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CHEMICAL KINETICS AND CATALYSIS

Role of Added Chloride Ions in Alteration of Reaction Pathway in the Oxidation of Cyclic Ketones by Dichloroisocyanuric Acid—A Kinetic Study[1]

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Abstract—Effect of added chloride ions on kinetics and pathway of reaction between cyclic ketones (five to eight membered rings) and dichloroisocyanuric acid (DCICA) was studied in aqueous acetic acid—perchloric acid medium. Formation of aliphatic dicarboxylic acids as the end products demonstrates the ring cleavage oxidation. Positive effect of acid and negative effect of dielectric constant on the reaction rate reveals a interaction between positive ion (oxidant in the form of H_2OCl^+) and dipolar substrate molecule. Zero and first orders by oxidant in absence and presence of added chloride ions illustrates the participation of substrate as enolic form of ketone and protonated ketone, respectively, in the rate determining steps. The observed order of reactivity of cyclic ketones (cyclohexanone > cyclooctanone > cyclopentanone > cycloheptanone) was explained on the bases of ring strain, change of hybridization and conformational considerations. The envisaged plausible mechanism based on order of reactants in presence and absence of added chloride ions was substantiated by the order of Arrhenius parameters.

Keywords: dichloroisocyanuric acid, cyclic ketones, kinetics, chloride ion, enolisation, reaction pathway.

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INTRODUCTION

According to the literature data, in some cases enol form of ketones participate in oxidation [1, 2] yielding carboxylic acids as the end products [3, 4] whereas in other cases, the protonated form of ketone undergoes the oxidation [5] to form diketones [6]. In few studies, authors reported halogenation of ketones by halogen/*N*-halogenated oxidants [7, 8].

Though, the effect of chloride ions on the kinetics of oxidation involving inorganic oxidants was explained on the basis of a chloride ion bridge activated transition state [9], very few such studies were carried out on the reactions involving *N*-halogenated oxidizing agents [10, 11] in which a pronounced effect of the added chloride ion was observed on the reaction of ketones with *N*-halogenated oxidizing agents following a change in reaction path compared to that without added chloride ion [11, 12]. Recently, we have communicated the kinetics of oxidation of acyclic ketones by DCICA in aqueous acetic acid and perchloric acid mixture, wherein products are corresponding carboxylic acids [13]. The present study is intended (a) to study the effect of added chloride ions on the kinetics and mechanism of oxidation of cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone) by DCICA in acetic acid—perchloric acid medium, (b) to learn the behavior of DCICA i.e., whether it acts as a halogenating agent and/or oxidizing agent towards ketones, (c) to ascertain the strength of DCICA with regard to cleavage of cyclic ketones and (d) to identify the active form (keto or enol) for the cylclic ketones.

EXPERIMENTAL

Cyclopetanone and cyclohexanone (Merck) were distilled before the experiments. Cycloheptanone (Fluka) was purified by vacuum distillation, and cyclooctanone (Fluka) was recrystallized. Dichloroisocyanuric acid was purchased from Fluka make and all other chemicals used were from SD Fine Chemicals. The concentration of unreacted DCICA was determined by iodometry at pH 1–2 in order to follow the reaction.

$$C_3O_3N_3H(Cl)_2 + 4I^- + 2H^+ \longrightarrow C_3O_3N_3(H)_3 + 2I_2 + 2Cl^-. \quad (1)$$

Under the employed reaction conditions, rates of self-decomposition of DCICA were negligible compared to the rates of studied reactions. Both in air and in a de-aerated atmosphere, the rate constants remained practically unaltered. In this study, average

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Table 1. Oxidation of cyclic ketones by DCICA in absence of added chloride ions [DCICA] = 0.0005 M; [Ketone] = 0.005 M; $[H^+]$ = 0.1 M; T = 35°C; solvent composition = 15 : 85 (AcOH : H_2O)

Variant	$k_0 \times 10^8$, mol L^{-1} s^{-1}			
	cyclo-hexanone	cyclo-pentanone	cyclo-heptanone	cyclo-octanone
[Ketone]				
0.0025	9.8	2.5	1.3	8.1
0.0050	18.2	6.7	3.1	16.6
0.0125	45.7	10.2	6.1	41.3
0.0250	119.0	20.8	17.8	113.5
0.0375	211.4	76.8	32.1	202.6
[Acid]				
0.0250	4.8	2.2	0.8	4.8
0.0500	8.9	5.3	2.3	7.7
0.1000	18.2	6.7	3.1	16.6
0.1500	26.7	12.3	4.6	22.6
0.3000	50.1	21.1	9.1	46.5
Solvent composition				
15%	18.2	6.7	3.1	16.6
25%	22.7	5.9	3.2	16.7
35%	23.4	6.6	3.4	17.9
45%	29.5	7.3	3.5	20.3
55%	39.2	8.0	4.0	21.2
70%	41.5	9.2	5.3	26.9
[Oxidant]				
0.00025	18.2	6.7	3.1	16.6
0.00050	18.2	6.7	3.1	16.6
0.0010	18.6	7.0	3.1	16.9
0.0020	18.7	6.8	3.1	16.8
Temperature, °C				
35	18.2	6.7	3.1	16.6
40	34.2	8.2	3.5	19.6
45	57.1	11.3	4.5	27.4
50	87.2	14.2	6.0	34.4

of two or more kinetic experiments is reported as the rate constant. Zero or first order rate constants were evaluated from the linear plots ($r^2 > 0.997$) of [reacted DCICA] or log [unreacted DCICA] against time. Rate constants and other determined values were reproducible within ±2%. The reaction products were characterized by IR spectroscopy using Perkin Elmer 1600 series FTIR Spectrophotometer. The samples for IR spectroscopy were prepared in form of KBr pellets.

RESULTS AND DISCUSSION

Reaction Orders by the Oxidant, Substrate, and Acid

In the absence of chloride ions, the time dependence of oxidant consumption was linear indicating zero order with respect to oxidant. The values of rate constant k_0 for different initial concentrations of oxidant were constant confirming the zero order by oxidant. However, in presence of added chloride ions, the reactions showed first order kinetics by oxidant, as seen from the constancy of k_1 values over the range of concentrations of DCICA studied.

First order by substrate was observed both in absence and in presence of chloride ions. An increase in the rate of the reaction was observed with an increase in $[H^+]$ indicating a direct participation of H^+ in the rate determining step and first order by $[H^+]$ was observed in both cases (Tables 1 and 2). The observed acid catalysis can be attributed to the nature of oxidant.

Effect of Variation of Solvent Composition

The effect of solvent composition (water–acetic acid) on the rate of reaction was studied. Both in presence and in absence of added chloride ions, an increase in the rate of reaction was observed with an increase in the percentage of acetic acid (Tables 1 and 2) which proves a highly polar transition state compared to that of reactants. The dielectric constants (D) of water—acetic acid mixtures were calculated from the dielectric constants of pure solvents. An interaction between a dipolar molecule and a positive ion can be implicit from positive slopes of plots of $\log k$ versus $1/D$. A similar solvent effect was observed in the oxidation of cyclic ketones by vanadium (V) [14], benzyltriethylammonium chlorochromate [15]. In the present case, the observed positive effect of acetic acid composition on the rate of reaction can be attributed to the catalytic nature of acetic acid/acetate ion in the process of enolisation which increases the enol concentration which is in corroboration with the work of Swain (1958) [16]. Solvent isotope studies in D_2O medium show a retardation of rate. It is well known that D_3O^+ is a stronger acid than hydronium ion and hence this observation supports the proposed mechanism.

Effect of Added Chloride Ions

A change in redox potential of pyridinium chlorochromate by binding of EDTA to chromium explains an increase in rate of oxidation of cycloalkanones [17]. An increase in the concentration of added chloride ions resulted in an increase in the rate of the reaction (Table 2) indicating that the reaction proceeded through a Cl^- mediated route. A fractional order by $[Cl^-]$ was observed from the plot of $\log k_1$ vs. $\log[Cl^-]$ which was a straight line with a slope of 0.25.

Absence of Induced Polymerization

The reaction was also studied in presence of acrylonitrile to reveal the formation and participation of free radicals [18]. Absence of induced polymerization of the acrylonitrile is evident from lack of the polymer precipitation as well as zero effect of acrylonitrile on reaction rate. The possibility of in situ generation of free radicals during the course of the reaction can be ruled out from the negative polymerization test, whereas, the involvement of free radicals was reported in the oxidation of cyclic ketones by dodecatungstocobaltate(III) [19].

Effect of Temperature

An increase in the rate of reaction was observed with an increase in the temperature in the temperature range 308 to 323 K (Tables 1 and 2). Activation parameters (E_a, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta G^{\neq}$) and $\log P_Z$ were determined from Arrhenius plot and Gibbs-Helmholtz relationship (Table 3). The values of activation energy indicate slow kinetics. Moderate values of activation energy support the proposed mechanisms. The positive values of $\Delta G^{\neq}$ and $\Delta H^{\neq}$ indicate that transition state is highly solvated. An ordered and compact transition state which has a fewer degrees of freedom is evident from negative values of entropy. Entropy values also explain that a fraction of collisions are stringent leading to a slow decomposition of the rigid activated complex.

Product Analysis and Stoichiometry

A reaction mixture of DCICA (1 mmol) and ketone (10 mmol) was taken in acetic acid-water mixture (15 : 85 by volume) and used to carry out the product analysis. To ensure the completion of reaction, the reaction mixture was allowed to stand for 24 h. The reaction mixtures were extracted with diethyl ether. Saturated sodium bicarbonate solution was added to neutralize the acetic acid in the ether layer. After washing with distilled water, the extract was dried over anhydrous sodium sulfate and evaporated. The obtained product was recrystallized from hot water and washed with chloroform. Thin layer chromatographic analysis (silica gel, benzene : petroleum ether (b.p. 40–60°C) 1 : 1, and spot tests revealed the formation of corresponding dicarboxylic acids [20] as oxidation products viz., glutaric acid, adipic acid, pimelic acid and suberic acid from cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone, respectively.

Formation of diketones as intermediates leading to dicarboxylic acids as final products was reported in case of other oxidants like, TCICA [11], DCDMH [21], and TCM [22]. Hence, in the present investigation, no diketones were found by the test showing, if positive, the pink-red color formation after warming with hydroxylamine hydrochloride solution in presence of sodium acetate buffer and addition of nickel acetate solution [23]. Formation of dicarboxylic acids as the end products is further confirmed by IR spectrum by the presence of an absorption band nearer to 2950 cm^{-1} (characteristic of O–H stretching) in addition to the peak of C=O stretching.

Table 2. Oxidation of cyclic ketones by DCICA in presence of added chloride ions [DCICA] = 0.0005 M; [Ketone] = 0.005 M; $[H^+]$ = 0.1 M; T = 35°C; [Chloride ion] = 0.00125 M; solvent composition = 15 : 85 ($AcOH : H_2O$)

Variant	$k_1 \times 10^5$, s^{-1}			
	cyclohexanone	cyclopentanone	cycloheptanone	cyclooctanone
[Ketone]				
0.0025	50.9	7.1	5.6	33.2
0.005	76.2	19.1	11.7	65.8
0.0125	285.5	53.8	28.6	188.5
0.025	601.8	189.0	61.3	409.9
0.0375	1103.0	194.7	146.4	807.1
[Acid]				
0.0250	15.0	5.1	3.3	12.5
0.0500	41.1	13.1	6.9	27.8
0.1000	76.2	19.1	11.7	65.8
0.1500	98.5	37.3	14.4	87.0
0.3000	189.0	55.7	28.7	128.1
Solvent composition				
15%	76.2	19.1	11.7	65.8
35%	85.7	25.0	11.9	81.8
55%	110.7	34.9	12.8	96.9
70%	132.6	42.4	23.7	119.9
[Oxidant]				
0.00025	76.8	20.7	12.1	66.8
0.0005	76.2	19.1	11.7	65.8
0.001	77.2	20.2	12.4	65.3
0.002	77.00	19.7	11.6	66.3
[Added Cl^-]				
0.00125	76.2	19.1	11.7	65.8
0.00250	84.7	26.0	12.0	79.7
0.00500	99.6	33.8	12.5	96.9
0.01000	117.9	35.5	18.3	105.4
Temperature, °C				
35	76.2	19.1	11.7	65.8
40	116.8	39.9	24.7	94.1
45	210.9	79.3	47.8	154.4
50	318.0	111.0	61.6	263.6

Table 3. Thermodynamic parameters for oxidation of cyclic ketones

Substrate	Addition of chloride ions	$\Delta E^{\neq}$, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$-\Delta S^{\neq}$, J/(mol K)	$\Delta G^{\neq}$, kJ/mol
Cyclohexanone	–	86	84	102	115
Cyclopentanone	–	43	40	252	118
Cycloheptanone	–	37	34	278	110
Cyclooctanone	–	42	39	248	116
Cyclohexanone	+	81	78	52	94
Cyclopentanone	+	99	96	3.4	97
Cycloheptanone	+	93	91	25	98
Cyclooctanone	+	73	70	79	94

In the presence of $HClO_4$ and at room temperature, the reaction mixtures containing varying proportions of DCICA and ketones were equilibrated for 24 h. Determination of the unreacted DCICA by iodometric method showed 3 : 2 (DCICA : ketone) stoichiometry.

Active Oxidizing Species in Absence of Chloride Ions

In acidic medium, the reactive species of dichloroisocyanuric acid may be HOCl or H_2OCl^+ or $DCICAH^+$ or DCICA itself. As there is no effect of added cyanuric acid on the rate of reaction, the leeway of either protonated or non-protonated oxidant molecules ($DCICAH^+$/DCICA) can be eliminated. In addition, as an increase in the rate of the reaction was observed with an increase in $[H^+]$, the possibility of HOCl as an oxidizing species can be ruled out. Therefore, under acidic conditions, H_2OCl^+ is the mere option remaining. The positive effect of $[H^+]$ on the rate of reaction further supports the formation of H_2OCl^+ due to protonation equilibrium. Hence, H_2OCl^+ can be considered as the reactive species in the present study which can be substantiated from the work reported by Anil Kumar and Sondu [24] in the case of trichloroisocyanuric acid. Previously published work also supports that hypohalous acidium ion is the active species in both oxidation as well as electrophilic substitution reactions [25].

Active Oxidizing Species in Presence of Chloride Ions

In the kinetics of oxidation of cyclic ketones by DCICA, the role of chloride ion is crucial as it is evident from its positive effect on the rate of the reaction. The pH of the medium dictates the type of oxidizing species and a steady formation of Cl_2 was observed in the case of various *N*-halogenated oxidants [26, 27]. As the reactions were catalyzed by chloride ions along with H^+ ions, the molecular chlorine can be considered as efficient oxidant due to reported higher activity of Cl_2 compared to other possible oxidising species in acidic conditions [28]. Similar reports are known from the literature on the oxidation of organic compounds [29, 30].

The set of following reactions explicitly enlighten the formation of molecular chlorine in the presence of added chloride ions.

$$DCICA + H_2O \rightleftharpoons MCICA + HOCl, \quad (2)$$

$$MCICA + H_2O \rightleftharpoons \text{Cyanuric acid} + HOC, \quad (3)$$

$$HOCl + H^+ \rightleftharpoons H_2OCl^+, \quad (4)$$

$$H_2OCl^+ + Cl^- \rightleftharpoons Cl_2 + H_2O. \quad (5)$$

Order of Activity of Cyclic Ketones

In the present study, the order of oxidation of cyclic ketones by DCICA is: cyclohexanone > cyclooctanone > cyclopentanone> cycloheptanone. A similar order of reactivity was observed in the oxidation of cyclic ketones by other oxidatants like quinolinium dichromate [31], benzyltriethylammonium chlorochromate [15], pyridinium chlorochromate [17], lead tetraacetate [32], whereas, in some cases cyclopentaone has shown a slightly higher rate of reaction compared to octanone when the oxidants were vanadium (V) [14], DCDMH [21].

In the present study, the observed jagged nature of cyclic ketones with respect to the number of carbon atoms in the ring might be probably due to I-strain value, the value of which depends on change in coordination number. The reactions are favoured when the charge of covalency is from 4 to 3 (or) 4 to 5 and are opposed when the change is from 3 to 4. Hence, five or seven membered rings experience a significant strain and at the same time, a strain free condition can be observed in six-membered rings [33]. It means that the observed reactivity order can be explained from the comparative ease in change of hybridization from sp^2 to sp^3 in the order [34]: $C_6 > C_8 > C_5 > C_7$. In fact, the NMR spectroscopic studies show that in aqueous medium, the content of enol form of cyclooctanone is highest (9.3%) compared to cyclohexanone (1.18%) and cycloheptanone (0.56%) [35]. But in the present

case acidic conditions are maintained and hence, rates of acid-catalyzed enolisation have to be considered and their relative rates for cyclopentanone, cyclohexanone, and cycloheptanone are 1.5 : 7, 43 : 1 [36]. This can be explained on the basis of:

(1) bond angle strain developed in transition state;

(2) $\log k_{obs}$ values were found to be −4.707, −3.985, and −4.877, respectively for 5, 6, and 7 membered rings respectively which were calculated from $\log k_{obs} = \log k_3 + pK_{BH^+} - H_x$, where k_3 is deprotonation rate constant, BH^+ is protonated ketone and H_x is acidity function;

(3) a variation of pK_{BH^+} with ketone structure [37].

Moreover, a higher rate of oxidation was observed with ketones having even number of carbons in ring (C6, C8) compared to odd number of carbons (C5, C7) which can be explained based on two points. (1) *Enol content* is higher for cyclic ketones having even number of carbon atoms compared to its adjacent homolog due to second order hyperconjugation [38]. (2) *Rate of enolisation* is controlled by variation in the steric factor in the transfer of ketone to a transition state which has an endocyclic unsaturated character and is greatly favoured in even numbered (8 and 6) cyclic ketones compared with odd numbered (5 and 7) ones [36].

Highest reactivity of cyclohexanone can be explained on the basis of following salient points.

(i) Formation of enol in higher concentration. Compared to the neighbor cyclic ketones, cyclohexanone has higher rate constant of enolisation [39]. This can be explained on the basis of (a) ready acceptance of a double bond in cyclohexanone compared to other homologs [40], (b) favored sp^2 to sp^3 conversion of hybridization state of ketone [41], (c) easier second step of enolisation (i.e., deprotonation of the α-carbon of the conjugate acid). The folded $(CH_2)_4$ fragment of cyclohexanone has negligible strain and its terminal hydrogen is able to satisfy the necessary stereochemical prerequisites to participate in hyperconjugation with the C=C bond present in the ring [42].

(ii) Alleviation of bond opposition strain. Inspite of absence of angle strain in cyclohexanone, the two equatorial hydrogen atoms on second and sixth carbons eclipse the oxygen of carbonyl group to contribute negligible quantity of bond opposition strain and even that strain is mitigated due to lessening of eclipse as well as alteration of hybridization of carbonyl oxygen from sp^2 to sp^3 during oxidation reaction.

(iii) Conformational features and their stability. The inter-conversions of different conformations of cyclohexanone (chair, twist-boat and half-chair) is possible by rotation around C_2 because all of these forms have C_{2v} symmetry [43]. Therefore, out of the studied cycloalkanones, cyclohexanone exhibits highest reactivity. Moreover, the extent of folding is low and hence, co-planarity is high in cyclohexanone. Therefore, enol form permits the half-chair conformation of cyclohexanone.

Higher and Medium Reactivities of Cyclooctanone and Cyclopentanone

The boat–chair conformation of cyclooctanone has the lowest conformational strain energy as the carbonyl group relics at position—1 or 5, where, nonbonded interactions as well as eclipsing strain are relieved [44]. The lower symmetry crown form of cyclooctanone explains its highest activity [45]. The symmetry group for deformed crown structure of cyclooctanone is C_{2v} and in total, cyclooctanone has six conformations, three each of axial and equatorial positions [46]. Compared to cyclohexanone, cyclooctanone is oxidized at slower rate because even after the process of oxidation, oxygen will not experience an appreciable release from compression, which arises from hydrogen atoms present on C_5 and C_1.

Cyclopentanone exists in C_2 *skew* conformation which was confirmed by spectral analysis [47]. The extent of enolisation is less in smaller rings (cyclopentanone) compared to the larger one (cyclohexanone) because in small rings, the puckered nature opposes the co-planarity and hence excludes half-chair form, a required form for enol [48]. In the case of cyclopentanone, the terminal hydrogen participate poorly in enol formation due to its attachment to almost flat $(CH_2)_3$ fragment present in it [42].

Lowest Reactivity of Cycloheptanone

Cycloheptanone exists in two forms (chair and boat) which are flexible, interconvertable, possess plane symmetrical forms and undergo pseudorotation. The pseudorotation eases H–H repulsion occurring across axial C_3 position. The least reactivity of cycloheptanone can be explained based on (1) stable nature of boat form (known as twist–chair conformation with C_2 axis of symmetry) due to minimum repulsion energy [49] and (2) formation of inferior quantity of enol due to least favored change in hybridization state from sp^2 to sp^3 [41].

Mechanism and Rate Law in Absence of Added Chloride Ions

Without addition of chloride ions, the reaction rate is dependent on enolisation rate as the reaction is zero order by oxidant. Similar reports were observed in literature [12, 50]. Participation of a diplole (enol form of ketone) and an ion (hypohalous ion) in a rate determining step can be ascertained from negative dielectric effect of solvent.

The stoichiometric studies show that each mole of cyclic ketone consumed three moles of DCICA. The rate orders in the absence of chloride ions can be justi-

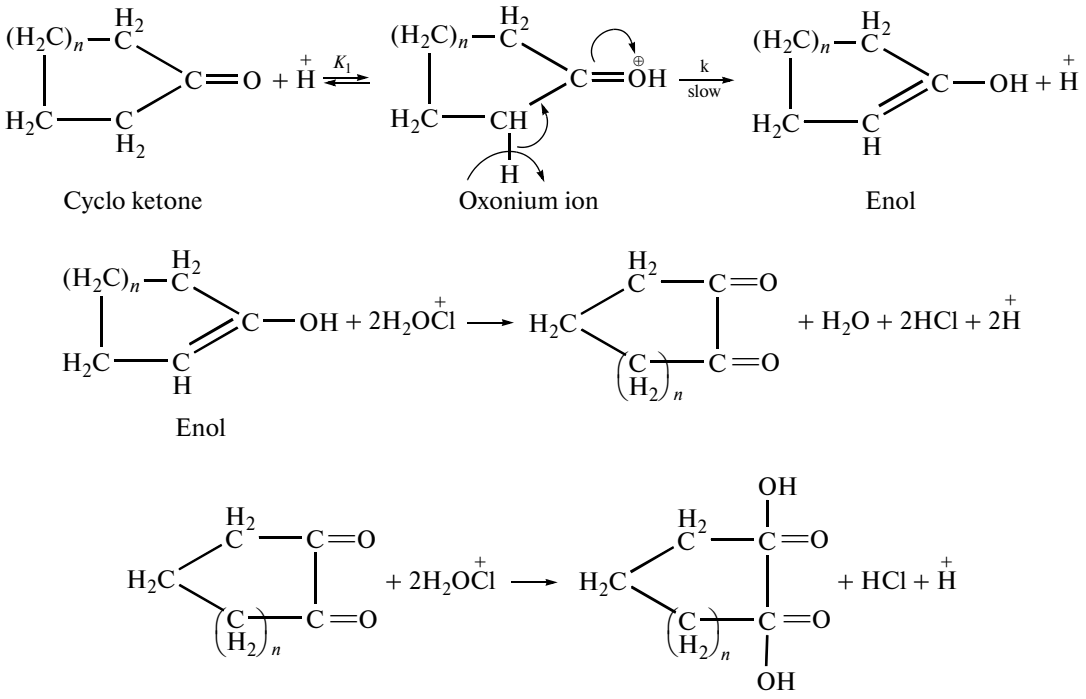
fied when the reaction progress by following the given below steps.

(a) In acidic medium, ketone is protonated to yield oxonium ion which further undergoes the process of enolisation in a slow step. A nucleophile like acetate removes alpha proton from the conjugate acid in a rate-determining step.

(b) The protonation of the oxidant species (HOCl) would make it more acquiescent towards nucleophilic attack by the enol form of the substrate on the electron-deficient H_2OCl^+.

(c) In a rapid step, the so formed enol is attacked by H_2OCl^+ to form α-mono chlorinated ketone which is again attacked by another H_2OCl^+ to form α,α-dichlorinated ketones.

(d) Dicarboxylic acids are formed following haloform route in a sequential attack of water molecule and then by one more H_2OCl^+ on α,α-dichlorinated ketones to resulting in C–C bond cleavage or α-diketone is formed when a water molecule is lost from α,α-dihydroxyketone which originate from hydrolysis of α,α-dichlorinated ketones. The so formed α-diketone is further attacked by third H_2OCl^+ to yield corresponding dicarboxylic acids.



Significant effect of deuterium isotope effect is in concurrence with the involvement of a cationic intermediate and a fast transfer of H^+ in acid catalyzed reaction that ascertain the participation of enol form of cyclic ketone but not the keto form. Though some of the earlier workers reported the formation of diketones as the end products in the oxidation of cyclic ketones in a slow step of with different oxidants [15, 45, 51], in the present case, dicarboxylic acids are found to be final products as enolic form of cyclic ketones were attacked by hypohalous ion.

The suggested mechanism can be further authenticated from the earlier reports on formation of dicarboxylic acids due to reaction between cyclic ketone and quinolinium dichromate [31], DCDMH [21], vanadium (V) [14], *N*-iodosuccinimide [52] and bromate [53].

Rate law, for the above mechanism, comes out as

$$\text{DCICA} + H_2O \rightleftharpoons \text{MCICA} + \text{HOCl}, \quad (6)$$

$$\text{MCICA} + H_2O \rightleftharpoons \text{Cyanuric acid} + \text{HOCl}, \quad (7)$$

$$\text{HOCl} + H^+ \overset{K_1}{\rightleftharpoons} H_2OCl^+, \quad (8)$$

$$S + H^+ \overset{K_2}{\rightleftharpoons} SH^+, \quad (9)$$

$$SH^+ \xrightarrow{k_0} EN + H^+, \quad (10)$$

$$EN + H_2OCl^+ \xrightarrow{\text{fast}_1} \text{Products}, \quad (11)$$

$$v = k_0[SH^+] = k_0K_2[S][H^+].$$

This rate expression is consistent with observed kinetics in the absence of chloride ion, viz., zero order with respect to [DCICA] and first order by [ketone] and $[H^+]$.

Mechanism and Rate Law in Presence of Added Chloride Ions

The first order dependence on oxidant as well as substrate concentration shows that perhaps the complex formation between them is not feasible or the so formed complex can be presumed as fragile in nature. The plausible steps in the oxidation of cyclic ketones by DCICA in the presence of added chloride ions and H^+ are as follows.

(1) In the presence of acid, both ketone and HOCl are protonated.

(2) The added chloride ions react with H_2OCl^+ (protonated form of HOCl) to form chlorine which further form a complex with protonated ketone in a rate determinating step.

(3) The so formed complex may break down to yield carboxylic acids in any one of the two routes viz., (a) a cascade of reactions via dihydroxyketone or (b) haloform route in which water molecule attacks carbonyl carbon with cleavage of C–C bond.

Hence, even in the absence of chloride ions, the final products of oxidation of cyclopentanone, cyclohexanone, cycloheptanone and cyclooctanone are glutaric, adipic, pimelic and suberic acids, respectively.

A rate law as shown below can be given, which explains the mechanism given above

$$H_2OCl^+ + Cl^- \overset{K_3}{\rightleftharpoons} Cl_2 + H_2O,$$

$$SH^+ + Cl_2 \xrightarrow{k_1} \text{Complex},$$

$$\text{Complex} \xrightarrow{\text{fast}} \text{Products},$$

$$\text{Rate} = k_1[SH^+][Cl_2] = \frac{k_1K_2K_3[HOCl]_T[H^+][Cl^-][S]}{(1 + K_3[Cl^-])}.$$

The given above rate law explains the observed reaction orders i.e., unit order in oxidant, substrate and acid, fractional order with respect to $[Cl^-]$.

CONCLUSIONS

In the oxidation of ketones by DCICA in acidic medium, hypohalous acidium ion (H_2OCl^+) and molecular chlorine (Cl_2) were the active oxidizing species in the presence and absence of added chloride ions, respectively. Without added chloride ions, the mechanism involved was acid catalyzed enolisation of ketones in a slow and rate determining step, followed by its subsequent fast interaction with H_2OCl^+ giving dicarboxylic acids as final products. However, in presence of chloride ions, the protonated ketone and molecular chlorine form an intermediate in a rate determining step and the intermediate breaks down to dicarboxylic acids.

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