Kinetics of Mercuric Chloride-catalysed Oxidation of Isopropyl Alcohol & of Acetone by Ceric Sulphate in Sulphuric Acid

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Kinetics of oxidation of isopropyl alcohol to acetone and of acetone to formic acid by ceric sulphate in sulphuric acid in the presence and absence of mercuric chloride have been studied. In both the oxidations, mercuric chloride catalyses the reaction. The oxidation of isopropyl alcohol is heterolytic in the presence of mercuric chloride; whereas it is homolytic in the absence of mercuric chloride. The oxidation of acetone is heterolytic in both the cases.

THE silver ion catalysis of oxidations with peroxydisulphate[1] and with Ce^{4+} has been reported[2]. The former is homolytic and the latter is heterolytic. In the first case the catalysis is due to Ag^{2+} and in second Ag^+. A likely simpler catalyst is mercuric chloride, where the electrophilic activity is related to its capacity for forming complex anions. This has been established for the solvolysis of alkyl chlorides[3] and for the hydrolysis of anions of esters[4]. In this paper we present the kinetic data of the Ce^{4+} oxidation of isopropyl alcohol and of acetone in the presence and absence of mercuric chloride.

Materials and Methods

A stock solution of ceric sulphate (BDH) was prepared in $1M$ sulphuric acid and standardized with standard ferrous sulphate. Isopropyl alcohol, acetone and other chemicals used were BDH (AR) grade.

Kinetic measurements — The reacting substances were allowed to equilibrate at the desired temperature. The cerium solution was the last to be added. Ceric ion consumption was followed by removing 10 ml aliquots which were added to solutions containing excess of ferrous ions. This excess was determined by back titration with standard ceric solution in the presence of ferroin indicator. As the rate of oxidation of acetone is very much higher than that of isopropyl alcohol, we adopted the following method for evaluating the rate constants for the oxidation of isopropyl alcohol to acetone. The experimentally determined value of x, the volume of titrant corresponding to the Ce^{4+} consumed, was multiplied by 2/10·6 (2 moles for the oxidation of alcohol[2] and 8·6 moles for the oxidation of acetone[5]) to get the cerium equivalent used for the alcohol alone. When this value was used in the integrated form of the first order rate equation, the values of the rate constants were steady (Table 1). The second order rate constants were obtained by dividing the first order rate constants with the concentration of the organic compound. All runs were conducted

in duplicate. The activation parameters were obtained for rate measurements at four temperatures. The method of least squares was used for obtaining the enthalpy of activation. The probable error in the values of activation parameters were found as follows: $\Delta H^{\ddagger} \pm 0 \cdot 2$ kcal; $\Delta S^{\ddagger} \pm 1$ (e.u.); $\Delta F^{\ddagger} \pm 0 \cdot 2$ kcal.

Results and Discussion

Sethuram and coworkers studied the kinetics of the reaction between ceric sulphate and isopropyl alcohol in sulphuric acid and reported that when the alcohol was in excess the rate of disappearance of Ce^{4+} follows first order kinetics and the stoichiometry of the reaction corresponds to the consumption of 2 moles of Ce^{4+} per mole of alcohol to yield one mole of acetone[2]. Shorter and Hinshelwood studied the kinetics of the reaction between acetone and Ce^{4+} in sulphuric acid and showed that one mole of acetone consumes 8·6 moles of Ce^{4+} forming 1·4 moles of formic acid and that this stoichiometry is independent of the concentration ratio of the ceric sulphate to acetone[5]. The authors noted that the rate of oxidation of acetone was much higher than that of isopropyl alcohol. In agreement with this, both for the normal and mercuric chloride catalysed oxidations, we found that when cerium was in excess one mole of isopropyl alcohol consumed 10·6 moles of Ce^{4+} and that the first order rate constants (k) for the oxidation of isopropyl alcohol with Ce^{4+} in sulphuric acid, with the alcohol in excess showed a sharp upward drift more than half-fold when the reaction has proceeded by about 60% (Table 1). We adopted a method (see materials and methods) for separately evaluating the rate constants (k_1) for the oxidation of isopropyl alcohol to acetone.

The second order rate constants for the oxidation of isopropyl alcohol in the absence of mercuric chloride (k_2) is independent of the polarity of the medium (Table 2). This observation supports the homolytic nature of the uncatalysed reaction. In the mercuric chloride-catalysed oxidation the second order rate constants increase with increase in

TABLE 1 — TYPICAL KINETIC RUN FOR THE OXIDATION OF ISOPROPYL ALCOHOL WITH CERIC SULPHATE

$\{[Ce^{4+}] = 0.0040M; \quad [\text{isopropyl alcohol}] = 1.306M; \quad [H_2SO_4] = 1.0M; \quad \text{temp.} = 54\}$

Time (min)	x	$2x/10.6$	$10^3 k$ (min^{-1})	$10^3 k_1$ (min^{-1})
0	0.00			
60	1.40	0.265	3.21	0.633
120	2.76	0.521	4.09	0.633
142	3.22	0.608	4.21	0.629
157	3.58	0.675	4.51	0.635
180	4.06	0.766	4.69	0.632
202	4.52	0.853	4.99	0.632
Infinity	7.12			

x represents ml of $0.00562M$ ceric sulphate.

TABLE 2 — KINETIC DATA FOR THE OXIDATION OF ISOPROPYL ALCOHOL AND ACETONE WITH CERIC SULPHATE

$\{[Ce^{4+}] = 0.0050M; [H_2SO_4] = 1.0M\}$

Substrate % (v/v)	[Substrate] mole	Uncatalysed [HgCl$_2$]=nil		Catalysed [HgCl$_2$]=0.100M	
		$10^3 k_1$ (min^{-1})	$10^3 k_2$ (litre mole^{-1} min^{-1})	$10^3 k_1$ (min^{-1})	$10^3 k'_2$ (litre mole^{-1} min^{-1})
		ISOPROPYL ALCOHOL; TEMP. 40°			
20	2.61	0.276	0.106	1.11	0.426
10	1.31	0.139	0.106	0.699	0.536
5	0.653	0.0686	0.105	0.387	0.593
		ACETONE; TEMP. 15°			
10	1.36	4.96	3.65	40.5	29.8
5	0.68	2.61	3.84	22.7	33.4
2	0.272			10.2	37.5
1	0.136			5.52	40.60

TABLE 3 — RATE CONSTANTS AND ACTIVATION PARAMETERS AT 25°C FOR THE OXIDATION OF ISOPROPYL ALCOHOL AND ACETONE WITH CERIC SULPHATE

$\{[Ce^{4+}] = 0.0050M; [H_2SO_4] = 1.0M\}$

Temp. °C	$10^3 k_2$ (litre mole^{-1} min^{-1})	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger}$ (e.u.)	$\Delta F^{\ddagger}$ (kcal/mole)
ISOPROPYL ALCOHOL, 1.306M; UNCATALYSED				
25.0	0.0105	28.1	+13	24.3
35.0	0.0506			
40.0	0.106			
50.0	0.452			
CATALYSED: [HgCl$_2$]=0.1M				
25.0	0.108	19.4	−12	22.8
35.0	0.415			
40.0	0.536			
45.0	0.897			
ACETONE, 1.360M; UNCATALYSED				
10.0	2.13			
15.0	3.65			
25.0	10.3	16.9	−11	20.2
28.0	13.6			
CATALYSED: [HgCl$_2$]=0.1M				
10.0	30.5			
15.0	51.7			
20.0	86.0			
25.0	141.0	16.5	−7	18.6

TABLE 4 — EFFECT OF MERCURIC CHLORIDE ON THE RATE OF OXIDATION OF ISOPROPYL ALCOHOL AND OF ACETONE WITH CERIC SULPHATE IN SULPHURIC ACID

$\{[Ce^{4+}] = 0.0050M; [H_2SO_4] = 1.0M\}$

[HgCl$_2$] M	$10^4 k'_2$ (litre mole^{-1} min^{-1})	
	(a)	(b)
0.00	1.06	36.5
0.025	3.62	168.0
0.050	4.17	298.0
0.075	4.80	410.0
0.100	5.36	517.0

(a) [Isopropyl alcohol]=1.306M; temp.=40°.
(b) [Acetone]=1.360M; temp.=15°.

polarity of the medium (Table 2), suggesting a polar transition state for the catalysed reaction. Support for this comes from the activation parameters. The $\Delta H^{\ddagger}$ value changes from 28.1 kcal in the uncatalysed to 19.4 kcal in the catalysed reaction (Table 3). There is also a decrease of entropy of activation from +13 e.u. to −12 e.u., suggesting an increased solvation of the transition state. The decrease in the free energy of activation is of the order of 1.5 kcal. The order with respect to catalyst is 0.47, (Table 4) and the catalytic coefficient, $k'_2 - k_2/k_2$ at 25° is 9.3 (k'_2 and k_2 are the second order rate constants in the presence and absence of mercuric chloride respectively).

In the oxidation of acetone by ceric sulphate when the acetone was in excess the rate of disappearance of ceric ions follows first order kinetics, both in the presence and absence of mercuric chloride. First order dependence of the reaction was also observed when Ce^{4+} was in excess. Shorter and Hinshelwood have argued that, although several steps are involved in the heterolytic oxidation of acetone by cerium, the rate determining step involves only two species — the enol form of acetone and the ceric sulphate[5].

We have observed that the enthalpy of activation for the catalysed and uncatalysed oxidations are nearly the same (Table 3). There is an increase in the entropy of activation for the catalysed oxidation from −11 to −7 e.u. and a decrease of free energy of by 1.6 kcal. The order with respect to mercuric chloride is nearly one (0.96) and the catalytic coefficient, $k'_2 - k_2/k_2$ at 25° is 12.7. Both for the catalysed and uncatalysed oxidations the second order rate constants increase with increase in polarity of the medium (Table 2). This supports the heterolytic nature of the reactions.

Further work with different alcohols and ketones is in progress. Till then we reserve our comments regarding the mechanism of the catalysed oxidations.

References

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