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Kinetics and Mechanism of Oxidation of Diethyl Sulfide by Pyridinium Chlorochromate

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The kinetics of oxidation of diethyl sulfide (DES) by pyridinium chlorochromate (PCC) have been studied in 50% acetic acid-50% water (v/v) mixture. The reaction is first-order each in [DES], [PCC] and [H^+]. Diethyl sulfoxide is the product of the reaction. A mechanism involving the formation of intermediate complex between protonated PCC and sulfide in a slow step has been proposed.

INTRODUCTION

The mechanism of Cr(VI) oxidation of organic sulfur compounds[1] has been investigated in aqueous acetic acid. Pyridinium chlorochromate (PCC) as a potential oxidant of secondary alcohols was first reported by Corey and Suggs[2]. The kinetics of oxidation of aryl methyl sufides[3] by PCC in dipolar protic and aprotic solvents have been studied. The results of this study showed that the solvent system has a pronounced effect on the mechanism of oxidation of sulfides. Panigrahi and Mahapatro[4] reported the kinetics of oxidation of alkyl sulfides by PCC in chlorobenzene-nitrobenzene mixture. We report herein the kinetics and mechanism of oxidation of diethyl sulfide (DES) by PCC in 50% acetic acid-50% water (v/v) mixture.

EXPERIMENTAL

Diethyl sulfide (Fluka) was used as such. Pyridinium chlorochromate was prepared by the method of Corey and Suggs[2]. Acetic acid was purified by standard procedure[5]. All other chemicals used were AR grade.

The kinetic studies were carried out under pseudo first-order conditions ([DES] $\gg$ [PCC]) by estimating the unreacted PCC by iodometric procedure. The pseudo first-order rate constant (k_1) in each kinetic run was evaluated from the slope of the linear plot of log [PCC] *vs.* time ($r > 0.995$) by the method of least-squares. The second-order rate constants (k_2) were obtained from $k_2 = k_1/[DES]$.

The reaction mixture from an actual kinetic run was extracted with ether and dried over anhydrous sodium sulfate, and the solvent was removed. The residue was analysed by TLC using the solvent system of 90% benzene-10% pet-ether (40–60°C) (v/v). The reaction mixture gave two spots, one corresponding to diethyl sulfide ($R_f = 0.94$) and the other due to diethyl sulfoxide ($R_f = 0.52$). Estimation of the unreacted PCC from reaction mixture where [PCC] > [sulfide] after the completion of the reaction showed that three moles of DES are oxidised for two moles of PCC. The stoichiometry is represented by

$$3C_2H_5SC_2H_5 + 2C_2H_5\overset{+}{N}HCrO_3Cl^- + 6H^+ \rightarrow 3C_2H_5SOC_2H_5 + 2C_5H_5\overset{+}{N}HCl^- + 2Cr(III) + 3H_2O$$

RESULTS AND DISCUSSION

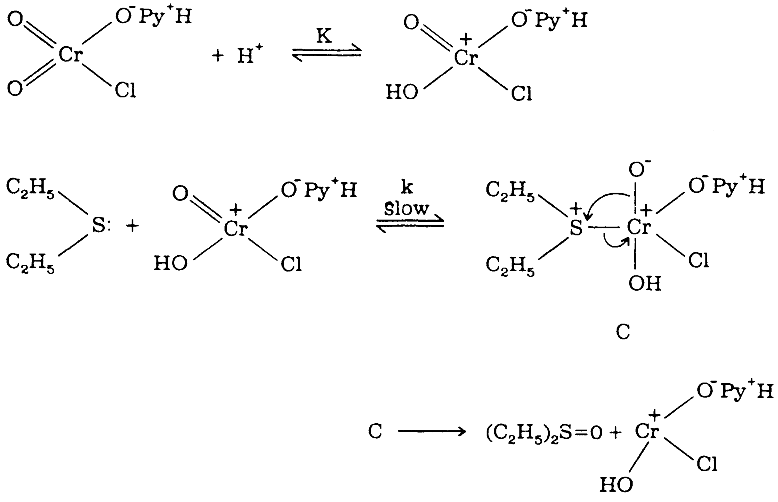
The reaction is first-order in PCC as shown by the linearity of the plots of log [PCC] versus time (r > 0.995) and also by the constant values of the pseudo first-order rate constants at different [PCC] at constant [DES] (Table-1). On varying [DES] at constant [PCC] the second-order rate constants gave concordant values (Table-1). Further the logarithm of psuedo first-order rate constants showed a linear dependence on the log [DES] with a slope of 0.98 (r = 0.993). These results indicate that the order with respect to [DES] is also unity.

TABLE-1
DEPENDENCE OF RATE ON [PCC] AND [DES]

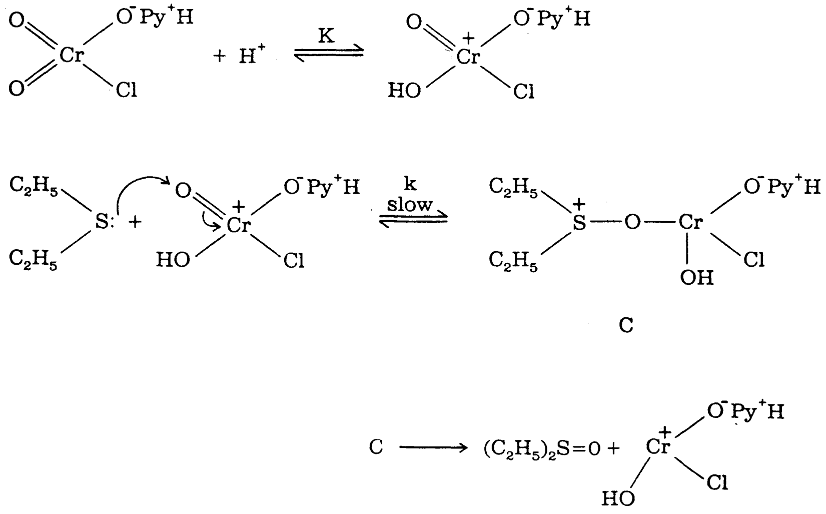
Solvent: 50% AcOH-50% H_2O (v/v) mixture, temperature = 25°C

10^4 [PCC] (mol dm^{-3})	10^2 [DES] (mol dm^{-3})	10^4 k_1 (s^{-1})	10^2 k_2 (dm^3 mol^{-1} s^{-1})
5.00	2.00	19.50	9.75
7.40	2.00	22.00	11.00
10.00	2.00	21.10	10.60
15.00	2.00	22.90	11.50
20.00	2.00	21.90	11.00
5.00	0.50	4.91	9.82
5.00	0.74	7.13	9.64
5.00	1.00	11.30	11.30
5.00	1.50	14.70	9.80

The reaction rate increased with an increase in the concentration of $HClO_4$ (Table-2) (in evaluating $[H^+]$, the dissociation of acetic acid was also taken into account). The unit slope obtained from the plot of log k_2 versus log $[H^+]$ (slope = 1.06, r = 0.998) shows that the order in $[H^+]$ is one. The rate of oxidation is unaffected by change in ionic strength brought about by the addition of sodium perchlorate (Table-2). This may presumably be due to the attack of an ion on a neutral molecule in the rate-determining step. The reaction rate increases with increase in acetic acid content in the reaction mixture (Table-2). A plot of log k_1 *vs.* 1/D is linear with positive slope (r = 0.994, slope = 59.3). This suggests[6] an interaction between a positive ion and a dipole and confirms that the rate-determining step involves a protonated Cr(VI) species. The pseudo first-order



Scheme-1



Scheme-2

rate constants for the oxidation of DES in the absence of acrylamide and in the presence of 0.005 mol dm^{-3} and 0.01 mol dm^{-3} acrylamide are 4.91, 5.06 and 5.29×10^{-4} s^{-1} respectively. Thus, acrylamide has no perceptible effect on the rate and no polymerization occurred. This clearly establishes the absence of free radical formation during the PCC oxidation of DES. The second-order rate constants at 25, 30, 35 and 45°C are 9.82, 14.9 18.1 and 26.0×10^{-2} dm^3 mol^{-1} s^{-1} respectively. The enthalpy and entropy of activation are 34.3 kJ mol^{-1} and -149 JK^{-1} mol^{-1} respectively. The negative value of the entropy of activation implies that the activated complex should have an exact specificity of orientation.

The results of kinetic studies indicate the formation of 1 : 1 complex between protonated PCC and sulfide in the slow step. The complex subsequently decomposes into products. The formation of the intermediate complex (C) and its decomposition into products can be shown as in Scheme-1 or Scheme-2.

Both schemes envisage an oxygen atom transfer from the oxidant and this is in accord with the earlier observation made for the diacetyl chromate oxidation of diphenyl sulfide[7]. It is pertinent to mention here that the oxidations of phenyl methyl sulfide[3] and alkyl sulfide[4] by PCC in chlorobenzene-nitrobenzene mixture followed Michaelis-Menten type kinetics.

Based on the proposed mechanism, the rate law for the PCC oxidation of DES in protic solvent may be written as

$$\frac{-d[PCC]}{dt} = kK[DES][PCC][H^+].$$

The proposed mechanism and rate law are in confirmity with the observed experimental features.

TABLE-2

EFFECT OF VARYING $[H^+]$, IONIC STRENGTH AND PERCENTAGE OF SOLVENT COMPOSITION ON THE RATE OF OXIDATION[a]

10^2 $[H^+]$ (mol dm^{-3})	10^2 k_2[b] (dm^3 mol^{-1} s^{-1})	10^2 I (mol dm^{-3})	10^2 k_2[c] (dm^3 mol^{-1} s^{-1})	AcOH-H_2O (% v/v)	10^4 k_1 (s^{-1})
1.20	10.50	1.25	9.82	40–60	3.07
1.70	15.20	1.70	10.40	50–50	4.91
2.20	21.40	2.20	11.80	60–40	10.40
2.70	25.20	3.20	11.00	65–35	18.10
3.20	28.80	4.20	10.50	70–30	24.80
4.15	39.60	—	—	—	—

[a] 10^3 [DES] = 5.00 mol dm^{-3}, 10^4 [PCC] = 5.00 mol dm^{-3}, temperature = 25°C

[b] 10^2 I = 4.20 mol dm^{-3}, solvent: 50% AcOH-50% H_2O (v/v) mixture.

[c] Solvent: 50% AcOH-50% H_2O (v/v) mixture.

REFERENCES

1. C. Srinivasan, A. Chellamani and S. Rajagopal, *J. Org. Chem.*, **50,** 1201 (1985).
2. E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
3. K. Rajasekaran, T. Baskaran and C. Gnanasekaran, *J. Chem. Soc., Perkin Trans.*, **2,** 1183 (1984).
4. G.P. Panigrahi and D.D. Mahapatro, *Int. J. Chem. Kinet.*, **13,** 85 (1981).
5. K.J.P. Orton and A.E. Bradfield, *J. Chem. Soc.*, 986 (1927).
6. E.S. Amis, Solvent Effects on Reaction Rates and Mechanism, Academic Press, New York, pp. 42, 43 (1966).
7. K.B. Wiberg, Oxidation in Organic Chemistry, Academic Press, New York, Part A, p. 182 (1965).

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