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Kinetics and Mechanism of the Oxidation of Substituted Benzyl Alcohols by Chloramine-T in Acid Solution

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The oxidation of benzyl alcohol and eight monosubstituted benzyl alcohols by chloramine-T in acid solution has been studied. The reaction is of first order with respect to the concentration of alcohol and oxidant. The rate constant is proportional to the square of hydrogen ion concentration. The kinetic isotope effect (k_H/k_D) is 4.13 at 303 K. The solvent isotope effect ($k(D_2O)/k(H_2O)$) is 5.93 at 303 K. The activation enthalpies and entropies are linearly related. The reaction exhibited a reaction constant $\rho^+ = -2.08 \pm 0.08$ at 303 K. The active oxidizing species is considered to be $(H_2OCl)^+$. A mechanism involving transfer of a hydride ion to the oxidant is suggested.

Chloramine-T (CAT) acts as an oxidizing agent in both acid and alkaline solutions. The kinetics of the oxidation by alkaline CAT has received much attention.[1,2] The reports on the oxidation by CAT in acid solutions are rather scanty. Mushran *et al.*[3] studied the oxidation of some primary alcohols in the pH range 4.0—5.2. Mahadevappa and Naidu[4] reported the oxidation of allyl alcohol by CAT in aqueous HCl medium.

This paper deals with the oxidation of monosubstituted benzyl alcohols by CAT in acid solution and the evaluation of the reaction constant. During the course of this investigation the oxidation of 2-propanol in acid solutions was reported by Natarajan and Thiagarajan.[5] Their results are also discussed.

Results

The oxidation of benzyl alcohol by CAT in acetic acid–water (1 : 1 (v/v)), in the presence of perchloric acid, results in the formation of benzaldehyde as the main product.

Stoichiometry. Excess of CAT was allowed to react with 0.02 M benzyl alcohol at various acidities. For some runs the carbonyl product was determined using an excess of benzyl alcohol. Values of Δ[CAT]/Δ[alcohol] and Δ[CAT]/Δ[benzaldehyde] in Table 1 show that the overall reaction corresponds to

$$PhCH_2OH + MeC_6H_4SO_2NCl^- \rightarrow PhCHO + MeC_6H_4SO_2NH_2 + Cl^-. \quad (1)$$

Rate Laws. The rate laws were determined for the oxidation of benzyl alcohol and the eight monosubstituted benzyl alcohols. Since the results are similar, only those of benzyl alcohol are reproduced.

Table 1. Stoichiometry of the oxidation of benzyl alcohol (BA) by CAT

$[H^+]$M	Δ[CAT]/Δ[BA]	Δ[CAT]/Δ[Benzaldehyde]
0.2	1.01	—
0.5	0.97	—
1.0	0.96	—
1.2	1.03	—
0.5	—	0.91
1.0	—	0.88
1.2	—	0.91

Table 2. Oxidant dependence of the reaction rate

[BA] 0.20 M $[H^+]$ 0.5 M Temp 303 K

[CAT] M	0.01	0.02	0.04	0.06
$10^7\ k_1$ s^{-1}	3.15	3.20	3.15	3.11

Table 3. Substrate dependence of the reaction rate

[CAT] 0.02 M $[H^+]$ 0.5 M Temp 303 K

[BA] M	0.10	0.20	0.40	0.60	1.0
$10^7\ k_1$ s^{-1}	1.60	3.15	6.31	9.50	15.8

Table 4. Acidity dependence of the reaction rate

[BA] 0.20 M [CAT] 0.02 M Temp 303 K

$[H^+]$ M	0.1	0.2	0.5	0.8	1.0
$10^8\ k_1$ s^{-1}	1.29	5.10	31.5	80.0	125
$10^6\ k_1/[H^+]^2$	1.29	1.27	1.26	1.25	1.25

When the alcohol is in excess, the rate of disappearence of CAT follows the first-order rate laws. The rate constant is independent of the initial concentration of CAT (Table 2), confirming that the order with respect to CAT is one. The reaction is of first order with respect to the alcohol concentration also (Table 3). The rate constant is proportional to the square of hydrogen ion concentration (Table 4). The rate law for the oxidation is therefore given as follows:

$$\text{Rate} = k[\text{CAT}][\text{Alcohol}][H^+]^2. \quad (2)$$

The rate law differs from those reported for the oxidation of primary alcohols and allyl alcohol in aqueous solutions.[3,4] However, it agrees with the results of Natarajan and Thiagarajan[5] obtained in the oxidation of 2-propanol in acetic acid–water (1 : 4 (v/v)).

The rate constants for the oxidation of benzyl alcohol and α,α-dideuteriobenzyl alcohol in acetic acid–water (1 : 1 (v/v)) at 303 K, are $10^6\ k = 6.32$ and 1.53 $l^3\,m^{-3}\,s^{-1}$, respectively. The kinetic isotope effect (k_H/k_D) is 4.13 at 303 K.

Benzyl alcohol was oxidized in 95% deuterium oxide and the rate constant was $16.7 \times 10^{-6}\ l^3\,m^{-3}\,s^{-1}$ at 303 K. The rate constant under similar conditions in water is $2.81 \times 10^{-6}\ l^3\,m^{-3}\,s^{-1}$. The solvent isotope effect ($k(D_2O)/k(H_2O)$) is 5.93 at 303 K. In this set of experiments no acetic acid was present.

The oxidation of benzyl alcohol in an atmosphere of nitrogen failed to induce polymerisation of acrylo-

Table 5. Oxidation of benzyl methyl ether by chloramine-T at 303 K in 1 : 1 (v/v) acetic acid-water

[Substrate] M	[CAT] M	[H$^+$] M	10^7 k_1 s^{-1}
0.10	0.02	1.0	5.01
0.20	0.02	1.0	10.0
0.40	0.02	1.0	20.2
0.20	0.01	1.0	10.1
0.20	0.04	1.0	9.90
0.20	0.02	0.5	2.43
0.20	0.02	0.8	6.50
0.20	0.02	1.6	26.2

$10^6 k = 5.04 \pm 0.07$ l^3 mol^{-3} s^{-1}.

Table 6. rate constants for the oxidation of substituted benzyl alcohol by chloramine-T

Substituent	10^8 k l^3 mol^{-3} s^{-1}				
	298	300	308	313	318 K
H	431	631	900	1410	1780
m-Me	596	850	1200	1680	2290
p-Et	1740	2400	3230	4360	5820
p-Me	1950	2630	3540	4680	6200
p-OMe	20000	23900	30200	37100	—
p-Cl	278	363	556	759	1050
m-Br	51.3	95.5	123	185	275
p-NO$_2$	8.95	15.1	24.8	40.3	64.6
m-NO$_2$	15.8	26.3	42.7	68.4	1.9

Table 7. Activation parameters for the oxidation

Substituent	H	*m*-Me	*p*-Et	*p*-Me	*p*-OMe
ΔH^* kJ mol^{-1}	55.4	52.0	47.0	45.8	34.4
$-\Delta S^*$ J mol^{-1} K^{-1}	165	169	182	184	203

Substiutent	*p*-Cl	*m*-Br	*p*-NO$_2$	*m*-NO$_2$
ΔH^* kJ mol^{-1}	59.6	66.4	77.7	75.6
$-\Delta S^*$ J mol^{-1} K^{-1}	158	145	123	124

nitrile. Thus a hydrogen abstraction giving rise to free radicals is unlikely.

The oxidation of benzyl methyl ether also follows similar rate laws, the ease of its oxidation being comparable to that of benzyl alcohol (Table 5).

The oxidation of benzyl alcohol and the monosubstituted benzyl alcohols was determined at various temperatures (Table 6) and the activation parameters were evaluated (Table 7). The average errors in the values of ΔH^* and ΔS^* are ± 4 kJ mol^{-1} and ± 11 J mol^{-1}K^{-1}, respectively.

Discussion

Chloramine-T is a strong electrolyte dissociating into ions in aqueous solution;[6)]

$$\mathrm{RNClNa} \rightleftharpoons \mathrm{RNCl^-} + \mathrm{Na^+}, \tag{3}$$

where R=*p*-MeC$_6$H$_4$SO$_2$. The anion is protonated in acid solution to give the acid. No free acid could be isolated since it undergoes hydrolysis;[4)]

$$\mathrm{RNCl^-} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{RNHCl} + \mathrm{H_2O}, \tag{4}$$

$$\mathrm{RNHCl} + \mathrm{H_2O} \rightleftharpoons \mathrm{RNH_2} + \mathrm{HOCl}. \tag{5}$$

However, the second order dependence on acidity and the magnitude of the solvent isotope effect suggest that a protonated species is involved in the rate-determining step. Thus Eq. 5 is followed by a protonation

$$\mathrm{HOCl} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{H_2OCl^+} + \mathrm{H_2O}. \tag{6}$$

This accords well with the suggestion of earlier workers[4,5)] that in the oxidation by CAT in acid solution, the active oxidizing species is (H$_2$OCl)$^+$. Natarajan and Thiagarajan[5)] have suggested an alternate oxidizing species (RNH$_2$Cl)$^+$ in the oxidation of 2-propanol. Some earlier workers[7)] however, have preferred HOCl as the oxidizing species in a weak acid solution. The sulfonamide group is not likely to be sufficiently basic to accept another proton.

The kinetic isotope effect, $k_\mathrm{H}/k_\mathrm{D} = 4.13$, is very close to the value obtained in the oxidation of benzyl alcohol by bromine.[8)] The mechanistic conclusion is that the rate-determining step involves a C–H bond rupture from the carbinol carbon.

The difference in the rate laws of the oxidation of allyl alcohol[4)] and benzyl alcohol can be explained on the basis of different reactivities of the two alcohols towards the oxidant. In the case of allyl alcohol, the oxidation is a fast step following the slow formation of HOCl or H$_2$OCl$^+$ (depending upon the reaction conditions), wheras the oxidation of benzyl alcohol is solwer than the formation of the oxidizing species. Thus the oxidation of benzyl alcohol should be slower than that of allyl alcohol. This is actually the case. The oxidation of allyl alcohol is so fast that it has been studied at 273 K.

The activation enthalpies and entropies of the nine compounds are linearly related ($r = 0.991$). The correlation was tested and found genuine by applying Exner's criterion.[9)] The isokinetic temperature computed from the plot is 540±35 K. Current views do not attach much physical significance to isokinetic temperature,[10)] though a linear relation is usually a necessary condition for the validity of the Hammett equation.

No systematic study of the effect of substituents on the oxidation of alcohols by CAT is available. The rates of the oxidation of monosubstituted benzyl alcohols correlate well with σ^+ values ($r = 0.996$). The reaction constant was $\rho^+ = -2.08 \pm 0.08$ at 303 K. The negative value of the reaction constant indicates an electron-deficient carbon center in the transition state.

Natarajan and Thiagarajan[5)] have suggested an initial formation of a hypochlorite in the oxidation of 2-propanol. However, the ester formation is unlikely in view of the almost equal ease of the oxidation of benzyl alcohol and its methyl ether. The large negative reaction constant thus arises only out of the differential effects of the substituents in the rate-determining step. The correlation with σ^+, together with the substantial deuterium isotope effect suggest a considerable carbonium ion character in the transition state.

From the results, a mechanism involving transfer of a hydride ion from the alcohol to the oxidant is suggested. Simultaneous release of hydroxylic proton is unlikely in view of the observed solvent isotope effect and the magnitude of the reaction constant. The polar requirement on the alcohol carbon for hydride release from C–H is opposite to that for proton release from O–H, the reaction constant being likely to be nearly zero in a concerted process:

$$\mathrm{PhCH_2OH + (H_2OCl)^+ \xrightarrow{slow} Ph\overset{+}{C}HOH + H_3O^+ + Cl^-} \quad (7)$$

$$\mathrm{Ph\overset{+}{C}HOH \xrightarrow{fast} PhCHO + H^+}. \quad (8)$$

It is of interest to recall here that in the oxidation of substituted benzyl alcohols by bromine[8)] and acid permanganate,[11)] which involve rate-determining transfer of a hydride ion, the reported values of ρ are -2.3 and -1.76 respectively.

Experimental

Materials. The preparation and specification of the alcohols used have been described earlier.[11)] Isotopic purity of α,α-dideuteriobenzyl alcohol, as determined by NMR, was 92±5%. Commercial benzyl methyl ether was purified by distillation from all glass apparatus. Aqueous solution of chloramine-T (E. Merck, pro analysi) was stored in dark bottles. Acetic acid was purified by the usual methods.[12)] Perchloric acid was used as a source of hydrogen ions.

Product Analysis. Benzaldehyde was characterized and estimated by the isolation of its 2,4-dinitrophenylhydrazone.

Kinetic Measurements. The reactions were carried out under pseudo-first-order conditions by keeping a large excess of the alcohol over CAT. The temperature was kept constant to ±0.1 K. The solvent used was acetic acid-water (1 : 1 (v/v)), unless otherwise stated. The reactions were followed iodometrically up to nearly three half-lives, the reactions being found smooth. The rate constants were evaluated from the plots of log [oxidant] against time and were reproducible within ±3%. Preliminary experiments showed that the oxidation is not sensitive to ionic strength, hence no attempt was made to keep it constant. The rate for the deuterated alcohol was corrected for the ordinary alcohol present. The usual concentration of the reactants in the reaction mixture was: the alcohol 0.05—1.0 M, CAT 0.01—0.08 M, and perchloric acid 0.1—1.5 M.

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