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KINETICS OF THE OXIDATION OF CYCLOPENTANONE AND CYCLOOCTANONE BY CERIUM (IV)

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ABSTRACT

Kinetic investigations of oxidation of Cyclopentanone and Cyclooctanone by Cerium (IV) in H_2SO_4 medium in acetic acid -water (1:1) solution have been made in the temperature range 50 - 80^0 C iodometrically. The reaction is first order with respect to both Ce (IV) and the substrate. Corresponding 1, 2- diaketones are found to be oxidation product. H_2SO_4 shows negative acid catalyzed effect on reaction rate, while positive effect of ionic strength on rate constant is observed. Reaction rate increases with acetic acid concentration. Magnitude of Arrhenius parameters indicates the bimolecular nature of the reaction. Salt effect and low energy values support the formation of intermediate complex, decomposition of which is slow and rate determining step. A suitable mechanism is proposed.

Key words: Cyclopentanone, Cyclooctanone, Ionic strength, Intermediate complex.

INTRODUCTION

Oxidation of cyclopentanone and cyclooctanone by cerium (IV) in acidic medium has 1:4 stoichiometry and exhibits unit order each in Ce(IV) and substrate . The reaction proceeds via formation of an oxidant-substrate complex and its subsequent decomposition in rate determining step to yield products. The effects of H^+ molarity , ionic strength ,dielectric constant and temperature on reaction rate have been studied. The reaction constants involved in the mechanism have been computed. Activation parameters have been calculated with respect to the slow step of the proposed mechanism of reaction.

Cerium (IV) is one of the strong oxidizing agents in aqueous solution with an oxidation potential of -1.43 ± 0.05 Volts in 1-8 N H_2SO_4.[1] The common valencies[2] of ceium salts are III and IV. Most probable unhybridised electronic configuration shows that monomeric Ce (IV) is one electron oxidant. A survey of literature reveals[3-5] that cerium is used for the oxidation of various organic compounds but a systematic kinetic study of the oxidation of cyclic ketones has not received much attention so far. In the present paper we report the kinetic investigations on the oxidation of cyclopentanone and cyclooctanone by Ce (IV) in acidic medium using aqueous acetic acid as solvent.

EXPERIMENTAL

Chemicals of A.R. or G.R. grade and freshly prepared double distilled water was used to prepare all solutions. Stock solution of the oxidant was prepared by dissolving accurately weighed amount of Ceric Ammonium Sulphate (C.A.S.) in 2N H_2SO_4 and kept in corning glass bottle. The strength of the solution was checked every time iodometrically. The substrate solutions were prepared by dissolving known amounts in glacial acetic acid. Aqueous hypo solution was prepared[6] and standardized against $K_2Cr_2O_7$ iodometrically using 0.5 % starch indicator. 20% KI solution was prepared and 5 ml of this was used in every titration.

Kinetic measurements

The reactions were studied under pseudo first order condition taking a known large excess of cyclic ketones over C.A.S. (at least 10 times) by

monitoring the decrease in the concentration of C.A.S. iodometrically. The temperature was kept constant at 60°C within ± 0.02°C. The solvent was 1:1 (v/v) acetic acid – water mixture. The pseudo first order rate constants were calculated using integrated form of first order rate equation and compared with the graphical values obtained from the linear plots of log (a/a-x) against time. To determine the stoichiometry a known excess of C.A.S. over the organic substrate was allowed to stand for 48 hours for the completion of oxidation reaction and the amount of unconsumed oxidant was estimated volumetrically.

RESULT AND DISCUSSION

The reactions were found to be first order with respect to oxidant as well as the substrate. Further, the pseudo first order rate constants were found to be independent of initial concentration of C.A.S. (Table - 1) with a slight initial retardation in the rate, which can be attributed to the formation of dimeric species $(Ce^{4+})_2$ and formation of complex with substrate both of which are chemically un-reactive. Rate constant k_1 increases with increase in initial concentration of substrate and constant k_2 obtained by k_1/[cyclic ketone] confirms the first order dependence on the substrate concentration. Linear plots of $1/k_1$ versus 1/[cyclic ketone] with a positive intercept on $1/k_1$ axis suggest the activated complex formation between Ce(IV) and cyclic ketone. The reaction rate decreases with increase in H_2SO_4 molarity. In Cerium (IV) oxidation it has been proposed that the inhibitory action is due to HSO_4^- [7] ion which converts the reactive form of Ce(IV) , $Ce(SO_4)_2$ to the un-reactive species $HCe(SO_4)^{3-}$ according to the following equilibrium:

$$Ce(SO_4)_2 + HSO_4^- \rightarrow HCe(SO_4)^{3+}$$

Linear plots of first order rate constant Vs H^+ molarity showing decreasing slopes with increasing ionic strengths confirm negative acid catalysis subject to positive salt effect (Table 1 & 2).

Table - 1: Rate constants for the Oxidation of Cyclopentanone and Cyclooctanone by Ceric Ammonium Sulphate at 333K

[Oxidant] X 10^3 mol dm^{-3}	[Cyclic ketone] X 10^2 mol dm^{-3}	$[H_2SO_4]$ mol dm^{-3}	$[CH_3COOH]$ percentage	K_1 X 10^3 min^{-1} Cyclopentanone	Cyclooctanone
1.00	8.00	2.00	50.00	7.25	10.52
2.50	8.00	2.00	50.00	7.21	10.41
4.50	8.00	2.00	50.00	7.17	10.27
6.00	8.00	2.00	50.00	7.01	10.20
8.00	8.00	2.00	50.00	7.00	10.13
4.50	5.00	2.00	50.00	4.27	6.54
4.50	6.50	2.00	50.00	5.56	8.36
4.50	8.00	2.00	50.00	7.01	10.20
4.50	9.50	2.00	50.00	8.43	12.04
4.50	11.00	2.00	50.00	9.45	14.16
4.50	8.00	0.50	50.00	20.80	34.20
4.50	8.00	1.00	50.00	16.45	21.57
4.50	8.00	2.00	50.00	07.00	10.20
4.50	8.00	3.00	50.00	4.35	6.82
4.50	8.00	3.50	50.00	3.59	5.72
4.50	8.00	2.00	30.00	5.81	7.45
4.50	8.00	2.00	40.00	6.28	8.41
4.50	8.00	2.00	50.00	7.12	10.18
4.50	8.00	2.00	60.00	8.55	12.27
4.50	8.00	2.00	70.00	10.75	15.96

Table - 2: Effect of H_2SO_4 variation at constant ionic strength

[Cyclic Ketones] = 8.0 X 10^{-2} mol dm^{-3} [AcOH] = 50%(v/v)
[Ceric Ammonium Sulphate] = 4.5 X 10^{-3} mol dm^{-3} Temperature = 333K

$[H_2SO_4]$ mol dm^{-3}	$[K_2SO_4]$ mol dm^{-3}	m Ionic Strength	K_1 X 10^3 min^{-1} Cyclopentanone	Cyclooctanone
1.00	0.00	1.00	13.15	21.62
0.60	0.40	1.00	14.33	22.67
0.20	0.80	1.00	15.65	23.85
2.00	0.00	2.00	7.10	10.19
1.20	0.80	2.00	8.36	11.37
0.40	1.60	2.00	9.58	12.49
3.00	0.00	3.00	5.20	6.93
1.80	1.20	3.00	6.46	7.71
0.60	1.40	3.00	7.58	8.56

Table - 3: Rate constants and Arrhenius parameters for Cerium (IV) oxidation of cyclic ketones in acetic acid - water mixture 1:1 (v/v)

Substrate	k_1 X 10^3 min^{-1} 323K	333K	343K	353K	ΔE Kcal.mol^{-1}	ΔH`" K .cal	ΔS`" e.u	A min^{-1}	ΔG`" K.cal
Cyclopentanone	3.46	7.01	13.68	25.51	15.10	14.46	-25.02	5.7 x 10^7	22.54
Cyclooctanone	5.29	10.20	19.12	34.32	14.18	13.54	-27.08	2.04x10^7	22.29

Influence of solvent on the oxidation rate was studied by varying the composition of AcOH – H_2O mixture and it is observed that initially the rate increases slowly with the increase in percentage of Acetic Acid in binary mixture then rises sharply. This may be attributed to the increase in the protonation[9] which decreases the formation of HSO_4^- ion responsible for the elimination of reactive oxidation species from the reaction field. To study the effect of temperature oxidation study in a temperature range of 30°C was done. The linear plots of log k_1 versus 1/T confirm the validity of Arrhenius equation. The magnitude of Arrhenius parameters indicates the bimolecular nature of the oxidation reaction in each case (Table 3). Large negative values of entropy and frequency factor also confirm bimolecular nature of the reaction and the low value of ΔH points out that in the rate determining activated complex the bond braking and bond formation are of almost equal magnitude.[10]

Reaction rate increases with decrease in acid molarity at various constant ionic strengths (Table 2).

Product analysis of the reaction done by TLC confirms the corresponding 1,2-diaketones as the reaction product in each case and the stoichiometric determinations indicate the following overall reaction:

Substrate + H_2O + 4Ce(IV) → Product + 4Ce(III) + $4H^+$

Considering the keto form of cyclic ketones as reactive species, on the basis of the experimental kinetic data following stepwise mechanism has been proposed:

$$Ce(SO_4)_2 + \text{Cyclic Ketone} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{Complex} \quad (1)$$

$$\text{Complex} \xrightarrow[\text{Slow \& RD}]{k_3} \text{Free Radical} + Ce(III) + H^+ \quad (2)$$

$$\text{Free Radical} + 3Ce(IV) + H_2O \xrightarrow[k_4]{} 1,2\text{-diaketone} + 3H^+ + 3Ce(III) \quad (3)$$

The rate of formation of complex is same as rate of disappearance of Ce (IV). Hence the rate of reaction may be expressed as

$$-\frac{d[Ce(IV)\}}{dt} = \frac{d[Complex]}{dt}$$

Rate law

Considering the above steps and applying the steady state treatment with a reasonable approximation, the rate law may be written in terms of rate of consumption of Ce (IV).

$$-\frac{d[Ce(IV)\}}{dt} = K[Ce(IV)][Cyclic\ \ ketone]$$

Where, $K = k_1 / k_{2\ddagger} k_3$

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