258 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57*, *258—260 (1984)* [Vol. 57, No. 1

Kinetics and Mechanism of the Oxidation of Alcohols by Pyridinium Fluorochromate

Manabendra N. Bhattacharjee, Mihir K. Chaudhuri,* and Himadri S. Dasgupta
Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

(Received February 1, 1983)

Pyridinium fluorochromate, $C_5H_5NHCrO_3F$, oxidizes benzyl alcohol, ethanol, and cyclohexanol to benzaldehyde, acetaldehyde, and cyclohexanone, respectively. While each of the oxidation, studied in acetonitrile–nitrobenzene (1 : 1, v/v) medium, is first order with respect to the oxidant, the rate is almost independent of the substrate concentration. The reactions are catalyzed by acid, the acid-catalyzed reactions being very fast, precluded determination of their order in acid medium. The effects of temperatures and solvent compositions were studied and activation parameters evaluated. Probable mechanisms are discussed.

There has been a continued interest in the development of new chromium(VI) reagents[1–6] for the effective oxidation of organic substrates, particularly alcohols, under mild conditions, and significant improvements were achieved, in recent years, by the use of new oxidizing agents.[2–6] We have very recently developed[7] a new reagent pyridinium fluorochromate, $C_5H_5NHCrO_3F$ (PFC) and found several advantages of our reagent over similar oxidizing agents in respects of amounts of oxidant and solvent required, short reaction times, and high yields. The mechanism of oxidations involving this important reagent has not yet been reported. The present paper describes the kinetics of oxidation of three typical alcohols *viz.*, benzyl alcohol, ethanol, and cyclohexanol, studied in medium acetonitrile–nitrobenzene (1 : 1, v/v), evaluates the reaction constants and discusses the probable mechanism.

Experimental

All chemical used were reagent grade products. The solvents were purified and dried by the literature methods.[8] *p*-Toluenesulfonic acid (TsOH) and benzoic acid were used in the attempts to study the acid-catalyzed reactions. Pyridinium fluorochromate, PFC, was synthesized by the method originally described in our previous paper.[7]

The reaction products benzaldehyde, acetaldehyde and cyclohexanone were characterized by spectral analyses and estimated as their 2,4-dinitrophenylhydrazones.

For kinetic measurements, the reactions were performed under pseudo-first-order conditions by maintaining a large excess (×5 or greater) of alcohol over PFC. The reactions were carried out at constant temperature (±0.1 K) and progress of the reactions were followed by iodometric estimation of unreacted chromium(VI), after quenching the reaction. The medium of reactions was always 1 : 1 (v/v) acetonitrile: nitrobenzene, unless otherwise stated. Acetonitrile–nitrobenzene system was chosen as the solvent because it was observed in our previous studies[7] that acetonitrile did not react with PFC. The reaction mixtures were homogeneous for the total period of kinetic investigation.

Computations of the rate constants were made from the plot of log[oxidant] against time. The values reported are the mean of at least duplicate runs and are reproducible to within ±4%.

Dielectric constants for the varying proportions of acetonitrile–nitrobenzene mixtures were estmiated from the dielectric constants of the pure solvents[9] and are set out in Table 3. A constant ionic strength could not be maintained owing to the nonaqueous nature of the reaction medium. It may, however, be mentioned that the variation in ionic strength did not bring about any change[10] in the oxidation of benzyl alcohol by chromium(VI) oxide in aqueous acetic acid medium.

The uncatalyzed reactions were studied with varying temperatures of 303, 308, 313, and 318 K (error limit ±0.1 K) respectively for all the three alcohols (Table 4). The frequency factors were determined on the basis of the results obtained thereof. The activation parameters were evaluated by the standard procedure,[11] within allowable average error limit (at 303 K) (Table 5).

Results and Discussion

The oxidation of benzyl alcohol, ethanol and cyclohexanol by PFC in 1 : 1 (v/v) acetonitrile–nitrobenzene leads to the formation of benzaldehyde, acetaldehyde and cyclohexanone respectively in very high yields (>90%), showing no indication of further oxidation of the carbonyls conforming to our earlier synthetic studies involving PFC.[7]

The stoichiometry of various oxidations studied herein were estimated by the reaction of the respective alcohol with an excess of oxidant (PFC) followed by estimating the unreacted Cr^{VI}. In some runs, however, an excess of alcohols were used followed by the estimation of the carbonyl product. The stoichiometry of the reactions can be represented as follows:

$$3RCH_2OH + 2Cr^{VI} \longrightarrow 3RCHO + 6H^+ + 2Cr^{III}. \quad (1)$$

The stoichiometry of the reactions with cyclohexanol was determined in an analogous manner,

$$3C_6H_{11}OH + 2Cr^{VI} \longrightarrow 3C_5H_{10}CO + 6H^+ + 2Cr^{III}. \quad (2)$$

Like the analogous PCC[12–14] reactions, all the three alcohols studied herein were found to be first order with respect to time, because the first order rates were constant at different times. The reactions were also observed to be clearly first order with respect to the oxidant (PFC) as the rate constants were found to be practically unaltered for most of the reaction times (Table 1) with varying concentration of oxidant. The most prominent difference in the oxidations involving PCC[12–14] and those involving PFC is that the order of the reactions of the three alcohols with respect to the substrate concentrations was found to be practically constant enabling us to infer that the rates are almost independent of substrate concentrations. However, a small but steady increase in the rate constant values for all the three alcohols with increasing concentrations of the substrate

TABLE 1. OXIDANT DEPENDENCE OF THE REACTION RATE
$T=303$ K

[Oxidant] / 10^{-3} mol dm^{-3}	$k_1/10^{-4}$ s^{-1}		
	[Ethanol] / 0.1 mol dm^{-3}	[Benzyl alcohol] / 0.01 mol dm^{-3}	[Cyclohexanol] / 0.01 mol dm^{-3}
1	6.765	8.413 (0.075) 12)	9.233
2	6.77 (0.10) 13)	7.95 (0.075) 12)	9.5
3	6.62	8.41 (0.072) 12)	9.34
4	6.56 (0.973) 13)	8.27 (0.077) 12)	9.59
5	6.64	8.21 (0.076) 12)	9.60

PCC oxidation data in parentheses.

TABLE 2. SUBSTRATE DEPENDENCE OF THE REACTION RATE
[PFC]$=0.001$ mol dm^{-3}; $T=303$ K

Ethanol		Benzyl alcohol		Cyclohexanol	
Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}	Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}	Concn / mol dm^{-3}	$k_1/10^{-4}$ s^{-1}
0.1	6.765 (0.10) 13)	0.01	8.413 (0.075[a]) 12)	0.01	9.233
0.2	7.87 (0.207) 13)	0.02	9.66 (0.152[a]) 12)	0.02	13.89
0.3	8.55	0.03	10.1	0.03	15.79
0.4	9.16 (0.41) 13)	0.04	10.52 (0.306[a]) 12)	0.04	17.78
0.5	10.6	0.05	11.54	—	—

PCC oxidation data in parentheses: a) Values at 298 K.

TABLE 3. DEPENDENCE OF REACTION RATE ON SOLVENT COMPOSITION
[Oxidant]$=0.002$ mol dm^{-3}; $T=303$ K

Nitrobenzene (%)	Acetonitrile (%)	Dielectric constant	[Ethanol] / 0.2 mol dm^{-3} $k_1/10^{-5}$ s^{-1}	[Benzyl alcohol] / 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}	[Cyclohexanol] / 0.02 mol dm^{-3} $k_1/10^{-4}$ s^{-1}
30	70	36.7	1.01	1.05	3.08
40	60	36.4	1.997	1.77	5.31
50	50	36.16	4.05	3.15	7.2
60	40	35.9	7.97	4.3	10.27
70	30	35.6	15.82	5.51	12.95

TABLE 4. RATE CONSTANTS FOR THE UNCATALYZED OXIDATION OF ALCOHOLS BY PYRIDINIUM FLUOROCHROMATE
[PFC]$=0.001$ mol dm^{-3}

Substrate	Concentration of substrate/mol dm^{-3}	$k/10^{-4}$ l mol^{-1} s^{-1} a)			
		303 K	308 K	313 K	318 K
Ethanol	0.1	6.765	7.112	7.447	7.798
		(1.0) 13)	(1.4) 13)	(1.93) 13)	(2.63) 13)
Benzyl alcohol	0.01	8.413	8.593	8.811	9.057
		(7.5) 12)	(11.2) 12)	(15.5) 12)	(21.6) 13)
Cyclohexanol	0.01	9.233	9.619	10.0	10.447
		—	(88.3) 14)	(133.3) 14)	(208.3) 14)

a) PCC oxidation data in parentheses.

TABLE 5. ACTIVATION PARAMETERS FOR THE OXIDATION OF ALCOHOLS BY PYRIDINIUM FLUOROCHROMATE

Substrate	ΔH^*/kJ mol^{-1} a)	$-\Delta S^*$/J mol^{-1} K^{-1} a)	ΔF^*/kJ mol^{-1} a)
Ethanol	7.657(51.8) 13)	280.51(153) 13)	92.65(98.2) 13)
Benzyl alcohol	3.89 (54.7) 12)	291.33(125) 12)	92.06(92.0) 12)
Cyclohexanol	6.127(93.0) 14)	282.98($-$18) 14)	91.82(87.4) 14)

a) PCC oxidation data in parentheses.

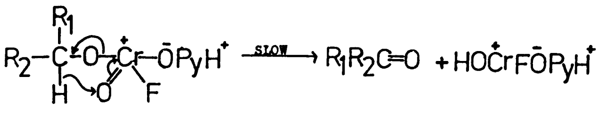
has been observed (Table 2) and a plot of log k_{obsd} against log [substrate] shows that the rates increase in very small fractions with the sequential increase in substrate concentration. This most probably implies that complex formation between the substrate and oxidant is taking place in present cases.

Our attempts to study the acid-catalyzed oxidations of the three alcohols were unsuccessful. Attempted acid-catalyzed reactions involving *p*-Toluenesulfonic acid or benzoic acid, and varying proportions of solvent compositions were observed to be too fast to measure the rate.

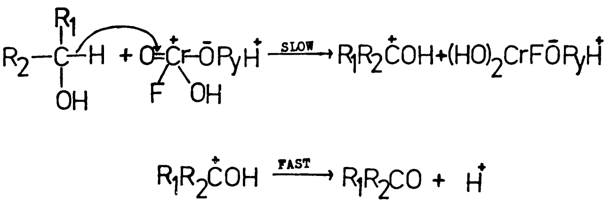
The results of uncatalyzed reactions with varying composition of the solvent components (Table 3) shows that the reaction rate decreases with increase in dielectric constant (though small) of the medium suggesting that the more polar solvents may require larger reaction times for the oxidation reactions. A plot of log k_1 against the inverse of dielectric constants of the media is a straight line with positive slope and implies the occurrence of an interaction between a dipole and a positive ion,[15] and also indicates the probable involvement of a protonated $\mathrm{Cr^{VI}}$ species, in the presence of an acid, in the rate determining step. However, since the range of dielectric constants varies between 35.6 and 36.7 showing a large increase in the rate, the observed change could as well be solvent specific rather than owing to the effect of change in dielectric constant.

The near constancy of the values of the free energies of activation of the three reactions (Table 5) suggest that a similar mechanism is operative in each of the three oxidations. Free energies of the acid-catalyzed reactions appear to be lower, as there has been a pronounced increase in the rate of catalyzed reactions suggesting thereby that a protonated $\mathrm{Cr^{VI}}$ species may be involved in the rate determining step in the presence of an acid. This is in accord with the involvement of such species well established in chromium(VI) oxide oxidations.[16]

The large negative entropy values obtained in the present studies, suggest that the solvent molecules are strongly oriented or 'frozen' around the ions thereby resulting in the loss of entropy,[17] the effect being larger in nonpolar solvents. This conforms to the contention that the decrease of polarity of the medium results in increase of the entropy value and the number of unbound molecules in the solution increases.[18] This also accounts for the lowering of rate coefficient values with increasing polarity of the medium. Comparatively greater reactivity of pyridinium fluorochromate (PFC) over that of the corresponding chlorochromate (PCC), as shown in our previous paper,[7] can now be understood from the relatively higher negative entropy values of the reactions. We believe that the bonding of F with chromium in PFC facilitates larger charge distribution in the transition state in the cases of PFC oxidation and correlates well with the observed entropy values.



Scheme 1.



Scheme 2.

In view of the above results it appears that a hydride transfer mechanism is involved in the rate determining step of the PFC oxidations. It is possible that the hydride transfer may take place either through the prior formation of chromate (Scheme 1), or directly (Scheme 2). The present data also suggest, like the similar oxidations involving chromic acid,[16] a chromate formation in the rate-determining step (Scheme 1) although the chances of Scheme 2 can not be totally ruled out. It is also expected that the chromate intermediate will be better stabilised in the less polar medium and will enhance the oxidation rate, thus conforming to the observations made by us.

The authors wish to thank the University for the award of a fellowship (U. G. C.) to one of them (M. N. B.) and also to Dr. A. K. Sil, for his interest in the work.

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