

Kinetics and mechanism of the oxidation of primary aliphatic alcohols by pyridinium bromochromate

P APARNA, SEEMA KOTHARI and KALYAN K BANERJI*

Department of Chemistry, J.N.V. University, Jodhpur 342 005, India

MS received 3rd October 1994; revised 1 January 1995

Abstract. Oxidation of nine primary aliphatic alcohols by pyridinium bromochromate (PBC) leads to the formation of corresponding aldehydes. The reaction is of overall second order, and of first order with respect to the each reactant. The reaction is promoted by hydrogen ions; the hydrogen-ion dependence has the form $k_{\text{obs}} = c + d[H^+]$. The oxidation of $[1, 1\text{-}^2\text{H}_2]$ ethanol (MeCD_2OH) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen organic solvents and the effect of solvent was analysed using Taft's and Swain's multiparametric equations. The oxidation is susceptible to both the polar and steric effects of the substituents. A suitable mechanism has been proposed.

Keywords. Alcohols; pyridinium halochromate; kinetics; mechanism; oxidation; correlation analysis.

1. Introduction

Pyridinium bromochromate (PBC) has been reported as a mild and selective oxidizing reagent in synthetic organic chemistry (Narayanan and Balasubramanian 1986). There seem to be only two reports on the mechanistic aspects of oxidations by PBC, those of benzhydrol and phosphorus oxyacid (Narayanan and Balasubramanian 1991; Grover *et al* 1994). We have been interested in the kinetics of reactions of complexed Cr(VI) species and have reported the kinetics and mechanism of oxidation of alcohols by pyridinium fluorochromate (PFC) and pyridinium chlorochromate (PCC) (Banerji 1978, 1988). It was observed that the oxidations of alcohols by PFC and PCC presented different kinetic pictures. In this paper we report the kinetics of oxidation of nine aliphatic primary alcohols by PBC in DMSO as solvent.

2. Experimental

2.1 Materials

PBC was prepared by the reported method (Narayanan and Balasubramanian 1986) and its purity checked by an iodometric method. Procedures used for purification of the alcohols have been described earlier (Banerji 1978). $[1, 1\text{-}^2\text{H}_2]$ Ethanol was prepared by the reported method (Kaplan 1958); Its isotopic purity, as ascertained by its NMR spectra, was $92 \pm 5\%$. *p*-Toluenesulphonic acid (TsOH) was used as the source of hydrogen ions. Solvents were purified by the usual methods (Perrin *et al* 1966).

*For correspondence

2.2 Product analysis

Product analysis was carried out under kinetic conditions. In a typical experiment, ethanol (2.30 g, 0.05 mol) and PBC (2.60 g, 0.01 mol) were made up to 50 cm³ in DMSO and kept in the dark for \approx 15 h to ensure completion of the reaction. The solution was then treated with an excess (200 cm³) of a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm⁻³ HCl and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol, and weighed again. The yields of DNP before and after recrystallization were 1.91 g (87%) and 1.61 g (72%) respectively. The DNP was identical (m.p. and mixed m.p.) with the DNP of acetaldehyde. Similar experiments were performed with other alcohols also.

Iodometric determinations of the oxidation state of chromium in completely reduced reaction mixtures indicated that the oxidation state of the reduced chromium species is 4.10 ± 0.16 .

2.3 Kinetic measurements

The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the alcohol over PBC. The solvent was DMSO, unless specified otherwise. The reactions were followed, at constant temperatures (± 0.1 K), by monitoring the decrease in [PBC] spectrophotometrically at 358 nm. No other reactant or product has any significant absorption at this wavelength. The pseudo-first order rate constant, k_{obs} , was evaluated from the linear ($r = 0.990 - 0.999$) plots of log [PBC] against time up to 80% reaction. Duplicate kinetic runs showed that the rate constants were reproducible to within $\pm 3\%$. The second order rate constant, k_2 , was obtained from the relation: $k_2 = k_{\text{obs}}/[\text{alcohol}]$, in the absence of added acid. Preliminary

Table 1. Rate constants for the oxidation of ethanol by PBC at 303 K.

$10^3[\text{PBC}]$ (mol dm ⁻³)	[EtOH] (mol dm ⁻³)	[TsOH] (mol dm ⁻³)	$10^5 k_{\text{obs}}$ (s ⁻¹)
1.0	0.01	0.0	3.50
1.0	0.03	0.0	10.3
1.0	0.05	0.0	17.4
1.0	0.08	0.0	27.5
1.0	0.12	0.0	41.6
1.0	0.24	0.0	35.2
2.0	0.08	0.0	27.7
4.0	0.08	0.0	27.3
8.0	0.08	0.0	28.0
1.0	0.08	0.0*	27.0
1.0	0.03	0.1	13.4
1.0	0.03	0.2	16.7
1.0	0.03	0.3	19.6
1.0	0.03	0.5	26.0
1.0	0.03	0.8	35.4
1.0	0.03	1.0	41.2

*Contained 0.001 mol dm⁻³ acrylonitrile

Table 2. Statistical analyses of hydrogen-ion dependence of rate of oxidation of primary alcohols, RCH₂OH, by PBC.

Substituent (R)	10 ⁵ <i>c</i>	10 ⁴ <i>d</i>	<i>r</i> ²
H	9.53 ± 0.4	3.60 ± 0.07	0.9985
Me	10.4 ± 0.1	3.10 ± 0.02	0.9998
Et	11.2 ± 0.3	2.70 ± 0.05	0.9984
Pr	10.4 ± 0.3	2.83 ± 0.05	0.9987
Bu	11.7 ± 0.2	2.62 ± 0.03	0.9996
Pr ⁱ	16.2 ± 0.1	3.06 ± 0.03	0.9994
ClCH ₂	11.5 ± 0.2	3.72 ± 0.04	0.9995
MeOCH ₂	14.2 ± 0.3	3.29 ± 0.06	0.9983
Bu ^t	84.7 ± 2.1	2.09 ± 0.03	0.9988

experiments showed that the reaction is not sensitive to changes in ionic strength, hence no attempt was made to keep it constant. Simple and multivariate linear regression analyses were carried out by the least-squares method on a personal computer.

3. Results

The rate laws and other experimental data were obtained for all the alcohols investigated. As the results are similar, only representative data are reproduced here.

The overall reaction may be written as



PBC undergoes a 2-electron change. This is in accord with the earlier observations with both PFC (Banerji 1988) and PBC (Grover *et al* 1994).

The reaction is first order with respect to PBC. Further, the pseudo-first order rate constant, k_{obs} , is independent of initial concentration of PBC. The reaction is of first order with respect to the alcohol also. The reaction is promoted by hydrogen ions, the $[\text{H}^+]$ dependence taking the form: $k_{\text{obs}} = c + d[\text{H}^+]$ (table 1). The least-squares values of *c* and *d* are recorded in table 2. Addition of a radical scavenger, acrylonitrile, had no effect on the rate (table 1).

Rates of oxidation of nine primary alcohols by PBC were determined at different temperatures and the activation parameters were calculated (table 3).

To ascertain the importance of the cleavage of the $\alpha\text{-C-H}$ bond in the rate-determining step, oxidation of $[1,1\text{-}^2\text{H}_2]$ ethanol was studied. Results showed the presence of a substantial primary kinetic isotope effect (table 3).

The oxidation of ethanol was studied in 19 different organic solvents. The choice of solvents was limited by the solubility of PBC and its reaction with primary and secondary alcohols. There was no reaction with the solvents chosen. Kinetics were similar in all the solvents. The values of k_2 are recorded in table 4.

4. Discussion

The correlation between activation enthalpies and entropies of the oxidation of the nine alcohols is not very good ($r^2 = 0.9672$). The values of the isokinetic temperature is 1578 ± 110 K. However, according to Exner (1964), an isokinetic relationship between

Table 3. Temperature dependence and the activation parameters of the oxidation of alcohols, RCH₂OH, by PBC in DMSO.

Subst. (R)	10 ⁴ k ₂ (dm ³ mol ⁻¹ s ⁻¹) at				ΔH ⁺ kJ mol ⁻¹	ΔS* J mol ⁻¹ K ⁻¹	ΔG* kJ mol ⁻¹
	303 K	313 K	323 K	333 K			
H	0.59	1.52	3.80	9.42	74.8 ± 0.7	-80 ± 2	98.5 ± 0.5
Me	34.7	68.7	139.0	265.0	54.5 ± 0.5	-113 ± 2	88.0 ± 0.4
Et	57.3	109.0	213.0	400.0	52.0 ± 0.7	-117 ± 2	86.8 ± 0.5
Pr	104.0	190.0	356.0	635.0	48.3 ± 0.5	-125 ± 2	85.2 ± 0.4
Bu	117.0	220.0	398.0	700.0	47.5 ± 0.1	-126 ± 1	84.9 ± 0.1
Pr ⁱ	163.0	298.0	542.0	939.0	46.6 ± 0.3	-126 ± 1	84.1 ± 0.2
ClCH ₂	1.00	2.25	5.11	11.6	66.0 ± 1.0	-105 ± 3	97.0 ± 0.9
MeOCH ₂	6.52	13.9	29.6	60.2	59.7 ± 0.4	-110 ± 1	92.3 ± 0.3
Bu ⁱ	1680.0	2650.0	4000.0	5880.0	32.5 ± 0.1	-153 ± 1	78.0 ± 0.2
MeCD ₂ OH	5.53	11.5	24.7	49.8	59.2 ± 0.7	-113 ± 2	92.7 ± 0.5

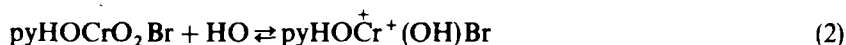
Table 4. Effect of solvents on the oxidation of ethanol by PBC at 303 K.

Solvent	10 ⁴ k ₂ (dm ³ mol ⁻¹ s ⁻¹)
Dimethylformamide	21.1
Chloroform	12.7
1,2-Dichloroethane	15.0
Dichloromethane	14.2
DMSO	34.7
Acetone	13.2
Butanone	10.6
Nitrobenzene	16.6
Benzene	5.95
Cyclohexane	1.04
Toluene	4.93
Acetophenone	17.7
Tetrahydrofuran	8.03
<i>t</i> -Butyl alcohol	6.82
Dioxane	8.27
1,2-Dimethoxyethane	4.80
Ethyl acetate	6.22
Carbon disulphide	3.03
Acetic acid	3.92

the calculated values of activation enthalpies and entropies is often vitiated by random experimental errors. Exner suggested an alternative method for establishing the isokinetic relationship. Exner's plot between log k_2 at 303 K and at 333 K was linear ($r^2 = 0.9989$). The value of isokinetic temperature evaluated from the Exner's plot is 647 ± 45 K. The linear isokinetic correlation implies that all the alcohols are oxidized by the same mechanism and that changes in the rate are governed by changes in both the enthalpy and entropy of activation.

The observed hydrogen-ion dependence suggests that the reaction follows two mechanistic pathways, one acid-independent and another acid-dependent. The acid-catalysis may

well be attributed to a protonation of PBC, (2), to yield a protonated Cr(VI) species which is a stronger oxidant and electrophile. Formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PCC (Banerji 1978).



The rate constants of oxidation, k_2 , in seventeen solvents (CS₂ and acetic acid were not considered as the complete range of solvent parameters were not available) were correlated in terms of linear solvation energy relationship of Kamlet *et al* (1983):

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha. \quad (3)$$

In this equation, π^* represents the solvent polarity, β the hydrogen bond acceptor basicities and α is the hydrogen bond donor acidity. A_0 is the intercept term. It may be mentioned here that out of the 17 solvents, 12 have a value of zero for α . The results of correlation analyses in terms of (3), a biparametric equation involving π^* and β , and separately with π^* and β are given below [(4)–(7)].

$$\log k_2 = -3.98 + 1.37\pi^* + 0.05\beta + 0.40\alpha, \quad (4)$$

$$(\pm 0.11) (\pm 0.09) (\pm 0.14)$$

$$R^2 = 0.9356; sd = 0.10; n = 17; \psi = 0.20.$$

$$\log k_2 = -3.91 + 1.26(\pm 0.12)\pi^* + 0.15(\pm 0.10)\beta, \quad (5)$$

$$R^2 = 0.8971; sd = 0.12; n = 17; \psi = 0.24.$$

$$\log k_2 = -3.88 + 1.31(\pm 0.13)\pi^* \quad (6)$$

$$r^2 = 0.8803; sd = 0.12; n = 17; \psi = 0.26.$$

$$\log k_2 = -3.17 + 0.39(\pm 0.28)\beta, \quad (7)$$

$$r^2 = 0.1155; sd = 0.33; n = 17; \psi = 0.84.$$

Here n is the number of data points and ψ is Exner's statistical parameter (Exner 1966).

Kamlet's (Kamlet *et al* 1983) triparametric equation explains $\approx 93\%$ of the effect of solvent on the oxidation. However, by Exner's criterion the correlation is not even satisfactory (4). The major contribution is of solvent polarity. It alone accounts for $\approx 88\%$ of the data. Both β and α play relatively minor roles.

The data on the solvent effect were also analysed in terms of Swain's equation (Swain *et al* 1983) of cation- and anion-solvating concept of the solvents,

$$\log k_2 = aA + bB + C. \quad (8)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. ($A + B$) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of (8), separately with A and B and with ($A + B$).

$$\log k_2 = 0.54(\pm 0.02)A + 1.33(\pm 0.01)B = -4.09, \quad (9)$$

$$R^2 = 0.9990; sd = 0.01; n = 19; n = 19; \psi = 0.02.$$

$$\log k_2 = 0.35(\pm 0.44)A - 3.17, \quad (10)$$

$$r = 0.0372; sd = 0.35; n = 19; \psi = 0.92.$$

$$\log k_2 = 1.29(\pm 0.10)B - 3.91, \quad (11)$$

$$r^2 = 0.9143; sd = 0.11; n = 19; \psi = 0.22.$$

$$\log k_2 = 1.07 \pm 0.10(A + B) - 4.00, \quad (12)$$

$$r = 0.8677; sd = 0.13; n = 19; \psi = 0.27.$$

The rates of oxidation of ethanol in the different solvents show an excellent correlation in Swain's equation (9) with the cation-solvating power playing the major role. In fact, the cation-solvation alone accounts for $\approx 91\%$ of the data. The solvent polarity, represented by $(A + B)$, also accounted for $\approx 87\%$ of the data. In view of the fact that the solvent polarity is able to account for $\approx 87\%$ of the data, an attempt was made to correlate the rate with the relative permittivity of the solvent. However, a plot of \log (rate) against the inverse of the relative permittivity is not linear ($r^2 = 0.5354$; $sd = 0.25$).

The rates of oxidation of the alcohols failed to yield any significant correlations separately with Taft's (Wiberg 1963) σ^* and E_s values:

$$\log k_2 = -2.22(\pm 0.41)\sigma^* - 2.21, \quad (13)$$

$$r^2 = 0.8060; sd = 0.52; n = 9; \psi = 0.34;$$

$$\log k_2 = -1.25(\pm 0.35)E_s - 2.79, \quad (14)$$

$$r^2 = 0.6488; sd = 0.70; n = 9; \psi = 0.46.$$

The rates were, therefore, correlated in terms of Pavelich and Taft's (1957) dual substituent-parameter equation,

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0. \quad (15)$$

The values of the substituent constants were obtained from the compilation by Wiberg (1963). The correlations are excellent: the reaction constant being negative (table 5). There is no significant colinearity ($r^2 = 0.2136$) between σ^* and E_s of the nine substituents.

The negative polar reaction constant indicates an electron-deficient carbon centre in the transition state of the rate-determining step. The negative steric reaction constant showed a steric acceleration of the reaction. This may be explained on the basis of high ground-state energy of the sterically crowded alcohols. Since the crowding is relieved in the product aldehyde as well as in the transition state leading to it, the transition state energy of the crowded and uncrowded alcohols do not differ much and therefore, steric acceleration, results.

The presence of a substantial kinetic isotope effect confirms the cleavage of α -C-H bond cleavage in the rate-determining step. The large negative value of the polar reaction constant together and the substantial deuterium isotope effect indicate that

Table 5. Temperature dependence of the reaction constants.

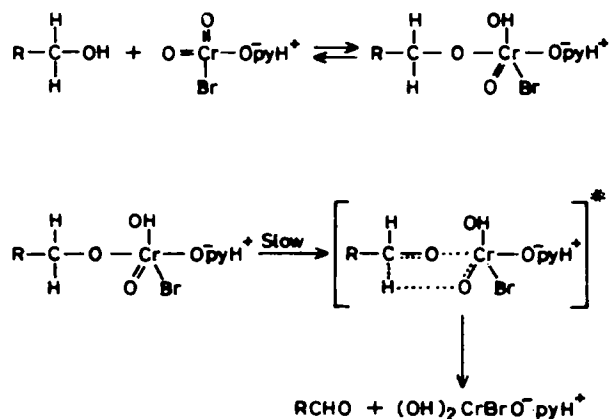
Temp (K)	ρ^*	δ	R^2	sd	ψ
303	-1.65 ± 0.02	-0.77 ± 0.01	0.9998	0.01	0.011
313	-1.58 ± 0.03	-0.72 ± 0.01	0.9997	0.02	0.013
323	-1.51 ± 0.02	-0.65 ± 0.02	0.9998	0.02	0.011
333	-1.43 ± 0.01	-0.60 ± 0.01	0.9998	0.01	0.011

the transition state approaches a carbocation in character. Hence, transfer of a hydride-ion from the alcohol to the oxidant is suggested. The hydride-ion transfer mechanism is also supported by the major role of cation-solvating power of the solvents.

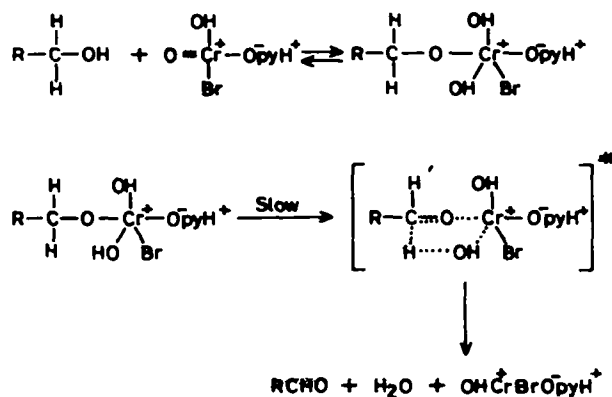
The hydride ion transfer may take place either by a cyclic process via an ester intermediate or by an acyclic one-step bimolecular process. Kwart and Nickel (1973) have shown that dependence of k_H/k_D on temperature can be successfully employed to determine whether the loss of hydrogen proceeds through a concerted cyclic process or by an acyclic one. The data for protio- and deuterio-ethanols, fitted to the familiar expression: $k_H k_D = A_H/A_D e(-\Delta H^*/RT)$, show a direct correspondence with the properties of a symmetrical transition state in which activation energy difference for protio and deuterio compounds are equal to the difference in the zero-point energy for the respective C-H and C-D bonds ($\approx 4.5 \text{ kJ mol}^{-1}$) and the entropies of activation of the respective reactions are almost equal (Kwart and Nickle 1973). Similar phenomena were observed earlier in the oxidation of benzhydrol by PCC (Banerji 1983) and that of alcohols by PFC (Banerji 1988).

Evidences against the hydrogen transfer occurring by a concerted one-step bimolecular process has been well documented by Bordwell (1972). It is clear in the present study also that hydrogen transfer does not take place by an acyclic bimolecular process. It is well established that intrinsically concerted sigmatropic reactions, characterized by transfer of a hydrogen in a cyclic transition state, are the only truly symmetrical processes involving a linear hydrogen transfer (Woodward and Hoffman 1969). Furthermore, a cyclic hydride-ion transfer in the oxidation of alcohols by Cr(VI) involves six electrons and being a Huckle-type system, is an allowed process (Littler 1971). Thus a transition state having a planar, cyclic and symmetrical structure can be envisaged for the decomposition of the ester intermediate. Hence the overall mechanism is proposed to involve the formation of a chromate ester in a fast pre-equilibrium and then a decomposition of the ester in a subsequent slow step via a cyclic concerted symmetrical transition state leading to the product (scheme 1 and 2).

It is of interest to compare here the mode of oxidation of alcohols by PCC (Banerji 1978), PFC (Banerji 1988), and PBC. The oxidation by PFC exhibited Michaelis-Menten type kinetics with respect to the alcohols, while the oxidation by PCC and PBC



Scheme 1.



Scheme 2.

presented similar kinetic pictures. The rate law, hydrogen-ion dependence, and kinetic isotope effect, are similar in both the cases. In the oxidation of alcohols by PFC and PBC excellent correlations were obtained in terms of Swain's equation with the cation-solvating power of the solvents playing the major role. Solvent effect was not studied in the oxidation by PCC. In all the three oxidations the polar reaction constants are negative. Though the data are not conclusive, it seems that the mode of oxidation depends on the nature of the halogen present in the Cr(VI) species.

Acknowledgement

Thanks are due to the University Grants Commission and the Council of Scientific and Industrial Research, New Delhi for financial support.

References

- Banerji K K 1978 *Bull. Chem. Soc. Jpn.* **51** 2732
 Banerji K K 1983 *Indian J. Chem.* **B22** 413
 Banerji K K 1988 *J. Chem. Soc., Perkin Trans. 2* 547
 Bordwell F G 1972 *Acc. Chem. Res.* **5** 374
 Exner O 1964 *Collect. Czech. Chem. Commun.* **29** 1094
 Exner O 1966 *Collect. Czech. Chem. Commun.* **31** 3222
 Grover A, Varshney S and Banerji K K 1994 *Indian J. Chem.* **A33** 622
 Kamlet M J, Abboud J L H, Abraham M H and Taft R W 1983 *J. Org. Chem.* **48** 2877, and references cited therein
 Kaplan L 1958 *J. Am. Chem. Soc.* **80** 2639
 Kwart H and Nickle J H 1973 *J. Am. Chem. Soc.* **95** 4835
 Littler J S 1971 *Tetrahedron* **27** 81
 Narayanan N and Balasubramanian T R 1986 *Indian J. Chem.* **B25** 229
 Narayanan N and Balasubramanian T R 1991 *J. Chem. Res. (S)* 336
 Pavelich W A and Taft R W 1957 *J. Am. Chem. Soc.* **79** 4935
 Perrin D D, Armstrong W L and Perrin D R 1966 *Purification of organic compounds* (Oxford: Pergamon)
 Swain C G, Swain M S, Powel A L and Alunni S 1983 *J. Am. Chem. Soc.* **105** 502
 Wiberg K B 1963 *Physical organic chemistry* (New York: Wiley) p. 415
 Woodward R B and Hoffman R 1969 *Angew. Chem., Int. Ed. Eng.* **8** 781