

Keiko Takashima

Depto. de Química - CCE - UEL - CP 6001 - 86051-970 - Londrina - PR

Recebido em 27/8/92; cópia revisada em 7/5/93

The oxidation kinetics of malic acid, HMal, by vanadium(V), V(V), in aqueous perchloric acid solution was studied at 30°C by monitoring the absorbance change at 760 nm. Under these conditions the rate of the reaction showed a first order dependence with respect to both the vanadium(V) and malic acid concentrations and fractional to the hydrogen ion concentration. Ionic strength variations of the medium had a small effect on the rate. The rate constant increased with the decrease of the dielectric constant of the medium. Energy of activation and activation parameters were calculated by studying the reaction at different temperatures (293 - 313 K). An oxidation mechanism is proposed.

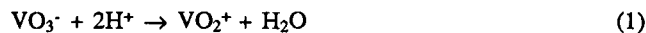
Keywords: oxidation kinetics; malic acid; vanadium (V) oxidation.

INTRODUCTION

The kinetics and mechanism of oxidation of some hydroxy acids by several oxidants such as N-bromobenzenesulphonamide,¹ N-bromacetamide,² diperiodatonickelate(V),³ trichloroisocyanuric acid,⁴ manganese(III),⁵ cerium(IV),^{6,7} chromium(VI)^{8,9}, vanadium(V)¹⁰⁻¹³ have been investigated. Being bifunctional compounds their oxidation can proceed by two general routes, either as alcohols or undergoing oxidative decarboxilation. Jones, Waters and Littler¹⁰ suggested that the oxidation of hydroxy acids involves a fast cyclic complex formation in the first step, a rupture of C-C bond, and the decarboxilation of this complex in the rate-determining step, kinetically similar to that of pinacol. On the other hand, Bakore & Narain⁸ suggested that hydroxy acid oxidation by chromic acid involves considerable C-H bond fission on the α -carbon in the rate-determining step. The present investigation was undertaken to study the malic acid oxidation by vanadium(V) in perchloric acid medium in order to show that the reaction does not change with the ionic strength.

EXPERIMENTAL

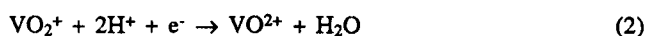
The stock solution of vanadium(V), V(V), was prepared by dissolving ammonium metavanadate, NH_4VO_3 (Merck, p.a.), in an appropriate amount of HClO_4 (Reagen) and producing a stable pervanadyl ion, VO_2^+ , of yellow colour. This solution was diluted to the desired concentration, the ionic strength being controlled by adding NaClO_4 solutions.



The malic acid, HMal (Sigma, purity > 98%) was used as received. All the solutions were prepared with deionized water just before the experiment, and all the reagents were of analytical grade.

Kinetic measurements

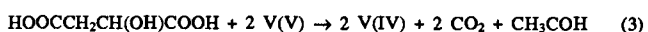
The reaction kinetics was followed by monitoring the appearance of vanadium(IV), V(IV) as vanadyl ion, VO^{2+} at 760 nm using a Varian spectrophotometer mod. DMS-80, with 1 cm pathlength cells and provided with cuvette holder thermostated at 30.0°C ($\pm 0.1^\circ\text{C}$).



Malic acid, HMal, oxidation was studied under pseudo-first order conditions by keeping a large excess over V(V), varying or not the ionic strength, at 30°C. The course of the reaction was followed through four or five half lives varying the concentration of one of the reagent species and maintaining fixed the others at constant temperature. The pseudo-first order rate constants, k_{obs} , were evaluated from the gradients of linear plots (correlation coefficient, $r > 0.9998$, standard deviation, $s \leq 2.0 \cdot 10^{-5}$) of $\ln[\text{V(V)}]$ against time and were reproducible within $\pm 5\%$. The linearity of these plots beyond this point indicates that none of the products formed during the reaction affected the rate. The gradients of such plots were carried out by least-squares method using a personal computer.

Reaction stoichiometry and product analysis

A reaction mixture containing an excess of V(V) (0.15 M) over HMal ($2.0 \times 10^{-3}\text{M}$) in the presence of perchloric acid (2.0 M) was thermostated at 40°C. The estimation of the residual oxidant showed that 1 mol of HMal liberated 2 moles of CO_2 , in a Warburg respirometer (B. Braun, mod. V-85). In addition, a reaction mixture containing a large excess of HMal (1.0 M) over V(V) (0.01 M) in perchloric medium (0.1 M) was allowed to stand for several hours at room temperature. The presence of aldehyde and/or ketone was characterized by the reaction with 2,4-dinitrophenylhydrazine.¹⁴ The differentiation was carried out through Tollens reagent.¹⁴ The reaction was positive for aldehyde. The characterization of form-aldehyde was carried out by chromotropic acid.¹⁵ The test was negative for this compound. Acetaldehyde was characterized through the formation of two moles of carbon dioxide.



Test for free radicals

The reaction between V(V) and HMal was carried out under kinetic conditions in the presence of 25% (w/v) of acrylamide. When the reaction mixture was allowed to stand for several hours a viscous solution was obtained. Controls from which either V(V) or HMal was excluded, indicated no

polymerization. These experiments indicate that the reaction between V(V) and HMal produces free radical species capable of initiating acrylamide polymerization.

RESULTS

Effect of reagent concentrations

The oxidation rate increased with the variation of the [HMal] in large excess at constant initial concentrations of vanadium(V), $[V(V)]_0$, and perchloric acid, $[HClO_4]_0$ ($r > 0.9993$, $s \leq 3.0 \times 10^{-5}$) (Table I). The formation of V(V) in function of time at different initial concentrations of malic acid, $[HMal]_0$, follows a first order kinetics in relation to $[V(V)]$ respectively ($r > 0.9998$, $s \leq 2.0 \times 10^{-5}$). The plot of \ln of observed first order constant, k_{obs} , against $\ln [HMal]_0$ was linear (Figure 1, $r > 0.9995$, $s \leq 0.013$) with a slope of unit showing a first order dependence on [HMal]. The rate of disappearance of V(V) also follows first order kinetics, since the rate constants remained practically constant by the variation in the initial $[V(V)]$ (Table II).

Table I. Effect of concentration of malic acid on the reaction rate at 30°C.

I/M	[S]/M	$k_{obs}/10^{-3}s^{-1}$				$k'/10^{-3}M^{-1}s^{-1}$
		0.50	0.75	1.00	1.20	
---		1.15	1.72	2.31	2.79	2.34
2.0		1.16	1.72	2.34	2.74	2.28

[S] = [HMal], $[V(V)] = 0.010$ M, $[HClO_4] = 1.0$ M.

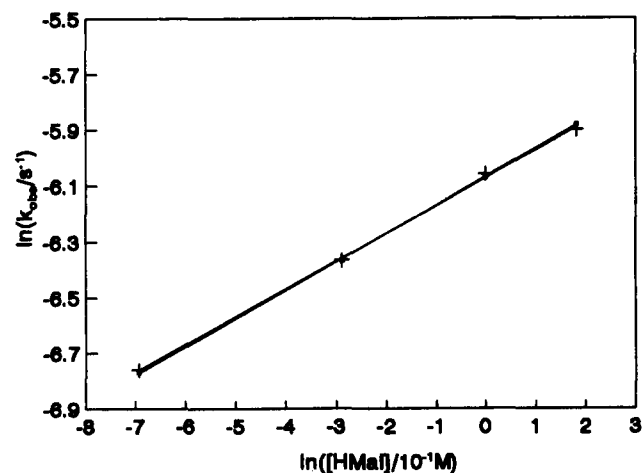


Figure 1. Plots between $\ln k_{obs}$ and $\ln [HMal]$ at 30°C. $[V(V)] = 0.010$ M, $[HClO_4] = 1.0$ M, (.) without ionic strength control; (+) $I = 2.0$ M.

Table II. Effect of the concentration of V(V) on the reaction rate at 30°C.

$[V(V)]/M$	$k_{obs}/10^{-3}s^{-1}$				
	0.005	0.10	0.015	0.020	0.025
	2.69	2.79	2.64	2.77	2.84

[HMal] = 1.2 M, $[HClO_4] = 1.0$ M.

Effect of ion hydrogen concentration

The reaction rate enhanced with the increase of $HClO_4$ concentration (Table III) at constant initial reagent concentration, controlling or not the ionic strength. The plots between the logarithm of k_{obs} and $[H^+]$, given by $[HClO_4]$, were linear (Figure 2, $r > 0.9905$, $s \leq 0.049$) with a same fractional slope ($n = 0.47$).

Table III. Effect of the concentration of $HClO_4$ on the reaction rate at 30°C.

I/M	$k_{obs}/10^{-3}s^{-1}$							n	
	$[H^+]/M$	0.25	0.50	0.75	1.00	1.25	1.50		1.75
---		1.18	1.58	1.84	2.31	2.29	2.75	2.99	0.47
2.0		1.24	1.64	2.13	2.34	2.70	2.91	3.00	0.47

$[H^+] = [HClO_4]$, [HMal] = 1.0 M, $[V(V)] = 0.010$ M.

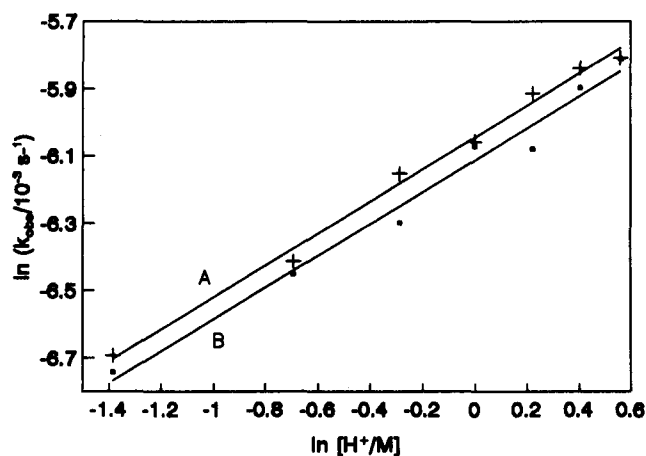


Figure 2. Plot between $\ln k_{obs}$ and $\ln [H^+]$ at 30°C. $[V(V)] = 0.010$ M, [HMal] = 1.0 M, $[H^+] = [HClO_4]$, (A) without strength control, (B) $I = 2.0$ M.

Effect of ionic strength

The ionic strength was varied by adding of concentrated solution of sodium perchlorate (5 M) to the reaction mixture. It was observed a small effect on the rate varying from 1.25 to 2.75 M. A plot between $\log k_{obs}$ and square root of the ionic strength, $I^{1/2}$, at 30°C, resulted a value of ionic charge product, z_+z_- , equal to 0.11^{16,17} ($r = 0.9655$, $s \leq 0.006$) as presented in Table IV.

Table IV. Effect of the ionic strength on the reaction rate at 30°C.

I/M	$k_{obs}/10^{-3}s^{-1}$							z+z-
	1.25	1.50	1.75	2.00	2.25	2.50	2.75	
	2.16	2.21	2.21	2.34	2.33	2.40	2.49	0.11

[HMal] = 1.0 M, $[HClO_4] = 1.0$ M

Effect of varying solvent concentration

The oxidation of HMal was investigated in solvent containing different proportions of methanol and water. The decrease of the dielectric constant of the medium by adding methanol led to an increase on the rate (Table V). Controls carried out with methanol showed negligible oxidation.

Table V. Effect of the dielectric constant on the reaction rate at 30°C.

MeOH/%	$k_{\text{obs}}/10^{-3}\text{s}^{-1}$				
	0	10	20	30	40
	2.31	2.71	3.29	3.92	4.72

[HMal] = 1.0 M, [V(V)] = 0.010 M, [HClO₄] = 1.0 M

Effect of the temperature on the rate

The reaction rate was determined at different temperatures (293 - 313K) maintaining constant all other experimental conditions. These results are given in Table VI ($r > 0.9905$, $s \leq 4.2 \times 10^{-5}$). From Arrhenius plot between \ln of second order constant, k' , and reciprocal absolute temperature, $1/T$ (Figure 3, $r = -0.9996$, $s \leq 0.023$), values of activation energy and other activation parameters were computed (Table VII).

Table VI. Effect of the temperature on the reaction rate.

$t/^\circ\text{C}$	[S]/M	$k_{\text{obs}}/10^{-3}\text{s}^{-1}$				$k/10^{-3}\text{M}^{-1}\text{s}^{-1}$
		0.50	0.75	1.00	1.20	
20	0.40	0.64	0.86	0.97	0.83	
25	0.70	1.07	1.42	1.66	1.38	
30	1.20	1.78	2.31	2.86	2.34	
35	1.98	2.91	3.94	4.76	3.98	
40	3.23	4.69	6.34	7.50	6.15	

[S] = [HMal], [V(V)] = 0.010 M, [HClO₄] = 1.0 M.

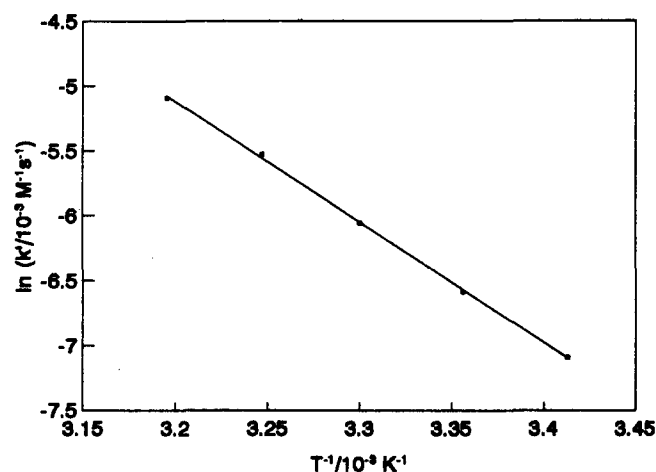


Figure 3. Plot between $\ln k'$ and T^{-1} . [V(V)] = 0.010 M, [HClO₄] = 1.0 M, [HMal] = 0.50 - 1.20 M.

Table VII. Thermodynamic parameters for the oxidation of malic acid by V(V) calculated from the values of k' .

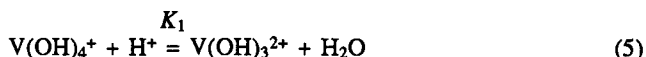
E^\ddagger	ΔH^\ddagger	ΔG^\ddagger	ΔS^\ddagger
kJ/mol	kJ/mol	kJ/mol	J/K.mol
77.8	75.3	89.3	-47

DISCUSSION

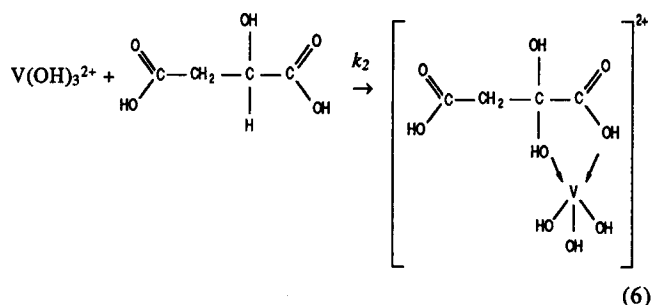
The main observations concerning to the oxidation of HMal by V(V) in perchloric acid medium may be summarized as follows. The rate law of the reaction was found to be proportional to the first power respectively to the oxidant and HMal concentrations, whereas, with respect to the hydrogen ion concentration, [H⁺] was fractionary (0.47). In this work we assumed that the perchloric acid behaves as strong acid, that is, as hydrogen ion.

$$\text{Rate} = k[\text{V(V)}][\text{HMal}][\text{H}^+]^x \quad (4)$$

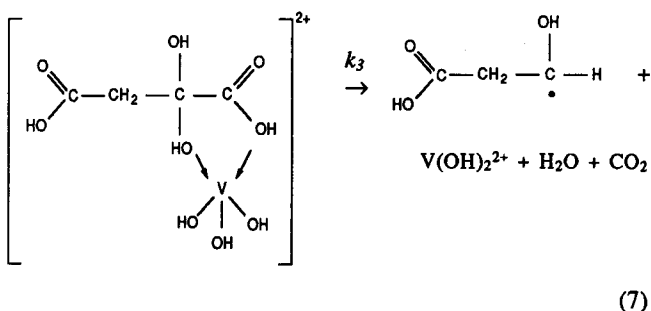
It was shown¹⁸ that the pervanadyl ion, VO₂⁺ is found as the hydrated species, V(OH)₄⁺ in equilibrium ($K_1 = k_1/k_{-1}$) with V(OH)₃²⁺ in perchloric acid medium according to the equation (5).



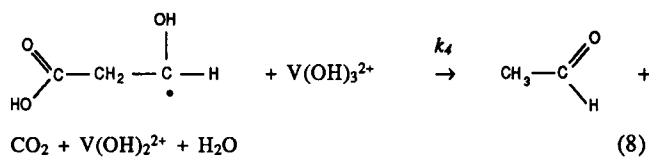
This species reacts in a next slow step with the HMal in the unionized form and produces an activated complex with a positive charge of 2+.



In a rapid subsequent reaction the rupture of the C-C bond takes place to give the first CO₂, and consequently the formation of a free radical and V(V).



The free radical is, then, attacked by another mol of V(V) immediately producing acetaldehyde and liberating the second mol of CO₂.



When this mechanism is taken into account the acid-dependent reaction rate becomes

$$R = -\frac{d[\text{V}(\text{V})]_t}{dt} = \frac{K_1 k_2 [\text{V}(\text{V})]_t [\text{H}^+] [\text{HMal}]}{(k_2/k_{-1}) [\text{HMal}] + 1 + K_1 [\text{H}^+]} \quad (9)$$

where the total or analytical concentration of V(V) is given by

$$[\text{V}(\text{V})]_t = [\text{V}(\text{OH})_4^+ + \text{V}(\text{OH})_3^{2+}]$$

Assuming that $k_2[\text{HMal}] \ll k_{-1}$, the equation (9) becomes

$$R = \frac{K_1 k_2 [\text{V}(\text{V})]_t [\text{H}^+] [\text{HMal}]}{1 + K_1 [\text{H}^+]} = k_{\text{obs}} [\text{V}(\text{V})]_t \quad (10)$$

where

$$k_{\text{obs}} = \frac{K_1 k_2 [\text{H}^+] [\text{HMal}]}{1 + K_1 [\text{H}^+]} \quad (11)$$

This rate law is in agreement with the experimental rate law (4). It supports the observed kinetic data in first order dependence on [V(V)] and [HMal] respectively and fractionary (0.47) one on [H⁺]. From the slope and intercept of the double reciprocal plots of the equation (11), $1/k_{\text{obs}}$ vs $1/[\text{H}^+]$ at constant malic acid concentration (Figure 4, $r > 0.9754$, $s \leq 43.36$) were obtained the equilibrium constant, K_1 , equal to 2.07 at 30°C and the value of the rate constant of the rate-determining step, k_2 , equal to $3.34 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ without ionic strength control. When this was adjusted to keep constant and equal to 2.0 M, these values were 1.95 and $3.66 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, respectively. The linear increase in the reaction rate with the acidity suggests the protonation of $\text{V}(\text{OH})_4^+$ to give a stronger oxidant, shifting the equilibrium to the right. On the other hand, plotting k_{obs} vs $[\text{H}^+]$ at constant [HMal] (Table III), a small

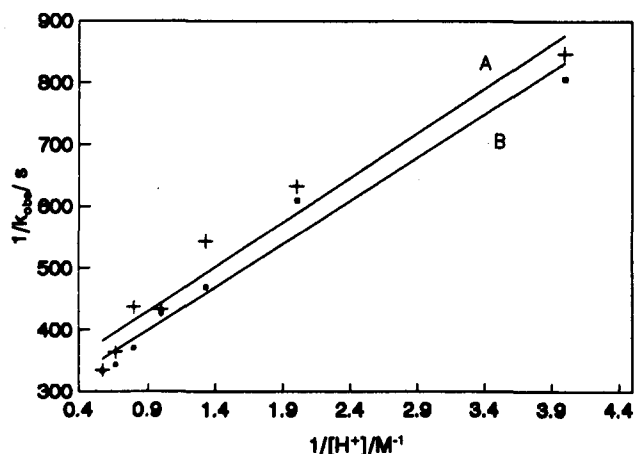


Figure 4. Plots between $1/k_{\text{obs}}$ and $1/[\text{H}^+]$ at 30°C obtained using the equation (11) with the values of the Table III, (A) without ionic strength control, (B) $I = 2.0 \text{ M}$.

influence over the rate constant from approximately $[\text{HClO}_4] 1.0 \text{ M}$ was observed, and the trend of the rate constant to achieve a constant value, which would correspond to the rate-determining step, k_2 . This means that k_2 may be slightly greater than $3.00 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and is consistent with the proposed mechanism, because at higher concentrations of the acid, $K_1[\text{H}^+] \gg 1$, the rate becomes independent of $[\text{H}^+]$, as shown by the rate law (11). This phenomenon may be associated to the decrease in the activity of perchloric acid medium with the increase of nominal concentration, and therefore a change in the order of the reaction from first to zero order. Hence, the experimental value of the rate constant, k' , controlling or not the ionic strength, around $2.3 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, is expected.

It has been shown earlier that most reactions involving V(V) proceed via a free-radical mechanism, wherein V(V) undergoes an one-electron reduction.¹⁸ In the present investigation, the addition of acrylamide to the reaction mixture gave a polymeric product indicating that V(V) behaves as an one-equivalent oxidant, and that free radicals are formed in the rate determining step.

As the ionic strength was increased, there was a small effect in the oxidation rate (Table IV), however due to the value of the ionic charge product, *z₊z₋*,¹⁷ to be equal to 0.11, it was taken into account as practically constant within experimental errors. This suggests that during the oxidation, at least, one of the reagents involved in the rate-determining step, is a neutral species. The obtained results are accordant with the mechanism where a charged species of V(V), $\text{V}(\text{OH})_3^{2+}$, would react with a neutral HMal producing a charged complex, which would decompose to produce a free radical in the subsequent step.

The effect of solvent on the reaction rate was studied varying the binary mixtures of methanol-water in different composition (Table V). It was observed that the decrease on the solvent polarity favoured the reaction. This means that one of the reactive species is positively charged, and that the radius of the activated complex is greater than the sum of the radii of the reagents,²⁰ that is, the transition state is less polar than the reactants, and this is consistent with the postulation of $\text{V}(\text{OH})_3^{2+}$ as the reactive oxidizing species. When $\text{V}(\text{OH})_3^{2+}$ and malic acid react, the charge spreads over a wider area in the transition state and the charge density is reduced by low polarity of the solvent.

The kinetic parameters in Table VII show that the moderate ΔH^\ddagger and small negative ΔS^\ddagger values point towards a transition state that leads directly to the formation of a free radical and carbon dioxide. This process requires rupture of C-C bond and is similar to the mechanism of the pinacol oxidation by chromic acid suggested by Chang and Westheimer²¹. It was estimated that such a process requires an energy of activation of about 75 kJ/mol and a small entropy of activation. On the other hand, Bakore et al.⁹ related that the oxidations of lactic, mandelic, malic and glycolic acids by chromic acid involve C-H bond rupture, whose values are between -133 and -165 kJ/mol. Therefore, our observed values for energy and entropy of activation (Table VII) and experimental rate law suggest that the oxidation of the malic acid takes place through the C-C bond rupture in the rate determining step independently or not of the maintenance of the ionic strength of the solution.

ACKNOWLEDGEMENTS

This work was possible through the financial support from FINEP, CNPq, CONCITEC and CPG/UEL. The author thanks to Prof. Dr. Omar El Seoud and his group (IQ-USP) by the use of the laboratory, to Prof. Dr. Faruk Nome (UFSC) and Prof. Dr. Tiemi Matsuo (UEL) by the valuable suggestions and Prof. Maria Helena Pimenta Pinotti (UEL) by the English revision.

REFERENCES

1. Mathur, A.; Sharma, V.; Banerji, K. K.; *Indian J. Chem.*, (1988), **27A**, 123.
2. Bishnoi, M. L.; Negi, S. C.; Banerji, K. K.; *Indian J. Chem.*, (1986), **25A**, 660.
3. Chandraiah, V.; Murthy, C. P.; Kandlikar, S.; *Indian J. Chem.*, (1989), **28A**, 162.
4. Radhakrishnamurthi, P. S.; Rath, B. N.; Panda, R. K.; *Indian J. Chem.*, (1988), **27A**, 963.
5. Levesley, P.; Waters, W. A.; *J. Chem. Soc.*, (1955), 217.
6. Krishna, B.; Tewari, K. C.; *J. Chem. Soc.*, (1961), 3097.
7. Amjad, Z.; McAuley, A.; *J. Chem. Soc.*, (1974), 2521.
8. Bakore, G. V.; Narain, S.; *J. Chem. Soc.*, (1963), 3419.
9. Bakore, G. V.; Deshpande, A. A.; *Z. Phys. Chem.*, (1964), **227**, 14.
10. Jones, J. R.; Waters, W. A.; Littler, J. S.; *J. Chem. Soc.*, (1961), 630.
11. Bakore, G. V.; Shanker, R.; *Can. J. Chem.*, (1966), **44**, 1717.
12. Nazer, A. F. M.; Wells, C. F.; *J. Chem. Soc. Dalton Trans.*, (1980), 2143.
13. Virtanen, P. O. I.; Karppinen, S.; *Finn. Chem. Lett.*, (1984), 34.
14. Brewster, R. Q.; Vanderwerf, C. A.; McEwen, W. E.; *"Unitized Experiments in Organic Chemistry"*, 4th. ed., Van Nostrand, New York, 1977, p. 511.
15. Feigl, F.; *"Spot Tests in Organic Chemistry"*, Elsevier, London, 1956, p. 331, 342.
16. Manov, G. G.; Bates, R. G.; Hamer, W. J.; Acree, S. F.; *J. Amer. Chem. Soc.*, (1943), **65**, 1765.
17. Steinfeld, J. I.; Francisco, J. S.; Hase, W. H.; *"Chemical Kinetics and Dynamics"*, Prentice-Hall, Englewood Cliffs, 1989, p. 164-168.
18. Sen Gupta, K. K.; Dey, S.; Banerjee, A.; *J. Chem. Soc. Perkin Trans. II*, (1985), 1503.
19. Littler, J. S.; Mallet, A. I.; Waters, W. A.; *J. Chem. Soc.*, (1960), 2761.
20. Amis, E. S.; *"Solvent effects on reaction rates and mechanisms"* Academic Press, New York, 1966, p. 45.
21. Chang, Y. N.; Westheimer, F. G.; *J. Amer. Chem. Soc.*, (1960), **82**, 1401.