Kinetics and Mechanism of the Oxidation of Substituted Benzyl Alcohols by Pyridinium Chlorochromate

By **Kalyan K. Banerji**, Department of Chemistry, University of Jodhpur, Jodhpur, India

The oxidation of benzyl alcohol by pyridinium chlorochromate is first order with respect to both the oxidant and the alcohol. The reaction is catalysed by acid, the catalysed reaction being nearly first order in acidity. The kinetic isotope effect, k_H/k_D, is 5.07 at 30 °C. The reaction does not induce polymerisation of acrylonitrile. The reaction constant ρ for the uncatalysed and acid-catalysed oxidation of benzyl alcohol and eight monosubstituted benzyl alcohols have the values -1.70 ± 0.08 and -1.45 ± 0.06, respectively at 25 °C. Probable mechanisms are discussed.

PYRIDINIUM CHLOROCHROMATE (PCC) is a complex of chromium trioxide, pyridine, and hydrochloric acid and is known as Corey's reagent.[1] Corey and Suggs[1] reported that this complex converts alcohols into carbonyl compounds smoothly at room temperature in yields well over 80%. There seems to be no report about the mechanism of this important reaction. The present communication reports the kinetics of oxidation of substituted benzyl alcohols by PCC and evaluates the reaction constant. Mechanistic aspects are discussed.

RESULTS

The oxidation of benzyl alcohol (BA) by PCC in 1 : 1 (v/v) methylene chloride–nitrobenzene results in the formation of benzaldehyde. No detectable oxidation of benzaldehyde could be observed under the experimental conditions.

Stoicheiometry.—Excess of PCC was allowed to react with 0.005M-benzyl alcohol at various acidities and the excess of Cr^{VI} estimated. For some runs, benzaldehyde was estimated, using an excess of the alcohol. Values of Δ[PCC]/Δ[BA] and Δ[PCC]/Δ[Benzaldehyde] in Table 1 suggest the overall reaction (1).

$$3\,PhCH_2OH + 2\,Cr^{VI} \longrightarrow 3\,PhCHO + 6\,H^+ + 2\,Cr^{III} \qquad (1)$$

TABLE 1

Stoicheiometry of the oxidation of benzyl alcohol by PCC

[TsOH]/M	Δ[PCC]/Δ[BA]	Δ[PCC]/Δ[Benzaldehyde]
0.0	0.62	
0.1	0.65	
0.3	0.70	
0.0		1.20
0.2		1.06
0.4		1.14

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 is found to be cleanly first order with respect to the oxidant as regards time (as evidenced by constancy of first-order rates at different times) and concentration (as evidenced by the time-order rate coefficient being independent of the initial concentration of the oxidant) (Table 2). The order with respect to the alcohol is also one (Table 3). The reaction is catalysed by acid. The catalysed reaction shows a near first-order dependence on acidity, the actual order being 0.87 ± 0.02 (Table 4). Because of the non-aqueous nature of the solvents, a constant ionic strength could not be maintained. However, the chromic acid oxidation of benzyl alcohol in aqueous acetic acid is not affected by changes in ionic strength.[2]

TABLE 2

Oxidant dependence of the reaction rate; [BA] 0.01M, t 25 °C

$10^3[Cr^{VI}]$/M	1.0	2.0	3.0	4.0	5.0
10^6k_1/s^{-1}	7.50	7.50	7.23	7.77	7.61

TABLE 3

Dependence of the reaction rate on substrate concentration; $[Cr^{VI}]$ 0.002M, t 25 °C

10^2[BA]/M	1.00	2.00	4.00	6.00	8.00
10^6k_1/s^{-1}	7.50	15.2	30.6	44.0	60.0

TABLE 4

Dependence of the reaction rate on acidity; [BA] 0.01M, $[Cr^{VI}]$ 0.002M, t 25 °C

[TsOH]/M	0.05	0.10	0.20	0.30	0.40
10^6k_1/s^{-1}	11.2	15.8	25.0	32.8	41.0

The rate of oxidation of αα-dideuteriobenzyl alcohol and benzyl alcohol at 30 °C are 10^3k 4.22 and 21.4 l^2 mol^{-2} s^{-1} respectively. The kinetic isotope effect k_H/k_D is 5.07 at 30 °C.

Effect of Solvent Composition.—The acid-catalysed oxidation of benzyl alcohol was studied in solutions containing varying proportions of methylene chloride and nitrobenzene (Table 5). The increase in the proportion of nitrobenzene reduces the reaction rate. This accords with Corey's observation that the use of more polar solvents in which the

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[1] E. J. Corey and W. J. Suggs, *Tetrahedron Letters*, **1975**, 2647.

[2] G. V. Bakore, K. K. Banerji, and R. Shanker, *Z. Phys. Chem.* (*Frankfurt*), **1965**, **45**, 129.

reactants are soluble lead to inconveniently long reaction times.[1]

TABLE 5

Dependence of the reaction rate on solvent composition; [BA] 0.02M, [Cr^{VI}] 0.002M, [TsOH] 0.1M, t 25 °C

Nitrobenzene (%)	20	30	50	60	70
D	14.2	16.8	22.0	24.5	27.1
$10^5k_1/s^{-1}$	8.73	5.37	3.16	2.31	1.88

The oxidation of benzyl alcohol, under nitrogen, failed to induce polymerisation of acrylonitrile. One-electron oxidation is thus unlikely, though not ruled out. In control experiments, with the alcohol absent, the concentration of PCC does not show any appreciable change during the period in which it is reduced to one-fifth in the presence of benzyl alcohol.

The uncatalysed and acid-catalysed oxidation of monosubstituted benzyl alcohol were studied at different temperatures (Tables 6 and 7). The activation parameters (25—40 °C) were evaluated by the standard procedure.[3] The error limits in the values of ΔH^*, ΔS^*, and ΔF^* (at 25 °C) are ± 5 kJ mol^{-1}, ± 10 J mol^{-1} K^{-1}, and ± 7 kJ mol^{-1}, respectively (Table 8).

TABLE 6

Rate constants for oxidation of substituted benzyl alcohols by pyridinium chlorochromate

Substituent	$10^5k/l\ mol^{-1}\ s^{-1}$ 25 °C	30 °C	35 °C	40 °C
H	75.0	112	155	216
m-Me	97.7	151	200	277
p-Et	126	186	263	355
p-Me	148	200	274	383
p-OMe	225	302	380	523
p-Cl	31.6	47.0	69.0	102
m-Br	15.2	26.3	40.7	70.0
m-NO_2	4.47	8.32	14.1	23.6
p-NO_2	3.64	6.62	11.8	20.0

DISCUSSION

A near constancy of the free energy of activation shows that the same mechanism is operative for all the alcohols.

TABLE 8

Activation parameters for oxidation of substituted benzyl alcohols by pyridinium chlorochromate

	Uncatalysed oxidation			Acid-catalysed oxidation		
Substituent	$\Delta H^*/kJ\ mol^{-1}$	$-\Delta S^*/J\ mol^{-1}\ K^{-1}$	$\Delta F^*/kJ\ mol^{-1}$	$\Delta H^*/kJ\ mol^{-1}$	$-\Delta S^*/J\ mol^{-1}\ K^{-1}$	$\Delta F^*/kJ\ mol^{-1}$
H	54.7	125	92.0	47.9	123	84.5
m-Me	56.4	115	89.1	46.7	125	84.0
p-Et	54.6	122	91.0	45.0	128	83.2
p-Me	51.7	130	90.4	44.0	131	83.0
p-OMe	43.1	155	91.3	36.4	154	82.3
p-Cl	59.9	110	92.8	58.9	84.1	84.0
m-Br	78.5	58.5	95.9	72.5	52.0	88.0
m-NO_2	87.1	39.8	98.9	82.4	27.0	90.4
p-NO_2	88.9	35.1	99.3	86.2	15.9	90.9

The free energy of activation of the catalysed oxidation is consistently lower than that of the uncatalysed reaction but are of the same order and indicate that the mechanism of the two reactions are essentially similar.

The increase in the oxidation rate with acidity suggests the involvement of a protonated chromium(VI) species in the rate-determining step, in the presence of an acid. Involvement of such species are well established in chromic acid oxidations.[4]

The kinetic isotope effect (k_H/k_D 5.07) indicates that the rate-determining step involves C–H cleavage from the alcohol carbon atom.

TABLE 7

Rate constants for the oxidation of substituted benzyl alcohol by pyridinium chlorochromate, in the presence of TsOH

Substituent	$10^4k/l^2\ mol^{-1}\ s^{-1}$ 25 °C	30 °C	35 °C	40 °C
H	158	214	285	386
m-Me	191	257	347	467
p-Et	251	339	447	575
p-Me	275	360	468	589
p-OMe	390	490	603	724
p-Cl	75.9	112	159	245
m-Br	42.7	61.7	100	151
m-NO_2	15.1	25.1	45.7	79.5
p-NO_2	12.5	22.4	38.9	69.2

The activation enthalpies and entropies of both the uncatalysed and acid-catalysed oxidations are linearly related (r 0.990 and 0.987 respectively). The correlations were tested and found genuine by applying Exner's criterion.[5] The isokinetic temperature computed from the plots between ΔH^* and ΔS^* are 430 and 375 K respectively. Current views do not attach much physical significance to isokinetic temperature,[6] though a linear correlation is usually a necessary condition for the validity of the Hammett equation.

Dielectric constants for the methylene chloride–nitrobenzene mixtures are not available but can be estimated approximately from the dielectric constants of the pure solvents.[7] The estimated dielectric constants for the solvent mixtures are given in Table 5. A plot of log k_1 against the inverse of dielectric constant gives a straight line (r 0.976) with a positive slope. This suggests an interaction between a positive ion and a dipole[8] and confirms that the rate-determining step, in the presence of an acid, involves a protonated Cr^{VI} species.

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[3] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley Eastern, New Delhi, 1970, p. 99.

[4] K. B. Wiberg, 'Oxidation in Organic Chemistry, Part A,' Academic Press, New York, 1965, p. 69.

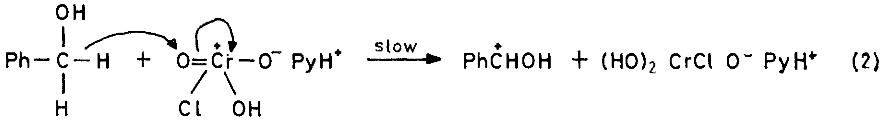
[5] O. Exner, *Coll. Czech. Chem. Comm.*, 1964, **29**, 1094.

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

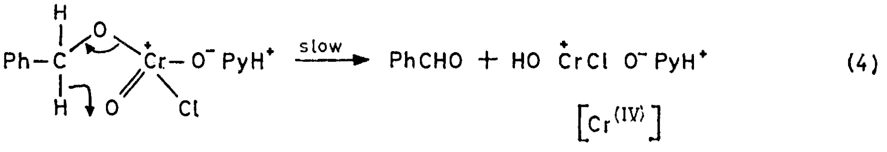
[7] C. N. R. Rao, 'A Handbook of Chemistry and Physics,' Affiliated East–West Press, New Delhi, 1967, p. 169.

[8] E. S. Amis, 'Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, New York, 1967, p. 42.

The rates of oxidation of substituted benzyl alcohols correlate well with Hammett's σ values, with negative reaction constants (Table 9).




SCHEME 1



SCHEME 2

The above results point to a hydride ion transfer in the rate-determining step. The hydride transfer may take place either directly (Scheme 1) or may involve the prior formation of a chromate ester (Scheme 2). The present data do not enable one to distinguish between the two mechanisms. Chromate ester formation is not likely to be susceptible to any considerable structural influence.[9,10] The large negative reaction constant can thus arise only from the differential effects of the substituents on the rate-determining step.

TABLE 9

Temperature dependence of the reaction constant for the oxidation of benzyl alcohols by pyridinium chlorochromate

	$-\rho$	
t/°C	Uncatalysed	Acid-catalysed
25	1.70 ± 0.08	1.45 ± 0.06
30	1.58 ± 0.10	1.30 ± 0.04
35	1.48 ± 0.05	1.16 ± 0.09
40	1.35 ± 0.06	1.01 ± 0.06

EXPERIMENTAL

Materials.—The preparations and specifiactions of the alcohols have been described earlier.[11] The solvents were purified and dried in the usual manner.[12] Toluene-*p*-sulphonic acid (TsOH) was used as a source of hydrogen ions. All reagents are of analytical grade.

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

Kinetic Measurements.—The oxidant was prepared by the method of Corey and Suggs [1] and the purity checked by estimating Cr^{VI} iodometrically.

The reactions were arranged to be under pseudo-first-order conditions by keeping a large excess (× 5 or greater) of the alcohol over PCC. The reactions were carried out at constant temperature (±0.1 °C) and were followed iodometrically. The rate constants were evaluated from the plots of log[oxidant] against time. The rate constants reported are the mean of at least duplicate runs and are reproducible to within ±3%. The solvent was always 1 : 1 (v/v) methylene chloride–nitrobenzene, unless mentioned otherwise. The reaction mixtures remain homogeneous in the solvent systems used. The usual initial concentration of the reactants were alcohol 0.01—0.20M, PCC *ca.* 0.002M, and TsOH 0.05—0.5M.

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[9] N. C. Deno and M. S. Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 3852.

[10] U. Klanning and M. C. R. Symons, *J. Chem. Soc.*, 1961, 3204, and references therein.

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

[12] D. D. Perrin, W. L. Armarego, and D. R. Perrin, ' Purification of Organic Compounds,' Pergamon Press, Oxford, 1966.