

Separation of polar and steric effects in the oxidation of ortho-substituted benzaldehydes by N-bromobenzamide

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Abstract. The kinetics of the oxidation of twelve ortho-substituted benzaldehydes by N-bromobenzamide (NBB) to the corresponding benzoic acids have been studied. The reaction is first order with respect to NBB, the aldehyde and hydrogen ions. The addition of benzamide has no effect on the reaction rate. $(\text{PhCONH}_2\text{Br})^+$ has been postulated as the reactive oxidising species. The correlation of rates with the single substituent-parameter equations is poor. The correlation with Charton's equation of inductive, resonance and steric parameters is satisfactory. However, excellent correlations were obtained, when Charton's steric parameter was used along with Taft's σ_I and σ_R^+ substituent constants. The polar reaction constants have negative values. The reaction is subject to steric hindrance by the ortho-substituents.

Keywords. Ortho-effect; correlation analysis; benzaldehydes; N-bromobenzamide; oxidation.

1. Introduction

The correlation of the rate and structure of ortho-substituted aromatic compounds is complicated because of the possible interaction of the substituent with the ortho-site through the polar effects, proximity effects, hydrogen bonding etc. Attempts have been made to quantitatively separate and analyse the contribution of various parameters to the ortho-effect (Pavelich and Taft 1957; Jones 1979; Charton 1969, 1971, 1975; Aslem *et al* 1981). Of these, Charton's treatment (Charton 1971, 1975; Aslem *et al* 1981) is considered the best method because of its wider applicability in explaining the nature of the ortho-effect.

A kinetic study of the oxidation of meta- and para-substituted benzaldehydes by N-bromobenzamide (NBB) has been reported from this laboratory (Banerji 1986). The rates of oxidation showed excellent correlation in Taft's dual substituent-parameter (DSP) equation (Dayal *et al* 1972).

The kinetics of the oxidation of twelve ortho-substituted benzaldehydes by NBB is being presently reported. The rates were correlated with various single parameter and multi parameter equations.

2. Experimental

2.1 Materials

o-Methylthio-, *o*-cyano-, *o*-acetyl-benzaldehydes and methyl *o*-formylbenzoate were prepared by reported methods (Fuslon and Daniels 1926; Stewart *et al* 1960;

Traynelis and Boragnaes 1972). Rest of the aldehydes were commercial products and were purified by either recrystallisation or distillation under reduced pressure. NBB was prepared by the reported method (Banerji 1986).

2.2 Product analysis

The oxidation of the aldehydes results in the formation of the corresponding benzoic acids. The quantitative analysis of the product (Banerji 1986) leads to the isolation of the corresponding benzoic acids in 85–92% yields.

2.3 Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by keeping a large excess of the aldehyde over NBB. The reactions were followed iodometrically for up to 70% of the consumption of NBB. The pseudo-first-order rate constant, k_1 , was determined from the linear plots of $\log [\text{NBB}]$ vs. time. Duplicate kinetic runs indicate that the rate constants are reproducible to within $\pm 4\%$. The solvent was 1:1 (v/v) acetic acid–water. The other details have been described earlier (Banerji 1986).

3. Results and discussion

The oxidation of the substituted benzaldehydes lead to the formation of the corresponding benzoic acids



The reaction is first order with respect to the aldehyde, NBB and hydrogen ions (table 1). The experimental rate law, therefore, has the following form (2).

$$-d[\text{NBB}]/dt = k[\text{NBB}][\text{ArCHO}][\text{H}^+] \quad (2)$$

Table 1. Rate constants of the oxidation of *o*-methoxybenzaldehyde by NBB at 298 K.

[Aldehyde] mol dm ⁻³	10 ³ [NBB] mol dm ⁻³	[H ⁺] mol dm ⁻³	10 ⁵ k ₁ s ⁻¹
0.5	2.0	0.5	9.90
0.5	3.5	0.5	9.78
0.5	5.0	0.5	9.90
0.5	7.5	0.5	10.2
0.5	10.0	0.5	9.81
0.5	15.0	0.5	9.78
0.1	5.0	0.5	2.00
0.2	5.0	0.5	3.93
0.3	5.0	0.5	5.94
0.6	5.0	0.5	12.0
0.8	5.0	0.5	15.7
1.0	5.0	0.5	19.8
0.5	5.0	0.1	1.95
0.5	5.0	0.4	7.92
0.5	5.0	0.6	11.9
0.5	5.0	0.8	15.6
0.5	5.0	1.0	19.7

The reaction rate is not affected by added benzamide. Thus, hydrolysis and/or disproportionation of the *N*-halogenoamide is not involved in the oxidation process. The linear increase in the rate with acidity suggests that NBB is protonated to give a stronger electrophile and oxidant.



The specific rate constants, k , for the twelve benzaldehydes were determined at various temperature and the activation parameters were evaluated (table 2).

A linear isokinetic relationship between $\log k$ at 293 K and 313 K ($r = 0.9992$, slope = 0.7330) for the oxidation of benzaldehyde and the *ortho*-substituted benzaldehydes shows that all the compounds are oxidised by the same mechanism (Exner 1973). The value of isokinetic temperature is 385 K. A linear isokinetic relationship is considered as a necessary condition for the validity of linear free energy relationships (Exner 1973).

The rates at 298 K were analysed separately in terms of Taft's polar and steric parameter equations (Charton 1969). The results are expressed as (4) and (5). The values of σ_o and E_s were those given by Charton and Jones (Charton 1969; Jones 1979).

$$\log k/k_o = -4.37 \sigma_o, \quad (4)$$

$$R = 0.9561; \text{ s.d.} = 0.83; n = 8,$$

$$\log k/k_o = 1.03 E_s, \quad (5)$$

$$R = 0.4202; \text{ s.d.} = 0.48; n = 11,$$

where R is the coefficient of correlation, s.d. is the standard deviation and n is the number of data points.

The rates for NHCOMe and COOMe compounds were not considered for (5) and those of the NHCOMe, COOMe, CF_3 , CN and SMe were not considered for

Table 2 Rate constants and activation parameters of the oxidation of *o*-substituted benzaldehydes by NBB

Substituent	$10^6 \text{ k/dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$					ΔH^*	ΔS^*	ΔG^*
	293 K	298 K	303 K	308 K	313 K	kJ mol^{-1}	$\text{J mol}^{-1} \text{ K}^{-1}$	kJ mol^{-1}
H ^a	140	206	303	440	615	54.2 ± 0.3	-133 ± 0.9	94.0 ± 0.1
NO ₂	3.17	5.12	8.57	12.8	20.6	68.5 ± 0.8	-116 ± 2.6	103 ± 0.6
F	35.4	52.0	76.4	115	166	56.7 ± 0.5	-136 ± 1.7	97.4 ± 0.4
Cl	10.7	16.3	24.1	37.5	56.7	61.0 ± 0.8	-131 ± 2.5	100 ± 0.6
Br	9.86	16.0	75.5	41.3	61.0	67.5 ± 0.6	-110 ± 2.1	100 ± 0.5
I	7.12	10.5	15.8	22.1	32.6	55.2 ± 0.5	-154 ± 1.7	101 ± 0.4
OMe	291	396	580	835	1100	49.4 ± 1.0	-144 ± 3.2	92.3 ± 0.8
Me	90.0	130	186	265	370	61.5 ± 0.7	-146 ± 1.3	95.2 ± 0.6
NHCOMe	66.0	98.5	147	202	308	55.4 ± 0.9	-135 ± 2.9	95.9 ± 0.7
SMe	69.2	103	153	215	325	55.9 ± 0.7	-133 ± 2.2	95.8 ± 0.5
COOMe	8.77	12.9	19.6	27.1	40.0	55.1 ± 0.7	-153 ± 2.2	101 ± 0.5
CN	4.25	6.90	11.3	17.3	29.1	70.1 ± 0.9	-108 ± 3.0	102 ± 0.7
CF ₃	2.06	3.32	5.41	8.77	12.8	68.0 ± 0.9	-121 ± 2.8	104 ± 0.7

^aData of Banerji (1986)

(4), since the substituent constants were not available. The results of the correlation analyses show that the observed reactivity of the ortho-substituted benzaldehydes towards NBB is not compatible with either the size of the substituents or their Taft's polar substituents constants.

Since the single substituent-parameter equations did not yield satisfactory correlations, the rate data were analysed using Charton's method (Charton 1975). The rate constants were correlated with (6) and (7). In (6) and (7), σ_I , σ_R and V are inductive, resonance and steric substituent constants respectively and the values used were those compiled by Aslem *et al* (1981).

The results of the analysis of the rate data at 298 K in terms of (6) are given in (8).

$$\log k_{\text{ortho}} = \alpha \sigma_I + \beta \sigma_R + h \quad (6)$$

$$\log k_{\text{ortho}} = \alpha \sigma_I + \beta \sigma_R + \phi V + h \quad (7)$$

$$\log k = -1.91 \sigma_I - 1.86 \sigma_R - 4.19 \quad (8)$$

$$R = 0.9173; \text{ s.d.} = 0.29; n = 13$$

In multiple linear regression using (6), the coefficient of correlation is poor and the standard deviation is high. The absence of significant correlation with (6) leads to the conclusion that the electric effects alone are not sufficient to account for the ortho-substituent effect in this reaction.

The correlation with (7) was performed using the rate data obtained at 293 K, 298 K, 303 K, 308 K, and 318 K, assuming both orthogonal and planar conformations for *o*-NO₂ and *o*-COOMe groups. It was observed that the correlation is consistent with the orthogonal conformation of both *o*-NO₂ and *o*-COOMe groups. The coefficient of multiple correlation, R , varied between 0.95 and 0.97, and the standard deviation ranged from 0.17 to 0.22. The correlation obtained at 298 K is given in (9).

$$\log k = -2.07 \sigma_I - 1.91 \sigma_R - 0.76 V - 3.71, \quad (9)$$

$$R = 0.9746; \text{ s.d.} = 0.17; n = 13.$$

The correlations are thus just satisfactory and not even good.

It may be recalled that the rates of oxidation of para-substituted benzaldehydes (Banerji 1986) showed excellent correlation with Taft's σ_I and σ_R^+ substituent constants (Dayal *et al* 1972). Therefore, the rates of oxidation of the ortho-substituted benzaldehydes were correlated in a triparametric equation using Taft's σ_I and σ_R^+ along with Charton's steric parameter, V . The values of Taft's σ_I and σ_R^+ constants were those given by Ehrenson *et al* (1973) except that of the methylthio group. Ehrenson *et al* (1973) have reported that no single σ_R^+ value for methylthio group could be agreed to and listed a large number of possible values ranging from -0.64 to -0.96. We tried all the values separately and found that the best results are obtained when a σ_R^+ value of -0.66 was assigned to the SMe group. The deletion of the datum of SMe does not adversely affect the significance of the correlation. The series of ortho-substituted benzaldehydes meets the minimal basic requirements of substituents for analysis by Taft's DSP equation (Shorter 1982). The behaviour of *o*-NO₂ and *o*-COOMe groups are consistent with their orthogonal conformations.

The significance of the correlation was tested by means of an *F*-test (Wine 1966). The confidence level of the *F*-test is > 99.9%. The confidence level for the significance of ρ_I , ρ_R^+ and ϕ terms was obtained by a Student's *t*-test. The confidence level of the *t*-test is > 99.9%, indicating operation of significant inductive, resonance and steric effects.

To test the significance of all the three substituent constants, multiple linear regression analyses were carried out with Taft's σ_I and σ_R^+ , Taft's σ_I and *V* and with σ_R^+ and *V*. The absence of significant correlations [(10)–(12)] showed that all the three σ_I , σ_R^+ and *V* substituent constants are significant.

$$\log k = -2.03 \sigma_I - 0.96 \sigma_R^+ - 4.09, \quad (10)$$

$$R = 0.9244; \text{ s.d.} = 0.28; n = 13,$$

$$\log k = -4.28 \sigma_I - 0.79 V - 3.32, \quad (11)$$

$$R = 0.7972; \text{ s.d.} = 0.44; n = 13,$$

$$\log k = -1.29 \sigma_R^+ - 1.40 V - 4.33, \quad (12)$$

$$R = 0.8627; \text{ s.d.} = 0.37; n = 13.$$

There is no significant collinearity between Taft's σ_I and *V*, σ_R^+ and *V*, and between Taft's σ_I and σ_R^+ values ($r = 0.3766$, 0.3884 and 0.2336 respectively) for the 13 substituents.

The regression coefficients of σ_I and σ_R^+ terms are negative indicating that the electron-releasing groups accelerate the reaction and electron-withdrawing groups retard it. Similar results were obtained in the oxidation of para- and meta-substituted benzaldehydes also (Banerji 1986). The negative regression coefficient for the steric term indicates that the reaction is subject to steric hindrance by the ortho-substituents. The contribution of the resonance effect to the total polar effect was calculated by using (13) (Charton 1975).

$$P_R = \frac{100 \times |\rho_R^+|}{|\rho_I| + |\rho_R^+|} \quad (13)$$

The contribution of the steric parameter (Charton 1975) to the total effect of the substituents, P_S , was determined by using (14).

$$P_S = \frac{|\phi| \times 100}{|\rho_I| + |\rho_R^+| + \phi} \quad (14)$$

The values of P_R and P_S are also recorded in table 3. The values of $P_R \approx 38\%$. The values of P_R for the oxidation of para-substituted benzaldehydes (Banerji 1986) range from 54 to 60%. This shows that the balance of inductive and resonance effects is different for the ortho- and para- positions, resonance effects being less pronounced in the former case. This may be due to the twisting away of the aldehyde group from the plane of the benzene ring. The value of P_S shows that the steric effect is considerable in this reaction.

Table 3 Temperature dependence of the reaction constants.

Temperature (K)	ρ_I	ρ_R	ϕ	R	s.d.	P_R	P_S
293	-1.80	-1.09	-1.08	0.9976	0.06	37.7	27.2
298	-1.74	-1.06	-1.06	0.9969	0.06	37.9	27.5
303	-1.69	-1.03	-1.04	0.9955	0.07	37.9	27.7
308	-1.62	-1.02	-1.04	0.9946	0.08	38.6	28.3
313	-1.57	-0.99	-1.02	0.9936	0.08	38.7	28.5

The magnitude of all the reaction constants decreases with an increase in the temperature. This points to a decrease in the selectivity at higher temperatures. Out of the two polar effects, the decrease in the inductive effect is proportionately more. This is reflected in the gradual increase in the value of P_R . The contribution of the steric factor to the total effect of the *o*-substituent also increases gradually with the increase in temperature.

A perusal of the data recorded in table 2 showed that except *o*-methoxybenzaldehyde, all the other benzaldehydes reacted at a rate slower than that of the parent compound. The resonance substituent constant for the OMe group has a large negative value (-1.02), while the inductive and steric substituent constants have small positive values (0.27 and 0.36 respectively). Therefore, the rate-enhancement caused by the resonance effect is more than the combined retardation in the rate due to the inductive and steric effects. Thus a net rate-enhancement results.

The large negative polar reaction constants, a correlation involving σ_R^+ values and a substantial deuterium isotope effect observed (Banerji 1986) in the oxidation of benzaldehyde point to a transition state in which the positive charge is highly localized on the aldehydic carbon atom. The transition state thus approaches a carbocation in nature. This agrees with the hydride transfer mechanism proposed earlier (Banerji 1986). The presence of an *o*-substituent hinders the approach of the oxidizing reagent to the aldehydic group. This causes the steric retardation of the rate.

4. Conclusion

The following conclusions emerge from this study: (i) Charton's inductive and resonance substituent constants are not sufficient to account for the polar effects of the ortho-substituents in this reaction, (ii) inductive, resonance and steric effects play important roles in determining the *ortho*-effect in the oxidation, (iii) there is a strong resonance interaction between a developing positive charge and the *o*-group in the transition state, and (iv) the results support a hydride transfer mechanism.

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