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Kinetics and Mechanism of the Oxidation of Alcohols by Pyridinium Chlorochromate

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The kinetics of the oxidation of ten primary alcohols by pyridinium chlorochromate has been studied. The main product of the oxidation is the corresponding aldehyde. The reaction is of first order with respect to the concentration of the alcohol and oxidant. The reaction is catalysed by acid, the catalysed reaction being nearly first order in acidity. The kinetic isotope effect, k_H/k_D is 5.71 at 303 K for ethanol. The reaction does not induce polymerisation of acrylonitrile. The reaction constant ρ^* for the uncatalysed and acid-catalysed oxidations have the values -1.93 and -1.75 at 303 K respectively. Probable mechanisms are discussed.

Pyridinium chlorochromate (PCC) is a complex of chromium trioxide, pyridine and hydrochloric acid.[1] Corey and Suggs[1] reported that this complex converts alcohols to carbonyl products in yields over 80%. There seems to be no previous report on the mechanism of this useful reaction. The present paper deals with the oxidation of some primary alcohols in 1 : 1 (v/v) dichloromethane–nitrobenzene solution and evaluates the reaction constant.

Results

The rate laws and other experimental data were obtained for all the alcohols investigated. Since results are similar, only those of ethanol are reproduced. The oxidation of ethanol by PCC results in the formation of acetaldehyde as the main product, which is isolable in 75±5% yield as its 2,4-dinitrophenylhydrazone.

Stoichiometry. Excess of PCC was allowed to react with 0.08 M of ethanol at various acidities and the unreacted oxidant estimated. For some runs the carbonyl product was estimated, using an excess of the alcohol. The overall reaction corresponds to

$$3RCH_2OH + 2Cr(VI) \longrightarrow 3RCHO + H^+ + 2Cr(III). \qquad (1)$$

Rate Laws. When the alcohol is in excess, the rate of disappearence of PCC follows first rate laws. The rate constant is independent of the initial concentration of PCC (Table 1). The reaction is of first order with respect to the alcohol concentration also (Table 2). The reaction is catalysed by acid. The catalysed reaction being nearly first order in acidity. The actual order is 0.88±0.02 (Table 3). Because of the non-aqueous nature of the solvent, constant ionic strength could not be maintained.

Table 1. Oxidant dependence of the reaction rate

[EtOH] 0.10 M	Temp 303 K				
10^3 [PCC] M	2.0	4.0	6.0	8.0	10.0
$10^6\,k_1$ s^{-1}	10.0	9.73	10.6	10.0	9.84

Table 2. Substrate dependence of the reaction rate

[PCC] 0.002 M	Temp 303 K				
[EtOH] M	0.05	0.10	0.20	0.40	0.80
$10^6\,k_1$ s^{-1}	5.13	10.0	20.7	41.0	78.3

Table 3. Acidity dependence of the reaction rate

[EtOH] 0.10 M	[PCC] 0.002 M		Temp 303 K		
[TsOH] M	0.05	0.10	0.20	0.30	0.40
$10^6\,k_1$ s^{-1}	14.4	18.9	27.0	38.1	44.9

Table 4. Dfpendence of the reaction rate on solvent composition

[EtOH] 0.10 M	[PCC] 0.002 M		[TsOH] 0.10 M		Temp 303 K
Percentage of nitrobenzene	30	40	50	60	70
Dielectric constant	16.8	19.4	22.0	24.5	27.1
$10^6\,k_1$ s^{-1}	50.1	28.2	18.9	13.5	10.6

The rate of the oxidation of ethan-1,1-d_2-ol and ethanol at 303 K are $10^5k=1.75$ and 10.0 l mol^{-1} s^{-1} respectively. The kinetic isotope effect, k_H/k_D is 5.72 at 303 K.

Effect of Solvent Composition. The acid-catalysed oxidation of ethanol was studied in solutions containing varying proportion of dichloromethane and nitrobenzene (Table 4). Increasing proportion of nitrobenzene in the solution reduces the rate.

The oxidation of ethanol, in an atmosphere of nitrogen, failed to induce polymerisation of acrylonitrile. In control experimetns, with the alcohol absent, the concentration of PCC does not change.

Table 5. Rate constants for the uncatalysed oxidation of primary alcohols, RCH_2OH, by pyridinium chlorochromate

Substituent (R)	$10^6\,k$ l mol^{-1} s^{-1}			
	303	308	313	318K
Me	100	140	193	263
Et	155	210	282	375
n-Pr	166	224	300	400
i-Pr	240	320	417	550
t-Bu	400	507	646	832
Cyclohexy.	182	246	327	432
H	11.5	18.2	28.2	43.1
$MeOCH_2$	10.2	16.2	25.7	39.9
$BrCH_2$	1.10	1.91	3.28	5.50
$ClCH_2$	1.00	1.76	3.06	5.20

Table 6. Rate constants for the acid-catalysed oxidation of primary alcohols, RCH_2OH, by pyridinium chlorochromate

Substituent (R)	$10^5 k$ l^2 mol^{-2} s^{-1}			
	303	308	313	318K
Me	189	251	336	443
Et	282	363	490	630
n-Pr	295	389	513	676
i-Pr	417	543	708	910
t-Bu	675	850	1070	1380
Cyclohexyl	330	427	550	725
H	27.0	38.9	56.2	79.5
$MeOCH_2$	24.0	34.7	50.1	72.5
$BrCH_2$	3.16	5.07	7.76	12.3
$CClCH_2$	2.95	4.68	7.24	11.5

The uncatalysed and acid-catalysed oxidation of the primary alcohols were studied at different temperatures (Tables 5 and 6) and the activation parameters evaluated (Table 7). The average error limits in the values of ΔH^*, ΔS^*, and ΔF^* (at 303 K) are ±6 kJ mol^{-1}, ±10 J mol^{-1} K^{-1}, and ±7 kJ mol^{-1} respectively.

Discussion

A near constancy of the free energy of activation shows that the same mechanism is operative in all the alcohols. The free energy of activation of the acid-catalysed oxidation is consistently lower than that of the uncatalysed reaction but are of the same order indicating that the mechanisms of the two reactions are essentially similar.

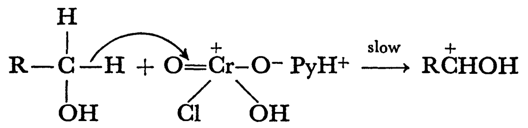
The linear increase in the oxidation rate with acidity suggests involvement of a protonated Cr(VI) species in the rate-determining step. Involvement of such species are well known in chromic acid oxidation.[2)] The kinetic isotope effect suggests that the rate-determining step involves a C–H bond rupture.

The activation enthalpies and entropies of both the uncatalysed and acid-catalysed reactions are linearly related (r=0.9993 and 0.9991 respectively). The correlations were tested and found genuine by applying Exner's criterion.[3)] The isokinetic temperatures computed from these polts are 436 and 502 K respectively. Current views do not attach much physical significance to isokinetic temperature,[4)] though a linear correlation is usually a necessary condition for the validity of linear free energy relationships.

Dielectric constants for dichloromethane–nitrobenzene mixtures are not available, but can be estimated approximately from the dielectric constants of the pure solvents.[5)] The estimated dieletctric constants of the solvent mixtures are recorded in Table 4. A plot of $\log k_1$ against the inverse of dielectric constant is a straight line with a positive slope. This indicates an interaction between a dipole and a positive ion.[6)] This accords with the observation regarding involvement of a protonated Cr(VI) species in the rate-determining step.

The oxidation rates of the primary alcohols correlate well with Taft's σ^* values with negative reaction constants (Table 8).

A hydrogen abstraction mechanism may be discounted in view of the failure to induce polymerisation of acrylonitrile and the magnitude of the reaction constant. In most hydrogen abstraction reactions the reaction constants have small magnitude.[7)] The large negative reaction constant together with the substantial deuterium isotope effect indicate a considerable carbonium ion character in the transition state. The above results points to a hydride-ion transfer in the rate-determining step. The hydride transfer may take place directly (Scheme 1) or may involve the prior formation of a chromate ester (Scheme 2). The similarity in the rate laws with chromic acid oxidations[2)] suggests a chromate ester formation. However, the observed kinetic isotope effect is rather



$$+ (HO)_2CrClO^- \ PyH^+ \qquad (2)$$

$$R\overset{+}{C}HOH \xrightarrow{\text{fast}} RCHO + H^+ \qquad (3)$$

Scheme 1.

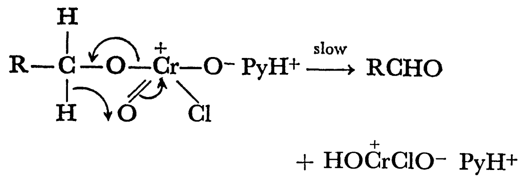
Table 7. Activation parameters for the oxidation of alcohols, RCH_2OH, by pyridinium chlorochromate

Substituent (R)	Uncatalysed			Acid-catalysed		
	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔF^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔF^* kJ mol^{-1}
Me	51.8	153	98.2	45.9	148	90.7
Et	47.3	164	97.0	43.6	153	90.0
n-Pr	47.2	164	96.9	43.4	153	89.8
i-Pr	44.1	171	95.9	41.9	155	88.9
t-Bu	39.3	183	94.7	38.0	164	87.7
Cyclohexyl	46.5	166	96.8	41.9	157	89.5
H	70.7	109	104	58.9	125	96.8
$MeOCH_2$	73.2	101	104	59.1	122	96.1
$BrCH_2$	86.1	77	109	72.1	95	101
$ClCH_2$	88.2	71	110	72.3	96	101

Table 8. Temperature dependence of the reaction constant and regression coefficient

Temp K	Uncatalysed		Acid-catalysed	
	$-\rho^*$	r	$-\rho^*$	r
303	1.93	0.9998	1.75	0.9997
308	1.83	0.9998	1.67	0.9998
313	1.73	0.9997	1.61	0.9997
318	1.64	0.9996	1.54	0.9998

large for the non-linear transition state implied in Scheme 2. The present data, thus do not enable one to distinguish between the two mechanisms. Chromate ester formation is not likely to be very much susceptible to structural influence.[8,9] The large negative reaction constant can thus arise only out of the differential effects of the substituents on the rate-determining step.



(4)

Scheme 2.

Experimental

Materials. The preparation and specification of the alcohols used have been described earlier.[10] Isotopic purity of ethan-1,1-d_2-ol, as determined by NMR, was 89±5%. The oxidant was prepared by the method of Corey and Suggs.[1] *p*-Toluenesulfonic acid (TsOH) was used as a source of hydrogen ions. The solvents were purified and dried in the usual manner.[11] All reagents were of analytical grade.

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

Kinetic Measurements. The reactions were carried out under pesudo-first-order conditions by keeping a large excess of the alcohol over PCC. The temperature was kept constant to ±0.1 K. The reactions were followed iodometrically. The rate constant were computed from the plots of log [oxidant] against time and were reproducible within ±4%. The solvent was dichloromethane-nitrobenzene —1:1 (v/v)—, unless otherwise stated. The reaction mixtures were homogenous in the solvent systems used. The rate for the deuterated alcohol was corrected for the ordinary alcohol present.

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