Kinetics and Mechanism of the Oxidation of Substituted Benzaldehydes by Hexamethylenetetramine-Bromine

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> ABSTRACT: The oxidation of thirty-six monosubstituted benzaldehydes by hexa-methylenetetramine-bromine (HABR), in aqueous acetic acid solution, leads to the formation of the corresponding benzoic acids. The reaction is first order with respect to HABR. Michaelis-Menten-type kinetics were observed with respect to aldehyde. The reaction failed to induce the polymerization of acrylonitrile. There is no effect of hexamethylenetetramine on the reaction rate. The oxidation of [2H]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 showed excellent correlations in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes correlated well with tetraparametric LDRS equation. The oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalization effect but the oxidation of ortho- and meta-substituted compounds displayed a greater dependence on the field effect. The positive value of γ suggests the presence of an electron-deficient reaction center in the rate-determining step. The reaction is subjected to steric acceleration when ortho-substituents are present. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 615-622, 2000

INTRODUCTION

Hexamethylenetetramine-bromine (HABR) has been reported as a mild and selective synthetic reagent for the oxidation of alcohol to carbonyl compounds and for the regeneration of carbonyl compounds from oximes and hydrazones [1,2]. There seems to be only a few reports on the mechanistic aspects of oxidation reactions of HABR [3–7]. In continuation of our earlier study, we report here the kinetics of oxidation of benzaldehyde and thirty-five monosubstituted benzaldehydes by HABR in aqueous acetic acid as solvent. The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

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EXPERIMENTAL

Materials

The aldehydes were commercial products. The liquid aldehydes were purified through their bisulfite addition compounds and distilling them, under nitrogen, just before use [8]. The solid aldehydes were recrystallized from ethanol. HABR was prepared and purified by the reported method [1]. [²H]Benzaldehyde (PhCDO) was prepared by the reported method [9]. Acetic acid (AcOH) was refluxed with chromic oxide and acetic anhydride for 6 h and fractionated [10].

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 HABR (4.59g, 0.01 mol) were made up to 100 cm³ 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, filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was dissolved in a minimum quantity of conc. HCl and cooled in crushed ice to yield crude acid (2.0 g), which was recrystallized from hot water to produce pure benzoic acid (1.76 g, 96%, m.p. 121° C).

Stoichiometry

To determine the stoichiometry, HABR (2.30 g, 0.005 mol) and benzaldehyde (0.11 g, 0.001 mol) were made up to 100 cm³ 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 HABR 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 HABR. 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 followed up to 80% reaction by monitoring the decrease in absorption due to HABR at 394 nm. The pseudo-firstorder rate constants, k_{obs} , were computed from the linear (r > 0.995) least-squares plots of log [HABR] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within $\pm 3\%$.

RESULTS

Oxidation of the aromatic aldehydes by HABR results in the formation of the corresponding benzoic acids. Analyses of products and stoichiometric determinations indicate the following overall reaction.

$$2 \operatorname{ArCHO} + (\operatorname{CH}_2)_6 \operatorname{N}_4 \operatorname{Br}_4 + 2 \operatorname{H}_2 \operatorname{O} \longrightarrow$$

$$2 \operatorname{ArCOOH} + (\operatorname{CH}_2)_6 \operatorname{N}_4 + 4 \operatorname{HBr}^- \quad (1)$$

Rate Laws

The reaction was found to be first order with respect to the HABR. The individual kinetic runs yielded a linear plot between log [HABR] and time. Further, the pseudo-first-order rate constant, k_{obs} , is independent of initial concentration of HABR. The reaction rate increases with an increase in the concentration of the aldehyde but not linearly (Table I). The order with respect to aldehyde is less than one. A plot of $1/k_{obs}$ versus 1/[aldehyde] is linear with an intercept on the rate-ordinate. Thus a Michaelis-Menten – type kinetics are observed with respect to aldehyde. This leads to the postulation of the following overall mechanism [equations (2) and (3)] and the rate-law equation (4):

Aldehyde + HABR
$$\xrightarrow{\kappa}$$
 [Complex] (2)

$$[Complex] \xrightarrow{\kappa_2} Product \qquad (3)$$

Rate =

$$k_2 K$$
[Aldehyde][HABR]/(1 + K[Aldehyde]) (4)

Table I	Rate Constants for the Oxidation of	
Benzalde	hyde by HABR at 298 K	

10 ³ [HABR] (mol dm ⁻³)	[PhCHO] (mol dm ⁻³)	$\frac{10^4 k_{ m obs}}{({ m s}^{-1})}$
1.0	0.10	3.79
1.0	0.20	5.63
1.0	0.40	7.45
1.0	0.60	8.35
1.0	0.80	8.89
1.0	1.00	9.24
1.0	1.50	9.75
1.0	3.00	10.3
2.0	0.20	5.72
4.0	0.20	5.86
6.0	0.20	5.54
8.0	0.20	5.60
1.0	0.40*	7.51*

* Contained 0.001 mol dm⁻³ acrylonitrile.

The dependence of the rate on the concentration of the aldehyde studied at different temperatures and the values of K and k_2 were calculated from the double reciprocal plots. The thermodynamic parameters of the formation of the intermediate and the activation parameters of its decomposition were calculated from the values of K and k_2 , respectively, at different temperatures (Tables II and III).

Effect of Hexamethylenetetramine

The oxidation is not affected by an addition of hexamethylenetetramine (HXA) (Table IV).

Induced Polymerization of Acrylonitrile

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 I).

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 III) showed the presence of a substantial kinetic isotope effect ($k_{\rm H}/k_{\rm D} = 5.47$ at 298 K).

 Table II
 Formation Constants and Thermodynamic Parameters of the Substituted Benzaldehyde-HABR Complexes

		$K (dm^3)$	$mol^{-1})$		ΔH ΔS	
Subst.	288 K	298 K	308 K	318 K	$(kJ mol^{-1})$	$(J \text{ mol}^{-1} \text{ K}^{-1})$
Н	6.15	5.25	4.36	3.44	-17.1 ± 0.8	-36 ± 3
<i>p</i> -Me	5.92	5.12	4.25	3.45	-16.2 ± 0.7	-33 ± 2
<i>p</i> -OMe	5.78	4.96	4.10	3.35	-16.4 ± 0.6	-34 ± 2
<i>p</i> -F	6.05	5.24	4.42	3.52	-16.5 ± 0.8	-34 ± 3
p-Cl	5.76	4.82	4.05	3.62	-16.7 ± 0.5	-35 ± 2
$p-NO_2$	6.28	5.46	4.58	3.67	-16.1 ± 0.9	-33 ± 3
p-CF ₃	5.98	5.15	4.32	3.53	-15.8 ± 0.6	-32 ± 2
<i>p</i> -COOMe	5.85	5.02	4.26	3.56	-15.1 ± 0.4	-29 ± 4
<i>p</i> -Br	5.65	4.72	3.95	3.15	-16.7 ± 0.7	-36 ± 2
<i>p</i> -NHAc	5.81	5.02	4.18	3.33	-16.5 ± 0.8	-34 ± 3
p-CN	5.88	5.12	4.32	3.49	-15.6 ± 0.8	-31 ± 3
<i>p</i> -SMe	5.75	5.00	4.25	3.46	-15.3 ± 0.7	-30 ± 2
<i>p</i> -NMe ₂	6.03	5.28	4.46	3.48	-17.0 ± 0.9	-37 ± 3
<i>m</i> -Me	5.66	4.82	3.97	3.13	-17.5 ± 0.8	-38 ± 3
<i>m</i> -OMe	5.86	5.02	4.20	3.38	-16.4 ± 0.7	-34 ± 2
m-Cl	6.02	5.27	4.40	3.52	-16.0 ± 0.9	-32 ± 3
<i>m</i> -Br	5.89	5.10	4.32	3.42	-16.1 ± 0.9	-33 ± 3
<i>m</i> -F	5.29	4.50	3.86	3.06	-16.1 ± 0.8	-34 ± 3
$m-NO_2$	5.45	4.62	3.85	3.08	-16.9 ± 0.7	-36 ± 2
m-CO ₂ Me	5.58	4.75	4.02	3.29	-15.8 ± 0.5	-32 ± 2
m-CF ₃	6.03	5.28	4.46	3.48	-16.2 ± 1.0	-33 ± 4
m-CN	5.56	4.85	4.02	3.26	-16.1 ± 0.8	-33 ± 3
<i>m</i> -SMe	5.82	5.05	4.23	3.40	-16.2 ± 0.9	-33 ± 2
<i>m</i> -NHAc	5.32	4.85	3.78	3.10	-16.3 ± 0.6	-34 ± 2
o-Me	5.87	5.02	4.27	3.40	-16.2 ± 0.8	-33 ± 3
o-OMe	5.73	4.97	4.02	3.18	-17.2 ± 0.7	-37 ± 2
o-NO ₂	5.96	5.12	4.32	3.48	-16.0 ± 0.7	-33 ± 2
o-COOMe	5.93	5.16	4.38	3.47	-15.9 ± 0.9	-32 ± 3
o-NHAc	6.12	5.34	4.55	3.62	-15.5 ± 0.9	-31 ± 3
o-Cl	5.58	4.75	4.02	3.29	-15.8 ± 0.5	-32 ± 2
o-Br	6.10	5.26	4.38	3.51	-16.5 ± 0.8	-34 ± 3
o-I	5.68	4.86	4.05	3.20	-16.9 ± 0.8	-36 ± 3
o-Cn	6.05	5.24	4.42	3.52	-16.1 ± 0.9	-33 ± 4
o-SMe	6.13	5.28	4.43	3.64	-15.7 ± 0.7	-31 ± 2
<i>o</i> -F	5.89	5.10	4.32	3.42	-16.1 ± 0.9	-33 ± 3
o-CF ₃	6.15	5.32	4.42	3.60	-16.0 ± 0.7	-32 ± 3
PhCDO	5.70	4.80	3.93	3.15	-17.5 ± 0.6	-38 ± 2

		$10^4 k_2 ({\rm dm})$	$^{3} \text{ mol}^{-1} \text{ s}^{-1}$)		ΛH^*	Δ.S*
Subst.	288 K	298 K	308 K	318 K	$(kJ mol^{-1})$	$(J \text{ mol}^{-1} \text{ K}^{-1})$
Н	4.37	11.0	27.6	69.1	67.5 ± 0.9	-75 ± 3
<i>p</i> -Me	9.02	22.3	54.0	135	56.6 ± 0.9	-76 ± 3
<i>p</i> -OMe	17.4	42.5	98.3	240	63.8 ± 0.9	-77 ± 3
<i>p</i> -F	3.62	9.39	23.7	61.0	69.0 ± 0.8	-72 ± 3
p-Cl	2.40	6.22	15.6	40.3	68.8 ± 0.9	-76 ± 3
$p-NO_2$	0.18	0.53	1.46	4.19	77.0 ± 0.9	-69 ± 3
p-CF ₃	0.57	1.55	4.12	10.8	72.1 ± 0.7	-76 ± 2
<i>p</i> -COOMe	0.80	2.11	5.54	14.3	70.6 ± 0.9	-79 ± 3
<i>p</i> -Br	2.30	6.10	15.3	39.7	69.5 ± 0.8	-74 ± 3
<i>p</i> -NHAc	8.65	21.4	52.8	127	65.7 ± 0.7	-76 ± 2
p-CN	0.32	0.93	2.52	7.00	75.5 ± 0.8	-69 ± 2
<i>p</i> -SMe	10.5	25.5	62.0	150	64.9 ± 0.9	-77 ± 3
<i>p</i> -NMe ₂	78.4	185	410	945	60.4 ± 0.7	-76 ± 2
<i>m</i> -Me	8.10	19.8	47.0	112	64.0 ± 0.7	-82 ± 2
<i>m</i> -OMe	10.0	24.0	57.1	135	63.5 ± 0.8	-82 ± 3
<i>m</i> -Cl	1.72	4.38	11.3	28.2	68.5 ± 0.8	-80 ± 3
<i>m</i> -Br	1.63	4.23	10.2	25.8	67.2 ± 0.9	-84 ± 3
<i>m</i> -F	2.30	5.71	14.3	35.6	66.0 ± 0.9	-83 ± 3
$m-NO_2$	0.15	0.47	1.34	3.91	79.9 ± 0.6	-60 ± 2
m-CO ₂ Me	0.75	2.05	5.51	14.8	73.1 ± 0.9	-71 ± 3
$m-CF_3$	0.55	1.50	4.06	11.0	73.0 ± 0.8	-73 ± 3
m-CN	0.28	0.82	2.31	6.41	76.8 ± 0.7	-66 ± 2
<i>m</i> -SMe	6.60	15.6	38.2	90.2	64.0 ± 0.9	-84 ± 3
<i>m</i> -NHAc	5.82	14.0	34.2	81.3	64.5 ± 0.9	-84 ± 3
o-Me	30.6	70.2	165	381	61.5 ± 0.9	-80 ± 3
o-OMe	31.0	73.6	172	388	61.6 ± 0.5	-79 ± 2
$o-NO_2$	0.43	1.20	3.21	8.80	73.9 ± 0.9	-73 ± 3
o-COOMe	2.75	7.00	17.9	45.3	68.6 ± 0.9	-76 ± 3
o-NHAc	41.1	92.6	210	476	59.6 ± 0.9	-84 ± 3
o-Cl	7.81	19.3	46.8	110	64.6 ± 0.5	-81 ± 2
o-Br	9.93	23.3	56.7	133	63.5 ± 0.9	-83 ± 3
<i>o</i> -I	16.0	36.9	88.2	203	62.1 ± 0.9	-83 ± 3
o-CN	0.85	2.33	6.14	16.6	72.7 ± 0.9	-71 ± 3
o-SMe	39.2	93.3	215	482	61.1 ± 0.4	-79 ± 1
<i>o</i> -F	5.47	13.5	33.8	82.2	66.3 ± 0.8	-78 ± 3
o-CF ₃	5.45	13.3	32.9	80.4	65.8 ± 0.9	-80 ± 3
PhCDO	0.78	2.01	5.18	13.2	69.2 ± 0.9	-84 ± 3
$k_{ m H}/k_{ m D}$	5.60	5.47	5.33	5.23		

 Table III
 Rate Constants and Activation Parameters of the Decomposition of Substituted Benzaldehyde-HABR

 Complexes
 Complexes

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. To determine whether the solvent composition is affecting the formation constant, K, and/or rate constant, k_2 , the variation of rate with the concentration of benzaldehyde was studied in solutions of different compositions. The results (Table V) showed the rate constants,

Table IV Effect of Hexamethylenetetramine (HXA) on the Rate of Oxidation of Benzaldehyde by HABR ([HABR] = $0.001 \text{ mol } dm^{-3}$, [benzaldehyde] = $1.0 \text{ mol } dm^{-3}$, Temp. = 298 K)

103 [HXA] / mol dm-3	0.0	0.5	1.0	2.0	3.0	4.0
$10^4 k_{\rm obs}/{\rm s}^{-1}$	9.24	9.33	9.00	9.85	9.63	9.44

PhCHO	10	$k_{\rm obs}/{\rm s}^{-1}$	[at % Ac	OH (v/v)]
$(\text{mol } \text{dm}^{-3})$	25	40	50	60	72
0.1	18.3	7.52	3.79	1.85	0.68
0.2	27.5	11.1	5.63	2.77	1.01
0.4	36.8	14.6	7.45	3.68	1.34
0.6	41.4	16.4	8.35	4.13	1.49
0.8	44.2	17.4	8.88	4.41	1.60
1.0	46.1	18.1	9.24	5.00	1.65
K (dm ³ mol ⁻¹)	4.93	5.42	5.25	5.08	5.35
$10^4 k_2 (s^{-1})$	55.4	21.4	11.0	5.49	1.96

Table V Dependence of Rate on the Concentration of Benzaldehyde in Solvents of Different Compositions ([HABR] = 0.001 mol dm⁻³, Temp. = 298 K)

 k_2 , vary considerably while the formation constant, K, remained practically independent of solvent composition.

DISCUSSION

A plot of log k_2 at 288 K is linearly related to log k_2 at 318 K (r = 0.9993, slope = 0.879 \pm 0.005). The value of the isokinetic temperature is 1269 \pm 23 K. A linear isokinetic relationship is a necessary condition for the validity of linear free-energy relationships [11]. It also implies that all the aldehydes for which the rates of oxidation are so correlated are oxidized by the same mechanism.

In solution, HABR may dissociate to form molecular bromine as Eq. (5).

$$(CH_2)_6 N_4 Br_4 \rightleftharpoons 2 Br_2 + (CH_2)_6 N_4 \qquad (5)$$

The probable oxidizing species in a solution of HABR are, therefore, HABR itself, molecular bromine, and its acetolysis product. An addition of HXA should result in the suppression of decomposition of HABR and thus a decrease in the reaction rate if bromine is the reactive oxidizing species. Therefore, the lack of an effect of HXA and strict first-order dependence on HABR rule out both bromine and its acetolysis product as the reactive oxidizing species.

A perusal of UV-VIS spectra of HABR (0.001 mol dm⁻³) and an equivalent amount of bromine (0.002 mol dm⁻³), in acetic acid at \approx 293 K, showed that the difference in the spectra of HABR and bromine was not very striking but their optical densities showed variations (Fig. 1). HXA had no appreciable absorption in this range. Further, the spectrum of HABR did not show any change in the experimental time period (ca. 2 h). When a solution of HABR in acetic acid was evaporated to dryness under reduced pressure, HABR was recovered unchanged. This confirmed that HABR retained its integrity in acetic acid. Therefore, we propose that in this reaction, the reactive oxidizing species is HABR itself.

Solvent Composition Effect

The increase in the rate constant of decomposition of the intermediate complex 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 Grunwald-Winstein [12] Eq. (6).

$$\log k_2 = \log k_0 + mY \tag{6}$$



Figure 1 UV-VIS spectra of (A) 0.001 mol dm⁻³ HABR and (B) 0.002 mol dm⁻³ bromine; Temperature: 293 K; Solvent: Acetic Acid.

The plot of log k_2 versus Y is linear (r = 0.9996) with $m = 0.78 \pm 0.01$. The value of m suggests that there is a considerable charge separation in the transition state of the rate-determining step.

Correlation Analysis of Reactivity

A perusal of data recorded in Tables II and III results indicates that the formation constants, K, for the ArCHO-HABR complexes are not very sensitive to the nature of the substituent in the aldehyde substrate. The rate constant for the decomposition of the complex k_2 , however, showed considerable variation as a function of substituent in the reductant. Similar observations have been previously recorded in the oxidation of benzyl alcohols [13] and mandelic acids [14] by ceric ammonium nitrate, aliphatic alcohols [4] and diols [5] by HABR, substituted benzaldehydes by bis(2,2'-bipyridyl) copper(II) permanganate [15] and aliphatic alcohols by pyridinium fluorochromate [16] and pyridinium hydrobromide perbromide [17].

The effect of substituents on reactivity has long been correlated with the Hammett equation [18] or with dual substituent-parameter equations [19,20]. In the late 1980s, Charton [21] introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities.

$$\log k_2 = \mathcal{L} \sigma_1 + \mathcal{D} \sigma_d + \mathcal{R} \sigma_e + h \tag{7}$$

Here, *h* is the intercept term, 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).

$$\sigma_{\rm D} = \eta \sigma_{\rm e} + \sigma_{\rm d} \tag{8}$$

where 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. [21], to account for the steric effects.

$$\log k_2 = \mathcal{L} \sigma_{\mathrm{l}} + \mathcal{D} \sigma_{\mathrm{d}} + \mathcal{R} \sigma_{\mathrm{e}} + \mathcal{S} V + h \quad (9)$$

where V is the well known Charton's steric parameter based on Van der Waals radii [22].

The rate constants, k_2 , of the disproportionation of the intermediate of the oxidation of ortho-, meta-, and para-substituted benzaldehydes show excellent correlations in terms of the LDR/LDRS equations (Table VI). All three series of substituted benzaldehydes meet the requirement of a minimum number of substituents for analysis by LDR and LDRS equations [20]. We have used the standard deviation (sd), the coefficient of multiple determination, R^2 , and Exner's [23] parameter, ψ , as the measures of goodness of fit. The value of ψ is 0.01 except in one case where it is 0.02.

To test the significance of localized, delocalised,

Table VITemperature Dependence for the Reaction Constants for the Oxidation of Substituted Benzaldehydes byHABR

T/K	L	D	R	S	η	R^2	h
			Para-substituted				
288	-1.72 ± 0.01	-1.86 ± 0.01	-1.32 ± 0.04	_	0.71	0.9998	-3.36
298	-1.63 ± 0.01	-1.80 ± 0.01	-1.31 ± 0.02	_	0.73	0.9999	-2.96
308	-1.58 ± 0.01	-1.73 ± 0.01	-1.24 ± 0.02	_	0.72	0.9998	-2.56
318	-1.51 ± 0.01	-1.68 ± 0.01	-1.18 ± 0.03	_	0.70	0.9998	-2.16
			Meta-substituted	l			
288	-1.86 ± 0.02	-1.57 ± 0.01	-0.94 ± 0.08	_	0.60	0.9996	-3.35
298	-1.76 ± 0.01	-1.46 ± 0.01	-0.93 ± 0.02	_	0.64	0.9999	-2.96
308	-1.69 ± 0.02	-1.39 ± 0.01	-0.95 ± 0.07		0.68	0.9997	-2.56
318	-1.61 ± 0.02	-1.30 ± 0.01	-0.90 ± 0.08		0.69	0.9996	-2.17
			Ortho-substituted	1			
288	-1.76 ± 0.01	-1.66 ± 0.01	-1.23 ± 0.06	1.11 ± 0.01	0.74	0.9997	-3.37
298	-1.68 ± 0.01	-1.60 ± 0.01	-1.13 ± 0.04	1.03 ± 0.01	0.71	0.9999	-2.96
308	-1.62 ± 0.01	-1.55 ± 0.01	-1.15 ± 0.04	0.99 ± 0.01	0.74	0.9998	-2.56
318	-1.56 ± 0.01	-1.46 ± 0.02	-1.14 ± 0.05	0.94 ± 0.01	0.78	0.9998	-2.16

and steric effects in the *ortho*-substituted benzaldehydes, multiple linear regression analyses were carried out with (i) $\sigma_{\rm l}$, $\sigma_{\rm d}$, and $\sigma_{\rm e}$, (ii) $\sigma_{\rm d}$, $\sigma_{\rm e}$, and V, and (iii) $\sigma_{\rm l}$, $\sigma_{\rm e}$, and V. The absence of significant correlations equations [(10)–(12)] showed that all the four substituent constants are significant.

$$\log k_2 = (-1.41 \pm 0.36)\sigma_1 - (1.61 \pm 0.29)\sigma_d + (-3.07 \pm 1.65)\sigma_e - 2.22 \quad (10)$$

 $R^2 = 0.8570, \quad \text{sd} = 0.25, \quad n = 12, \quad \Psi = 0.31$

$$\log k_2 = (-1.70 \pm 0.42)\sigma_{\rm d} - (1.67 \pm 2.58)\sigma_{\rm e} + (0.73 \pm 0.48)v - 3.06 \quad (11)$$

$$R^2 = 0.6948, \quad \text{sd} = 0.37, \quad n = 12, \quad \Psi = 0.47$$

$$\log k_2 = (-1.86 \pm 0.66)\sigma_1 - (0.35 \pm 3.15)\sigma_e + (1.12 \pm 0.59)v - 2.26 \quad (12)$$

$$R^2 = 0.5430, \quad \text{sd} = 0.45, \quad n = 12, \quad \Psi = 0.58$$

Similarly, in the cases of the oxidation of *para*- and *meta*-substituted benzaldehydes, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant collinearity between the various substituent constants for the three series.

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 , increasing the electron-donating power of the substituent and its capacity to stablize a cationic species. The positive value of S indicates that the reaction is subject to steric acceleration by an ortho-substituent.

The percent contribution [21] of the delocalized effect, $P_{\rm D}$ is given by the following Eq. (13):

$$P_{\rm D} = \frac{(|{\rm D}| \times 100)}{(|{\rm L}| + |{\rm D}|)} \tag{13}$$

Similarly, the percent contribution of the steric parameter [21] to the total effect of the substituent, $P_{\rm S}$, was determined by using Eq. (14).

$$P_{\rm S} = \frac{(|{\rm S}| \times 100)}{(|{\rm L}| + |{\rm D}| + |{\rm S}|)} \tag{14}$$

The values of $P_{\rm D}$ and $P_{\rm S}$ are also recorded in Table VI. The value of $P_{\rm D}$ for the oxidation of *para*-substituted benzaldehydes is ca. 52%, whereas the corresponding values for the *meta*- and *ortho*-sobstituted aldehydes are ca. 45 and 47%, 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 from the *para*-position may be due to the twisting away of the aldehydic group from the plane of the benzene ring. The value of the $P_{\rm S}$ (ca. 24%) shows that the steric effect is significant in this reaction.

Mechanism

The cleavage of the aldehydic C-H bond in the ratedetermining step is confirmed by the presence of a substantial kinetic isotope effect. The failure to induce polymerization of acrylonitrile and the lack of effect of the radical scavenger on the reaction rate point against the operation of a one-electron oxidation, giving rise to free radicals. The negative values of the localization and delocalization electrical effects, that is, 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 hydride-ion transfer in the rate-determining step is suggested (Scheme I). The observed effect of solvent composition on the reaction rate also supports a mechanism involving the transfer of a hydride-ion. The benzoyl cation is reported to have a considerable ketene character [24] and is thus linear. The linear structure of acylium cation has been confirmed by X-ray crystallography also [25]. The change from sp^2 to sp results in steric relief. This relief will be greater in crowded reductants and is reflected in observed steric acceleration.

ArCHO + Br...Br...N <
$$\stackrel{\kappa}{\Longrightarrow}$$

Ar-C=O...Br...Br...N < $\stackrel{l}{\underset{H}{\overset{H}{\longrightarrow}}}$
Ar-C=O...Br...Br...N < $\stackrel{k_2}{\longrightarrow}$
H
Ar-C=O + HBr + Br⁻ + N <

$$Ar - \stackrel{+}{C} = O + H_2 O \xrightarrow{\text{fast}} ArCOOH + H^+$$

Scheme I

The observed negative entropy of activation supports the above mechanism also. As the charge separation takes place, in the transition state of the ratedetermining step, the charged 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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