STUDIA UNIVERSITATIS BABEŞ–BOLYAI, CHEMIA, XLV, 1-2, 2000

THE OXIDATION OF TOLUENE BY POTASSIUM PERMANGANATE IN PERCHLORIC ACID MEDIUM

CLAUDIA MUREŞANU[1], IOAN BÂLDEA[2]

Department of Physical Chemistry, Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University of Cluj - Napoca, 11 Arany Janos Str., 3400-Romania.

ABSTRACT. The reaction of potassium permanganate with toluene, catalyzed by Mn^{2+}, was studied spectrophotometrically. Permanganate ion is consumed mainly by two reaction routes: one is the direct oxidation of toluene and the other the reduction by the manganous ion. Both pathways exhibit a first - order dependence with respect to permanganate ion. Our kinetic study includes also the influence of toluene, hydrogen ion and manganous ion concentration upon reaction rate. The rate laws for the two reaction routes and for the global reaction were established. Several possible reaction mechanisms are discussed for C – H bond breaking in the case of direct oxidation of toluene by permanganate and for Mn^{3+} generation by reduction of MnO_4^- with Mn^{2+}.

KEYWORDS: toluene, potassium permanganate, catalysis, redox reactions, kinetics.

Potassium permanganate is a well-known oxidant for various organic compounds, in acidic and basic media. We mention here only a few examples, like the oxidation of olefins[1], oxalic[2 - 4] and formic acid[5], 2,6-dinitrophenols[6], toluene[7], substituted toluenes[8] and ethylbenzene[9].

Related to the subject of our paper are the earlier works of Cullis and Ladbury[7-9]. They studied the oxidation of aromatic hydrocarbons with potassium permanganate, in a 50% aqueous acetic acid medium, by means of an iodometrical method. The main product was the corresponding aldehyde, for toluene and substituted toluenes oxidation and acetophenone in the case of ethylbenzene oxidation, when a stoichometric ratio of initial concentrations of reactants was used. Besides side chain oxidation aromatic ring disruption was also observed, especially for the oxidation of xylenes. The results of the kinetic studies about the oxidation of aromatic hydrocarbons mentioned above[7-9] revealed that, all reactions are first-order with respect to MnO_4^- concentration. Toluene, chlorotoluene and ethylbenzene oxidations are first order with respect to the organic compound, while for m- and p-xylene this order was less than one. A clear autocatalytic effect of Mn(II), involving the Mn(III) intermediate, could not be proved. It seemed rather that the mechanism of these reactions has two pathways, one in which Mn(III) is implied and one independent of this species[7-9]. The recent papers of Gardner and Kuehnert deal with the oxidation of alkylbenzenes in aqueous buffer[10] and in neat toluene[11]. They developed a hydride transfer mechanism for toluene oxidation in aqueous buffer and a radical mechanism if the reaction was performed in organic solvent. Benzyl alcohol[12-14] and benzaldehyde[15-17] oxidation with MnO_4^- were studied in acid medium while for toluene oxidation no recent kinetic are available in

---

[1] *muresanu@chem.ubbcluj.ro;* [2] *ibaldea@chem.ubbcluj.ro*

this medium. That is why we considered it interesting to devote this paper to a more detailed investigation of toluene oxidation by potassium permanganate in perchloric acid medium.

EXPERIMENTAL

The chemicals used in this study were of reagent grade purity and were acquired from commercial sources (Reactivul Bucuresti and Merck).

Kinetic measurements were performed by means of a Zeiss Spekol spectrophotometer, provided with a temperature jacket surrounding the cell holder. The jacket was connected to a Wobser U-10 recirculatory water bath. Reaction mixtures were prepared directly into the spectrophotometer glass cell, of 5-cm path length. The reaction was started by adding a measured amount of $KMnO_4$ stock solution over the mixture of toluene, $HClO_4$, $MnSO_4$, $NaClO_4$ in twice distilled water. Absorbance was measured at 520 nm, where $KMnO_4$ UV/VIS spectrum exhibits a maximum.

RESULTS AND DISCUSSIONS

Kinetic runs were performed in the presence of toluene and Mn(II) excess. Absorbance readings were processed according to the integrated form of a first-order rate law:

$$\ln(A - A_\infty) = \ln(A_0 - A_\infty) - k_{obsd}\cdot t \qquad (1)$$

where: A_0, A_∞ and A are the measured values of absorbance at the beginning, the end and at different time moments of the reaction;
k_{obsd} is the observed first-order rate constant.

Semilogarithimic plots $\ln(A - A_\infty)$ *versus* t, at several excess concentrations of toluene were linear (***Fig.1***) up to 90 % of completion, so that it is obvious that reaction order with respect to MnO_4^- is one. If the reaction was approaching its end a slight downward curvature was noticed.

Observed rate constants were determined from the slopes of linear plots, of eq. (1), using a least square method. Two to four replicate kinetic runs were carried out for each set of conditions.

It is considered that the depletion of MnO_4^-, in the presence of Mn^{2+}, occurs by two pathways:

Pathway 1, which means the direct oxidation of toluene by permanganate;

Pathway 2, which is the autocatalytic, first order reduction of MnO_4^- by the manganous ion.

Our results, summarized in ***Table 1***, revealed that enlarged concentrations of toluene lead to increased values of first-order rate constants according to:

$$k_{obsd} = (2.4\pm0.5)\cdot10^{-4} + (0.34\pm0.04)\cdot[\text{Toluene}]_0 \qquad \text{at } 45^0\text{C} \qquad (2)$$

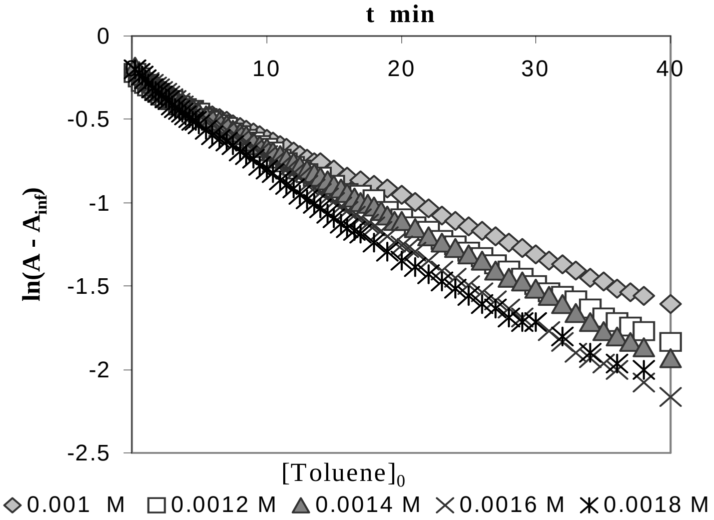


Fig.1 First order semilogarithmic plots at several excess concentrations of toluene; $[MnO_4^-] = 7\cdot10^{-5}$; $[HClO_4] = 1.4$; $[MnSO_4] = 10^{-2}$ $mol\cdot dm^{-3}$ and $\mu = 1.5$ $mol\cdot dm^{-3}$ at 45^0C.

where the term of zero-order with respect to toluene represents the consumption of MnO_4^- due to the reaction:

$$MnO_4^- + 4Mn^{2+} + 8H^+ \rightarrow 5Mn^{3+} + 4H_2O \qquad (3)$$

The rate constant determined in the absence of toluene, $k_0 = 3.9\pm0.2$ s^{-1}at $[H^+] = 1.4$, $\mu = 1.5$ $mol\cdot dm^{-3}$ and 45^0C, is a close value to the intercept of eq.(3).

Table 1.

The dependence of first-order rate constants for toluene oxidation on the excess concentration of toluene; $[MnO_4^-] = 7\cdot10^{-5}$; $[HClO_4] = 1.4$; $[MnSO_4] = 10^{-2}$ $mol\cdot dm^{-3}$ and $\mu = 1.5$ $mol\cdot dm^{-3}$ at 45^0C.

$10^3\cdot[Toluene]_0$ $(mol\cdot dm^{-3})$	1.0	1.2	1.4	1.6	1.8
$10^4\cdot \bar{k}_{obsd}$ (s^{-1})	5.8±0.6	6.5±0.3	7.2±0.2	7.9±0.3	8.6±0.2
$10^4\cdot \bar{k}^*_{obsd}$ (s^{-1})	3.4±0.4	4.1±0.3	4.8±0.3	5.5±0.2	6.4±0.3

The values of first – order rate constants corrected for reduction of permanganate by manganous ion, $k^*_{obsd} = k_{obsd} - 2.4\cdot10^{-4}$, exhibited a first – order influence with respect to toluene concentration:

$$k^*_{obsd} = (1.5\pm0.5)\cdot10^{-6} + (0.34\pm0.04)[Toluene]_0 \qquad \text{at } 45^0C \qquad (4)$$

$$k^*_{obsd} \approx (0.34\pm0.04)[Toluene]_0$$

The influence exerted by hydrogen ion concentration was investigated in the limits of 1 to 1.5 mol·dm^{-3} at constant toluene and Mn(II) concentration. The results presented in **Table 2** prove a linear dependence of the rate constant on the [H$^+$], of the form:

$$k_{obsd} = (2.7\pm0.8)\cdot10^{-4} + (2.7\pm0.2)\cdot10^{-4}\cdot[H^+] \qquad \text{at } 45^0\text{C} \qquad (5)$$

A similar correction procedure, as for the influence of organic substrate, was used also in this case: $k^*_{obsd} = k_{obsd} - k_0$, where k_0 are the rate constants of pathway 2 obtained from kinetic runs in the absence of toluene (**Table *2***).

$$k_0 = (2.7\pm1.1)\cdot10^{-5}+(1.7\pm0.1)\cdot10^{-4}\cdot[H^+] \qquad \text{at } 45^0\text{C} \qquad (6)$$

$$k^*_{obsd} = (2.4\pm0.1)\cdot10^{-4}+(9.34\pm0.6)\cdot10^{-5}\cdot[H^+] \qquad \text{at } 45^0\text{C} \qquad (7)$$

This relationship is valid in strong acid media. At low acid concentration it is to expect a downward curvature of the k_{obsd} = f(t) dependence, tending to a constant value, like that obtained by Cullis and Ladbury[7], because $KMnO_4$ keeps it oxidizing effect upon organic substrates also in low acidic, neutral media and alkaline media.

Table 2.

The dependence of first-order rate constants for toluene oxidation on [H$^+$]; [Toluene]$_0$=1.2·10^{-3}; [MnO_4^-] = 7·10^{-5}; [$MnSO_4$] = 10^{-2} mol·dm^{-3} and μ = 1.5 mol·dm^{-3} at 45^{0}C.

[H$^+$] (mol·dm^{-3})	1	1.1	1.2	1.3	1.4	1.5
$10^4\cdot\overline{k}_{obsd}$ (s^{-1})	5.4±0.1	5.7±0.1	6.0±0.2	6.2±0.2	6.5±0.1	6.8±0.1
$10^4\cdot\overline{k}_0$ (s^{-1})	2.0±0.1	2.2±0.2	2.4±0.1	2.5±0.2	2.7±0.1	2.9±0.2
$10^4\cdot\overline{k}^*_{obsd}$ (s^{-1})	3.4±0.1	3.6±0.1	3.8±0.2	3.8±0.2	3.4±0.1	3.9±0.2

Because several autocatalytic oxidations of organic compounds by $KMnO_4$ are mentioned in literature[2-6], we have studied the influence of Mn(II) upon the reaction rate. But, as it can be seen (***Fig.2***) no sigmoid curve was obtained for the change of absorbance with time, in the absence of Mn(II). Although we couldn't identify any autocatalytic effect, the reaction evolves much faster in the presence of Mn(II), proving the catalytic influence of manganous ion. A similar situation has been observed by other authors[7-9] in the case of toluene, xylenes, chlorotoluene and ethylbenzene.

The first-order rate constant exhibits a second - order dependence on manganous ion concentration, with a small intercept:

$$k_{obsd} = (3.2\pm0.3)\cdot10^{-4} + (3.08\pm0.13)\cdot[Mn(II)]^2 \qquad \text{at } 45^0\text{C} \qquad (8)$$

where the first term corresponds to the rate constant of toluene oxidation in the absence of Mn(II).

A similar dependence is obtained by processing data from kinetic runs in the absence of toluene:

$$k_0 = (6.65\pm0.06)\cdot10^{-5} + (3.23\pm0.11)\cdot[Mn^{2+}]^2 \qquad 45^0C \qquad (9)$$

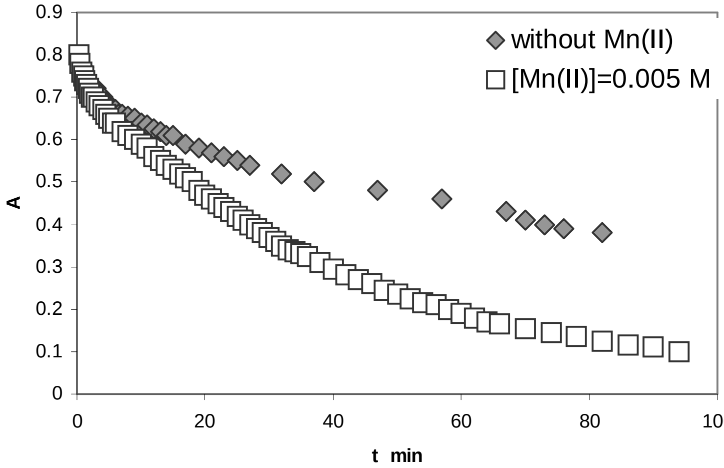


Fig. 2 The variation of absorbance with time in the absence and in the presence of Mn(II) catalyst $[Toluene]_0=1.2\cdot10^{-3}$; $[MnO_4^-] = 7\cdot10^{-5}$; $[HClO_4] = 1.4$ mol·dm^{-3} and $\mu = 1.5$ mol·dm^{-3} at 45^0C.

where the intercept represents the rate constant for solvent oxidation by permanganate ion. The manganous ion influences only the second pathway, this is why the dependence of the rate constants eq. (6) and (7) exhibits approximately the same slope.

Table 3.

The dependence of first-order rate constants for toluene oxidation on $[Mn^{2+}]$; $[Toluene]_0=1.2\cdot10^{-3}$; $[MnO_4^-] = 7\cdot10^{-5}$; $[H^+] = 1.4$ and $\mu = 1.5$ mol·dm^{-3} at 45^0C.

$10^2\cdot[Mn^{2+}]$ (mol·dm^{-3})	0.5	1	1.5	2
$10^4\cdot\bar{k}_{obsd}$ (s^{-1})	3.5±0.7	6.4±0.1	10.4±0.1	15.5±0.4
$10^4\cdot\bar{k}_0$ (s^{-1})	1.4±0.1	3.9±0.2	7.9±0.1	13.6±0.2

The rate law represents the sum of the rates for the two pathways:

$$r = -\frac{d[MnO_4^-]}{dt} = (k_0\cdot[Mn(II)^2] + k\cdot[Toluen]_0)[H^+][MnO_4^-] \qquad (10)$$

CONCLUSIONS

The oxidation of toluene by Mn(VII) yields benzaldehyde and benzoic acid, for reactions performed in aqueous acetic acid[7], aqueous buffer[10] and in neat toluene[11].

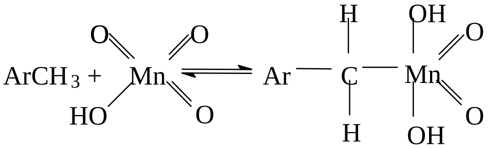
Therefore it is reasonable to consider the formation of same products if the reaction takes place in aqueous $HClO_4$ solution.

Many kinetic studies underline the large isotopic effect observed for the oxidation of organic compounds, like toluene, benzyl alcohol, tolylvaleric acids and for substituted mandelate ions[10, 13, 18, 19, 20] with permanganate. Such a behavior indicates the C – H bond cleavage is the rate determining step. The oxidation of the C – H bond by $KMnO_4$ may proceed by: **A.** proton transfer abstraction[11,12]; **B.** hydrogen atom abstraction[20]; **C**. hydride abstraction[10]; **D**. a [2 + 2] addition of a reactive C – H bond[18, 19] to an Mn = O bond ; **D.** formation of a manganese ester[17, 21].

Literature information, together with the experimental rate law, eq. (10) are to be accommodate by the reaction mechanism. In our opinion these requests are satisfied by three of the above mentioned reaction mechanisms, considering that oxidation proceeds by permanganate ion (pathway 1).

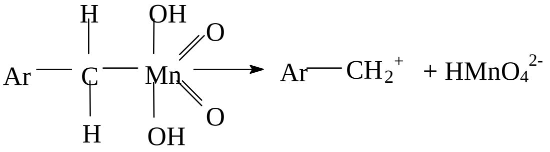
- A [2+2] addition of a C – H bond to the Mn = O bond, continued by homolytic or heterolytic bond cleavage in the rate determining step and subsequent reaction of the intermediate with the solvent.

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4 \qquad K, \text{ fast} \qquad (11)$$



$$ArCH_3 + HO-MnO_3 \rightleftharpoons Ar-CH_2-Mn(OH)_2O_2$$

K₁, fast (12)



$$Ar-CH_2-Mn(OH)_2O_2 \longrightarrow Ar-CH_2^+ + HMnO_4^{2-}$$

k₂, slow (13)

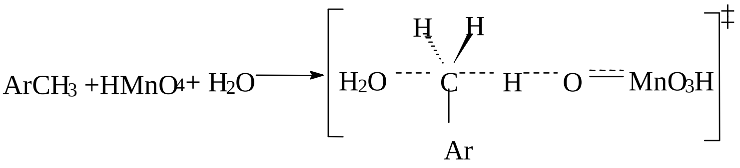
$$Ar-CH_2^+ + H_2O \longrightarrow Ar-CH_2OH + H^+ \qquad k_3 \qquad (14)$$

A free radical intermediate was excluded because experiments undertaken with toluene and benzylic alcohol in aqueous medium ruled out this possibility[10, 13]. The resulting rate law will depend on permanganate, reductant and hydrogen ion concentration according to:

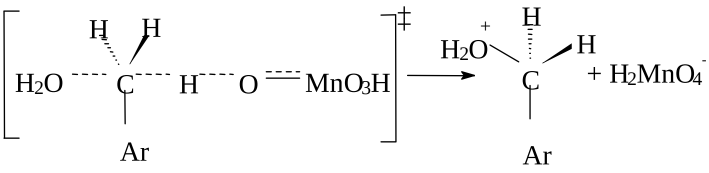
$$r = k_2K_1K[ArCH_3][MnO_4^-][H^+] \qquad (15)$$

- Hydride abstraction which in this case occurs similar to a SN_2 mechanism: With the rate law:

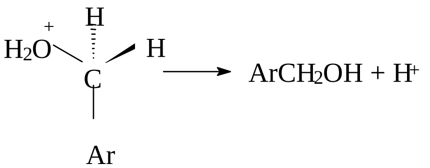
$$MnO_4^- + H^+ \rightleftharpoons HMnO_4 \qquad K \quad (16)$$



fast, K_1 (17)



slow, k (18)

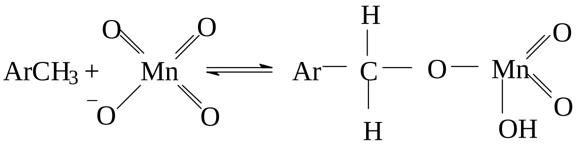


fast (19)

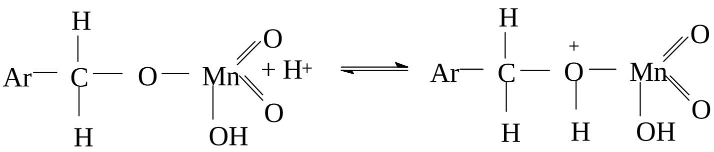
$$r = kKK_1[ArCH_3][H^+][H_2O][MnO_4^-] \qquad (20)$$

Although the association constant for $HMnO_4$ is very low[17] ($K = 2.99\cdot10^{-3}$) there are cases for which a greater reactivity of $HMnO_4$ compared to MnO_4^- is mentioned[22, 23]

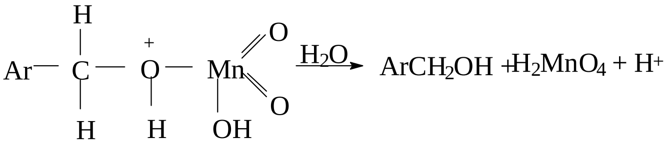
- The formation of an ester between permanganate ion and toluene, followed by the acid catalyzed hydrolysis of the ester.



fast, K^*_1 (21)



fast, K^*_2 (22)



slow, k_3 (23)

This mechanism will lead to a rate law similar to that deduced above:

$$r_1 = k_3K^*_1K^*_2[ArCH_3][MnO_4^-][H^+][H_2O] \qquad (24)$$

All these three mechanisms lead to a rate law of first order with respect to MnO_4^-, H^+ and toluene, similar to that obtained by us for the first pathway.

In high acidic medium several redox and dismutation reactions between manganese species might occur, which explains why no MnO_2 formation was observed:

$$5H_2MnO_4 + 8H^+ \longrightarrow 4MnO_4^- + Mn^{2+} + 4H_2O \qquad (25)$$

$$2H_3MnO_4 + 4H^+ \longrightarrow H_2MnO_4 + MnO_2 + 2H_2O \qquad (26)$$

$$MnO_2 + 4\,Mn^{2+} + 4H^+ \longrightarrow 2Mn^{3+} + 2H_2O \qquad (27)$$

Hydrogen ion abstraction will be the rate determining step[24, 25. 26-28], when Mn^{3+} is the oxidizing species (pathway 2), followed by other reactions of the formed intermediate:

$$ArCH_3 + Mn^{3+} \xrightarrow{k} ArCH_2^{\bullet} + H^+ + Mn^{2+} \qquad \text{slow} \quad (28)$$

$$ArCH_2^{\bullet} + Mn^{3+} \longrightarrow ArCH_2^+ + Mn^{2+} \qquad \text{fast} \quad (29)$$

$$ArCH_2^+ + H_2O \longrightarrow ArCH_2OH + H^+ \qquad \text{fast} \quad (30)$$

Recent literature on this subject, suggests for the generation of the Mn^{3+} intermediate, the formation of a monomeric and a dimeric Mn^{2+} complex (I), with a bridging ligand[4], or the formation of a dinuclear complex between MnO_4^- and Mn^{2+} with oxo bridge[22], followed by the reduction of the complex by Mn^{2+} to Mn^{3+}. Our reaction mixtures contained only ClO_4^- and SO_4^{2-} anions, which are weak in complexing Mn^{2+}, that is why we considered the formation of the MnO_4^- - Mn^{2+} complex:

$$Mn^{2+} + MnO_4^- \rightleftarrows I \qquad K_c \qquad (31)$$

$$I + Mn^{2+} \longrightarrow 2Mn^{3+} + H_2O \qquad k_0 \qquad (32)$$

The influence of hydrogen ion may be explained in two ways: if it is considered that the permanganic acid forms the binuclear complex with Mn^{2+}, or if it is considered that the hydrogen ion is involved in reduction of the complex. The formation of Mn^{3+} was considered as the rate-determining step, and the deduced rate law came to the form:

$$r_2 = k_0[MnO_4^-][Mn^{2+}]^2[H^+] \qquad (33)$$

Although the rate law is quite similar to our experimental rate law eq.(10), we will continue the experimental investigations to come to a better understanding of the overall mechanism.

REFERENCES

1. Lee D. G. and Chen T. : *J. Am. Chem. Soc.*, **1989**,*111*, 7534-7538.
2. Wawrezenczic E. M. and Vronska M. : *Z. Phys. Chem. (Leipzig)*, **1980**, *261(2)*, 306-312.
3. Powell R. T. Oskin, T. and Ganapatshubramanian N. : *J. Phys. Chem.*, **1989**, *93*, 2718-2721.
4. Pimienta V. , Lavabre D. , Levy G. and Micheau J. C. : *J. Phys. Chem.*, **1994,** *98*, 13294-13299.
5. Mann D. R. and Tompkins F. C. : *Trans. Faraday Soc.*, **1941,** *37*, 201-209.
6. Alexander E. A. and Tompkins F. C. : *Trans. Faraday Soc.*, **1939,** *35*, 1156-1165.
7. Cullis C. F. and Ladbury J. W. : *J. Chem. Soc.*, **1955**, 555-560.
8. Cullis C. F. and Ladbury J. W. : *J. Chem. Soc.*, **1955**, 1407-1412.
9. Cullis C. F. and Ladbury J. W. : *J. Chem. Soc.*, **1955**, 2851-2854.
10. Gardner K. A. and Mayer J. M. : *Science*, **1995**, *269*, 1849 – 1851.
11. Gardner K. A. , Kuehnert L. L. and Mayer J. M. : *Inorg. Chem.*, **1997**, *36*, 2069 – 2078.
12. Corma A. , Lambies V. , Melo F. V. and Palou J. : *Anal. Quim.*, **1980**, *76*, 304-310.
13. Banerji K. K. : *J.C.S. Perkin 2*, **1973**, 435 – 437.
14. Mathur S. , Gupta A. and Banerji K. : *Ind. J. Chem.*, **1988**, *27A*, 581 – 583.
15. Tompkins F. C. : *Trans. Faraday Soc.*, **1943**, *39*, 280 – 287.
16. Wiberg K. B. and Stewart R. : *J. Am. Chem. Soc.*, **1955**, *77*, 1786 – 1795.
17. Sen Gupta K. K. , Sen P. K. and Mukhopadhyay G. : *Trans. Met. Chem.*, **1993**, *18*, 369 – 371.
18. Lee D. G. and Chen T. : *J. Org. Chem.*, **1991**, *56*, 5341 – 5345.
19. Lee D. G. and Chen T. : *J. Am. Chem. Soc.,* **1993**, *115*, 11231 – 11236.
20. Braumann J. I. and Pandell A. J. : *J. Am. Chem. Soc.*, **1970**, *92*, 329 – 335.
21. Wiberg K. and Fox A. S. : *J. Am. Chem. Soc.*, **1963**, *85*, 3487 – 3491.
22. Simoyi R. H. , De Kepper P. , Epstein I. R. and Kustin K. :*Inorg. Chem.*, **1986**, *25*, 538 – 542.
23. Bhatia I., Banerji K. K : *J.C.S. Perkin Trans. 2*, **1983**, 1577 – 1580.
24. Venkatachalapathy M. S. , Ramaswamy R. and Udupa H. V .K. : *Bull. Acad. Pol. Scien. (Ser. Chim.)*, **1959**, *7*, 629 – 631.
25. Venkatachalapathy M. S. , Ramaswamy R. and Udupa H. V .K : *Bull. Acad. Pol. Scien. (Ser. Chim.)*, **1958**, *6*, 487 – 489

26. Heiba E. I. , Dessau R. M. and Koehl W. J. :*J. Am. Chem. Soc.*, **1969**, *91*, 138 – 145.
27. Hanotier J. , Hanotier – Bridoux M. and Radzetzky P. :*J.C.S. Perkin 2*, **1973**, *4*, 381 – 386.
28. Andrulis P. ,. Dewaer M. J. S , Dietz R. and. Hunt R. L : *J. Am. Chem. Soc*., **1966**, *88*, 5473 – 5478