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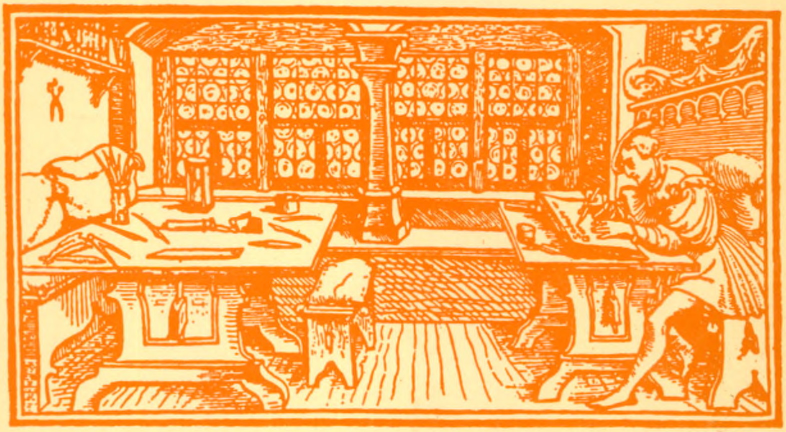

ANUL XLI 1996

STUDIA
UNIVERSITATIS BABEŞ-BOLYAI

CHEMIA

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PROF. DR. DOC. ION CĂDARIU

Profesorul Ion Cădariu s-a născut la 28 octombrie 1910, dintr-o familie de dascăli, în localitatea Caporal Alexa, Jud. Arad. Ştiind a scrie şi a citi la 5 ani, a fost primit direct în clasa a 3-a a şcolii primare. A urmat secţia reală a liceului "Moise Nicoară" din Arad şi în continuare cursurile secţiei de Chimie a Facultăţii de Ştiinţe, Universitatea "Regele Ferdinand I" din Cluj, luându-şi licenţa în Chimie cu "distincţie" în anul 1932 şi licenţa în Fizică cu "foarte bine" în 1934.

În 1933 este numit preparator la Laboratorul de Chimie Generală a Universităţii din Cluj, unde lucrează până în 1936. În 1935 îşi susţine cu succes şi Examenul de Capacitate pentru învăţământul secundar în specialităţile Fizico-chimice şi Matematici. În vacanţele de vară (1933 şi 1937) este chimist practicant la Uzinele Dermata din Cluj şi la Fabrica de ciment din Turda.

Şi-a luat doctoratul sub conducerea profesorului Adrian Ostrogovich în 1938 cu calificativul "magna cum laude", susţinând teza "Cercetări asupra triazinelor simetrice" şi tezina asupra aluminiului.

În această perioadă cunoaşte pe studenta din anul I de la Facultatea de Ştiinţe Naturale, domişoara Maria Achim, cu care se căsătoreşte la terminarea facultăţii, în 1941, şi cu care a împărţit bucuriile şi durerile vieţii timp de 55 de ani. In 1942 se naşte fiica lor Undina, care şi-a urmat părintele in alegerea profesiei de chimist.

Din 1936 până în 1940 este profesor la Liceul de Băieţi din Dej, fiind detaşat în anii şcolari 1937/38 şi 1939/40 la Seminarul Pedagogic Universitar din Cluj. După refugiu lucrează o perioadă scurtă la Liceul de Construcţii Civile şi Edilitare din Bucureşti, pentru a ocupa în 1940 postul de chimist la Uzinele Chimice Nitrogen din Târnăveni, post ce-l ocupă până în 1944, când este numit şef de lucrări la Catedra de Chimie fizică a Universităţii din Cluj-Timişoara, la care era Şef de Catedră profesorul Aurel Ionescu, post ocupat efectiv în iulie 1945. Activitatea de Şef de lucrări din acea vreme consta în coordonarea activităţii de laborator a studenţilor şi îndrumarea asistenţilor. Dar, chiar din primul an şi apoi odată cu mutarea profesorului Aurel Ionescu la Catedra de Fizică experimentală, a trebuit să preia şi prelegerile de Chimie Fizică ale acestuia. Din 1947 pâna la pensionare a predat Chimia Fizică (întreagă sau părţi ale ei) necontenit.

Conferenţiar între 1949 şi 1951, este numit profesor, şi în 1953, Şef al Catedrei de Chimie fizică. Acest post îl ocupă pâna la pensie, cu o întrerupere de un an, datorată comasării catedrelor de Chimie Generală şi Chimie Fizică din motive greu de înţeles astăzi.

In 1970, la vârsta de 60 de ani, preferă pensionarea la cerere. A continuat să funcţioneze ca profesor consultant, atâta timp cât această activitate nu a fost plătită.

Conduce doctoranzi din anii 50, până la obţinerea dreptului de a conduce, sub auspiciile Acad. Raluca Ripan - din dorinţa de a asigura pregătirea şi cercetarea în Chimie fizică a tinerilor colaboratori de la catedră - apoi în virtutea acestui drept, până când deteriorarea vederii nu i-a mai permis să citească.

Cercetarea ştiinţifică l-a pasionat din tinereţe. A continuat-o atât în perioada în care a funcţionat ca profesor la liceu, cât şi în industrie, unde a contribuit la realizarea primei linii de producţie a aluminiului din România, la Târnăveni. O plachetă comemorativă realizată din prima şarjă de aluminiu fabricat în ţară şi păstrată de profesorul Cădariu, aminteşte de acest eveniment.

Cele circa 60 de substanţe din clasa triazinelor, descoperite şi sintetizate in cadrul tezei de doctorat şi în lucrări ulterioare, au făcut obiectul a 7 articole (6 publicate în Gazz. Chim. ital.) şi au fost studiate şi în continuare împreună cu colaboratorii mai tineri, seria de lucrări pe această temă, iniţiată de profesorul Ostrogovich, ajungând la peste 50 de articole, publicate în mare majoritate în reviste din străinătate.

Perioada de activitate din industrie a fost de asemenea productivă sub aspect ştiinţific, 12 articole publicate în ţară şi în străinătate cu lucrări efectuate sau iniţiate în această perioadă stau mărturie preocupărilor din domeniile chimiei analitice, preparative, şi chimiei fizice. Multe dintre acestea au apărut în reviste străine, cum ar fi Z. analyt. Chem., Chem. Zeitung, Bull. de la Soc. Franc. des Electriciens.

Un alt domeniu abordat de profesorul Cădariu, în care a îndrumat mulţi dintre colaboratorii săi este cel al complecşilor aluminiului şi fierului cu oxiacizi organici, numărul articolelor pe această temă ridicându-se la circa 30, precum şi studiul altor echilibre de formare a complecşilor şi cinetica unor reacţii redox.

Activitatea didactică a fost o dominantă în viaţa profesorului Cădariu. Cum am putea uita, noi cei care l-am ascultat, cursurile magistrale de chimie fizică, conferinţele ţinute cu diverse ocazii, întotdeauna pregătite exemplar, cu un rar cult al perfecţiunii. A fost un exemplu nu numai pentru tinerii sau mai bătrânii colaboratori de la catedră, dar şi pentru cei de la alte catedre şi alte universităţi, care au avut şansa deosebită de a-l audia.

Cursul de Chimie fizică, litografiat încă într-o primă forma în 1950 şi reeditat mai amplu (1300 de pagini) în 1952, a fost tipărit de Editura Tehnică în 3 volume împreună cu colaboratorii mai tineri de la catedră în anul 1967, profesorul Cădariu scriind în întregime volumul I Structura atomului şi moleculei, ca şi volumul de Termodinamică chimică, apărut in 1971 în Editura Didactică şi Pedagogică.

Îndrumător atent al tinerelor generaţii, a avut calitatea de nepreţuit de a lăsa colabotratorilor libertatea să-şi dezvolte propriile idei, îndrumându-i discret şi cu mult tact. Avea întotdeauna grijă să scoată în evidenţă meritele colaboratorilor mai tineri. Corectitudinea şi modestia lui erau proverbiale; nu şi-ar fi pus semnătura pe un articol la care nu a lucrat efectiv, pentru nimic în lume. Aşa se explică faptul că nu a acceptat să figureze coordonator la cele trei volume de Chimie fizică, cu toate că a citit şi celelate două scrise de colaboratori, şi a dat sugestii şi îndrumări de îmbunătăţire, iar planul lucrării îi aparţinea. A semnat numai primul volum scris de el în întregime.

Preocupările sale variate de om de cultură sunt scoase în evidenţă de cele 25 de conferinţe pe care le-a ţinut în faţa studenţilor şi cadrelor didactice de la universităţile din Cluj, Timişoara, Iaşi, tematica lor întinzându-se dincolo de limitele chimiei, de la energia atomică, biologie, astronomie şi zbor cosmic, pînă la istorie (Hannibal, Continuitatea românilor) şi artă. Printre conferinţele cu caracter ştiinţific de chimie menţionăm "Reacţia de culoare a amidonului cu iodul", "Reacţii la presiune înaltă", "Reacţii în fascicule încrucişate", "Supratensiunea hidrogenului". Pe lângă prezentarea clară şi interesantă a stadiului actual al ştiinţei într-o interpretare personală, nu rareori avansa idei noi, cum ar fi explicarea supratensiunii hidrogenului prin formarea intermediara a moleculelor H_3O cu caracter de metal alcalin (în 1980), din păcate nevalorificate în lucrări ştiinţifice.

A fost un pasionat cititor de literatură şi un documentat cunoscător de artă plastică. Dintre scriitori l-a preferat pe Edgar Poe, din proza căruia a tradus şi chiar a publicat, iar dintre pictori, datorită multilateralităţii sale, pe Leonardo da Vinci. Cei care au fost onoraţi cu acceptarea de către profesorul Cădariu a ţinerii unui "curs festiv" cu ocazia întâlnirilor la un număr rotund de ani de la absolvire, au avut privilegiul rar de a fi călauziţi într-un univers aparte, creat convingător de marea lui artă de a-şi expune ideile în conferinţele sale, alcătuite cu aceeaşi rigoare, ca şi lucrările ştiinţifice şi cursul de Chimie fizică.

Neimplicarea politică i-a adus multe necazuri în toate etapele vieţii, aflându-se practic tot timpul în opoziţie cu cei care deţineau puterea, mai ales când aceasta a fost nu numai arogantă, ci şi incompetentă.

La 1 august 1996 prin trecerea lui în nemurire, Clujul a pierdut un însemnat om de cultură, iar Universitatea clujană un inegalabil dascăl.

STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLI, 1, 1996

SOME PROBLEMS OF PREEQUILIBRIUM KINETICS

Dedicated to the memory of the
outstanding teacher and scientist
Prof. dr. doc. Ion Cadariu

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ABSTRACT

The order of reactions involving intermediate compounds in equilibrium with the reactants, depends upon the concentrations taken as reaction variables. The case of monitoring the concentration of the intermediate complexes is of special interest. Monomolecular decomposition of the intermediate complex, the reaction between two complex molecules, and that between the intermediate and one of the reactants are examined. At equal concentrations of the reactants the reaction order may increase with as much as 0.5 units when monitoring the intermediate at high versus low concntrations, for the first two cases, and one unit for the last. The diffrerences in reaction order and possible interpretations are given taking the cases of the iron-thiosulfate and copper-thiosulfate reactions.

INTRODUCTION

The kinetics of reactions with preequilibrium is well known, it is discussed in every physical chemistry book and in many general chemistry texts. When an experimental study is undertaken, some problems may arise concerning the determination of the reaction order and the rate constant, since the observed reaction order depends upon the recorded concentration: that of reactants, intermediate compound or reaction products.

RESULTS AND DISCUSSION

1. Monomolecular decomposition of the intermediate or bimolecular reaction between intermediate molecules

For the reaction between reactants A and B with the formation at equilibrium of an intermediate X and eventually yielding the product P in a monomolecular or bimolecular reaction between two such complex molecules:

$$A + B \Leftrightarrow X, \quad \text{and} \quad X \rightarrow P \quad \text{or} \quad X + X \rightarrow P \tag{1}$$

with the equilibrium constant

$$K = \frac{x}{ab} \tag{2}$$

where a, b and x are the the concentration of compounds A, B and X respectively, the rate law expressing the appearance of the product species is

$$\frac{dp}{dt} = kx^n , \tag{3}$$

with n standing for reaction order (1 or 2) and p for concentration of P. Substituting x from (2) the rate law takes the form

$$\frac{dp}{dx} = kK^n(ab)^n \tag{4}$$

or for a stoichiometric mixture of A and B

$$\frac{dp}{dt} = kK^n a^{2n}. \tag{5}$$

As may be seen, the increase of the product concentration *p* per unit time follows a higher order rate law regarding the reactants (eqs. 4 and 5) as regarding the intermediate compound X (eq. 3).

None of these equations can be integrated, until *dp/dt* can be explicitly expressed as function of either *x*, *a* and *b* (or at least *a* for stoichiometric initial mixtures of A and B). Alternatively concentrations of at least two species should be monitored versus time, in order to determine the reaction order *n*, in some of the usual ways.

In many cases the intermediate compound X is a coloured complex - as in some redox reactions of thiosulfate and other sulphur compounds (with Fe^{3+} [1-5], CrO_4^{2-} [6-9], MnO_4^- [10], Cu^{2+} [11]) - which is suitable to spectrophotometric concentration measurements. Therefore the interpretation of the rate law requires the substitution of *dp/dt* with *dx/dt*. For this purpose the equations of mass balance can be used:

$$a_o = a + x + p \tag{6}$$

$$b_o = b + x + p. \tag{7}$$

Supposing A as the limiting component, the following set of equations will result in the desired rate law:

$$b = b_o - a_o + a \tag{8}$$

$$K = \frac{x}{a(b_o - a_o + a)} \tag{9}$$

$$a = -\frac{b_o - a_o}{2} + \sqrt{(\frac{b_o - a_o}{2})^2 + \frac{x}{K}} \tag{10}$$

$$\frac{dp}{dt} = -\frac{da}{dt} - \frac{dx}{dt} \tag{11}$$

$$\frac{da}{dt} = \frac{1}{K\sqrt{(b_o - a_o)^2 + \frac{4x}{K}}} \frac{dx}{dt} \tag{12}$$

$$-\frac{dx}{dt}[1 + \frac{1}{K\sqrt{(b_o - a_o)^2 + \frac{4x}{K}}}] = kx^n \tag{13}$$

and

$$\boxed{-\frac{dx}{dt} = \frac{\sqrt{K^2(b_o - a_o) + 4Kx}}{1 + \sqrt{K^2(b_o - a_o) + 4Kx}} kx^n}. \tag{14}$$

There are several limiting cases of interest.

1°. $b_o \quad a_o$, the initial concentrations are the same. Equation (14) simplifies to:

$$\boxed{-\frac{dx}{dt} = \frac{2\sqrt{K}}{1 + 2\sqrt{Kx}} kx^{(n+0.5)}} \tag{15}$$

2° $\sqrt{K^2(b_o - a_o) + 4Kx} >> 1$. For large excess of b_o or large values of *K* the rate law has a simple form, the reaction order with respect to *x* being the same as equation (3) given above:

$$-\frac{dx}{dt} = kx^n \tag{16}$$

3°. $\sqrt{K^2(b_o - a_o) + 4Kx} << 1$. At low concentrations of X and/or low values of *K*

$$-\frac{dx}{dt}=\sqrt{K^2(b_o-a_o)+4Kx}.kx^n \quad . \tag{17}$$

For the stoichiometric mixture the reaction order with respect to x is 0.5 higher than required by equation (3):

$$\boxed{-\frac{dx}{dt}=2\sqrt{K}kx^{(n+0.5)}} \tag{18}$$

The linear form of the equation (15) can be used to find the reaction order n:

$$\ln(-\frac{dx}{dt})+\ln(1+2\sqrt{Kx})=\ln(2k\sqrt{K})+(n+0.5)\ln x\,. \tag{19}$$

By plotting $\ln(-dx/dt)+\ln(1+2\sqrt{Kx})$ as function of $\ln x$ a straight line with slope n+0.5 is obtained. The classical plot of logarithm of the rate versus logarithm of the concentration gives a straight line only at low concentrations of X and/or low values of the equilibrium constant K, when the first term in the left hand side is negligible (corresponding to the lineari form of equation (18)). In this case the intercept is $\ln(2k\sqrt{K})$ instead of $\ln k$

At low concentrations, for monomolecular decomposition of the intermediate complex, the observed reaction order will be 1.5, while for the bimolecular reaction of two complex molecules, 2.5, instead of 1, respectively 2, as requested by equation (3).

2. Reaction between the intermediate and a reactant. Reactant catalized reaction.

While for simple reactions calalysis by reactants is meaningless, in the case of formation of intermediate complexes at equilibrium such reactions can occure according to the following sequence:

$$\mathrm{A + B \Leftrightarrow X;} \qquad \mathrm{X + A \rightarrow P + A.} \tag{20}$$

The rate law of such reactions is

$$\frac{dp}{dt}=kax\,, \tag{21}$$

with three concentration variables, p, a and x. The substitution of a and dp/dt as functions of x, from equations (10), (11) and (12) gives

$$-\frac{dx}{dt}=[\frac{-(b_o-a_o)\sqrt{K^2(b_o-a_o)^2+4Kx}+K(b_o-a_o)^2+4x}{1+\sqrt{K^2(b_o-a_o)^2+4Kx}}]\frac{k}{2}x\,. \tag{22}$$

At equal initial concentrations of A and B, equation (22) simplifies to:

$$\boxed{-\frac{dx}{dt}=\frac{2kx^2}{1+2\sqrt{Kx}}}\,, \tag{23}$$

or in linear form:

$$\ln(-\frac{dx}{dt})+\ln(1+2\sqrt{Kx})=\ln(2k)+2\ln x\,. \tag{24}$$

Equations (23) and (24) are similar to equations (15) and (19), except of the missing factor $\sqrt{K}$ and the reaction order 2 instead of n + 0.5, i.e. 1.5 or 2.5 for monomolecular or bimolecular reactions respectively, of the intermediate complex.

At high concentrations of the intermediate x, or large formation constant K, the reaction order is 1.5:

$$-\frac{dx}{dt}=\frac{k}{\sqrt{K}}x^{1.5}\,, \tag{25}$$

while at low x and/or small [illegible] the reaction order n reaches 2:

$$-\frac{dx}{dt}=2kx^2 \tag{26}$$

In a large excess of B the rate law has the form

$$-\frac{dx}{dt} = \frac{k}{1+Kb}x^2 \tag{27}$$

and in excess of A, the form

$$-\frac{dx}{dt} = \frac{Ka_0^{2}k}{1+a_0K}x , \tag{28}$$

or, writing k' for the constant fraction, the reaction order for x is 1:

$$-\frac{dx}{dt} = k'x . \tag{29}$$

For this mechanism the reaction order may change from the first order in excess of A to second order in excess of B or at equal initial and low concentrations of A and B. At high stoichiometric concentrations of A and B, the reaction order is 1.5.

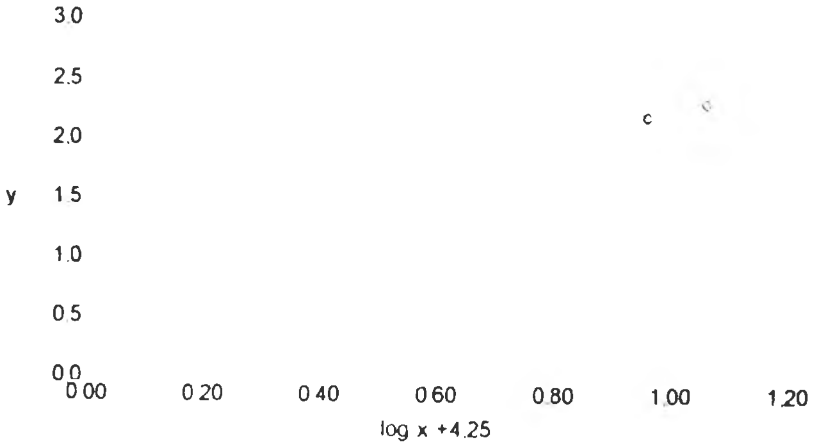
3. The reaction between Fe^{3+} and $S_2O_3^{2-}$

The reduction of Fe(III) to Fe(II) by $Na_2S_2O_3$ in acidic solutions takes place by formation of a violet intermediate complex which fades away with time. While the formation of $FeS_2O_3^+$ is unamimously accepted over the last decades, the kinetics of its decomposition is still controversal. Some facts might be summarized, based on data from the literature and from own experieces

1° At low concentrations of the intermediate complex ($FeS_2O_3^+$ concentrations between $6\ 10^{-5}$ $6.5\ 10^{-4}$) and pH about 3 the photometrically determined reaction order was 1.96 [5]. The formation constant of the complex was calculated to be 126 M^{-1}. Under these conditions $2\sqrt{Kx}$ in the denominator of equation (23) varies between 0.2 and 0.6, the denominator itself from 1.2 to 1.6 and its logarithm with only 0.1 units. Therefore the plot of $\log(-dx/dt)$ vs $\log x$ should give also a straight line, except the slope should be interpreted as corresponding to n+0.5. Using data from [5], the plot required by equation (24) is shown in fig. 1

Fig.1 Plot of equation (24)

for data of Williamson and Rimstidt[5]



The ordinate is the first member of equation (24)

$$y = \log(-\frac{dx}{dt}) + \log(1+2\sqrt{Kx}) \tag{30}$$

The slope of the plot in figure 1 is 2.08, in agreement with a reactant catalized reaction.

The same experimental data gave a very good straight line $\log(-dx\ dt)$ vs. $\log x$ [5], but the conclusion of the mentioned authors about a bimolecular mechanism is questionable. Rather a mechanism

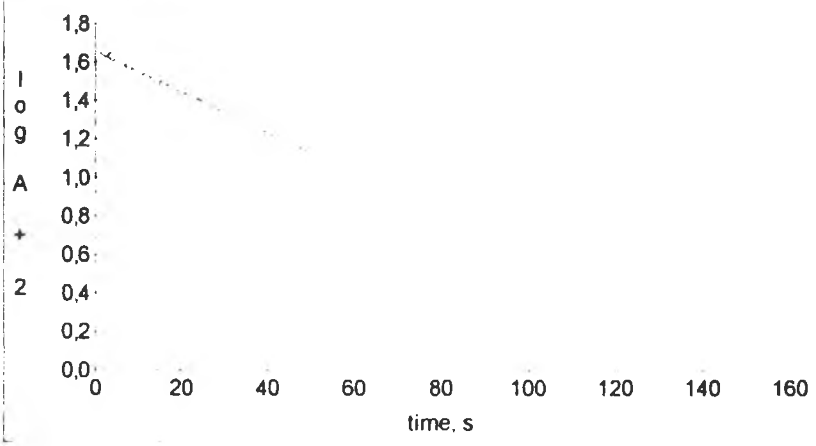
$$Fe^{3+} + S_2O_3^{2-} \Leftrightarrow FeS_2O_3^{+} \quad (31)$$

$$FeS_2O_3^{+} + S_2O_3^{2-} \rightarrow Fe^{2+} + S_2O_3^{-} + S_2O_3^{2-}, \quad (32)$$

suggested by equation (24) should be considered. The free radicals combine to tetrathionate in a fast step. An alternative but kinetically undistiguishable pathway could involve the formation of $S_2O_3 \therefore S_2O_3^{3-}$ free radical, instead of (32), suggested by the existence of similar radicals of organic thiols [12] and their possible formation during oxidation of thiols with chromate [13].

2°. Under the thiosulfate excess conditions the reaction order is close to 1, as expected. Colorimetric recording of concentrations of the complex (concentration of thiosulfate 0.0182 mol/l and of iron 0.0049 mol/l), at several nitric acid concentrations (between 0.006 and 0,06 mol/l) and ionic stregth 0.184, gave straight lines by plotting log A (absorbance) vs. time [4]. Figure 2 shows an example (with no acid added).

Fig. 2. The iron-thiosulfate reaction



3°. Frozen solutions at -80 °C of the freshly prepared complex and containing methylmetacrylate monomer, while meltig, generate a large amount of polymer, proving the involvement of free radicals. This fact is also consistent with the proposed mechanism.

4°. In alcoholic solution, the formation of the $Fe(S_2O_3)_2^-$ anion, containing two reducing agent ions in the first coordination sphere of the Fe(III) as well as an induction period is observed, suggesting a possible alternative pathway of the reaction.

4. The reaction between Cu^{2+} and $S_2O_3^{2-}$

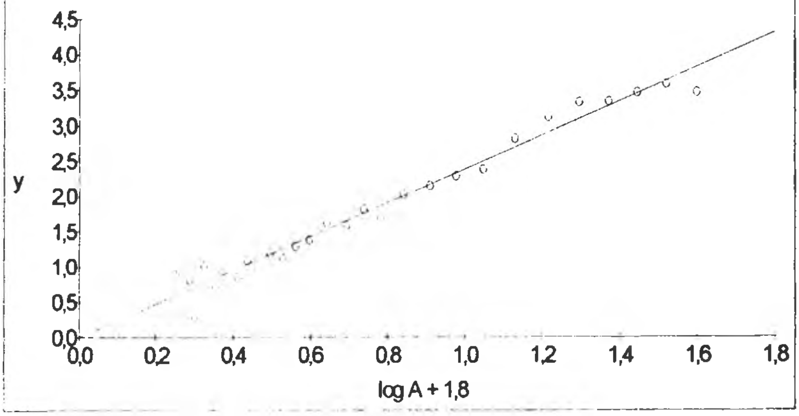
The reaction between copper and thiosulfate ions occurs also with the formation of an intermediate complex, CuS_2O_3, similar to the iron-thiosulfate complex, but uncharged. The kinetics of fading away of this complex can be followed spectrophotometrically, but its half time is three to four orders of magnitude shorter than for the former, therefore a stopped-flow apparatus is needed for its study.

Plots of absorbace versus time vere recorded for this reaction at Stanford University (with Prof. Dr. Henry Taube) some years ago. The plots of logarithm of the rate vs. the logarithm of the absorbance gave straight lines with slopes between 2 and 2 5, as may be illustrated by figure 3, where the reaction order n = 2 37 was calculated with initial conentrations of 0 05 M for both reactants in aqueous acidic solution (0.01 M $HClO_4$) at 20 °C.

The found reaction order is consistent with the mechanism involving in the first step the fast formation of the complex and in the second, the reaction between two complex molecules.

Fig.3. The copper-thiosulfate reaction

$y = \log(-dA/dt) + 4.5$



CONCLUSIONS

The interpretation of kinetic runs for the reactions involving an intermediate complex in a preequilibrium, should carefully consider possible bias in the formal kinetics of supposed mechanisms, since under certain conditions reaction orders obtained by following the decay of the intermediate complex, can be altered by as much as one unit.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLI, 1, 1996

^{1}H - NMR - STUDY OF CONDENSATION PRODUCTS OF 1-(2- PYRIMIDINYL)-3-METHYLPYRAZOLIN-5-ONES WITH THE HETEROCYCLIC ALDEHYDES

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ABSTRACT.
The structure of condesation products obtained from the corresponding 1-(2-pyrimidinyl)-3-methylpyrazolin-5-ones **1a-c** with heterocyclic aldehydes **2** and **3** was established by means of ^{1}H-NMR spectra. This structure corresponds to dimethin- **4** and monomethin- **5** merocyanines. The chemical and spectral properties of the obtained compounds are reported.

INTRODUCTION

The 1-(2-pyrimidinyl)-3-methylpyrazolin-5-ones **1**, relatively recently discovered [1,2], were converted to methinic dyes by the condensation with aromatic aldehydes under acidic and basic catalysis [3-6]. This possibility was based on the analogy with 1-phenyl-3-methylpyrazolin-5-one which has furnished by condensation with aromatic and heterocyclic aldehydes, a series of methinic dyes [7-9].

Because only the compounds resulted by condensation with heterocyclic aldehydes are produced industrially [7], we have also condensed 1-(2-pyrimidinyl)-3-methylpyrazolin-5-ones **1** with such aldehydes, namely "Fischer's base" aldehyde **2** and 5-methyl-2-phenyloxazole-4-carboxaldehyde **3**, respectively [10].

The purpose of present paper is to report the structural assignments for the obtained compounds.

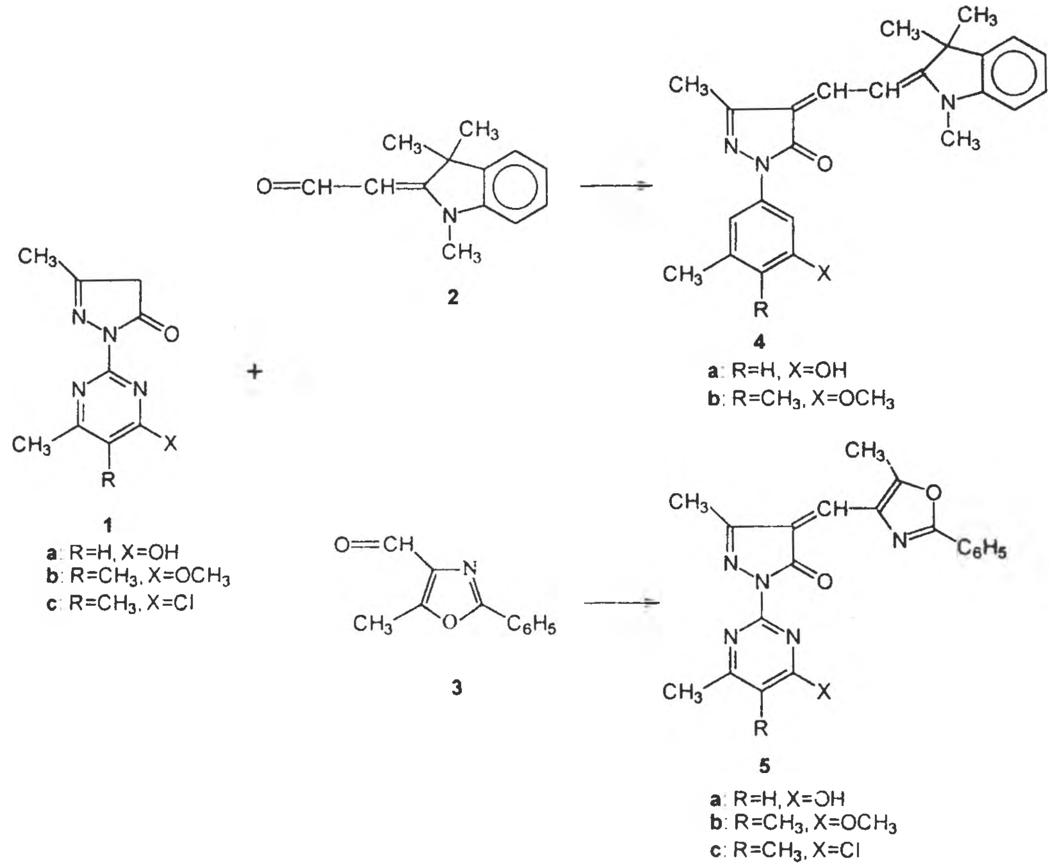
RESULTS AND DISCUSSION

The condensation products of 1-(6-methyl-5-R-4-X-2-pyrimidinyl)-3-methylpyrazolin-5-ones **1** with heterocyclic aldehydes **2** and **3**, are coloured materials (from yellow to red), with strong and sharp absorption bands in the visible region (λ_{max} = 450-500 nm, ε_{max}~50000), while the starting materials are colourless (λ_{max} = 290-350 nm). The coloured products have dyeing properties for synthetic fibres. Some physico-chemical data of the examined compounds are presented in Tables 1 and 2.

Based on elemental microanalysis and ^{1}H-NMR spectral data presented inTables 1 and 2, the structure of the condensation products obtained from 1-(6-methyl-5-R-4-X-2-pyrimidinyl)-3-methylpyrazolin-5-ones **1** and heterocyclic aldehydes **2** and **3**, was established; it corresponds to dimethin- **4** and monomethin-**5** merocyanines. These resulted by a dimolecular crotonic condensation of the methylenic group of one of the tautomeric forms of pyrazolinones **1** and the formyl group of the aldehydes **2** and **3**.

Thus, the microanalysis data are compatible only with dimolecular condensation products, the trimolecular condensation products [11] which can be formed by condensation of one molecule of aldehyde with two molecules of 1-substituted-3-methylpyrazolin-5-ones , being excluded.

In the disscused reactions, the dimolecular condensation products can also be formed by water elimination between formyl group of aldehydes **2** ,**3**, and one of active methyl groups of pyrazolinones **1**, or between 5-pyrazolinone carbonyl group and the active methyl group of 5-methyl-2-phenyloxazole-4-carboxaldehyde **3** [9].



1
a: R=H, X=OH
b: R=CH$_3$, X=OCH$_3$
c: R=CH$_3$, X=Cl

2

3

4
a: R=H, X=OH
b: R=CH$_3$, X=OCH$_3$

5
a: R=H, X=OH
b: R=CH$_3$, X=OCH$_3$
c: R=CH$_3$, X=Cl

Table 1. Physico-chemical data of the compounds **4a,b** and **5a-c**.

Compd.	M.p.°C	Yield %	Microanalysis (calcd / found)						Application on polyester and polyamide
			C%		H%		N%		
4a	295-296	80	67.86	67.8	5.91	6.1	17.99	18.3	orange
4b	245-246	53	69.06	68.7	6.47	6.6	16.78	17.1	orange
5a	241-243	48	64.0	64.3	4.53	4.7	18.66	18.4	brownish orange
5b	234-236	30	65.5	65.1	5.21	4.9	17.36	17.6	yellow
5c	230-231	70	61.84	62.2	4.41	4.3	17.17	16.8	yellow

These posibilities are excluded, however, by ^{1}H-NMR spectra of the obtained compounds **4**, **5**, where the signals corresponding to methylenic (or methinic) protons and formyl proton are absent, while in the case of the last suggested possibilities, they must be conserved at their characteristic chemical shift values of 3.4-5.4 ppm (δ C_4-H pyrazolone) [4,6,12] and 9.6 ppm (δ CHO-oxazole) respectively (see Table 2).

Table 2. ^{1}H-NMR spectral data of the compounds **1a-c**, **4a,b**, **5a-c**, (δ ppm, J Hz).

Compd.	Pyrazolone ring		Pyrimidine ring			Vinylic protons	Formyl protons	3-H-indole ring			Oxazole ring	
	C_3-CH_3 s	C_4-H s	C_5-R s	C_6-CH_3 s	C_4-X s			C_6H_4 $C(CH_3)_2$ m	s	N-CH_3 s	C_6H_5 m	C_5CH_3 s
1a	2.20	5.30	6.10	2.10								
1b	2.18	5.31	2..01	2.31	4.01							
1c	2.18	5.30	2.15	2.43								
4a	2.15		5.68	2.18		7.01(d) 7.47(d) j = 14		6.6-7.2	3.36	1.58		
4b	2.18		1.97	2.36	3.95	7.33(d) 7.59(d) j = 14		6.6-7.3	3.32	1.55		
2						5.26(d) j = 9	9.85(d) j = 9	6.6-7.3	3.09	1.51		
5a	2.39		5.71	2.15		6.86(s)					7.1-7.9	2.61
5b	2.43		2.02	2.40	3.98	7.37(s)					7.3-8.2	2.70
5c	2.47		2.26	2.52		7.42(s)					7.3-8.2	2.72
3							9.46(s)				7.2-8.1	2.38

Multiplicity: s (singlet), d (doublet), m (multiplet).

Naturally the above mentioned absence of signals corresponding to methylenic (or methinic) protons proves the elimination of these protons by condensation with the formyl group of aldehydes and consequently, the assigned structures **4** and **5**. The absence of signal of formyl proton and the appearance in the ^{1}H-NMR spectra of the condensation products of new signals in the range 6.8-7.6 ppm, that can be assigned to one proton of methinic bridge [6,13,14], also supports the structures **4** and **5**.

Actually by condensation, the formyl proton becomes a methinic one, which produces an upfield shift greater than 2 ppm in the ^{1}H-NMR spectra. Alike great shift, but downfield, undergoes the signal of methinic proton from ^{1}H-NMR spectrum of "Fischer's base" aldehyde **2**, as a result of its transformation into the condensation products **4**. The assigned structures **4** and **5** were also sustained by all others ^{1}H-NMR data of examined condensation products, as follows:

a) the 1:1 ratio of the singlets intensities of singular methyl groups from the two constitutive parts of the condensation products originated from methylenic and carbonylic component (see δ C_3-CH_3 pyrazolone, δ N-CH_3 3-H-indole, and δ C_5-CH_3 oxazole).

b) the conservation with some little shifts, of the signals in the ^{1}H-NMR spectra of the condensation products, for all types of protons from starting materials which are not involved in condensation.

The assignement of signals for the different protons, especially of the methyl groups, is based on the comparison with ^{1}H-NMR spectral data for starting materials and other similar condensation products [4-6,12-14].

We mention also that the values between 2.15-2.5 ppm of the chemical shift of the pyrazolone C_3-CH_3 group protons plead for a *Z*-configuration of the exocyclic double bond from the position 4 of pyrazolone ring [6,13], while the value J=14Hz for the coupling constant of the protons from the dimethinic bridge in dimethinmerocyanines **4** indicates an *E*-configuration for these protons [14].

EXPERIMENTAL

Melting points were determined in capillaries and are uncorrected. ^{1}H-NMR spectra were recorded with a Tesla BS 487 (80 Mhz) spectrometer using hexamethyldisiloxane as an internal standard in $CDCl_3$. Electronic spectra were recorded in MeOH on a "Specord" spectrophotometer.
1-(6-Methyl-5-R-4-X-2-pyrimidinyl)-3-methylpyrazolin-5-ones **1** [2], "Fischer's base" aldehyde **2** [15] and 5-methyl-2-phenyloxazole-4-carboxaldehyde **3** [16] were synthesised according to quoted references.

General procedure for synthesis of dimethin 4 and monomethin 5 merocyanines

A mixture of 1-pyrimidinyl-3-methylpyrazolin-5-ones **1** (0.01 mol), heterocyclic aldehyde **2** or **3** (0.01), piperidine (0.1 ml) and ethanol (10 ml) was heated under reflux for 7 hrs and 2 hrs respectively, and then allowed to stand at room temperature over night. The coloured precipitate was filtered off, washed with ethanol (3 times, 3 ml) and dried, finally at 120^{0}C. The physico-chemical data of synthetized dyes are given in Table 1 and 2.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLI, 1, 1996

OXIDATION - REDUCTION PROCESSES OF CADMIUM ELECTRODE IN ALKALINE ELECTROLYTE

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ABSTRACT

The electrochemical behaviour of cadmium plate electrode in 6N KOH electrolyte has been investigated by cyclic voltammetry The anodic and cathodic curves were recorded at different sweep rates and the peaks were associated with the electro-oxidation and electroreduction processes which occurred.

INTRODUCTION

The electrochemical behaviour of cadmium electrodes in alkaline solutions has been the object of many studies because of their wide applications in nickel- cadmium and silver-cadmium batteries [1-7]

Cadmium can be reversibly charged and discharged through the reaction formally written as:

$$Cd + 2OH^- \underset{charge}{\overset{discharge}{\rightleftarrows}} Cd(OH)_2 + 2e^-, \qquad \varepsilon^0 = -0{,}809V/NHE \qquad (1)$$

In charged state the active material is metallic Cd and in discharged state it is $Cd(OH)_2$. In practice, the electrode reaction is more complex due to the formation of different modifications of discharged active material: α, β and γ - $Cd(OH)_2$, CdO and CdO_2 [8].

In spite of many studies, the reaction mechanism is still incompletely understood. For example, recently, two different mechanisms have been proposed the dissolution-precipitation mechanism involving solution phases [9,10] and the solid state mechanism involving ionic transport through the $Cd(OH)_2$ active material film [11,12].

The formation of CdO in anodic polarisation was studied [13,14] CdO can be formed as the primary product before its conversion to $Cd(OH)_2$, as a result of a secondary reaction after the $Cd(OH)_2$ is formed, and in parallel with the $Cd(OH)_2$ formation.

EXPERIMENTAL

The cyclic voltammetry was applied to study the electrochemical behaviour of a 99,99% pure cadmium plate in 6N potassium hydroxide electrolyte

The measurements were made in a conventional three-electrode cell using SCE as reference, connected through a Luggin capillary, and a platinum wire as counter electrode.

All the potentials given in this paper are referred to SCE.

The apparent surface area of the working electrode was 1cm^2. The 6N KOH electrolyte was prepared from analytical grade KOH and distilled water.

The experiment were performed by means of an Wenking HP 72 potentiostat, a PV_2 programmer and an Endim 620.02 X-Y recorder.

The surface of the cadmium plate was polished with fine emery degreased and rinsed with distilled water . Before the investigations, the cadmium electrode was polarised at 1,75V/SCE, for 5 minutes, to eliminate the impurities from its surface.

RESULTS AND DISCUSSION

Figure 1 shows the voltammograms obtained with the cadmium plate electrode, in 6N KOH, at three potential sweep rates: 20mV/s, 6,66 mV/s and 3,33mV/s respectively.

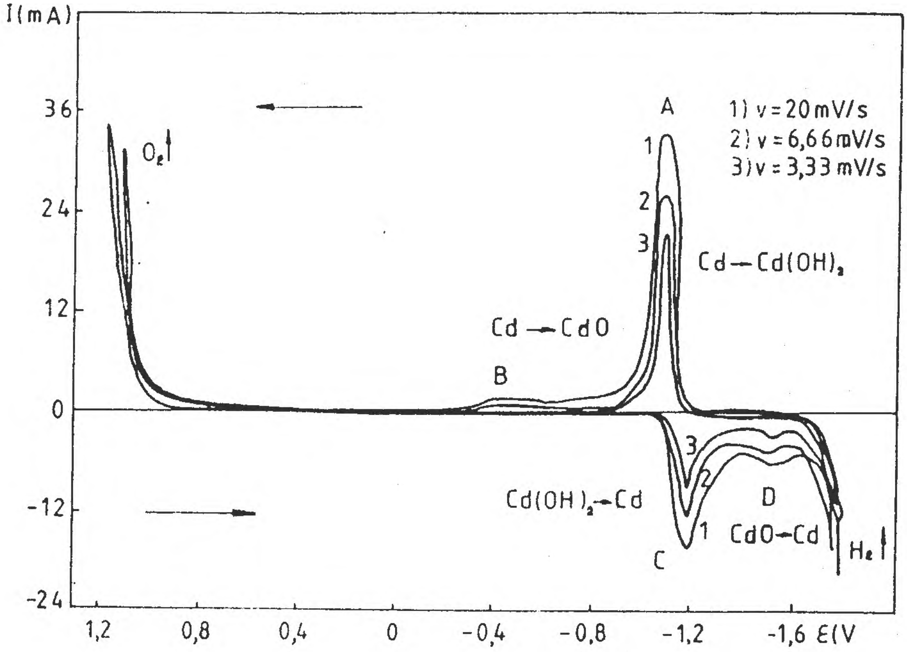

Fig. 1 Cyclic voltammograms of cadmium plate electrode in 6N KOH at: v=20mV/s(1), v=6,66mV/s(2) and v=3,33mV/s(3).

In the positive going potential scan two anodic current peaks (A and B) were recorded. The peak A was associated with the oxidation of Cd to Cd(OH)$_2$ and the peak B with the formation of CdO. At high anodic potentials (>1V/SCE) oxygen evolution reaction (OER) occurs:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \qquad (2)$$

In the negative going potentials scan two cathodic current peaks (C and D) were recorded. The peak C was associated with the reduction of $Cd(OH)_2$ to Cd and the peak D with the reduction of CdO to Cd. At extreme cathodic potentials (<-1,6V/SCE) hydrogen evolution reaction (HER) occurs

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3)$$

The results of cyclic voltammetry measurements of Cd plate electrode, related to the main peaks (A and C) are tabulated in Table 1

Table 1. Cyclic voltammetry measurements of Cd plate electrode.

Sweep rate (mV/s)	**$\varepsilon_{a,p}$(A) (V/SCE)**	**$\varepsilon_{c,p}$(C) (V/SCE)**	**$\Delta\varepsilon_{a,c}$ (V)**	**ε' (V/SCE)**	**$I_{a,p}$ (A) (mA)**	**$I_{c,p}$(C) (mA)**	**$\frac{I_{c,p}}{I_{a,p}}$**
20	**-1,090**	**-1,190**	**0,100**	**-1,140**	**34**	**17**	**0,6**
6,66	**-1,100**	**-1,180**	**0,080**	**-1,140**	**26**	**13**	**0,5**
3,33	**-1,120**	**-1,160**	**0,040**	**-1,140**	**21**	**10,5**	**0,5**

The average potential, ε'=-1,140V/SCE, is taken as an estimation of the reversible potential, being comparable with the theoretical value of the reversible potential, calculated for 6N KOH electrolyte and T=20°C, ε_r =-1,088V/SCE [15].

If the difference in the anodic and cathodic peak positions ($\Delta\varepsilon_{a,c}$) is taken as an estimation of the reversibility of the reaction, it is evident that the reversibility of process increases with decreasing of sweep rates

The ratio of the cathodic to anodic peak currents is 0,5 and demonstrates that the charge recovered on the cathodic sweep was considerably smaller than the previous anodic sweep, suggesting the inefficient reduction of $Cd(OH)_2$ on the planar surface.

The current intensities of the peaks were plotted against the square root of four sweep rates (figure 2)

The linear dependence suggests that the involved reactions behave as diffusion controlled electrochemical processes. But the non-zero value of I ,for v=o ,points out that the processes also include non-diffusional contributions (ohmic and charge transfer)

According to Will's investigations [16] the oxidation of Cd to $Cd(OH)_2$ occurs through a complex mechanism involving 2 steps:

- the dissolution of Cd with the formation of complex cadmiate ions, at the electrode surface:

$$Cd + 3OH^- \rightarrow [Cd(OH)_3]^- + 2e^- \quad (4)$$

- the precipitation of $Cd(OH)_2$ after saturation with $[Cd(OH)_3]^-$

$$[Cd(OH)_3]^- \rightarrow Cd(OH)_2 + OH^- \quad (5)$$

The formation of CdO (peak B) occurs, probably, in solid state, as demonstrated Zytner et al. [17]:

$$Cd + OH^- \rightarrow [Cd(OH)_{ads}] + e^- \quad (6)$$

$$[Cd(OH)_{ads}] + OH^- \rightarrow CdO + H_2O + e^- \quad (7)$$

The reduction of $Cd(OH)_2$ during the cathodic sweep (peak C) occurs either by Eq (4) and (5) in reverse order and/or by solid state reaction:

$$Cd(OH)_2 + 2e^- \rightarrow Cd + OH^- \quad (8)$$

It is very probably the involvement of both mechanisms in the reduction of $Cd(OH)_2$ to Cd [16].

The reduction of CdO to Cd (peak D) takes place preferentially through a solid state process due to the semiconductor properties of CdO [18]:

$$CdO + H_2O + 2e^- \rightarrow Cd + 2OH^- \quad (9)$$

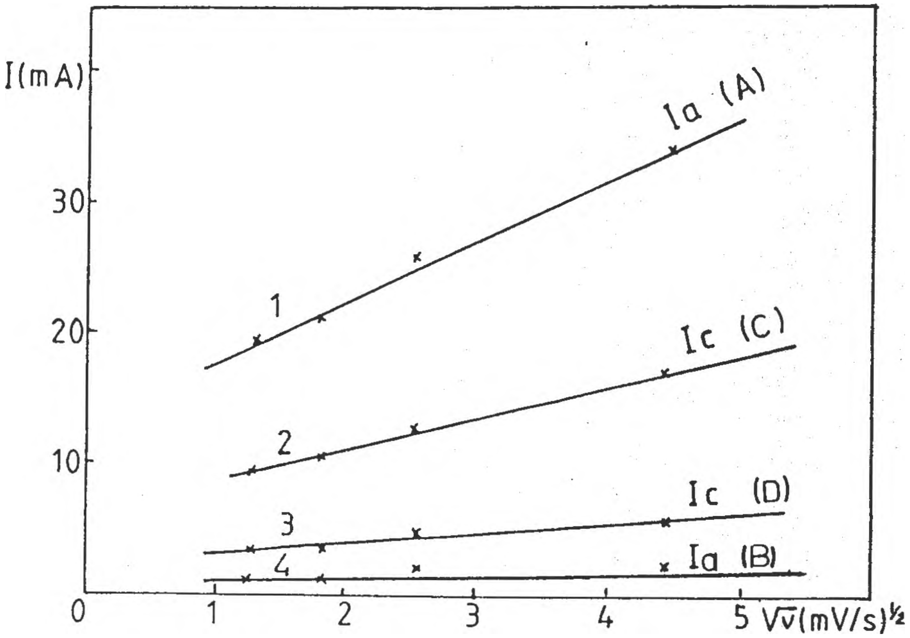

Fig 2. The dependence of the anodic (1,4) and cathodic (2,3) peak current intensity of $v^{1/2}$

The voltammograms depicted in figure 3 were recorded in order to inves[illegible]e the effect of solution stirring on the mechanisms of processes.

Under stirring, the height of peaks A and C is changed, suggesting the involvement of precipitation-dissolution mechanism in the formation of $Cd(OH)_2$ and its reduction.

The peaks B and D are unchanged confirming the supposition that the corresponding processes occur in solid state.

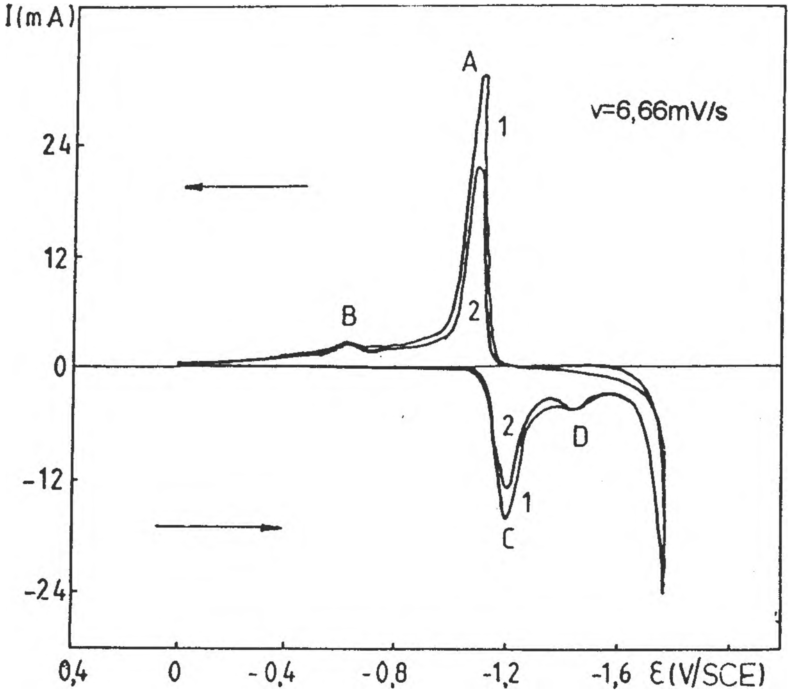

Fig. 3. Voltammograms of Cd plate electrode at v=6,66mV/s, in unstirred electrolyte (curve 1) and in stirred electrolyte (curve 2).

From our experiments presented above it should be pointed out that:

- the low sweep rates are favourable for the reversibility of processes;
- from the dependence of anodic and cathodic peak current intensity of $v^{1/2}$ we can suggest that the electrode processes are controlled in the most great part by diffusion, but there are also non diffusional contributions.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLI, 1, 1996

AROMATICITY OF THIAZOLES. I. TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH THE 2,5-THIAZOLYLENE BRIDGE

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ABSTRACT

The propagation of electronic effects from position 2 to position 5 of thiazole was investigated by correlating the chemical shifts of C-5 protons in 2-(4-substituted-phenyl)-4-thiazolecarboxal-dehydes, **1**, with substituent constants in Hammett plots. The contributions of mesomeric and field effects to the overall influence exerted by the substituents on the chemical shifts were analyzed by an original variant of the Swain-Lupton method. A value of 0.38 ± 0.02 was assigned to the transmission coefficient of the 2,5-thiazolylene bridge.

INTRODUCTION

Although the practical importance of thiazole derivatives in many fields of science and technology entailed copious theoretical investigations, some basic problems of thiazole chemistry still form the object of rather contradictory statements. The purpose of this paper is to present new data concerning the chemical and physical behaviour of the extended π system of the thiazole heterocycle, with special emphasis on the quantitative aspects of aromaticity [1, 2]. According to the general image of thiazole emerged as a result of classical investigations [3-5] , this heterocycle represents a term of the aromatic series [6, 7]. Thermodynamic [8, 9], chemical [3, 5], NMR [10-12] and mass spectrometry data [13, 14] might be quoted to substantiate this statement. However, a closer inspection reveals that, apart from the coplanarity of the ring atoms [15] and of the existence of a diamagnetic ring current [10], all other characteristics of thiazole display more or less evident departures from what is usually understood by "aromatic character". In fact, if one compares the physical and chemical behaviour of benzene and thiazole, the differences are more important then similitudes, from a pragmatical point of view.

With the advent of modern methods in quantum-mechanical calculations [16-18], the existence of two divergent lines in the evolution of the chemistry of thiazole became more obvious. Thus, while the preparative chemistry used the aromatic heterocycle image as a starting point and an interpretative tool, other research fields put more and more emphasis on the electronic and structural unevenness of this system; it culminated with the very elaborated work of Metzger's group [19, 20] which described thiazole as a cyclic conjugated diene, with strongly localized double bonds, and little of the sulphur electronic doublet to the extended conjugation. It was felt by present authors that new experimental data are needed for further refining the actual concepts on this problem.

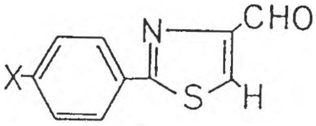
Since conjugated, and especially aromatic, compounds are characterized by a long-range transmission of electronic effects, we started by reinvestigating the propagation across the thiazole ring of the influences exerted by substituents.

Imoto *et al.* [21, 22] who determined the pKa of substituted thiazolecarboxylic acids, and the alkaline hydrolysis rates of some esters of these acids, found acceptable correlations with

Hammett's σ constants for 2,5-disubstituted series, and with σ_m for the 2,4-disubstituted ones, and concluded that the thiazole ring is a poorer transmitter of electronic effects than benzene.

A series of papers by Noyce and co-workers [23-25] reported another aproach to the transmission of electronic effects by the heterocyclic system of thiazole, namely, by monitoring the rates of solvolysis of α-chloro- and α-*p*-nitrobenzoxyethyl thiazoles. Their results were at variance with those of the japanese workers in at least two important points, namely, they did not find acceptable correlations with σ_m (or σ_m^+) in the case of 2,4-disubstituted derivatives and their values in the thiazole series were greater than those for the benzene series, thus presenting thiazole as a better transmitter of electronic perturbations [26].

In our investigations, we studied the influence of the substituent X on IR- and NMR-parameters, characterizing the formyl group and the proton at C-5 in 2-(*p*-substituted-phenyl)-4-thiazolecarboxaldehydes **1**.



1

The present paper is confined to the presentation of results obtained by correlating the ^{1}H-NMR chemical shifts of the C-5 proton with the substituent constants of the group located in a *para*-position on the phenyl at C-2.

EXPERIMENTAL

The 2-(*p*-substituted-phenyl)-4-thiazolecarboxaldehydes were synthesized according to literature data [27-30] except for the *p*-methoxy-derivative (*vide infra*). The ^{1}H-NMR spectra were recorded on a Tesla BS-478-B 80 MHz-Spectrometer, by using saturated solutions in CCl_4 and DMSO, with TMS as internal reference and lock.

2-(*p*-methoxyphenyl)-4-thiazolecarboxaldehyde.

A mixture of 3.5 g 2-(*p*-methoxy-phenyl)-4-chloromethyl-thiazole, 2.3 g hexamethylene-tetramine and 15 ml $CHCl_3$ was refluxed for 0.5 hrs., cooled, the hexamethylenetetramine salt isolated by filtration, treated with 20 ml 50% acetic acid and refluxed for 1 hr., then poured on water to give a 45% yield of aldehyde, yellowish crystals, m.p. 97-98° (two recrystallizations from aq. ethanol).

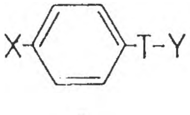
$C_{11}H_9NO_2S$ (219.26) Calcd. N 6.39%, found N 6.40%

RESULTS AND DISCUSSION

We used the method of Jaffe [31], further developed by Charton [32] and especially by Miller *et al.* [33] in measuring the transmission through a structural element of the effect exerted by a substituent X on a "reaction center" Y in two series of compounds **2** and **3**. This method consists of determining the ratio:

$$\pi'_T = \rho_2/\rho_3$$

of the slopes of the respective Hammett plots.



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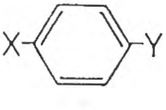


3

The ^{1}H-NMR spectra of compounds **1**, in both CCl_4 and DMSO clearly showed a distinct singlet for the C-5 proton at 80 MHz. Its position was found to vary significantly with both the solvent and the substituent, as shown in Table 1.

Table 1. ^{1}H-NMR chemical shifts of the C-5 proton in 2-Aryl-4-Thiazolecarboxaldehydes, 1.

X	Chemical Shifts, Hz	
	CCl_4	DMSO
Me O	658	705
Me	662	714
NHCOMe	663	713
H	667	714
Cl	670	720
Br	670	720
NO_2	677	728

The influence of the solvent, amounting to 50 Hz (cca. 0.65 ppm) on passing from CCl_4 to DMSO, is quite noteworthy and, in our opinion, points out not only to the existence of important interactions between the oxygen atom of DMSO and the C-5 proton, but also to a distortion of the charge density distribution over the ring. We shall return to this point in the following paper, in the context of solvent effects on the transmission coefficients of 2,4- and 2,5-thiazolylene bridges.

As to the observed substituent effects, we attempted to rationalise them in several ways, namely, by means of Hammett's σ_p and σ_m (as listed by McDaniel and Brown [34]) and Brown and Okamoto's σ_p^+ constants [35], on the one hand, and by using the function of Swain and Lupton: $\sigma_x = f\mathcal{F} + r\mathcal{R}$, on the other hand. Taking into account both classical [36] and more recent [37] warning against mixing substituents with too different mesomeric abilities in the same linear correlation, and having noted the failure of $-NH_2$ or $-NMe_2$ groups to fall on the straight lines in the correlation reported by Imoto [21, 22], we also carried out these correlation analyses with, and without including the MeO group. The researcher must be aware of the fact that dispersion of data due to substituent effect should be relatively uniform in the whole range [37]. It is recommended to avoid data sets with one cluster of points and a single point far away from the cluster. The distribution of experimental points along substituent parameter axis should be uniform. The results of the correlation with σ_p^+, σ_p, σ_m, σ_{x1} and σ_{x2} constants are presented in Table 2.

The statistical analysis shows the existence of a definite trend towards improved correlation on passing from σ_m to σ_p^+, with a somewhat better colinearity of the points in the case of CCl_4. This trend is conserved in the series without MeO in CCl_4, but is replaced by an opposite tendency in the last column (DMSO, MeO excluded). This demonstrates that, indeed, the strong mesomeric electron-donating effect of the methoxy group is not accepted in the same way by the formyl-thiazole moiety in the two solvents.

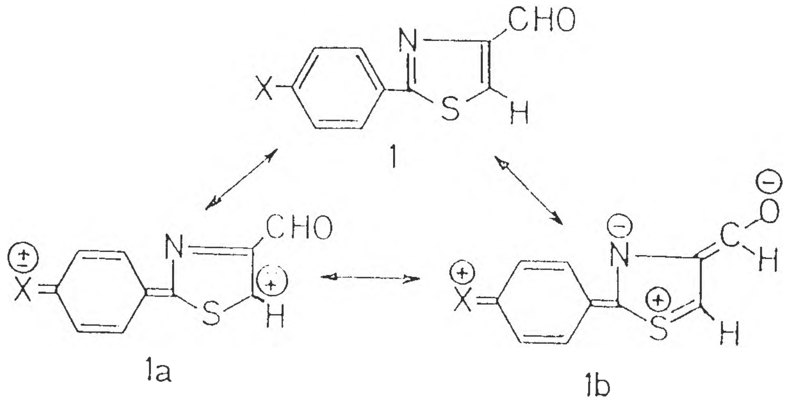
The same conclusion is arrived at if one compares the relative values of the slopes: with only one exception (σ_p^+, CCl_4), the slopes are larger for the series including methoxy, and this difference is systematically larger in DMSO than in CCl_4. This indicates that the point corresponding to the *p*-methoxy compound would fall under the straight lines which best correlate the other points, as a result of a stronger shielding of the C-5 proton, hence, of an increased mesomeric transfer of negative charge from the substituent to the thiazole ring.

The above mentioned facts are to be interpreted, in our opinion, as an indication for the predominance, especially in CCl_4 solutions, of the expected "through-conjugation" involving both C-5 and the substituent located in the position *para* on the phenyl ring (**1**<--->**1a**); along with it, there is, particularly in DMSO solutions, a contribution of polar, "zwitterionic" resonance structures (**1b**), in which the mesomeric charge is developed at the neighbouring sulphur atom, thus giving C-5 the status of a *meta* position [38]. The enhanced electron-donating effect of themethoxy group is thus easily understood, as well as the failure of $-NH_2$ and $-NMe_2$ substituents to follow the overall correlation in the investigations reported by Imoto *et al.* [21,22]

Table 2. Correlation parameters of substituent effects on ^{1}H-NMR chemical shifts by using σ_p^+, σ_p, σ_m, σ_{x1} and σ_{x2} constants.

Substituent constant	Correlation parameter	Solvent			
		CCl$_4$		DMSO	
		including MeO	excluding MeO	including MeO	excluding MeO
σ_p^+	ρ[a]	12.85	13.72	14.54	13.94
	intercept[b]	667.24	667.03	716.88	717.02
	r[c]	0.987	0.984	0.976	0.958
	s[d]	1.094	1.084	1.710	1.871
	F[e]	194.822	124.380	102.128	43.098
σ_p	ρ	17.55	15.93	19.74	16.72
	intercept	664.74	665.36	714.06	715.22
	r	0.964	0.965	0.948	0.968
	s	1.830	1.617	2.522	1.594
	F	66.488	53.650	44.266	60.846
σ_m	ρ	19.02	17.09	21.96	18.49
	intercept	662.73	663.56	711.69	713.19
	r	0.930	0.891	0.929	0.982
	s	2.700	2.782	2.933	2.480
	F	27.700	15.487	31.438	22.783
σ_{x1}=0.86 [illegible]+ 0.14[illegible]	ρ	29.92	-	33.89	-
	intercept	668.73	-	718.56	-
	r	0.944	-	0.934	-
	s	2.288	-	2.821	-
	F	40.736	-	34.394	-
σ_{x2}=0.72 [illegible]+ 0.28 [illegible]	σ	29.41	-	33.148	-
	intercept	666.081	-	715.572	-
	r	0.978	-	0.960	-
	s	1.495	-	2.167	-
	F	101.898	-	61.750	-

[a] Slopes of correlation straight lines in Hertz per σ unit of the given kind; [b] in Hertz from TMS; [c] correlation coefficients; [d] standard deviations; [e] the regression values.



In order to obtain a better image of the amount of mesomeric interaction between the substituent X and the C-5 position of thiazole, we analysed the dependence of the correlation coefficient in the least-squares analysis on the percentage of ℛ, the measure of mesomeric abilities of a given substituent in the Swain and Lupton's approach [39].

Figure 1 presents the results for the series including MeO in both solvents, whereas the series excluding MeO are given in Figure 2.

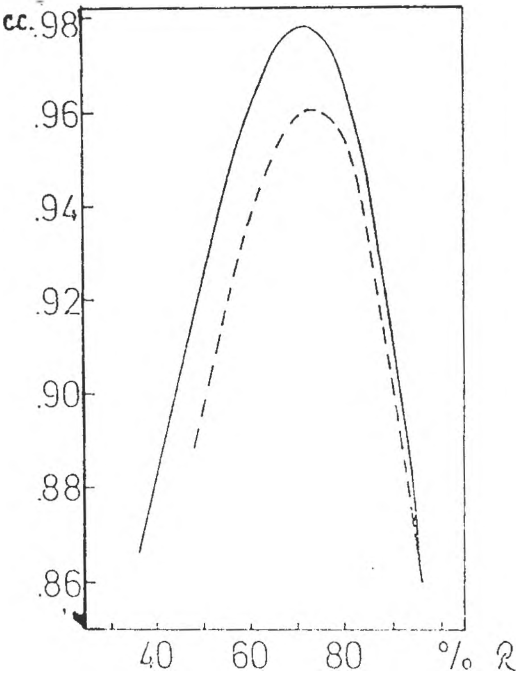


Figure 1. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents in the series of aldehydes **1**, 2-(4-methoxy-phenyl) -thiazole-4-carboxaldehyde included. Full line: in CCl_4; Broken line: in DMSO

In the first case, a rather sharp maximum is obtained at 72-74% resonance, thus substantiating the important part played by the electron interactions depicted by the structure **1a**. In the second case the correlation remains fair to good over a broader range of resonance participation, with maxima at 60% (in CCl_4) respectively 50% resonance (in DMSO), a very high value, especially if one takes into account the limited mesomeric abilities of these substituents.

These data have a bearing on the rather controversial problem of the geometry of phenylthiazole. In fact, it was to be expected that notable substituent effects as those implied by the data of Table 1 had to be primarily mesomeric in nature, but the existence of such interactions, and particularly of the through-conjugation represented by the resonance structure **1a**, requires a high degree of coplanarity in the 2-(*p*-substituted-phenyl)-thiazole.

The problem of coplanarity is inherent to the method of Miller, since it tacitly assumes that the only change on passing from the $X\text{-}C_6H_4\text{-}Y$ series to the $X\text{-}C_6H_4\text{-}T\text{-}Y$ one consists in the insertion of T, and the electronic effects of X are exclusively affected by the attenuation induced by this structural element. However, in those cases when T possesses a delocalized π system of its own, one must take into account the specific interactions between the latter and the 1,4-phenylene bridge, an asp which has been neglected so far in the application of the Jaffe-Miller method of estimating the transmission factors of conjugated cyclic systems [40-43].

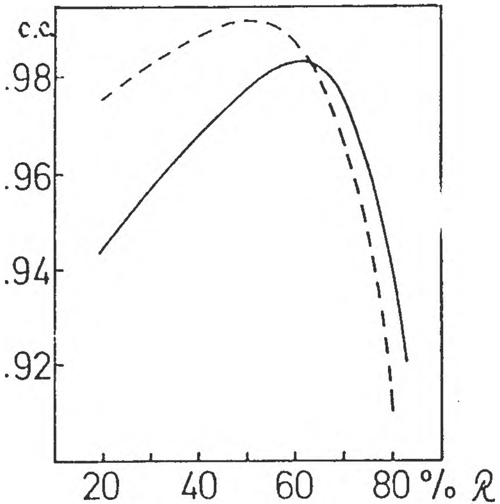


Figure 2. Variation of the correlation coefficient with the amount of the mesomeric contribution to the electronic effects of the substituents in the series of aldehydes **1**, the 4-methoxy derivative excluded. Full line : in CCl_4 ; broken line: in DMSO.

The 1,4-phenylene bridge acts as a filtering system which tends to eliminate all interactions which are solely due to the close vicinity of X and Y, respectively of X and T, and to relay almost "pure" electronic effects. The advantages of this method are obvious in the context of the work of Byron *et al.* [44] on 2'-substituted biphenyl-4-carboxylic acids, which clearly stresses the complications arising when the substituent is too close to the system T-Y being investigated. Thus, instead of being affected directly by various X groups, T is experiencing in our case the inductive and mesomeric effects of the phenyl nucleus (which remains qualitatively the same throughout the series) and are only quantitatively modulated by the group X, the polar effects of the latter adding to, or substracting from the -I and ±M effects of the phenyl nucleus. With systems such as phenyl-thiazole, this is true only as long as the two rings are coplanar and X can influence Y by both its inductive and mesomeric effects in exactly the same way as it does in the reference X-C_6H_4-Y series. It is obvious that if the two rings were held in a reciprocally perpendicular position, the charge induced by X at the carbon atom located *para* to it would exert only an inductive effect on C-2 of thiazole, and no matter how efficiently it would be relayed, by mesomeric interactions, from C-2 to C-5, the percentage of $\mathcal{R}$ in the Swain-Lupton equation would remain significantly lower than in the reference series.

In our case, the chemical shifts of the *para* protons in monosubstituted benzenes represent the X-C_6H_4-Y reference. We used the data of Speisecke and Schneider [45], obtained in cyclohexane (a solvent which can be assimilated with CCl_4, used in our determinations, as far as the polarity is concerned) for the following X: -NH_2, -OMe, -F, Cl, -Br, -H and -NO_2. In agreement with the generally accepted point of view, we found that these chemical shifts give only fair correlation with σ_p^+ and σ_p, the first being better. In exchange, as shown in Figure 3, very good correlation were obtained by using substituent parameters which include higher contributions of the mesomeric effects, the largest values of the correlation coefficients being found at 86% $\mathcal{R}$.

Since in monosubstituted benzene the mesomeric effects of the substituents manifest themselves in position *para* to the maximum extent compatible with the specific nature of the experiment being performed, we think that if the two rings were coplanar throughout the series of 2-aryl-4-thiazolecarboxaldehydes, the contribution of $\mathcal{R}$ should remain constant and close to the one in the reference series, within experimental errors.

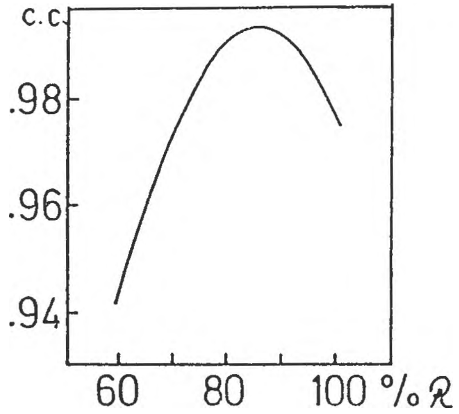


Figure 3. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents in the series of the monosubstituted benzenes.

Consequently, our data can be interpreted as an evidence for the existence of deviations from coplanarity in the system of 2-phenylthiazole since there is a diminished mesomeric contribution to the overall effects exerted by the substituents X.

To achieve the last goal of the present investigation, we compared the propagation of substituent effects in our series of compounds and in the reference one, by determining the ratio of the corresponding slopes. The large amount of mesomeric contribution in the substituent effects observed in the series of monosubstituted benzenes prompted us to adopt the slope of the correlation with σ_p^+ (34.41 Hz/unit σ_p^+ corrected for 80 MHz) as a reference value; since the chemical shifts of our compounds are also best correlated by σ_p^+, (the regression value [illegible] is, too, more significant than others). The transmission coefficient of the 2,5-thiazolylene bridge is straightforward determined by

$$\pi'_{2,5\,thz} = 12.85/34.41 = 0.373$$

In the regression analyses carried out by means of Swain and Lupton's parameters, the highest correlation coefficients are not encountered in exactly the same groups of data, since the reference series gives the best straight lines when the plots are made against substituent parameters containing 86% $\mathcal{R}$, whereas the thiazolecarboxaldehydes correlate at 72% $\mathcal{R}$.

Similar analyses involving the series in which MeO was excluded lead to the value $\pi' = 0.398$ for σ_p^+; as expected the transmission coefficient is not significantly different.

We take, consequently, the value 0.38 ± 0.02 as the attenuation coefficient of the transmission of electronic effects by the 2,5-thiazolylene bridge. These values will be given a full discussion together with the ones for the 2,4-thiazolylene bridge in a subsequent paper of this series; however, we wish to present here two concluding remarks. First, it appears that the 2,5-thiazolylene bridge relays to position 5 cca. 38% of the electronic perturbation applied at position 2; the same should be true for a reversed location of X and Y, as demonstrated by Noyce and Fike [25], who corrected, in this point too, the conclusions of Imoto [21, 22].

Finally, it is demonstrated that the 2,5-thiazolylene bridge ($\pi' = 0.38$) is a better transmitter of substituent effects than the 1,4-phenylene bridge ($\pi' = 0.24$), in contradiction with the statements of Imoto; however, our π' value appears to be slightly lower than the one for the 2,5-thienylene (0.44 [42] resp. 0.54 [43]) and definitely lower than the corresponding parameter in the furan series (0.64 [40] resp. 0.65 [43]).

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AROMATICITY OF THIAZOLES. II. TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH THE 2,4-THIAZOLYLENE BRIDGE

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ABSTRACT

The propagation of electronic effects from position 2 to position 4 of thiazole was investigated by correlating the C=O stretching frequencies in IR spectra, and CHO-proton chemical shifts in ^{1}H-NMR spectra of 2-(4-substituted-phenyl)-4-thiazolecarboxaldehydes **1** with substituent constants, by means of the Hammett equation, and by using the Swain-Lupton analysis. Both IR- and NMR- data led to the same value of the transmission coefficient of the 2,4-thiazolylene bridge, 0.42±0.02.

INTRODUCTION

In the first paper of this series [1] we reported that the influence exerted by a substituent on position 2 of thiazole is attenuated by a factor of 0.38 during its propagation to position 5 of the same heterocycle. In order to obtain more information on the polarizability of the electronic system of thiazole, we found that it would be necessary to determine the value of the transmission coefficient of the 2,4 thiazolylene bridge, which corresponds to what is usually called a "pseudo-*meta*" relationship [2-4] of the two substituents in five-membered rings. Although there are data in literature on the estimation of 2,5-heteroarylene bridges in the case of furan [5, 6] and thiophene [6, 7] no attempt has been reported as yet of expressing in quantitative terms the attenuation of electronic substituent effects by the corresponding 2,4-bridges.

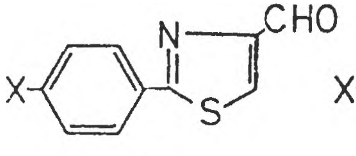
We wish to report in this paper the results obtained by correlating with substituent constants, by means of the Hammett equation, the C=O stretching vibrations in the IR spectra, and the CHO proton chemical shifts in the ^{1}H-NMR spectra of 2-(*p*-substituted)-thiazolecarboxaldehydes in several solvents.

EXPERIMENTAL

The preparation of the compounds **1** and the conditions for the recording of the NMR spectra were previously described [1]. The IR spectra were recorded on a Carl Zeiss Jena UR-10 double-beam recording spectrophotometer under conditions ensuring an accuracy better than ±0.5 cm^{-1}.

RESULTS AND DISCUSSION

The method used for estimating the factor $\pi'_{2,4\,thz}$ is principially the same as the one described in the previous paper [1] for measuring of $\pi'_{2,5\,thz}$ and consists in the determination of the ratio $\rho 1/\rho 2$ of the slopes characterizing the correlation of the properties of -CHO groups with substituent constants in the investigated **1** and reference **2** series.



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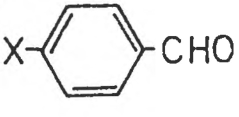

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The influence of the substituents was expressed in quantitative terms by means of Hammett's σ_p and σ_m constants [8] and by Brown and Okamoto's electrophilic σ_p^+ constants [9].

We also carried out a detailed analysis of the relative contributions of inductive and mesomeric effects of the substituents by using the Swain and Lupton's function [10]

$$\sigma_x = f\mathcal{F} + r\mathcal{R}$$

The determination of the transmisssion coefficient of the 2,4-thiazolylene bridge from IR spectrometric data.

The C=O stretching vibrations of **1**, determined in CCl_4 and $CHCl_3$ solutions are presented in Table 1. These data point out the existence of a measurable influence of both the substituents and the solvents.

Table 1. Carbonyl stretching frequencies of 2-aryl-4-thiazolcarboxaldehydes 1

Solvent	Substituent						
	MeO	Me	MeCONH	H	Cl	Br	NO_2
CCl_4	1706.0	1707.0	1707.5	1708.0	1709.0	1709.5	1711.0
$CHCl_3$	1703.5	1704.5	1705.0	1706.5	1707.5	1708.0	1710.5

As a first observation, we wish to note that, unlike 2-aryl-5-formyl-furans [5] and thiophenes [7], which give rise to bands located 20-24, resp. 28-35 cm^{-1} lower than the corresponding benzaldehydes, the $\nu_{C=O}$ frequencies of **1** are a few cm^{-1} apart from the ones in the reference series. This proves that in our case there is a considerably less important conjugation between ring and substituent π electrons that in the hetarylcarboxaldehydes mentioned above, and the comparison with the series **2** can be made much easier; this also substantiated the close similitudes between position 4 of thiazole and those of the benzene ring, derived from chemical [11, 12], physical [13] and theoretical [14, 15] investigations.

The solvent effects provide another opportunity for comparing **1** with 2-aryl-5-formylfurans and thiophenes. Inspection of Table 1 reveals that the frequencies measured in $CHCl_3$ are systematically 1.5-2.5 cm^{-1} lower than those determined in CCl_4, and this difference presents a slight trend towards attenuation as the electron-withdrawing abilities of X increase. A similar phenomenon, but involving much larger variations, was observed in the case of 4-substituted benzaldehydes (4-18 cm^{-1}), 2-aryl- 5-thiophenecarboxaldehydes (7-12 cm^{-1}) [7] and 2-aryl-5-furaldehydes (10-13 cm^{-1}) [5], the least affected by the change of the solvent being always the nitroderivative and the frequencies in $CHCl_3$ being constantly lower. The correlations of $\nu_{C=O}$ values of **1** with substituent constants are presented in Table 2.

Consenquently, in spite of changes due to the "pseudo-*meta*" disposition of the interacting groups, and to the specific structure of thiazole, the basic phenomena remain qualitatively the same in all the series under discussion, and only quantitative differences are observed, thus allowing a meaningful comparison of physico-chemical parameters of 1 and 2. The analysis was carried out on parallel series of compounds, with, and without the methoxy group, the one with strong mesomeric abilities, taking into account the already presented literature arguments, and the results for the 2,5-thiazolylene bridge [1].

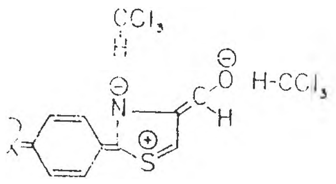
A comparison of the data in Table 2 with the corresponding ones for the correlation of the chemical shifts of C-5 protons of the same compounds in the ^{1}H-NMR spectra [1] demonstrates the existence of at least two fundamental features which are common to these two correlations, albeit the physical nature of the experiments and the relative positions of the interacting groups are different.

Table 2. Correlation parameters of the least squares analyses of substituent effects on carbonyl stretching frequencies in IR spectra of 1 by using σ_p^+, σ_p, σ_m and σ_x constants.

Substituent constant	Correlation parameter	Solvent			
		CCl$_4$		CHCl$_3$	
		including MeO	excluding MeO	including MeO	excluding MeO
σ_p^+	ρ[a]	3.678	4.473	4.836	5.463
	intercept[b]	1708.150	1707.967	1706.700	1706.553
	r[c]	0.902	0.908	0.978	0.984
	s[d]	0.936	0.907	0.549	0.452
	F[e]	21.793	18.864	109.488	133.253
σ_p	ρ	5.038	4.972	6.707	6.348
	intercept	1707.432	1707.457	1705.744	1705.882
	r	0.883	0.922	0.971	0.964
	s	1.016	1.135	0.632	0.651
	F	17.760	10.622	81.340	52.664
σ_m	ρ	5.230	5.107	7.261	6.861
	intercept	1706.905	1706.958	1704.980	1707.153
	r	0.868	0.944	0.926	0.879
	s	1.277	1.426	0.993	1.082
	F	9.405	5.262	29.995	16.490
$\sigma_x=0.68\mathcal{R} + 0.32\mathcal{F}$	ρ	8.181	8.304	6.853	10.509
	intercept	1707.622	1707.593	1705.384	1706.062
	r	0.891	0.862	0.957	0.966
	s	0.985	1.100	0.756	0.632
	F	19.500	11.549	55.260	56.100

[a] Slope in cm^{-1}/units of the given kind; [b] in cm^{-1}; [c] correlation coefficients; [d] standard deviation; [e] Fischer parameters.

First, the best correlation in the group including methoxy is found for σ_p^+ and σ_p, that is, the sets of constants which reflect better the mesomeric influences of the substituents. However, the former are only slightly better that the latter, whereas in the case of the 2,5-thiazolylene bridge the correlation coefficients for σ_p^+ were clearly dominating the scene. Second, the series without methoxy are closer to the best fit straight line that the other series, and the trends of their evolutions with respect to the substituent constants are again opposite for the polar solvent and for the non-polar one. The important fact is that in the 2,4-disubstituted series the situation is reversed with regard to that in 2,5-series, namely, in CCl$_4$ the highest correlation coefficients are for σ_m and in the more polar CHCl$_3$ a value as high as 0.984 is reached for σ_p^+. In fact, this is exactly what was to be expected if limiting structures like **1a**, stabilized by solvation in the polar solvent, and perhaps by hydrogen bonding, would bring an important contribution to the state of the molecule in the chloroform solutions.



1a

Such a distorsion of the electron distribution gives position 5, as already mentioned [1], the status of a "*meta*" position, since it is now located "*ortho*" to the charge developed by mesomeric interactions, while position 4 becomes, in turn, a "*para*" position, and through-conjugation of CHO and X groups is now possible. This phenomenon can only be observed when MeO is excluded, because the very high mesomeric electron-donating activity of the latter brings about the changes in geometry already discussed [1]. However, the fundamental "pseudo-*meta*" nature of position 4 still remains detectable, as there are only minute improvements in correlation on passing from σ_p to σ_p^+ , as compared with the case of the interaction between positions 2 and 5.

The Swain-Lupton analyses were carried out as previously described [1] and showed again well-defined maxima in the plots of correlation coefficients against % ℛ for the series including methoxy.

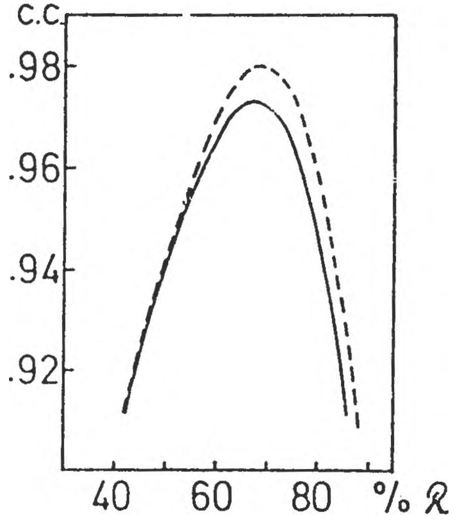


Figure 1. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents in the series of aldehydes **1**, IR-spectra, 2-(4-methoxyphenyl)-thiazole-4-carboxaldehyde included. Full line: CCl_4, broken line: $CHCl_3$.

As it is described by Figure 1, the maxima are found at 68% ℛ for both CCl_4 and $CHCl_3$ solutions, that is, 4-6% lower that for the 2,5-bridge, a tendency in agreement with the "pseudo-*meta*" character of position 4, which diminishes to some extent the contribution of mesomeric interactions. The percentage of ℛ still remains very high, due to the already presented reasons [1], and to the particular property of five-membered rings, pointed out by Noyce [3, 15] to relay from position 2 to position 4 a higher amount of mesomeric interaction than would be expected for a "*meta*" relationship.

We would like to point out that, in accord with the hypothesis of an increased importance of forms like **1a** in $CHCl_3$, the maximum of the plot for this solvent is slightly, but definitely, shifted towards higher %ℛ. As expected, this shift is more marked in the plots corresponding to the series without methoxy (fig. 2), which present the same flat appearance as in the case of the 2,5-interactions [1].

The present authors are fully aware of the criticisms directed toward the Swain-Lupton method; a comparison of data in Tables 2 and 5 is clearly demonstrating that in our case, when rather good correlations are obtained with σ_p and σ_p^+ , the σ_x values, (even in the best possible case, as shown by our method of optimisation of resonance contributions) give correlations usually situated in between those obtained by "classical" sets of constants [16].

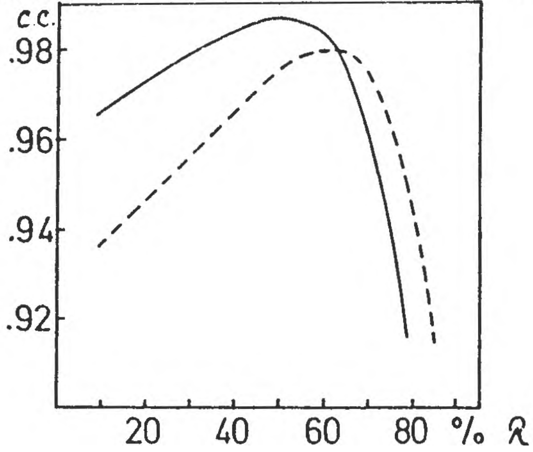


Figure 2. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents in the series of aldehydes **1**; IR-spectra, the 4-methoxy derivative excluded. Full line: CCl_4; broken line: $CHCl_3$.

In the determination of the transmission coefficient of the 2,4-thiazolylene bridge we have to use the Hammett plots of the $\nu_{C=O}$ for **2** as reference data. Since the most elaborated reports on the matter, those of Rao [17] and Perjessy [5] gave somewhat different values, we also investigated, under the same conditions as used for **1**, a limited number of 4-X-substituted-benzaldehydes (X= NMe_2, H, Cl, NO_2).
The relevant data of the corresponding statistical analysis for CCl_4 solutions are given in Table 3. Correlation with σ include both 4- and 3-substituted benzaldehydes, since it is well established that the corresponding points fall on the same straight line, provided the appropriate σ_p or σ_m constants used.

Table 3. Regression analysis parameters for the correlation of $\nu_{C=O}$ with substituent constants for substituted benzaldehydes in CCl_4.

Substituent constant	Origin of data	Parameters			
		intercept cm^{-1}	slope cm^{-1} / unit σ	r	Standard deviation
σ_p^+	Rao[17]	1707.0	9.1	0.989	3.1
	Perjessy[5]	1711.5	9.16	0.991	1.0
	Present work	1710.5	8.22	0.997	0.8
σ	Rao	1704.0	10.9	0.872	2.8
	Perjessy	1709.4	13.75	0.959	2.1
	Present work	1708.0	12.74	0.975	2.3

Since the slopes and the statistical weights are not too scattered in the three cases, we decided to use average values as ρ_2 (8.83); we also choosed the correlations with σ_p^+, which give the best fits in both the reference and the investigated series. The value 0.415 is thus arrived at for the transmission coefficient of the 2,4-thiazolylene bridge in CCl_4, by means of IR spectrometric data.By using the $\nu_{C=O}$ frequencies of benzaldehydes determined by Perjessy in $CHCl_3$, we calculated a slope of 15.70 cm^{-1}/ σ_p^+ unit (r=0.989) and this value led us to the transmission coefficient $\pi'_{2,4\,thz(CHCl3)} = 0.308$.

The determination of the transmission coefficient of the 2,4-thiazolylene bridge from ^{1}H-NMR data.

The signals of the aldehydic protons in ^{1}H-NMR spectra represent another probe for the investigation of the propagation of substituent effects through the 2,4-bridge of **1**. Table 4 summarises the experimental data and Table 5 displays the correlation parameters.

Table 4. Chemical shifts of aldehydic proton in ^{1}H-NMR spectra of compounds 1, (δ in Hz from TMS).

Solvent	Substituent						
	MeO	Me	MeCONH	H	Cl	Br	NO_2
CCl_4	822	824	826	826	829	829	834
DMSO	810	812	813	813	814	815	818

Table 5. Correlation parameters of least squares analyses of substituent effects on the chemical shifts of the aldehydic proton in the ^{1}H-NMR spectra of 1 by using σ_p^+, σ_p, σ_m and σ_x constants.

Substituent constant	Correlation parameter	Solvent			
		CCl_4		DMSO	
		including MeO	excluding MeO	including MeO	excluding MeO
σ_p^+	ρ^a	7.90	8.67	5.08	5.27
	intercept^b	827.47	827.29	813.78	813.74
	r^c	0.975	0.971	0.983	0.973
	s^d	0.996	0.941	0.507	0.552
	F^e	96.622	66.041	141.609	70.975
σ_p	ρ	11.23	10.53	7.06	6.36
	intercept	825.87	826.14	812.77	813.05
	r	0.990	0.995	0.977	0.989
	s	0.600	0.402	0.576	0.344
	F	253.232	378.677	108.786	189.314
σ_m	ρ	12.54	11.89	7.82	7.04
	intercept	824.52	824.80	811.93	812.27
	r	0.965	0.967	0.954	0.944
	s	0.959	0.994	0.825	0.787
	F	95.960	58.723	50.425	32.858
$\sigma_x=0.68\sigma_I+$ $0.32\sigma_R$	ρ	18.47	18.06	11.76	10.99
	intercept	826.75	826.82	813.32	813.44
	r	0.984	0.977	0.983	0.980
	s	0.757	0.832	0.498	0.473
	F	156.857	85.543	147.187	97.86

^{a}Slopes (Hertz/unit σ of the given kind); ^{b}in Hertz from TMS; ^{c}correlation coefficients; ^{d}standard deviation; ^{e}Fischer parameters.

As it was expected, the general trends were the same as those found by inspecting the figures in Table 2, and obviously they were interpreted in the same manner. The only differences to be noted are those derived from the specific ways in which the two physical methods, IR- and NMR- spectroscopy, reflect the influences of the substituents in the series of arylcarboxaldehydes; the best correlation in the series of 4-substituted-benzaldehydes are obtained with σ_p^+ in IR and with σ_p in NMR spectra. We checked the literature data in our conditions on the same set of 2 that we used for IR-measurements (*vide supra*) and found that the correlation coefficient reaches 0.992 in CCl_4 and 0.995 in DMSO when the CHO proton chemical shifts were plotted against σ_p and was only 0.969 in CCl_4 and 0.959 in DMSO when σ_p^+ were used as the substituent constants. This explains why although σ_p^+ were again slightly better than σ_p in the series including methoxy, the other series constantly showed the best correlation with σ_p [18]. However, a comparison of the correlation coefficients for σ_p^+ and σ_m reveals that the opposite evolution of the correlations for the polar and the unpolar solvent remains exactly the same as in the case of the data derived from IR-spectroscopy. The variation of the correlation coefficients with the mesomeric contribution to the substituent effects shows maxima at 72% $\mathcal{R}$ for both solvents (fig.3) in the groups including methoxy, and at 58% $\mathcal{R}$ (CCl_4) and 64% $\mathcal{R}$ (DMSO) in the ones excluding MeO (fig.4).

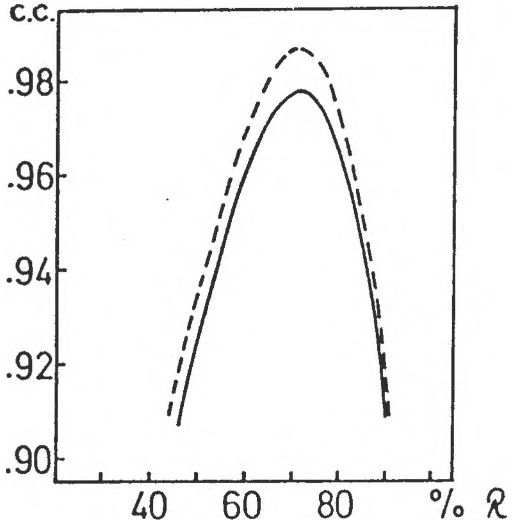


Figure 3. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents in the series of aldehydes **1**, NMR-spectra, the 4-methoxy derivative included. Full line: CCl_4; broken line: DMSO.

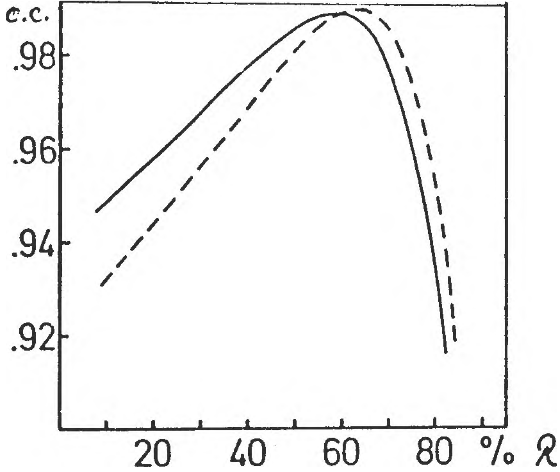


Figure 4. Variation of the correlation coefficient with the amount of mesomeric contribution to the electronic effects of the substituents the series of aldehydes **1**, NMR-spectra, the 4-methoxy derivative excluded. Full line: CCl_4; broken line: DMSO.

Taking into account that the best fits were obtained with σ_p in the reference series, and that, even in the series including methoxy, σ_p gives correlation coefficients which are inferior by only 0.4-0.6% of the nominal value, the comparison of the slopes in the investigated and reference series has to be made by using the figures obtained in the σ_p correlations. The transmission coefficient thus determined has the value 0 440 in CCl_4 and 0.310 in DMSO.

CONCLUSION

The close similarity between the response of $\nu_{C=O}$ frequencies and of aldehydic protons chemical shifts to substituent effects demonstrates that both phenomena have the same underlying physical reason, namely, the specific transmission through the 2,4-thiazolylene bridge of the electronic perturbations produced by the substituents.

The value of transmission coefficients determined from IR and NMR data agree very well, 0.415 and 0.440, respectively (in CCl_4), and we conclude that the 2,4-thiazolylene bridge can be characterised by the value $\pi'_{2,4 thz} = 0.42 \pm 0.02$ in solvents of low polarity.

A comparative discussion of the transmission of substituent effects through the two thiazolylene bridges is given in the following paper of this series.

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A NOVEL NONTAUTOMERIC OXOPYRIMIDINE: SYNTHESIS AND CHARACTERIZATION OF 2-DIETHYLAMINO-5,5,6-TRIMETHYL-4(5H)-PYRIMIDINONE

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ABSTRACT

Reaction of ethyl 2,2-dimethylacetoacetate **2** with *N,N*-diethylguanidine nitrate **3** affords 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**, a novel nontautomeric oxopyrimidine, characterized by ^{1}H and ^{13}C NMR, DRIFTS and MS spectrometry. The NMR spectral parameters of **1** reveal the diastereotopicity of the two prostereogenic methyl groups attached to C5 (Dd_H = 0.08 ppm; Dd_C = 4.79 ppm). The semiempirical PM3 method is employed to estimate the optimal geometry of **1** in gas-phase and in aqueous media, which is qualitatively correlated with the physico-chemical properties of **1**. The ^{1}H and ^{13}C NMR spectra of *N,N*-diethylguanidine nitrate **3** along with the ^{13}C NMR spectrum of ethyl 2,2-dimethylacetoacetate **2** are reported here for the first time.

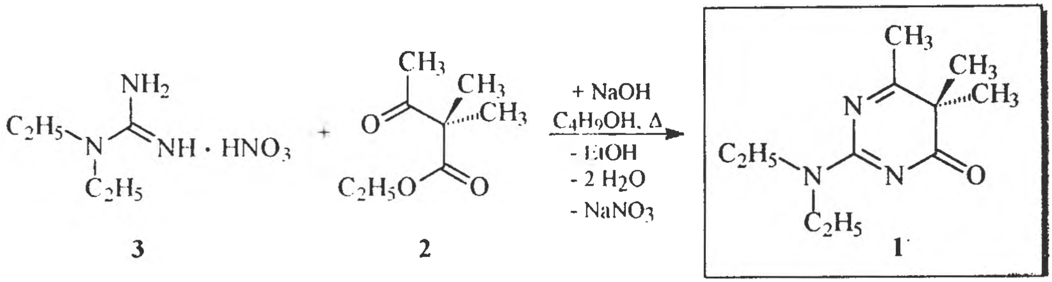
INTRODUCTION

The pyrimidine system is an important structural unit in numerous natural products of biological importance [1], as well as in compounds of pharmaceutical interest [2] and agrochemicals [3]. The pyrimidine ring bearing various substituents can be formed directly by cyclization of one or more fragments or by modification (ring expansion, ring contraction, rearrangement) of other heterocycles [4]. The condensation of two fragments, with any preattached substituents, one to provide N1+C2+N3 and the other to provide C4+C5+C6 of the resulting pyrimidine ring, is the foremost procedure and is known accordingly as the "Principal Synthesis" [5]. Due to their accessibility, β-keto esters have been used more extensively than other synthones in the Principal Synthesis. They react with amidines [6], guanidines [7], ureas [8] and thioureas [9] to afford the corresponding pyrimidines. In the search for novel pyrimidines [10], we have looked at the Principal Synthesis employing β-keto esters, as a route to new nontautomeric pyrimidinones. Qualitative correlations of the spectral characteristics of nontautomeric or fixed pyrimidinones with those of tautomeric ones, can help to predict and evaluate the nature and extent of pyrimidine tautomerism.

Herein, we report the synthesis of 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**, a novel nontautomeric 4-pyrimidinone prepared from the condensation reaction of ethyl 2,2-dimethylacetoacetate **2** with *N,N*-diethylguanidine nitrate **3**, and characterized by ^{1}H and ^{13}C NMR, DRIFTS [11] and MS spectrometry. The semiempirical PM3 method [12] is used to estimate the optimal geometry of **1** in gas-phase and in aqueous media. The ^{1}H and ^{13}C NMR spectra of *N,N*-diethylguanidine nitrate **3** and the ^{13}C NMR spectrum of ethyl 2,2-dimethylacetoacetate **2** are reported here for the first time.

RESULTS AND DISCUSSION

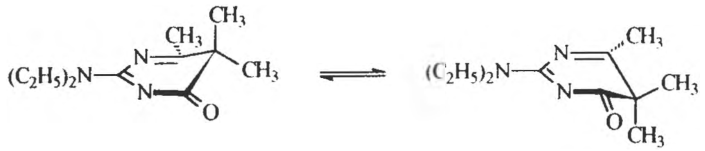
2-Diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1** was synthesized by condensation of ethyl 2,2-dimethylacetoacetate **2** with *N,N*-diethylguanidine nitrate **3**, (Scheme 1). The b-keto ester **2** and *N,N*-diethylguanidine nitrate were obtained according to literature procedures and were characterized by ^{1}H and ^{13}C NMR. Thus, ethyl 2,2-dimethylacetoacetate **2** was prepared by alkylation of ethyl acetoacetate with methyl iodide in EtOH/EtONa (or *tert*-amyl alcohol / sodium *tert*-amyloxide) [13], and *N,N*-diethylguanidine nitrate **3** was synthesized from diethylammonium nitrate and calcium cyanamide [14].



Scheme 1. Synthesis of 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**

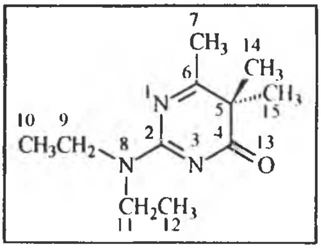
^{13}C NMR spectroscopy has been shown to provide a clear distinction in a variety of nitrogen heterocyclic systems between dissimilar tautomeric forms [15]. In order to make use of the fixed tautomeric structure in 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**, which can serve as a comparison for other tautomeric pyrimidinones, we completed the individual assignments of the ^{13}C NMR signals of **1** (Table 1) from its 2D HMQC spectrum.

The contour plot of the ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) [16] spectrum of **1** (in D_2O) is shown in Figure 1. Contour peaks appear only between protons and their directly coupled carbon atoms. The advantage of the HMQC technique over the classical H,C-COSY [17], which gives essentially the same spectrum, is that the experimental time is drastically shortened because of the higher sensitivity for ^{13}C in this method. We attributed the ^{13}C NMR signals based on the proton assignments and the H/C correlations from the HMQC spectrum. In addition, the ^{1}H and ^{13}C NMR spectra of **1** revealed the diastereotopicity of the two methyl groups attached to C5 (Dd_H = 0.08 ppm; Dd_C = 4.79 ppm). A temperature dependence NMR experiment (in D_2O) showed identical chemical shift differences even at 80°C. The asymmetry of the pyrimidinonic ring along the C2-C5 axis places the two methyl groups in different environments. Thus, the two methyls at C5 are *cis* and *trans*, respectively, to the carbonyl at C4, the methyl at C6 and the diethylamino group at C2, (Scheme 2). Since there is no chiral center in **1**, this diastereotopicity makes the two methyls at C5 prostereogenic, and thus, replacement of one methyl by a different group would create not a chiral, in the conventional interpretation, but a stereogenic center [18].



Scheme 2. The low-frequency out-of-plane vibration of C5 (PM3 calculated value of 30 cm^{-1}) in 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**

Table 1. ^{1}H and ^{13}C NMR chemical shifts of 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1** in D_2O



Position	δ (ppm) ^{1}H	δ (ppm) ^{13}C
2	-	159.18
4	-	190.43
5	-	48.08
6	-	87.85
7	1.32	24.19
9, 11	3.25	45.15
10, 12	0.97	15.22
14, 15[a]	0.90, 0.98	20.17, 24.96

[a] The signals corresponding to H_{14} and H_{15}, C_{14} and C_{15}, have not been assigned individually

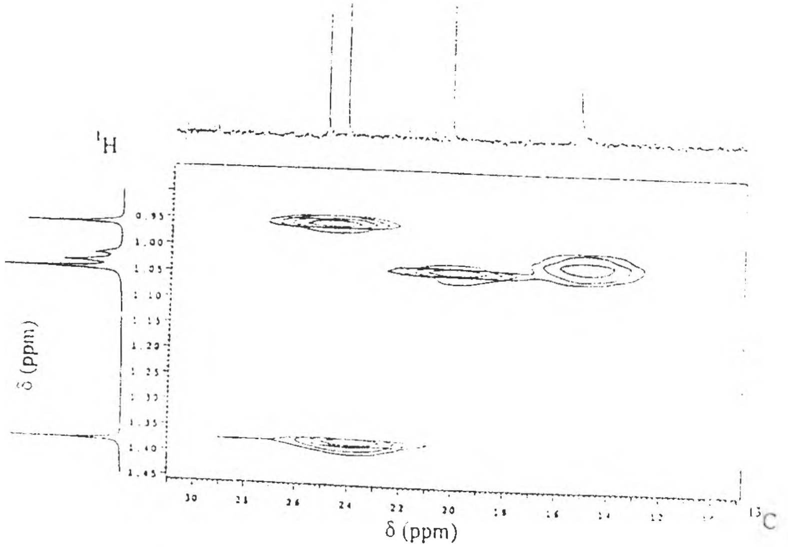


Fig. 1. The partial HQ[illegible] spectrum of 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**.

Surprisingly, 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1** is soluble in water and insoluble in common organic solvents. 4(*3H*)-Pyrimidinone **4** shows similar behavior [19]; nevertheless the solubility of **4** in water is enhanced by the hydrogen bonding ability of the NH group, which compound **1** lacks. The hydrophilicity of **1** could be due to the ring nitrogens and the prevalence of zwitterionic structures I-IV (Scheme 3), which allow limited dipol-dipol interactions and hydrogen bonding with the solvent at these sites. The DRIFTS spectrum of **1** (KBr powder) shows two IR bands in the region of the C=O stretching absorption, at 1630 and 1566 cm^{-1} (more intense). These extremely low frequencies indicate also extensive delocalization at the carbonyl [20], in agreement with molecular orbital calculations presented below.

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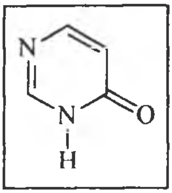
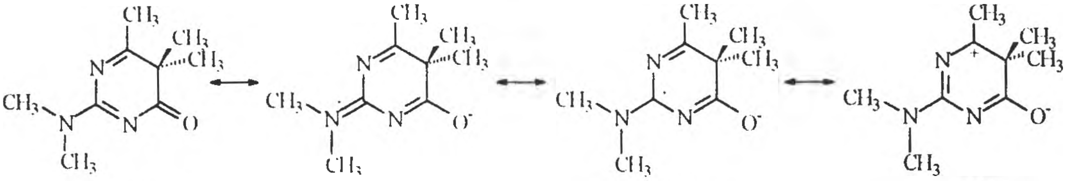




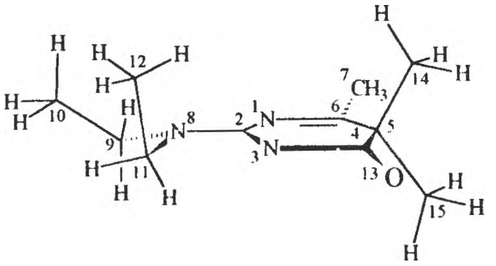
I II III IV

Scheme 3. Resonance structures of 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**

Semiempirical PM3 calculations [12] were performed to estimate the optimal geometry of **1** in gas-phase (GP) and in water (Table 2). Both calculations, in GP and in water, show the lone-pair of the exocyclic amine orthogonal on the plane of the ring (N8 is *ca.* 3-4° out of the ring plane). Accordingly, 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**, can benefit from the resonance of the exocyclic tertiary amine with the pyrimidinonic ring. The calculated geometries, atomic charges and bond orders (Table 3) indicate the canonical form II as having an important contribution to the resonance hybrid.

The accuracy of the PM3 method, as of any semiempirical molecular orbital method, is limited to the accuracy of the experimental data used for parametrization. However, semiempirical methods are fast enough and accurate enough for routine applications, and the computed results can be used for qualitative estimations. For example, the semiempirical MNDO method [21] has been previously used to calculate geometries for various pyrimidinones and the results were shown to be in good agreement with available experimental data [22]. Previous studies using the PM3 method found average errors of 0.036 Å for bond lengths, 3.9° for bond angles and 14.9° for dihedral angles, which make the method reliable for prediction of molecular geometries [23]. Nevertheless, semiempirical methods are not suited for more elaborated computations, such as the relative stability of pyrimidinonic tautomers, where extensive ab initio methods are needed for accurate predictions [24].

Table 2. Selected PM3 calculated bond distances (r, in Å), bond angles ($\angle$, in degrees °) and dihedrals (q, in degrees °) in 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**[a]



Parameter	Gas-phase	Water[b]
$r(N_1-C_2)$	1.4393	1.4361
$r(C_2-N_3)$	1.3244	1.3457
$r(N_3-C_4)$	1.4293	1.4113
$r(C_4-O_{13})$	1.2135	1.2268
$r(C_2-N_8)$	1.4010	1.3765
$\angle(C_2N_8C_9)$	119.80	121.4294
$\angle(C_4C_5C_6)$	111.64	111.3211
$q(C_6N_1C_2N_3)$	0.18	0.75
$q(C_2N_3C_4O_{13})$	1.34	0.49
$q(C_2N_1C_6C_7)$	0.34	0.29
$q(C_5C_4C_6N_1)$	0.85	1.01

[a] All PM3 calculations (Table 2, Table 3) were performed with complete geometry optimization. Program used: Spartan version 4.0, running on a cluster of SGI Indigos. See W. J. Hehre, L. D. Burke and A. J. Shusterman, A SPARTAN Tutorial. Wavefunction Inc., Irvine, CA, 1995.

[b] The solvation model used for water was developed by Dixon, Leonard and Hehre, based on the earlier SM2 model. See R. W. Dixon, J. M. Leonard and W. J. Hehn, *Isr. J. Chem.*, **1993**, *33*, 427.

Both calculations, in GP and in water, show the lone-pair of the exocyclic amine orthogonal on the plane of the ring (N8 is *ca.* 3-4° out of the ring plane). Accordingly, 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**, can benefit from the resonance of the exocyclic tertiary amine with the pyrimidinonic ring. The calculated geometries, atomic charges and bond orders (Table 3) indicate the canonical form **II** as having an important contribution to the resonance hybrid.

The accuracy of the PM3 method, as of any semiempirical molecular orbital method, is limited to the accuracy of the experimental data used for parametrization. However, semiempirical methods fast enough and accurate enough for routine applications, and the computed results can be used for qualitative estimations. For example, the semiempirical MNDO method [21] has been previously used to calculate geometries for various pyrimidinones and the results were shown to be in good agreement with available experimental data [22]. Previous studies using the PM3 method found average errors of 0.036 Å for bond lengths, 3.9° for bond angles and 14.9° for dihedral angles, which make the method reliable for prediction of molecular geometries [23]. Nevertheless, semiempirical methods are not suited for more elaborated computations, such as the relative stability of pyrimidinonic tautomers, where extensive ab initio methods are needed for accurate predictions [24].

Table 3. Selected PM3 calculated electrostatic atomic charges and bond orders in 2-diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone **1**

Charge/Bond order	Gas-phase	Water
C_2	0.96	0.86
N_3	-0.90	-0.96
C_5	-0.15	-0.09
C_6	0.38	0.41
N_8	-0.55	-0.33
O_{13}	-0.56	-0.68
C_2-N_3	1.59475	1.43792
C_2-N_8	1.18660	1.32182
N_3-C_4	1.00484	1.07533
C_4-O_{13}	1.88703	1.32182

The 2-, 4-, and 6-positions of pyrimidines are naturally deficient in p-electrons due to the electron localization at the ring-nitrogen atoms, and accordingly are predisposed to direct nucleophilic substitutions [25]. However, NMR samples of **1** in D_2O after prolonged storage (several hours) show extensive decomposition with the appearance of two new ^1H NMR peaks at d 2.03 (s) and 1.10 ppm (s), in the relative ratio of 1:2 (1×CH_3:2×CH_3). This result suggests ring cleavage by nucleophilic attack of D_2O at C6, and is noteworthy in comparison with the stability of the pyrimidinonic ring in such reactions. One explanation could be that the aromaticity of the pyrimidinic (4-pyrimidinonic) ring is interrupted by substitution at C5, therefore making the ring more susceptible to decomposition. Further studies to identify the hydrolysis products and to employ this unusual reactivity in subsequent transformations of **1** are underway.

EXPERIMENTAL

Ethanol and butanol were distilled from Na. All other reagents were used as obtained from commercial sources and purified according to standard procedures.

Melting points were measured with a Thomas Hoover capillary melting point apparatus and were uncorrected. Diffuse reflectance infrared spectra (DRIFTS) were recorded using a Perkin-Elmer Spectrum-2000 FT-IR spectrometer equipped with a Harrick diffuse reflectance attachment. ^1H and ^{13}C NMR spectra were recorded on a Varian FT-NMR 300 MHz spectrometer at ambient temperature. Chemical shifts are given in ppm on the d scale, relative to solvent signals (^1H NMR: 7.24 for $CDCl_3$, and 4.63 for D_2O; ^{13}C NMR: 77.0 for $CDCl_3$), and multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The ^{13}C NMR spectra in D_2O are referenced to Na TMSP (sodium trimethylsilylpropionate), d = 0. The HQMC spectrum of **1** was recorded on a Varian FT-NMR 500 MHz. The mass spectrum of **1** was obtained using a VG Trio-1 GC-MS spectrometer

Ethyl 2,2-dimethylacetoacetate 2

Ethyl 2,2-dimethylacetoacetate **2** was prepared according to literature procedures [13] from ethyl acetoacetate and methyl iodide in EtONa/EtOH: n_D^{25} = 1.4165 (lit. [13b], n_D^{25} = 1.4162); b.p. 60.5-61.5°C at 12 torr; ^{1}H NMR (300 MHz, $CDCl_3$) d 1.19 (t, *J* = 7.1 Hz, 6H), 1.29 (s, 6H), 2.09 (s, 3H), 4.12 (q, *J* = 7.1 Hz, 4H), in agreement with previous literature reports [26]; ^{13}C NMR (300 MHz, $CDCl_3$) d 13.91, 21.72, 25.62, 55.61, 61.22, 173.50, 205.85.

N,N-Diethylguanidine nitrate 3

N,N-Diethylguanidine nitrate **3** was prepared from diethylammonium nitrate and calcium cyanamide, $CaCN_2$, according to the literature procedure [14]: m.p. = 169°C (lit. 170-171°C); ^{1}H NMR (300 MHz, D_2O) d 1.01 (t, *J* = 7.2 Hz, 6H), 3.18 (q, *J* = 7.2 Hz, 4H); ^{13}C NMR (300 MHz, D_2O/Na TMSP) d 14.56, 46.10, 158.05.

2-Diethylamino-5,5,6-trimethyl-4(*5H*)-pyrimidinone 1

A solution of 4.1 g sodium hydroxide (0.102 moles) in 100 ml of ethanol and 18 g of *N,N*-diethylguanidine nitrate **3** (0.101 moles) was refluxed for 30 minutes, 100 ml 1-butanol were added and the mixture was vacuum distilled to about half its volume, cooled in ice and filtered. Ethyl 2,2-dimethylacetoacetate **2** 16 ml (0.100 moles) in 100 ml 1-butanol were added dropwise (*ca.* 2 hours), under stirring, to the filtrate. The reaction mixture was stirred for 1 hour at room temperature and refluxed for 2 hours. After cooling, the solvent was vacuum distilled, 200 ml acetone were added, and the mixture was stored in the refrigerator until the next day when white crystals separated from the yellowish liquid. Recrystallization from nitromethane gave 7.7 g (37 %) of white needle crystals: m.p. = 140°C (1×HCl m.p. = 171-174°C); DRIFTS (KBr powder): 723, 1082, 1120, 1335, 1448, 1475, 1490, 1566, 1630, 2939, 2986, 3223 cm^{-1}; ^{1}H NMR (300 MHz, D_2O) d 3.25 (q, *J* = 7 Hz, 4H), 1.32 (s, 3H), 0.98 (s, 3H), 0.97 (t, *J* = 7 Hz, 6H), 0.90 (s, 3H); ^{13}C NMR (300 MHz, D_2O/Na TMSP) d 190.43, 159.18, 87.85, 48.08, 45.15, 24.96, 24.19, 20.17, 15.22; MS (EI) m/e for $C_{11}H_{19}N_3O$ 209 ($[M]^+$), 194 ($[M]^+$-15), 166 ($[M]^+$-43), 97 ($[M]^+$-112), 69 ($[M]^+$-140]).

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A NEW POLYMORPHIC FORM OF DIPHENYLARSINIC ACID

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ABSTRACT

A second monoclinic modification of diphenylarsinic acid containing two independent molecules in the asymmetric unit has been isolated. The compound is obtained as one component of the mixture which results when bis(diphenylarsine) oxide is oxidised with iodine.

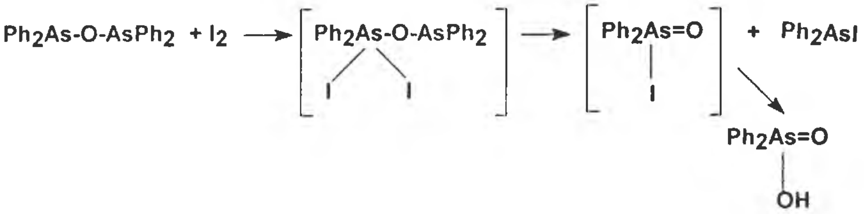
INTRODUCTION

We have been interested lately in the oxidation of a number of organoarsenic(III) compounds, including bis[diphenylarsenic(III)] oxide, with various oxidation systems (t-butylhydroperoxide to give, for example, the bis(arsine) oxide, $[AsPh_2(O)]_2O$; sulfur, to give $[AsPh_2(S)]_2O$, etc.). Our interest stems from the expected versatility such compound would have as ligands towards both main group and transition elements. We have previously reported that oxidation of the corresponding bis[diphenylarsenic(III)] sulfide, followed by crystallisation of the product in the open atmosphere, gives a mixed diphenylarsinic acid - diphenylmonothioarsinic acid [1]. An X-ray structure showed that the product is a novel hydrogen bonded, centrosymmetric, tetranuclear species, $[AsPh_2(O)OH\ AsPh_2(S)OH]_2$, where the oxo group of the arsinic acid simultaneously hydrogen bonds to the hydroxo groups of both acids. Rather surprisingly, the same compound is also obtained when sulfur is added to bis[diphenylarsenic(III)] oxide and the product crystallised in the air, implying that the expected oxidation products, $[AsPh_2(O)SAs(O)Ph_2]$ and $[AsPh_2(S)OAs(S)Ph_2]$ respectively, are hydrolytically unstable. Stability is, however, gained not by forming a mixture of the individual acids but rather by a supramolecular association to give the discrete tetranuclear product.

We now report on the reaction that takes place when $(AsPh_2)_2O$ is oxidised by elemental iodine. The reaction is clearly not a simple oxidation to give the expected As(III)/As(V) compound, $AsPh_2OAsPh_2I_2$, but a complex reaction mixture was obtained. We have previously reported the structure of $AsPh_2I$ [2], one of the products of this reaction. This paper presents the structure of diphenylarsinic acid, another compound formed and isolated as white crystals from the above mentioned reaction. The X-ray investigation showed that the crystals belong to a different monoclinic modification ($P2_1/a$) from that already known (space group $P2_1/b$ with one unique molecule) [3]. The latter was obtained by crystallisation from a mixture of ethyl acetate and ethanol.

RESULTS AND DISCUSSION

The oxidation of bis(diphenylarsine)oxide with iodine does not proceed in a straight forward fashion. Although the preparation was carried out under nitrogen, stringent precautions to exclude oxygen and water were not applied and hydrolysis, in particular, cannot be ruled out. The initial product of this 1:1 reaction was expected to be a mixed As(III)/As(V) compound, $AsPh_2OAsPh_2I_2$ but further reactions led to the isolation of diphenylarsenic iodide and diphenylarsinic acid. The formation of $AsPh_2I$ can arise by nucleophilic attack of an iodine on the As(III) centre followed by cleavage of the As(III)-O bond to give the observed monoiodide and presumably $AsPh_2(O)I$, which was not isolated.



It is quite probable for the latter to be hydrolytically unstable and, as stringent precautions to exclude moisture were not applied hydrolysis to the free acid which was isolated could occur. The infrared spectrum of diphenylarsinic acid shows the expected absorption bands at 755, 770 and 875 cm^{-1}, associated with arsenic-oxygen stretching modes and a broad band centered at ca. 2400 cm^{-1} assigned to the hydrogen bonded OH groups of As(O)OH moiety.

An X-ray structure determination shows that a new polymorphic form of diphenylarsinic acid has been identified which contains two independent molecules in the asymmetric unit. Important bond distances and angles for the new modification are collected in Table 1 and ORTEP diagrams of the structure, showing the atom numbering scheme, are in Figure 1 and 2. The hydrogen bond association of the molecules is also shown for each chain.

There are some differences in the dimensions of the independent molecules and these are mentioned below, but there is an overall similarity with the structure of the single molecule in the diphenylarsinic structure already determined [3]. Structural similarities are continued as the individual molecules in the new form are interlinked by hydrogen bonds to give infinite chains, as in the previous determination, but here there are two independent chains based, respectively, on the As(1) and As(2) molecules. This arrangement appears to be the preferred supramolecular arrangement for a diphenylarsinic acid. Infinite chains are also observed for divinylarsinic acid [4], while the dimethyl [5] and dibutyl [6] analogues crystallise in an alternative arrangement as centrosymmetric dimer.

A NEW POLYMORPHIC FORM OF DIPHENYLARSINIC ACID

Table 1. Important bond lenghts (A) and angles (°) for $AsPh_2(O)OH$, with e.s.d.s. in parentheses

As(1) - O (1)	1.71 (1)
As(1) - O (2)	1.71 (1)
As(1) - C (11)	1.92 (1)
As(1) - C (21)	1.92 (1)
As(2) - O (3)	1.62 (1)
As(2) - O (4)	1.69 (1)
As(2) - C (31)	1.86 (1)
As(2) - C (41)	1.90 (1)
O(1)...O (2')	2.52 (1)
O(3)...O (4')	2.55 (1)
O(1) - As(1) - O (2)	114.6 (5)
O(1) - As(1) - C (11)	111.2 (5)
O(2) - As(1) - C (11)	107.7 (5)
O(1) - As(1) - C (21)	103.3 (5)
O(2) - As(1) - C (21)	108.8 (5)
C(11) - As(1) - C(21)	111.2 (3)
O(3) - As(2) - O(4)	113.1 (5)
O(3) - As(2) - C(31)	110.7 (6)
O(4) - As(2) - C(31)	110.3 (5)
O(3) - As(2) - C(41)	110.6 (6)
O(4) - As(2) - C(41)	102.4 (5)
C(31) - As(2) - C(41)	109.4 (4)
As(1) - O (1) ... O(2 ')	118.5 (6)
As(1) - O (2) ... O(1 ')	111.9 (6)
As(2) - O (3) ... O(4 ')	114.1 (6)
As(2) - O (4) ... O(3 ')	120.0 (6)

Atoms carrying a prime are related by the symmetry operation o . 5 + x , 0 . 5 - y , z

Rather surprisingly, although the As-O separations in As(2) molecules [1.62(1) and 1.69(1) Å] are comparable with those [1.639(2) and 1.713(2) Å] in the earlier structure, those in the As(1) molecule are equal [1.70(1) and 1.71(1) Å] within the estimated standard deviations, even though one involves a formally doubly bonded oxygen and the second an OH group. A second difference is in the As—C bonds, which are equal [1.92(1) Å] at As(1), while at As(2) the separations are 1.86(1) and 1.90(1) Å. Each arsenic atom shows distorted tetrahedral geometry with angles ranging between 103.3(5) and 114.6(5)^{O} at As(1) and 102.4(5) and 113.1(5)^{O}

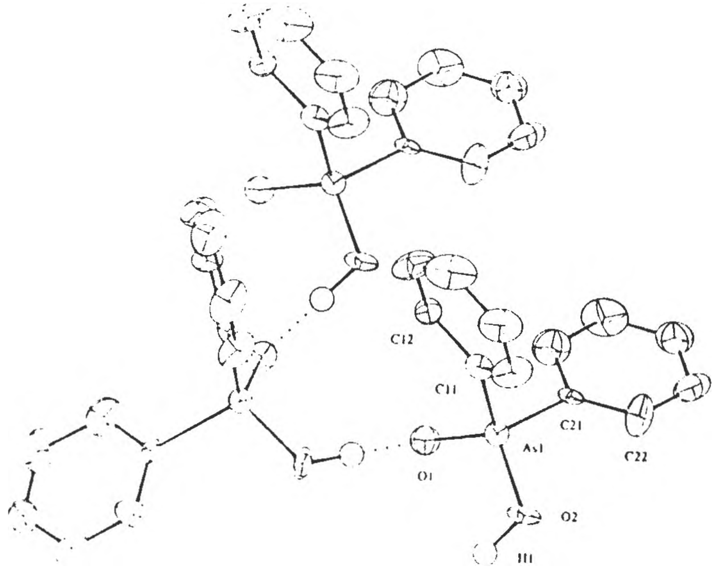


Fig 1 The ORTEP diagram of the As(1) chain in the $AsPh_2(O)OH$ crystal with the atom numbering scheme

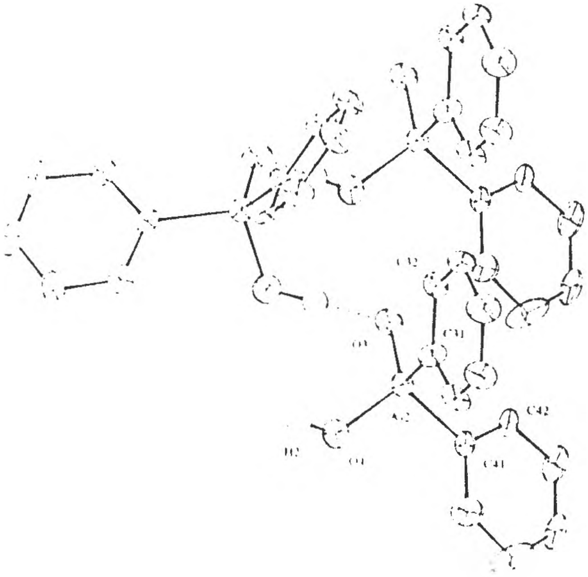


Fig 2 The ORTEP diagram of the As(2) chain in the $AsPh_2(O)OH$ crystal with the atom numbering scheme

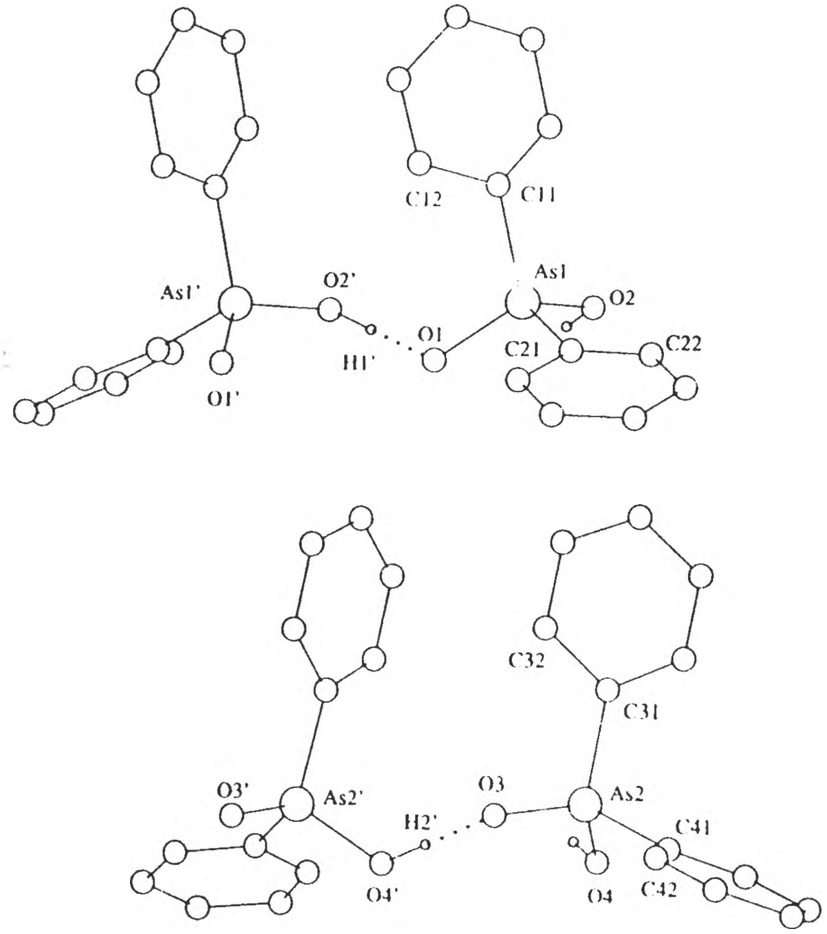


Fig.3 Structure of $AsPh_2(O)OH$ showing the relative position of the two independent chains

at As(2) and in each case the largest angle is between the oxygen atoms while the smallest is that between one of the phenyl groups and an oxygen atom The O O separations, 2 52(1) and 2.55(1) A, and the As—O O angles point to the presence of conventional hydrogen bonding The two chains are independently packed in the crystal, as shown by the fragments in Fig 3 which illustrates their reciprocal orientation It is obvious from this figure that the voluminous phenyl groups keep the inorganic H-bonds chains at a noninteracting distance

EXPERIMENTAL

Bis[diphenylarsenic(III)] oxide was prepared from a Grignard reaction between arsenic(III) oxide and phenylmagnesium bromide as described previously [7].

Reaction of bis[diphenylarsenic(III)] oxide with iodine.

A solution of bis[diphenylarsenic(III)] oxide in CCl_4 was treated at room temperature with a solution containing an equimolar amount of elemental iodine in the same solvent. The iodine colour was discharged and the yellowish solution was allowed to evaporate slowly at room temperature. The first solid (pale yellow) to separate was identified as $AsPh_2I$, which was removed by filtration. Further evaporation of the filtrate led to the separation of colourless crystals of diphenylarsinic acid with m. p. 173 ^oC. (Found: C 55,15, H 4.32 %; Calc. for $C_{12}H_{11}AsO_2$: C, 54.96; H, 4.19 %.

Table 2. Fractional atomic coordinates for $AsPh_2(O)OH$, with e.s.d.s. in parentheses

Atom	x/a	y/b	z/c	U (equ)
As(1)	0.9436(2)	0.16624(9)	0.28331(8)	0.0354
As(2)	0.7428(2)	0.1671 (1)	0.78052(8)	0.0364
O(1)	1.110 (2)	1.2115 (5)	0.3407 (6)	0.0494
O(2)	0.672 (2)	0.1826 (5)	0.2913 (6)	0.0379
O(3)	1.000 (2)	0.1812 (5)	0.7901 (7)	0.0452
O(4)	0.584 (2)	0.2126 (5)	0.8395 (6)	0.0498
C(11)	1.019 (2)	0.1684 (4)	0.1668 (7)	0.0212
C(12)	1.235 (2)	0.1840 (4)	0.1441 (9)	0.0388
C(13)	1.294 (3)	0.1869 (5)	0.063 (1)	0.0603
C(14)	1.137 (4)	0.1736 (5)	0.002 (1)	0.0785
C(15)	0.931 (3)	0.1587 (5)	0.026 (1)	0.0663
C(16)	0.883 (3)	0.1570 (4)	0.111 (1)	0.0586
C(21)	0.994 (2)	0.0883 (6)	0.3300 (5)	0.0248
C(22)	0.838 (3)	0.0478 (8)	0.3345 (7)	0.0684
C(23)	0.877 (3)	-0.0074 (9)	0.3664 (8)	0.0693
C(24)	1.082 (4)	-0.0225 (9)	0.3947 (7)	0.0717
C(25)	1.245 (4)	0.018 (1)	0.3907 (7)	0.0719
C(26)	1.200 (3)	0.075 (1)	0.3575 (7)	0.0737
C(31)	0.658 (2)	1.1710 (4)	0.6688 (8)	0.0376
C(32)	0.812 (2)	0.1893 (4)	0.607 (1)	0.0456
C(33)	0.754 (3)	0.1898 (4)	0.523 (1)	0.0515
C(34)	0.544 (3)	0.1727 (4)	0.4992 (9)	0.0505
C(35)	0.397 (2)	0.1551 (4)	0.557 (1)	0.0498
C(36)	0.454 (2)	0.1541 (4)	0.640 (1)	0.0262
C(41)	0.677 (2)	0.0901 (6)	0.8239 (6)	0.0328
C(42)	0.831 (2)	0.0475 (6)	0.8304 (6)	0.0394
C(43)	0.790 (3)	- 0.0083 (7)	0.8616 (7)	0.0543
C(44)	0.577 (3)	- 0.0201 (7)	0.8886 (7)	0.0616
C(45)	0.411 (3)	0.0212 (8)	0.8840 (7)	0.0665
C(46)	0.468 (3)	0.0762 (7)	0.8518 (7)	0.0611

A NEW POLYMORPHIC FORM OF DIPHENYLARSINIC ACID

Crystal Structure of AsPh$_2$(O)(OH)

Crystal data. $C_{12}H_{11}AsO_2$, M = 262.1, monoclinic, space group *P21/a*, a = 6.148(2), b = 22.316(6), c = 15.993(4) Å, b = 90.06(2)°; U = 2194.2 Å^3, Z = 8, D_c = 1.59 g cm^{-3}, $F(000)$ = 1059, μ =32.4 cm^{-1}, Mo-K$_\alpha$ radiation, l = 0.710 69 Å, crystal size = 0.01 x 0.06 x 0.5 mm^3.

A suitable crystal was mounted on a glass fibre and data were collected using a Hilger and Watts four circle diffractometer for 4385 reflections ($-8 < h < 8$, $0 < k < 26$, $0 < l < 19$ in the range $0 < \theta < 20°$). 2569 reflections with $I > 3\sigma(I)$ were considered observed giving1603 unique reflections (merging R = 0.033). The data were corrected for Lorentz and polarisation effects and for absorption (DIFABS) [8].

Structure determination. The structure was solved by direct methods using SIR92 [9] and refined by full matrix least squares methods on F using the CRYSTALS programs [10] and scattering factors, including the imaginary part, for neutral atoms [11]. After refinement of the non-hydrogen atom positions with anisotropic thermal parameters, the phenyl group hydrogens were placed at their calculated positions [d(C-H) 1.0 Å] and refined riding on their respective carbon atoms with a common U[iso] value 1.3 times that of the attached carbon atom. Modification for anomalous scattering and extinction were applied, together with a Chebyshev weighting scheme. Final convergence (272 least squares parameters, maximum shift:esd 0.2) occurred at R = 0.091 (R_w = 0.056). Final atomic coordinates are collected in Table 2.

Tables of anisotropic thermal parameters and hydrogen atom coordinates can be obtained from the authors.

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STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, XLI, 1, 1996

SULFUR OXIDATION OF 16H, 18H-DIBENZO[c,l]-7,9-DITHIA-16,18-DIAZA-PENTACENE

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ABSTRACT:

The paper reports the chemical oxidation of 16H,18H-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 1 leading to the corresponding sulfoxide and sulfone. IR and ^{1}H-NMR spectra of intremediates and main products are discussed.

INTRODUCTION:

16H,18H-Dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 1 has been synthesised by us [1] in our efforts to extend the area of phenothiazine derivatives in order to include oligophenothiazines with interesting electrical and magnetic properties. Our investigations concerning the chemical oxidation of 1 leading to sulfur oxidised compounds are reported here. The similar oxidation of phenothiazine has been studied by Bodea and Silberg [2], [3], [4].

RESULTS AND DISCUSSION:

The oxidation of 16H,18H-Dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 1 involves the reaction sequence showed in scheme 1

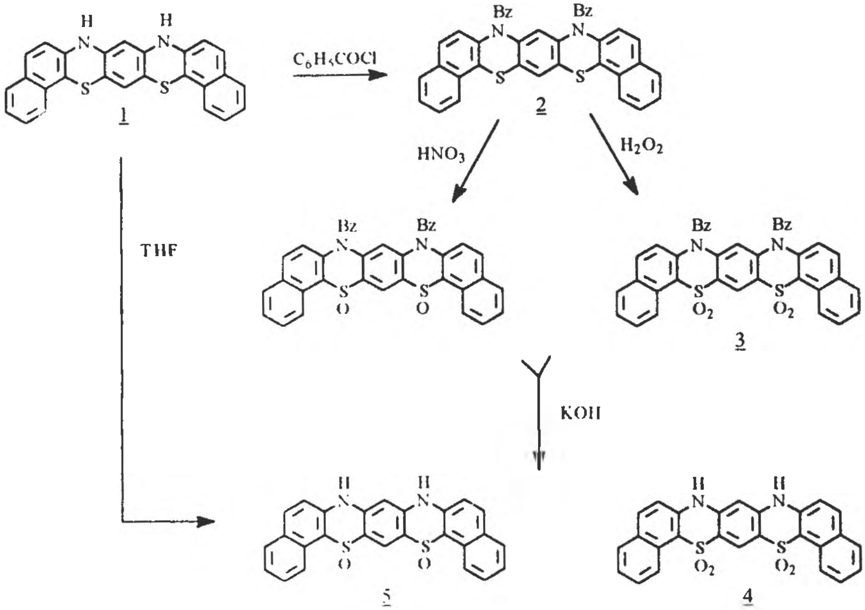
The first step consists of the protection of the amino group by benzoylation with benzoyl chloride and leads to 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza pentacene 2 which is a white precipitate. The presence of the benzoyl group in the molecule is shown by IR spectrum which displays the absorption band due to carbonyl vibration at 1680 cm^{-1}. Mass spectrum shows the molecular peak at the value m/e = 628 which corresponds to the benzoylation of both amino groups present in the molecule of the heterocycle.

The oxidation of 2 to16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene-7,7,9,9-bis-dioxide 3 takes place by treatment with hydrogen peroxide at 120^{0}C (refluxing in acetic acid).

The IR spectrum of 3 displays the ν_{CO} absorption at 1710 cm^{-1} strongly influenced by the electron withdrawing SO_2 group. The bands due to the SO_2 group vibrations are situated at 1160 cm^{-1} and 1280 cm^{-1}.

The benzoyl group is removed by hydrolysis in ethanolic potassium hydroxide leading to the target oxidised molecule 16H,18H-Dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene-7,7,9,9-bis-dioxide 4. The IR spectrum of 4 shows the same two bands at 1160 and 1280 cm^{-1} due to the SO_2 group vibrations, and no band in the 1700 cm^{-1} region which shows that the benzoyl groups have been removed. 4 is a white greenish solid with an extremely high melting point (over 360^{0}C), soluble in DMF and DMSO.

The 300 M Hz ^{1}H-NMR of 1 shows two signals at δ (ppm) = 6.25 (s, 1H) and 6,76 (s, 1H) assigned to the protons situated on the central benzene nucleus between the nitrogen atoms and the sulfur atoms respectively.



Scheme I

For the assignment of the protons attached to the naphthyl groups we used a 2D homocorrelation experiment (COSY) which is shown in figure 1. The amino protons appear at δ (ppm) = 8.85 (s, 2H) as unusually sharp signal.

For the sulfone 4 the 300 M Hz ^{1}H-NMR, shows the most shielded signal at δ(ppm) = 7,1 (s, 1H), a dramatic shift that we attribute to the neighbouring electron withdrawing SO_2 groups.

The oxidation of 1 to 16H,18H-Dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene -7,9-bis-oxide 5 can be performed starting from 1 in THF solution enriched with peroxides, or starting from benzoyl derivative 2 oxidised in acetic acid solution with HNO_3 (d = 1.5) followed by hydrolysis of the benzoyl group. The IR spectrum of 5 shows the absorption band due to SO group vibration at 1070 cm^{-1}.

The ^{1}H-NMR spectrum of 5 appears more deshielded than heterocycle's spectra. The amino protons appear at δ (ppm) = 11.6 (s, 2H) strongly acidified (comparable with the phenothiazine sulfoxide δ (ppm) = 10.9). The protons bonded to naphthyl part of the molecule appear in the region 7.4 - 8.8 ppm and have almost the same pattern like the parent heterocycle (a better separation between signals of the protons H_B, δ (ppm)= 8.18 (d, 2H) and H_C, δ (ppm) = 8.02 (d, 2H) can be observed and also the deshielding of H_A, δ (ppm)= 7.62 (d, 2H) bigger than H_D δ (ppm) = 7.54 (m, 2H). The two singlet signals assigned to the protons situated on the central benzene nucleus are at the edges of the aromatic region of this spectra δ (ppm) = 7.42 (s, 1H) and δ (ppm) = 8.92 (s, 1H).

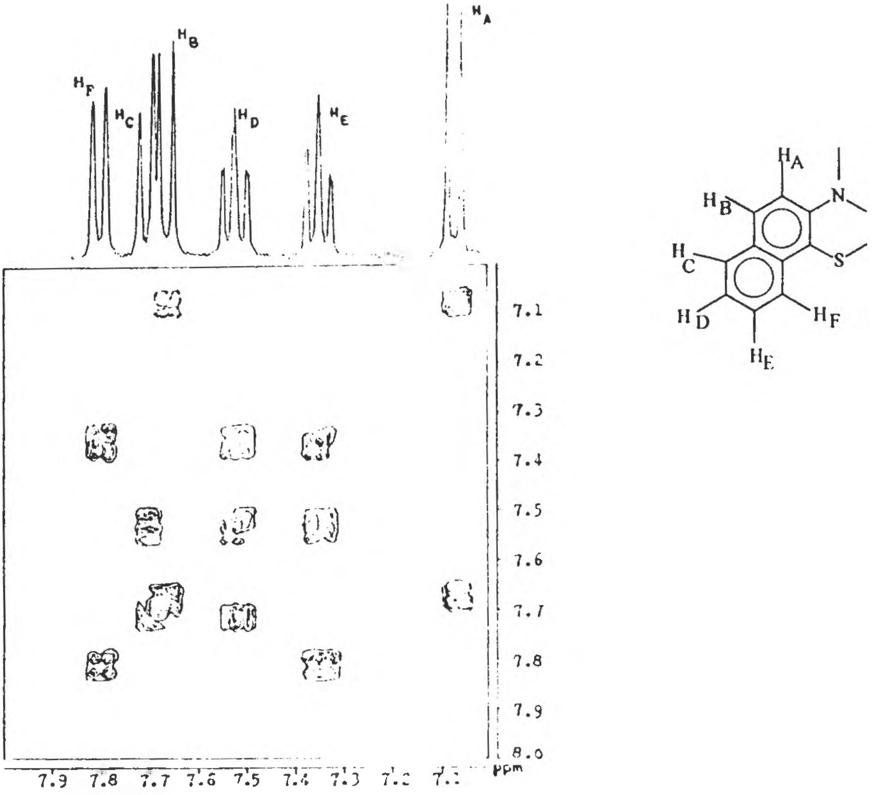


Figure 1. ^{1}H-NMR , COSY experiment for the naphthyl part of the structure of 16H,18H-Dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene 1

In conclusion, the chemical oxidation of 16H,18H-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene are similar to those of the phenothiazine, and the products are poorly soluble solids with high melting points.

EXPERIMENTAL

1) 16,18-Dibenzoyl-Dibenzo[c,l]-7,9-Dithia-16,18-Diaza-Pentacene-7,7,9,9-bis-Dioxide

At 0.4 g 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene solved in 15 ml boiling acetic acid 10 ml H_2O_2 30% had been added, and the boiling had been continued for one and a half hour, adding 2 ml H_2O_2 at every half hour. After cooling and staying after night the product had been filtered. Yields 0.3 g (50%) yellow precipitate. Spectral data: IR (cm^{-1}) : 1710, 1280, 1160.

2) 16H,18H- Dibenzo[c,l]-7,9-Dithia-16,18-Diaza-Pentacene-7,7,9,9-bis-Dioxide

0.2 g 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene-7,7,9,9-bis-dioxide had been boiled to reflux with 10 ml ethanol solution of potassium hydroxide 10% for 2 hours. The reaction mixture had been poured [illegible] 25 ml cool water. The white greenish precipitate had been filtered and washed with water. Yields 0.1 g (70%). Spectral data: IR (cm^{-1}) 1160, 1280.

3) 16H,18H- Dibenzo[c,l]-7,9-Dithia-16,18-Diaza-Pentacene-7,9-bis-Oxide

a) 0.2 g 16H,18H- dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene is solved in 50 ml THF enriched in peroxides. After 10 minutes the colour of the solution turns from green to red. The mixture had been allowed to stay after night at room temperature. The reaction is complete after refluxing the reaction mixture for 30 minutes. The precipitate separated after cooling had been filtered. Yields 0.1 g (50%) m.p. 300 ^{0}C with decomposition. Spectral data: IR (cm $^{-1}$) 1070.

b) 0.17 g 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene are treated with a mixture of 10 ml acetic acid and 1.2 ml HNO_3 (d = 1.5) under continuous stirring. After 2 hours the reaction mixture is poured into water. The yellow - green precipitate is filtered Yields 0.1 g (60%) 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene-7,9-bis-oxide The crude 16,18-dibenzoyl-dibenzo[c,l]-7,9-dithia-16,18-diaza-pentacene-7,9-bis-oxide had been solved in 15 ml ethanol and heated to reflux; after 5 min. 5 ml NaOH 10% aqueous solution had been added and the mixture boiled to reflux for 2 hours. After cooling, a pale yellow precipitate separated and it had been filtered. Yields 0.05 g (83%).

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STUDIA UNIV.BABES-BOLYAI, CHEMIA, 41, 1, 1996

THE KINETIC OF SOLID-LIQUID EXTRACTION (HIPPOPHAE FRUCTUS OIL SEPARATION)

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ABSTRACT

This paper presents the kinetic curves of Hippophae Fructus Oil extraction with acetone, benzene, ethyl alcohol, ethyl acetate, petroleum ether and a mixture of petroleum ether, acetone, methanol, the efficiency of total extract vs. the amount of dry material which was initially introduced; the quantitative and the qualitative analysis of the extracts and discussions of the results.

INTRODUCTION

The obtaining of the vegetable oils usually involves the retrieving of these from the vegetable mass by solid-liquid extraction.
The characteristics of solid depend on the nature of species within the same species. For the same species characteristics depend on the structure of plant part in which the metabolic products are accumulated: root, stalk, leaves, fruits or seeds.

Both variables characteristic overlap in time and by the comparison of geographical zone and with the solvent effects used.

The vegetable oils retrieving is generally made by the solid-liquid extraction. The retrieving of Hippophae Fructus Oil represents a special interest because of its composition: vitamins B_1, B_2, C, PP; carothenoides, folic acid, fat oil (non-saturated and saturated fatty acids), fitosterols, flavonoides, leucoantocians, organic acids, aminoacids, terpenes, and its pharmacological action as: revitaminizing, burnout treatments [1].
We used different solvents that were appropriate on the vegetable oils extraction [2] and we paid attention to the total efficiency of extracted oil and to the operating time until the solid material is out of stock.

EXPERIMENTAL

The oil extraction from the Hippophae Fructus with solvent was made through the following procedures: one step extraction, extraction with Soxhlet apparatus and extraction in fixed bed [3, 4], in the last two processes with distillate solvent (Figure 1).

RESULTS AND DISCUSSION

The results of determinations in comparison with the procedure that it was used and with the type of the solvent are shown in Table 1.
The total efficiency was established by bringing to "dry" the extract in comparison with raw material that was introduced into the process. We worked with 10: 1 = liquid : solid mass ratio.

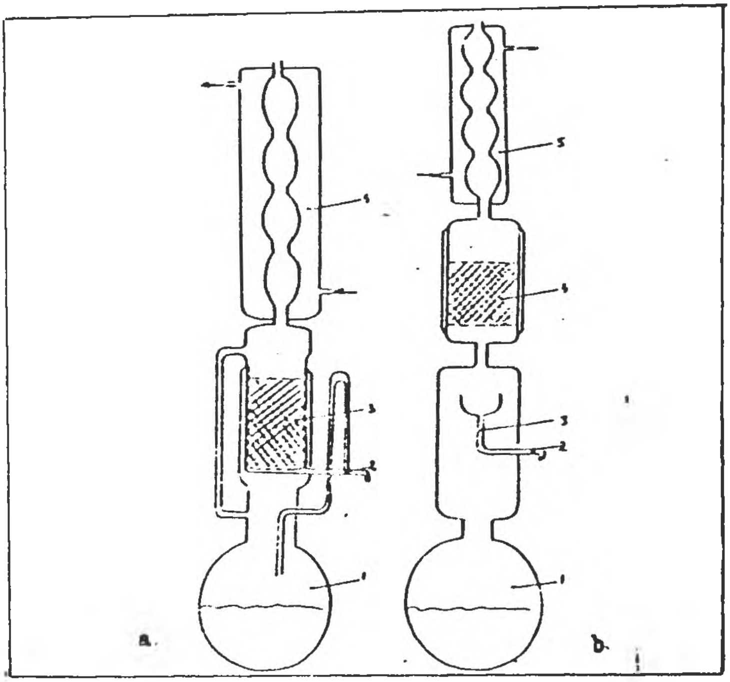

Fig 1. Extraction with distillate solvent, experimental installations
a. Soxhlet apparatus, b. fixed bed.

Table 1. Experimental results

Extraction procedure	Temperature (°C)	Solvent	Total output (%)
One step extraction	20	acetone	8.5
	40	acetone	10.5
Soxhlet apparatus	56	acetone	31.7
	79	ethyl alcohol	50.0
	40	petroleum ether	30.0
	78	ethyl acetate	38.0
	48	mixture	45.5
Fixed bed	56	acetone	34.5
	40	petroleum ether	31.0
	79	ethyl alcohol	53.5
	78	ethyl acetate	40.5
	80	benzene	35.8
	48	mixture	48.35

The vegetable material was grinded in a ball mill, sorting a product having the granularity between 0,1 - 1,0 mm. The granularity offered a more confortable way of working and increased the total efficiency (Table 2).

Table 2. The granularity influence

Extraction procedure	Temperature (°C)	The material	Total output (%)
One step extraction (acetone)	20	non-brooked	5.0
	20	brooked	8.5
Soxhlet apparatus (acetone)	56	non-brooked	22.7
	56	brooked	31.7
Fixed bed (acetone)	56	non-brooked	28.4
	56	brooked	34.25

Kinetic measurements were carried out spectrofotometrically by means of a Specord UV-VIS Carl Zeiss Jena at 455 nm [5, 6].
The oil concentration was established by an ethalon curve using the solvent which was used for each of the extraction (Figure 2).

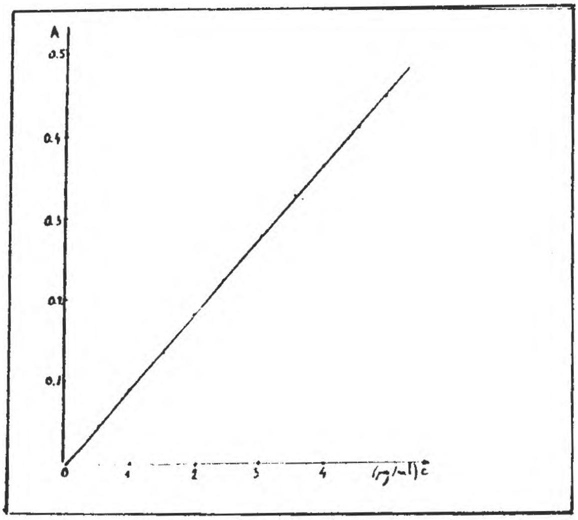

Fig. 2. Ethalon curve

The evolution of concentration for acetone was represented in the Figure 3. The exhausted time was shorter in the fixed bed process, at atmospheric pressure.

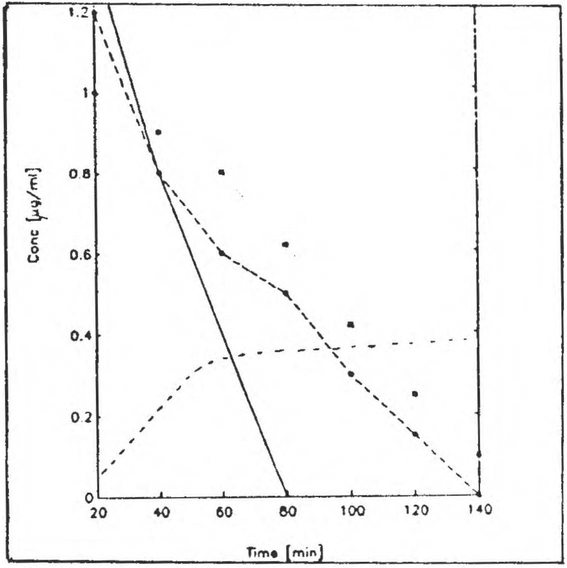

Fig. 3. Extraction with acetone

* Extraction with Soxhlet apparatus
conc. = $0.988 + 2.629\ 10^{-3}\ T - 1.274\ 10^{-4}\ T^2 + 4.513\ 10^{-7}\ T^3$

o Extraction in fixed bed at subatm. press.
conc. = $1.686 - 2.971\ 10^{-2}\ T + 2.47\ 10^{-4}\ T^2 - 8.68\ 10^{-7}\ T^3$

. Extraction in fixed bed atm. press.
conc. = $1.4\ 10^{-4} - 1\ 184\ 10^{-2}\ T + 1.018\ 10^{-3}\ T^2 - 2.019\ 10^{-5}\ T^3$

The development of the macerate concentration was asymptotic to the saturation concentration which led to a lower efficiency extraction.
The evolution of concentration with ethyl alcohol is given in the Figure 4.

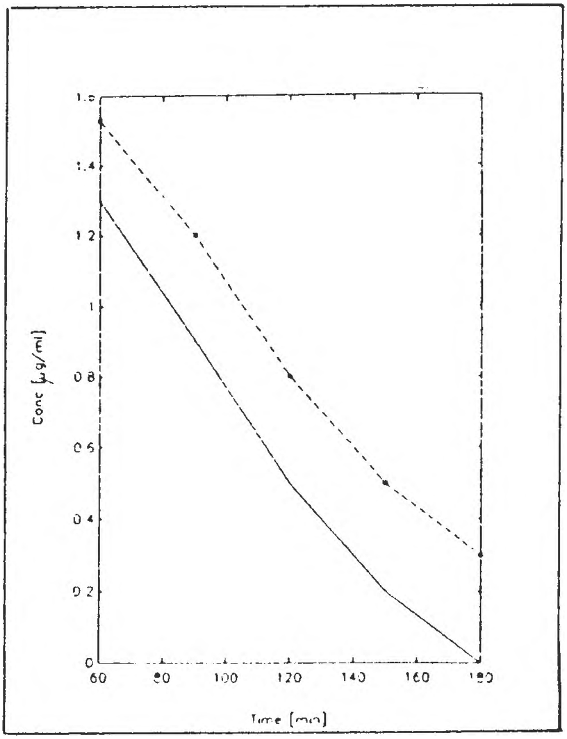

Fig. 4. Extraction with ethanol
* Extraction with Soxhlet apparatus
conc. = $1.98 - 8.135\ 10^{-3}\ T - 7.14\ 10^{-5}\ T^2 + 3.086\ 10^{-7}\ T^3$
. Extraction in fixed bed at atm. press.
conc. = $1.776 + 3.67\ 10^{-3}\ T - 1.6\ 10^{-4}\ T^2 + 5.24\ 10^{-7}\ T^3$

The exhausting time depended on the oil solubilization into the solvent. The oil solubilization increases in the serie: mixture to acetone, ethyl acetate and ethyl alcohol.

The kinetic curves that were obtained using the results of extraction on fixed bed with all the solvents are shown in the Figure 5.
The same representation was shown in Figure 6 for the extraction with the Soxhlet apparatus.

The time out of stock increases in the following serie: mixture, acetone, benzene, ethyl acetate, ethyl alcohol, like in the case of extraction with Soxhlet apparatus.
The fact is understandable, the solubility of constituents in solvent doesn't depend on the process of extraction.

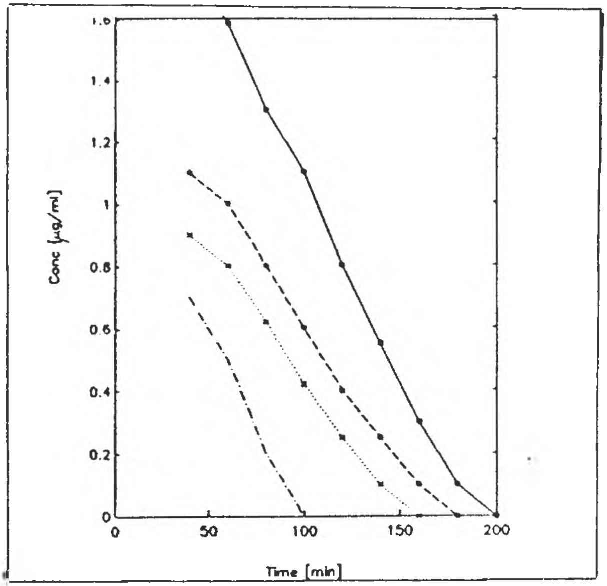

Fig. 5. Extraction with Soxhlet apparatus

* Ethanol: conc. = 2.197 - 8.58 10^{-3} T - 3.72 10^{-5} T^2 +1.04 10^{7} T^3
o Ethyl acetate: conc. = 1.107 + 5.41 10^{-3} T - 1.56 10^{4} T^2 + 1.56 10^{-7} T^3
x Acetone: conc. = 0.867 + 6.82 10^{-3} T - 1.7 10^{4} T^2 + 5.9 10^{7} T^3
. Mixture
\+ Benzene

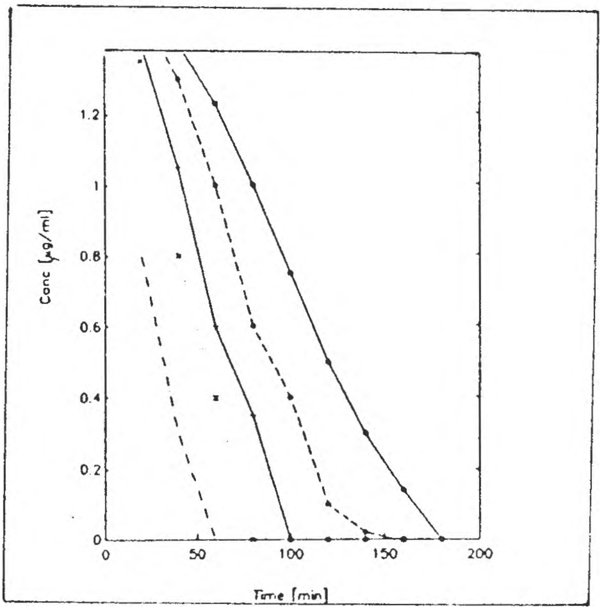

Fig. 6. Extraction in fix bed

* Ethanol: conc. = 1.7 - 4.38 10^{-3} T - 7.97 10^{-5} T^2 + 2.77 10^{-7} T^3
o Ethyl acetate: conc. = 1.588 + 1.74 10^{-3} T - 2.37 10^{-4} T^2 + 1.11 10^{-6} T^3
. Mixture: conc. = [illegible]8 - 2.48 10^{-2} T - 6.87 10^{-5} T^2
x Acetone
\+ Benzene

The total extract was analysed using the advisable literature [6, 7] for the identification of carothenoides and fatty acids content. The results are given in the Table 3.

Table 3. The oil fatty acids content

	Fatty acids in	total extract [%]	
with mixture		with ethanol	
palmitic	32.1	palmitic	31.01
stearic	0.58	stearic	1.53
oleic	34.3	oleic	29.68
linoleic	4.1	linoleic	8.8
linolenic	1.0	linolenic	3.14
linolic	27.5	linolic	24.67
???	0.42	arahic	0.25
		miristic	0.57
		palmitoleic	24.67
		???	0.35

Carothenoides	acetone	ethyl alcohol	benzene	mixture
(mg/g)	0.151	0.170	0.131	0.170

The analysis of total extract was carried out chromatography. The dependence of the concentration versus time was given by equations.

CONCLUSIONS

The obtaining of the Hippophae Fructus Oil with a good efficiency and a shorter time requires the use of a mixture of petroleum ether: acetone: methanol (5:3:1)
It is also possible to use the ethanol alcohol when the oil is rich in carothenoides and fatty acids.
The milling of raw material at a fineness not too advanced leads to the increase of the efficiency of the total extract and the decrease of the extraction time.
Besides, the extraction on fixed bed leads to a shorter extraction time and a higher efficiency then in the Soxhlet apparatus or in one step extraction.

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POTENTIOMETRIC AMMONIA SENSOR

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ABSTRACT

The functional characteristics of the potentiometric ammonia sensor elaborated by us , are presented. The influence of the following factors was studied : composition and concentration of the internal filling solution , type (nature) and thickness of the ammonia permeable membrane , thickness of the internal filling solution film formed between the sensitive surface of the indicator electrode and the ammonia permeable membrane, measuring procedure. The optimum parameters were established. The ownmade potentiometric ammonia sensor has comparable response characteristics with a Mettler ammonia sensor.

INTRODUCTION

The quantitative determination of ammonia is of special interest in the quality control of environment (water and air pollution) and in medicine (human and veterinary). The spectrophotometric methods based on the Berthelot reaction [1] and on the use of the Nessler reagent [2] are tedious as to the reagents and the devices used. The potentiometric ammonia sensor is a convenient and faster alternative yielding comparable accuracy.

The potentiometric ammonia sensor with permeable membrane combines the functional characteristics of an indicator electrode with the permselective qualities of an ammonia permeable membrane. Literature date presents the use of glass H^+-sensitive [3-6], metal H^+-sensitive [7] and NH^+_4-sensitive [8-10] electrodes as indicator electrodes. The most used ammonia permeable membrane is Teflon [11-14].

The principle of a potentiometric ammonia sensor with ammonia permeable membrane is: the ammonia , released from the sample, diffuses through the ammonia permeable membrane into a film of internal filling solution formed between the sensitive surface of the indicator electrode and the ammonia permeable membrane. Consequently, for the species for which the indicator electrode is sensitive, a change of the concentration occurs. This change is proportional to the concentration of the diffused ammonia. The potential of an ammonia sensor is expressed by the relation :

$$E = \text{konst.} - 2.3\ RT \log[NH_3] / F \qquad (1)$$

The paper presents a study of the influence of a number of factors on the behavior of the ownmade potentiometric ammonia sensor and its functional characteristics, as well.

RESULTS AND DISCUSSIONS

The ownmade potentiometric ammonia sensor with ammonia permeable membraneconsists of the following parts: a combined glass electrode with flat H^+- sensitive membrane, as indicator electrode, which is introduced into an external PVC body with two functions: reservoir for the internal filling solution and fastening the ammonia permeable membrane. The indicator electrode has the following functional characteristics: linear response range:1-11 pH, sensitivity 53 mV/pH at 25°C, flat sensitive surface : ϕ=4 mm. The flat surface of the sensitive membrane yields an uniform contact with the ammonia permeable membrane and a controlled geometry of the film of internal filling solution formed between them. This, generally, has a positive effect on the reproducibility of the sensor.

The behavior of the sensor is influenced by a number of factors which will be discussed below.

By its composition and concentration the internal filling solution influences the response range of the sensor. Table nr.1 shows the data obtained when a Teflon membrane of 0.075mm thickness was used.

Table nr.1. The influence of the internal filling solution on the response range of the sensor

Internal filling solution	Response range $[NH_3]$
NH_4Cl 10^{-2}M	8.10^{-4} - 8.10^{-1}
NH_4Cl 10^{-2}M+NaCl 10^{-2}M	5.10^{-4} - 8.10^{-1}
NH_4Cl 10^{-3}M	5.10^{-5} - 8.10^{-1}
NH_4Cl 10^{-3}M+NaCl 10^{-2}M	10^{-5} - 10^{-1}

The experimental data show that the response range of the sensor increases when the concentration of NH_4Cl solution decreases and when NaCl solution is added. The addition of NaCl to the internal filling solution yields a decrease of the osmotic pressure between the sample and the filling solution (the ionic strength of the sample is 10^{-1} M and that of the internal filling solution NH_4Cl 10^{-3}M+NaCl 10^{-2}M is 1.1 10^{-2} M). The volume of the internal filling solution, in the PVC body, was varied between 0.1-3 ml without any significant effect on the response of the sensor. We choosed as internal filling solution 0.7 ml of the solution NH_4Cl 10^{-3} M+NaCl 10^{-2} M, in which case the sensor had the widest response range.

An other factor which influences the behavior of the sensor is the ammonia permeable membrane. Two types of membranes were considered Teflon and Nylon 66. Table nr 2 shows the experimental results obtained when 0.7ml of NH_4Cl 10^{-3} M+NaCl 10^{-2} M solution were used as internal filling solution.

Table nr.1 Influence of the ammonia permeable membrane thickness on the functional characteristics of the sensor.

Membrane type	Membrane thickness (mm)	Linear response range $[NH_3]$	Sensitivity mV/pNH_3	Response time (min)
Teflon	0.040	5.10^{-5}-10^{-1}	54	3
Teflon	0.075	5.10^{-5}-10^{-1}	54	3
Teflon	0.150	5.10^{-5}-10^{-1}	52	5
Nylon 66	0.125	5 10^{-5}-10^{-1}	51	7

One may observe in Table nr 2 that for a given type of membrane the increase in thickness yields a slight decrease of the sensitivity and an increase of the response time of the sensor. For membranes of different types and similar thicknesses the sensitivity of the sensor was almost the same but the response times differ. Among the considered ammonia permeable membranes we choosed the Teflon membrane with 0.075 mm thickness since it has a higher mechanical strength and the sensor has the highest sensitivity and shortest response time in the linear response range.

The influence of other factors was studied using 0.7 ml NH_4Cl 10^{-3} M+NaCl 10^{-2} M solution as internal filling solution and the Teflon of 0.075 mm thickness as ammonia permeable membrane.

The thickness of the internal filling solution film formed between the sensitive surface of the indicator electrode and the ammonia permeable membrane may be controlled with a spacer. The behavior of the sensor was studied with and without spacer .When spacers were used two kinds were considered:cellulose type (ϕ=4 mm, thickness 0.06 mm) and nylon net (ϕ=4 mm, thickness 0.1mm). The sensitivity and the response range of the sensor were not affected by the presence of the spacer but the response time increased over 5 minutes at 0.1 mm thickness of the spacer. Therefore the spacer was removed and a very thick film of the internal filling solution was formed by pressing the sensitive surface of the indicator electrode onto the ammonia permeable membrane.

The measuring procedure is an other factor that influences the response characteristics of the sensor. When measurements were performed in the low to high concentration's order followed by high to low concentration's order, a decrease of the reproducibility of the measurements was observed, especially at low concentrations. In the 10^{-5}-5.10^{-5} M concentration range, a difference of 3-4 mV between the readings for the same concentration was noted. This feature is clearly yielded by the diffusion rate of ammonia out of the internal filling solution film, which is slower than the diffusion rate of ammonia into the film. Consequently, the response time of the sensor increases when measurements are performed from high to low concentrations and differ from one concentration level to another. Therefore we chosen to perform the measurements only in the low to high concentration's order followed by a 10 minute's recovery of the sensor by washing it in distilled water, with slow stirring. The reproducibility of the readings was better than 2 mV, even in the 10^{-5} -5.10^{-5} M concentration range.We note that at concentrations above 5.10^{-5} M, the potential reproducibility is about 1 mV.

Taking into account the experimental results we established the general functional characteristics of the ownmade sensor (Table nr.3)

Table nr.3 General functional characteristics of the ownmade ammonia sensor

Functional characteristic	Nominal value
Linear response range [M]	5 10^{-5}-10^{-1}
Sensitivity (mV/pNH_3)	53±1
Response time (min.)	3
Recovery time (min.)	10

The response characteristic of the ownmade ammonia sensor was compared with that of a Mettler ammonia sensor . The calibration curves in the 5.10^{-5}-10^{-1}M concentration range show that both sensors have nearly Nernstian response (Fig 1)

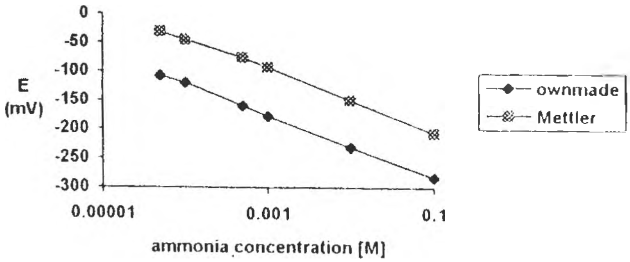

Fig 1 Calibration graphs for ammonia sensors

CONCLUSIONS

The functional characteristics of the ownmade potentiometric ammonia sensor, with ammonia permeable membrane are influenced by: the composition and concentration of the internal filling solution, the type (nature) and the thickness of the ammonia permeable membrane, the thickness of the internal filling solution film formed between the sensitive surface of the indicator electrode and the ammonia permeable membrane and the measuring procedure. Our study allowed us to establish the optimum parameters for the ownmade sensor that has comparable functional characteristics with the Mettler ammonia sensor.

Experimental

The solutions used to check the functional characteristics of the indicator electrode and the ammonia sensors (ownmade and Mettler) were: buffers with pH 1.64;7.09;9.26, NH_4Cl solutions in the concentration range 10^{-5}-10^{-1}M and NaOH 10M solution.
The apparatus used were: digital pH-meter, ownmade and Mettler ammonia sensors, U10-type thermostat (±0.2°C) and magnetic stirrer.

The response characteristics of the indicator electrode was established by consequently measuring the potential in the buffers of pH=7.09,pH=1.64and pH=9.26.The response characteristic of the ammonia sensors was checked as follows: The sensors were introduced in 20 ml of NH_4Cl solutions (10^{-5}-10^{-1}M) and 0.2 mlNaOH 10M solution were added under stirring. The reading of the potential was made 3 min after the last drop of NaOH 10M solution was added.

Measurements were performed from low to high concentrations, than the sensors were washed for 10 min.,in distilled water under stirring.

Measurements were performed in the low to high concentrations order followed by high to low concentrations order too.All samples were measured at 25°C by using the precision thermostat.

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STUDY OF THE ACCURACY OF THE DETERMINATION OF pH WITH METAL ELECTRODES

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ABSTRACT

The H^+-sensitive metal electrodes are recommended for pH measurements in continuous measurements in different industrial processes, first a study was made on the change Than the change of the accuracy of the pH measurements in continuous flux was followed for 20 days.The accuracy of the measurements of pH was estimated by comparison with measurements made with a H^+-sensitive glass electrode.In the studied processes the good functioning period of the metal electrodes is 6 days. When a method is used to forestall the covering of surface of the electrodes (e.g. mechanical or ultrasound cleansing) the period of good functioning is prolonged to 10 days.

INTRODUCTION

The metal H^+-sensitive electrodes (Sb, Bi, W) are recommended by the literature [1-7] for continuous measurements in industrial and hard working conditions such as, high alkalinity, high concentrations of HF, HCl, foams and bulk particles. Comparatively to the glass H^+-sensitive electrodes,the metal electrodes are more robust. That's why their surface may be renewed easily.

With a view to establish the most adequate electrode for a certain industrial process, the chemical resistance of the Me/MeO type electrodes was studied in laboratory conditions. Then the accuracy of the pH measurements in time was followed during the flotation process of obtaining sugar and respectively of Na_2CO_3 production.

The accuracy of the pH measurements was evaluated by comparison with measurements made with the H^+-sensitive glass electrode

RESULTS AND DISCUSSION

In agreement with literature [12] the studied H^+-sensitive metal electrodes have a measurement error of ± 0.2 pH and a linear functioning range as follows: 2-12 pH for Sb electrode and 9-13 pH for Bi and W electrodes respectively

The results of the study made in laboratory (fig. 1) shows that in strong acid media

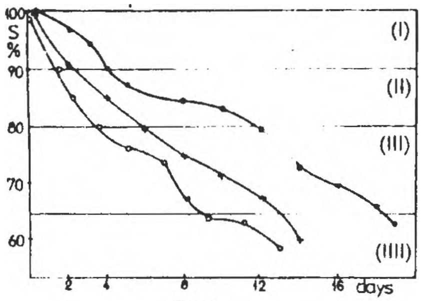

Fig. 1

Figure 1. The change of the sensitivity of the Sb electrode, in the pH range: 1.68-6.88 x-10^{-2}M HF, •-10^{-3}M HF, o-10^{-2}M HF
(I)-error of the measurement less than 0.1 pH; (II)- error of the measurement less than 0.2 pH; (III)- error of the measurement less than 0.2 pH with a new calibration; (IIII)- error of the measurement higher 0.2 pH.

(HF 10^{-2}M, HCl 10^{-2}M) the sensitivity of the electrode decrease as follows: -after 3-4 days to 90% of its initial value (I); -after 6-7 days to 80% of its initial value (II); -after 9-12 days to 65% of its initial value (III)

Figure 2 shows the change of the sensitivity of Bi and W electrodes in strong alkaline media

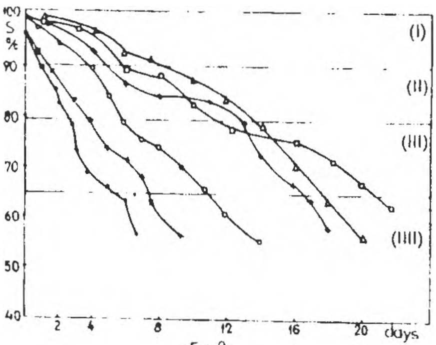

Fig 2

Figure 2. The change of the sensitivity of the Bi and W electrodes, in the pH range:9.20-12.00. W-electrode: •- in 10^{-3}M NaOH; x- in 10^{-3}M NH_4OH;o- in 10^{-3}M $Ca(OH)_2$; Bi-electrode: - in 10^{-3}M NaOH; Δ- in 10^{-3}M NH_4OH; +- in 10^{-3}M $Ca(OH)_2$; (I)- error of the measurement less than 0.1 pH; (II)- error of the measurement less than 0.2 pH; (III)- error of the measurement less than 0.2 pH with a new calibration; (IIII)- error of the measurement higher than 0.2 pH.

DETERMINATION OF pH WITH METAL ELECTRODES

In NH_4OH or NaOH 10^{-3}M the following changes took place at the W electrode: after 1.5-2 days according to (I), after 3-4 days according to (II) and after 6-8 days according to (III). For the Bi electrode the changes were according to (I) after 6-8 days, according to (II) after 12-14 days and according to (III) after 18-20 days.

In $Ca(OH)_2$ 10^{-3} M medium, the sensitivity of the Bi electrode changes as follows: according to (I) after 3-4 days, according to (II) after 6 days and according to (III) after 11 days. It results that the Bi electrode has a high chemical stability, because of a better resistance to the alkaline attack of the Bi_2O_3layer comparatively with WO_3 that is dissolved by the alkalis.

In figures 1 and 2 the good functioning periods of the metal electrode (I,II) are also showed, when the electrodes are attached to an ownmade industrial pH-meter.

When the sensitivity of the electrode decreases under 80% of its initial value (II) is necessary to recalibrate the pH-meter, for an accuracy better than 0.2 pH.

It may be observed that the diminishing of the sensitive surface from rod to pellet and ring type does not affect the response of the electrodes. The pellet and ring electrodes have an increased mechanical resistance (excepting for W which is a hard metal) and also saves the row material.

The results of the measurements in industrial processes are shown in tables 1, 2 and 3. In sugar industry the pH of the second saturation step was measured. The working temperature was 95°C and the pH varied between 9-11, the optimum being 9.5 pH. During this step of the process a crust formation occured

The W electrode allows an accurate measurement of pH for 4 days (the deviation from the pH measured with glass H^+-sensitive electrode is under 0.2 pH).

Table no.1. pH determination in flux in sugar production using W electrode

Functioning period (hours)	Without cleansing pH	Without cleansing Error versus the glass electrode	Mechanical cleansing pH	Mechanical cleansing Error versus the glass electrode
5	9.65	-0.20	9.75	-0.01
10	9.45	0.15	9.40	+0.01
50	9.40	0.02	9.30	+0.01
80	9.35	0.02	9.25	+0.10
114	9.50	0.25	9.40	+0.15
128	9.55	0.25	9.25	-0.05
132	9.45	0.35	9.25	+0.15
145	9.50	0.30	9.35	+0.15
156	9.60	0.30	9.20	-0.10
175	9.45	0.35	9.20	+0.10
212	9.55	0.45	9.30	+0.20
243	9.50	0.50	9.30	+0.30

The W electrode with a renewed surface by mechanical cleansing gives an accurate response for 9 days. After this period the electrode must be reconditioned (the oxide layer on the surface of the electrode is renewed by electrochemical oxidation).

In the process of Na_2CO_3 production, in the ammonia recovery step, the pH was measured with W electrode and with Bi electrode. The optimum working parameters are 80°C and pH:9.5-11. Comparatively with the W electrode that works correctly for 18 hours, the Bi electrode measures with an accuracy of minimum 0.2 pH, after 10days of functioning,too.

Table no.2. pH determination in flux, in the ammonia recovery process, in the Na_2CO_3 production

Functioning period (hours)	W-electrode pH	W-electrode Error versus the glass pH electrode	Bi-electrode pH	Bi-electrode Error versus the glass pH electrode
3	10.10	+0.10	10.10	+0.10
7	10.25	-0.20	10.20	-0.15
18	10.25	-0.25	10.40	-0.10
56	10.40	+0.25	10.30	+0.10
83	11.25	-0.35	11.50	-0.10
120	12.30	-0.30	12.50	-0.20
168	12.40	-0.30	12.50	-0.20
216	12.35	-0.35	12.50	-0.20

In mining industry, during the flotation process of the nonferrous ores, the difficulty in measuring the pH results because of the presence of HF foams and solid particles. The measurement of pH is made at medium temperature (10-20^{0}C). The results of this measurement in continuous flux show that the Sb electrode measures correctly for 6 days, without being necessary to renew its surface. When mechanical or ultrasound cleansing device is attached the period of good functioning of the electrodes is prolonged to 9 days, respectively more than 12 days.

Table no. 3. Accuracy of pH determination with Sb electrode, in the presence of HF (mining industry)

Functioning period (hours)	Error versus glass electrode (pH) Without cleansing	Error versus glass electrode (pH) Mechanical cleansing	Error versus glass electrode Ultrasound cleansing
2	-0.05	-0.05	-0.05
15	-0.05	0.00	0.00
36	+0.05	+0.05	-0.05
56	-0.10	+0.15	0.00
74	-0.05	0.00	0.00
118	+0.15	+0.05	+0.05
152	-0.20	+0.10	0.00
160	-0.35	+0.15	+0.05
216	-0.30	+0.25	+0.10
282	-0.30	+0.20	+0.05

CONCLUSIONS

The experimental data obtained in checking the industrial processes show that the H^+-sensitive metal electrodes attached to an industrial pH-meter which allows the compensation of the decrease of the sensitivity of the electrode till 65% of the initial value, ensures an accuracy of the measurement of ±0.2 pH only for 5-6 days. After this period the electrodes must be reconditioned.

This period of good accuracy is prolonged to 10-16 days when the electrodes are used in laboratory conditions, in a similar chemical media as in the studied industrial processes.

The period of good functioning of the electrodes in industrial conditions may be prolonged to 10 or more than 10 days when a method to forestall the covering of the surface of the electrode is used.(e.g. cleansing devices).

EXPERIMENTAL

The H^+-sensitive metal electrodes are achieved from Sb, Bi, W [8,9,10] (rod pellet or ring type). The electrodes are provided with a diode that allows the compensation of the variation of the sensitivity with temperature. The electrodes were kept for 18-20 days in HCl, NaOH,HF, $Ca(OH)_2$, NH_4Oh solutions that are present in many industrial processes. From time to time the sensitivity of the electrodes was verified. The potential values vs. an Ag/AgCl reference electrode were determined in two buffers by a pH/mV-meter. The buffers had the following pH values: 1.68 and 6.88 for Sb electrode, respectively 9.22 and 12 for the W electrode.

The pH measurements in the industrial processes were made directly in flux. The electrodes were attached to an ownmade pH-meter, specific for metal electrodes. This pH-meter may compensate the decrease of the sensitivity of the metal electrode to aprox. 65% of its initial value.

The accuracy of the pH measurements with metal electrodes was established towards the values obtained with glass electrode.

The surface of the electrode was renewed by using a mechanical cleansing device [11] having textolite lamellae and electrically divided or using ultrasounds (polish generating set type:ELWRO,N.5830).

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SYNTHESIS, STEREOCHEMISTRY AND NMR SPECTRA OF SOME NEW 5,5-SUBSTITUTED 1,3-DIOXANES

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Abstract: The stereochemistry of new 1,3-dioxane compounds obtained by the condensation reaction of 2,2-diethyl-1,3-propanediol with several carbonyl compounds was studied by NMR methods. The investigations showed anancomeric or flexible structures, in correlation with the free conformational energies of the substituents located in the acetal part of the heterocycle. The influence of the chiral center (belonging to the equatorial substituent of position 2), in the compound obtained starting from benzoine, was observed by the diastereotopicity of the positions 4 and 6 of the heterocycle.

INTRODUCTION

Some interesting aspects concerning the stereochemistry of 1,3-dioxane compounds bearing substituents in the positions 2 and 5 of the ring were revealed in previous works [1-8]. This type of compounds are involved in the conformational equilibrium (Scheme 1):

R=CH_3, $COOCH_2CH_3$

Scheme 1

The compounds displaying only one substituent in position 2 (R_2=H, obtained by the acetalization reaction of aldehydes) show anancomeric structures, the characteristic conformational equilibrium (Scheme 1) being strongly shifted towards the conformation A that exhibits the bulky substituent (R_1) of position 2 in equatorial orientation. The compounds with identical geminal substituents (resulted from symmetrical ketones, R_1=R_2) show flexible structures. The two degenerated conformers (A and B) exist at the equilibrium in the same ratio. They pass rapidly one into the other, the free enthalpy of activation for the inversion of the 1,3-dioxane ring ($\Delta G^{\#}$< 10 kcal/mol) being to small to freeze (at room temperature) the flipping rings [9,10].

A peculiar case is represented by the compounds bearing different substituents in position 2 (obtained from unsymmetrical ketones, $R_1 \neq R_2$) which can be anancomeric or flexible in correlation with the differences of the free conformational energies between the two substituents located in the ketal part of the heterocycle (R_1 and R_2). The compounds show anancomeric structures if this difference is enough high (e.g. Me and Ph [11, 12]) and they are flexible if the values of the free conformational enthalpies of the two substituents are close (e.g. Me and CH_2COOR [13]).

The conformational behaviour of the compounds was inferred by their NMR spectra. Thus, the spectra of the anancomeric compounds display different signals for the equatorial and axial protons of the heterocycle, as well as for the equatorial and axial similar substituents located at C^5. The spectra of the flexible compounds display unique signals (at mean values of the chemical shifts) for the axial and equatorial positions of the protons of the ring or of the similar substituents belonging to the aliphatic or to the ketalic part of the molecule..

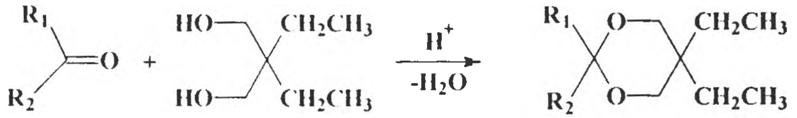
At the same time if one of the substituents located in the ketal part of the 1,3-dioxane ring is chiral, the influence of the chirality was observed by means of the diastereotopicity of protons and carbon atoms.

The different influence of the oxygen atoms of the heterocycle on the pattern of the ^{1}H NMR spectra corresponding for the protons of the groups located at C^5 was revealed. A significant deshielding through space on the protons of the axial groups has been observed.

It was considered of interest to develop the investigation of a series of compounds obtained from 2,2-diethyl-1,3-propanediol and to determine their stereochemistry by NMR investigations.

RESULTS AND DISCUSSION

New 1,3-dioxanes were obtained by the condensation reaction of 2,2-diethyl-1,3-propanediol with several aldehydes and ketones under usual conditions (Scheme 2):



R^2=H, R^1=CH_3 **1**
R^2=H, R^1=i-C_3H_7 **2**
R^2=C_6H_5,R^1=CH(OH)C_6H_5, **3**
R^2=R^1=C_2H_5 **4**
R^2=CH_3,R^1= $CH_2COOC_2H_5$, **5**

Scheme 2

Compounds **4** and **5** display flexible structures. Their NMR spectra are very simple and show unique signals (Table 1) for the protons of positions 4 and 6 (singlet) and for the methylene (quartet) and methyl (triplet) protons of the ethyl groups belonging to the position 5 of the ring. Thus, the ^{1}H NMR spectrum (Figure 1) of compound **4** shows one singlet (δ=3.51 ppm) corresponding to the protons of positions 4 and 6 and two quartets and two triplets belonging to the protons of the two type of ethyl groups located at C^2 (δ_q=1.69 and δ_t=0.87 ppm) and located at C^5 (δ_q=1 38 and δ_t=0.78 ppm).

Table 1 ^{1}H NMR data (δ, ppm) of compounds **1-5**

Compound	C4,C6		5-Et			
			-CH2-		CH3	
	ax	eq	ax	eq	ax	eq
1	3.27	3.68	1.65	0.98	0.77	0.70
2	3.25	3.71	1.63	0.97	0.77	0.70
3	3.38	3.64	1.76	0.88	0.88	0.64
4	3.51		1.38		0.78	
5	3.87		1.30		0.73	

Compound **5** shows a flexible structure despite the different substituents located at C^2. The difference between the conformational free enthalpies of the two groups (CH_3 and $CH_2COOC_2H_5$) is too small to induce the anancomericity of the system. Thermodynamic data reported in the literature underline the existence of insignificant differences between the free conformational enthalpies of the groups CH_3 and CH_2-X (if X is a polar substituent, *e. g.* Cl or Br) [11].

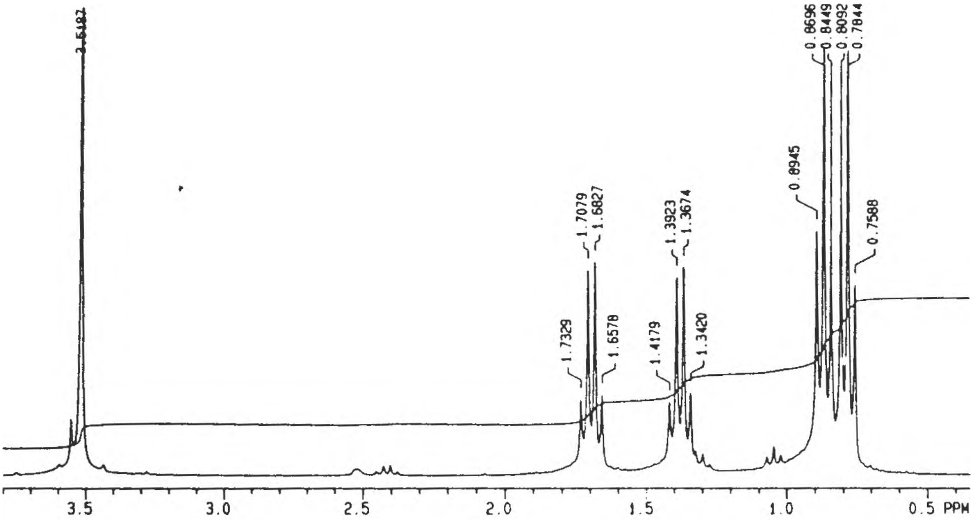
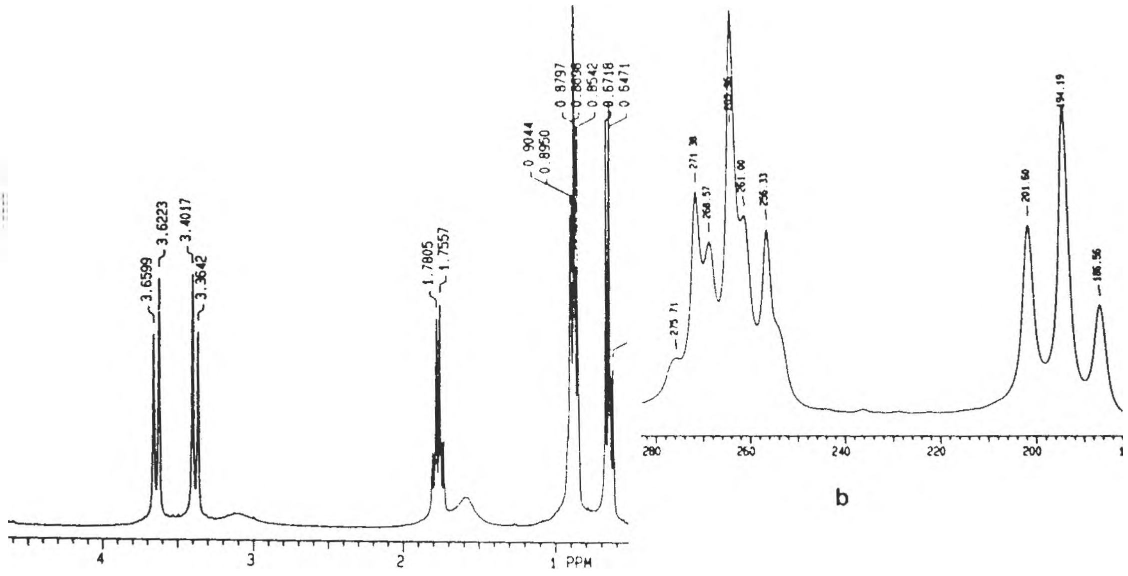


Figure 1. ^{1}H NMR spectrum of compound **4**.



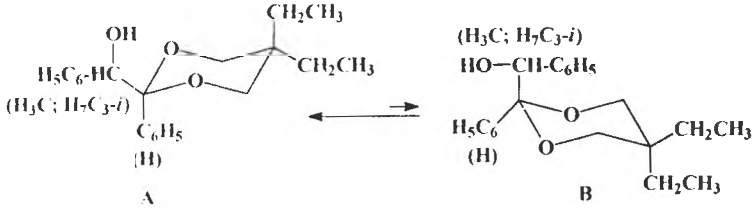
a

b

Figure 2. ^{1}H NMR spectrum of compound **3** (fragment a, detail b)

Compounds **1-3** exhibit anancomeric structures, the conformational equilibrium (Scheme 3) being shifted towards the conformer that displays the bulkier substituent of position 2 in equatorial orientation (A). The NMR spectra of these compounds show distinct signals for the equatorial and axial protons of position 4 and 6 and for the axial and equatorial ethyl groups located at C^5. The equatorial protons belonging to the ring are in a usual way more deshielded then the axial ones whereas the protons of the axial group located at C^5 are more deshielded as those of the ethy group situated in the equatorial position.

The differences among the chemical shifts of the equatorial and axial protons of the heterocycle ($\Delta\delta_{eq\text{-}ax}$=0.26-0.46 ppm) are close to the data reported in the literature [1,2,5,6,12].



Scheme 3

Interesting aspects were observed comparing the chemical shifts of the protons belonging to the axial and equatorial ethyl groups of position 5. Thus, the differences between the chemical shifts (spectra run in $CDCl_3$) of the axial and equatorial methylene protons (compounds **1** and **2**, $\Delta\delta_{ax\text{-}eq}$=0.66-0.67 ppm) are significantly higher then the differences measured in previous works [1-3] between the chemical shifts of the methylene protons of the axial and equatorial $COOCH_2CH_3$ groups ($\Delta\delta_{ax\text{-}eq}$=0.10-0.12 ppm). For the protons belonging to the methyl groups in both substituents CH_2-CH_3 and $COOCH_2CH_3$, the differences between the chemical shifts of the axial and equatorial positions are close (CH_2CH_3, compounds **1** and **2**, $\Delta\delta_{ax\text{-}eq}$=0.07 ppm) and ($COOCH_2CH_3$, $\Delta\delta_{ax\text{-}eq}$=0.04-0.07 ppm).

The protons of the axial groups located at C^5 are more deshielded as those of the similar geminal equatorial groups as a consequence of their interactions through space with the oxygen atoms of the ring. The methylene protons of the ethyl substituent are more deshielded as those of the ester group ($COOCH_2CH_3$) because they are more close to the heteroatoms of the ring.

The ^{1}H NMR spectrum of compound **3** (Figure 2) shows significantly higher differences of the chemical shifts for the axial and equatorial positions of the protons belonging to the ethyl substituents located at C^5 [$\delta(CH_2)_{ax}$=1.76, $\delta(CH_2)_{eq}$=0.88, $\Delta\delta_{ax\text{-}eq}$=0.88 and $\delta(CH_3)_{ax}$=0.88, $\delta(CH_3)_{eq}$=0.64, $\Delta\delta_{ax\text{-}eq}$=0.24 ppm]. The quartet belonging to the equatorial methylene protons and the triplet corresponding to the axial methyl protons are overlapped. These higher values of the differences of chemical shifts compared to the values found for compounds **1** and **2**, are explained by an influence through space of the axial phenyl group linked at C^2. As it also was revealed for other 1,3-dioxanes bearing an axial aromatic substituent at C^2 [2,14], there is a hindrance of the rotation of the aromatic group and that determines a rigid gonal rotamer for the axial aryl group. In this rotamer the magnetic anisotropy of the aromatic substituent leads to a shielding of the protons belonging to the equatorial substituent. In the same time the polar equatorial substituent located at C^2 determines (interactions through space) a more deshielding of the protons of the axial ethyl group located at C^5. Compound **3** exhibits a chiral center [$C^*H(OH)C_6H_5$] and the positions 4 and 6 become diastereotopic ones. The data of the literature [5-8] show the recording, in the ^{1}H NMR spectra, of different signals for the axial protons of the positions 4 and 6 as well as for the protons belonging to the equatorial mentioned positions. In compound **3** the differences between the magnetic environments of the protons of the two positions 4 and 6, are too small and with a 300 MHz apparatus it was not possible to separate the signals of these diastereotopic protons. Thus, the pattern of the ^{1}H NMR spectrum of compound **3** (Figure 2) displays for the protons of the heterocycle only two doublets, one for the axial (δ=3.38 ppm) and another one for the equatorial protons (δ=3.64 ppm) of the ring. The spectrum shows more a singlet (δ=4.69 ppm) belonging to the proton of the chiral center, a extended signal (δ=1.5-1.7 ppm) corresponding to the proton of the hydroxyl group and to the traces of water of the solvent and an overlapped group of signals (δ=6.98-7.26 ppm) for the aromatic protons.

The diastereotopicity of these positions could be observed only in ^{13}C NMR spectrum. The value of the diastereotopicity ($\Delta\delta$=0.09 ppm) is close to the data reported in the literature [5-8,15].

EXPERIMENTAL

^1H-and ^{13}C-NMR spectra were recorded at room temperature, using $CDCl_3$ as solvent, in 5 mm tubes, on a Varian Gemini 300 Fourier transform NMR spectrometer, equipped with a multinuclear head, operating at 300 MHz for protons and 75 MHz for carbon atoms.
M.ps were measured with Electrothermal melting point apparatus and are uncorrected.

*New compounds **1-5**, general procedure.* - Equimolecular amounts of 1,3-diol and carbonyl compound (0.1 mol) with catalytic amounts of p-toluenesulphonic acid (0.1 g) were solved in 200 ml benzene. The mixture was refluxed and the water resulted in the reaction was removed using a Dean-Stark trap. When 80 % of the theoretical water was separated, after cooling at room temperature, the catalyst was neutralized (under stirring 0.5 h) with CH_3-COONa powder in excess (0.2 g). The reaction mixture was washed twice with 100 ml water. After drying (with Na_2SO_4) the benzene was removed and the 1,3-dioxane compounds were purified by crystallisation from ethanol or by vacuum distillation.

5,5-Diethyl-2-methyl-1,3-dioxane ***1***.

Liquid, b.p.=77-78° C (1 mm col.Hg). Yield 55.6%. $C_9H_{18}O_2$, M=158.28. Found: C, 68.48; H, 11.61; required C, 68.31; H, 11.47. ^1H-NMR ($CDCl_3$) δ 0.70[t, 3H,J=7.7 Hz, 5-$CH_2C\underline{H}_3$(eq.)], 0.77[t, 3H,J=7.6 Hz, 5-$CH_2C\underline{H}_3$(ax.)], 0.98[q, 2H,J=7.7 Hz, 5-$C\underline{H}_2CH_3$(eq.)], 1.22(d, 3H,J=4.9 Hz, 2-CH_3), 1.65[q, 2H,J=7.6 Hz, 5-$C\underline{H}_2CH_3$(ax.)], 3.27(d,2H,J=11.2 Hz, 4,6-ax.), 3.68(d,2H,J=11.2 Hz, 4,6-eq.), 4.48 ppm(q, 1H, J=4.9 Hz, 2-H).

5,5-Diethyl-2-isopropyl-1,3-dioxane ***2***.

Liquid, b.p.=82-83° C (1 mm col.Hg). Yield 56.2%. $C_{11}H_{22}O_2$, M=158.28. Found: C, 70.72, H, 11.77; required C, 70.92; H, 11.90. ^1H-NMR ($CDCl_3$) δ 0.70[t, 3H,J=7.6 Hz, 5-$CH_2C\underline{H}_3$(eq.)], 0.77[t, 3H,J=7.4 Hz, 5-$CH_2C\underline{H}_3$(ax.)], 0.86[d, 6H, J=6.8 Hz, 2-$CH(C\underline{H}_3)_2$], 0.97[q, 2H,J=7.6 Hz, 5-$C\underline{H}_2CH_3$(eq.)], 1.63[q, 2H,J=7.4 Hz, 5-$C\underline{H}_2CH_3$(ax.)], 1.70[doublet of heptet, overlapped peaks, 1H,J=4.5, J'=6.8 Hz, 2-$C\underline{H}(CH_3)_2$], 3.25(d,2H,J=11.1 Hz, 4,6-ax.), 3.71(d,2H,J=11.1 Hz, 4,6-eq.), 4.06 ppm(d, 1H, J=4.5 Hz, 2-H).

5,5-Diethyl-2-phenyl-2-(phenyl-hydroxymethyl)-1,3-dioxane ***3***

Solid, m.p.=96-97° C. Yield 66.8%. $C_{21}H_{26}O_3$, M=326.44. Found C, 77.42, H, 8.17; required C, 77.27; H, 8.03. ^1H-NMR ($CDCl_3$) δ 0.64[t, 3H,J=7.5 Hz, 5-$CH_2C\underline{H}_3$(eq.)], 0.88[t, 3H,J=7.5 Hz, 5-$CH_2C\underline{H}_3$(ax.)], 0.88[q, 2H,J=7.5 Hz, 5-$C\underline{H}_2CH_3$(eq.)], 1,5-1,7(anvelope, 1H, -OH), 1.76[q, 2H,J=7.5 Hz, 5-$C\underline{H}_2CH_3$(ax.)], 3.38(d,2H,J=11.3 Hz, 4,6-ax.), 3.64(d,2H,J=11.3 Hz, 4.6-eq.), 4.69(s, 1H, 2-H), and 6.98-7.26 ppm(overlaped peaks,10H, aromatic protons). ^{13}C-NMR ($CDCl_3$) δ 6.35[5-$CH_2\underline{C}H_3$(eq.)], 7.59[5-$CH_2\underline{C}H_3$(ax.)], 22.27[5-$\underline{C}H_2CH_3$(eq.)], 24.18[5-$\underline{C}H_2CH_3$(ax.)], 30.08(C^5) 68.82(C^4), 68.91(C^6), 96.20(C^2), 126.96, 127.40, 127.82, 128.12, 128.31, 128.69 ppm aromatic carbon atoms

2,2,5,5-Tetraethyl-1,3-dioxane ***4***

Liquid, b.p.= 90° C (1 mm col.Hg). Yield 60.6%. $C_{12}H_{24}O_2$, M=200.32. Found C, 71.78; H, 11.94; required C, 71.95; H, 12.08. ^1H-NMR ($CDCl_3$) δ 0.78(t, 3H,J=7.5 Hz, 5-$CH_2C\underline{H}_3$), 0.87(t, 3H,J=7.6 Hz, 2-$CH_2C\underline{H}_3$), 1.38(q, 2H,J=7.5 Hz, 5-$C\underline{H}_2CH_3$), 1.69(q, 2H,J=7.6 Hz, 2-$C\underline{H}_2CH_3$), 3.51 ppm(s,4H ,4,6-H).

5,5-Diethyl-2-(ethyloxycarbonyl)methyl-2-methyl-1,3-dioxane ***5***

Liquid, b.p.=84-86° C (1 mm col.Hg). Yield 53.8%. $C_{13}H_{24}O_4$, M=244.33. Found: C, 63.78; H, 9.81; required C, 63.91; H, 9.90. ^1H-NMR ($CDCl_3$) δ 0.73(t, 3H,J=7.0 Hz, 5-$CH_2C\underline{H}_3$), 1.18(t, 3H,J=7.0 Hz, 2-CH_2-COO-$CH_2C\underline{H}_3$), 1.30(q, 2H,J=7.0 Hz, 5-$C\underline{H}_2CH_3$), 1.44(q, 2H,J=7.0 Hz, 5-$C\underline{H}_2CH_3$), 2.69(s, 2H, 2-$C\underline{H}_2$-COO-CH_2CH_3), 3.87(s,4H, 4,6-H), 4.06 ppm(q, 2H, J=7.0 Hz, 2-CH_2-COO-$C\underline{H}_2CH_3$)

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NITRATE-SELECTIVE MEMBRANE ELECTRODE WITH PROLONGED LIFE

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ABSTRACT

Nitrate-selective membranes were made using quaternary ammonium salts, plastified PVC and THF as solvent. The electrodes accomplished with these membranes had Nernstian response in the 10^{-1}-5.10^{-4}M concentration range.

The electrodes kept their sensitivities (54±3mV/decade) for more than two years of use.

The response characteristic of the electrode in presence of: ClO_4^-, Bph_4^-, I^-, Cl^-, Br^-, NO_2^-, HCO_3^-, $H_2PO_4^-$ and SO_4^{2-} was studied.

INTRODUCTION

The nitrate ion selective electrode is a typical example of the success of a liquid-membrane configuration.

The literature describes a great number of methods for obtaining NO_3^- selective membranes [1-9] whose sensitive electrode components are included in different classes: quaternary ammonium, arssonium and phosphonium salts, triphenyl methane dies, different metal complexes and different doped conducting polymers.

The poly(vinylchloride) (PVC) membrane, containing a quaternary ammonium nitrate ion-exchanger and a certain plasticized such as o-nitrophenyl octyl ether, or dioctyl phthalate which are the most popular [10,11].

Thomas [12] presented some aspects of the optimisation of the PVC matrix membrane and showed that a content of about 30% PVC was appropriate. The plasticising solvent mediator must have a high viscosity for longer functional life-time of the electrode.

This paper describes the fabrication and the characteristics of the nitrate-selective membrane electrode based on PVC, tricresylphosphate, tricaprilmethyl ammonium nitrate (Aliquat) and tetrahydrofurane (THF) as solvent.

The following abbreviations are used: PVC-poly(vinylchloride); TCPh-tricresylphosphate; AQ-aliquat NO_3; THF-tetrahydrofurane.

RESULTS AND DISCUSSION

The membranes which have a PVC content below 20% do not correspond as concerning their physical properties.

Some of the experimental data are given in Table 1

Table 1. Membrane composition and calibration data.

The membranes composition wt(%)			Linear response range (M)	Slope (mV/decade)
PVC	TCPh	AQ		
24	64	12	5.10^{-4}-10^{-1}	49
30	40	30	5.10^{-4}-10^{-1}	52
30	50	20	5.10^{-4}-10^{-1}	56
30	60	10	5.10^{-4}-10^{-1}	53
30	65	5	10^{-3}-10^{-1}	46
38	24	38	5.10^{-4}-10^{-1}	50
38	42	20	5.10^{-4}-10^{-1}	52
38	47	15	5.10^{-4}-10^{-1}	50
38	52	10	5.10^{-4}-10^{-1}	49
38	57	5	10^{-3}-10^{-1}	47

The membrane prepared with a small quantity of TCPh and AQ respectively, have a poor sensitivity. Among the membrane compositions with different PVC contents, the best properties are achieved by that one with 30% PVC, 50% TCPh and 20% AQ, which achieves 96% from theoretical sensitivity value at 20°C.

The effect of the pH on the potential response of NO_3^--selective membrane electrode is given in Figure 1 The maximum volume of H_2SO_4 and NaOH (0.5M), necessary to change the pH of a 50 ml sample was 0.25ml.

The optimum pH range is between 3-11 pH.

The effect of ionic strength on the electrode response was established. The results are given in Figure 2.

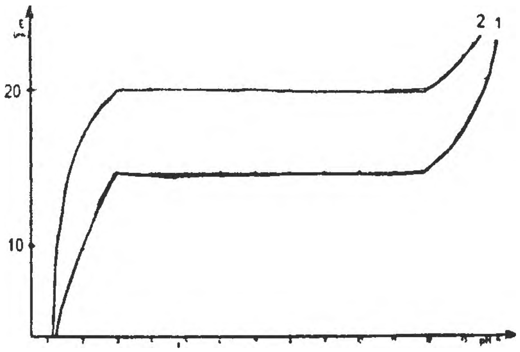

Figure 1. Effect of the pH on the potential response of the electrode.
1- 10^{-2}M $NaNO_3$; 2- 10^{-3}M $NaNO_3$

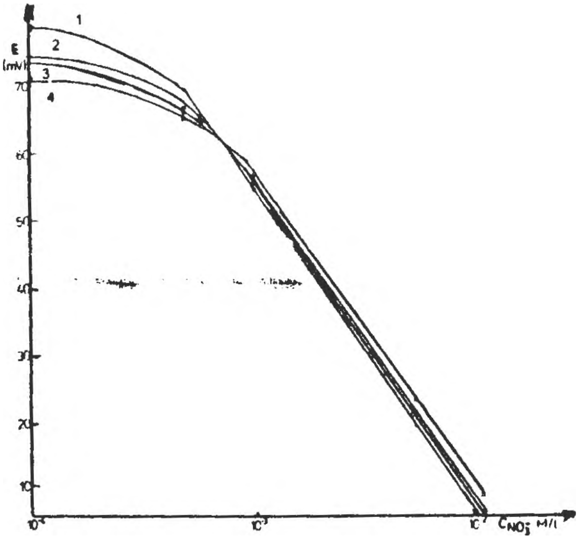

Figure 2. Effect of ionic strength on the response of the electrode
1- J= 0.1; 2- J= 0.3; 3- J= 0.6; 4= J=1.2

It can be seen that while an increase of J takes place, a slight drift of the calibration graphs and a slight diminishing of the linear response range occurs.

The results of the selectivity study by the mixing solution method [13,14] are shown in Figure 3.

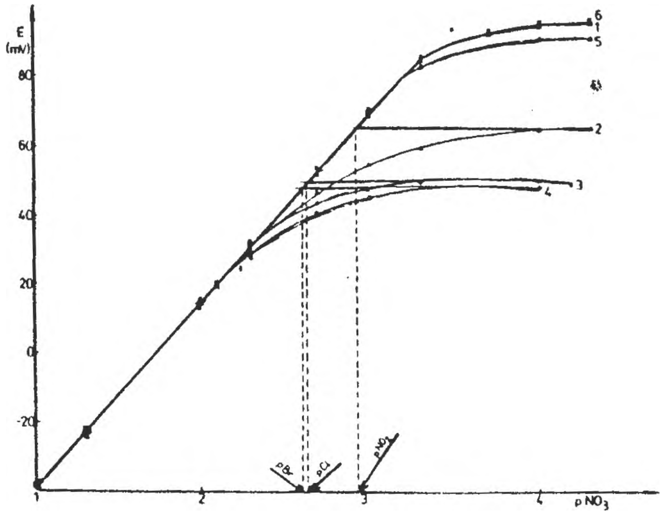

Figure 3. The selectivity study of the nitrate selective membrane electrode
1- NO_3^-M; 2- NO_2^- 10^{-2}M; 3- Cl^- 10^{-1}M; 4- Br^- 10^{-2}M; 5- HCO_3^- 10^{-2}M; 6- $H_2PO_4^-$ 10^{-2}M

I^-,ClO_4^- and Bph_4^- are interferents; Cl^-, Br^- and NO_2^- are slight interferents and $H_2PO_4^-$, HCO_3^- and SO_4^{2-} are not interfering at all. The following selectivity coefficients KNO_3^-,X^- were obtained: KNO_3^-,Cl^-=2.3x10^{-2}, KNO_3^-,Br^-=2.5x10^{-1}, KNO_3^-,NO_2^-=1.3x10^{-1}.

The operational life-time of the electrode was tested during a period of more than two years. The electrodes were permanently kept in a 10^{-2} M $NaNO_3$.
During this period, the physical properties (colour, elasticity) of the membranes were unaffected. The results for calibration curve in the same period are shown in Table 2.
These data show that: the linear response range of the electrode remained unchanged; the slope decreased only with 3% from initial proper value. Practically, the drift of the potential for each concentration level affected only the intercept of the calibration curve.

Table 2. Calibration data during different period of time.

NO_3^- concentration (M)	E(mV) after 24h	|ΔE| (mV)			
		a week	six months	a year	two years
10^{-4}	72	2	6	8	8
5.10^{-4}	66	1	1	10	6
10^{-3}	56	0	5	11	9
5.10^{-3}	17	2	6	9	7
10^{-2}	-2	1	5	8	10
5.10^{-2}	-39	3	7	10	12
10^{-1}	-56	2	8	10	12
S (mV/decade)	55.2	55.0	55.2	54.0	53.5
$S/S_{teor,\ 20\ C}$x100%	95.2	95.0	95.2	93.1	92.2
E_0 (mV)	-111	-113	-119	-121	-123

CONCLUSIONS

The analytical performance of NO_3^--selective electrode are:
-Linear concentration range 10^{-1}-5.10^{-4}M/l;
-pH range: 3 - 11pH;
-Slope: 54± 3 mV/decade.
-Electrical resistance: under 100 KΩ;
-Response time: a few seconds;
-Operational life-time: minimum two years,
-Memory effect: absent;
-Interferents: I^{-1}, ClO_4^- and BPh_4^-.

EXPERIMENTAL

Apparatus and reagents

NO_3-selective membrane electrode; double-junction Saturated Calomel Electrode (Na_2SO_4 0.33M in the second salt bridge) pH/mV-meter with a precision of ±0.2mV; magnetic stirrer and thermostatically controlled bath at 20± 0.1°C.

NITRATE - SELECTIVE MEMBRANE ELECTRODE

The following reagent of analytical reagent grade were used: Poly(vinyl chloride) - PVC Romania; Tricaprylmethyl ammonium chloride (Aliquat 336) - Fluka Switzerland; Tricresylphosphate (TCPh) - Chemicals Ltd - England; Tetrahydrofurane (THF) - Carlo Erba - Italy; $NaNO_3$; Na_2SO_4; H_2O; NaCl; NaBr; NaI; $NaHCO_3$; $KClO_4$; KH_2PO_4; KNO_2 - Romania and $NaBPh_4$ - Riedel - DI Haen AG - Germany.

Aliquat-NO_3^- was prepared from Aliquat-Cl^- by using the known procedure [15]

The NO_3^--selective membrane based on: PVC, TCPh, AQ and THF as solvent, have been prepared. Different compositions in THF were prepared: PVC: 15-38%; TCPh: 82-24%; AQ: 3-38% (weight percents).

The homogenous composition was casted on a plane surface and than slowly evaporated at room temperature for 48 hours.

The configuration of the nitrate-selective membrane electrode is shown in Figure 4.

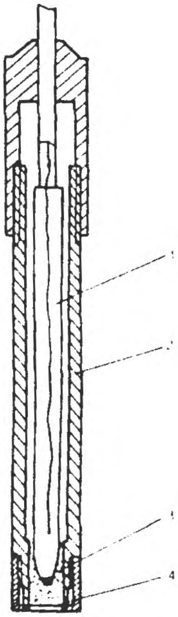

Figure 1 Nitrate-selective membrane electrode : 1- internal reference; 2- electrode body; 3- internal solution; 4- nitrate selective membrane

The conditioning of the electrodes was made by keeping them in 10^{-}M $NaNO_3$ solution for 24 hours.

The testing solutions were prepared in the concentration range of 10^{-4}-10^{-1}M $NaNO_3$ at J= 0.1 (Na_2SO_4 as ionic strength adjustor).

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THE APPLICATION OF POTENTIOMETRIC DIFFERENTIAL Cu(II)-MICRODETECTOR IN CLINICAL ANALYSIS

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ABSTRACT

A Potentiometric Differential Microdetector equipped with two similar Cu(II)- selective membrane was used for the determination of a number of amino acids and total proteinsin serum,in clinical analysis .
The results of the method for total proteins were compared with the biuret method.
The system is suitable for the determination of total proteins in clinical analysis in the interested range with a relative error better than 3.6% at a sampling rate of 100 samples h^{-1}.

INTRODUCTION

The formation of copper complex with amino acids is the base of potentiometric determinations of this with different types of electrodes : copper wire, copper ion selective membranes [1-3], silver wire [4-5].

In usual clinical determinations of proteins, the biuret reaction [6]is used in spectrophotometrical analysis.

Hitchman and Nyasulu [7] have found that in indirect potentiometry of amino acids and proteins with metallic ions the response at organic ligand concentration can be linear over a range of tenths millivolts and a general model is presented in terms of an electrode of the second kind and then an experiment for a number of amino acids and proteins applied in Flow Injection Analysis [FIA]

Our work presents the application of two solid membranes sensitive to Cu(II) as an integrated part of potentiometric differential microdetector (Cu-MD) in FIA for total proteins in sanguine serum. The detector has also been used in comparative studies with copper ion selective electrode (Cu-ISE).

RESULTS AND DISCUSSION

The calibration graphs for amino acids and proteins are shown in Figs. 2 and 3. The calibration graph for bovine serum albumin was used for the determination of total proteins in serum, in clinical analysis. The samples from the sanguine serum were prepared in the same way as the standard solutions.

The performance and reproducibility of the proposed system on real concentrations of total proteins are shown in Table 1.

Table 1 Performance and reproducibility of the proposed flow injection system for total proteins in serum

Sample no.	Proteins concentrations g/%		Recovery %
	Spectrophotometric method	Proposed FIA system	
1	5.00	4.96	97.25
2	6.20	6.27	101.13
3	6.73	6.89	102.38
4	7.58	7.61	100.39
5	6.82	6.83	100.15
6	6.95	7.10	102.16
7	6.85	7.10	103.64
8	7.20	7.30	101.38

The calibration graph slopes obtained with Cu-MD are inferior to those obtained under static conditions with Cu-ISE. The calibration graph stability depends on the solution's stability: for alanine and histidine it is of the order of 3-4 days, but in the case of albumin the calibration solutions must be prepared daily.

The data in Table 1 recommend the utilization of the FIA method with Cu-MD for albumin determinations in the human or veterinary clinical laboratories.

For ensuring optimum measuring precision, it is necessary that a high-precision apparatus should be used (o.1 mV).

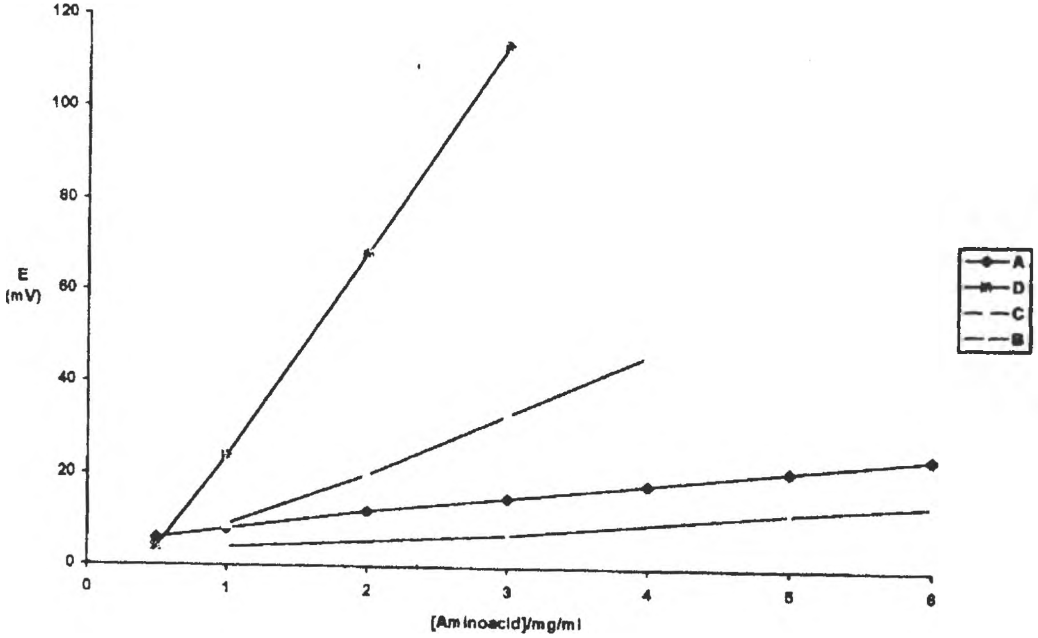

Figure 2. Calibration graphs for aminoacids;
A,D- alanine,histidine (ISE); B,C- alanine,histidine (FIA)

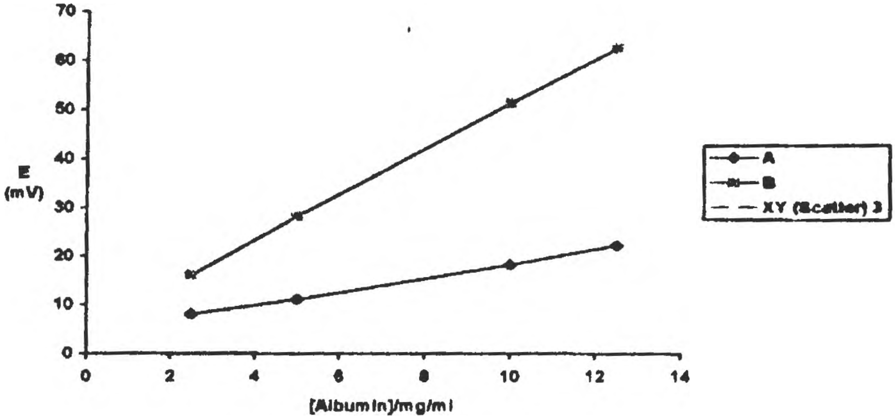

Figure 3. Calibration Graphs for Albumin; A - FIA, B - ISE

EXPERIMENTAL

Reagents and solutions :

For preparing all aqueous solutions double distilled water and analytical-reagent grade chemicals were used.Amino acids and protein : bovine serum albumin (Merck), L-alanine (Fluka) and L-histidine (Fluka).Carrier solution: potassium nitrate 10^{-1} mol dm^{-3}, prepared in acetic buffer (pH=6.3) and containing copper nitrate 10^{-4} mol dm^{-3}, for a good stability of the base line.Amino acids and albumin stock solutions: L-alanine/L-histidine 10^{-1} mol dm^{-3}, bovine albumin 10^{-1} mol dm^{-3} .Copper stock solution : copper nitrate 10^{-1} mol dm^{-3}.

Apparatus and working conditions

In static method we used a pair of electrodes formed by Cu-ISE and double junction saturated calomel electrode, a millivoltmeter (o.1 mV precision) and a magnetic stirrer.
In the dynamic method we used a potentiometric differential Cu(II)-microdetector, arrangement, as in Fig.I

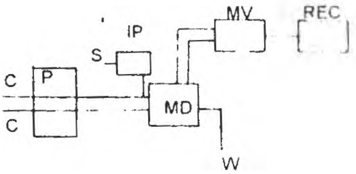

Figure 1. Schematic diagram of the flow system
C- carrier; S- sample; P- peristaltic pump; IP- injection peristaltic pump; MD- potentiometric differential microdetector; M- millivoltmeter. REC- recorder; W- waste
-sample injection volume- 300μl;
-sampling rate- 100 h^{-1};
-carrier stream at a constant flow- rate of - 0.13ml min^{-1};
-ionstrength for carrier and sample j=0.03

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CAPACITIVE-TYPE HUMIDITY SENSOR USING METHACRYLIC TERPOLYMER

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ABSTRACT

A capacitive type humidity sensor was prepared using a methacrylic terpolymer. The electrical capacitance changes linearly with relative humidity (RH) over the range of 12 - 75 %. It shows a deviation upwards at RH >75 %; the sensitivity at 95 % was about 1.56 The sensitivity was enhanced by progressive cross-linking reaction and by the presence of the 2-hydroxyethyl-methacrylate. The hysteresis was small (≈ 3.5 % RH) and the response time was fast. The present humidity sensor is suitable for practical use.

INTRODUCTION

Humidity is one of the most important parameters in a variety of industrial and agro-industrial processes. Consequently, a vast amount of humidity sensors operating by different working principles have been developed [1] They have their specific advantages, disadvantages and areas of application. The humidity-sensitive materials used in sensors are classified into three groups: organic polymers, porous ceramics and electrolytes [2 - 6]. It is well known that cellulose derivatives and polyimide are suitable capacitive-type humidity sensing materials [6], but there are problems concerning the hysteresis and long term stability. We have reported that the most important requirements for manufacturing capacitive-type humidity sensors are low hygroscopicity and a rigid structure of the sensing polymer [7.8].. As a consequence, research towards the synthesis of new sensing materials, polymeric thin films for applications in capacitive-type humidity sensors has been intensified over recent years.

In the present paper we have chosen poly[(methyl-methacrylate)-*co*-(vinyl- crotonate)-*co*-((2-hydroxyethyl)-methacrylate))] as sensing material to make a capacitive-type humidity sensor (Fig.1). The main characteristics of the sensor are presented here.

EXPERIMENTAL

For the measurement of the sensing characteristics, a sandwich-type device was prepared, according to the following procedure: a monomers mixture of 75 % (molar) methyl methacrylate +10 % (molar) hydroxyethyl methacrylate + 0.5 % (molar *vs.* double bonds) benzoyl peroxide was prepolymerized by thermal initiation until an appropriate viscosity. An amount of 16 % (molar) of vinyl crotonate (VCr) was added after cooling and the solution was heated again until its viscosity began to increase.

The solution was cast by spin coating onto a ceramic substrate [7] that had a pair of gold electrodes deposited by vacuum evaporation technique. The thin film on the substrate was thermally treated at 120 °C to completely polymerise it. The upper aluminium electrode (*cca* 10 ÷ 20 nm in thickness) was prepared by vacuum evaporation technique and the area of the sensing device was

4 - 6 mm. The electrical properties were measured using an RLC meter at 1 kHz (E 0711 IEMI Bucureşti)..

All data presented here refer to experiments at room temperature (20 ± 1 °C). The sensor is mounted in the test chambers, which consist of closed vessels partially filled with saturated salt solutions in order to obtain well-defined relative humidity levels [9]

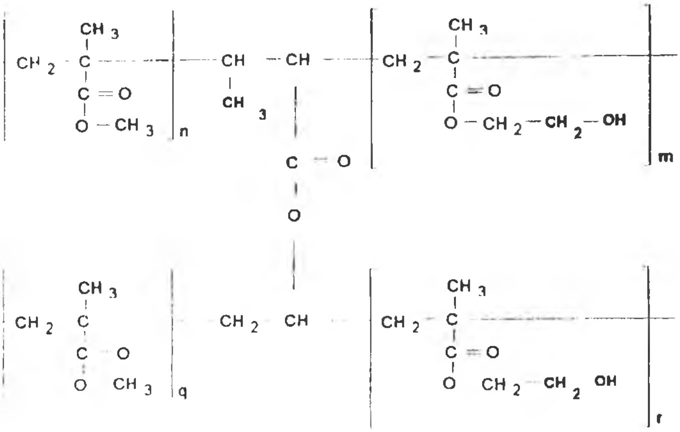

Fig. 1 The polymer structure

RESULTS AND DISCUSSIONS

The polymer structure is determined by the ratio of the three *co*-monomers and by the parameters of the polymerisation process : ***(I)*** the type and the concentration of the ***co***-monomers, ***(ii)*** the pre-polymerisation temperature, ***(iii)*** the final heat treatment. The monomers' ratio can determine an optimum concentration of the hydrophilic groups in the polymer composition The aim of that is to regularise the sorption capacity of material by modifying its hydrophilic and/or hydrophobic character . It is known that an increased hydrophilic character is responsible for a large amount of sorbed water in polymer even at low and medium RH and an enhanced hydrophobic character causes a very low sensitivity even at high RH. The type and the concentration of the initiator are very important because the moment of pre-polymerisation determines the size of the macromolecules. On the other hand, the residual products resulted from the decomposition of the initiating reagent can influence the dielectric properties of the material. In order to avoid this, we have chosen benzoyl peroxide as initiating reagent because of its low temperature decomposition (≈ 60 °C); also, the secondary product is benzene which can be easy stripped from the polymer by heat treatment. The benzoyl peroxide concentration is low and it causes the increasing of the macromolecules' length . The aim of the final heat treatment is to finish the polymerisation and the cross-linking process, and to clean the material of the undesirable low molecular size products resulted from the secondary reactions. In this way, the electrical characteristics are rather due to polymeric material instead of the impurities. The electrical capacitance of the present sensor was examined as a function of relative humidity at 1 kHz as shown in Fig. 2.

The capacitance increases linearly with relative humidity over the range of 12 - 75 % and it has a noticeable increase above RH = 75 %. The sensitivity (capacitance at "x" % RH/capacitance at 12 % RH) (Fig. 2) depends on the polymer hygroscopicity. MMA and Vcr are hydrophobic and the increase of sensitivity above 75% is derived from the enhancement of the water content along with an increase of the hygroscopicity because of the presence of the 2-hydroxyethyl-methacrylate.

2-hydroxyethyl-methacrylate has a hygroscopic character and this gives the behaviour of the sensor. Also, the sensitivity is enhanced by cross-linking the polymer because of the increase of the free space around the polar sites.

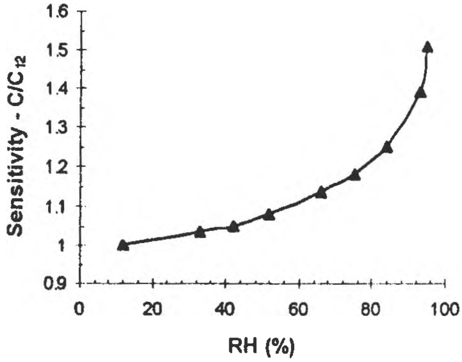

Fig. 2 The sensitivity (C/C_{12}) vs. RH ($T = 20$ °C, $\nu = 1$ kHz)

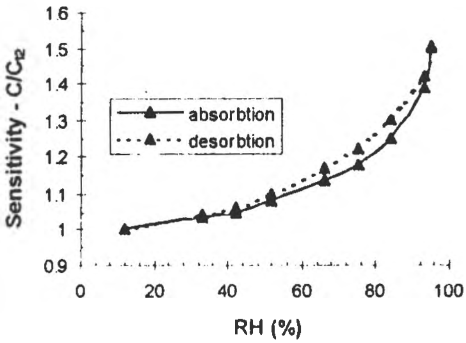

Fig. 3 The sensitivity vs RH in an absorption/desorption process ($T = 20$ °C, $\nu = 1$ kHz)

The increment of sensitivity tends towards the increment of hysteresis. The cause of hysteresis is the formation of clusters of sorbed water [7, 8]. The present results are consistent with that interpretation. The hysteresis was strongly affected by the history of exposure to a humid atmosphere as shown in Fig. 3. From this figure we can see that the sensitivity observed in desorption process increases with an increase in the highest humidity of exposure. These results show that the formation of clusters of sorbed water was initiated by increasing the water content at a higher relative humidity region and desorption became difficult in the desorption (desiccation) process. The adsorbed water vapours consist of chemisorbed as well as physisorbed water which have different relaxation mechanisms.

Also, the changes occur in the relative abundance of each species as the amount of adsorbed water increases with relative humidity. The loss tangent *vs.* RH (Fig. 4) illustrates this behaviour. At low humidity levels (12 - 75 % RH) the loss tangent is almost linearly and it presents an increase at RH > 75 % because of the amount of adsorbed water. The curve fit for the loss tangent dependence has two components: ***(I)*** at low humidity levels (12 - 75 %RH) there is a linear dependence $y = 0.0007x + 0.0747$ and *R-squared value* $R^2 = 0.939$; ***(ii)*** at larger values of relative humidity, there is a polynomial

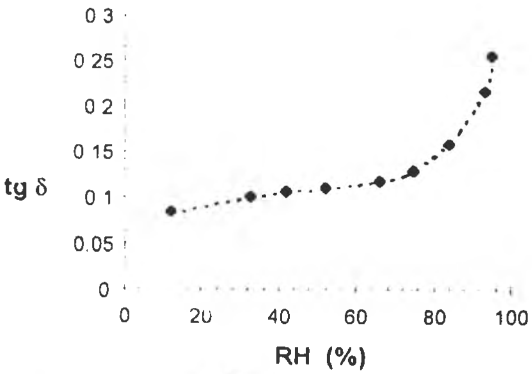

Fig. 4 Loss tangent vs. RH ($T = 20$ °C, $\nu = 1$ kHz)

dependence $y = 0.0011x^2 - 0.1956x + 8.534$ and *R-squared value* $R^2 = 1$. However, the hysteresis was small, *cca.* 3.5 % RH, including experimental errors.

The response time of the sensor is good (the 63 % max. response was within 1.5 min, obtained by changing the relative humidity from 12 % RH in the vessel to 60 % RH in the laboratory atmosphere).

CONCLUSIONS

We have prepared a capacitive type humidity sensor based on poly[(methyl-methacrylate)-*co*-(vinyl crotonate)-*co*-((2- hydroxyethyl)-methacrylate))]. The sensor prepared has a good sensitivity and small hysteresis. The sensitivity was enhanced: ***(i)*** by cross-linking the polymer because of the increase in the free space around the polar sites and ***(ii)*** by the presence of 2- hydroxyethyl)-methacrylate which increases the hygroscopicity of the polymer. The hysteresis was small, less than 3,5 % RH, including the experimental errors. The response time was fast. Consequently the poly[(methyl-methacrylate)-*co*-(vinyl crotonate)-*co*-((2-hydroxy ethyl)-methacrylate))] sensor is suitable for practical and reliable capacitive-type humidity sensor.

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Monoatomic Carbon and its Chemistry

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Introduction

In recent years, after the discovery and synthesis of fullerenes, C_1 and C_2 in particular have been the object of increasing interest. C_1 is proposed as the fundamental brick in the building of fullerenes through the formation of linear chains that subsequently produce rings and fullerenes; their fragmentation, in turn, is considered to proceed with continuos loss of C_1 and C_2.[1]

The chemistry of particular reactive atomic carbon, C_1, and small chains C_2, C_3, C_4, mainly produced by carbon arc, deserve nowadays steady attention. The monoatomic carbon is not only the brick in fullerenes formation but, far more important, is the fundament of life on Earth. Understanding its chemical behavior is a must in understanding the fundamental rules which govern our planet and the chemistry of the Universe.

Atomic carbon is, by its self, one of the most fascinating intermediates encountered in chemistry, due to its extremely high energy and its particularly interesting electronic configuration. From the possible fifteen electronic states, the triplet ground state $C(^3P)$ and the two low-lying excited metastable singlet states, $C(^1D)$ and $C(^1S)$, are thought to be involved in most of the reactions in which monatomic carbon is generated, considering that the energy split betwen them (~30 kcal/mol) is relatively small compared with the total amount of energy involved in the generation of atomic carbon, present at the reaction site.

The following informations are trying to update and reorganize the data available in literature about carbon atom chemistry. It should be mentioned that the only two reviews about this subject are almost fifteen years old. [2, 3]

Generation of atomic carbon

In order to generate atomic species, one should start with the stable allotropic forms of elemental carbon and invest a tremendous amount of energy to vaporize it. The other

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* The idea about this reviw started from a presentation that the author has to perform during her Ph.D. program at Michigan State University, Department of Chemistry, MI, USA.

alternative is to start with an extremely energetic species which decomposes to generate atomic carbon, C_1. In the first case, graphite is the source and the energy used for evaporation is electrical or thermal. In the second one, species which photolyticaly or thermally decompose to monoatomic carbon are used, as carbon suboxide C_3O_2.

Table 1: Methods used for carbon atom generation

Source	Method	Advantages	Disadvantages	Notes
C graphite	A. Nuclear recoil methods	-no dimers -^{11}C radioactive	-excess of E_{kin}. -low amount of ^{11}C -only radiochemical detection	-manly used for ^{11}C and ^{14}C -$^{14}N(n, p)^{14}C$ -$^{14}N(p, a)^{11}C$
	B. Graphite vaporization technique			graphite used as source of C and source of energy
	a)C arc	-from -196° to 2500° C. -low pressure -higher yields	-presence of molecular species -large amount of UV light	
	b)Heating		-C_3 is predominant	
	c)Laser heating	-more C_1		
	d)Explosion of filaments			-mainly used for studies of reactions with H_2
C_3O_2 N_3-CN R_2CN_2 N + CN·	C. Photolytic Thermal	-temp ~ 100° -no excess of E_{kin}		-flash photolysis studies
	E. Other methods			
C_3O_2	a)Microwave discharge			
$^{14}C^+$	b)Neutralization of ionic beam			

An other method used for generating highly energetic atomic carbon atoms is through nuclear reactions.[2] The method offers the advantage of low concentration in monoatomic carbon (~10^{-7} M) and, consequently, avoids the presence of C_2 and C_3 species. Also, the radioactivity of ^{11}C and ^{14}C generated in this way allows radiochemical detection. But, due to the nature of the method, the atomic carbon is extremely energetic and, as a consequence, the excess of its kinetic energy is a source of distorted information about its reactivity, especially in comparison with other methods.

In **Table 1** are classified the methods used for generating monoatomic carbon,[2] according with the source of carbon, along with the advantages and disadvantages involved by the use of each of these methods.

Carbon Arc. Among the methods which start with graphite as the source, the carbon arc is the most popular. It involves the use of the apparatus described by Skell *et al.*[1] which allows working under high vacuum. The procedure offers a wide range of temperatures for performing the subsequent reaction, from 2500 to 77 K, by cooling the walls of the reaction vessel at the desired temperature. The carbon atoms, generated at the electrodes, are thought to travel to the walls fast enough to reach the reaction site in one of the three low-lying electronic states ^3P, ^1D or ^1S. Any one of these may be considered as reactive species in the conditions of the arc. Analysis of the carbon vapors generated by arc method shows that 70% of the carbon consumed from the electrodes participated in the subsequent reaction; out of it, 40% is thought to be C_1. For the composition of carbon vapors

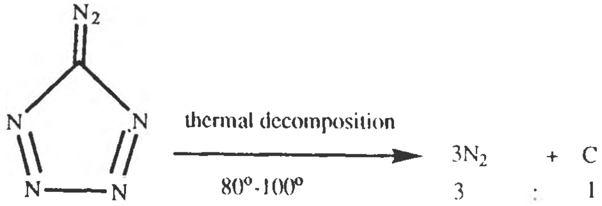
see **Table 2.**

Table 2: Relative molar concentrations of carbon species generated by arc:

Species	Arc	Thermalized
C_1	100	100
C_2	35-48	20
C_3	7-10	61
C_4	0.6-1.0	

The values are obtained by chemical analysis of the products in the reaction with chlorine gas; the percentages are confirmed by mass-spectroscopic detection.

Decompozition of other species. Among the methods which are using highly reactive species as starting compounds, the one using diazotetrazole is the most popular.[4,5,6] The diazotetrazole is prepared in tetrahydrofurane (THF) solution and the solvent is evaporated while the walls of the reaction flask are evenly coated with the diazonium compound. The substrate may be added in the initial solution of THF or after the evaporation and than the system is UV irradiated or heated at 80°-100° C; during this procedure the diazocompound decomposes in nitrogen gas N_2 and monoatomic carbon in a 3: 1 ratio (**Scheme 1**).



Scheme 1

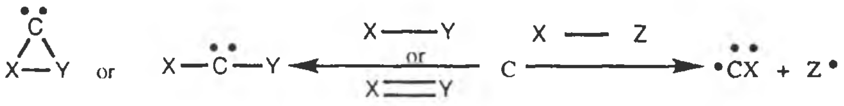
The advantages of the method consist in producing monatomic carbon with low kinetic energy along with moderate running temperatures for the subsequent reaction of the substrate with carbon.

A closer look on each of the methods mentiond in Table 1 allows one to conclude that there is no simple method to generate monoatomic carbon without complications. The most frequent problems are related with:

- the presence of C_2 and C_3 species,
- the excess of kinetic energy available for C_1
- the possible excitation of the substrate, the reaction partner of C_1, due to the energy involved in the generation of monoatomic carbon.

The chemistry of monoatomic carbon

In interaction with organic substrates, atomic carbon follows two possible routes: insertion in σ or π bonds and atom abstraction (**Scheme 2**).



Scheme 2

The products observed, at the conclusions of the reactions, are formed by subsequent transformations of the intermediates generated in the primary reaction of the carbon atom with the substrate. The intermediates may by monovalent species known as methylynes, divalent carbenes or radicals, all of them highly reactive (see their experimental heats of formation, H_f, available in **Table 3**).

Table 3: Experimental heats of formation* (in kcal/mol):

Species	H_f (exp)	Species	H_f (exp)	Species	H_f (exp)
$C_1(^3P)$	171	CH	142.4	iso-C_3H_7	22.3
$C_1(^1D)$	201	$^1CH_2$	99.8	H_2C=CH	63.4
$C_1(^1S)$	233	$^3CH_2$	92.3	H_2C=CH_2CH_2	40.0
C_2	200.2	CH_3	34.8	HO	9.3
C_3	196	n-C_3H_7	16.8	H_2N	45.1

* from: Lias, J. L.; Bartmess. J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. "Gas Phase Ion and Neutral Thermochemistry" *J. Phys. Chem Ref. Data*, 1988, *17*, Supl 1

Befor concluding about the chemical behavior of monoatomic carbon in interaction with a certain substrate, one should consider different aspects which may influence the results and their interpretation. The most obvious aspects which have to be considered will be presented below.

a). The electronic state of the reacting monoatomic carbon.

Given the relatively small gap between the ground state triplet and the two low-lying excited singlet states of carbon, all three of them have to be considered as possible reacting species. In **Fig.1** a simplified representation of the electronics of this three states along with their heats of formation is presented.

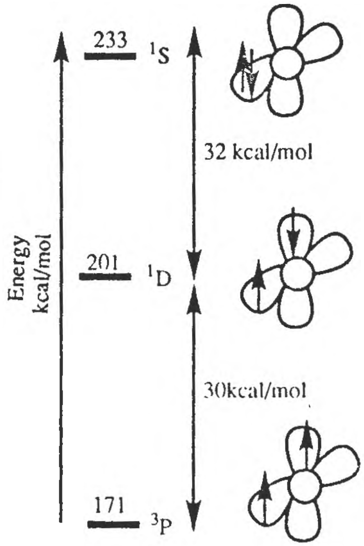


Fig 1

For sorting out which of these states is involved in a reaction, one has two handles: the electronic state of the reacting partner and the electronic state of the product. For the involvement of triplet ground state C(^{3}P), usually molecular oxygen is added to the system and its influence on the overall and particular yields is used as an indication of the participation of the triplet state in the reaction. The use of O_2 as a scavenger for C(^{3}P) is based mainly on the conservation of spin rule which governs the interaction of triplet carbon with triplet oxygen molecule. Also, theoretical calculations are an useful tool for analyzing the electronic state of carbon atom and give informations related with the possible crossing points on the potential energy surface (PES) of the reaction.

As a general trend, in good agreement with the informations available in literature, the most reactive species seems to be the singlet ^1D followed by the triplet ^3P and the less reactive singlet ^1S. Given the fact that singlet ^1D exists as two different substrates, one closed shell and one open shell, very close in energy, one should keep in mind that the problem of which electronic state of carbon atom reacts is not an easy one to be solved.

b).The presence and involvement of poliatomic species.

Only-carbon molecules, as C_2, C_3, C_4, were detected and characterized in the process of monoatomic carbon generation. The presence of C_2 and C_3 is more likely in the vapor mixture obtained by arc or heat generated carbon (see **Table 2**).
These species were characterized by spectroscopic means, and their ground and excited states are known, but yet their involvement is hard to be clearly stated. If such species are generated along with monoatomic carbon, the question is if they are in their ground state or in one of the low-lying excited state. C_2, by the way, is a singlet molecule in its ground state but the excited triplet is lying only 1.75 kcal/mol above it. Their way of interacting with the substrate is similar to the atomic carbon, insertion in σ and π bonds, and atom abstraction. The initial products obtained through their reaction may decompose or further react with the substrate complicating the spectrum of the final products.

The involvement of C_2 and C_3 species may be followed by mass spectrometry detection or by radioactivity measurements, in the case of nuclear recoil methods, used for ^{11}C and ^{14}C generation.

c).The presence of methylyne, methylene and methyl radicals.

Often, the organic reaction partner of monoatomic carbon, the substrate, contain hydrogen atoms. In such case, hydrogen abstraction by monoatomic carbon competes with other possible routs for chemical interaction. Species like methylyne CH, methylene CH_2, or methyl radicals CH_3 are generated. It may be more likely that the abstraction of an hydrogen atom generates initially CH, which reacts further with the substrate by hydrogen abstraction forming CH_2. The methylene forms subsequently the methyl radical through an other hydrogen abstraction reaction (see **Scheme 3**).

$$C + HR \longrightarrow \cdot\overset{\cdot\cdot}{C}H \xrightarrow{+HR} \overset{\cdot\cdot}{C}H_2 \xrightarrow{+HR} \cdot CH_3$$

Scheme 3

The possibility of methylene formation by carbon atom stripping simultaneously two hydrogen atoms have also to be considered. The presence of these species, as the result of the primary process, rise the question of their electronic state and their interaction with the substrate; one should keep in mind that their chemistry is basically the same as the one of the investigating monoatomic carbon, insertion in σ or π bonds and atom abstraction.

The complications added through their presence may be clarified nowadays starting with the new experimental data about their heat of formation (**Table 3**) and by the use of the advanced methods in spectroscopy along with the support of the more and more sophisticated available computational means.

d). The electronic state of the reactive substrate

Under the conditions used for carbon atom generation, the existence of the substrate in its ground state become questionable. Especially for the cases where the amount of energy is huge, as the carbon arc or the recoil method, the substrate may encounter the vapors of carbon after its reaches one of its excited state. As an example, the case of methanol may be cited, where several possible ions and radicals may be the partners in the reaction. In a case like this, the products will not be simply the results of chemistry between carbon atom and the desired ground state of the substrate.

Considering the aspects mentioned above, it is clear that studying the chemistry of monoatomic carbon is not a simple problem at all. Special attention should be directed to differentiate among the initial process and the subsequent ones which involves species generated in the primary reaction. Also, for the primary process, distinction is required among the reacting states of C_1. Than, a rigorous search of each possible channel for reactions, opened by each of the intermediates primary generated, is requested. Whit all this in mind, the task of following monoatomoc carbon chemistry turns in a challenging one.

Table 4: Reactions of atomic carbon

Reaction	Competition with:	Carbon state	Obs.	Ref.
C-H insertion				
saturated H-C	H abstraction	^1D, ^1S	no influence of O_2 on yield	7,8,9
unsat. H-C	H abstraction			
	add. C=C	^1D, ^3P		
benzenes	add. C=C	^3P, ^1S	possible involv. of :CH_2	16,17, 18
alcohols	O-H insertion	^1D	radicals from excited alcohols	
	C-O ylide formation	^1D		
heteroaromatics	add. C=C			19,20
C-X insertion				
X = O, ethers			no insertion noticed	
X = F			no insertion noticed	21,22
X = Cl				21,23
N-H insertion			noticed in NH_3 + C	
O-H insertion			noticed in H_2O + C	12
C=C insertion				10,11
unsaturated HC	H abstraction	^1S	no influence of O_2 on yield	
unsaturated FluoroC				
heteroaromatics	H abstraction	^1D		19,20
Atom abstraction				
H				
saturated HC	C-H insertion		C_2 present	
unsaturated HC	add. C=C			
benzene	add.C=C	^3P		
	C-H insertion			
alcohols				
F, Cl				
O				24,25, 26,27, 28
etheres		^1D		13
carbonyl compds.		^1D		
N				
aziridine				14
S				
thioetheres		^1D		15

The summary in **Table 4** intend to present the reactions of atomic carbon with some of the most common organic compounds, classified according to the type of interaction (atom abstraction or bond insertion). The scheme contains also the most likely electronic state of atomic carbon thought to be responsible for observed chemistry. Under the "notes" other possible species which might be involved in are listed along with some informations considered usefull.

Carbon Atom as Electrophile

Due to the nature of its outer electronic shell, atomic carbon acts as an electrophile, searching for the site with the highest electronic density in the substrate. This major aspect of its reactivity governs the competition among insertion in σ or in π bonds and atom abstraction. But, despite its high energy, monoatomic carbon presents, in several cases, an **unexpected selectivity.**

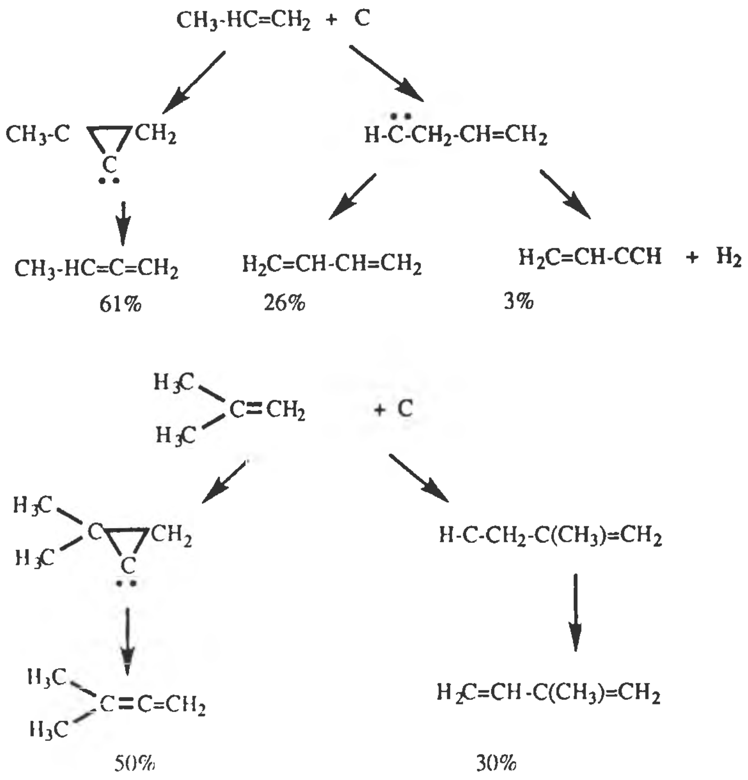
In reactions with saturated hydrocarbons, atomic carbon presents the same preference toward the weakest of the σ bonds of the partner, regardless the method used for its generation and its excess of energy.[7] As an example, the insertion in secondary C-H σ bond (94 kcal/mol) of propane is preferred toward the primary one (97 kcal/mol). Even more, in competition with cyclopropane (106 kcal/mol for the C-H bonds), propane if preferred.[8,9] Such a high selectivity for an energetic species, as C_1, is remarkable.

When the σ bond competes with π bond, the addition to the π system is more likely to occur.[10, 11] The yield of ethylene reaction with carbon, generated by different methods, are presented in Scheme 4; they are clearly illustrating the preference for addition *vs.* insertion.

	Addition	Insertion
^{11}C gas phase	3.7	1
^{11}C condensed phase	2.6	1
arc generated C in Ne matrix /condensed	2.5	1
chemically generated C /gas phase	1.6	1
low intensity C arc high vacuum, 77 K	1.3	1

Scheme 4

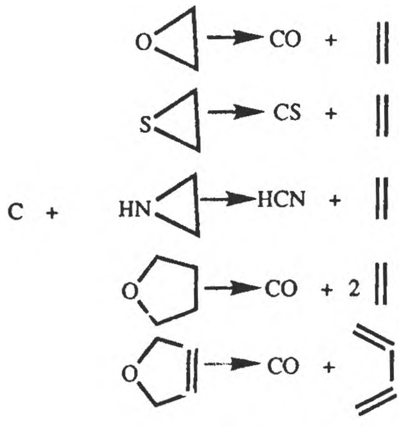
If there are allylic bonds available, they are preferred toward the vinylic ones, as may be seen from the yields presented in Scheme 5.



Scheme 5

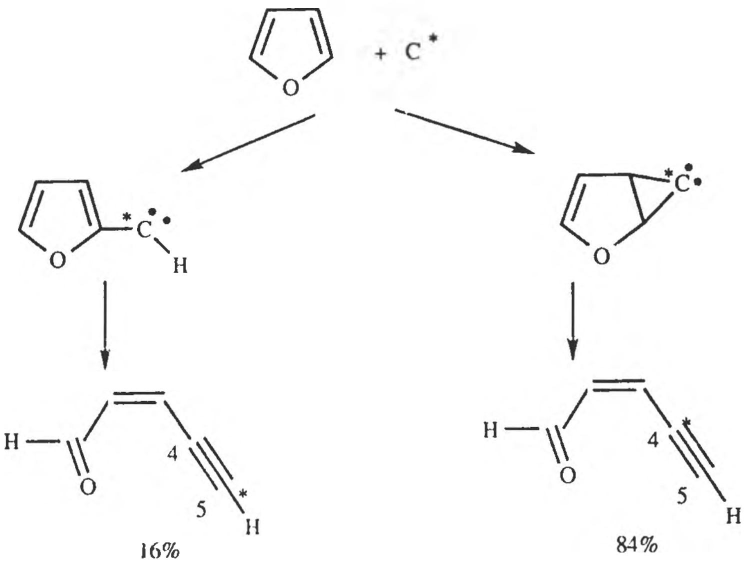
If others sorts of σ bonds are present, as in alcohols O-H, or amines N-H, the competition with atom abstraction became prevalent. In such cases the involvement of mono- and divalent species (CH and CH_2) have to be considered as the result of the primary process. To get an idea of the complexity of the system, one may look at the studies of Voigt *et al.* on the reaction of ethanol and methanol with carbon atoms, from a beam of $^{14}C^+$ ions.[12]

The presence of heteroatoms with their unbounded electrons, as in the case of ethers, thioethers or aziridines, directs the attack of carbon toward the electron lone pair. The main course of the reaction is, in such cases, atom abstraction with the formation of CO, CS, or HCN (see **Scheme 6**).[13, 14, 15]



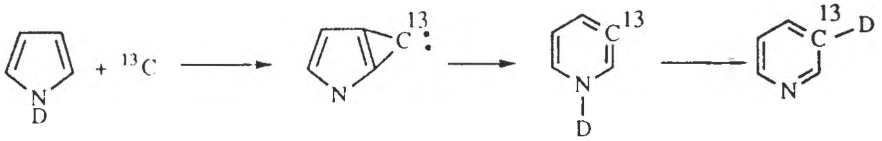
Scheme 6

In contrast, when the heteroatom is part of an aromatic system as in the case of furan or pyrrole, no interaction of carbon with the hetreoatom was noticed. Instead, addition to the π system, similar with the benzene case,[16, 17, 18] with the rearrangement of the initial adduct is thought to best fit the final products obtained. This behavior of carbon atom is once again stressing its reactivity toward highest electronic density site of the molecule. In furan and pyrrole the HOMO has no electron density on the heteroatom and, as a consequence, the attack is directed toward the π system. In **Scheme 7** the suggested mechanism involved in the reaction of chemically generated carbon with furan is presented;[19] the course of the reaction was followed by ^{13}C NMR. From the yields is noticed the preference toward addition *vs.* bond insertion (84:16)



Scheme 7

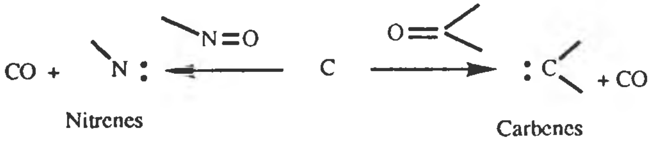
In **Scheme 8** a similar mechanism proposed for pyrrole is detailed along with the labeling results to support it.[20]



Scheme 8

Interesting enough is the behavior of carbon atom toward halocarbons.[21] If one consider the strength of the C-halogen bond as a measure, the preference for inserting into the C-Cl bond but not into the C-F may be explained (see **Table 3**). In the same time, the halogen abstraction reaction is more likely the primary process with the generation of monovalent CF or CCl intermediates.[22, 23] This way of producing them is suggested as a possible route to study their chemistry.

In the reaction with carbonyl or nitroso compounds the main product is carbon monoxide, along with the corresponding carbene or nitrene.[24,25] The reaction is used as a method to generate carbenes and nitrenes (**Scheme 9**).



Scheme 9

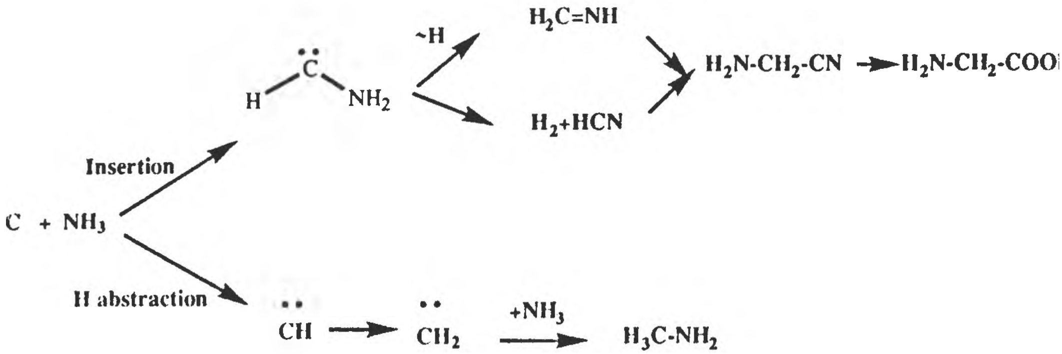
Their chemistry may be followed without the possible involvement of the carbene precursor.[26, 27, 28] According to the spin state of the carbenes or nitrenes obtained through this method, the singlet C(^{1}D) is the attacking species. Theoretical calculations on formaldehyde [26] suggest the possible generation of methylene in its first excited singlet state and open the prospective for an other interesting area for investigations.

The overview presented above is meant to give a general idea about the main channels of interaction among carbon atom and organic substrates. It is meant also to emphasize the complexity of the problem and the variety of questions that should be addressed for a complete understanding of the chemistry of "simple" carbon atom.

Carbon Atom and The Origin of Life

This is one of the most fascinating aspects of carbon atom chemistry, opening the discussion about its possible contribution, as a monoatomic species, at the origin of life, as we know and understand it, on Earth. Supporting this idea are the results of carbon atom reacting with simple molecules as H_2O or NH_3, at reduced temperatures (as low as 77 K). These conditions reproduce also those available outside of the Earth atmosphere and may shine a bit of light on the origin of simple carbohydrates and aminoacids in the extraterrestrial space.

The arc generated carbon reacts with NH_3 and produces some aminoacids among which glycine is the most abundant.[29,30,31] The mechanism considered consists of an initial insertion of a carbon into the N-H bond (see Scheme 10).



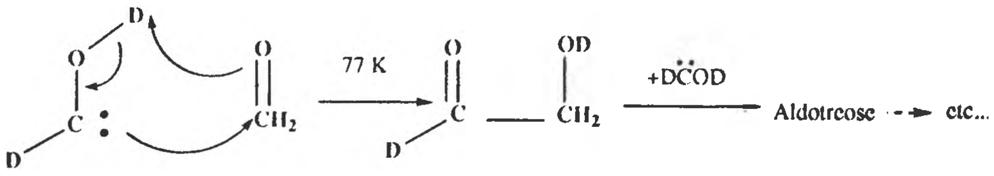
Scheme 10

The aminocarbene generated, rearranges to aminomethylene and reacts further with the other product of the primary process, HCN, to form the corresponding cyanide which during the workup of the reaction produces the corresponding aminoacid (**Table 5**).

Table 5: Quantitative results for aminoacids formation

Reaction mixture	Quantity (from ref 29)	Quantity (from ref 30)
urea	6.1×10^{-7}	-
aspartic acid	1×10^{-9}	4.4×10^{-5}
threonine	1×10^{-9}	-
serine	8×10^{-10}	-
glutamic acid	5×10^{-10}	-
glycine	4.5×10^{-8}	6×10^{-2}
alanine	1×10^{-9}	1.6×10^{-2}
b-alanine	-	2×10^{-3}
N-Me-glycine	-	4.8×10^{-2}

In reaction with H_2O, a similar insertion into O-H bond followed by hydrogen migration leads, via hydroxycarbene, to formaldehyde.[32, 33] The nucleophilic attack of hydroxycarbene to formaldehyde is considered to produce simple carbohydrates with up to five carbons (see **Scheme 11**).



Scheme 11

Table 6: Quantitative results in the carbohydrates formation

Product Aldose (from ref 33)	$C + H_2O$	$C + D_2O$
glycolaldehyde*	0.25 ± 0.11	0.27 ± 0.08
erythrose	0.11 ± 0.08	0.09 ± 0.05
threose	0.15 ± 0.14	0.08 ± 0.03
aldopentoses	low yield and overlapping peaks made quantitation difficult	

*** the absolute yield of glycolaldehyde in an experiment in which 54 mmol C was reacted with 277 mmol H_2O was 0.045 mmol**

In the reaction with completely deoxygenated H_2O mono- and dicarboxylic acids are also obtained,[34] in the yields presented in Scheme 12.

$$C + H_2O \longrightarrow R\text{-}COOH + HOOC\text{-}(CH_2)_n\text{-}COOH$$

Scheme 12

Table 7: Quantitative results for the carboxylic acids formation

Monocarboxylic acids	Amounts (nmol)	Dicarboxylic acids	Amounts (nmol)
Acetic acid	196	Oxalic acid	624
Propionic acid	63.3	Malonic acid	166
2-Me-Propionic acid	5.4	Fumaric acid	6.7
Butanoic acid	10.6	2-Me-Succinic acid	4.9
Propenoic acid	5.5	Succinic acid	44.7
2-Me-Butanoic acid	2.4	Maleic aid	3.8
Pentanoic acid	1.8		
2-Butenoic acid	1.5		
Haxanoic acid	0.7		

All these informations are meant to reorient the search in the direction to new possible ways to understand the origin of life in the extremely drastically condition outside of Earth atmosphere and in the "primordial soup" conditions on Earth.

Conclusions

From the unexpected large amount of informations available on the chemistry of atomic carbon, some general conclusions may be withdrawn:

–generating monoatomic carbon implies huge energy or special highly energetic precursors

–the actual electronic state of carbon atom involved in the process is difficult to be stated

–the presence of only-carbon molecules, as C_2 or C_3, may interfere with the chemistry of C_1

–the reaction partner of C_1, the substrate, is influenced by the light or heat used for graphite vaporization, prior to its subsequent reaction with monoatomic carbon.

–the possible ways of reacting, characteristic to C_1, atom abstraction and bond insertion are overlapping with the same type of reactivity displayed by the intermediates formed in the initial processes. The separation among the initial process products and the subsequent steps, is difficult and may not be solved with traditional means of organic chemistry.

The progresses in femptosecond laser spectroscopy along with a better interference among the classical organic chemistry methods and the new advanced analysis procedures, supported by the modern computational tools, should revigorate the area of research in the monoatomic carbon chemistry.

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THE ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON FLAT METALLIC CATHODES I. ELECTROREDUCTION PERFORMED ON "sp" GROUP METAL ELECTRODES

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ABSTRACT

A new approach is made to summarize the most important methods of electrochemical reduction of carbon dioxide on flat metallic cathodes. Unlike the usual classification systems, solely based on the products of the electroreduction, in this paper the procedures are grouped according to the both the nature of the cathode ("sp" or "d" group metalelectrodes) and the nature of the supporting electrolyte (aqueous or non-aqueous solutions). Thus, in this part of the paper we discuss the electroreduction of carbon dioxide performed on "sp" metal electrodes. In this review different subsections are dedicated to experiments performed in aqueous and in non-aqueous media. In addition to synthetic aspects, the most important reduction mechanisms are examined. The selective preparation of formic acid and procedures for manufacturing hydrocarbons and alcohols are discussed.

Keywords: Carbon dioxide, electrochemical reduction of CO_2, electrocatalysis by "sp" group metals, formic acid.

1. INTRODUCTION

The large numbers of recent papers dealing with the electrochemical reduction of carbon dioxide are of both fundamental and preparative interest. The fundamental research is stimulated by the similarity of CO_2 electroreduction to photosynthesis, the latter being one of the most important reactions in nature and indeed the basis to all living activity[1,2]. Since the beginning of life on the earth, photosynthesis has converted sunlight and simple inorganic minerals into energy-rich organic compounds[2]. As the most important result of this process, the storage of energy was achieved in biosystems, according to the general reaction (Eq.1)[3].

$$CO_2 + 2\,H_2A + h\nu \text{ -----> } CH_2O + A_2 + H_2O \qquad (1)$$

where A is the oxygen in the case of chlorophyll, and sulfur or organic acids in the case of bacteria. In optimal conditions the light energy is converted to chemical energy stored under the form of carbohydrates with an overall efficiency of 36%. The process requires 8 quanta for each reduced CO_2 molecule[3]. It has been the aim of chemists to utilize this naturally occurring process of carbon fixation as a model for manufacturing synthetic fuels[4]. Since 1870 there have been many attempts to find nonbiological approaches to the reduction of CO_2 to various organic compounds[2]. Different ways to reduce CO_2 have been investigated, such as radiochemical, chemical, thermochemical, photochemical, electrochemical and biochemical procedures[3]. As plenty of carbon dioxide is available in nature and huge amounts are generated by human activities, CO_2 is a practically infinite carbon source for the chemical industry for the manufacturing of alcohols, aldehydes, hydrocarbons and carboxylic acids. Among these products methanol is an environmentally neutral liquid energy source, that can be obtained by the electroreduction of CO_2 from enriched high concentration emissions with an overall efficiency of 50%[5,6]. This yield is comparable to that attained in hydrogen generation, followed by liquefaction, when 55% of the electric energy is converted into chemical energy. Furthermore, the synthesis of hydrocarbons by the electrochemical reduction of CO_2 might be of practical interest for fuel production, storage of solar energy, and the production of raw materials for the chemical industry[7]

As seen in **Figure 1** the number of papers referring to the electroreduction of CO_2 reached a maximum in 1986-1987, slightly decreased until 1990, and has continuously increased since then This growth of the topic is due to the promising results of the electrochemical method, which has proven suitable for industrial scale applications.

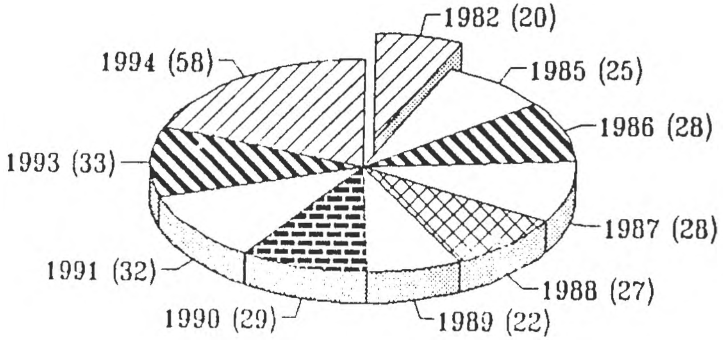

Figure 1 Number of papers published in the last decade on the electrochemical reduction of CO_2 of flat metallic electrodes.

Several procedures are currently being patented All these electroreductions had to overcome the difficulty of finding electrodes with both a good electrocatalytic activity and a satisfactory lifetime Another problem to be solved was the relatively low solubility of the CO_2 in aqueous solutions Methods for improving the solubility of CO_2 had to be found.

It is generally known that the electroreduction of CO_2 can be achieved in aqueous or non-aqueous solution on bulk metal (or metal oxide) electrodes with proper electrocatalytic activity, and on chemically modified electrodes, as well[8,9] However, the choice of the appropriate metal for the cathode is only the first step in designing an efficient procedure Next, a large number of experimental conditions should be evaluated and optimized, as each of them may affect the pathway of the electrochemical reaction and determine the identity of the reaction products Such parameters are: the cathode potential, the composition and the concentration of the supporting electrolyte, the temperature, the pressure, the efficiency of the mass transfer and the current density[10]. As seen in **Table 1** the magnitude of the cathodic potential is related to the number of electrons involved in the process[3,11] The greater the number of electrons transferred in the process, the less negative the cathode potential is Thus the multi-electron reductions of CO_2 are thermodynamically favored upon the monoelectronic or bielectronic reduction (compare examples 4-6 to 1-3 in **Table 1**) Examples 7-9 (**Table 1**) refer to electroreduction processes that involve two CO_2 molecules, i e a dimerization step It is generally accepted that the rate determining step for all these reactions is the transfer of the first electron to the CO_2 substrate molecule (example 1, **Table 1**)

Table 1: Standard electrode potentials for the main products of electrochemical CO_2 reduction[3,11]

	Process	E° [V vs SHE]
1.	$CO_2 + e^- \text{----->} CO_2^- (aq)$	- 1.84
2.	$CO_2(g) + 2 H^+(aq) + 2 e^- \text{----->} HCOOH(aq)$	0.11 .... -0.199
3.	$CO_2(g) + 2 H^+(aq) + 2 e^- \text{----->} CO(g) + H_2O(l)$	-0.10 .... -0.103
4.	$CO_2(g) + 4 H^+(aq) + 4 e^- \text{----->} CH_2O(aq) + H_2O(l)$	-0.028....-0.071
5.	$CO_2(g) + 6 H^+(aq) + 6 e^- \text{----->} CH_3OH(aq) + H_2O(l)$	+0.031....+0.030
6.	$CO_2(g) + 8 H^+(aq) + 8 e^- \text{----->} CH_4(g) + 2 H_2O(l)$	+0.175....+0.169
7.	$2 CO_2(g) + 2 H^+(aq) + 2 e^- \text{----->} (COOH)_2(aq)$	-0.382....-0.475
8.	$2 CO_2(g) + 12 H^+(aq) + 12 e^- \text{----->} C_2H_4(g) + 4 H_2O(l)$	+0.094

The C_1 transformations that accompany the stepwise electrochemical reduction of CO_2 that involve coupled proton/electron transfer steps, are shown in Eq.2[12]

$$CO_2 \text{---->} HCOOH \text{---->} H_2C{=}O \text{---->} CH_3OH \text{---->} CH_4 \qquad (2)$$

Another pathway of the process from CO_2 to methane may involve as the first step the reduction of CO_2 to CO (Eq 3)

$$CO_2 \text{---->} CO \text{---->} HCOOH \text{---->} H_2C{=}O \text{---->} CH_3OH \text{---->} CH_4 \qquad (3)$$

The conversion of formic acid to formaldehyde is thermodynamically unfavorable[13] The process can be achieved, however, by choosing metallic electrodes with favorable electrocatalytic activity. Thus, the overpotential is reduced and rapid methanol and methane formation is promoted[12] The electrochemical reduction of carbon dioxide has been studied for over one hundred years[14-25]. The most important reaction products that can be formed in the electrochemical reduction of carbon dioxide are shown in (Eq 4):

$$CO_2 + x\, e^- + x\, H^+ \text{----->} CO, HCOOH, HOOC\text{-}COOH, CH_4, C_2H_4, CH_3OH, C_2H5OH \qquad (4)$$

Most of the authors evidenced the presence of formic acid among the reaction products, for electroreductions performed in aqueous solution. Papers published starting in the early seventies, stressed the difference between the electrocatalytic behavior of electrodes made of **sp** group metals and of **d** group metals[26-37]. Thus, when used in aqueous supporting electrolytes, **sp** group metal cathodes (Hg, In, Sn and Pb) favored the electroreduction of CO_2 to formic acid[26-29,34], while on **d** group metals (Pt and Pd) carbon monoxide was formed as the main product[36,38] Another typical **d** group metal, Ru, was found suitable for the preparation of various organic compounds: hydrocarbons (methane and ethylene), alcohols (methanol and ethanol), as well as formic aldehyde[39-41]

However, the same groups of metals behaved differently in non-aqueous supporting electrolytes: on **sp** group metals (Tl, Pb and Hg) oxalic acid was selectively produced; on several **d** group metals (Fe, Cr, Mo, Ti and Nb) oxalic acid and CO were the main products, there is a class however, of mixed **sp** group (In, Sn, Cd, Zn, Cu, Ag and Au) and **d** group metal electrodes (Pd, Pt and Ni) which produced mainly carbon monoxide[42-47]

Our discussion on the electroreduction of CO_2 will consider both the importance of the cathode metal and that of the solvent. Therefore, the review comprises two main sections according to the type of electrodes used as the cathode material (**sp** and **d** group metals). Given the major influence of the solvent on the nature of the products, in each section separate sub-sections are dedicated to experiments performed in aqueous and in non-aqueous media

2. ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON *"sp"* GROUP METALS

According to Kita[30] the **sp** metal group includes the transitional metals with completely filled d-orbitals in addition to the metals of the principal groups of the periodic table. This means that metals with d^{10} electronic configuration: Zn, Cd, Hg, Cu, Ag and Au, are considered **sp** group metals.

2.1. Electroreduction performed in aqueous solutions

2.1.1. Electrodes formed of main group metals

Metals of the **sp** group have been continuously used as the cathode material from the early stages of the research until now. Copper and zinc have probably been the most lengthy used cathodes in the electrochemical reduction of CO_2. In 1870, Royer[17] employed Zn electrodes in sodium bicarbonate supporting electrolyte to obtain formic acid. Three decades later Coehn and Jahn[22] improved Royer's procedure by using Zn amalgam cathodes. They prepared formic acid with current yields up to 88.6%. Ehrenfeld[23] successfully raised the current efficiency (r_F) of this process to 95% by using a divided cell equipped with Zn amalgam vs. Pt electrodes, and ammonium bicarbonate supporting electrolyte. Fischer and Prziza[24] were the first to utilize pressurized electrolysis cells in CO_2 electroreduction. At pressures of 5-50 atm, on Zn amalgam and Pb cathodes, they obtained formic acid with almost quantitative yields. Both lead amalgam with 0.2 wt% Pb[25] and rotating amalgamated Cu cathodes[47] have proven efficient in the manufacturing of HCOOH. In order to eliminate the polluting mercury involved in amalgam electrodes Kesarev and co-workers[27] re-introduced Royer's metallic Zn cathode, one hundred years after its first use. Watanabe and co-workers[48,49] examined the electrocatalytic activity of Cu-based alloys. They performed experiments at 275 K, with Cu-Sn and Cu-Zn alloys, and with elemental Cu, Sn and Zn, as well. On these cathode materials, formic acid, methanol and carbon monoxide were produced. Noda and co-workers[44,45] found that in addition to Hg and Pb, metallic In and Sn were selective for the production of formic acid, while metallic Al and Ga had a scarce electrocatalytic activity in CO_2 electroreduction.

The introduction of copper and copper-coated metallic electrodes for the reduction of CO_2 to hydrocarbons[38,50-57] and alcohols[58,59], or both hydrocarbons and alcohols[60-66] in aqueous media represented a real a breakthrough[3]. These reductions were performed at ambient temperature and pressure and at high current density (i.e. with favorable reaction rates). In addition, the faradaic efficiency attained in neutral solution was of the order of 100%[67-73].

One difficulty in using Cu electrodes is their deactivation, which was usually observed 20-30 min after the beginning of the electrolysis[63]. A periodic anodic activation procedure allowed high hydrocarbon yields to maintain over prolonged electrolysis runs. Similar conclusions were drawn by Cook and co-workers[67]; their work also revealed that the electrocatalytic activity of copper was dependent on the renewal of the electrode surface. On a clean Cu surface the achieved r_F was 73% for CH_4, and 25% for C_2H_4. The use of rotating disk electrodes ensured the clean copper surface[64]. The mechanism of CO_2 electroreduction on Cu is still not completely understood. No sufficient explanations were found for the effect exerted by supported copper electrodes, and for the influence of Cu^+ ions present in the supporting electrolyte[57,64-66]. A recent study by Hwang and co-workers[67] aimed to evaluate the experimental factors affecting the r_F of methane and ethylene formation on Cu/glassy carbon cathodes. In their aqueous solution experiments the highest r_F (*ca.* 70%) was obtained at pH 7 (at room temperature) and at pH 2 (at ice temperature). Also the surface area of the electrode (both its size and the number of Cu deposits on the glassy carbon) played an important role in the electroreduction of CO_2. The presence of Cu-complexing agents in the supporting electrolyte, such as ammonia, ethylenediamine or pyridine, enhanced the efficiency of the electrochemical reduction. Though similar in their electronic configuration and alike in their main chemical properties, Cu and Ag behaved differently in the electroreduction of CO_2. Watanebe and co-workers[74] explained this difference by means of an ab initio MP_4 calculation: they concluded that CO did not interact with Ag, but it was adsorbed on the Cu electrode, the C-O bond being weakened in the latter case. The optimized geometry and vibrational wavenumbers of $CuCO^-$ were determined, but a bound state of $AgCO^-$ could not be evidenced.

Ito and co-workers[28] reported the excellent electrocatalytic activity of several **sp** group metals for the synthesis of HCOOH. They performed experiments in a divided electrochemical cell, in aqueous carbonate supporting electrolyte, at room temperature. Indium and cadmium, metals with an average overpotential for the hydrogen discharge reaction, were utilized as the cathode. At current densities of 5-10 mA cm^{-2} faradaic yields of 70-80% were reached. It is notable that In not only reduced CO_2 efficiently, but inhibited the hydrogen evolution, as well.

As seen from curve 1, **Figure 2**, fair r_F was recorded at low current densities (5 mA cm^{-2}). By using Sn cathodes (curves 2 and 3, **Figure 2**) the electrosynthesis of HCOOH could be performed at higher current densities, that is: under kinetically favorable conditions. Unfortunately, the r_F of the electroreduction decreased, so that the advantage of the increasing productivity was canceled by the poor selectivity. On other **sp** group metals (**Fig. 2**, curves 4-6) Zn, Pb and Cd, formic acid was formed only at low or average current efficiency. Work performed in 1985 by Bagotskii and co-workers[26] confirmed Ito's former results[28] on the electrocatalitic activity of **sp** group metals.

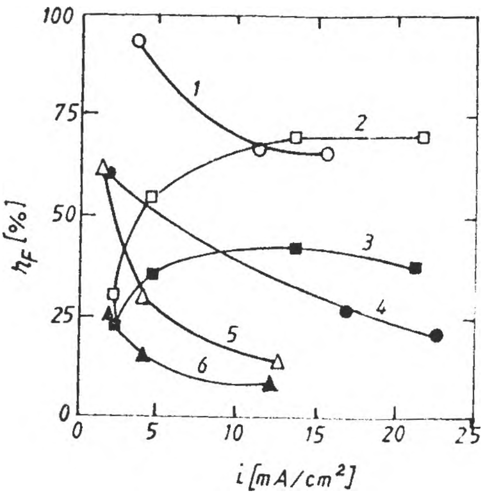

Figure 2: Faradaic yields of formic acid synthesized on different sp group metal electrodes in function of the current density
1 - In, 2 and 3 - Sn, 4 - Zn, 5 - Pb, 6 - Cd[28]

In a more recent paper Ito and co-workers[29] discussed the product distribution on In, Pb, Zn and Sn cathodes as a function of the cathode potential (**Table 2**)

Table 2: Faradaic yields of the main products of CO_2 electroreduction as a function of the electrode material and the cathode potential[29]

Cathode metal	Potential [V vs. SCE]	HCOOH [%]	CO [%]	H_2 [%]
In	-2.0	87.6	6.8	4.9
	-2.4	83.2	4.2	13.2
Pb	-2.0	72.9	2.0	15.6
	-2.4	78.9	2.1	14.3
Zn	-2.0	46.6	35.6	12.4
	-2.4	53.4	16.8	35.2
Sn	-2.0	67.5	9.1	29.9
	-2.4	37.6	4.2	61.6

It was reconfirmed that In electrodes at moderate cathode potentials ensured both a high r_F (87 6%) and an excellent selectivity (92.8%) of HCOOH synthesis. In addition, at a cathode potential of -2.0 vs. SCE the evolution of H_2 was almost suppressed. The best current efficiencies for HCOOH were obtained on Hg, In and Pb, in aqueous tetraethylammonium phosphate (TEAP) supporting electrolyte. The faradaic yield of HCOOH on In was as high as 70.0%[75]. When Sn and Zn cathodes were employed in 0.1 mol · L^{-1} aqueous TEAP the current efficiencies ranged from 38 to 70%.

Enhanced current efficiencies were obtained in high-pressure electroreductions of CO_2. In experiments carried out at 30 atm Hara and co-workers[76] achieved outstanding r_F for the formation of HCOOH on several main-group metal electrodes: 95.5% on Pb, 92.3% on Sn, 90.1% on In, and 82.7 on Bi. Despite the similitude of In and Al, the latter metal had scarce activity in CO_2 reduction and produced almost exclusively molecular hydrogen (86.5%)[76].

It should be noted here that in high-pressure electrolysis glassy carbon and n-Si wafer cathodes reduced CO_2 efficiently to CO and HCOOH (on carbon) and 46.3% HCOOH (on n-Si)[76]. On glassy carbon electrodes the pH of the supporting electrolyte was found important, slightly acidic oxalate solution being recommended[77]. It was necessary to activate the glassy carbon electrode by applying a 30 s anodic pulse at +1.2 V vs. SCE[78]. Such an electrode showed improved activity in the electrochemical CO_2 reduction; the reduction potential being shifted toward lower cathodic potentials relative to the potential of the glassy carbon electrode with no anodic treatment[79].

The critical overview of the published results lead to the conclusions that in most cases: (1) the main product on **sp** metals in aqueous supporting electrolytes was formic acid; and (2) the electrocatalytic activity of the cathode decreased in the following order: In > Hg > Pb > Sn > Zn » Cu.

There is a large number of reaction mechanisms suggested by several authors[47,76, 80-82] for the electroreduction of CO_2 in aqueous solutions. Udupa[47], Paik and Eyring[80,81] assumed independently that the reactive species were the neutral hydrated CO_2 molecules, that undergo the first electronation step to yield in an adsorbed $CO_2^{\cdot-}$ radical anion (**Figure 3a-b**).

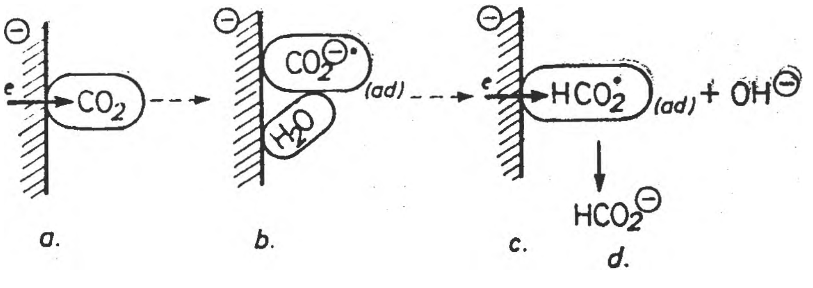

Figure 3: The mechanism of the electroreduction of CO_2 on sp group metal electrodes[47,80,81]. Neutral hydrated CO_2 molecules (a) undergo electronation to yield in adsorbed $CO_2^{\cdot-}$ radical anions (b). The latter reacts with adsorbed water molecules to form adsorbed HCO_2 radicals, that are further reduced to formate ions (c).

The latter reacts with adsorbed water molecules to form adsorbed $HCO_2^{\cdot}$ radicals, that are further reduced to formate ions (**Figure 3c**). Such a mechanism is likely for most of the **sp** group metal cathodes. However, analogous mechanisms were proposed for reactions proceeding on **d** metal electrodes.

As seen in **Figure 4**, when a mercury electrode was used the Tafel slope at low current densities was found of about 450 mA cm^{-2}/V (segment **a**), while at high current densities the slope was much lower, of only 3600 mA cm^{-2}/V (segment **b**).

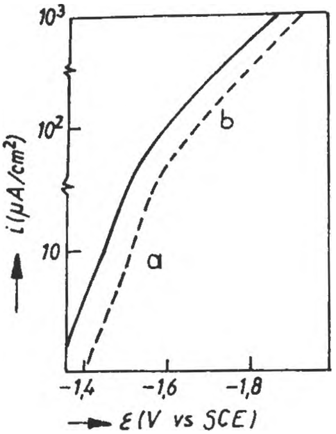

Figure 4: Polarization curves for the electroreduction of CO_2 on Hg cathode The slopes are: 450 mA cm^{-2}/V for segment a and 3600 mA cm^{-2}/V for segment b[75]

This significant difference can be attributed to different rate determining steps. It was suggested that an anion radical could be formed by photoemission[35,75]. Similar shapes but different Tafel slopes of the polarization curves were recorded on other metals[26]. Several studies revealed that the current efficiency of CO_2 electroreduction was also influenced by the nature of both the cation and the anion present in the solution. It was concluded that the presence of CO_3^{2-} or SO_4^{2-} anions in the supporting electrolyte increased the current yield, while PO_4^{3-} did not[8,29,34-37].

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The positive influence of CO_3^{2-} and HCO_3^- on the r_F was probably due to the direct participation of these anions in the mechanism of CO_2 electroreduction. Therefore, the real mechanism of CO_2 electroreduction appears to be more complicated than the one initially assumed. Spichiger-Ulmann and Augustinski[36,37] attributed the high cathodic currents recorded during CO_2 electroreduction in aqueous $CsHCO_3$ solution, to the involvement of HCO_3^- ions. The authors considered that HCO_3^- ions were the species to undergo electroreduction, rather than the neutral CO_2 molecules. For different anions present in the supporting electrolyte the r_F of HCOOH formation increased from 35 to 87.5% in the order: $PO_4^{3-} < SO_4^{2-} < CO_3^{2-} < HCO_3^-$. These experimental data were explained based upon the electrosorption of the hydrated ions at the electrode surface. This phenomenon has also been known to occur in other electrochemical reductions[8,10,83-87]. Small cations, such as Li^+ and Na^+ are not adsorbed at the electrode surface, due to their strong hydration. In addition, small cations carry to the cathode a large number of water molecules, that supply protons for the electroreduction[83]. Conversely, the poorly hydrated bulky cations are being preferentially adsorbed at the cathode. Depending on the different cations present in the supporting electrolyte the r_F of the process increased from 47 to 90% in the order: $Rb^+ < K^+ < Na^+ < Li^+$. In a recent paper Kyriacou and Anagnostopoulos[88] reported that the r_F of ethylene formation increased with the cation in the order $Cs^+ \gg K^+ > Li^+$, apparently in a manner related to the cation radius. However, the authors of this review paper also believed that the hydration of the metal ions played a key role in controlling the selectivity of CO_2 electroreduction. The nonmetallic cation NH_4^+ allowed only hydrogen evolution with almost quantitative r_F (*ca.* 92%).

Potentiostatic CO_2 reduction studies performed by Ito and co-workers[28,29,89], at -1.7 V vs. SCE, in in neutral aqueous $KHCO_3$ solution showed that: (1) Hg, In, Sn and Pb favored the formation of HCOOH and $HCOO^-$; (2) Zn and Cd, both with d^{10} electronic configuration (i.e. **sp** group metals) exhibited poor electrocatalytic properties for formic acid formation, e.g. on Zn 20% $HCOO^-$ and 40% H_2 were obtained, while on Cd 39% of $HCOO^-$ and 39% H_2 were yielded; (3) the main product on any other metals was hydrogen; and (4) the favorable properties of In suggested the opportunity of employing other metals of the 3rd group as the cathode.

Several new electroreduction products were obtained by Eggins and co-workers[90] by using an aqueous quaternary ammonium salt (QAS) solution as the supporting electrolyte. Thus, on Hg and graphite oxalate anions formed, on Pb glyoxylic acid was yielded, while on Hg malic acid was obtained. Similar results were reported by Bewick[91,92], Wolf and Rollin[93] and Kuhn[94]. The presence of glyoxylic acid among the reaction products was in agreement with the previously known reduction of oxalate to glyoxalate on Pb cathodes[95]. The reaction mechanism of glyoxalate formation was investigated by cyclic voltammetry in 1 mol dm^{-3} aqueous tetraethylammonium chloride solution. Two monoelectronic reduction steps were evidenced at -0.68 and -1.4 V vs. SCE. The authors suggested the following mechanism (Eq.5-7):

$$CO_2 + e^- \dashrightarrow CO_2^{\cdot -} \qquad (5)$$

$$CO_2^{\cdot -} + CO_2^{\cdot -} \dashrightarrow {}^-O_2C\text{-}CO_2^- \text{ (oxalate)} \qquad (6)$$

$$ {}^-O_2C\text{-}CO_2^- + 3\,H^+ + 2\,e^- \dashrightarrow {}^-O_2C\text{-}CH(OH)_2 \dashrightarrow \underset{\text{(glyoxalate)}}{{}^-O_2C\text{-}CHO} + H_2O \qquad (7)$$

Hence, the oxalate formation involved the monolelectronic reduction of CO_2 (Eq.5), followed by the dimerization of the radical anions (Eq.6). The latter step was favored in the presence of a QAS in the aqueous supporting electrolyte. The reduction may stop here or the dinegative oxalate ion may eventually undergo further reduction to glyoxalate (Eq.7).

Customarily the analytical control of the electroreduction was achieved by HPLC[9,34], mass spectrometry[3,4], as well as by classical methods, such as acid-base titration and redox titration with $KMnO_4$.

The preparative electrosynthesis carried out on graphite electrode (at -0.900 V vs. SCE) yielded in oxalate with almost quantitative faradaic efficiency, but the nature of the products varied in function of the applied cathode potential (**Table 3**)[94]. Also, good oxalate yields were obtained with Pb cathodes, at low catode potentials (-1.26 V vs. SCE, **Table 3**,[95]

Table 3. Faradaic efficiency (%) of several CO_2 electroreduction products (on graphite[94] and Pb[95] electrodes in aqueous 0.1 mol dm^{-3} NH_4Cl supporting electrolyte, at room temperature)

Electrode	E_c [V vs. SCE]	Oxalate	Formate	Glyoxylate
Graphite	-0.900	100	-	-
	-1.05	10	78	12
	-1.26	17	74	7
	-1.70	15	72	-
	-1.88	6	65	28
Pb	-1.26	44	55	-
	-1.40	9	90	-
	-1.49	25	74	-
	-1.65	1	62	35

Several studies are concerned with the electroreduction of CO_2 on Au and Ag electrodes. Ito[49] obtained on gold CO, hydrogen and $HCOO^-$. The identity of each of the products was determined by the cathode potential, e.g. from -1.3 to -1.6 V vs. SCE exclusively CO and H_2 could be obtained. Hori and co-workers[50-52] performed galvanostatic CO_2 electroreduction experiments that yielded in $HCOO^-$, CO, CH_3OH, CH_4 and C_2H_4. The presence of CO, ethane and methane among the reaction products was assessed by Noda and co-workers[41]. Again, the products obtained were extremely sensitive to the cathode potential. It was noticed that the most appropriate cathodic potentials for the preparation of different products were:

$HCOO^-$	CO	C_2H_4	CH_4	
-1.4	-1.52	-1.58	-1.70	(E_c, V vs. Ag, AgCl)
32.4	36.8	38.8	42.1	(r_F, %)

A variety of possible pathways could be responsible for this potential sensitivity of the product formation. In these experiments new reaction products such as alcohols and aldehydes were detected. At a cathode potential of -1.65 V vs. Ag, AgCl, 14% of ethanol was formed.

2.2. Electroreduction performed on sp group metal electrodes in non-aqueous media

One major advantage of using organic solvents as the supporting electrolyte is that for most organic solvents the solubility of CO_2 is much higher than in water, and the solubility of CO_2 is unrelated to the dielectric constant of the solvent[3]. Thus the solubility of CO_2 in dimethyl sulfoxide (DMSO) and acetonitrile (AN) is about 4 times that in water, while its solubility in propylene carbonate (PrC) is about 8 times greater. Dimethylformamide (DMF) has proven the best solvent of CO_2, with a 20 times greater solubility than in water[96]. However, recently Chang and co-workers[97] found that at elevated pressure CO_2 showed the highest solubility in cyclo-hexanone, next in toluene and the least in DMF.

Carbon dioxide electroreductions performed on Pb, Tl and Hg electrodes in non-aqueous media yielded in oxalate ions[3], according to the mechanism shown in Eq 5 and 6. On other **sp** group metals: In, Zn, Sn and Au, the reductive disproportionation of CO_2 took place along with the formation of CO and carbonate ions (Eq 8)

$$CO_2^{\cdot-} + CO_2 \text{ -----> } CO + CO_3^{2-} \tag{8}$$

This process was identified by Saveant and co-workers[98,99] in their studies of the uncatalyzed electroreduction of CO_2. (The radical anion $CO_2^{\cdot-}$ formed in the monoelectronic reduction of the CO_2 molecule, according to Eq 5)

In chronopotentiometric electroreduction of CO_2 performed on Au and Hg electrodes in anhydrous DMSO, Haynes and Sawyer[15] assessed the presence of CO. Similar reduction mechanisms were assumed for both metals, the rate determining step was the electron transfer to CO_2 (Eq 3). However, the standard reduction rate constants were significantly lower for Hg (3.2×10^{-25} cm s^{-1}) than for Au (4×10^{-12} cm s^{-1}). No evidence was found for the participation of the solvent in the redox process (Eq 6), and no reasonable explanation could be provided for the very low rate constant at the Hg.

Vassiliev and co-workers[100] investigated the electroreduction of CO_2 on Sn, In, Pb and Hg in various aprotic solvents (DMFA, DMSO, AN). In all of these experiments the main reaction to occur was the dimerization yielding in oxalate ions. The reaction mechanism suggested by the authors involved 3 steps (Eq 9-11)

$$CO_{2ad} + e^- \text{ ----- } CO_{2ad}^{\cdot-} \tag{9}$$

$$CO_{2ad}^{\cdot-} + CO_{2ad} \text{ ----> } (O_2C\text{-}CO_2^{\cdot-})_{ad} \tag{10}$$

$(O_2C\text{-}CO_2^{-})_{ad} + e^{-} \text{ -----> } {}^{-}O_2C\text{-}CO_2^{-}$ (11)

Unlike the mechanism in aqueous solutions which involved the dimerization of two radical anions (Eq.6), in non-aqueous media an attack of the adsorbed radical anion by an adsorbed CO_2 molecule was assumed (Eq.10). This step was considered fast at all potentials.

Electroreductions of CO_2 were performed by Ito and co-workers[42] in an electrolyte formed of DMSO or propylene carbonate (PrC) and QAS (tetraethylammonium perchlorate, TEAP). The main product on Pb electrodes was oxalic acid with r_F up to 80%, while on Sn and In carbon monoxide was primarily produced. On Zn electrodes operated under the similar conditions, a mixture of oxalic acid, glyoxylic acid and CO was yielded with an overall r_F of *ca.* 40%. The same authors[43] extended their investigation (in TEAP/PrC supporting electrolyte) to Pb, Tl and Hg electrodes that have proven suitable for the selective production of oxalic acid (r_F up to 84%). Oxalic acid (under the form of its Zn salt) was obtained on the preparative scale on Pb cathode vs. a soluble Zn anode, used in an undivided cell (the supporting electrolyte was tetrabutylammonium perchlorate in DMF). Both the material yield of oxalic acid (*ca.* 85%) and its r_F (80%) were excellent[46]. When the reduction of CO_2 was performed on Pb cathode, at -2.8 V *vs.* SCE (in 0.1 mol dm^{-3} TEAP/PrC electrolyte), the concentration of oxalic acid increased almost linearly up to 423 K[43]. Above this temperature glyoxylic acid and some glycolic acid started to form[43]. These observations were in agreement with previously suggested mechanisms in which glyoxylic and glycolic acid were yielded in the further reduction of oxalic acid (see Eq.5)[95]. Glyoxylic acid could also be obtained on Cd[43], however, for this metal CO was the main reduction product.

Recent CO_2 electroreduction experiments were performed on Cu cathode in benzalkonium chloride/methanol supporting electrolyte[53,54] at low temperatures. At 258 K the composition of the reduction products was: CO (24.0%), methane (39.1%) and ethylene (4.4%)[54]. Hence the r_F for methane and ethylene was better in pure methanol than in aqueous catholytes. Another advantage was that the solubility of CO_2 in methanol was about five times that in water at ambient temperature. In 1995, Mizuno and co-workers[101] improved this method by cooling the same supporting electrolyte to a lower temperature (243 K); under optimal conditions the r_F of methane exceeded 42%. In addition, at low temperatures the efficiency of the competing hydrogen evolution was diminished to less than 8%. As methanol is being used in industry as a CO_2 absorber, the systems above may have industrial applications in large-scale methane production.

In summary, the most significant difference between neutral aqueous and non-aqueous electrolytes using **sp** group metal electrodes is that the major product formed in the aqueous solution was the formate ion (or formic acid), while in non-aqueous solution oxalic acid was preponderant[102].

3. CONCLUSIONS

A new approach is made to summarize the most important methods of electrochemical reduction of carbon dioxide on flat metallic cathodes. Unlike the usual clasification systems, solely based on the products of the electroreduction, the electroreduction procedures are grouped according to both the nature of the cathode ("sp" or "d" group metal electrodes) and the solvent used for the supporting electrolyte (aqueous or non-aqueous solutions). Thus, in the first part of the paper we discuss electrochemical reduction of CO_2 on electrodes made of "sp" metals. It has been shown that the products of the electrochemical CO_2 reduction depend on the electrocatalytic activity of the cathodic metal. A large number of examples have been provided to stress the contrasting behaviour of electrodes made of "sp" or "d" group metals. This significant difference allows a new classification, based on the nature of the cathode material. Of great importance are also the composition of the supporting electrolyte (aqueous or non-aqueous solutions), and the experimental parameters (cathode potential, current density, temperature and pressure), as well. Spectacular faradaic efficiencies have been achieved in high pressure experiments at "sp" group metal electrodes with high overpotential for hydrogen evolution such as Pb, Hg and In. Especially indium, known for its noteworthy selectivity in the synthesis of formic acid at ambient pressure, has been recently used in the high-pressure experiments[103]. At 60 atm in aqueous $KHCO_3$ solution HCOOH was obtained at a remarkable current density (560 mA · cm^{-2}). Mercury and graphite manifested different electrocatalytic activities when used in aqueous quaternary ammonium salt supporting electrolytes. However, the major product for both electrodes were acids : oxalic and malic acid.

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THE ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE ON FLAT METALLIC CATHODES
II. ELECTROREDUCTION ON *"d"* GROUP METAL ELECTRODES

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ABSTRACT
In Part II of this review article the electroreductions accomplished on "d" group metals are examined. Different subsections are dedicated to experiments performed in aqueous and in non-aqueous media. Mechanistic details of the most important processes are given, and the selective preparation of formic, oxalic, glyoxylic and glycolic acids are discussed. Procedures the manufacturing of hydrocarbons and alcohols are described.

Keywords : Carbon dioxide, electrochemical reduction of CO_2, electrocatalysis by "d" group metals, formic acid, oxalic acid, glyoxylic acid, glycolic acid.

1. Electroreduction of CO_2 on metals of the 8th group in aqueous solutions
1.1. Ni, Pd and Pt electrodes

Platinic metals generally exhibit excellent electrocatalytic properties for the electroreduction of CO_2 due to the strong adsorption of CO_2 on these metals. When carbon dioxide was electrochemically reduced on platinic metals, the same active species were generated as those encountered in the oxidation of methane[1,2]. However, the products formed on Pt, Pd and Ni cathodes largely depend on the experimental conditions[3-27]. Transition metal (and metal oxide) electrodes with higher pseudocapacity values in CO_2-saturated solutions than in N_2-saturated solutions had an enhanced efficiency for the electrochemical reduction of CO_2. Cyclic voltammetry performed at the Pt cathode evidenced the formation of three different intermediates from the adsorbed CO_2[28]. The influence exerted by the temperature and pre-polarization time of the electrode on the adsorption of CO_2 on Pt was studied by Maier and co-workers[10]. At higher temperatures, after a short anodic prepolarization at +0.520 V vs. SCE, adsorbed (COOH) species were assessed. When the pre-polarization was done at a slightly more positive potential value (+0.650 V vs. SCE for 30 min), the adsorbed intermediates were mainly $(CO)_{ads}$. The oxidation peak at +0.280 V vs. SCE found in cyclic voltammograms were assigned to the adsorption product $(HCOOH)_{ads}$.

An impressive number of fundamental studies have been done for the electrochemical reduction of CO_2 on the three basal planes of Pt: Pt(100), Pt(110) and Pt(111)[11-13]. In acidic solution the most active was the Pt(110) surface, giving CO, while Pt(111) surface was inactive. The amount of reduced CO_2 increased when defects were present at the surface, blocking the (100) terraces, whereas edge sites were less active for the adsorption. Fourier-transform IR spectra confirmed the formation of linear CO and traces of multibonded CO at the Pt(100) surface[12]. No differences in the nature of "reduced CO_2" were observed at different adsorption potentials. Even well-ordered Pt(111) single crystal electrodes were made active for CO_2 adsorption by cycling them in the Pt oxide region[13]. This treatment induced disorder on the surface, and its activity for CO_2 reduction increased.

While in contact with CO_2 containing solution, the surface of Pt became covered with a strongly attached "reduced CO_2" layer[29]. This adsorption layer hindered further electroreduction of CO_2, so that it could never be quantitatively reduced on Pt, and the main process remained molecular hydrogen. This statement seems to be questioned by the recent work of Inuzuka[9], who patented an and effective apparatus for the electrochemical reduction of CO_2 to methane and methanol. His cell was based on a proton-conductive solid electrolyte with a porous Pt anode on one side and a porous catalytic metal cathode on the other side.

Studies performed by using bulk Pd cathodes[30,31] showed that HCO_3^- was the electrochemically active species. The electrocatalytic properties of Pd paralleled its outstanding catalytic properties already proven for the chemical reduction of CO_2[3]. This allowed the electroreduction of carbon dioxide to $HCOO^-$ with high r_F[4-6].

Using the insertion of hydrogen, Ayers and Farley[7] proposed a new reduction method of the CO_2 / HCO_3^- mixture on flat bipolar Pd electrodes (**Figure 1**):

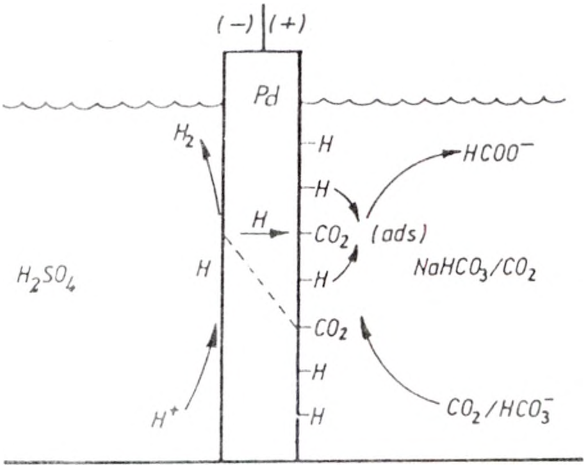

Figure 1. The mechanism of CO_2 electroreduction on a bipolar Pd electrode

In this procedure the atomic hydrogen penetrated the negative side of the bipolar Pd electrode. By arriving to the opposite, positively polarized side of the electrode, the hydrogen reduced the neutral CO_2 molecule, according to the following mechanism (Eq 1-3)

$$(HCO_3^- / CO_2)_{ads} + 2\ Pd\text{-}H \text{ ------> } HCOOH + 2\ Pd \quad (1)$$

$$(HCO_3^- / CO_2)_{ads} + 4\ Pd\text{-}H \text{ ------> } HCHO + H_2O + 4\ Pd \quad (2)$$

$$(HCO_3^- / CO_2)_{ads} + 6\ Pd\text{-}H \text{ ------> } CH_3OH + H_2O + 6\ Pd \quad (3)$$

The slightly positive face of Pd bound the CO_2 molecules by electrosorption, without oxidizing the intermediate products. The CO_2 electroreduction may not stop at alcohols. Thus, Azuma[8] researched the experimental conditions for obtaining C_1-C_6 hydrocarbons. In these experiments only low current efficiencies were achieved on bulk Pd electrodes. Similar studies were performed by Ohkawa and co-workers[32-33] who observed an increase of the r_F of CO and HCOOH production following the adsorption of hydrogen into the Pd electrode. This improvement of r_F was a consequence of the suppression of H_2 evolution. Adsorbed hydrogen could also participate in the electrochemical reduction of CO_2 by directly reacting with the reaction intermediates. The Tafel behavior of CO_2 electroreduction on H-loaded Pd was compared to that of the H-free Pd electrode[33]. The competing desorption of hydrogen was found to enhance the electrochemical reduction of CO_2. Hashimoto and co-workers[34] used the hydrogen accumulated in a Pd working electrode for the reduction of CO_2. In aqueous $KHCO_3$ solution HCOOH and CO were yielded. The same authors[34] also employed electrodes made of a combination of sp and d group metals: Cu and Pd, respectively. In addition to HCOOH methane and methanol were obtained. For Cu electrodes modified with Pd the current efficiencies for the three products were larger than for Pd electrodes modified with Cu. The enhancement of the process efficiency was caused by the amount of hydrogen adsorbed by the working electrode, rather than by the change in the lattice morphology or the oxidation state of copper.

Both Pt and Pd electrodes were successfully used for the preparation of methanol[14,15]. A slightly acidic supporting electrolyte (pH 5.0) was employed, to which a homogeneous catalyst was added under the form of pyridinium ions. Faradaic yields up to 30% were reached by means of the molecular hydrogen released from two sources: the electroreduction of H^+ and of the pyridinium ions. The main advantage of this procedure was that the electrochemical reduction of CO_2 proceeded at low overpotentials. Several new apparatus were patented in the last years for the electrochemical reduction of CO_2 on platinum group metals[16,17]. The electrolysis cell used by Inuzuka[16] was equipped with a sandwich-type three-layer electrode, formed of a porous platinum-group metal anode, a proton-conductive solid electrolyte, a porous electrocatalytic metal cathode, and a second anode, facing the side of the cathode, that is opposite to the first anode. The electrolytic solution contained dissolved CO_2 and an ultrasonic vibrator completed the system. Due to the construction of the cell and to the electrocatalytic activity of the cathode layer, this set-up allows for the efficient reduction of CO_2 over a long time period. The other cell, suitable for the synthesis of formic acid, had a gas-diffusion electrode A (formed of a reactive layer supported with Pd or its alloy), opposed by another gas-diffusion electrode, B, with a reactive layer supported with a Pt catalyst[17]. An ion-exchange diaphragm was positioned between the electrodes. In this system CO_2 was supplied from the back side of electrode A, while H_2 was fed from the back side of electrode B. Aqueous carbonate and hydroxide solutions were introduced in the spaces between the electrodes. This setup allowed both the efficient formation of a CO / HCOOH mixture and the simultaneous generation of electricity. Presently preparative syntheses of HCOOH are commonly being carried out on Pd electrodes, at potentials higher than the reversible hydrogen potential, with current efficiencies close to 100%[18,19]. For reductions performed in alkaline aqueous supporting electrolytes (pH 8-10), at ambient pressure, the current yield for $HCOO^-$ was close to 100%. It was assumed that adsorbed hydrogen atoms took part in the slow step of HCO_3^- electroreduction.

Nickel has been used intensively in CO_2 electroreductions[35]. According to Hori and co-workers[36] when the electrolyte was neutral or mildly acidic, mostly H_2 evolved. In addition to hydrogen Frese[37] some carbon monoxide was obtained on Ni (r_F of only 9%). In recent studies Osamu and co-workers[20,21] found 99.99% pure Ni electrodes suitable for hydrocarbon and ethanol production. When performed in aqueous supporting electrolytes the process yielded methane, ethylene and ethane with the simultaneous formation of molecular hydrogen[20]. During the electroreduction of carbon dioxide, CO was formed and strongly adsorbed at the Ni surface. This adsorbed CO layer occupied most of the surface site where hydrogen evolution could proceed, and thus inhibited the H_2 formation. The presence of adsorbed CO was confirmed by Fourier-transform IR spectroscopy[21]. Hydrocarbons and traces of ethanol were obtained by the same authors[21] on a pure Ni electrode (in pH 6.8 phosphate buffer solution and at ambient temperature), under Ar and CO_2 atmosphere. The faradaic efficiencies for the different products were: CH_4 (3.7%), C_2H_4 (0.1%), C_2H_6 (0.7%), and ethanol (0.1%), respectively. Voltammetric studies revealed that under inert atmosphere (Ar) the evolution of H_2 started at -0.45 V vs. SHE, an anodic oxidation of metallic Ni occurred at -0.18 V, and that CO_2 was reduced to CO simultaneously with the H_2 evolution. Koga and co-workers[22] assessed the presence of CO molecules adsorbed at the Ni electrode, in the electrochemical reduction of CO_2 to CH_4, C_2H_4 and C_2H_6.

Nickel cathodes are commonly being used in high pressure CO_2 electroreduction experiments[23,24]. As already mentioned, the low solubility of CO_2 in aqueous solutions is one of the major problems to overcome in the electroreduction of carbon dioxide. The concentration of CO_2 in water at 298 K is of only 0.033 mol L^{-1}. Fortunately, this concentration can be risen at room temperature to 1.17 mol L^{-1} by increasing the pressure to 60 atm, a pressure value close to the liquefied pressure (approximately 70 atm). Ito and co-workers[25,26] reported that at high pressures (50-60 atm) several Group VIII metal electrodes, such as Fe, Co, Ni, Pd and Pt, showed r_F values up to 62% in the electrochemical CO_2 reduction.

Recently, Kudo and co-workers[23] focused their research on the high-pressure electrochemical reduction of CO_2 at the Ni cathode. All of their experiments were performed in 0.1 mol L^{-1} $KHCO_3$ aqueous supporting electrolyte, on high purity (99.7%) nickel electrode, by using purified CO_2 (99.9%). It was found that increasing CO_2 pressures favored the faradaic efficiency of CO_2 reduction and diminished the H_2 evolution by water reduction. Electrolyses carried out at 303 K and -1.6 V vs. Ag/AgCl, showed a maximum of the faradaic yield for the hydrocarbon formation. The r_F for both CO and HCOOH improved with increasing cathodic polarization. Also, the weight distribution of the hydrocarbons agreed with the Schultz-Flory distribution, suggesting that the formation mechanism was similar to the Fischer-Tropsch reaction by thermal catalysis. A probable scenario for the hydrocarbon formation at the Ni surface may involve the following steps: the electrochemical reduction of CO_2 to CO (Eq.4), simultaneous with water reduction (Eq.5), followed by the chemical reduction of CO (Eq.6) and the formation of hydrocarbons by surface polymerization of carbene groups (Eq.7):

$$CO_2 + e^- \dashrightarrow CO_{ads} \tag{4}$$
$$H_2O + e^- \dashrightarrow H_{ads} \tag{5}$$
$$CO_{ads} + H_{ads} \dashrightarrow (CH_2)_{ads} \tag{6}$$
$$(CH_2)_{ads} \dashrightarrow \text{Hydrocarbons} \tag{7}$$

At cathode potentials more negative than -1.6 V vs. Ag/AgCl, the formation of CO and HCOOH were favored.

Hori and co-workers[27] assessed the presence of adsorbed CO on the Ni cathode in phosphate buffer solution. For this a novel in-situ IR spectroscopy technique, SNIFTIRS (subtractively normalized interfacial Fourier transform IR spectroscopy), was used. In CO-saturated solution adsorbed carbon monoxide was present at the Ni electrode surface in the potential range from -0.4 to -0.8 V vs. NHE. Both linear and bridged adsorbed CO molecules were detected.

A general conclusion of the work carried out on Ni cathodes was that the electrocatalytic properties of this metal were favorable for paraffin formation (methane, ethane, propane, *n*- and *i*-butane were yielded), unlike Cu, on which methane and ethylene were produced selectively[36,38,39-46].

Promising high pressure electrolyses were performed by Bandi and co-workers[28] on platinum cathodes. They carried out experiments both in the aqueous solution, and in supercritical CO_2 and tetraalkylammonium salts.

1.2. Fe, Ru and Os electrodes

Iron cathodes have been widely examined for their use in CO_2 electroreduction. Hori and co-workers[36] found that in neutral and mildly acidic solutions Fe cathodes form hydrogen more readily and this product dominates by far. However Frese and Canfiled[37] obtained on Fe electrodes significant amounts of CO. Recently, Hara and co-workers[46] obtained in high pressure experiments (at 30 atm) formic acid as the main product, methane as the by-product and traces of ethane and ethylene, as side-products. However, about half of the current was consumed on hydrogen evolution.

Ruthenium was the first metal found to catalyze the electrochemical methanation of CO_2[4,5]. Nevertheless, in other experiments on Ru electrodes the main product was methanol (r_F = 25%)[6]. In addition, CH_4 was formed with almost similar efficiency as methanol (r_F = 30%). The presence of carbon and CO among the reduction products was explained by two-electron reductions (Eq 8 and 9):

$$CO_2 + H_2O + 2\,e^- \text{ ----> } CO + 2\,OH^- \qquad (8)$$
$$CO + H_2O + 2\,e^- \text{ ----> } C + 2\,OH^- \qquad (9)$$

Metallic osmium cathodes at a cathode potential of -0.69 V *vs.* SCE and at low current densities were selective for methanol formation (r_F = 57%), while CO formed with only r_F = 0.11%[37]. However, when Os electroplated on carbon was used as the electrode the formation of methanol stopped.

1.3. Co, Rh and Ir electrodes

On cobalt electrodes mainly carbon monoxide was yielded (r_F up to 26%). Slightly acidic sodium sulfate or neutral $LiHCO_3$ supporting electrolytes were used, at 333 K[37]. Usually almost no reduction occurred on Rh and Co electrodes although, when used at ambient pressure, the predominant product was H_2 from the reduction of water[46]. Nevertheless, at a pressure of 30 atm and at large current densities (163-700 mA cm^{-2}) CO and HCOOH were also obtained (along with H_2). Under these conditions Rh electrodes yielded mainly in CO (61.0%) and formic acid (19.5%). Iridium electrodes primarily decomposed water to H_2 (48.3%) with only limited amounts of HCOOH (22.3%) and CO (17.5%) being produced[46].

2. Electroreduction of CO_2 on metals of the 8th group in non-aqueous media

Vassiliev and co-workers[47] performed electroreduction experiments on Pt electrodes in non-aqueous supporting electrolytes. As a result CO and CO_3^{2-} were produced, according to the mechanism proposed by Haynes and Sawyer[48] (Eq 10 and 11):

$$CO_{2ad} + e^- \text{ ----> } CO^{\cdot-}_{2ad} \qquad (10)$$
$$CO^{\cdot-}_{2ad} + CO_{2ad} \text{ ----> } CO + CO_3^{2-} \qquad (11)$$

Nickel and platinum electrodes in TEAP/PrC electrolyte, at a cathode potential of -2.8 V *vs.* Ag-AgCl formed CO and HCOOH (in a ratio of 6:1 - 8:1, wt/wt) and traces of oxalic acid[49]. However, in similar experiments performed on Pd electrodes significant amounts of oxalic acid (CO/HOOC-COOH = 2:1, wt/wt) and only traces of oxalic acid were yielded[49].

Iron cathodes have proven excellent for the selective preparation of oxalic acid; when used in TEAP/PrC supporting electrolyte, the product ratio of HOOC-COOH/CO/H_2 was approximately 3:1:2[49]. In DMSO and AN, the r_F of oxalic acid was in the range of 50-60%.

3. Reduction of CO_2 on other "d" metals in aqueous solutions

3.1. Cr, Mo and W electrodes

Molybdenum electrodes were investigated by Summers and Frese[50] in detail because they were among the first metals to show electrocatalytic activity for CH_3OH

formation. In fact, a Mo electrode is a metal/metal oxide system. When used in CO_2 saturated sodium sulfate solution (pH 4.2), at room temperature and at a potential of -0.7 to -0.8 V *vs.* SCE, methanol was the principal product (r_F of 50-100%). Methanol was also generated in dilute sulfuric acid solution (0.05 mol dm^{-3}) with yields of 20 to 46%. Usually the by-products were CO (1 to 20%) and CH_4 (0.1 to 3 %). Cycling the voltage of the Mo electrode between +0.2 and -1.2 V vs. SCE was beneficial on the formation rate of methanol. A reaction mechanism in two steps was suggested (Eq.12 and 13):

$$2\,CO_2 + 3\,Mo + 4\,H_2O \longrightarrow 2\,CH_3OH + 3\,MoO_2 \qquad (12)$$

$$3\,MoO_2 + 12\,H^+ + 12\,e^- \longrightarrow 3\,Mo + 6\,H_2O \qquad (13)$$

In CO_2 electroreductions performed with Mo cathodes in PrC, DMSO and AN, oxalic acid was obtained with r_F in the range of 20-35%, while CO formed as the by-product in amounts of 5-30%[49].

Tungsten electrodes operated at 333 K and at low current densities (32 mA cm^{-2}) in Na_2SO_4 solution (pH 4), produced methanol with the r_F of 76% (the by-product was CO, 22%)[37]. In high-pressure electrolysis experiments carried out on W cathodes, Hara and co-workers[46] synthesized 31.9% oxalic acid as the main carbon-containing product; the r_F of the process was diminished by the evolution of 53.1% H_2.

In addition to large amounts of molecular hydrogen some CO was yielded with a low current efficiency (6.2%) on chromium electrodes[37]. At increased pressures (30 atm) about 20% of the electricity produced carbon-based products (11.8% CO and 8.2% HCOOH)[46].

3.2. Ti, Zr, Nb, Ta and Mn electrodes

There are only a few experimental works of CO_2 electroreduction on Ti, Zr, Nb and Ta electrodes. When operated under pressure (30 atm) all four electrodes produced a small amount of formic acid (3.5-7.6%) along with significant amounts of H_2[46]. However, on Zr a notable quantity of CO was also generated (32.5%).

The same authors found that on Mn electrodes, operated under a pressure of 30 atm, 78.8% H_2 was evolved and only 6.5 of the CO_2 was reduced (to 2.8% CO and 2.8% HCOOH)[46].

4. Reduction of CO_2 on other "d" metals in non-aqueous media

Several metals found inactive in the aqueous CO_2 electroreduction have proven some activity in non-aqueous media[49]. Dimerization of the $CO_2^{\cdot-}$ anion radical to oxalate ions is prevalent in non-aqueous supporting electrolytes. For electroreductions performed in TEAP/PrC on Ti, Nb and Cr electrodes the reaction proceeded according to the mechanism shown in Eq.14-16.

$$2\,CO_2^{\cdot-} \longrightarrow {}^-OOC\text{-}COO^- \qquad (14)$$

$${}^-OOC\text{-}COO^- + 2\,H^+ + 2\,e^- \longrightarrow {}^-OOC\text{-}CHO + OH^- \qquad (15)$$

$${}^-OOC\text{-}CHO + 2\,H^+ + e^- \longrightarrow {}^-OOC\text{-}CH_2OH \qquad (16)$$

The dinegative oxalate ion yielded in the dimerization of the $CO_2^{\cdot-}$ radical anion (Eq.14) can undergo further reduction to glyoxalate (Eq.15), and as a final reduction step to glycolate anions (Eq.16). No glyoxylic acid was obtained on Mo electrodes, the main product was proven to be the oxalate[49].

CONCLUSIONS

The main processes of carbon dioxide electroreduction were summarized based upon the nature of the cathode metal. In this review we have discussed the electroreduction of CO_2 performed on "d" type metal cathodes. It was shown that by using metals that belong to the 8th group the electroreduction yielded various active intermediates. These intermediates were capable to undergo subsequent reactions in which valuable products were formed. Typically, on palladium cathodes formate ions and hydrocarbon molecules were obtained, while the main products on ruthenium were methanol and methan. Copper remains on of the most promising cathode materials for the manufacturing of hydrocarbons. Nevertheless, the current efficiency for methan and ethan depends on the renewal on the electrode surface. Rotating disk electrodes had an efficiently renewed surface. The large number of mechanism suggested for the electroreduction of carbon dioxide indicate that this topic has still not been elucidated. One should emphasize that the electrochemistry of CO_2 is a continuously growing field. Novel procedures and even new reduction products are being reported. Gold electrodes have been recently introduced for analytical purposes[51-53], namely for the development of a new microelectrode CO_2 sensor. In the described application CO_2 is being electrochemically reduced at unshielded gold microdisc electrodes in DMSO, in standard reaction cell. Shibata and co-workers[54] obtained urea by the simultaneous reduction of CO_2 with nitrate and nitrite ions. Copper-loaded gas-diffusion electrodes were used in aqueous $KHCO_3$ supporting electrolyte, to which arbitrary concentrations of KNO_3 or KNO_2 were added. The increasing number of patents in this field [9,16,17,55] support the conclusion that the electroreduction of carbon dioxide at the industrial scale is not an unrealistic dream any more, for it has promising chances of being achieved in the near future

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