Kinetics and Mechanism of the Oxidation of Aliphatic Aldehydes by Benzyltrimethylammonium Chlorobromate

J. Chem. Research (S),
1999, 308–309
J. Chem. Research (M),
1999, 1343–1356

Anupama Bohra, Pradeep K. Sharma and Kalyan K. Banerji*
Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

Oxidation of aliphatic aldehydes by benzyltrimethylammonium chlorobromate to the corresponding carboxylic acid proceeds *via* the transfer of a hydride ion from the aldehyde hydrate to the oxidant.

Benzyltrimethylammonium chlorobromate (BTMACB) has been used as a halogenating reagent in synthetic organic chemistry.[1–3] However, there seems to be no report on the kinetics of oxidation by BTMACB. We report here the kinetics of the oxidation of six aliphatic aldehydes by BTMACB in aqueous acetic acid solutions.

BTMACB was prepared by the reported method[1] and its purity checked by an iodometric method. The reactions were carried out under pseudo-first-order conditions by keeping a large excess of the aldehyde (×15 or more) over BTMACB. The solvent was acetic acid–water (1:1, v/v). The reactions were followed up to *ca.* 80% reaction, by monitoring the decrease in the [BTMACB] at 364 nm at constant temperatures (±0.1 K).

The aldehydes were oxidized to the corresponding carboxylic acids. Product analysis indicated the following overall reaction [eqn. (1)].

$$\begin{aligned}\mathrm{RCHO} + [\mathrm{PhCH_2NMe_3}]\mathrm{Br_2Cl} + \mathrm{H_2O} \rightarrow \\ \mathrm{RCO_2H} + [\mathrm{PhCH_2NMe_3}]\mathrm{Cl} + 2\mathrm{HBr}\end{aligned} \qquad (1)$$

The reactions were found to be first order with respect to BTMACB and the aldehyde. The experimental specific rate constants, k_{ex}, was obtained from the relation: $k_{\mathrm{ex}} = k_{\mathrm{obs}}/[\mathrm{aldehyde}]$.

Addition of benzyltrimethylammonium chloride (BTMACl) or bromide ion had no effect on the rate of oxidation.

The oxidation of deuteriated acetaldehyde (MeCDO) indicated the presence of a substantial primary kinetic isotope effect ($k_{\mathrm{H}}/k_{\mathrm{D}} = 6.14$ at 298 K). This confirmed the cleavage of the aldehydic C–H bond in the rate-determining step.

Conductivity measurements showed that an addition of BTMACB increases the conductivity of glacial acetic acid. Conductivity measurements of BTMACB in solvents containing different proportions of acetic acid (100–30%) and water showed that the conductivity increases sharply as the water content is initially increased but reaches a limiting value in *ca.* 60% acetic acid–water mixture. Therefore, BTMACB can be considered as an ionic compound which exists under our reaction conditions as benzyltrimethylammonium and chlorobromate ions [eqn. (2)]. No effect of added benzyltrimethylammonium ion also indicates that the equilibrium (2) lies far towards the right. The absence of any effect of bromide or chloride ion led us to propose that the reactive oxidizing species is the chlorobromate ion.

$$\mathrm{PhCH_2NMe_3Br_2Cl} \rightleftharpoons \mathrm{PhCH_2NMe_3}^{+} + \mathrm{Br_2Cl}^{-} \qquad (2)$$

Solvent Effect.—The rate of oxidation of aldehydes increases with decrease in the amount of acetic acid in the solution. This indicates that an increase in the solvent polarity facilitates the reaction. This can be explained if one assumes that in the rate-determining step the transition state is more polar than the reactants. The effect of solvent composition was analysed using the Grunwald–Winstein[13] equation (5).

$$\log k_{\mathrm{ex}} = mY + \log k_0 \qquad (5)$$

A plot of log k_{ex} *vs.* Y was linear ($r^2 = 0.9963$) with $m = 0.53 \pm 0.02$. The value of m indicates that a large charge separation takes place in the transition state of the rate-determining step.

Aliphatic aldehydes are known to be hydrated to varying extent in aqueous solution. From the values of k_{ex} and of the equilibrium constant[14] of the hydration reaction, two sets of rate data were computed. The values of k_{Hy} were obtained by assuming that only the hydrated form participates in the oxidation process and the rate law has the form (7). The data are reported in Table 5.

$$\mathrm{Rate} = k_{\mathrm{Hy}}[\mathrm{BTMACB}][\mathrm{RCH(OH)_2}] \qquad (7)$$

Similarly the values of k_{A} were calculated assuming participation of only the free aldehyde form, according to the rate law (8).

$$\mathrm{Rate} = k_{\mathrm{A}}[\mathrm{BTMACB}][\mathrm{RCHO}] \qquad (8)$$

The rates of oxidation of the aldehyde hydrate, k_{Hy}, correlates very well with Taft's σ^* substituent constants,[15] the reaction constants being negative. On the other hand, no such correlation exists with the rates of oxidation of the free aldehyde form. In particular, formaldehyde and trichloroacetaldehyde (chloral) react much faster compared to other aldehydes. If one assumes that the aldehyde reacts *via* the hydrate form [eqn. (7)], the rate of oxidation of formaldehyde and chloral compares favourably with reactivities of the other aldehydes. If the oxidation of the aldehyde form is assumed then formaldehyde and chloral are *ca.* 250 and 400 times more reactive than other aldehydes. This makes a direct hydrogen transfer from the free aldehyde and oxidant highly unlikely. The existence of a good structure–reactivity correlation in the oxidation of aldehyde hydrate further

Table 5 Rate constants for the oxidation of hydrate and free aldehyde forms at 298 K

		10^3 (Rate constant)/ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$		
Aldehyde	K_{d}	k_{ex}	k_{A}	k_{Hy}
HCHO	5.5×10^{-4}	3.18	6360.0	3.18
MeCHO	0.67	13.5	33.8	22.5
EtCHO	1.40	14.1	24.3	33.6
PrCHO	2.10	11.6	17.1	36.2
$\mathrm{Pr^iCHO}$	2.30	14.7	21.0	49.0
$\mathrm{CCl_3CHO}$	3.6×10^{-5}	0.38	10556.0	0.38

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* To receive any correspondence.

supports the involvement of aldehyde hydrates in the oxidation process.

Mechanism.—The oxidation of aldehydes, by BTMACR, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, addition of acrylonitrile had no effect on the rate. Thus a hydrogen abstraction mechanism leading to the formation of free radicals may be discounted. The negative polar reaction constant points to an electron-deficient carbon centre in the transition state. The large negative reaction constant and a substantial kinetic isotope effect suggest a considerable carbocation character in the transition state. Therefore, the mechanism shown in Scheme 1 is suggested.

$$RCH(OH)_2 + Br_2Cl^- \overset{slow}{\rightarrow} \overset{+}{R}C(OH)_2 + Cl^- + HBr + Br^-$$

$$\overset{+}{R}C(OH)_2 \overset{fast}{\rightarrow} RCO_2OH + H^+$$

Scheme 1

Thanks are due to the Council of Scientific and Industrial Research (India) for financial support.

Techniques used: spectrophotometry, correlation analysis

Equations: 8

References: 16

Table 1: Rate constants for the oxidation of acetaldehyde by BTMACB at 298 K

Table 2: Effect of benzyltrimethylammonium chloride/bromide ion on the rate of oxidation of acetaldehyde by BTMACB

Table 3: Kinetic isotope effect in the oxidation of acetaldehyde by BTMACB

Table 4: Effect of solvent composition in the oxidation of acetaldehyde by BTMACB

Table 6: Rate constants and activation parameters of the oxidation of aldehyde hydrates, $RCH(OH)_2$, by BTMACB

Table 7: Temperature dependence of the reaction constants

Received, 5th January 1999; Accepted, 28th January 1999
Paper E/9/00107G

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