

## Kinetics of Acid Bromate Oxidation of Benzyl Alcohols: Substituent Effect

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The oxidation of benzyl alcohol and substituted benzyl alcohols by bromate in the presence of mercury(II) ions follows the rate law:  $-d[\text{Br(V)}]/dt = k[\text{benzyl alcohol}][\text{Br(V)}]$ . Increasing acidity of the medium enhances the rate and the rate constant correlates well with the acidity function  $H_0$ . From the effect of ionic strength and dielectric constant the reaction has been found to be between a +ve ion and a dipole, and the values of  $r^0$  have been evaluated. Benzyl alcohol is oxidised by bromate at a rate 1.6 times faster than  $\alpha, \alpha$ -dideuteriobenzyl alcohol at 40°C. The order of reactivities among the studied benzyl alcohols is:  $p\text{-OCH}_3 > p\text{-CH}_3 > \text{-H} > p\text{-Br} > m\text{-NO}_2 > p\text{-NO}_2$ . Plot of  $\log k_2$  versus Hammett's substituent constant ( $\sigma$ ) is a curve (concave upward), which has been ascribed to the continuous change in the transition state with change in substituent in the substrate from electron-donating to electron-withdrawing group. The rate-limiting step involves both the C-H bond breaking and C-O bond formation in a concerted manner. However, the two processes are influenced in two different ways as revealed by the curved Hammett plot, the electron-withdrawing groups favouring bond-formation while the electron-donating groups facilitating bond-breaking.

Natarajan and Venkatasubramanian<sup>1</sup>, observed during the oxidation of secondary alcohols by bromate that the formation of alcohol bromate ester occurred in the rate-determining step and there was no  $\alpha\text{-C-H}$  bond cleavage. This contrasted with the behaviour of primary alcohols where the decomposition of the bromate ester was found to be<sup>2</sup> the rate-determining step and  $\alpha\text{-C-H}$  bond cleavage was also observed. Vijayalaxmi<sup>2</sup> also observed that, while the rate constants of all the primary alcohols studied fitted in a linear Taft's plot benzyl alcohol deviated substantially. This prompted us to undertake the oxidation of benzyl alcohol and substituted benzyl alcohols by bromate, in order to have an insight into the mechanism and the effect of substituents on the rate of reaction.

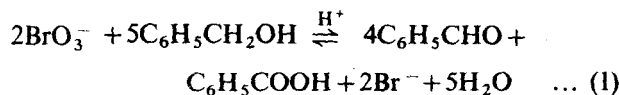
### Materials and Methods

All the chemicals used were of either Fluka or BDH(AR) quality and were further purified either by distillation or recrystallisation.  $\alpha, \alpha$ -Dideuteriobenzyl alcohol of isotopic purity  $92 \pm 5\%$  was prepared by reducing ethyl benzoate with lithium aluminium deuteride<sup>3</sup>. Absorption measurements were carried out with the Shimadzu spectrophotometer MPS-5000.

Solutions of Br(V) (or Br<sub>2</sub>) and substrate were thermally equilibrated for 1.5 hr in requisite proportions separately, mixed and the progress of the reaction was followed iodometrically to a starch end point. The rate constants were the average of two or more experiments, the accuracy being  $\pm 3\%$  or better. Solvent decomposition is negligible.

### Stoichiometry and product analysis

Though benzyl alcohol was inert to bromate oxidation under basic and neutral conditions, it was found to give benzaldehyde and benzoic acid as the final products of oxidation under conditions  $[\text{BrO}_3^-] < [\text{benzyl alcohol}]$ , in the presence of mineral acid and Hg(II) ions in accord with Eq. (1).



Benzoic acid was the only product when bromate was in excess. No brominated products were obtained in both the cases. Benzoic acid was determined spectrophotometrically at 235 nm, benzaldehyde by preparing its 2,4-DNP and bromide by AgNO<sub>3</sub> method.

### Results

The reduction product Br<sup>-</sup> ion leads to the formation of Br<sub>2</sub> which interferes in the oxidation of benzyl alcohol. When the alcohol is in excess, the plot of  $\log[\text{Br(V)}]$  against time gives two intersecting lines (Fig 1A), indicating that the reaction is composed of two successive reactions, an initial slow reaction followed by a faster reaction. Such an observation has also been recorded in NBS oxidation by Venkatasubramanian and coworkers<sup>4,5</sup> and the faster reaction has been attributed to bromine oxidation. In the present system appearance of a yellow colour after the reaction has proceeded to 25% perhaps may be due to liberated bromine. Further initial addition of KBr

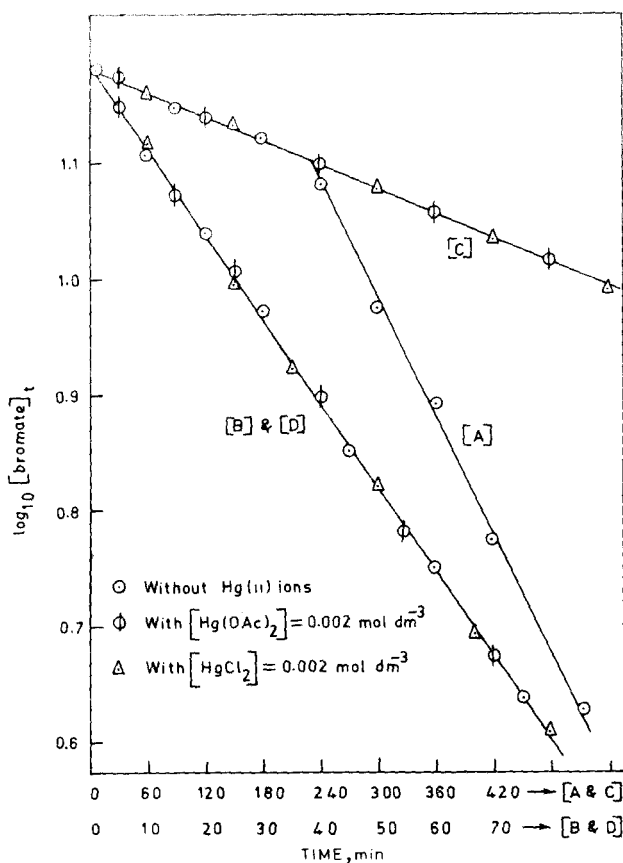


Fig. 1—Plots of  $\log[\text{bromate}]_t$  against time of bromate ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) oxidation of *p*-nitrobenzyl alcohol ( $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ); (A) without Hg(II) ions; (C) with  $[\text{Hg}(\text{OAc})_2]/[\text{HgCl}_2]$  ( $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) at  $0.2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ,  $45^\circ\text{C}$  and 40-60% (v/v) acetic acid-water; and (B) without Hg(II) ions; (D) with  $[\text{Hg}(\text{OAc})_2]/[\text{HgCl}_2]$  ( $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) at  $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ ,  $40^\circ$  and 30:70% (v/v) acetic acid-water.

completely suppresses the first part of the reaction and the rate constants are nearly the same as that obtained either for the second stage of the reaction or for the bromine oxidation under identical conditions. The rate of oxidation by bromate ion increases with increase in acid strength whereas that by  $\text{Br}_2$  decreases. While carrying out the oxidation of benzyl alcohols by bromate at  $1.0 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  and 30% (v/v) acetic acid, no break is observed in the first order plot (Fig. 1B), though the yellow colour due to bromine is present. The liberated bromine does not oxidise the substrate under these conditions whereas below  $0.20 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ , the oxidation by bromine is evident indicating that the oxidation by bromine is suppressed at higher acid concentrations an observation recorded earlier in the oxidations of benzyl alcohol<sup>6</sup>, benzaldehydes<sup>7</sup> and hydroxy acids<sup>8</sup> by bromine. It is interesting to note that the rate constant in the presence of bromide ion scavenger, such as mercuric acetate or chloride is the same as that obtained from the first part of the plot (Fig. 1A), below  $0.2 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . Different concentrations of added  $\text{Hg}(\text{OAc})_2/\text{HgCl}_2$  over a ten-fold range do not affect the rate constants and there is no change even in the presence of  $\text{NaOAc}/\text{KCl}$ . The reactions, therefore, are carried out with an optimum  $[\text{Hg}(\text{OAc})_2]$  of  $0.002 \text{ mol dm}^{-3}$ .

The reaction shows first order dependence in  $[\text{bromate}]$  since at constant ionic strength and at different concentrations of reactants pseudo-first order rate constants are independent of  $[\text{bromate}]_{\text{initial}}$  (Table 1). The plots of  $\log[\text{bromate}]$  versus time are also linear upto three half-lives. Second order rate

Table 1—Dependence of Rate on  $[\text{Bromate}]_{\text{initial}}$  in Bromate Oxidation of Unsubstituted and Substituted Benzyl Alcohols.

$[\text{Substrate}] = 0.01 \text{ mol dm}^{-3}$ ;  $[\text{Hg}(\text{OAc})_2] = 0.002 \text{ mol dm}^{-3}$ ;  $[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$ ; acetic acid-water = 30:70% (v/v); temp =  $40 \pm 0.01^\circ\text{C}$

Benzyl alcohol	$10^4 \times k_1 (\text{s}^{-1}) \times 10^4$ at $[\text{bromate}] (\text{mol dm}^{-3})$						
	2.00	4.00	8.00	10.00	12.00	16.00	20.00
—H	2.33 (1.47)	2.30 (1.46)	2.31 (1.48)	2.30 (1.46)	2.29 (1.46)	2.28 (1.47)	2.29 (1.46)
* <i>p</i> -OCH <sub>3</sub>	2.66	2.70	2.69	2.68	2.68	2.66	2.67
* <i>p</i> -CH <sub>3</sub>	2.44 (1.56)	2.45 (1.55)	2.46 (1.55)	2.46 (1.56)	2.45 (1.57)	2.44 (1.57)	2.42 (1.55)
<i>p</i> -Br	2.13	2.15	2.14	2.14	2.12	2.13	2.14
<i>m</i> -Br	1.39	1.40	1.40	1.42	1.41	1.42	1.40
<i>m</i> -NO <sub>2</sub>	1.24 (0.76)	1.22 (0.74)	1.24 (0.74)	1.23 (0.76)	1.22 (0.75)	1.24 (0.74)	1.23 (0.76)
<i>p</i> -NO <sub>2</sub>	1.19	1.20	1.21	1.19	1.19	1.20	1.18

\* At  $25^\circ\text{C}$ .

Values in parentheses are in perchloric acid ( $1.0 \text{ mol dm}^{-3}$ ) medium.

Table 2—Effect of Added Salts on  $k_2$  in the Benzyl Alcohol-Bromate System<sup>(a)</sup>

[NaClO <sub>4</sub> ] <sup>b</sup> (mol dm <sup>-3</sup> )	[NaHSO <sub>4</sub> ] <sup>b</sup> (mol dm <sup>-3</sup> )	$10^2 \times k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )						
		-H	* <i>p</i> -OCH <sub>3</sub>	* <i>p</i> -CH <sub>3</sub>	<i>p</i> -Br	<i>m</i> -Br	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>
0.25	—	1.52	1.67	1.64	1.24	1.00	0.80	0.77
—	0.25	2.34	2.80	2.63	2.22	1.45	1.47	1.36
0.50	—	1.89	1.92	1.88	1.85	1.22	1.02	0.90
—	0.50	2.42	3.15	3.02	2.42	1.80	1.89	1.77
0.75	—	2.31	2.46	2.39	2.10	1.86	1.26	1.13
—	0.75	3.04	3.62	3.54	3.32	2.10	2.01	1.93
1.00	—	2.95	3.01	2.92	2.82	2.00	1.81	1.75
—	1.00	3.54	4.00	4.12	3.85	3.23	2.95	2.80
1.50	—	3.88	4.11	4.01	3.28	3.01	3.71	1.89
—	1.50	4.76	5.14	5.37	4.77	4.12	3.89	3.65

<sup>a</sup>[BrO<sub>3</sub><sup>-</sup>] = 0.001 mol dm<sup>-3</sup> and other conditions as in Table 1.

<sup>b</sup>The effects of NaClO<sub>4</sub> and NaHSO<sub>4</sub> have been studied in perchloric acid and sulphuric acid medium respectively.

\* At 25°C.

Table 3—Dependence of Rate on [Acid] in Bromate Oxidation of Benzyl Alcohol<sup>a</sup>

[H <sub>2</sub> SO <sub>4</sub> ] (mol dm <sup>-3</sup> )	$10^2 \times k_2$ (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )						
	-H	* <i>p</i> -OCH <sub>3</sub>	* <i>p</i> -CH <sub>3</sub>	<i>p</i> -Br	<i>m</i> -Br	<i>m</i> -NO <sub>2</sub>	<i>p</i> -NO <sub>2</sub>
0.50	0.62 (0.36)	0.61	—	0.55	0.34	0.35	—
0.75	—	1.44	1.40	1.18	—	—	0.54
1.00	2.30 (1.46)	2.68	2.40	2.13	1.43	1.23	1.19
1.25	4.04	5.24	4.78	3.84	2.58	—	—
1.50	7.68 (4.57)	9.60	8.96	7.11	4.24	3.88	3.64
1.75	11.51	—	19.19	—	—	—	5.54
2.00	23.30 (11.17)	—	27.68	18.58	9.80	7.92	7.80
2.50	— (27.54)	—	—	—	—	19.82	18.42
<i>n</i> †	1.62 (1.57)	1.70	1.89	1.62	1.56	1.52	1.47

<sup>a</sup>I = 2.5 mol dm<sup>-3</sup> and other conditions as in Table 1

\* at 25°C

† Slopes obtained from Zucker-Hammett plot

Values in parentheses are obtained in perchloric acid medium.

constants have been calculated as  $k_2 = k_1/[\text{substrate}]$ , at different [substrate].

The second order kinetics have also been followed and the plots of  $1/[\text{BrO}_3^-]$  against time, under identical conditions are linear upto 75% completion, confirming the first order dependence of the reaction rate on both [bromate] and [benzyl alcohol]. Rates remain unchanged when reactions are carried out under nitrogen.

The value of  $k_2$  increases with increase in ionic strength (varied by adding NaClO<sub>4</sub> and NaHSO<sub>4</sub>). Although the concentrations employed in studying the effect of ionic strength on the reaction rate are such that the total ionic strength of the system is far greater than that permitted by the Debye-Hückel treatment

(Table 2), the results in terms of Brønsted-Bjerrum-Christiansen equation are consistent with the assumed reaction involving the positively charged species and a neutral molecule. Also the  $k_2$  values increase with decrease in dielectric constant of the medium. The plot of  $\log k_2$  and  $1/D$  is linear with a positive slope, supporting that the oxidation under study is of an ion-dipole type.

The rate of oxidation is also enhanced with increase in [acid] at constant ionic strength (Table 3), thus exhibiting acid catalysis. Unlike in primary<sup>2</sup> and secondary alcohols<sup>1</sup>, the plot of  $\log k_2$  against  $\log[H^+]$  is a curve the slope of which changes with increase in [acid]. But, the plots of  $\log k_2$  against  $H_o$ , rather than  $H_R$  are linear with slopes ranging from 1.5

Table 4—Thermodynamic Parameters for Acid Bromate Oxidation of Unsubstituted and Substituted Benzyl Alcohols  
 $[H_2SO_4] = 1.0 \text{ mol dm}^{-3}$ ;  $[BrO_3^-] = 0.001 \text{ mol dm}^{-3}$ ;  $[\text{substrate}] = 0.01 \text{ mol dm}^{-3}$ ;  $[Hg(OAc)_2] = 0.002 \text{ mol dm}^{-3}$ ; dielectric constant = 53.18; temp = 40°

Benzyl alcohol	$10^2 \times k_2$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$^* \Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$-\Delta S^\ddagger$ ( $\text{JK}^{-1} \text{ mol}^{-1}$ )	log <i>PZ</i>
<i>p</i> -OCH <sub>3</sub>	14.45	86.1 ± 5	81.9 ± 5	83.5 ± 5	-5 ± 6	13.0
<i>p</i> -CH <sub>3</sub>	8.22	63.1 ± 5	83.3 ± 5	60.5 ± 5	73 ± 6	9.0
-H	2.30	60.9 ± 3	86.7 ± 3	58.3 ± 3	91 ± 4	8.1
<i>m</i> -Br	1.42	59.8 ± 4	87.8 ± 4	57.2 ± 4	98 ± 4	7.7
<i>p</i> -Br	2.13	55.8 ± 3	87.1 ± 3	53.2 ± 3	108 ± 5	7.1
<i>m</i> -NO <sub>2</sub>	1.23	50.0 ± 3	88.3 ± 2	47.4 ± 3	131 ± 6	5.9
<i>p</i> -NO <sub>2</sub>	1.19	46.3 ± 3	88.3 ± 3	43.7 ± 3	143 ± 8	5.3

\* The observed range of experimental  $\Delta H^\ddagger$  is  $> 2\delta$ .

to 2.0 for all alcohols studied, indicating  $H_0$  as a more satisfactory measure rather than stoichiometric concentration of acid.

The rate constants for the oxidation of benzyl alcohol and  $\alpha, \alpha$ -dideuteriobenzyl alcohol (both  $0.01 \text{ mol dm}^{-3}$ ) with bromate ( $0.001 \text{ mol dm}^{-3}$ ) in 50-50% (v/v) acetic acid-water at 40°C are  $8.24 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $5.11 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively. The kinetic isotope effect ( $k_H/k_D = 1.6$ ) leads to the conclusion that the  $\alpha$ -C-H bond is ruptured in the rate-determining step.

Thermodynamic parameters have been computed from the data obtained from the temperature effect on the reaction rate and are recorded in Table 4.

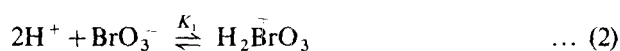
The presence of free radicals has been ruled out by the absence of polymerisation of acrylonitrile or acrylamide under nitrogen.

### Discussion

We have already established that the reaction under study is of an ion-dipole type. From the ionic strength and dielectric constant effects it can be suggested that the reaction is between a +ve ion and dipole. The dependence on [acid] indicates that the protonation of either bromate ion or alcohol may take place. The reacting species may thus be (a)  $H_2BrO_3^+$  (refs. 9, 10) and benzyl alcohol or (b)  $HBrO_3$  and the protonated benzyl alcohol.

The rates of oxidation of *n*-butanol, *sec*-butanol and *tert*-butanol under similar conditions follow the order: *n*-butanol  $>$  *sec*-butanol  $>$  *tert*-butanol. The rate constants of oxidation of methyl phenylcarbinol and dimethyl phenylcarbinol are found to be  $1.06 \times 10^{-4} \text{ s}^{-1}$  and  $0.24 \times 10^{-4} \text{ s}^{-1}$ , respectively under identical conditions. The order of reactivities is benzyl alcohol  $>$  methyl phenylcarbinol  $>$  dimethyl phenylcarbinol. If the protonated alcohol were the relative species, then the order should have been reversed. Hence the reaction between  $HBrO_3$  and protonated

benzyl alcohol is ruled out. This shows that the reacting species are neutral molecules of benzyl alcohol and  $H_2BrO_3$  obtained by the protonation of  $BrO_3^-$  (Eq. 2).

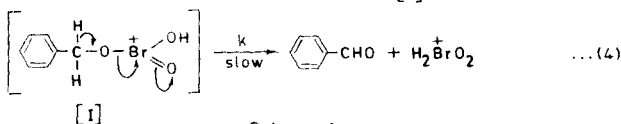
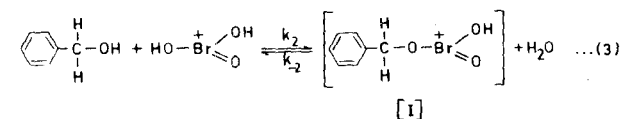


with a protonation constant of  $0.211^2 \text{ mol}^{-2}$  at 40° (ref. 11).

In view of the above facts, the mechanism of oxidation of benzyl alcohol to benzaldehyde may be represented by Scheme 1.

The dependence of the rate on the structure of the substrate and the presence of kinetic isotope effect ( $k_H/k_D = 1.6$ ) in the reaction show that Eq. (4) in the above mechanism is the rate-determining step which involves the cleavage of a C-H bond and is influenced by structural changes in the substrate as has been observed. On the other hand, if step (3) involving the formation of bromate ester is assumed to be the slow step, it will not be in accord with the observed kinetic isotope effect and the dependence of rate on the structure of the substrate. In the primary alcohol-bromate system<sup>2</sup>, an  $\alpha$ -C-H bond rupture in the rate-determining step has been suggested, but there seems to be no evidence for C-H bond rupture.

The formation of the bromate ester (I) is visualised through a nucleophilic attack at the hydroxyl group of the substrate by the oxidant species. The ester intermediate (I) is then assumed to breakdown concertedly in a slow step (4) producing aldehyde.  $Br(III)$  thus formed in step (4) reacts with either alcohol



Scheme 1

or aldehyde in fast steps to give bromide as the end product. Since the bromide can react with the unreacted bromate to form molecular bromine, initial addition of  $\text{Hg}(\text{OAc})_2$  is justified.

If the steady state concentration of ester intermediate is invoked, the above mechanism leads to the rate expression (5)

$$-d[\text{Br(V)}]/dt = Kk[\text{C}_6\text{H}_5\text{CH}_2\text{OH}][\text{BrO}_3^-]H_0 \dots (5)$$

where  $K = K_1k_2/k_{-2} + k$

The mechanism is supported by the observed rate law, first order dependence each in [oxidant] and [substrate], and the primary kinetic isotope effect. This is further corroborated by the solvent influence on the reaction rate. The intermediate ester is less polar than the reactants due to dispersal of charge, hence decreasing polarity of the solvent is expected to stabilize the bromate ester in preference to the reactants thereby enhancing the rate. Such a solvent influence has actually been observed.

A linear plot between  $\log PZ$  and  $1/\sqrt{E_a}$  (Fig. 2A) indicates that the Arrhenius parameters are controlling the reaction. The plot of  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  is linear (Fig. 2B) and the isokinetic temperature,  $\beta = 260 \text{ K}$ , which is less than the experimental range of temperature (298 to 323 K). From the value of  $\beta$  it is

evident that the reaction is entropy-controlled. This is further supported by  $\Delta S^\ddagger$  values where the entropy of activation for the fastest reaction is the lowest (magnitude) and vice versa. The Exner<sup>12</sup> plot of  $\log k_{323\text{K}}$  against  $\log k_{303\text{K}}$  is linear (Fig. 2C) suggesting that, all the substrates are being oxidised by an identical mechanism. The isokinetic temperature determined from the slope (1.33) of Exner's plot is 256 K which is fairly in good agreement with that obtained from the isokinetic relationship (260 K).

The rates of oxidation of various substrates are in the order: *p*-methoxy > *p*-methyl > *-H* > *p*-bromo > *m*-bromo > *m*-nitro > *p*-nitro, i.e. a faster reactivity for electron-releasing substituents compared to the electron-withdrawing substituents. The energy and entropy of activation also follow the same sequence. Correction of  $\log k_2$  with Hammett's substituent constant ( $\sigma$ ) gives a smooth curve as shown in Fig. 3. Such a curve is obtained at all temperatures studied and it remains unchanged in shape even when  $\log k_2$  is correlated with either  $\sigma^+$  or  $\sigma^-$  instead of  $\sigma$ . Hence the deviation from linearity in Hammett's plot is not due to change in  $\sigma$ .

The curvature may be due to any of the following three factors: (i) a gradual change in the reaction mechanism when one passes from electron-donating to electron-withdrawing substituents, (ii) a change in the rate-determining step with change in the nature of the substituent and (iii) a change in the nature of the transition state.

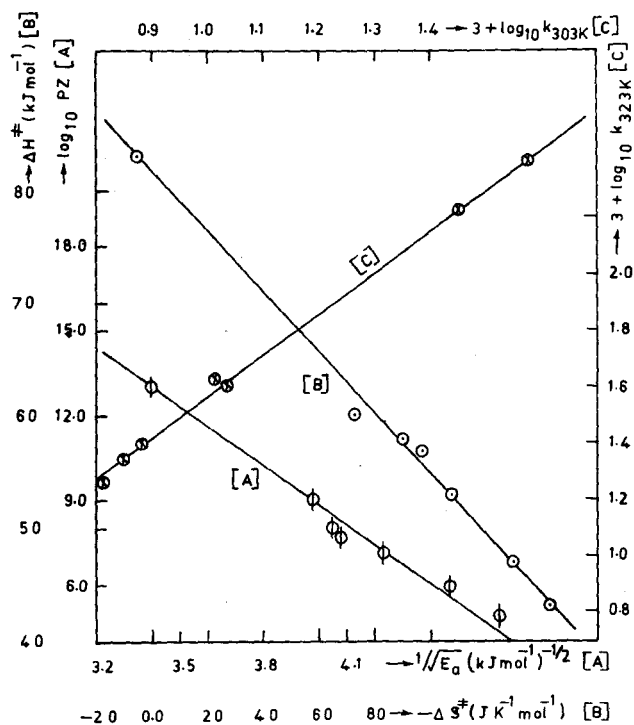


Fig. 2—Plots of (A)  $\log_{10} PZ$  against  $1/\sqrt{E_a}$  at  $40^\circ\text{C}$ ; (B)  $\Delta H^\ddagger$  against  $\Delta S^\ddagger$  at  $40^\circ\text{C}$  and (C)  $\log k_{323\text{K}}$  against  $\log k_{303\text{K}}$  at dielectric constant of the medium = 53.18, [sulphuric acid] =  $1.00 \text{ mol dm}^{-3}$ , [substrate] =  $0.01 \text{ mol dm}^{-3}$ , [bromate] =  $0.001 \text{ mol dm}^{-3}$  and [mercuric acetate] =  $0.002 \text{ mol dm}^{-3}$ .

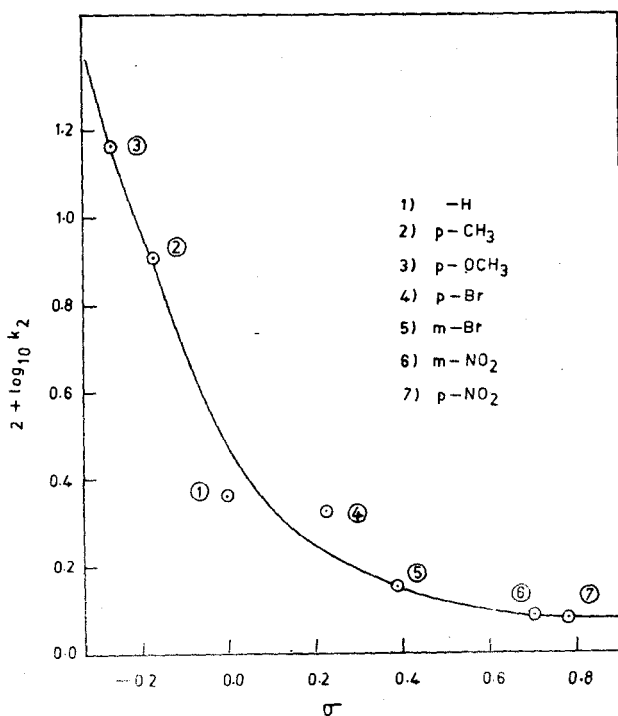


Fig. 3—Plot of  $\log k_2$  against Hammett's substituent constants ( $\sigma$ ) at  $40 \pm 0.01^\circ\text{C}$  [Experimental conditions as in Table 4]

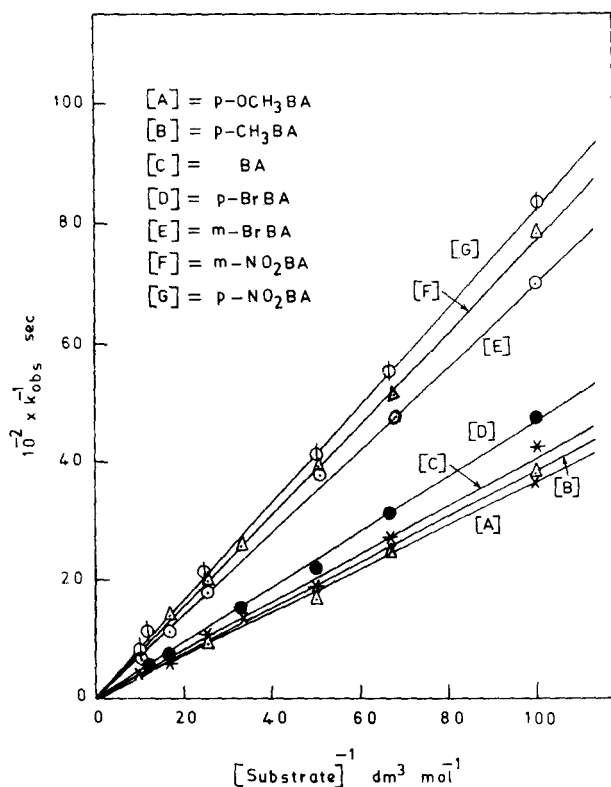


Fig. 4 -- Representative Michaelis-Menten plots for benzyl alcohols at  $40 \pm 0.01^\circ\text{C}$  [Other conditions as in Fig. 2]

In the present case the linearity obtained in the Exner's plot and the isokinetic plot (Fig. 2B and C) and nearly constant values of  $\Delta G^\ddagger$  (Table 4) indicate that probably same mechanism operates with all the substrates. The curvature in  $\rho$ - $\sigma$  plot cannot be attributed to the change in the rate-determining step, since the Michaelis-Menton's plot with all the substrates does not yield an intercept (Fig. 4).

The observed curvature in the Hammett's plot (Fig. 3) may be due to change in the transition state and many instances are available in literature<sup>13-15</sup> in support of this assumption.

In the proposed Scheme 1, the rate-limiting step(4) involves both C-H bond breaking and C-O bond formation. However, these two processes are influenced in two different ways. With electron-withdrawing groups C-O bond formation may be more extensive than C-H bond breaking and the

electron-donating group probably lead to a transition state in which the C-H bond breaking has progressed to a greater extent than C-O bond formation, thus resulting in a curvature.

The activation parameters, viz  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  also support this view. The values of  $\Delta H^\ddagger$  are seen to decrease with increasing electron-attracting ability of the substituents (Table 4). At the same time  $\Delta S^\ddagger$  becomes more negative, reflecting a more heavily solvated transition state. For the electron-attracting group like nitro the bond formation is apparently more important, since substitution of *m*-NO<sub>2</sub> decreases  $\Delta H^\ddagger$ , resulting in an increase in solvation.

The values of frequency factor (*PZ*) given in Table 4 show a significant variation with the nature of the substituent on the phenyl moiety. The variation in *PZ* may be attributed to solvation of benzyl alcohols to different degrees. This is also evident from the entropy values.

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