Bull. Chem. Soc. Jpn., *76*, 2335–2339 (2003)

Kinetics and Mechanism of the Oxidation of Some α-Hydroxy Acids by Benzyltrimethylammonium Dichloroiodate

Archana Goyal and Seema Kothari*

Department of Chemistry, J N V University, Jodhpur 342005, India

Received January 14, 2003; E-mail: seema@goraexports.com

The oxidation of lactic acid, mandelic acid, and ten monosubstituted mandelic acids by benzyltrimethylammonium dichloroiodate (BTMACI) in glacial acetic acid leads to the formation of the corresponding oxo acid. The reaction is first order with respect to hydroxy acid, BTMACI, and zinc chloride. An addition of benzyltrimethylammonium chloride enhances the rate slightly. $[PhCH_2Me_3N]^+[IZn_2Cl_6]^-$ is postulated to be the reactive oxidizing species. The oxidation of α-deuteriomandelic acid exhibited the presence of a substantial kinetic isotope effect ($k_H/k_D = 5.97$ at 298 K). The rate of oxidation of the substituted mandelic acids showed an excellent correlation with Brown's σ^+ values. The reaction constants are negative. A mechanism involving the transfer of hydride ion to the oxidant is postulated.

Benzyltrimethylammonium polyhalides are widely used as halogenating agents in synthetic organic chemistry.[1–3] These compounds are more suitable than molecular halogens because of their solid nature, ease of handling, stability, selectivity, and excellent product yields. However, not many reports are available on their use as oxidizing agents in synthetic organic chemistry.[4–6] We are interested in the kinetic and mechanistic studies of the newer oxidizing agents and have reported, perhaps for the first time, the use of benzyltrimethylammonium dichloroiodate (BTMACI) in the oxidation of organic compounds.[7,8] A perusal of the literature showed that the kinetics and mechanism of the oxidation of hydroxy acids by BTMACI has not been investigated so far. Hydroxy acids may be oxidized either as alcohols yielding corresponding oxo acids,[9] or may undergo decarboxylation to yield an aldehyde.[10] In the present article the kinetics of oxidation of lactic acid (LA), mandelic acid (MA), and ten substituted mandelic acids by BTMACI in glacial acetic acid in the presence of zinc chloride have been described. Attempts have been made to correlate the rate and structure in this reaction. Mechanistic aspects are discussed.

Experimental

Materials. BTMACI was prepared by the reported method,[1] and its purity was checked iodometrically. LA, MA, and nitromandelic acids were commercial products of the highest purity available and were used as such. Halogeno-, alkyl-, and *p*-methoxymandelic acids were prepared from the corresponding benzaldehydes by cyanohydrine formation followed by acid hydrolysis.[11] Solutions were standardized by alkalimetry. α-Deuteriomandelic acid (DMA) was prepared by the method of Kemp and Waters.[12] The isotopic purity, as ascertained by its NMR spectrum, was 94 ± 5%. Glacial acetic acid was purified by refluxing it with CrO_3 and acetic anhydride for 6 h followed by distillation.[13]

BTMACI is only slightly soluble in acetic acid at room temperature. However, the addition of zinc chloride renders it readily soluble in acetic acid. We found that in the absence of zinc chloride, the strength of a saturated solution of BTMACI in acetic acid is 0.0005 mol dm^{-3}. The addition of zinc chloride (0.002 mol dm^{-3}) increased the solubility of BTMACI and a saturated solution of BTMACI, under these conditions, has strength of 0.0016 mol dm^{-3}.

Product Analysis. The formation of oxo acids as the product of the oxidation was confirmed by their characteristic positive spot test, given by a completely reduced reaction mixture.[14] The quantitative estimation of the oxo acids was carried out under kinetic conditions. In a typical experiment, mandelic acid (0.1 mol) and BTMACI (0.01 mol) were dissolved in 100 mL of glacial acetic acid in the presence of 0.03 moles of zinc chloride. The reaction mixture was allowed to stand in the dark for ca. 6 h to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The solution was then treated with an excess (250 mL) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 2.20 g (90%) and 1.98 g (81%) respectively. The identity of the product was established by comparing the mp of the DNP derivative with the literature value.[15] The DNP was found to be identical (mp = 190 °C and mixed mp = 193 °C) with the DNP of phenylglyoxylic acid (mp = 196–7 °C).[15] In similar experiments with other hydroxy acids, the yield of the corresponding oxo acids was in the range of 77–87% after recrystallization.

Stoichiometry. To determine the stoichiometry, BTMACI (0.05 mol) and MA (0.01 mol) were mixed with 100 mL of glacial acetic acid in the presence zinc chloride (0.15 mol). The reaction was allowed to stand for ca. 10 h to ensure the completion of the reaction. The residual BTMACI was determined spectrophotometrically at 364 nm. Several determinations, with different concentrations of MA, showed that the stoichiometry is 1:1.

Spectral Studies. UV–vis spectra of 0.0005 mol dm^{-3} of BTMACI alone and in the presence of 0.002, 0.003 and 0.006 mol dm^{-3} of $ZnCl_2$ were obtained using an HP-diode array spectrophotometer (Model 8452A), at 298 ± 3 K. The solvent and blank were glacial acetic acid. The scanning speed was 600 nm s^{-1}.

Published on the web December 15, 2003; DOI 10.1246/bcsj.76.2335

Kinetic Measurements. The reactions were studied under pseudo-first-order conditions by keeping an excess (×20 or greater) of the hydroxy acid over BTMACI. The solvent was glacial acetic acid. The reactions were carried out at constant temperature (±0.1 K) in the presence of zinc chloride (0.003 mol dm^{-3} unless stated otherwise) and were followed by monitoring the decrease in [BTMACI] spectrophotometrically at 364 nm for up to 80% of the reaction. Beer's law is valid for BTMACI within the concentration range used in our experiments. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.9990$) of log[BTMACI] against time. Duplicate kinetic runs showed that the rates were reproducible to within ±4%. The third order rate constant, k_3, was calculated by the following relation: $k_3 = k_{\mathrm{obs}}/$[hydroxy acid] [ZnCl$_2$].

Results

The rate and other experimental data were obtained for all the hydroxy acids. Since the results are similar, only representative data are reported here.

The oxidation of the hydroxy acids by BTMACI results in the formation of the corresponding oxo acids. Analyses of products and stoichiometric determinations indicate the following overall reaction.

$$\begin{aligned}&\mathrm{RCH(OH)COOH} + [\mathrm{PhCH_2Me_3N}]\mathrm{ICl_2}\\&\quad\rightarrow \mathrm{RCOCOOH} + \mathrm{PhCH_2Me_3NCl} + \mathrm{HCl} + \mathrm{HI}\end{aligned} \tag{1}$$

Rate Laws. The reactions are first order with respect to BTMACI, as evidenced by a linear plot of log[BTMACI] vs time (Fig. 1). The pseudo-first-order rate constants do not depend on the initial concentration of BTMACI (Table 1). This further confirms the first-order dependence of rate on the oxidant concentration. The reaction rate increases linearly with an increase in the concentration of the hydroxy acid (Table 1). A plot of log k_{obs} vs log[hydroxy acid] is linear ($r^2 > 0.9990$) with a slope $= 0.99 \pm 0.01$, indicating that the order with respect to the hydroxy acid is also one (Fig. 2).

Induced Polymerization of Acrylonitrile. The oxidation of hydroxy acids, under a nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate (Table 1).

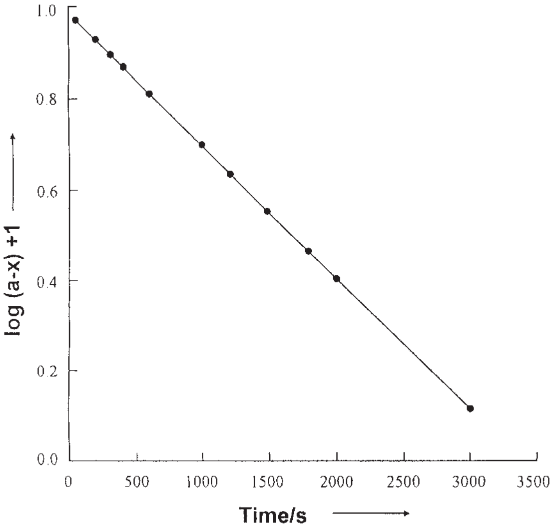


Fig. 1. Oxidation of mandelic acid (3.0 mol dm^{-3}) by BTMACI (0.001 mol dm^{-3}) at 318 K.

Table 1. Rate Constants for the Oxidation of Mandelic Acid by BTMACI at 318 K

[MA] /mol dm^{-3}	10^3 [BTMACI] /mol dm^{-3}	10^4 k_{obs} /s^{-1}
0.2	1.0	0.45
0.4	1.0	0.93
0.6	1.0	1.30
1.0	1.0	2.25
2.0	1.0	4.61
3.0	1.0	6.69
2.0	0.2	4.68
2.0	0.4	4.55
2.0	0.6	4.60
2.0	0.8	4.71
2.0	1.0	4.64[a)]
2.0	1.0	4.57[b)]

a) and b) contained 0.002 and 0.005 mol dm^{-3} acrylonitrile respectively.

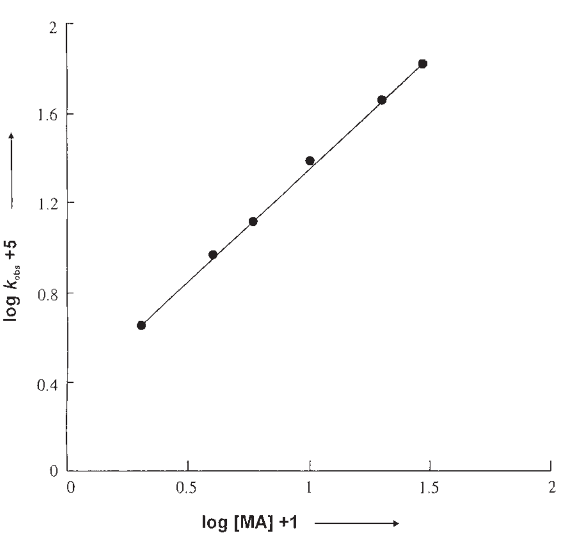


Fig. 2. A log–log plot for the oxidation of mandelic acid (0.2–3.0 mol dm^{-3}) by BTMACI (0.001 mol dm^{-3}) at 318 K.

Effect of Temperature. The rates of oxidation of hydroxy acids were determined at different temperatures between 298 K and 328 K and the activation parameters were calculated (Table 2).

Kinetic Isotope Effect. To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, the oxidation of DMA was studied. The results showed (Table 2) that the reaction exhibited a substantial kinetic isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}} = 5.97$ at 298 K). The rates for the deuteriated mandelic acid were corrected for the amount of the protio mandelic acid present.

Effect of Zinc Chloride. With an increase in the concentration of zinc chloride, the reaction rate increases linearly (Table 3). A plot of k_{obs} versus [ZnCl$_2$] is linear ($r^2 = 0.9990$) and passes through the origin.

Effect of Benzyltrimethylammonium Chloride. An addition of benzyltrimethylammonium chloride (BTMAC) enhances the reaction rate slightly (Table 4).

Table 2. Rate Constants and Activation Parameters of the Oxidation of Substituted Mandelic Acids by BTMACI[a)]

Subst.	$10^4\ k_3/\mathrm{dm^6\,mol^{-2}\,s^{-1}}$				ΔH^*	ΔS^*	ΔG^*
	298 K	308 K	318 K	328 K	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{J\,mol^{-1}\,K^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
H	185	379	750	160	55.6 ± 1.1	-92 ± 4	83.0 ± 0.9
p-F	277	531	1080	2280	54.5 ± 1.6	-93 ± 5	82.0 ± 1.2
p-Cl	101	221	438	979	58.4 ± 1.3	-88 ± 4	84.5 ± 1.0
p-Br	82.0	187	381	851	60.3 ± 1.0	-83 ± 3	84.9 ± 0.8
p-Me	995	1700	3070	6190	46.7 ± 2.1	-108 ± 7	78.9 ± 1.6
p-Pr^i	839	1520	2770	5670	48.8 ± 1.8	-103 ± 6	79.3 ± 1.4
p-OMe	13000	17000	27100	49000	33.4 ± 3.3	-132 ± 9	72.6 ± 2.6
m-Cl	21.2	54.6	120	278	66.6 ± 0.8	-73 ± 2	88.3 ± 0.6
m-NO_2	4.80	12.2	31.7	83.5	74.8 ± 1.3	-58 ± 4	92.0 ± 1.1
p-NO_2	2.52	8.50	19.5	52.0	78.1 ± 2.2	-52 ± 7	93.4 ± 1.7
m-Br	20.5	52.7	116	271	67.4 ± 0.9	-71 ± 3	88.4 ± 0.7
LA	57.8	120	253	492	55.7 ± 0.4	-101 ± 1	85.8 ± 0.3
DMA	31.0	65.0	131	286	57.3 ± 1.2	-102 ± 4	87.4 ± 0.9
k_H/k_D	5.97	5.83	5.73	5.59			

a) [Oxidant] = 0.001 mol dm^{-3}; [hydroxy acid] = 1.0 or 5.0 mol dm^{-3} depending on the reactivity of the hydroxy acid.

Table 3. Effect of Zinc Chloride on the Rate of Oxidation of Mandelic Acid by BTMACI

$10^3\ [\mathrm{ZnCl_2}]/\mathrm{mol\,dm^{-3}}$	3.0	4.0	6.0	8.0	10.0	15.0	20.0
$10^4\ k_{obs}/\mathrm{mol\,dm^{-3}}$	2.25	3.10	4.61	6.35	7.65	11.6	16.0

[MA] = 1.0 mol dm^{-3}; [BTMACI] = 0.001 mol dm^{-3}; Temperature = 318 K.

Table 4. Effect of Benzyltrimethylammonium Chloride on the Rate of Oxidation of Mandelic Acid by BTMACI

$10^3\ [\mathrm{BTMAC}]/\mathrm{mol\,dm^{-3}}$	0.0	0.4	0.6	1.0	2.0	3.0	4.0
$10^4\ k_{obs}/\mathrm{mol\,dm^{-3}}$	2.25	2.68	2.90	3.25	3.50	3.85	4.66

[MA] = 1.0 mol dm^{-3}; [BTMACI] = 0.001 mol dm^{-3}; Temperature = 318 K.

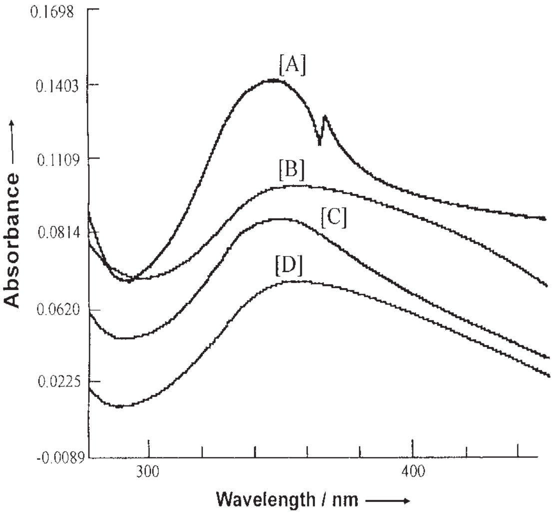


Fig. 3. UV–vis spectra of [A] 0.0005 mol dm^{-3} BTMACI, [B] 0.0005 mol dm^{-3} BTMACI + 0.002 mol dm^{-3} $ZnCl_2$, [C] 0.0005 mol dm^{-3} BTMACI + 0.003 mol dm^{-3} $ZnCl_2$, [D] 0.0005 mol dm^{-3} BTMACI + 0.006 mol dm^{-3} $ZnCl_2$. Solvent: Glacial acetic acid; Temperature: 298 ± 3 K.

Spectral Studies. A comparison of the UV–vis spectra (Fig. 3) of BTMACI alone and in the presence of different concentrations of $ZnCl_2$ showed that the nature of the spectra is not much different in the presence or absence of zinc chloride. However, there is an initial sharp decrease in the absorbance followed by a regular but gradual decrease in the absorbance of BTMACI on further addition of $ZnCl_2$. This clearly shows that a strong complex [A] is formed initially which undergoes further complexation to give complex [B] whose concentration increases with an increase in the concentration of $ZnCl_2$.

Discussion

From our data on the solubility of BTMACI[7] in the absence and presence of $ZnCl_2$, the value of the equilibrium constant, K_1, comes to be ca. 2400 mol^{-1} dm^3. This indicates that even at the lowest concentration of $ZnCl_2$ used, almost whole of BTMACI will be in the form of complex [A] (Eq. 2). The linear increase in the rate with an increase in the concentration of $ZnCl_2$ points to a further complexation to give complex [B] (Eq. 3). The role of $ZnCl_2$ is to co-ordinate with ICl_2^-. Interhalogen compounds are known to form complexes with Lewis acids like zinc chloride.[16]

$$[\mathrm{PhCH_2Me_3N}]^+\ \mathrm{ICl_2}^- + \mathrm{ZnCl_2} \overset{K_1}{\rightleftharpoons} \underset{[\mathrm{A}]}{[\mathrm{PhCH_2Me_3N}]^+\ [\mathrm{IZnCl_4}]^-} \tag{2}$$

$$[\mathrm{A}] + \mathrm{ZnCl_2} \overset{K_2}{\rightleftharpoons} \underset{[\mathrm{B}]}{[\mathrm{PhCH_2Me_3N}]^+\ [\mathrm{IZn_2Cl_6}]^-} \tag{3}$$

In the complexes [A] and [B], the formal oxidation state of iodine is +1. Despite the lack of evidence for the existence of discrete I^+ ions, its stable complexes with donors have been known for a long time.[16,17] The formation of positive iodine species in the sulfuric acid medium has been reported recently.[18] Acetic acid is a relatively poor ionizing solvent, and the formation of ion-pairs in it is a distinct possibility. Therefore, it is probable that complexes [A] and [B] exist as ion-pairs in the solvent.

The observed dependence on the concentration of zinc chloride indicates that the equilibrium between [A] and [B] is rapid, that the equilibrium constant, K_2, is small that the reaction is not complete even at high concentrations of $ZnCl_2$, and that only complex [B] is reactive. The small rate-enhancing effect of BTMAC suggests that iodine monochloride (Eq. 4) is not involved in the oxidation process.

$$[PhCH_2Me_3N]^+ \ ICl_2^- \overset{K_3}{\rightleftharpoons} [PhCH_2Me_3N]^+ \ Cl^- + ICl \tag{4}$$

Therefore, [B] is the only reactive oxidizing species in the oxidation of hydroxy acids. The formation of the complex is also supported by spectral studies. The existence of the anion $[Zn_2Cl_6]^{2-}$ in tertahydrofuran has been confirmed by X-ray crystallography.[19] Various metallic salts of $[Zn_2Cl_6]^{2-}$ are known.[20]

The linear correlation between $\log k_3$ of twelve hydroxy acids at 298 K and 328 K ($r^2 = 0.9998$; slope $= 0.805 \pm 0.003$) shows that an isokinetic relationship exists in the oxidation of hydroxy acids by BTMACI.[21] The value of the isokinetic temperature is 562 ± 7 K. An isokinetic relationship is a necessary condition for the validity of linear free energy relationships. It also implies that all the hydroxy acids with this correlation are oxidized by a similar mechanism.[21]

Correlation Analysis of Reactivity. The rate constants of the oxidation of MA and ten monosubstituted mandelic acids were correlated in terms of the Hammett equation,[22] but they failed to yield a significant correlation with Hammett's σ values, Eq. 5. The main deviating points correspond to para-substituents capable of electron-donation by resonance viz. methoxy, methyl, isopropyl, fluoro, etc. Their rates are higher than those required by their Hammett's σ values.

$$\log k_3 = -3.03 \pm 0.26\sigma - 1.36, \tag{5}$$

$$r^2 = 0.9372;\ \text{sd} = 0.29;\ n = 11;\ \psi = 0.26;$$
$$\text{Temperature} = 298\ \text{K}.$$

Here, n is the number of data points.

The rate constants were, therefore, correlated in terms of Brown's σ^+ values (Eq. 6).[23] An excellent correlation (Fig. 4) with large reaction constants was obtained (Table 5).

$$\log k_3 = \rho^+\sigma^+ + \log k_0. \tag{6}$$

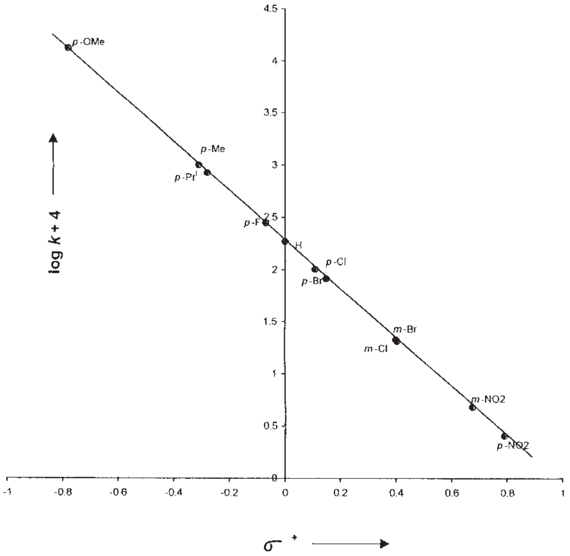


Fig. 4. Brown plot at 298 K.

Here, k_0 is rate constant for MA.

Mechanism. A hydrogen abstraction mechanism leading to the formation of free radicals may be discounted in view of the failure to induce the polymerization of acrylonitrile,[24] and the large value of the reaction constants. In most hydrogen abstraction reactions, the reaction constants, ρ, have small magnitude.[22]

The observed kinetic isotope effect suggested that the α-C–H bond is cleaved in the rate determining step. The value of the kinetic isotope effect ($k_H/k_D = 5.97$ at 298 K) is of the order of the values obtained in the oxidation of MA by pyridinium hydrobromide perbromide[25] ($k_H/k_D = 5.07$ at 323 K) and pyridinium bromochromate ($k_H/k_D = 6.35$ at 298 K).[26] Both these oxidations suggest the cleavage of a α-C–H bond in the rate determining step. This supports the proposition of the cleavage of the α-C–H bond in the rate-determining step of the oxidation of hydroxy acids by BTMACI.

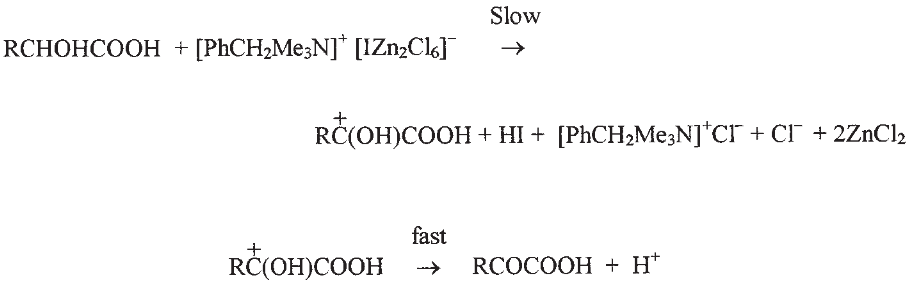
The correlation analysis of the substituent effect indicated the presence of a highly electron-deficient reaction centre in the rate-determining step. The fact that an excellent correlation is obtained with Brown's σ^+ values suggests that there is a resonance interaction in the transition state between a developing positive centre at the reaction site and the substituent. Thus, the transition state approaches a carbocation in character. Below, the transfer of a hydride-ion from the acid to the oxidant is indicated (Scheme 1).

We were unable to study the effect of polarity, which might have given supportive evidence to our mechanism, because of the decomposition of the oxidant in water and its insolubility in

Table 5. Temperature Dependence of the Reaction Constant for the Oxidation of Substituted Mandelic Acids by BTMACI[a)]

Temp/K	ρ^+	r^2	sd	ψ	h[b)]
298	-2.36 ± 0.01	0.9999	0.004	0.010	−1.73
308	-2.13 ± 0.02	0.9995	0.023	0.023	−1.42
318	-2.01 ± 0.01	0.9998	0.010	0.015	−1.13
328	-1.90 ± 0.01	0.9998	0.008	0.015	−0.79

a) No. of data points = 11. b) h = intercept.



$$\mathrm{RCHOHCOOH} + [\mathrm{PhCH_2Me_3N}]^+ [\mathrm{IZn_2Cl_6}]^- \xrightarrow{\text{Slow}} \mathrm{R\overset{+}{C}(OH)COOH} + \mathrm{HI} + [\mathrm{PhCH_2Me_3N}]^+\mathrm{Cl}^- + \mathrm{Cl}^- + 2\mathrm{ZnCl_2}$$

$$\mathrm{R\overset{+}{C}(OH)COOH} \xrightarrow{\text{fast}} \mathrm{RCOCOOH} + \mathrm{H}^+$$

Scheme 1.

any other suitable solvent. The proposed mechanism is, however, supported by the observed negative entropy of activation for the conversion of the reactant molecules into the activated complex. As the process involves a large charge separation in the transition state which results in an increase in the total number of charges, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

Thanks are due to University Grants Commission (India) for financial support.

References

1 S. Fujisaki, S. Kajigaeshi, T. Kakinami, H. Yamasaki, and T. Okamoto, *Bull. Chem. Soc. Jpn.*, **61**, 600 (1988).

2 S. Kajigaeshi, T. Kakinami, M. Moriwaki, T. Tanaka, S. Fujisaki, and T. Okamoto, *Bull. Chem. Soc. Jpn.*, **62**, 439 (1989).

3 S. Mitra and K. Sreekumar, *Indian J. Chem., Sect. B*, **36**, 133 (1997).

4 S. Kajigaeshi, H. Kawamuki, and S. Fujisaki, *Bull. Chem. Soc. Jpn.*, **62**, 2585 (1989).

5 S. Kajigaeshi, Y. Morikawa, S. Fujisaki, T. Kakinami, and K. Nishihara, *Bull. Chem. Soc. Jpn.*, **64**, 336 (1991).

6 T. Kakinami, S. Kajigaeshi, Y. Morikawa, S. Fujisaki, and K. Nishihara, *Bull. Chem. Soc. Jpn.*, **64**, 1060 (1991).

7 P. S. C. Rao, D. Suri, S. Kothari, and K. K. Banerji, *J. Chem. Res., Synop.*, **1998**, 510; *J. Chem. Res., Miniprint*, **1998**, 2251; P. Gupta and S. Kothari, *Indian J. Chem., Sect. A*, **40**, 474 (2001).

8 G. Goswami, S. Kothari, and K. K. Banerji, *Indian J. Chem., Sect. B*, **38**, 1270 (1999).

9 K. K. Banerji, *J. Chem. Res., Synop.*, **1978**, 193; *J. Chem. Res., Miniprint*, **1978**, 2561.

10 P. Levesley and W. A. Waters, *J. Chem. Soc.*, **1955**, 217.

11 A. I. Vogel, "A Text Book of Practical Organic Chemistry," Longmans Green, London (1956), p. 774.

12 T. J. Kemp and W. A. Waters, *J. Chem. Soc.*, **1964**, 1194.

13 K. J. P. Orton and A. Bradfield, *J. Chem. Soc.*, **1924**, 960; **1927**, 983.

14 F. Feigl, "Spot Tests in Organic Analysis," Elsevier Publishing Co., Amsterdam (1966), p. 485.

15 "Dictionary of Organic Compounds," ed by J. R. A. Pollock and R. Stevans, Eyre and Spottiswoode Publishers Limited, London (1964), Vol. 1, p. 359.

16 A. J. Downs and C. J. Adams, "Comprehensive Inorganic Chemistry," ed by J. C. Bailer, H. J. Emeleus, R. N. Yholm, and A. F. Tritman-Dickenson, Pergamon Press, Oxford (1973), Vol. II, p. 1344.

17 Supplement to Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," ed by H. V. A. Briscoe, A. A. Eldridge, and G. M. Dyson, Longmans, London (1956), Vol. II, p. 500.

18 V. K. Chaikovski, T. S. Kharlova, V. D. Filimonov, and T. A. Saryucheva, *Synthesis*, **1999**, 748.

19 F. A. Cotton, S. A. Duraj, M. W. Extine, G. E. Lewis, W. J. Roth, C. D. Schmulbach, and W. Schwotzer, *J. Chem. Soc., Chem. Commun.*, **1983**, 1377.

20 H. J. Emeleus, "Inorganic Chemistry (MTP International Review of Science)," Butterworths, London (1973), Vol. I, p. 53.

21 O. Exner, *Prog. Phys. Org. Chem.*, **10**, 411 (1973).

22 K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, New York (1963).

23 H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

24 R. Mehnert and O. Brede, *Radiat. Phys. Chem.*, **23**, 463 (1984).

25 P. Aparna, S. Kothari, and K. K. Banerji, *Indian J. Chem., Sect. A*, **32**, 1086 (1993).

26 P. Aparna, S. Kothari, and K. K. Banerji, *J. Chem. Res., Synop.*, **1994**, 367; *J. Chem. Res., Miniprint*, **1994**, 2123.