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Kinetics and mechanism of the oxidation of formic and oxalic acids by benzyltrimethylammonium dichloroiodate

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Abstract. The oxidation of formic and oxalic acids by benzyltrimethylammonium dichloroiodate (BTMACI), in the presence of zinc chloride, leads to the formation of carbon dioxide. The reaction is first order with respect to BTMACI, zinc chloride and organic acid. Oxidation of deuteriated formic acid indicates the presence of a kinetic isotope effect. Addition of benzyltrimethylammonium chloride enhances the rate. It is proposed that the reactive oxidizing species is $[(PhCH_2Me_3N)^+ (IZn_2Cl_6)^-]$. Suitable mechanisms have been proposed.

Keywords. Polyhalogens; benzytrimethylammonium dichloroiodate; organic acids.

1. Introduction

Benzyltrimethylammonium polyhalides are widely used as halogenating reagents in synthetic organic chemistry[1–3]. However, they have been rarely used as oxidizing agents[4–6]. These compounds are more suitable than molecular halogens because they are solids and therefore easy to handle, and owing to their stability, selectivity and excellent product yields. We are interested in the kinetic and mechanistic studies of new oxidizing agents and have recently reported the oxidation of substituted benzyl alcohols[7] and aliphatic aldehydes[8] by benzyltrimethylammonium dichloroiodate (BTMACI). In the present article, kinetics of oxidation of formic (FA) and oxalic (OA) acids by BTMACI, in glacial acetic acid, in the presence of zinc chloride have been described and their mechanistic aspects are discussed.

2. Experimental

2.1 *Materials*

BTMACI was prepared by the reported method[1] and its purity was checked by iodometry. The organic acids were commercial products of the highest degree of purity available and were used as supplied. The solution of formic acid was standardized by alkalimetry while that of oxalic acid was prepared by direct weighing. a-Deuterioformic acid (DCOOH or DFA) was prepared by the reported method[9] and its isotopic purity, ascertained by NMR spectra, was 94 ± 5%. Acetic acid was refluxed with chromic oxide and acetic anhydride for 6 h and then fractionated[10].

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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 had earlier observed[7] that in the absence of $ZnCl_2$, the strength of a saturated solution of BTMACI in acetic acid is 0·0005 mol dm^{-3}. Addition of $ZnCl_2$ (0·002 mol dm^{-3}) increased the solubility of BTMACI and a saturated solution of BTMACI, under these conditions, has a strength of 0·0016 mol dm^{-3}.

2.2 *Stoichiometry*

The oxidation of oxalic and formic acids leads to the formation of carbon dioxide. No quantitative determination of carbon dioxide formed was carried out.

To determine the stoichiometry, BTMACI (0·005 mol) and the organic acid (0·001 mol) were made up to 100 ml in glacial acetic acid in the presence of zinc chloride (0·015 mol dm^{-3}). The solutions were allowed to stand for ≈ 10 h to ensure the completion of the reaction. The residual BTMACI was determined spectrophotometrically at 364 nm. Several determinations, with both formic and oxalic acids showed that the stoichiometry is 1:1.

2.3 *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 300 ± 3 K. Both solvent and blank were glacial acetic acid. Scanning speed was 600 nm s^{-1}.

2.4 *Kinetic measurements*

The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the acid (× 15 times or more) over BTMACI, at constant temperature (± 0·1), in glacial acetic acid as solvent. The reactions were carried out 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 at least three half-lives. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear ($r^2 > 0{\cdot}995$) plots of log[BTMACI] against time. Duplicate kinetic runs showed that the rate constants were reproducible to within ± 3%. The experimental third order rate constant, k_3, was determined from the relationship, $k_3 = k_{obs}/[\text{acid}]\,[ZnCl_2]$.

3. Results and discussion

Stoichiometric determination indicated the following overall reactions for the oxidation of OA and FA respectively,

$$(COOH)_2 + PhCH_2Me_3NICl_2 \rightarrow 2\,CO_2 + PhCH_2Me_3NCl + HI + HCl, \tag{1}$$

$$HCOOH + PhCH_2Me_3NICl_2 \rightarrow CO_2 + PhCH_2Me_3NCl + HI + HCl. \tag{2}$$

3.1 *Rate laws*

The reaction is of first order with respect to BTMACI. Further, the pseudo-first-order rate constants do not depend on the initial concentration of BTMACI. The reaction rate increases linearly with increase in concentration of the acid (table 1). With increase in the concentration of zinc chloride also, the reaction rate increases linearly (table 2). A plot of k_{obs} *vs* [$ZnCl_2$] is linear ($r^2 > 0{\cdot}9980$) and passes through the origin. An addition of benzyltrimethylammonium chloride (BTMACl) enhances the reaction rate slightly (table 3).

3.2 *Induced polymerization of acrylonitrile*

Oxidation of the acid, under nitrogen atmosphere, failed to induce polymerization of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate (table 1).

3.3 *Effect of temperature*

Rates of oxidation of both the acids were determined at different temperatures and activation parameters calculated (table 4).

3.4 *Kinetic isotope effect*

To ascertain the importance of the cleavage of the α-C–H bond in the rate-determining step, the oxidation of DFA was studied. The results showed (table 4) the presence of a primary kinetic isotope effect ($k_H/k_D = 5{\cdot}11$ at 313 K).

3.5 *Spectral studies*

A comparison of the UV-Vis spectra (figure 1) 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 and absence of zinc chloride. However, there is initial sharp decrease in absorbance followed by regular but gradual decrease in the absorbance of BTMACI on further addition of $ZnCl_2$. This clearly shows that a strong complex is

Table 1. Rate constants for the oxidation of organic acids by BTMACI at 313 K.

10^3[BTMACI] (mol dm^{-3})	[Acid] (mol dm^{-3})	$10^5\ k_{obs}$ (s^{-1}) FA	OA
1·0	0·1	1·02	35·8
1·0	0·2	2·11	70·7
1·0	0·3	3·17	105
1·0	0·5	5·55	180
1·0	1·0	10·9	360
1·0	1·5	16·0	520
1·0	2·0	20·9	712
0·2	1·0	10·5	370
0·4	1·0	11·1	358
0·6	1·0	10·2	372
0·8	1·0	11·5	355
1·0	1·0	10·7*	362*

*Contained 0·005 mol dm^{-3} acrylonitrile

Table 2. Effect of zinc chloride on the rate of oxidation of organic acids by BTMACI.
[BTMACI] = 0·001 mol dm^{-3}, [acid] = 1·0 mol dm^{-3}, temperature = 313 K.

	$10^3[ZnCl_2]$(mol dm^{-3})					
$10^5\ k_{obs}\ (s^{-1})$	2·0	3·0	4·0	5·0	8·0	10·0
FA	6·99	10·9	15·1	18·2	29·7	38·5
OA	230	360	480	600	970	1200

Table 3. Effect of benzyltrimethylammonium chloride on the rate of oxidation of organic acids by BTMACI.
[BTMACI] = 0·001 mol dm^{-3}, [acid] = 1·0 mol dm^{-3}, temperature = 313 K.

	10^3[BTMACl](mol dm^{-3})					
$10^3\ k_{obs}\ (s^{-1})$	0·0	0·4	0·6	1·0	3·0	4·0
FA	10·9	11·7	13·4	16·5	19·0	20·8
OA	360	381	440	542	615	676

Table 4. Temperature dependence of reaction rate and activation parameters for the oxidation of organic acids by BTMACI.

	$k_3(dm^6\ mol^{-2}\ s^{-1})$ at						
Acid	303 K	308 K	313 K	318 K	ΔH^* (kJ mol^{-1})	ΔS^* (J $mol^{-1}\ K^{-1}$)	ΔG^* (kJ mol^{-1})
FA	11·1	17·8	28·1	44·3	71·3 ± 0·5	–48 ± 2	85·4 ± 0·4
OA	770	962	1193	1468	31·9 ± 0·2	–142 ± 1	74·2 ± 0·2
DFA	2·04	3·38	5·50	8·75	75·2 ± 0·4	–49 ± 2	89·6 ± 0·3
k_H/k_D	5·44	5·27	5·11	5·06			

formed initially which undergoes further complexation and whose concentration increases with increase in concentration of $ZnCl_2$.

From our data [7] on the solubility of BTMACI in the absence and the presence of $ZnCl_2$, the value of the equilibrium constant, K_1, is about 2400 $mol^{-1}\ dm^3$. This indicates that even at the lowest concentration of $ZnCl_2$ used, almost the whole of BTMACI is in the form of complex (A). Linear increase in the rate with increase in the concentration of $ZnCl_2$ points to further complexation. 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 [11].

$$[PhCH_2Me_3N]^+\ ICl_2^- + ZnCl_2 \overset{K_1}{\qquad} \underset{(A)}{[PhCH_2Me_3N]^+\ [IZnCl_4]^-} \tag{3}$$

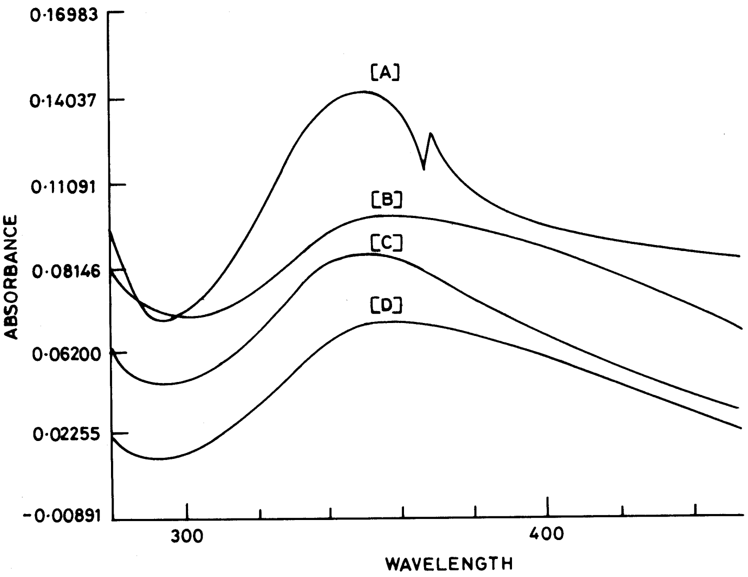

Figure 1. UV-Vis spectra of [A]: 0·0005 mol dm^{-3} BTMACI, [B]: [A] + 0·002 mol dm^{-3} $ZnCl_2$, [C]: [A] + 0·003 mol dm^{-3} $ZnCl_2$, [D]: [A] + 0·006 mol dm^{-3} $ZnCl_2$. Solvent: Glacial acetic acid. Temperature: 300 ± 3 K.

$$(A) + ZnCl_2 \quad \overset{K_2}{} \quad \underset{(B)}{[PhCH_2Me_3N]^+ [IZn_2Cl_6]^-}. \tag{4}$$

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[11,12]. The formation of positive iodine species in the sulphuric acid medium has been reported recently[13]. Acetic acid is a relatively poor ionizing solvent and 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, the reaction is not complete even at high concentration of $ZnCl_2$, and that only the complex (B) is reactive. The small rate-enhancing effect of BTMACl suggests that iodine monochloride is not involved in the oxidation process.

$$[PhCH_2Me_3N]^+ ICl_2^- \quad \overset{K_3}{} \quad [PhCH_2Me_3N]^+ Cl^- + ICl. \tag{5}$$

Therefore, (B) is the only reactive oxidizing species in the oxidation of acids. The formation of the complex is supported by the spectral studies also. The existence of the anion, $[Zn_2Cl_6]^{-2}$, in tetrahydrofuran has been confirmed by X-ray crystallography[14]. Various metallic salts of $[Zn_2Cl_6]^{-2}$ are known[15].

3.5 *Mechanism*

In view of the absence of any effect of acrylonitrile on the rate of reaction and the failure to induce polymerization of acrylonitrile, it is unlikely that a one-electron oxidation, giving rise to free radicals, takes place in the reaction. The presence of a substantial primary kinetic isotope effect confirms that the a-C–H bond is cleaved in the rate-determining step. Based on the kinetic results and above considerations, it is proposed that the rate-determining step, in the oxidation of formic acid, involves the transfer of a hydride-ion to the oxidant (see (6) below). The relatively large decrease in the entropy of activation in the oxidation of oxalic acid suggests the involvement of both the carboxylic acid groups in the transition state ((7) below).

$$\mathrm{HCOOH} + [\mathrm{PhCH_2Me_3N}]^+\,[\mathrm{IZn_2Cl_6}]^- \xrightarrow{\text{slow}} \mathrm{CO_2} + \mathrm{HI} + 2\,\mathrm{ZnCl_2} + [\mathrm{PhCH_2Me_3N}]^+ + 2\mathrm{Cl}^- + \mathrm{H}^+, \qquad (6)$$

$$(\mathrm{COOH})_2 + [\mathrm{PhCH_2Me_3N}]^+\,[\mathrm{IZn_2Cl_6}]^- \xrightarrow{\text{slow}} 2\mathrm{CO_2} + \mathrm{HI} + 2\mathrm{ZnCl_2} + [\mathrm{PhCH_2Me_3N}^+ + 2\mathrm{Cl}^- + \mathrm{H}^+. \qquad (7)$$

The proposed mechanism is supported by the observed negative entropy of activation. As charge separation takes place in the transition state, the two ends become highly solvated. This results in an immobilization of a large number of solvent molecules, reflected in the loss of entropy.

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