STUDIA UBB CHEMIA, LVIII, 3, 2013 (p. 75-84)
(RECOMMENDED CITATION)

ELECTROCHEMICAL REDUCTION OF CO_2 ON LEAD ELECTRODE. I. CYCLIC VOLTAMMETRY AND LONG TIME ELECTROSYNTHESIS STUDIES

FLORIN ALIN HANC-SCHERER[a], PETRU ILEA[a]

ABSTRACT. Carbon dioxide electrochemical reduction (CDER) was investigated on Pb electrode in a conventional three electrodes cell and a filter-press electrochemical reactor at ambient temperature and pressure. The electrolysis was conducted in Na_2SO_4, Na_2SO_4+Na_2CO_3 and Na_2CO_3 solutions for 4h. The formation of formate as a product of reduction depends on the type of electrolyte and pH value. The highest current efficiency (35%) was obtained in sulphate solution at 5mA/cm^2 current density.

Keywords: *carbon dioxide reduction, formic acid production, lead electrode*

INTRODUCTION

Carbon dioxide (CO_2) is recognized as a major contributor to climate change due to human activities (human factor). The main areas of activities that emit CO_2 and have greatly increased CO_2 concentrations in the atmosphere are the combustion of fossil fuels (oil, natural gas, coal), the transportation of goods and people and deforestation (making it difficult to remove CO_2 from the atmosphere).

The reduction of CO_2 emissions was examined *via* different paths, among the most important ones are the following: chemical [1], thermochemical [2], photochemical [3, 4] and electrochemical reduction [1-5]. The last mentioned way is a promising and efficient process that allows recycling of CO_2 to valuable products (CO, HCOOH, MeOH, CH_4, C_2H_4) [6-9].

Electrochemical conversion of CO_2 depends on a number of specific parameters (electrode material, electrolyte solution, temperature, pressure) that can lead to high current yields of products [6, 7, 10].

Since hydrogen evolution is a competing reaction (HER), metals with high overpotential for hydrogen evolution, such as *sp* group (Hg, In, Pb, Cd, Sn) have higher efficiencies for CO_2 reduction. These electrodes tend to favor the formation of formic acid with high current efficiency [9, 11-13].

---

[a] *Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering, 11 Arany Janos Street, Cluj-Napoca, 400028, Romania, pilea@chem.ubbcluj.ro*

Formic acid as a reduction product on Pb, Sn, Cd electrodes is important because it represents an alternative fuel for direct liquid fuel cells (DLFCs). Direct formic acid fuel cells (DFAFC) have higher open circuit potentials (1.45 V) and current densities [14-17]. Lead has the advantage that it is easy to process and is available on the market at a reasonable price. The most important thing is that the overpotential for hydrogen evolution reaction on Pb is higher than that on the other metals (In, Sn, Cd) [18].

Based on the above considerations the present work is focused on the study of electrochemical reduction of CO_2 in different aqueous electrolytes (Na_2SO_4 and Na_2CO_3) using a lead cathode. The ultimate goal of the research was to convert carbon dioxide into fuel (formic acid/formate) for use in fuel cells.

RESULTS AND DISCUSSION

Voltammetric experiments

To highlight the cathodic reduction of CO_2, cyclic voltammetry (CV) studies were carried out at lead electrode. The reactions that occurred on lead electrode in alkaline media at 25°C and their electrochemical potential vs standard hydrogen electrode (SHE) are shown below [19]:

$$CO_2(aq) + H_2O + 2e^- \rightarrow HCOO^- + OH^- \qquad E^o = -1.02\ V/SHE \qquad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^o = -0.83\ V/SHE \qquad (2)$$

In order to study the carbon dioxide electrochemical reduction (CDER) first experiments were performed using Na_2CO_3 0.5M (deaerated by bubbling Ar) and saturated with CO_2 (Figure 1). In the presence of carbonate ions a wave is observed at a potential of ca. -1.45 V/ Ag/AgCl/KCl$_{sat}$ due to reduction of the ions. When CO_2 is bubbled a well-defined reduction peak is observed at -1.6V due to CO_2 reduction.

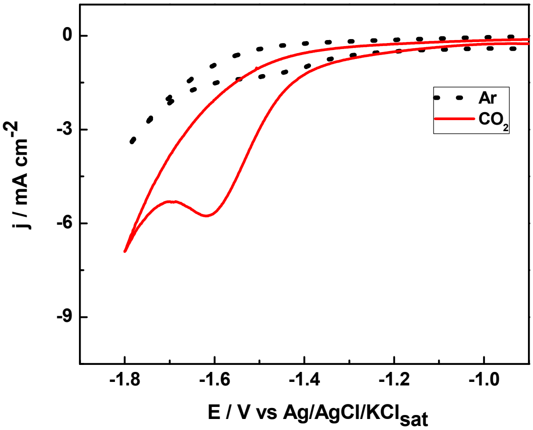

Figure 1. Cyclic voltammograms on Pb electrode at 50 mV s^{-1} in 0.5 M Na_2CO_3 with and without CO_2.

The current density peak (-5.6 mA/cm^2) for CO_2 reduction to formate is close to the data from literature [20, 21].

Cyclic voltammograms recorded in Na_2SO_4 electrolyte are presented in (Figure 2A).

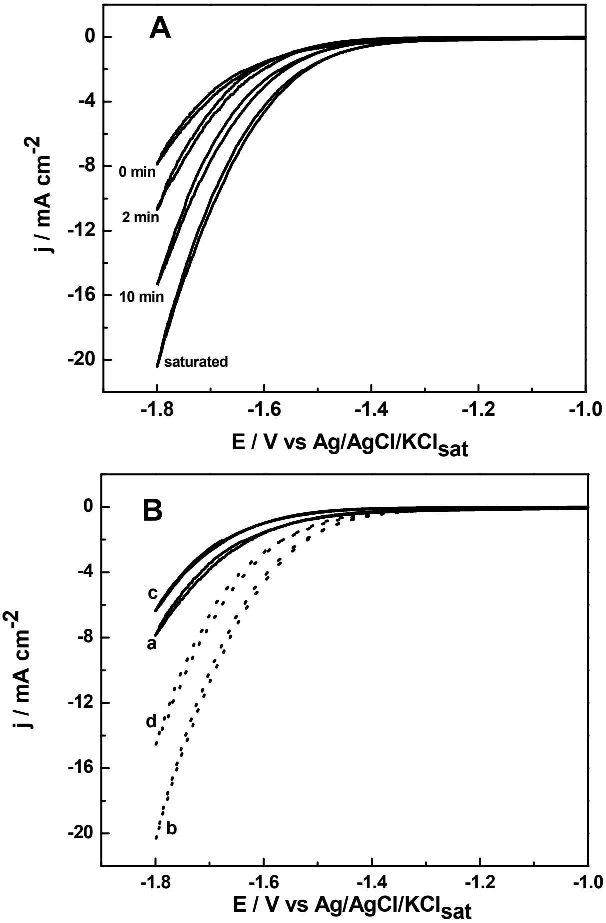

Figure 2. Cyclic voltammograms on Pb electrode at 50 mV s^{-1} in: (**A**) Na_2SO_4 0.6 M, at different times of bubbling CO_2, in (**B**) (**a**) Ar atmosphere Na_2SO_4 0.6M, (**b**) CO_2 saturated Na_2SO_4 0.6M (**c**) Ar atmosphere Na_2SO_4 0.6M+Na_2CO_3 0.1M, (**d**) CO_2 saturated Na_2SO_4 0.6M +Na_2CO_3 0.1M.

When the voltammetry was made under Ar atmosphere, only HER is active. The cathodic current, obtained in CO_2-saturated Na_2SO_4 solution, started to increase at more positive potential (ca.-1.4 V) than cathodic current obtained in Ar atmosphere (-1.49 V). In view to observe the influence of CO_2 concentration, the gas was bubbled at different intervals of time. After each bubbling time cyclic voltamograms were recorded (Figure 2A). The onset potential of the cathodic current shifts more positively with increasing CO_2 concentration.

Current efficiency for product depends on the ratio CO_2-H_2O in the electrolyte solution. For a molecular ratio CO_2-H_2O about 0.25 current efficiency of HCOOH is equal to current efficiency of H_2. Values under 0.25 encourage hydrogen evolution reaction and CO_2 reduction significantly decreases [10].

Cyclic voltammograms obtained in Na_2SO_4 electrolyte with Na_2CO_3 are presented in (Figure 2B). In this case the cathodic current obtained is much smaller than that obtained in the absence of Na_2CO_3.

The presence of Na_2CO_3 in the electrolyte increases the pH of the solution. The predominant species in high alkaline solution are the carbonate ions, according to the E-pH diagram performed by Hori [22], which means that this compound is not reactive at the electrode surface. By lowering the pH solution due to CO_2 bubbling, CO_2 reacts with CO_3^{2-} ions which are converted into HCO_3^- as described in equation 3 [10]:

$$CO_3^{2-} + CO_2(aq) + H_2O \rightarrow 2HCO_3^- \qquad (3)$$

At pH = 8.5 equilibriums states between CO_{2aq}, HCO_3^- and CO_3^{2-} are achieved:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)} \qquad (4)$$

$$CO_{2(aq)} + HO^- \leftrightarrow HCO_3^- \qquad K_1=2.57 \times 10^{11} \qquad (5)$$

followed by:

$$HCO_3^- + HO^- \leftrightarrow CO_3^{2-} \qquad K_2=8.13 \times 10^3. \qquad (6)$$

The formation of bicarbonate ions simultaneously with the consumption of carbonate and OH^- ions results in decreasing of the pH value in the bulk solution [23]. This may explain the decrease of the speed for CDER in the presence of CO_3^{2-} ions. This observation is confirmed by the mechanism of electrosynthesis of formate ions, on lead electrode, which according to the literature [10] consists of the following steps:

$$CO_{2\,(aq)} + e^- \rightarrow CO_2^{\bullet -}{}_{ads} \qquad (7)$$

$$CO_2^{\bullet -}{}_{ads} + H_2O \rightarrow HCOO^{\bullet}{}_{ads} + OH^- \qquad (8)$$

$$HCOO^{\bullet}{}_{ads} + e^- \rightarrow HCOO^- \qquad (9)$$

Based on cyclic voltammetry data the current efficiency (CE) can be estimated for each type of electrolyte by dividing the amount of charge consumed for CDER (Q_{CDER}) to total amount of charge consumed (Q_{total}) as described in Table1.

Tabel 1. Current efficiency evaluated by CV measurements for different types of electrolytes

Type of electrolyte	pH	Q_{total} (mAs)	Q_{CDER} (mAs)	CE (%)
Na_2CO_3(0.5M) + CO_2	10.6	10.4	4.0	38
Na_2SO_4 (0.6M)+ CO_2	6.3	12.8	7.9	62
Na2SO4(0.6M)+Na_2CO_3(0.1M) + CO_2	7.5	8.7	5.0	58

From the values presented in Table 1 it can be seen the electrolyte solution saturated with CO_2 is beneficial to the process regardless of the type of electrolyte.

Long time electrosynthesis (LTE) of formate in filter-press electrochemical reactor with metallic lead cathode

Following the results obtained by cyclic voltammetry experiments, studies were continued by electrolysis measurements. These experimental data are necessary because they could determine the formation of formate ions during the electrolysis by quantitative chemical analysis

In the cathodic compartment of the reactor, CO_2(aq) is reduced to formate according to equation (1) in parallel with equation (2), while the reaction at anode is:

$$O_2 + 4H^+ + 4\,e^- \rightarrow 4\,OH^- \qquad E^o=+0.41\ V/SHE \qquad (10)$$

Current efficiencies calculate for formate ions during LTE are presented in Figure 3A.

Changing sulphate anion with carbonate anion or adding carbonate to sulphate solution leads to a decrease in current efficiency. The modification in CE appears to be influenced by changes in pH (what was observed in cyclic voltammetry experiments).

The Na_2CO_3 and Na_2SO_4 0.6M + Na_2CO_3 0.1M solutions have a pH value greater than 10 which makes the reaction (1) to be less favourable. In this case adsorbed CO_2 in solution will react with carbonate to bicarbonate according to the reaction (3).

The poor current efficiencies obtained in the carbonate presence is due to CO_3^- species whose reaction with CO_2 reaction (3) competing reaction (1) and leading to an inhibition of the formation of formate.

LTE measurements were also performed at different current densities (Figure 3B).

As can be observed in Figure 3B, increasing the current density typically lowers the formate current efficiency. This was observed by Udupa et al. [24] and can be attributed mainly to CO_2 concentration polarization [19].

The experiments undertaken by Koleli et al. [25] on Pb electrode showed a dependence of the formate current efficiency on current density, while results obtained on Sn [26] show an increasing of current efficiency with decreasing current. We observed a similar trend (decreasing in current efficiency with increasing current) for carbonate/sulphate solutions.

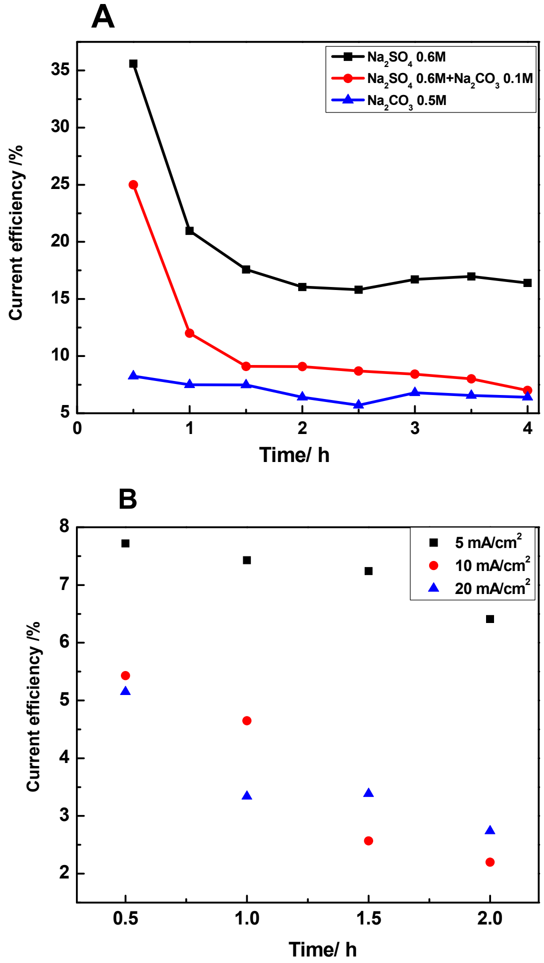

Figure 3. (**A**) Current efficiencies for formate evolution during LTE for different type of electrolyte saturated with CO_2 at 5 mA/cm^2; (**B**) in 0.5 mol L^{-1} Na_2CO_3 saturated with CO_2 at different current densities

Due to the H_2-evolution, the current efficiencies for the $HCOO^-$ formation decreases with the rising of the electrolysis time.

After 30-45 minutes of electrolysis, a cathode deactivation was observed (the corresponding current efficiencies decreased with 15% in the case of Na_2SO_4 electrolyte-Figure 3A).

"Poisoning" of the cathode over time has been observed for CO_2 electroreduction on copper electrodes [27-31], and some effects of this deactivation have been indicated on *sp* group (In, Pb, Sn) electrodes. Koleli and al. [32] show that the current efficiency decreased in time during electrolysis thus the highest current efficiency for formic acid production obtained in carbonate solution on Pb after 30 min. was 39% and after 120 min. CE was 10% respectively. Kapusta and al. [33] showed that low efficiency was due to the formation of organometallic complexes on the tin electrode, this situation favouring hydrogen evolution reaction as a competitive reaction.

CONCLUSIONS

The electrochemical reduction of CO_2 on lead plate electrode in aqueous Na_2CO_3 and Na_2SO_4 electrolyte by cyclic voltammetry and LTE in a filter-press electrochemical reactor was studied.

Measurements showed that CO_2 electroreduction at formate depends on the type of electrolyte and pH value. The highest current efficiency for $HCOO^-$ production (35%) (see figure 3A) was obtained in sulphate solution. Long time electrosynthesis showed that CE is favored by low current densities (5mA/cm^2). Further research is needed to minimize the disadvantage of operating at low current densities.

EXPERIMENTAL SECTION

Voltammetric experiments

Experiments were carried out in an undivided conventional three electrodes cell (V = 12 cm^3) at 25 °C. The working electrode consisted of a lead wire with a geometric surface area of 0.12 cm^2. The current densities were normalized with the geometric surface area. The reference electrode used in all measurements was $Ag/AgCl/KCl_{sat}$ and the counter electrode used was a Pt wire. The electrolytes used were Na_2CO_3 0.5M and Na_2SO_4 0.6M solutions prepared from the solid salt and double distilled water (Double D Still, JENCONS, England). Measurements have been done with a computer controlled tripotentiostat DXC 240. Carbon dioxide and argon gases were purchased from Linde.

Filter-press electrochemical reactor

A filter-press type electrochemical reactor was used in this study. The cell contained two compartments one cathodic and one anodic separated by a Nafion 324 cation-exchange membrane. The working electrode (cathode) was a lead plate (99.99% Pb), while a Dimensionally Stable Anode (DSA/O_2)

plate was used as the counter- electrode (anode). The area of the working and DSA electrodes was 10 cm^2. The reference electrode Ag/AgCl/KCl$_{sat}$ was placed close to the Pb cathode. A schematic representation of the filter-press electrochemical reactor is shown in Figure 4.

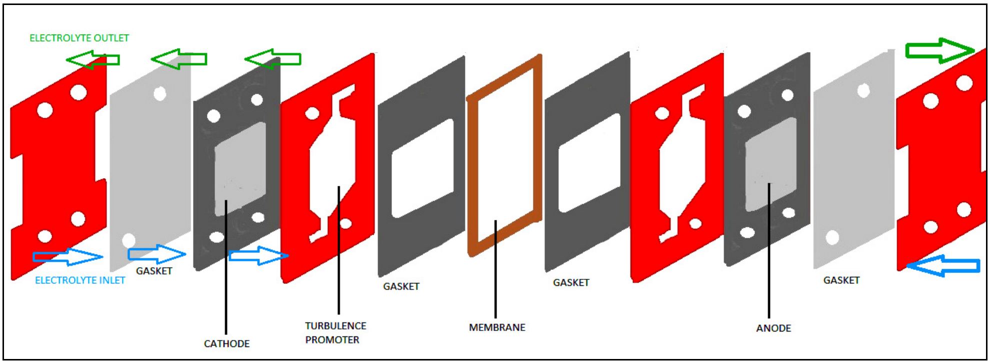

Figure 4 Scheme of the filter-press electrochemical reactor

Electrochemical experiments were carried out in continuous mode for 4h under ambient temperature and pressure conditions. Each electrolyte was circulated through its own compartment using peristaltic pumps with a flow rate of 200mL min^{-1}. Measurements have been done galvanostaticaly with PC controlled PARSTAT 2273 and Datronix Electrochemical System, composed by DXC 236 potentiostat connected to a PC through National Instruments (NI) DAQ hardware. The software packages used have been developed in our laboratory in NI Labview soft.

The aqueous solution used in our experiments as catholyte and anolyte were Na_2CO_3 and Na_2SO_4. Before the start of each experiment, catholyte was deaerated with Ar for 30 minutes then CO_2 was bubbled into the catholyte solution until saturation, and then continuous CO_2 bubbling was maintained throughout the experiment. The lead cathode was ground flat with fine emery paper, then polished with alumina powder and rinsed with double distilled water.

Samples were taken from 30 to 30 minutes and the formate content was analysed by the permanganate method. This procedure consisted of: 1) reacting the sample solutions with an excess of potassium permanganate solution, 2) adding an excess of oxalic acid solution and 3) re-titrating the solution with $KMnO_4$ [34].

ACKNOWLEDGMENTS

The authors wish to thank for the financial support of the Sectorial Operational Programme for Human Resources Development 2007 – 2013, co-financed by the European Social Fund, under the project number POSDRU/107/1.5/S/76841 with the title “Modern Doctoral Studies: Internationalization and Interdisciplinarity”.

REFERENCES

[1] M. Aulice Scibioh, B. Viswanathan, *Proc. Indian Natn. Sci. Acad.*, **2004**, *70*, A, 3, 407-462.

[2] C.E. Bamberger, P. R. Robinson, *Inorg. Chim. Acta*, **1980**, *42*, 133-137.

[3] G. Centi, S. Perathoner, *Catalysis Today*, **2009**, *148*, 191-205.

[4] K. Kalyanasundaram and M. Graetzel, *Current Opinion in Biotechnology*, **2010**, *21*, 298-310.

[5] Y. Lu, Z. Jiang, S. Xu, H. Wu, *Catalysis Today*, **2006**, *115*, 263-268.

[6] M. Jitaru, D.A. Lowy, M. Toma, B.C. Toma, L. Oniciu, *J. Appl. Electrochem.*, **1997**, *27*, 875-889.

[7] C.M. Sánchez-Sánchez, V. Montiel, D.A. Tryk, A. Aldaz and A. Fujishima, *Pure and Applied Chemistry*, **2001**, *73*, 12, 1917-1927.

[8] R.P.S. Chaplin, A.A. Wragg, *J. Appl. Electrochem.*, **2003**, *33*, 1107-1123.

[9] B. Eneau-Innocent, D. Pasquier, F. Ropital, J.-M. Léger, K.B. Kokoh, *Applied Catalysis B: Environmental*, **2010**, *98*, 65-71.

[10] Y. Hori, "*Electrochemical CO_2 reduction on Metal Electrodes*". *Modern Aspects of Electrochemistry,* Number 42, Springer, New York, **2008**.

[11] F. Koleli, T. Atilan, N. Palamut, A.M. Gizir*, J. Appl. Electrochem.*, **2003**, *33*, 447-450.

[12] S. Ikeda, T. Takagi, K. Ito, *Bull. Chem. Soc. Jpn.*, **1987**, *60*, 2517-2522.

[13] M. Todoroki, K. Hara, A. Kudo, T. Sakata, *J. Electroanal. Chem.*, **1995**, *394*, 199-203.

[14] S. Ha, C.A. Rice, R.I. Masel, A. Wieckowski, *J. Power Sources*, **2002**, *112*, 655-659.

[15] X Wang, J. Hu, I-M. Hsing, *J. Electroanal. Chem.*, **2004**, *562*, 73–80.

[16] J-H. Choi, K-J. Jeong, Y. Dong, J. Hanb, T-H. Limb, J-S. Lee, Y.-E. Sung, *J. Power Sources*, **2006**, *163*, 71-75.

[17] X. Yu, P.G. Pickup, *J. Power Sources*, **2008**, *182*,124-132.

[18] Allen J. Bard, Encyclopedia of Electrochemistry of the Elements, Marcel Dekker, Inc. New York and Basel, **1973**, Volume IX, Part A.

[19] H. Li, Colin Oloman, *J. Appl. Electrochem.*, **2006**, *36*, 1105-1115.

[20] Y. Hori, K. Kikuchi, S. Suzuki, *Chemistry letters*, **1985**, 1695-1698.

[21] Y. Hori, H. Wakebe, T.,Tsukamoto, O, Koga, *Electrochimica Acta* **1994**, *39*,1833.

[22] Y. Hori, S. Suzuki, *Bull. Chem. Soc. Jpn.*, **1982**, *55*, 660.

[23] B. Innocent, D. Pasquier, F. Ropital, F. Hahn, J.-M. Leger, K.B. Kokoh, *Applied Catalysis B: Environmental*, **2010**, *94*, 219-224.

[24] K.S. Udupa, G.S. Subramanian and H.V.K. Udupa, *Electrochimica Acta*, 1971, *16*, 1593-1598.

[25] F. Koleli, D. Balun, *Applied Catalysis A: General*, **2004**, *274*, 237-242.

[26] Hui Li, Colin Oloman, *J. Appl. Electrochem.*, **2005**, *35*, 955-965.

[27] D.W. DeWulf, T. Jin, A.J. Bard, *J. Electrochem. Soc.* **1989**, *136*, 1686-1691.

[28] S. Wasmus, E. Cattaneo, *Electrochimica Acta*, **1990**, *35*, 771-775.

[29] G. Kyriacou, A. Anagnostopoulos, *J. Electroanal. Chem.*, **1992**, *322*, 233-246.

[30] B. Jermann, J. Augustynski*, Electrochimica Acta,* **1994**, *39*, 1891-1896.

[31] Jaeyoung Lee, Yongsug Tak, *Electrochimica Acta,* **2001**, *46*, 3015-3022.

[32] F. Koleli, T. Atilan and N. Palamut, *J. Appl. Electrochem.,* **2003**, *33*, 447-450.

[33] S. Kapusta and N. Hackerman, *J. Electrochem. Soc.,* **1983**, *130*, 3, 607-613.

[34] F. Albert, N. Barbulescu, C. Holszky, C. Greff, “Analiză chimică organică”, Ed. Tehnică, Bucureşti, **1970**.