Asian Journal of Chemistry Vol. 22, No. 10 (2010), 7833-7840

Kinetics and Mechanism of Periodate Oxidation of N,N-Diethyl-*m*-toluidine in Acetone-Water Medium

R.D. Kaushik*, Manmeet Kaur, Jaspal Singh and Rajdeep Malik
Department of Chemistry, Gurukul Kangri University, Haridwar-249 404, India
E-mail: rduttkaushik@yahoo.co.in

Main reaction product of the periodate oxidation of N,N-diethyl-*m*-toluidine (DET) in acetone-water medium is methyl-1,4-benzoquinone. It was isolated and characterized. The kinetics of the reaction has been followed by monitoring the increase in the absorbance of reaction intermediate, C. The reaction followed second order behaviour, being first order in each reactant. Results under pseudo first order conditions, $[IO_4^-] >> [DET]$, are in agreement with the rate law: $d[C]/dt = kKKw [S] [IO_4^-]_0[H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\}$, where kK is the empirical composite rate constant, K_w is ionic product of water, K_2 is acid dissociation constant of $H_4IO_6^-$, K_b is base dissociation constant of DET and $[IO_4^-]_0$ represents the concentration of periodate that has been taken in excess. In agreement with the rate law the $1/k_2$ *versus* $[H^+]$ profile passes through the minimum. Increase in ionic strength increases the rate of reaction. Further, the rate of reaction increases with increase in dielectric constant of the medium. Free radical scavengers do not affect the reaction rate. Thermodynamic parameters evaluated are: $\Delta E = 23.2$ kJ mol^{-1}, A = 2208.6 dm^3 mol^{-1} s^{-1}; $\Delta S^{\#} = -190.0$ J mol^{-1} K^{-1}, $\Delta G^{\#} = 79.5$ kJ mol^{-1} and $\Delta H^{\#} = 20.92$ kJ mol^{-1}.

Key Words: Kinetics and mechanism, Periodate oxidation, N,N-Diethyl-*m*-toluidine, Methyl-1,4-benzoquinone.

INTRODUCTION

The kinetic studies reported for the non-Malapradian periodate oxidation of aromatic amines are rather few[1-5] and contradictory in regard to the ionic or free radical mechanism being followed. Recent reports include the periodate oxidation of 3,3',5',5'-tetramethyl benzidine[6] and oxidation of L-proline by *bis*(hydrogen periodato) argentate(III) complex anion[7]. In continuation to our earlier studies[8-16], the results of periodate oxidation of N,N-diethyl-*m*-toluidine (DET) in acetone-water medium are being presented and discussed in the present communication. These studies have been aimed to decide the mechanism of the reaction and rate law particularly for seeking an explanation for the unique rate-pH profile observed.

EXPERIMENTAL

Sodium meta-periodate (Loba Chemie), N,N-diethyl-*m*-toluidine (Sigma-Aldrich), acetone (E. Merck) and all other chemicals of analytical reagent/guaranteed reagent grade were used after redistillation/recrystallization. Triply distilled water was used for preparation of the solutions. Thiel, Schultz and Koch buffer[17], consisting of different volumes of 0.05 M oxalic acid, 0.02 M boric acid, 0.05 M succinic acid, 0.05 M sodium sulphate and 0.05 M borax, was used for maintaining the pH, measured on Systronics digital pH-meter-802. The reactions were studied in a spectrophotometric cell and initiated by adding temperature equilibrated $NaIO_4$ solution of known concentration to the reaction mixture containing the DET and buffer and maintained at the desired temperature (± 0.1 ºC).

Procedure for kinetic studies: The progress of the reaction was followed by recording the absorbance on Shimadzu double beam spectrophotometer (UV Pharmaspec-1700), at 535 nm, *i.e.*, the λ_{max} of the violet colour reaction mixture. λ_{max} was not found to change with change in pH. High precision thermostatically controlled water bath with an accuracy of ± 0.1 ºC was employed for maintaining the desired temperature.

Product analysis: Reaction mixture containing oxidant in excess was left overnight to ensure completion of the reaction. Initially the solution turned violet, thereafter yellow and finally the product was precipitated on standing. It was filtered and the filtrate was extracted with petroleum ether (40-60 ºC). The extract was evaporated at room temperature to get a yellow product which was found to be TLC single. It was recrystallized in ether and characterized as methyl-1,4-benzoquinone on the basis of positive test for quinone[18], m.p. 67 ºC (sublimes) (literature value 69 ºC[19]), UV spectrum (in ethanol absorption maxima at 247, 310, 430 and 440 nm (literature values 246, 312, 429 and 438 nm for methyl-1,4-benzoquinone[20]). The IR spectrum of compound (in KBr) showed the presence of bands at 2713 cm^{-1} (s) (due to isolated C-C stretching of CH_3), 1632 cm^{-1} (s) (indicating the presence of C=O on benzoquinone pattern with the possibility that the position of this band got lowered due to + I effect of methyl group[21]), 3255 cm^{-1} (s) (may be due to overtone of C=O stretch). Further, the bands at 1514 and 1469 cm^{-1}(s) may be due to C=C ring stretch. The bands at 1383-1352 cm^{-1} (m) may be due to the symmetrical bending vibrations of CH_3 group and at 768 cm^{-1} (s)(m) and 692 cm^{-1} (s) (due to out of plane C=C bending mode). The observed values are in good agreement with those reported/expected for methyl-1,4-benzoquinone.

Determination of stoichiometry of the reaction: Stoichiometry of the reaction was determined by allowing a known excess of $NaIO_4$ to react with substrate. After completion of the reaction, the precipitated product was filtered out and in the filtrate unconsumed $NaIO_4$ was determined iodimetrically. The results indicate the stoichiometry to be 1 mol DET: 2 mol periodate as in eqn. 1.

$$CH_3C_6H_4N(C_2H_5)_2 + 2IO_4^- + 2H^+ + 2H_2O \rightarrow CH_3C_6H_3O_2 + 2HIO_3 + 2C_2H_5OH + NH_3 \qquad (1)$$

RESULTS AND DISCUSSION

On mixing the reactants, the solution becomes violet which later changes in to yellow. On keeping for long time it finally gives the product. These observations indicate the formation of more than one intermediate prior to the formation of final reaction product. The rapid scan of the violet solution showed the λ_{max} of the intermediate C to be 535 nm. The UV-visible spectra of IO_4^- and DET indicated these to show no absorption in visible region. Hence for following the kinetics the absorbance changes were recorded at 535 nm at which only the intermediate C absorbs. Plane mirror and Guggenheim's methods, respectively were used for evaluation of initial rates in terms of change in absorbance with time, (dA/dt) and pseudo first order rate constants, k_{obs}.

The kinetics was studied under pseudo order conditions, *viz.*, $[IO_4^-]_0 >> [S]$ and $[S]_0 >> [IO_4^-]$. Under both these conditions the reaction displayed first order. Under the condition, $[S]_0 >> [IO_4^-]$, the results (Table-1) were defined by the eqn. 2 and pseudo first order rate constant, k_{obs}, was equal to $k_2[S]_0$.

$$d[C]/dt = k_2[IO_4^-][S]_0 \qquad (2)$$

where k_2 is a pH-dependent second order rate constant.

TABLE-1
EFFECT OF VARIATION OF CONCENTRATION OF REACTANTS, IONIC STRENGTH AND DIELECTRIC CONSTANT ON THE REACTION RATE
Temperature = 30 ± 0.1 °C, pH = 7

$[NaIO_4]$ [mol dm^{-3}]	[DET] [mol dm^{-3}]	Acetone [% (v/v)]	[NaCl] [mol dm^{-3}]	$k_{obs} \times 10^3$ [s^{-1}]	k_2 [dm^3 mol^{-1} s^{-1}]
0.0002	0.002	5.0	–	0.30	0.15
0.0002	0.003	5.0	–	0.45	0.15
0.0002	0.004	5.0	–	0.60	0.15
0.0002	0.005	5.0	–	0.70	0.14
0.0002	0.006	5.0	–	0.84	0.14
0.0100	0.001	5.0	–	2.11	0.21
0.0120	0.001	5.0	–	2.40	0.20
0.0140	0.001	5.0	–	2.70	0.19
0.0160	0.001	5.0	–	3.00	0.19
0.0180	0.001	5.0	–	3.30	0.18
0.0200	0.001	5.0	–	3.50	0.17
0.0100	0.001	5.0	0.005	2.40	0.24
0.0100	0.001	5.0	0.006	2.70	0.27
0.0100	0.001	5.0	0.007	3.10	0.31
0.0100	0.001	5.0	0.008	3.60	0.36
0.0100	0.001	5.0	–	2.11	0.21
0.0100	0.001	7.5	–	1.73	0.17
0.0100	0.001	10.0	–	1.44	0.14
0.0100	0.001	12.5	–	1.10	0.11

On the other hand under the condition $[IO_4^-]_0 >> [S]$, the rate was defined by eqn. 3 and k_{obs} was equal to $k_2[IO_4^-]_0$.

$$d[C]/dt = k_2[IO_4^-]^0[S] \qquad (3)$$

In eqns. 2 and 3 $[IO_4^-]_0$ and $[S]_0$ represent the initial concentrations of reactants in excess. The values of k_2 determined from k_{obs} values clearly indicate a clear cut first order in each of periodate and DET.

The effect of pH was examined in the range 5-9. Rate-pH profile indicates a maximum at pH = 8 (Table-2), which could be due to change in nature of species and their relative reactivity when the pH is changed.

TABLE-2
EFFECT OF VARIATION IN pH ON THE REACTION RATE
Temperature = 30 ± 0.1 °C

$[NaIO_4]$ [mol dm^{-3}]	[DET] [mol dm^{-3}]	Acetone [% (v/v)]	[NaCl] [mol dm^{-3}]	pH	$k_{obs} \times 10^3$ [s^{-1}]	k_2 [dm^3 mol^{-1} s^{-1}]
0.01	0.001	5	–	5.0	0.40	0.04
0.01	0.001	5	–	5.5	0.50	0.05
0.01	0.001	5	–	6.0	0.90	0.09
0.01	0.001	5	–	6.5	1.70	0.17
0.01	0.001	5	–	7.0	2.11	0.21
0.01	0.001	5	–	7.5	2.50	0.25
0.01	0.001	5	–	8.0	2.70	0.27
0.01	0.001	5	–	8.5	1.80	0.18
0.01	0.001	5	–	9.0	1.20	0.12

An increase in ionic strength, μ, led to an increase in the rate and the plot of log k_2 *versus* μ was almost linear. An increase in dielectric constant increased the rate of reaction as indicated by a linear plot between log k_2 *versus* 1/D, where D is the dielectric constant of the medium. Both these effects (Table-1) indicate an ion-dipole type interaction in the rate-determining step and that the reacting ion is possibly an anion. Free radical scavengers acrylamide and allyl alcohol had no effect on the reaction rate.

By determining the rate constants at four different temperatures (30-45 ºC), the values of different thermodynamic parameters were found to be: $\Delta E = 23.2$ kJ mol^{-1}, A = 2208.6 dm^3 mol^{-1} s^{-1}; $\Delta S^\# = -190.0$ J mol^{-1} K^{-1}, $\Delta G^\# = 79.5$ kJ mol^{-1} and $\Delta H^\# = 20.92$ kJ mol^{-1} at [DET] = 0.001 mol dm^{-3}, $[NaIO_4] = 0.01$ mol dm^{-3}, pH = 7 and acetone = 5 % (v/v).

Some important features of this reaction, which provide clue to the possible mechanism, are as follows: firstly, there is appearance of violet colour which continues to darken with increase in the concentration of the intermediate, C and finally the product settles on standing for long time. Obviously, the coloured intermediate is formed on a time scale of minutes and the final product on a time scale of hours. In real sense the overall reaction involves several steps and possibly several transient intermediates, in addition to comparatively stable one C, are formed during the oxidation of DET into benzoquinone. Secondly, the kinetic order of one in periodate but requirement of the two periodate molecules for each DET molecule as per stoichiometry indicates the involvement of only one periodate in the rate determining step and second IO_4^- ion is consumed in a fast reaction in the formation of the intermediate, C. It also indicates the violet coloured intermediate is quite stable and its concentration is not in steady state. In such ase, there should be no change in its concentration with time. On the contrary, concentration of C increases continuously with time and reaches a limiting value. This has been used in following the kinetics of this reaction. Thirdly k_2-pH profile indicates the presence of at least three differently reactive reactant species in the pH region chosen for study.

Before presenting a mechanism, it is necessary to discuss the speciation of DET and periodate species in aqueous solutions. In aqueous solutions, periodate exists in three forms governed by the equilibria:

$$H_5IO_6 \rightleftharpoons H_4IO_6^- + H^+, \qquad K_1 = 2.3 \times 10^{-2} \qquad (4)$$

$$H_4IO_6^- \rightleftharpoons H_3IO_6^{2-} + H^+, \qquad K_2 = 4.35 \times 10^{-9} \qquad (5)$$

The value of K_1 indicates that in the pH range 5-9 species H_5IO_6 shall be practically non-existent and hence only species $H_4IO_6^-$ and $H_3IO_6^{2-}$ need be considered for explaining observed pH-dependence. In case of DET[22], in aqueous solution the following acid-base equilibrium with $K_b = 1.32 \times 10^{-7}$ operates.

$$CH_3C_6H_4N(C_2H_5)_2 + H_2O \rightleftharpoons CH_3C_6H_4N^+H(C_2H_5)_2 + OH^- \qquad (6)$$

In the studied pH-range, both $CH_3C_6H_4N(C_2H_5)_2$ and $CH_3C_6H_4N^+H(C_2H_5)_2$ shall exist and both of these have been considered. Based on the observed kinetic rate laws (2-3) and pH-dependence, the following mechanism, which assumes, $CH_3C_6H_4N(C_2H_5)_2$ and $H_4IO_6^-$ to be the reactive species, is proposed.

$$CH_3C_6H_4N(C_2H_5)_2 + [IO_4^-] \overset{K}{\rightleftharpoons} [A] \qquad (7)$$

$$[A] \xrightarrow{k} \text{Intermediate [B] (slow)} \qquad (8)$$

$$[B] + IO_4^- \rightarrow \text{Intermediate [C] (fast)} \qquad (9)$$

The intermediate, C, appears to undergo very slow reorganization/hydrolysis to yield the reaction product.

$$\text{Intermediate [C]} \rightarrow \text{Product [D]} \qquad (10)$$

In the mechanism for simplicity, $H_4IO_6^-$ has been written as IO_4^-. Since the elementary reactions in liquid phase are a rarity, the formation of a transient intermediate [C], which could be a collisional complex/reactant pair in a rapid step having a low value of equilibrium constant, K, is assumed in the proposed gross mechanism.

The mechanistic steps (8-9) lead to the rate law:

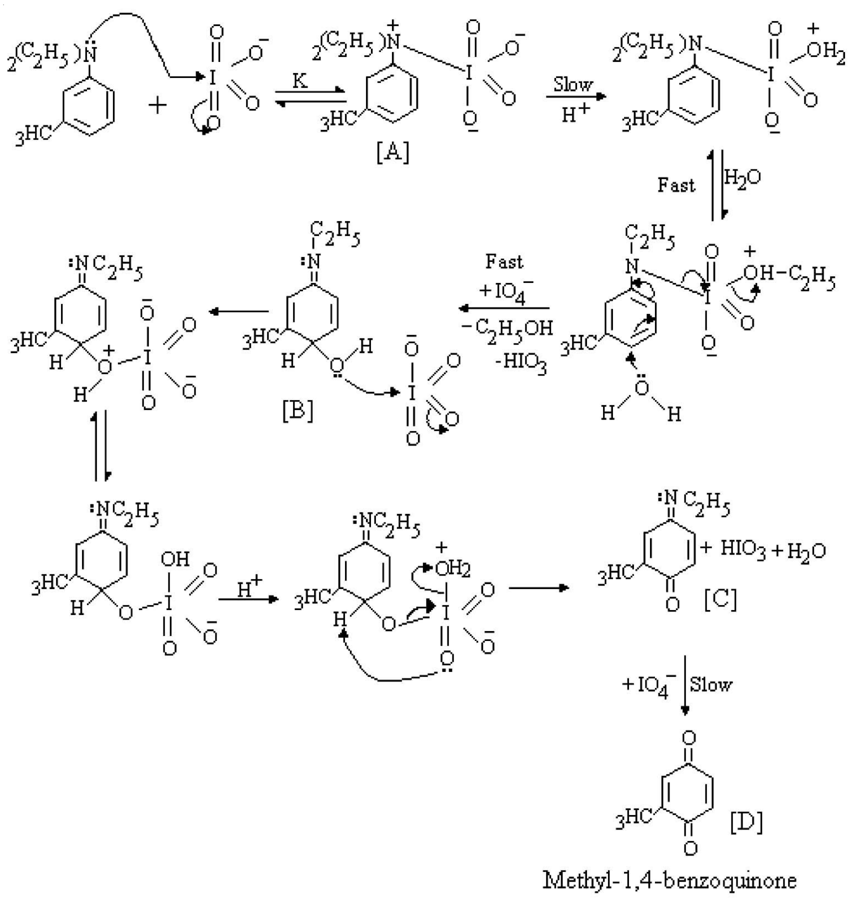
$$d[C]/dt = k[A] \qquad (11)$$

$$= kK[CH_3C_6H_4N(C_2H_5)_2][IO_4^-] \qquad (12)$$

Since the observed kinetics shows first order in each of $[CH_3C_6H_4N(C_2H_5)_2]$ and $[IO_4^-]$, the value of K must be low.

At a fixed pH, under the condition $[S]_0 >> [IO_4^-]$, the rate of formation of intermediate, C, is given by eqn. 13.

$$d[C]/dt = kK[IO_4^-][S]_0/(1 + K[S]_0) \qquad (13)$$



Scheme-I

Likewise, under the condition $[IO_4^-]_0 >> [S]$

$$d[C]/dt = kK[IO_4^-]_0[S]/(1 + K[IO_4^-]_0) \qquad (14)$$

Since the reaction shows a clean-cut first order in each of [S] and $[IO_4^-]$, the inequalities $K[S]_0 << 1$ and $K[IO_4^-]_0 << 1$ should operate in eqns. 13 and 14, respectively leading to the rate laws in eqns. 2 and 3.

On substituting the values of concentrations of the reactive species $[CH_3C_6H_4N(C_2H_5)_2]$ and $[IO_4^-]$ in terms of equilibria (4-5) and (6), respectively, in eqn. (12), the complete rate law including $[H^+]$-dependence becomes:

$$d[C]/dt = kK\{([S][OH^-]/([OH^-] + K_b)\}\{([IO_4^-]^0[H^+]/(K_2 + [H^+])\} \qquad (15)$$

On replacing $[OH^-][H^+]$ by K_w and $[OH^-]$ by $K_w/[H^+]$ in denominator and on rearranging,

$$d[C]/dt = kKK_w[S][IO_4^-]_0\,[H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\} \qquad (16)$$

On comparing eqns. 3 and 16, we get

$$k_2 = kKK_w[H^+]/\{K_2K_w + (K_w + K_bK_2)[H^+] + K_b[H^+]^2\} \qquad (17)$$

Eqn. 17 on rearranging becomes eqn. 18.

$$1/k_2 = (K_2/kK[H^+]) + \{(K_w + K_bK_2)/kKK_w\} + K_b[H^+]/kKK_w \qquad (18)$$

The nature of the rate law shows that a plot of $1/k_2$ *versus* $[H^+]$ shall pass through a minimum as clear from the already available literature[23]. On differentiating $1/k_2$ with respect to $[H^+]$ in eqn. 18, we get the values of $d^2[1/k_2]/d[H^+]^2$. The value of second derivative is found to be positive showing the plot of $1/k_2$ *versus* $[H^+]$ to pass through a minimum. Thus, on setting $d[1/k_2]/d[H^+]$ equal to zero for obtaining hydrogen ion concentration at which the $1/k_2$ *versus* $[H^+]$ profile will pass through minimum, we obtained:

$$[H^+]_{min.} = (K_2K_w/K_b)^{1/2}$$

On substituting the values of K_2, K_w and K_b, we found:

$$[H^+]_{min.} = 1.82 \times 10^{-8} \text{ mol dm}^{-3}$$

It is gratifying to note that the calculated value of $[H^+]_{min}$ is in excellent agreement with the experimental value of $[H^+]_{min}$ of 1×10^{-8} mol dm^{-3} obtained from $1/k_2$ *versus* $[H^+]$ plot (Fig. 1).

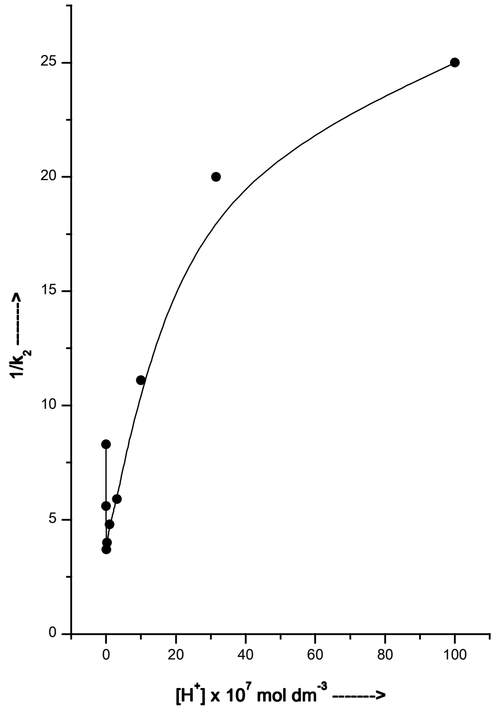


Fig. 1. $[H^+]$ profile at [DET] = 0.001 mol dm^{-3}, $[NaIO_4]$ = 0.01 mol dm^{-3}, acetone = 5 % (v/v), temperature = 30 ± 0.1 °C

It is necessary and interesting to discuss the possible molecular mechanism of the reaction. Mechanism proposed in **Scheme-I** shows the first step as a reversible bimolecular reaction between DET and $[IO_4^-]$. The formation of a charged intermediate complex [A] taking place by the attack of [IO_4^-] on the nitrogen of anilino group and stabilization of positive charge on this nitrogen are well supported by our earlier LFER studies on this type of reaction series[24]. The high negative value of entropy of activation supports the involvement of solvation effects in this reaction. The formation of another intermediate [B] followed by its reaction with another IO_4^- to form quinoneimine [C] in a fast step are the expected steps of the mechanism involved. The last step (10) seems to be the slow hydrolysis and rearrangement of (C) to give methyl-1,4 -benzoquinone (D), *i.e.*, the main product of the reaction that has been isolated, separated and characterized.

REFERENCES

1. G. Dryhurst, Periodate Oxidation of Diols and Other Functional Groups, Analytical and Structural Applications, Pergamon Press (1970).
2. V.K. Kalinina, *Kinet. Katal.*, **12**, 100 (1971).
3. V.K. Pavolva, Ya. S. Sevchenko and K.B.Yatsmiriskii, *Zh. Fiz. Khim.*, **44**, 658 (1970).
4. M.P. Rao, B. Sethuram and T.N. Rao, *Indian J. Chem.*, **17(A)**, 52 (1979).
5. S.P. Srivastava, G. Bhattacharjee, V.K. Gupta and Satya Pal, *React. Kinet. Catal. Lett.*, **13**, 231 (1980).
6. M.K. Beklemishev, E.N. Kiryushchenkov, E.K. Skosyrskaya and A.M. Petrenko, *J. Anal. Chem.*, **61**, 1067 (2006).
7. H.W. Sun, H.M. Shi, S.G. Shen and Z.F. Guo, *Chin. J. Chem.*, **26**, 615 (2008).
8. S.P. Srivastava, M.C. Jain and R.D. Kaushik, *Nat. Acad. Sci. Lett.*, **2**, 63 (1979).
9. V.K. Gupta, R. Bhushan, R.D. Kaushik, M.C. Jain and S.P. Srivastava, *Oxid. Commun.*, **7**, 409 (1984).
10. R.D. Kaushik, R.P. Singh and Shashi, *Asian J. Chem.*, **15**, 1655 (2003).
11. R.D. Kaushik, Amrita, M. Dubey and R.P. Singh, *Asian J. Chem.*, **16**, 831 (2004).
12. R.D. Kaushik, Amrita, R. Malik, Manila and A. Kumar, *Asian J. Chem.*, **22**, 2090 (2010)
13. R.D. Kaushik, P. Sundriyal, T. Kumar and P. Singh, *Asian J. Chem.*, **22**, 2136 (2010).
14. R.D. Kaushik, D. Kumar, A. Kumar and R. Malik, *Asian J. Chem.*, **22**, 2155 (2010).
15. R.D. Kaushik, A. Kumar, M. Kaur and P. Singh, *J. Indian Coun. Chem.*, **26**, 175 (2009).
16. R.D. Kaushik, R. Malik and A. Kumar, *J. Indian Chem. Soc.*, **87**, 317 (2010).
17. H.T.S. Britton, Hydrogen Ions, D. Von Nostrand Co., p. 354 (1956).
18. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A.R. Tatchell, Vogel's Text Book of Practical Organic Chemistry, Addison-Wesley Longman LTD., edn. 5, p. 1221 (1998).
19. J. Buckingham, Eds.: Dictionary of Organic Compounds, Chapman and Hall, N. York, edn. 5, 4, p. 2137 (1982).
20. J.P. Phillips and F.C. Nachod (eds.), Organic Electronic Spectral Data, Interscience Publishers, N. York, 2, p. 108 (1958-1959).
21. P.S. Kalsi, Spectroscopy of Organic Compounds, New Age International Ltd., N. Delhi, edn. 2 (1996).
22. N. Inoue and Y. Matsunaga, *Bull. Chem. Soc. (Japan)*, **46**, 3345 (1973).
23. K.S. Gupta and Y.K. Gupta, *J. Chem. Educ.*, **61**, 972 (1984).
24. S.P. Srivastava, V.K. Gupta, M.C. Jain, M.N. Ansari and R.D. Kaushik, *Thermochim. Acta*, **68**, 27 (1983).

(*Received*: 24 February 2010; *Accepted*: 27 July 2010) AJC-8908