Kinetics and Mechanism of the Oxidation of Substituted Benzyl Alcohols by Sodium *N*-Chlorobenzenesulphonamide

By **Jogeshwar Mukherjee** and **Kalyan K. Banerji,*** Department of Chemistry, University of Jodhpur, Jodhpur 342001, India

The kinetics of the oxidation of benzyl alcohol and eight monosubstituted benzyl alcohols by sodium *N*-chlorobenzenesulphonamide in acid solution has been studied. The reaction is of first order with respect to each of the oxidant, the alcohol, and the acidity. The primary kinetic isotope effect (k_H/k_D) is 4.41 ± 0.08 at 308 K. The solvent isotope effect (k_{H_2O}/k_{D_2O}) is 0.413 at 303 K. The activation enthalpies and entropies are linearly related. The reaction exhibited a reaction constant ρ^+ of −2.14 at 298 K. The probable oxidising species is $PhSO_2NHCl$. A mechanism involving transfer of a hydride ion to the oxidant is suggested.

WHEN halogens, except fluorine, are joined to nitrogen or oxygen they acquire a positive oxidation state. Such compounds are known as positive halogen compounds and are used as oxidising and halogenating agents. Well known among them are chloramine T (CAT) and *N*-bromosuccinimide (NBS). Another compound of this category is sodium *N*-chlorobenzenesulphonamide (chloramine B or CAB). Reports are available in literature [1,2] about the mechanism of oxidation by CAT and NBS. However, no information is available about the mode of reaction of CAB. We now report the kinetics of the oxidation of substituted benzyl alcohols in aqueous acetic acid solution in the presence of perchloric acid. The mechanistic conclusions are discussed.

RESULTS

The oxidation of benzyl alcohol (BA) by CAB in 1 : 1 (v/v) acetic acid–water in the presence of perchloric acid results in the formation of benzaldehyde. No detectable oxidation of benzaldehyde could be observed under the experimental conditions.

Stoicheiometry.—Excess of CAB was allowed to react with 0.05M-benzyl alcohol at various acidities and residual CAB estimated. For some runs, using an excess of alcohol, benzaldehyde was estimated. Values of Δ[CAB]/Δ[BA] and Δ[Benzaldehyde]/Δ[CAB] in Table 1 suggest the overall reaction (1).

TABLE 1

Stoicheiometry of the oxidation of benzyl alcohol by chloramine B

$[H^+]$/M	Δ[CAB]/Δ[BA]	Δ[Benzaldehyde]/Δ[CAB]
0.05	0.93	
0.10	1.02	
0.20	0.94	
0.30	1.05	
0.30		0.83
0.20		0.80
0.10		0.79

$$PhSO_2NCl^- + PhCH_2OH \longrightarrow PhCHO + PhSO_2NH_2 + Cl^- \quad (1)$$

Rate Laws.—The rate laws and other experimental data were obtained for all the alcohols investigated. As the results are similar only those of benzyl alcohol are reproduced.

The reaction was found to be first order with respect to the oxidant. Individual kinetic runs were strictly first order with respect to the oxidant. Further the first-order rate coefficients did not vary with the initial concentration of oxidant (Table 2). The order with respect to alcohol is also one (Table 3). Under the conditions of constant ionic strength the reaction is first order with respect to the acidity (Table 4).

TABLE 2

Oxidant dependence of the reaction rate: [BA] 0.05M, $[H^+]$ 0.5M, *T* 308 K

10^3[CAB]/M	2.0	4.0	5.0	7.0	10.0
$10^5\,k_1/s^{-1}$	7.12	6.88	7.05	7.23	7.12

TABLE 3

Dependence of the reaction rate on substrate concentration: [CAB] 0.005M, $[H^+]$ 0.5M, *T* 308 K

10^2[BA]/M	1.0	3.0	5.0	7.0	10.0	15.0
$10^5\,k_1/s^{-1}$	1.40	4.28	7.05	9.80	14.2	21.0

TABLE 4

Dependence of the reaction rate on acidity: [CAB] 0.005M, [BA] 0.05M, *T* 308 K, *I* 1.0

$[H^+]$/M	0.10	0.30	0.50	0.75	1.00
$10^5\,k_1/s^{-1}$	1.39	4.30	7.05	10.5	14.2

The oxidation of αα-dideuteriobenzyl alcohol ($PhCD_2OH$) indicated k_H/k_D of 4.41 ± 0.08 at 308 K.

Addition of benzenesulphonamide does not affect the oxidation rate.

The oxidation of benzyl alcohol was studied in 95% deuterium oxide. The rate constants for the oxidation in D_2O and H_2O at 303 K are $10^3\,k$ 2.83 and 1.17 $l^2\,mol^{-2}\,s^{-1}$, respectively. The solvent isotope effect, k_{H_2O}/k_{D_2O}, is

TABLE 5

Kinetic isotope effect in the oxidation of benzyl alcohol and αα-dideuteriobenzyl alcohol: [CAB] 0.005M, $[H^+]$ 0.5M, *T* 308 K

[BA]/M	Type	$10^5\,k_1/s^{-1}$	*T* 308 K
0.05	αα-$^1H_2$	7.05	
0.10	αα-$^1H_2$	14.2	$10^4\,k_H$ 28.1 ± 0.2 $l^2\,mol^{-2}\,s^{-1}$
0.15	αα-$^1H_2$	21.0	
0.10	αα-$^2H_2$	3.24	
0.05	αα-$^2H_2$	4.78	$10^4\,k_D$ 6.38 ± 0.09 $l^2\,mol^{-2}\,s^{-1}$
0.20	αα-$^2H_2$	6.30	

k_H/k_D 4.41 ± 0.08

0.413 at 303 K. In this set of experiments, no acetic acid was present.

Increase in the amount of acetic acid in the solvent mixture increases the rate slightly (Table 6).

The oxidation of monosubstituted benzyl alcohols were studied at different temperatures and the activation parameters evaluated (Tables 7 and 8). The average error in the values of ΔH^*, ΔS^*, and ΔG^* (at 298 K) are ± 4 kJ mol^{-1}, ± 6 J mol^{-1} K^{-1}, and ± 5 kJ mol^{-1}, respectively.

TABLE 6

Effect of solvent composition on the reaction rate: [BA] 0.05M, [CAB] 0.005M, [H$^+$] 0.5M, T 303 K

Percentage of acetic acid	0	20	30	50	60	70
$10^5\,k_1/\mathrm{s}^{-1}$	2.92	3.55	4.02	4.80	5.23	6.25

TABLE 7

Rate constants for the oxidation of substituted benzyl alcohols by chloramine B

	$10^5k/\mathrm{l}^2\,\mathrm{mol}^{-2}\,\mathrm{s}^{-1}$				
Substituent	298 K	303 K	308 K	313 K	318 K
H	132	193	282	410	605
m-Me	191	275	385	551	797
p-Et	550	760	1 050	1 380	1 870
p-Me	603	830	1 150	1 510	1 050
p-OMe	5 630	6 950	8 460	10 300	12 400
p-Cl	75.9	118	174	260	380
m-Br	19.0	31.6	49.0	79.0	130
m-NO_2	4.80	8.71	14.4	24.0	43.7
p-NO_2	2.82	5.25	9.12	15.5	27.5

TABLE 8

Activation parameters for the oxidation of substituted benzyl alcohols

Substituent	ΔH^*/kJ mol^{-1}	$-\Delta S^*$/ J mol^{-1} K^{-1}	ΔG^*/kJ mol^{-1}
H	58.7	105	90.1
m-Me	54.5	117	89.4
p-Et	47.9	130	86.7
p-Me	47.8	129	86.3
p-OMe	31.3	166	80.8
p-Cl	63.1	95.5	91.6
m-Br	73.3	72.5	94.9
m-NO_2	82.5	53.4	98.4
p-NO_2	87.7	40.2	99.7

DISCUSSION

The rate law for the oxidation of benzyl alcohol by CAB is given by equation (2). Not much information is

$$d[\mathrm{CAB}]/dt = k[\mathrm{CAB}][\mathrm{Alcohol}][\mathrm{H}^+] \qquad (2)$$

available about the equilibria present in acidified CAB solution, though the same has been reported in detail for CAT in acid solution.[3-5] Zilberg[6] has shown that acidification of CAB gives dichloramine B ($PhSO_2NCl_2$) and benzenesulphonamide. Mogilevskii *et al.*[7] have reported the presence of HOCl in acidified CAB. Mahadevappa and his co-workers have shown[8,9] that conductometric and potentiometric behaviours of acidified CAB solution are similar to those noted for the CAT-HCl system.

The possible equilibria present in aqueous acidified CAB solutions are (3)—(5). The probable oxidising species are $PhSO_2NHCl$, $PhSO_2NCl_2$, and HOCl.

Dichloramine B ($PhSO_2NCl_2$) can be ruled out as the active oxidising species in view of the strict first-order dependence on CAB. As there is no effect of benzenesulphonamide on the oxidation rate this also rules out both $PhSO_2NCl_2$ and HOCl as the oxidising species.

$$PhSO_2NCl^- + H_3O^+ \rightleftharpoons PhSO_2NHCl + H_2O \qquad (3)$$

$$2\,PhSO_2NHCl \rightleftharpoons PhSO_2NH_2 + PhSO_2NCl_2 \qquad (4)$$

$$PhSO_2NHCl + H_2O \rightleftharpoons PhSO_2NH_2 + HOCl \qquad (5)$$

Thus $PhSO_2NHCl$ is the most probable oxidising species in the present reaction.

The primary kinetic isotope effect (k_H/k_D 4.41) confirms that the rate-determining step involves a C–H bond rupture from the alcohol carbon.

The activation enthalpies and entropies of the nine alcohols are linearly related (r 0.999 7). The correlation was tested and found genuine by applying Exner's criterion.[10] The isokinetic temperature computed from the plot is 449 K. Current views do not attach much physical significance to isokinetic temperature,[11] though a linear correlation is usually a necessary condition for the validity of linear free energy relationships.

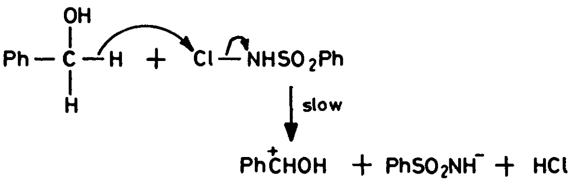
The rates of oxidation of substituted benzyl alcohols correlate well Brown's σ^+ values[12] with negative reaction constants (Table 9). Correlation with Hammett's σ values was poor. The negative reaction constant points to an electron-deficient carbon centre in the transition state. The above results indicate a hydride ion transfer in the rate-determining step.

TABLE 9

Temperature dependence of the reaction constant for the oxidation of substituted benzyl alcohols by chloramine B

T/K	298	303	308	313	318
$-\rho^+$	2.14	2.02	1.93	1.83	1.71
Correlation coefficient (r)	0.9992	0.9987	0.9999	0.9990	0.9989

Natarajan and Thiagarajan[13] have suggested a hypochlorite ester formation in the oxidation of propan-2-ol by acidified CAT. However, the solvent isotope effect (k_{H_2O}/k_{D_2O} 0.413) does not indicate any involvement of the hydroxy-group either in the rate-determining step or in pre-equilibria. Correlation with σ^+ values also suggests an intermolecular hydride ion transfer. The observed kinetic isotope effect is rather large for the non-linear transition state implied in the ester mechanism.



$$\mathrm{Ph\overset{+}{C}HOH} + PhSO_2NH^- + HCl \qquad (6)$$

$$PhSO_2NH^- + HCl \xrightarrow{\text{fast}} PhSO_2NH_2 + Cl^- \qquad (7)$$

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

The mechanism of reactions (6)—(8) may then be proposed.*

EXPERIMENTAL

Materials.—The preparations and specifications of the alcohols have been described earlier.[14] CAB was prepared by passing chlorine through a solution of benzenesulphonamide in 4M-NaOH at 343 K.[15] The resultant solid mass was filtered off, dried, and recrystallised from water. The purity was checked by estimating the amount of chlorine present iodometrically. Acetic acid was purified by the usual methods.[16] Perchloric acid was used as a source of hydrogen ions. All reagents were of analytical grade.

Product Analysis.—Benzaldehyde was estimated and characterised as its 2,4-dinitrophenylhydrazone.

Kinetic Measurements.—The reactions were arranged to be under pseudo-first-order conditions by keeping a large excess (× 5 or greater) of the alcohol over CAB. The reactions were carried out at constant temperature (±0.1 K) and were followed iodometrically. The rate constants were evaluated from the plots of log [oxidant] against time. The rate constants reported are mean of at least duplicate runs and are reproducible to within ±3%. The solvent was always 1 : 1 (v/v) acetic acid–water unless mentioned otherwise. The usual concentrations of the reactants in the reaction mixtures were alcohol 0.1—1.0M, CAB 0.002—0.01M, and perchloric acid 0.1—1.0M.

[9/865 *Received, 5th June,* 1979]

REFERENCES

[1] M. M. Campbell and G. Johnson, *Chem. Rev.*, 1978, **78**, 65.

[2] N. Venkatasubramanian and V. Thiagarajan, *Canad. J. Chem.*, 1969, **47**, 694.

[3] E. Bishop and V. J. Jennings, *Talanta*, 1955, **1**, 197.

[4] J. C. Morris, J. R. Salazar, and M. A. Winemann, *J. Amer. Chem. Soc.*, 1948, **70**, 2036.

[5] T. Higuchi and A. Hussain, *J. Chem. Soc.* (*B*), 1967, 549.

[6] I. G. Zilberg, *J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 2145 (*Chem. Abs.*, 1948, **42**, 144).

[7] M. S. Mogilevskii, V. I. Malchevskaya, and E. P. Voinarovskaya, *Gigiena i Sanit*, 1959, **24**, 77 (*Chem. Abs.*, 1959, **53**, 22749).

[8] D. S. Mahadevappa and R. Swamy, *Indian J. Chem.*, 1973, **11**, 811; *Rev. Roumaine De Chemie*, 1977, **22**, 1233.

[9] R. Swamy and D. S. Mahadevappa, *Indian J. Chem.*, 1976, **14A**, 463.

[10] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094.

[11] J. E. Leffler, *J. Org. Chem.*, 1966, **31**, 533.

[12] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, 1957, **22**, 485.

[13] M. M. Natarajan and V. Thiagarajan, *J.C.S. Perkin II*, 1975, 1590.

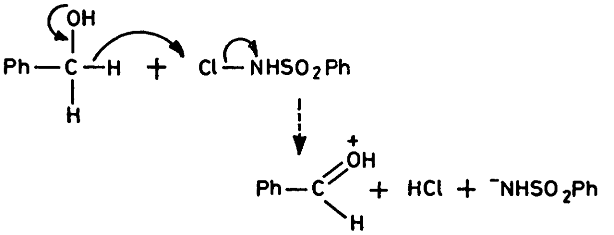
[14] K. K. Banerji, *J.C.S. Perkin II*, 1973, **435**.

[15] A. Chrzaszczewska, *Bull. Soc. Sci. et Lettres Lodz, classe III*, 1952, **3**, 16 (*Chem. Abs.*, 1955, **49**, 212).

[16] K. J. P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 1924, 960; 1927, 983.

---

* One of the referees has suggested an alternative rate-determining step (6a). The cation visualized in reaction (6a) is actually one of the possible canonical forms of the resonance-stabilized carbonium ion. Thus there is no essential difference between the reactions (6) and (6a).



(6a)