

CHEMICAL KINETICS
AND CATALYSIS

Shift of Reaction Pathway by Added Chloride Ions in the Oxidation of Aromatic Ketones by Dichloroisocyanuric Acid—A Kinetic Study¹

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Abstract—Role of added chloride ions on the shift of reaction pathway of oxidation of aromatic ketones (acetophenone, desoxybenzoin) by dichloroisocyanuric acid (DCICA) was studied in aqueous acetic acid—perchloric acid medium. Participation of enolic and protonated forms of ketones in the rate determining steps is manifested from zero and first orders with respect to the oxidant in absence and presence of added chloride ions, respectively. Positive and negative effects of acid and dielectric constant on the reaction rate were observed. The observations deduce plausible mechanisms involving (i) rate-determining formation of enol from the conjugate acid of the ketone (SH^+) in the absence of added chloride ions and (ii) rapid formation of molecular chlorine species from HOCl (hydrolytic species of DCICA) in the presence of added chloride ions, which then interacts with SH^+ in a rate-determining step prior to the rapid steps of product formation. The order of Arrhenius parameters substantiate the proposed plausible mechanisms based on order of reactants both in presence and absence of added chloride ions.

Keywords: dichloroisocyanuric acid, acetophenone, desoxybenzoin, kinetics, chloride ion, enolization, reaction pathway.

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INTRODUCTION

Recent literature survey shows that kinetics of oxidation of aromatic ketones by different inorganic oxidants like potassium permanganate [1], thallium (III) perchlorate [2], iodate [3], permanganate ion [4], quinolinium dichromate [5], as well as in the presence of amino acids [6] and cetyltrimethylammonium bromide [7, 8] is well studied. The earlier works reported that end products are carboxylic acids [9, 10] formed via enol form of ketones [11, 12] and diketones [13] via the protonated form of ketone which undergoes the oxidation [14]. However, halogenation of ketones was reported with halogen/*N*-halogenated oxidants [15, 16].

Though, the effect of chloride ions on the kinetics of oxidations involving inorganic oxidants was explained on the basis of a chloride ion bridge activated transition state [17], very few such studies were carried out on the reactions involving *N*-halogenated oxidizing agents [18, 19]. Recently the authors have reported a pronounced effect of the added chloride ion on the oxidation of aliphatic ketones [20] and cyclic ketones [21] with *N*-halogenated oxidizing agent in which a change in reaction path was observed compared to that of absence of added chloride ion. In con-

tinuation, the present study of kinetics of oxidation of acetophenone and desoxybenzoin by DCICA in aqueous acetic acid—perchloric acid medium in absence and presence of added chloride ions is intended (i) to learn about the active species out of the two possible forms (enol and keto) of aromatic ketones (ii) to understand the nature of DCICA i.e., whether it halogenates and/or oxidizes these ketones (iii) to study the effect of added chloride ions on the kinetics and mechanism of oxidation of aromatic ketones (acetophenone and desoxybenzoin) by the present *N*-halogenated reagent (iv) as the oxidation of ketones frequently provides a useful synthetic route to α -hydroxyketones, α -diketones, carboxylic acids, etc. and aromatic ketones are convenient substrates in that the reaction site is localized by the flanking phenyl rings leading to minimization of secondary reactions. The nature of end products can be understood easily in this case.

EXPERIMENTAL

AR grade acetophenone and desoxybenzoin were redistilled and recrystallized, respectively, before use. Dichloroisocyanuric acid was from Fluka. All other chemicals used were of Excelsior grade from Glaxo.

¹ The article is published in the original.

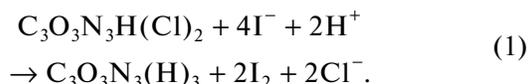
Table 1. Oxidation of aromatic ketones by DCICA in absence of added chloride ions ([DCICA] = 0.0005 M, [Substrate] = 0.005 M, [H⁺] = 0.1 M, temperature = 35°C, solvent composition (AcOH : H₂O) = 70 : 30 vol/vol

Varied conditions		$k_0 \times 10^8, \text{ mol L}^{-1} \text{ s}^{-1}$	
		acetophenone	desoxybenzoin
[DCICA]	0.00025	2.39	1.31
	0.0005	2.36	1.34
	0.001	2.40	1.36
[Substrate]	0.00125	—	0.34
	0.0025	1.31	0.57
	0.00375	—	0.85
	0.005	2.36	1.34
	0.0125	4.62	—
[H ⁺]	0.025	11.5	—
	0.375	23.9	—
	0.025	1.40	0.95
	0.05	2.09	1.02
	0.1	2.36	1.34
Solvent composition AcOH : H ₂ O (vol/vol)	0.15	4.52	1.40
	0.3	6.86	—
	15 : 85	1.16	—
	35 : 65	1.58	—
	55 : 45	1.68	—
Temperature (°C)	70 : 30	2.36	1.34
	80 : 20	2.73	1.58
	90 : 10	4.35	1.93
	35	2.36	1.34
	40	4.06	3.58
	45	6.61	6.87
	50	11.2	—

Table 2. Oxidation of aromatic ketones by DCICA in presence of added chloride ions ([DCICA] = 0.0005 M, [Substrate] = 0.005 M, [H⁺] = 0.1 M, temperature = 35°C, solvent composition (AcOH : H₂O) = 70 : 30 vol/vol, [Cl⁻] = 0.00125M)

Varied conditions		$k_1 \times 10^{-5}, \text{ s}^{-1}$	
		acetophenone	desoxybenzoin
[DCICA]	0.00025	34.1	27.5
	0.0005	35.2	26.6
	0.001	34.9	25.0
[Substrate]	0.00125	—	7.03
	0.0025	20.3	12.7
	0.00375	—	15.2
	0.005	35.2	26.6
	0.0125	88.2	—
[H ⁺]	0.025	126.0	—
	0.0375	245.0	—
	0.025	38.4	26.1
	0.05	33.4	25.0
	0.1	35.2	26.6
[Cl ⁻]	0.15	34.2	42.1
	0.3	31.3	89.4
	0.00125	35.2	26.6
	0.0025	40.0	31.0
	0.005	51.9	38.4
Temperature (°C)	0.01	63.6	46.1
	35	35.2	26.6
	40	44.1	34.3
	45	52.9	69.3
	50	96.3	101.0

The reaction was followed by estimating the concentration of unreacted DCICA by iodometry at pH 1–2.



Compared to the rates of present reaction, self decomposition rates of DCICA were negligibly smaller under the conditions employed. The rate constants remained practically unaltered in air or in a de-aerated atmosphere. Only a representative set of the average values of kinetic data in aqueous acetic acid medium was presented here. Zero or first order rate constants were evaluated from the linear plots ($r^2 > 0.993$) of [reacted DCICA] or log [unreacted DCICA] against time. Rate constants and other determined values were reproducible to $\pm 2\%$.

RESULTS AND DISCUSSION

Reaction Orders of the Oxidant and Substrate

In the oxidation of aromatic ketones (acetophenone and desoxybenzoin) by DCICA in absence of added chloride ions, the reactions have been found to be zero order in oxidant (DCICA) concentration as evidenced by the linear plots of x versus time (Table 1). Such a zero order dependence on oxidant was observed in the oxidation of acetophenone in acidic medium using Tl (III) perchlorate in perchloric acid media [2], *N*-bromosuccinimide [22] in which enolized form of ketone is involved in the rate determining step whereas, it was first order in the oxidation of acetophenone by potassium permanganate [1], the reaction is first order with respect to [oxidant], as ketone was the active form of ketone. Hence, based on the

zero order nature of oxidant in the present case, it is evident that enolized ketone form involves in the rate determining step. However, in the presence of added chloride ions, the oxidation of acetophenone and desoxybenzoin were first order with respect to [DCICA], as seen from the constancy of k_1 values (Table 2) obtained with different initial oxidation concentrations and the plots of $\log(a-x)$ versus time are linear confirming unit dependence with respect to [DCICA]. Both in the absence and presence of added chloride ions, the reaction order on substrates (acetophenone and desoxybenzoin) concentration is unit (Tables 1, 2).

Effect of Variation of Acid Concentration

In the absence of added chloride ions, as the rate of reaction increased with an increase in $[H^+]$ (Table 2), it is evident that the reaction (enolization) is catalyzed in the presence of acid, and enol form is active species. In the absence of added chloride ions, the reactions have positive fractional order with respect to acid concentration. In the presence of added chloride ions, the oxidation of acetophenone is acid independent and in the case of desoxybenzoin, initially it is acid concentration independent and later first order.

Effect of Variation of Solvent Composition

Rates of the reactions increased with an increase in the percentage of acetic acid in the aqueous—acetic acid medium (Table 1) and the observation can be substantiated with an increase in the rate of enolization of acetophenone with the increase in acetic acid [23] and similarly in the case with desoxybenzoin. However, a decrease in rate of the oxidation of acetophenone by potassium permanganate with increase in the acetic acid content was studied in 50% aqueous acetic acid-medium [1] and those results were explained on the basis of a decrease in the water content in the reaction mixture, which is essential for rate determining decomposition of the intermediate. But, it may be the case when the composition of acetic acid is more than 95% in aqueous—acetic acid mixture. In the present case, plots of $\log k_0$ vs. $1/D$ gave straight lines with positive slopes indicating that the reaction is between dipolar molecule and a positive ion. In corroboration with the work of Swain [24], the observed

positive effect of acetic acid composition on the rate of reaction can be attributed to an improvement of enol concentration due to catalytic nature of acetate ion/acetic acid on the process of enolization. Retardation in reaction rate was observed by carrying out solvent isotope studies in the medium of heavy water which can be explained on the fact that D_3O^+ is a stronger acid than hydronium ion and hence this observation supports the proposed mechanism.

Effect of Temperature

To investigate the effect of temperature and to evaluate the various Arrhenius activation parameters the oxidation of acetophenone and desoxybenzoin by DCICA has been carried out at different temperatures in absence and presence of added chloride ions (Tables 1, 2) and thermodynamic parameters were calculated from plots of $\log k_0$ vs. $1/T$ and tabulated (Table 3). In the absence of added chloride ions, the fairly high positive value of ΔH^\ddagger indicates that, the transition state is highly solvated. The high negative value of entropy in the oxidation of acetophenone favors the formation of a compact and a more ordered transition state compared to the oxidation of desoxybenzoin. Almost constant values of ΔG^\ddagger for both aryl ketones may be indicative of the operation of the same mechanism of oxidation, namely a fast nucleophilic attack of oxidant on enol forms of ketones to form the products.

Absence of Induced Polymerization

To understand if the involvement of free radicals is present or not, the reactions were studied in presence of added acrylonitrile [25]. Non-appearance of precipitate formation (due to lack of induced polymerization of the acrylonitrile) gives evidence to absence of induced polymerization. No effect of acrylonitrile on rate of the reaction and the negative polymerization test rules out the possibility of in situ generation of free radicals during the course of the reaction.

Product Analysis and Stoichiometry

To conduct the product analysis, reaction between ketone (10 mmol) and DCICA (1 mmol) was carried

Table 3. Arrhenius parameters for oxidation of acetophenone and desoxybenzoin

Substrate	Addition of chloride ions	ΔE^\ddagger , kJ/mol	ΔH^\ddagger , kJ/mol	$-\Delta S^\ddagger$, J K ⁻¹ /mol	$\log P_z$	ΔG^\ddagger , kJ/mol
Acetophenone	–	85.32	82.76	122.68	6.84	120.54
Desoxybenzoin	–	133.23	130.67	–28.64	14.74	121.85
Acetophenone	+	52.75	50.19	149.14	5.46	96.13
Desoxybenzoin	+	77.77	75.21	70.27	9.58	96.85

out in a mixture of acetic acid–water (70 : 30 vol/vol). The reaction mixture was allowed to stand for 48 h to make sure of completion of reaction. From the reaction mixtures, the organic layer was extracted with diethyl ether. The acetic acid in the ether layer was neutralized with saturated sodium bicarbonate solution. The extract was washed with distilled water, dried over anhydrous sodium sulphate and evaporated. Obtained product was recrystallised from hot water and washed with chloroform.

Formation of benzoic acid and formic acid in the oxidation of acetophenone and, benzoic acid in the oxidation of desoxybenzoin was observed from spot tests [26, 27]. Formation of benzoic acid is evident from thin layer chromatographic analysis in which product is eluted on a silica gel G TLC plate (ethanol : ammonia—9 : 1). Air dried plate was sprayed with peroxide—ferric chloride reagent (mixture of equal volumes of freshly prepared 2% ferric chloride and 0.5% hydrogen peroxide solution) where benzoic acid shows a mauve colored spot ($R_f = 0.5$) [28]. The presence of an absorption band corresponding to characteristic of O—H stretching (nearer to 2950 cm^{-1}) in addition to the peak of C=O stretching in IR spectrum confirms the formation of benzoic and formic acids.

The literature survey shows that in the of oxidation of acetophenone, ester was the product by peroxomonosulphate [29], benzoic acid was the product of potassium permanganate oxidation [1], benzoic acids and formic acid were the products using Tl (III) [2], phenylglyoxal using *N*-bromosuccinimide [22], benzoic acid and formaldehyde using manganese (III) [30] and quinolinium dichromate [5]. Oxidation of desoxybenzoin with 1 M HNO_3 at gives benzoin (46%), benzil (11%), and the degradation products (41%) (due to C—C bond fission products, i.e., benzoic and *p*-nitrobenzoic acids and benzaldehyde) [31]. In the chromic acid oxidation of desoxybenzoin in 91% acetic acid, benzoin was shown to be the intermediate in the reaction, and the source of the products,

Table 4. Relative rates of oxidation of ketones by DCICA ([DCICA] = 0.0005 M, [Substrate] = 0.005 M, $[\text{H}^+] = 0.1\text{ M}$, temperature = 35°C , solvent composition (AcOH : H_2O) = 70 : 30 vol/vol)

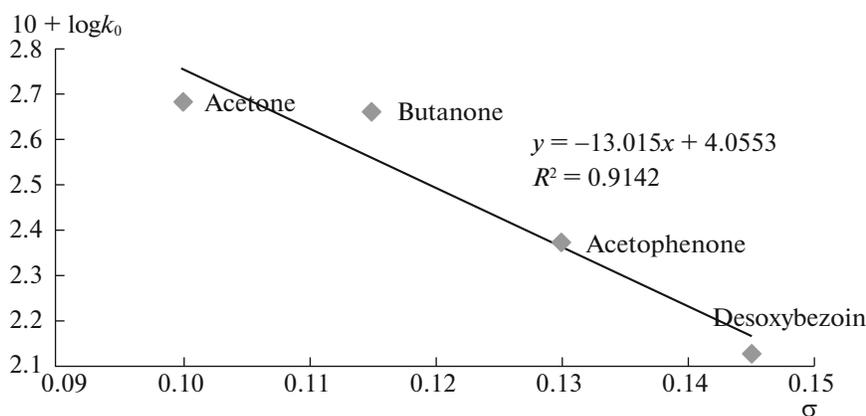
Substrate	σ	$k_0 \times 10^8, \text{ mol s}^{-1}$
Acetone	0.1	4.80
2-Butanone	0.115	4.60
Acetophenone	0.13	2.36
Desoxybenzoin	0.145	1.34

benzil, benzaldehyde, and benzoic acid [32]. Formation of benzoin as the final product in the oxidation of desoxybenzoin can be denied on the basis earlier observation that the oxidation of benzoin occurs at a rate 500 times as great as that of desoxybenzoin [32]. In addition, in the recent publication of [5], it was reported that in the oxidation arylalkyl ketones by QDC, cleavage of the carbon—carbon bond yields carboxylic acids.

Reaction mixtures of varying proportions of ketones and DCICA were equilibrated for 48 h at room temperature in perchloric acid medium. The unreacted DCICA was determined by iodometry and the stoichiometry was found to be 3 : 2 (DCICA : ketone). The stoichiometry also confirms the above said products formation.

Lower Rate of Desoxybenzoin

Both in the absence and presence of added chloride ions, the lower order of reactivity of desoxybenzoin compared to acetophenone (Tables 1, 2) is in accordance with the structural changes. Addition of one more phenyl group to alkyl side of acetophenone enhances electron density at the carbon atom adjacent to the carbonyl group. The ease of deprotonation from this carbon atom in desoxybenzoin would decrease as compared that in acetophenone.



Hammett's plot for oxidation of ketones by DCICA in absence of added chloride ions.

Table 5. Effect of acid containing chloride ($[\text{DCICA}] = 0.0005 \text{ M}$, $[\text{Substrate}] = 0.005 \text{ M}$, solvent composition ($\text{AcOH} : \text{H}_2\text{O}$) = 70 : 30 vol/vol, temperature = 35°C)

Acid	Conc. of acid, M	$k_0 \times 10^8 \text{ mol L}^{-1} \text{ s}^{-1}$	
		acetophenone	desoxybenzoin
HClO_4	0.1	2.36	1.34
HCl	0.1	21.23	22.04

The Hammett's Plot

To understand the nature of substrates in the oxidation by DCICA, Hammett's plot was drawn from the rate constants obtained at similar conditions of reactants (Table 4 and figure). The Hammett's plot is linear and a reaction constant of -13.01 is obtained. This value indicates that electron-donating groups retard the process which is in agreement with the suggested mechanism.

Effect of Variation of Chloride Concentration

The reaction rates increased with an increase in Cl^- concentration in the oxidation of both the substrates (Table 2) indicating that the reaction proceeded through a Cl^- mediated route. Such an increase in the rate of oxidation of chalcones by trichloroisocyanuric acid [33], aliphatic and cyclic ketones [20, 21] was observed with an increase in concentration of chloride ions. In the present case, plots of $\log k_1$ vs. $\log[\text{Cl}^-]$ gave straight lines with slopes of 0.292 and 0.268 respectively in the oxidation of acetophenone and desoxybenzoin, respectively, indicating positive fractional order with respect to chloride. The catalytic nature of chloride ions is further evidenced from the kinetic studies of replacing HClO_4 with HCl (which supplies free chloride ions) where an increase in rate of reaction was observed which further augments the proposed involvement of chloride ions in the generation of active oxidizing agent—chlorine (Table 5).

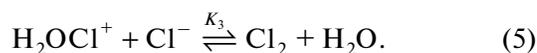
H_2OCl^+ Is the Active Oxidizing Species in Absence of Chloride Ions

The pH of the medium dictates the type of oxidizing species and different reactive species of dichloroisocyanuric acid in acidic medium may be either unprotonated (HOCl/DCICA) or protonated forms ($\text{H}_2\text{OCl}^+/\text{DCICAH}^+$) [20, 21]. The possibility of participation of either unprotonated/protonated oxidant molecules ($\text{DCICA}/\text{DCICAH}^+$) can be eliminated as there is no effect of added cyanuric acid. Out of the remaining two species, involvement of HOCl can be ruled out from positive effect of acid concentration on rate of reaction and hence, in acidic medium the remaining only one option is H_2OCl^+ which forms in protonation equilibrium. Active participation of

H_2OCl^+ in the present case is further substantiated from the earlier reports [20, 21, 33] in the case of trichloroisocyanuric acid. In both oxidation and electrophilic substitution reactions, hypohalous acidium ion was reported to be the active species [34].

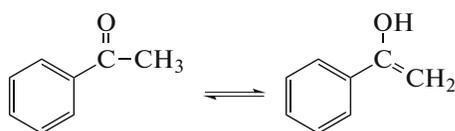
Molecular Chlorine Is the Active Oxidizing Species in Absence of Chloride Ions

The added chloride ions play a vital role in the kinetics of oxidation of aromatic ketones by DCICA as they have a positive effect on the rate of the reaction. Formation of molecular chlorine (Cl_2) was observed with different *N*-halogenated oxidants [20, 21, 35, 36]. Apart from H^+ ions, chloride ions also exhibited catalytic effect in the present case and molecular chlorine was reported to be the efficient active oxidizing species in acidic medium [37] and similar reports can be observed in the literature in the oxidation of organic compounds [38, 39]. Hence, in the present case, molecular chlorine is formed from DCICA in presence of added chloride ions and it is the active oxidant. The set of following reactions clearly explain the formation of molecular chlorine in the presence of added chloride ions.



Mechanism and Rate Law in Absence of Added Chloride Ions

In the oxidation of acetophenone and desoxybenzoin in acetic acid—perchloric acid medium in absence of added chloride ions, the rate controlling step is enolization of arylketones in view of (i) zero order dependence on oxidant (ii) increase in rate constant with increase in concentration of hydrogen ion as enolization is acid catalyzed reaction. This is in corroboration with reports in literature [20, 21, 40]. Participation of a dipole (enol form of ketone) and an ion (hypohalous ion) in a rate determining step can be ascertained from negative dielectric effect of solvent. This is further supported by the effect of ionic strength on the rate of reaction as there is no effect of ionic strength, the reaction might be between an ion and molecule. In acidic solutions the acetophenone undergoes fast enolization as represented by equation [9] as given below.

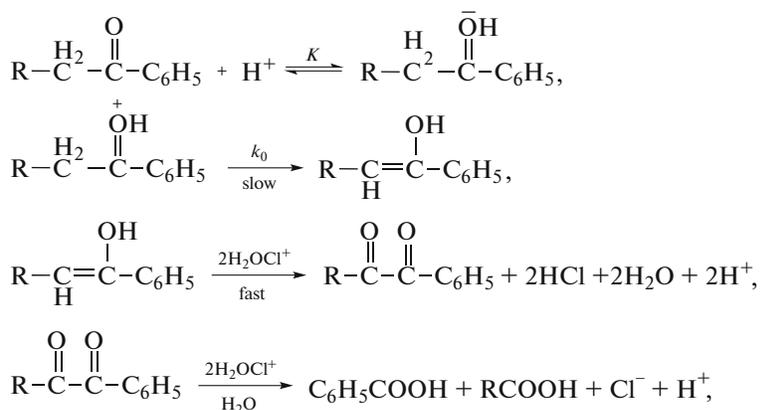


Based on the reaction conditions, ketones can react directly or via its enol form. In general, ketone is the active species when (i) the rate of oxidation is faster compared to the enolization rate, (ii) oxidant transfers one electron in the reactions, and (iii) mechanism involves a free radical. Direct oxidation of ketone form was observed in the oxidation of ketones by various oxidants like Ce(IV), Mn(IV) [41], Co^{3+} [42].

Active participation of enol form can be observed if (i) rate of oxidation equals enolization (ii) oxidant transfers two electron in the reactions, and (iii) zero order dependence on [oxidant]. Participation of enol form was observed in the oxidation of ketones by oxidants like Tl(III), MnO_4^- , and Hg(II) [43], BrO_3^- [44] and manganic pyrophosphate [45]. Based on the experimental observation in the present investigation,

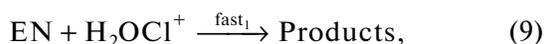
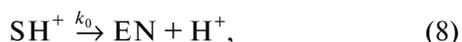
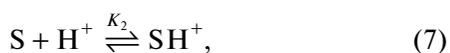
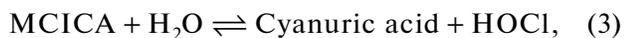
enolization involve in the rate determining step. Such a rate controlling step of keto-enolization was proposed in the oxidation of acetophenones using Tl (III) perchlorate in perchloric acid media [2].

The kinetics of oxidation of acetophenone/desoxybenzoin by dichloroisocyanuric acid (DCICA), the reaction stoichiometry is [ketone] : [DCICA] : 2 : 3 i.e., [ketone] : [HOCl] : 1 : 3 (because each DCICA releases two HOCl molecules). The kinetic and thermodynamic parameters strongly suggest the mechanism of a fast protonation of the ketone (S) to give (SH^+), followed by slow and rate-determining conversion of SH^+ to enol (EN) by keto-enol tautomerism. The enol (EN) is quickly attacked by two H_2OCl^+ in concomitant fashion to give diketones, which react in a fast a step with another H_2OCl^+ to decompose into the products. In the oxidation of acetophenone the products were benzoic and formic acids, whereas, benzoic acid was the only product from oxidation of desoxybenzoin.



where $\text{R}=\text{H}/\text{C}_6\text{H}_5$.

Rate Law in Absence of Added Chloride Ions



$$[\text{S}]_{\text{T}} = [\text{S}] + [\text{SH}^+] = [\text{S}] + K_2 [\text{S}] [\text{H}^+]$$

$$= [\text{S}]\{1 + K_2 [\text{H}^+]\},$$

$$[\text{S}] = \frac{[\text{S}]_{\text{T}}}{1 + K_2 [\text{H}^+]},$$

$$\text{Rate} = k_0[\text{SH}^+] = k_0 K_2 [\text{S}] [\text{H}^+],$$

$$\text{rate} = \frac{k_0 K_2 [\text{S}]_{\text{T}} [\text{H}^+]}{1 + K_2 [\text{H}^+]}$$

The given above rate law explains the observed reaction orders i.e., zero order in [oxidant], first order in [substrate], and fractional order in [acid].

*Mechanism and Rate Law in Presence
of Added Chloride Ions*

As the reactions are first order in concentrations of both oxidant and substrate, probably, the formation of complex between them is not viable or the so formed complex can be assumed as fragile in nature. The possible steps in the oxidation of aromatic ketones by DCICA in the presence of added chloride ions and H^+ are summarized below.

(a) In acid medium, the protonated forms oxidant (H_2OCl^+) and ketone (SH^+) exist.

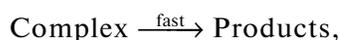
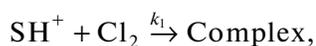
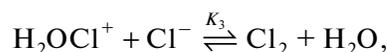
(b) Molecular chlorine is formed due to reaction between H_2OCl^+ and added chloride ions.

(c) In a rate determining step, complex formation takes place between molecular chlorine and SH^+ .

(d) Carboxylic acids are yielded due to decomposition of the above complex through either any one of the two routes viz., (i) a cascade of reactions via dihydroxy ketone or (ii) haloform route in which water molecule hit carbonyl carbon to rupture C–C linkage of complex.

Hence, even in the presence of added chloride ions, the end products are same as in the case of absence of added chloride ions.

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



$$[S] = \frac{[S]_T}{1 + K_2[H^+]},$$

$$\text{rate} = k_1[SH^+][Cl_2]$$

$$= \frac{k_1 K_2 K_3 [HOCl]_T [H^+] [Cl^-] [S]}{(1 + K_3 [Cl^-])}$$

$$= \frac{k_1 K_2 K_3 [HOCl]_T [H^+] [Cl^-] [S]_T}{(1 + K_3 [Cl^-]) (1 + K_2 [H^+])}.$$

The given above rate law explains the observed reaction orders i.e., unit order in concentrations of oxidant and substrate, fractional order with respect to $[Cl^-]$. The equation also explains acid independent oxidation of acetophenone as well as initial independence and unit order latter in $[H^+]$ in the oxidation of desoxybenzoin.

CONCLUSIONS

In the absence and presence of added chloride ions, hypochlorous acidium ion (H_2OCl^+) and molecu-

lar chlorine (Cl_2) were the active oxidizing species in the oxidation of ketones. The oxidation of aromatic ketones by DCICA is acid catalyzed in absence of added chloride ions. Hence, the protonated ketone undergoes enolization in a rate determining step and subsequently, the enol interacts with H_2OCl^+ in a faster step to give benzoic acid and formic acid in oxidation of acetophenone, where as benzoic acid was the product in oxidation of desoxybenzoin. In the presence of chloride ions, same dicarboxylic acids are produced by decomposition of an intermediate which is formed in a slow step due to reaction between protonated ketone and molecular chlorine.

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