Kinetics and Mechanism of the Oxidation of Substituted Benzaldehydes by Benzyltrimethylammonium Chlorobromate

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The oxidation of 35 monosubstituted benzaldehydes by benzyltrimethylammonium chlorobromate (BTMACB) in aqueous acetic acid leads to the formation of the corresponding benzoic acids. The reaction is first order with respect to both benzaldehyde and BTMACB. The reaction failed to induce the polymerization of acrylonitrile. There is no effect of benzyltrimethylammonium chloride or potassium bromide on the reaction rate. The oxidation of [^{2}H]benzaldehyde (PhCDO) indicated the presence of a substantial kinetic isotope effect. The effect of solvent composition indicated that the reaction rate increases with an increase in the polarity of the solvent. The rates of oxidation of meta- and para-substituted benzaldehydes were correlated in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes was correlated with the tetraparametric LDRS equation. The oxidation of para-substituted benzaldehydes is more susceptible to the delocalization effect, whereas the oxidation of ortho-and meta-substituted compounds displayed a greater dependence on the field effect. The positive value of η suggests the presence of an electron-deficient reaction center in the rate-determining step. The reaction is subjected to steric hindrance by the ortho substituents.

Benzyltrimethylammonium chlorobromate (BTMACB) is one of the number of quaternary ammonium polyhalides that have been used as effective halogenating and oxidizing agents in synthetic organic chemistry.[1−3] Recently, polymeric benzyltrimethylammonium dichloroiodate and dibromoiodate have been used for the addition of halogens to olefins.[4] The polyhalides are more suitable than molecular halogens because of their solid nature, ease of handling, stability, selectivity, and excellent product yield. We have been interested in kinetic and mechanistic aspects of oxidation by polyhalide compounds, and many reports have emanated from our laboratory.[5−8] There seems to be no report on the kinetics of oxidation by BTMACB, except that of aliphatic aldehydes.[9] In continuation of our earlier study, we report here the kinetics of oxidation of 35 monosubstituted benzaldehydes by BTMACB in aqueous acetic acid as solvent. The major objective of this investigation was to study the structure−reactivity correlation for the substrate undergoing oxidation.

Results

Oxidation of the aromatic aldehydes by BTMACB results in the formation of the corresponding benzoic

Table 1. Rate Constants for the Oxidation of Benzaldehyde by BTMACB at 298 K

10^4[BTMACB] (mol dm^{-3})	[PhCHO] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
1.0	0.10	1.62
1.0	0.20	3.21
1.0	0.40	6.46
1.0	0.60	9.71
1.0	0.80	13.0
1.0	1.00	16.1
1.0	1.50	24.4
2.0	0.20	3.46
4.0	0.20	3.05
6.0	0.20	3.61
8.0	0.20	3.30
1.0	0.40^a	6.52^a

^{a} Contained 0.001 mol dm^{-3} acrylonitrile.

acids. Analyses of products and stoichiometric determinations indicate the following overall reaction:

$$ArCHO + [PhCH_2Me_3N]^+Br_2Cl^- + H_2O \rightarrow$$
$$ArCOOH + [PhCH_2Me_3N]^+ + Cl^- + 2H^+ + 2Br^- \quad (1)$$
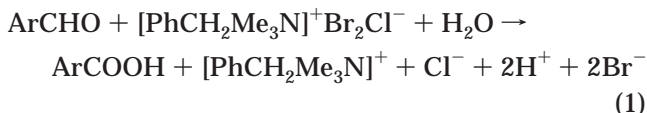
The reactions were found to be first order with respect to BTMACB. In the individual kinetic runs, the plots of log [BTMACB] versus time were linear ($r^2 > 0.995$). Further, the pseudo-first-order rate constants, k_{obs}, do not depend on the initial concentration of BTMACB. The reaction rate increases linearly with an increase in the concentration of benzaldehydes (Table 1).

Induced Polymerization Test. The oxidation of benzaldehyde, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table 1).

Effect of Substituents. The rate of the oxidation of 35 monosubstituted benzaldehydes was determined at different temperatures, and the activation parameters were calculated (Table 2).

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Table 2. Rate Constants and Activation Parameters of the Oxidation of Substituted Benzaldehydes by BTMACB

	$10^4 k_2$ (dm^3 mol^{-1} s^{-1})				ΔH^*	ΔS^*	ΔG^*
subst	288 K	298 K	308 K	318 K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
H	2.26	6.10	16.1	42.4	71.8 ± 0.8	−66 ± 3	91.3 ± 0.7
p-Me	4.65	12.2	31.5	80.3	69.7 ± 0.8	−67 ± 3	89.6 ± 0.6
p-OMe	8.88	22.7	57.2	142	67.8 ± 0.7	−68 ± 2	88.0 ± 0.6
p-F	1.91	5.17	13.9	36.6	71.7 ± 0.9	−67 ± 3	91.6 ± 0.8
p-Cl	1.27	3.50	9.45	25.3	73.3 ± 0.8	−65 ± 3	92.7 ± 0.6
p-NO$_2$	0.10	0.32	0.94	2.77	81.5 ± 0.6	−58 ± 2	98.7 ± 0.5
p-CF$_3$	0.31	0.90	2.56	7.24	77.4 ± 0.9	−63 ± 3	96.0 ± 0.7
p-COOMe	0.42	1.23	3.42	9.57	76.6 ± 0.7	−63 ± 2	95.3 ± 0.6
p-Br	1.25	3.43	9.27	24.9	73.3 ± 0.9	−66 ± 3	92.7 ± 0.7
p-NHAc	4.47	11.7	30.3	77.1	69.7 ± 0.8	−67 ± 2	89.7 ± 0.6
p-CN	0.19	0.55	1.59	4.58	78.2 ± 1.0	−64 ± 4	97.2 ± 0.9
p-SMe	5.36	14.0	35.7	90.3	69.1 ± 0.7	−68 ± 2	89.2 ± 0.6
p-NMe$_2$	40.2	96.8	232	537	63.3 ± 0.6	−71 ± 2	84.5 ± 0.5
m-Me	3.59	9.45	24.2	62.2	69.7 ± 0.8	−69 ± 3	90.2 ± 0.6
m-OMe	3.32	8.67	21.9	54.9	68.5 ± 0.7	−74 ± 2	90.4 ± 0.5
m-Cl	0.76	2.15	5.91	16.0	74.7 ± 0.7	−65 ± 2	93.9 ± 0.6
m-Br	0.74	2.11	5.83	15.6	74.8 ± 0.5	−65 ± 2	94.0 ± 0.5
m-F	0.90	2.48	6.74	17.6	72.9 ± 0.6	−69 ± 2	93.5 ± 0.5
m-NO$_2$	0.11	0.35	1.12	3.33	84.2 ± 0.8	−48 ± 3	98.4 ± 0.6
m-CO$_2$Me	0.48	1.40	4.02	11.3	77.6 ± 0.8	−59 ± 3	94.9 ± 0.6
m-CF$_3$	0.35	1.03	3.02	8.57	78.7 ± 0.9	−58 ± 3	95.7 ± 0.7
m-CN	0.19	0.59	1.77	5.14	81.1 ± 0.6	−54 ± 2	97.1 ± 0.5
m-SMe	2.40	6.36	16.5	42.4	70.3 ± 0.8	−71 ± 2	91.2 ± 0.6
m-NHAc	2.22	5.92	15.4	39.9	70.7 ± 0.8	−70 ± 3	91.4 ± 0.6
o-Me	1.17	3.25	8.80	24.1	74.1 ± 0.9	−63 ± 3	92.8 ± 0.8
o-OMe	2.60	7.05	18.9	51.4	73.1 ± 1.0	−60 ± 3	90.9 ± 0.8
o-NO$_2$	0.04	0.14	0.43	1.36	86.5 ± 0.7	−48 ± 2	101 ± 0.5
o-COOMe	0.13	0.38	1.12	3.35	79.8 ± 1.4	−62 ± 4	98.1 ± 1.0
o-NHAc	0.60	1.71	4.84	13.9	77.1 ± 1.1	−59 ± 4	94.4 ± 0.9
o-Cl	0.26	0.79	2.32	6.86	80.4 ± 0.9	−54 ± 3	96.4 ± 0.7
o-Br	0.19	0.61	1.81	5.42	82.3 ± 0.7	−50 ± 2	97.0 ± 0.5
o-I	0.17	0.50	1.48	4.48	80.4 ± 1.3	−58 ± 4	97.4 ± 1.1
o-CN	0.07	0.22	0.64	1.98	81.9 ± 1.1	−60 ± 4	99.6 ± 0.9
o-SMe	0.81	2.32	6.50	18.4	76.6 ± 0.9	−58 ± 3	93.7 ± 0.8
o-F	0.73	2.13	6.06	17.3	77.7 ± 0.9	−55 ± 3	93.9 ± 0.7
o-CF$_3$	0.03	0.11	0.33	1.06	87.3 ± 0.9	−48 ± 3	101 ± 0.8
PhCDO	0.42	1.15	3.07	8.15	72.6 ± 0.8	−77 ± 3	95.4 ± 0.6
k_H/k_D	5.38	5.30	5.24	5.20			

Table 3. Effect of Benzyltrimethylammonium Chloride or Bromide Ions on the Rate of Oxidation of Benzaldehyde by BTMACB

[BTMACB] = 0.001 mol dm^{-3}	[benzaldehyde] = 1.0 mol dm^{-3}				T = 298 K	
10^3[BTMACl] or [KBr]/mol dm^{-3}	0.00	0.5	1.0	2.0	3.0	4.0
$10^4 k_{obs}/s^{-1}$						
BTMACl	16.1	16.3	15.4	16.8	15.7	16.0
KBr	16.1	15.8	16.4	15.5	16.7	16.5

Kinetic Isotope Effect. To ascertain the importance of the cleavage of the aldehydic C−H bond in the rate-determining step, the oxidation of [²H]benzaldehyde (PhCDO) was studied. The results (Table 2) showed the presence of a substantial kinetic isotope effect (k_H/k_D = 5.30 at 298 K).

Effect of Benzyltrimethylammonium Chloride or Potassium Bromide. The addition of benzyltrimethyl-ammonium chloride (BTMACl) or potassium bromide (Table 3) did not affect the rates of oxidation.

Effect of Solvent Composition. The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with an increase in the amount of water in the solvent mixture (Table 4).

Discussion

A plot of log k_2 at 288 K is linearly related to log k_2 at 318 K (r^2 = 0.9988, slope = 0.8645 ± 0.004). The value

Table 4. Effect of Solvent Composition in the Oxidation of Benzaldehyde by BTMACB

| [BTMACB] = 0.001 mol dm^{-3}	[benzaldehyde] = 1.0 mol dm^{-3}			T = 298 K	
% AcOH	25	40	50	60	72
$10^4 k_{obs}/s^{-1}$	53.8	29.0	16.1	10.3	5.72

of the isokinetic temperature is 955 ± 82 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.[10] It also implies that all the aldehydes for which the rates of oxidation are so correlated are oxidized by the same mechanism.[10]

We have carried out some conductivity measurements to determine the nature of BTMACB in aqueous acetic acid solution.[9] It was observed that acetic acid has very low conductivity. Addition of BTMACB increases the conductivity of acetic acid. We measured the conductivity of BTMACB in solvents containing different proportions of acetic acid (100−30%) and water also. We found that the conductivity increases sharply as the water content is initially increased but reaches a limiting value in about 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 (eq 2). No effect of added ben-zyltrimethylammonium ion also indicates that the equilibrium (2) lies far toward the right.

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

$$PhCH_2Me_3NBr_2Cl \rightleftharpoons PhCH_2Me_3N^+ + Br_2Cl^- \quad (2)$$

The following equilibria may also exist in the solution.

$$Br_2Cl^- \rightleftharpoons Br_2 + Cl^- \quad (3)$$

$$Br_2 + H_2O \rightleftharpoons HOBr + HBr \quad (4)$$
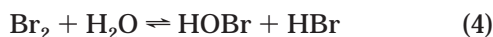
The probable oxidizing species in a solution of BT-MACB are, therefore, chlorobromate ion, molecular bromine, or hypobromous acid. The equilibria (3) and (4) likely to be suppressed by the addition of BTMACl or potassium bromide. No effect of BTMACl or bromide ion on the reaction rate rules out any role of Br_2 and HOBr in the oxidation process. The oxidation of benzaldehyde by bromine, in the pH range 1−4, is retarded by the addition of bromide ions,[11] whereas the oxidation by BTMACB is unaffected by bromide ions. This also indicates that in this reaction bromine is not the active oxidizing species. For comparison, the oxidation of benzaldehyde by hypobromous acid was studied. The oxidation was very slow initially but became faster later. Similar results were obtained in the oxidation of acetaldehyde by HOBr.[12] It has been attributed to the faster oxidation of the aldehyde by bromine, formed by the reaction of HOBr and bromide ion. Such a kinetic picture is not obtained in the oxidation by BTMACB. Similar results were obtained in the oxidation of aliphatic aldehydes by BTMACB.[9] Thus, in the present reaction also the reactive oxidizing species is the chlorobromate ion.

Solvent Composition Effect. The increase in the rate of oxidation with an increase in the polarity of the medium suggests that the transition state is more polar than the reactants. The solvent effect was analyzed using the Grunwald−Winstein equation.[13]

$$\log k_2 = \log k_0 + mY \quad (5)$$

The plot of $\log k_2$ versus Y is linear ($r^2 = 0.9912$) with $m = 0.53 \pm 0.02$. The value of m suggests that there is a considerable charge separation in the transition state of the reaction. However, the solvent composition may simply affect the ground state stability of benzaldehyde. Solvents of high polarity is likely to stablize the ionic canonical form of benzaldehyde (eq 6).

$$Ph-CH=O \leftrightarrow Ph-CH^+-O^- \quad (6)$$

Therefore, a reaction leading to the formation of a cation is likely to be favored in solutions of high polarity.

Correlation Analysis of Reactivity. The effect of substituents on reactivity has long been correlated with the Hammett equation[14] or with dual substituent-parameter equations.[15,16][15,16] In the late 1980s, Charton[17] introduced a triparametric LDR equation (eq 7) for the

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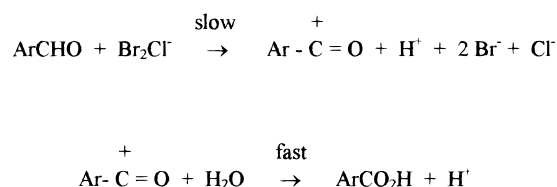(17) Charton, M.; Charton, B. *Bull. Soc. Chim. Fr.* **1988**, 199 and references therein.

quantitative description of structural effects on chemical reactivities.

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + h \quad (7)$$

Here, σ_l is a localized (field and/or inductive) effect parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when active-site electronic demand is minimal, and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by eq 8.

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (8)$$

Here, η represents the electronic demand of the reaction site and is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For ortho-substituted compounds, the LDR equation has been modified to the LDRS eq 9[17] to account for the steric effects

$$\log k_2 = L\sigma_l + D\sigma_d + R\sigma_e + SV + h \quad (9)$$

where V is the well-known Charton's steric parameter based on van der Waals radii.[18]

The rates of oxidation of ortho-, meta-, and para-substituted benzaldehydes show excellent correlations in terms of the LDR/LDRS equations (Table 5). All three series of substituted benzaldehydes meet the requirement of a minimum number of substituents for analysis by LDR and LDRS equations.[17] We have used the standard deviation (sd), the coefficient of multiple determination (R^2), and Exner's[19] parameter, ψ, as the measures of goodness of fit.

The comparison of the L and D values for the substituted benzaldehydes showed that the oxidation of para-substituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of ortho- and meta-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, L, D, and R, are negative, indicating an electron-deficient carbon center in the activated complex for the rate-determining step. The positive value of η adds a negative increment to σ_d (eq 8), reflecting the electron-donating power of the substituent and its capacity to stablize a cationic species. The negative value of S indicates that the reaction is subject to steric hindrance by an ortho substituent.

The percent contribution of the delocalized effect, P_D, and the percent contribution of the steric parameter to the total effect of the substituent, P_S, were determined by Charton's method.[18] They are recorded in Table 5. The value of P_D for the oxidation of para-substituted benzaldehydes is ca. 52%, whereas the corresponding values for the meta- and ortho-sobstituted aldehydes are ca. 39% and 49%, respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzaldehydes. The less pronounced resonance effect from the ortho- position than

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Table 5. Temperature Dependence for the Reaction Constants for the Oxidation of Substituted Benzaldehydes by BTMACB

T/K	L	D	R	S	η	R^2	sd	ψ	P_D	P_S
				Para-Substituted						
288	−1.66	−1.83	−1.34		0.73	0.9998	0.008	0.01	52.4	
298	−1.59	−1.75	−1.31		0.75	0.9999	0.001	0.02	52.4	
308	−1.53	−1.69	−1.25		0.74	0.9997	0.001	0.02	52.6	
318	−1.47	−1.62	−1.18		0.73	0.9999	0.001	0.01	52.3	
				Meta-Substituted						
288	−1.72	−1.16	−0.75		0.65	0.9998	0.006	0.01	40.3	
298	−1.64	−1.08	−0.72		0.67	0.9999	0.004	0.01	39.7	
308	−1.54	−1.00	−0.70		0.70	0.9997	0.006	0.02	39.4	
318	−1.48	−0.93	−0.69		0.74	0.9998	0.002	0.01	38.6	
				Ortho-Substituted						
288	−1.72	−1.62	−1.20	−1.11	0.74	0.9992	0.002	0.02	48.5	24.9
298	−1.61	−1.53	−1.10	−1.03	0.79	0.9999	0.006	0.01	48.7	24.7
308	−1.54	−1.50	−1.06	−1.00	0.71	0.9998	0.002	0.01	49.3	24.8
318	−1.46	−1.45	−1.01	−0.95	0.70	0.9998	0.001	0.01	49.8	24.6

Scheme 1

$$\text{ArCHO} + \text{Br}_2\text{Cl}^- \xrightarrow{\text{slow}} \text{Ar-}\overset{+}{\text{C}}=\text{O} + \text{H}^+ + 2\,\text{Br}^- + \text{Cl}^-$$

$$\text{Ar-}\overset{+}{\text{C}}=\text{O} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{ArCO}_2\text{H} + \text{H}^+$$

from the para-position may be due to the twisting away of the aldehydic group from the plane of the benzene ring. The magnitude of the P_S value shows that the steric effect is significant in this reaction.

Mechanism

The cleavage of the aldehydic C–H bond in the rate-determining step is confirmed by the presence of a substantial kinetic isotope effect. A one-electron oxidation, giving rise to free radicals, is unlikely in view of the failure to induce polymerization of acrylonitrile and no effect of the radical scavenger on the reaction rate.[20] The negative values of the localization and delocalization electrical effects i.e., of L, D, and R, points to an electron-deficient reaction center in the rate-determining step. It is further supported by the positive value of η, which indicates that the substituent is better able to stabilize a cationic or electron-deficient reactive site. Therefore, a mechanism involving formation of an acylium cation in the rate-determining step is suggested (Scheme 1). Formation of acylium cation has been earlier been proposed in the oxidation of benzaldehyde[11] and acetaldehyde[12] by bromine also. The proposed mechanism is supported by the observed negative entropy of activation. As the charge separation takes place in the transition state, the charged ends get extensively solvated. This results in the immobilization of a large number of solvent molecules. This is reflected in the loss of entropy. The observed effect of solvent composition on the reaction rate also supports a mechanism involving the formation of an acylium cation. The observed steric hindrance by the ortho substituent may be due to the hindrance to approach of the oxidizing species by the ortho substituent.

Experimental Section

Materials. The aldehydes were commercial products. The liquid aldehydes were purified through the their bisulfite addition compounds and distilling them, under nitrogen, just before use.[21] The solid aldehydes were recrystallized from ethanol. BTMACB was prepared and purified by a reported method.[1] [^{2}H]Benzaldehyde (PhCDO) also was prepared by a reported method.[22] Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and fractionated.

Product Analysis. The product analysis was carried out under kinetic conditions. In a typical experiment, freshly distilled benzaldehyde (5.25 g, 0.05 mol) and BTMACB (6.9 g, 0.02 mol) were made up to 100 mL in 1:1 (v/v) acetic acid–water. The reaction mixture was allowed to stand for ca. 6 h to ensure completion of the reaction. It was rendered alkaline with NaOH and filtered and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in minimum quantity of dilute HCl and cooled in crushed ice to yield crude acid (2.0 g), which was recrystallized from hot water to produce pure benzoic acid (1.74 g, 71%, mp 121 °C). The percentage yield of benzoic acid has been calculated on the basis of BTMACB used.

Stoichiometry. To determine the stoichiometry, BTMACB (1.73 g, 0.005 mol) and benzaldehyde (0.11 g, 0.001 mol) were made up to 100 mL in 1:1 (v/v) acetic acid–water. The reaction was allowed to stand for ca. 10 h to ensure the completion of the reaction. The residual BTMACB was determined spectrophotometrically at 394 nm. Several determinations, with differently substituted benzaldehydes showed that the stoichiometry is 1:1.

Kinetic Measurements. The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the aldehyde (×15 or more) over BTMACB. The solvent was a 1:1 (v/v) acetic acid–water mixture (pH = 2.04), unless otherwise mentioned. The reactions were carried out at a constant temperature (±0.1 K) and were followed up to 80% reaction by monitoring the decrease in absorption due to [BTMACB] at 394 nm. The pseudo-first-order rate constants, k_{obs}, were computed from the linear ($r^2 > 0.995$) least-squares plots of log [BTMACB] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within ±4%.

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