Separation of Polar & Steric Effects in Oxidation of ortho-Substituted Benzyl Alcohols by Acid Permanganate

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The kinetics of the oxidation of ten ortho-substituted benzyl alcohols by acid permanganate have been studied. The reaction is first order each with respect to [alcohol], [permanganate] and [H⁺]. The correlation of the rates of oxidation with Charton's extended Hammett equation, involving inductive, resonance and steric parameters, is excellent. The polar reaction constants have negative values. The reaction is subject to steric acceleration by the ortho-substituents. The mechanistic aspects are discussed.

Correlation of rate and structure of ortho-substituted aromatic compounds is complicated because of the possible interaction of the substituent with the ortho site through polar effects, proximity effect, hydrogen bonding etc. Many attempts have been made to separate and analyse the contributions of various parameters to the ortho-effects[1-6]. Of these, Charton's treatment[4-6] is considered the best because of its wider applicability in explaining the nature of the ortho-effect.

Following our report[7] on the kinetics of the oxidation of para- and meta-substituted benzyl alcohols by permanganate ion in 1 : 4 (v/v) acetic acid-water in the presence of perchloric acid, we now report the kinetics of the oxidation of ortho-substituted benzyl alcohols. The rate data are correlated with various single parameter and multi parameter equations involving field, resonance and steric parameters.

Materials and Methods

o-Methylthio- and o-acetylamino-benzyl alcohols were prepared by the reported procedures[8,9]. The other alcohols were commercial products and were purified by recrystallization or distillation under reduced pressure.

Product analysis

To analyse the products, the alcohol (0.05 mol) and permanganate (0.005 mol), dissolved in 100 ml of 1 : 1 (v/v) acetic acid-water, in the presence of perchloric acid (0.2 mol dm⁻³), were allowed to stand for nearly 12 hr and then treated overnight with an excess of 2,4-dinitrophenylhydrazine (2,4-DNP). The solid 2,4-DNP derivative obtained was recrystallized from ethanol and found to be identical (m.p. and mixture m.p.) with an authentic sam-

ple of the corresponding benzaldehyde 2,4-dinitrophenylhydrazone; yield 87-93%.

Kinetic measurements

The reactions were followed under pseudo-first order conditions, i.e. [alcohol] ≫ [permanganate]. The reactions were followed spectrophotometrically at 525 nm on a kinetic spectrophotometer (Photoelectric Instruments, Jodhpur). The solvent was 1 : 4 (v/v) acetic acid-water. Sodium fluoride (0.005 mol dm⁻³) was added to each reaction mixture to suppress the reactions of $Mn(III)/Mn(IV)$. The other experimental details have been described earlier[7].

Simple and multivariate linear regressions were carried out by the least squares method using a Workhorse II (HCL) microcomputer.

Results and Discussion

The oxidation of ortho-substituted benzyl alcohols by acid permanganate leads to the formation of the corresponding benzaldehydes. At the end of the reaction, the solutions were colourless indicating that MnO_4^- has been reduced to Mn^{2+}. The overall reaction may be represented by Eq (1).

$$5 X\text{-}C_6H_4CH_2OH + 2MnO_4^- + 6H^+ \rightarrow$$
$$5 X\text{-}C_6H_4CHO + 2Mn^{+2} + 8H_2O \qquad \ldots (1)$$
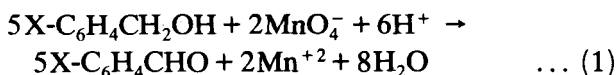
The rate of oxidation of alcohols is first order each in [oxidant], [alcohol] and [H⁺] (Table 1). Thus the experimental rate law has the form[7] (Eq 2).

$$-d[MnO_4^-]/dt = k[MnO_4^-][\text{alcohol}][H^+] \qquad \ldots (2)$$

The oxidation of $[\alpha,\alpha\text{-}^2H_2]$benzyl alcohol is known to exhibit a primary kinetic isotope effect[7].

The values of specific rate constant, k, for the oxidation of alcohols were determined at different tem-

Table 1 — Rate Constants for Oxidation of o-Bromo-
benzyl Alcohol by Acid Permanganate at 298 K

[Alcohol] (mol dm^{-3})	10^4 [MnO$_4^-$] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	$10^4 k_1$ (s^{-1})
0.05	2.0	0.05	4.93
0.05	5.0	0.05	4.85
0.05	7.5	0.05	4.90
0.05	10.0	0.05	4.78
0.05	15.0	0.05	4.85
0.05	20.0	0.05	4.90
0.01	5.0	0.05	1.00
0.03	5.0	0.05	2.87
0.06	5.0	0.05	5.82
0.08	5.0	0.05	7.83
0.12	5.0	0.05	11.5
0.15	5.0	0.05	14.4
0.05	5.0	0.03*	3.00
0.05	5.0	0.08*	7.76
0.05	5.0	0.10*	9.62
0.05	5.0	0.15*	14.7
0.05	5.0	0.20*	19.7
0.05	5.0	0.25*	24.0
0.05	5.0	0.30*	29.3

*I = 0.50 mol dm^{-3}

peratures and the activation parameters were evaluated (Table 2). The average errors in the values of $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ (at 298 K) are ± 1.5 kJ mol^{-1}, ± 3 J mol^{-1} K^{-1}, and 1 kJ mol^{-1} respectively.

A linear isokinetic relationship between log k at 298 K and 318 K ($r = 0.9912$, slope $= 0.9219$) for the oxidation of benzyl alcohol and the ten ortho-substituted benzyl alcohols shows that all the compounds are oxidised by the same mechanism[10]. The value of isokinetic temperature is 1587 K. Current views do not attach much physical significance to isokinetic temperature[11]; however, an isokinetic relationship is a necessary condition for the validity of linear free energy relationships[12].

The rates at 298 K were analysed separately in terms of Taft's polar and steric parameter equations[1], but the results failed to yield signifiant correlations. Thus the observed reactivity of the ortho-substituted benzyl alcohols towards permanganate is not compatible with either the size of the substituents or their Taft's polar substituent parameters.

Since the single-substituent parameter equations did not yield satisfactory correlations, the rate data were analysed using Charton's method[5]. The rate constants were correlated with Eqs (3) and (4). In these equations σ_I, σ_R and V are inductive, resonance and steric substituent constants respectively and values used were those compiled by Aslam et al[6].

The result of the analysis of the rate data at 298 K in the terms of Eq. (3) is given in Eq. (5).

$$\log k_{ortho} = \alpha \sigma_I + \beta \sigma_R + h \qquad \ldots (3)$$

$$\log k_{ortho} = \alpha \sigma_I + \beta \sigma_R + \phi V + h \qquad \ldots (4)$$

$$\log k = -2.34 \sigma_I - 1.51 \sigma_R - 2.54 \qquad \ldots (5)$$

$$R = 0.8215; SD = 0.44; n = 11.$$

In multivariate linear regression analysis using Eq. (3), the coefficient of correlation is poor and the standard deviation is high. The absence of significant correlation with Eq. (3) leads to the conclusion that electric effects alone are not sufficient to account for the ortho-substituent effect in this reaction.

The correlations with Eq. (4) were performed with the rate data obtained at 298 K, 303 K, 308 K, 313 K and 318 K and the results are presented in Table 3. The effect of o-NO$_2$ group is consistent with the orthogonal conformation.

The significance of the correlation was tested by means of an F-test[13]. The confidence level of the F-test was $> 99.9\%$. The confidence leavels for the significance of the α, β, and ϕ terms were obtained by means of a Student's t-test[13]. The significance level of the t-test was $> 99.9\%$, indicating the operation of significant field, resonance and steric effects. There was no significant correlation of the rates with σ_I and V, and with σ_R and V. The results show that this reaction belongs to the case 1 of the classification given by Charton[5].

The regression coefficients of σ_I and σ_R terms are negative indicating that electron-releasing groups accelerate the reaction and electron-withdrawing groups retard it, as was found for meta- and para-substituted benzyl alcohols[7]. The positive regression coefficient for the steric term indicates that the reaction is subject to steric acceleration by the ortho substituent.

The contribution of the resonance effect to the polar effect[5] was calculated using Eq. (6).

$$P_R = \frac{100 \times |\beta|}{|\alpha| \times |\beta|} \qquad \ldots (6)$$

The contribution of the steric parameter[5] to the total effect of the substituent, P_s, was determined using Eq. (7).

$$P_s = \frac{|\phi| \times 100}{|\alpha| + |\beta| + |\phi|} \qquad \ldots (7)$$

The values of P_R and P_s are also recorded in Table 3. The values of P_R indicate that the field effect is more

Table 2—Rate Constants and Activation Parameters for Oxidation of
ortho-Substituted Benzyl Alcohols by Acid Permanganate

Substituent	$10^3 \, k \, (\mathrm{dm^6 \, mol^{-2} \, s^{-1}})$ at temp. (K)					$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	$\Delta G^{\ddagger}$ (kJ mol^{-1})
	298	303	308	313	318			
H[a]	139	189	251	336	443	43.2	−116	77.3
NO$_2$	6.80	9.84	13.7	18.1	28.2	51.6	−113	85.2
Cl	138	170	262	320	438	43.7	−115	77.8
Br	194	268	330	517	600	43.2	−113	76.9
I	355	434	606	904	1080	43.9	−107	75.5
Me	2100	2570	3740	4200	5600	36.0	−118	71.1
OMe	815	1240	1700	2150	2600	41.7	−106	73.7
SMe	817	1050	1550	1830	2530	41.7	−107	73.4
NHCOMe	1200	1650	2210	2900	4010	44.2	−95	72.4
CF$_3$	167	245	305	400	540	42.0	−119	72.2
F	98.0	127	200	242	325	45.3	−112	78.6

[a]Data from ref. 7 except k at 298 K

Table 3—Temperature Dependence of Reaction Constants

Temp. (K)	α	β	ϕ	R	SD	P_R	P_s
298	−2.79	−1.82	1.54	0.9993	0.030	39.5	25.0
303	−2.75	−1.79	1.52	0.9991	0.034	39.4	25.1
308	−2.69	−1.83	1.43	0.9982	0.048	40.6	24.0
313	−2.63	−1.77	1.45	0.9984	0.042	40.2	24.8
318	−2.57	−1.72	1.37	0.9988	0.038	40.1	24.2

dominant than the resonance effect. The value of P_R is 50% for the *para* position by defination[4]. The observed value of P_R (40%) shows that the balance of the field and resonance effects is different for *ortho* and *para* positions, resonance effect being less pronounced in the former case. This may be due to the twisting away of the primary alcohol group from the plane of the benzene ring. The values of P_s show that the steric effect is considerable in the reaction. The magnitude of all the reaction constants decreases with increase in temperature indicating a decrease in the selectivity at higher temperature. The decrease is of similar order for all the three α, β, and ϕ reaction constants, reflected in almost constant values of P_R and P_s.

The reactivity of the *ortho*-substituted benzyl alcohols accords with the hydride-transfer mecahnism proposed earlier[7]. The large negative polar reaction constants support a transition state in which the positive charge is localized on the carbinol carbon atom. The steric acceleration of the rate by the *ortho*-substituents can be explained on the basis of high ground state energy level of the starting material. Since the crowding is relieved in the pro-

duct aldehyde as well as in the transition state leading to it, the transition state energy of the crowded (*ortho*-substituted) and uncrowded alcohols, do not differ much and steric aceleration, therefore, results.

Acknowledgement

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