A Novel Reaction of Some Enolisable Ketones *not* involving the Rate-determining Enolisation Step. Kinetics of the Reaction of Ketones with Trichloroisocyanuric Acid in the Presence of Added Chloride Ion in Acid Medium

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Kinetics of the reaction between some enolisable ketones (S) and trichloroisocyanuric acid (TCICA) in aqueous acid–acetic acid medium at 35 °C follow pseudo-zero-order and pseudo-first-order disappearance of $[\mathrm{TCICA}]_0$ in the absence and the presence of added Cl^-, respectively. The rate constants for the latter system exhibit a linear dependence each on $[\mathrm{S}]_0$ and $[\mathrm{H}^+]$, and an increasing and limiting dependence on added $[\mathrm{Cl}^-]$. The results are interpreted in terms of probable mechanisms involving (i) rate-determining enol formation from the conjugate acid of the ketone (SH^+) in the absence of added Cl^- and (ii) rate-determining interaction of SH^+ with the most effective molecular chlorine species produced by the hydrolysis of TCICA (rather than a rate-determining interaction of enol with Cl_2) in the presence of added Cl^-, prior to the rapid steps of product formation.

It is well established that reactions of enolisable ketones with oxidising and halogenating agents more often than not proceed through rate-determining enolisation steps. Halogenation of acetone in acid medium generally exhibited kinetic-rate dependences on the initial concentrations of the substrate (S) and H^+, but remained independent of the nature and extent of the halogen used; the mechanism thus involved, in general, acid-catalysed enolisation as the rate-determining process, the subsequent and kinetically very rapid step(s) being the reaction(s) of the molecular enol with the halogen. This conformed with the measured pseudo-zero-order kinetics for the disappearing halogen.[1] However, in several cases,[1,2] where the rate of halogenation might depend on the concentration of the halogen, it was assumed that by reducing the [halogen] to a very low value (*i.e.* below some threshhold concentration, *ca.* 10^{-5}M or less) and at relatively high $[\mathrm{H}^+]$ (>0.1M), the rate of its attack on the enol could become lower than the rate of enol formation so that attack by halogen turned out to be rate controlling. The overall rate was proportional to [halogen] in that event. For example, the rate of chlorination of acetone by molecular chlorine (Cl_2) in acid medium corresponded to the enol–Cl_2 reaction (1).[1,2] This suggested that (a) at low

$$\mathrm{S} + \mathrm{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{EN} + \mathrm{H}^+, \quad \mathrm{EN} + \mathrm{Cl}_2 \xrightarrow{k_2} \text{Products} \qquad (1)$$

$$\text{Rate} = V = \frac{k_1k_2[\mathrm{H}^+][\mathrm{Cl}_2][\mathrm{S}]}{k_{-1}[\mathrm{H}^+] + k_2[\mathrm{Cl}_2]} \qquad (2)$$

$[\mathrm{H}^+] < 0.1$M and $[\mathrm{Cl}_2] > 10^{-4}$M, when $k_{-1}[\mathrm{H}^+] \ll k_2[\mathrm{Cl}_2]$ so that $V = k_1[\mathrm{H}^+][\mathrm{S}]_0$, the rate was pseudo-zero order in halogen[1] and (b) that at relatively high $[\mathrm{H}^+]$ (>0.1M) and low $[\mathrm{Cl}_2]$ ($<10^{-5}$M), when $k_{-1}[\mathrm{H}^+] \gg k_2[\mathrm{Cl}_2]$ so that $V = [\mathrm{S}][\mathrm{Cl}_2]k_2k_1/k_{-1}$, the rate was pseudo-first order in halogen.[1,2] The operation of this latter mechanism cannot be universal because in the reaction of acetone with CAT (*i.e.*, chloramine T or sodium *N*-chlorotoluene-*p*-sulphonamide) in acid medium, for example, different results were obtained.[3]

Recent investigations in the absence of added Cl^- exhibited pseudo-zero-order disappearance of TCICA[4,5] and indicate that reactions of enolisable ketones do follow the rate-determining acid-catalysed enolisation mechanism for a wide range of $[\mathrm{TCICA}]_0$. In the presence of added Cl^-, however, the same reaction exhibits pseudo-first-order kinetics for the disappearance of TCICA under almost identical conditions. In view of the diversity observed in the reactions of enolisable ketones as substrates (S) with different chlorinating agents, we report here the kinetics of the same reaction in the presence of added Cl^- in order to establish that rate-determining enol formation need not be general and also to attempt a more reasonable explanation for the deviations from this mechanism.

Experimental

Materials and Methods.—The experimental procedure was briefly described earlier.[4] Reagents used were of guaranteed grade. Trichloroisocyanuric acid, *i.e.*, 1,3,5-trichloro-1*H*,3*H*,5*H*-1,3,5-triazine-2,4,6-trione[6] (TCICA) was from Fluka; its concentration was estimated iodometrically in acid medium in accordance with reaction (3).

$$\underset{\text{(TCICA)}}{\mathrm{C_3O_3N_3(Cl)_3}} + 6\mathrm{I}^- + 3\mathrm{H}^+ \longrightarrow \underset{\text{(ICA)}}{\mathrm{C_3O_3N_3(H)_3}} + 3\mathrm{I}_2 + 3\mathrm{Cl}^- \qquad (3)$$

The kinetics were monitored by estimating the disappearing [TCICA] at various time intervals. Rate constants were reproducible to ±5%. Self-decomposition rates of TCICA were negligibly small under the conditions employed $[\mathrm{SL}]_0 > [\mathrm{TCICA}]_0$,† compared with the rates of the present reaction. The rate constants remained practically unaltered in air or in a deaerated atmosphere; the addition of edta (added as the disodium salt of ethylenediaminetetra acetic acid) also did not bring about any significant change in the rates. Only a representative set of the average values of kinetic data at 35 (±0.1) °C in aqueous acetic acid medium (water–acetic acid 85—15 v/v) is presented here.

Stoicheiometry and Products.—Stoicheiometric runs employing $[\mathrm{TCICA}]_0 > [\mathrm{S}]_0$ (*e.g.* $[\mathrm{TCICA}]_0$ 2×10^{-3}—4×10^{-2}M, $[\mathrm{S}]_0$ 2×10^{-4}—5×10^{-3}M) at $[\mathrm{HClO}_4]$ 0.5M, $[\mathrm{Cl}^-]$ 0.5M, aqueous acetic acid 15% (v/v), and 35 °C were not meaningful as the self-decomposition of TCICA in these cases was appreciable.

Although the initial products of the reaction of enolisable

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† SL = substrate ligand.

Table 1. Pseudo-first-order rate constants for the reaction of ketones with TCICA in the presence of added Cl^-.[a] $[S]_0$ 1×10^{-2}M, $[H^+]$[b] 4×10^{-2}M, $[Cl^-]_{ad}$ 5×10^{-2}M

		$10^5k_{obs}/s^{-1}$			
(S)	$10^4[TCICA]_0$/M	3	5	12	20
Acetone		18	14	5.3	3.2
Cyclopentanone		33	24	10	6

[a] In water–acetic acid 85:15 (v/v) at μ 1M and 35 °C (and in the other Tables). [b] $HClO_4$ was used in all experiments.

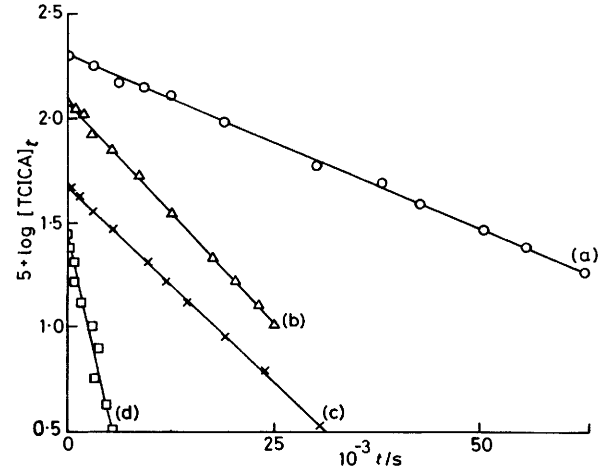


Figure 1. The pseudo-first-order disappearance plots. $[Acetone]_0$ 1×10^{-2}M, $[H^+]$ 4×10^{-2}M, $[Cl^-]_{ad}$ 5×10^{-2}M. $10^4[TCICA]_0$/M: 20 (a); 12 (b); 5 (c); 3 (d)

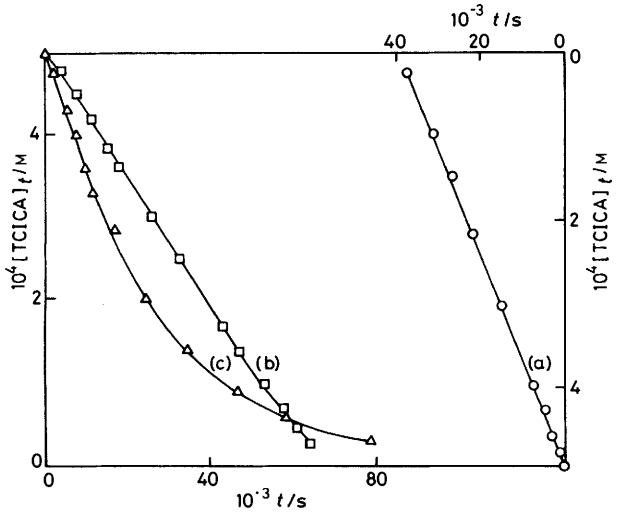


Figure 2. Representative experimental plots. $[Acetone]_0$ 1×10^{-2}M, $[H^+]$ 1×10^{-2}M, $[TCICA]_0$ 5×10^{-4}M. $10^4[Cl^-]_{ad}$/M: nil (a); 1 (b); 500 (c)

Table 2. Representative values of the computed pseudo-first-order and pseudo-zero-order rate constants for the reaction of acetone with TCICA in the presence of added Cl^-. $[Acetone]_0$ 1×10^{-2}M, $[TCICA]_0$ 5×10^{-4}M, $[H^+]$ 1×10^{-2}M

Computed rate constant	$10^4[Cl^-]_{ad}$/M	0	0.5	1	5	10	100	500
10^8k_0/l mol^{-1} s^{-1}		1.2[a,b]	1.0[b]	0.6[b]	0.2[b]			
$10^5k'_1$/s^{-1}			0.3[c]	0.5[c]	1.7[c]	2.4[d]	3.5[d]	3.7[d]

[a] Value from ref. 4. [b,c] Values obtained using equation (4). [d] $k_{obs} = k'_1$.

ketones with many chlorinating agents are halogen-substituted derivatives, the actual products of the reaction under the present conditions could not be ascertained due to experimental difficulties. Moreover, there was much decomposition of TCICA in many other solvent media. Therefore, the following procedure was adopted for representative product studies. To an aqueous solution of acetone (50 ml; 0.01 mol) containing 1M-$HClO_4$ and 0.5M-Cl^-, solid TCICA (0.02 mol) was added, and the mixture was allowed to react for 50 h. The mixture was neutralised with alkali and extracted with diethyl ether. The aqueous layer was acidified and then again thrice ether-extracted. Ether was evaporated and the resulting product was subjected to t.l.c. [silica gel, benzene–light petroleum ether (b.p. 40—60°) (1:1)]; acetic acid and formic acid were qualitatively identified. Similar treatment of cyclohexanone furnished adipic acid. The product of the reaction of acetophenone under similar conditions could not be obtained because of the poor solubility of the latter in aqueous medium.

Results

While the disappearance of TCICA in the reaction of substrate ketone (S) with TCICA in acid medium in the absence of added Cl^- was pseudo-zero order[4] in $[TCICA]_0$, the same reaction in the presence of added Cl^- ($[Cl^-]_{ad}$ 1×10^{-3}—50×10^{-3}M) exhibited pseudo-first-order kinetics; plots of log $[TCICA]_t$ *versus* time were perfectly linear for more than four half-lives of disappearance of TCICA in individual runs, even for different initial concentrations of TCICA (Figure 1). However, the pseudo-first-order rate constants (k_{obs}) were found to show a decreasing trend with increasing $[TCICA]_0$ (Table 1) and plots of $(k_{obs})^{-1}$ *versus* $[TCICA]_0$ were linear.

At sufficiently low $[Cl^-]_{ad}$ (*e.g.*, 5×10^{-5}—5×10^{-4}M), the disappearance rates of TCICA did not follow either a pseudo-zero-order or a pseudo-first-order pattern (*viz.*, plots of $[TCICA]_t$ *versus* *t* or log$[TCICA]_t$ *versus* *t*, respectively, were not perfectly linear); it appeared that the pseudo-zero-order rate of the 'unmediated reaction' and the pseudo-first-order rate of the 'Cl^--mediated reaction' were somewhat 'mixed' at these low $[Cl^-]_{ad}$ values. Figure 2 reproduces some experimental plots. For these experiments at very low $[Cl^-]_{ad}$, the rate of disappearance of TCICA was found to obey equation (4)[7]

$$-d[TCICA]/dt = k'_1[TCICA] + k_0$$

$$\text{or} \quad \left[\frac{[TCICA]_{t_n} - [TCICA]_{t_{(n+1)}}}{t_{(n+1)} - t_n}\right] = k'_1\left[\frac{[TCICA]_{t_n} + [TCICA]_{t_{(n+1)}}}{2}\right] + k_0 \quad (4)$$

where k'_1 and k_0 refer to the pseudo-first-order and pseudo-zero-order rate constants respectively, and $[TCICA]_{t_n}$ and $[TCICA]_{t_{(n+1)}}$ refer to the measured concentrations at time t_n and $t_{(n+1)}$, respectively. Plots of the left-hand side of equation (4) *versus* $1/2\{[TCICA]_{t_n} + [TCICA]_{t_{(n+1)}}\}$ furnished the k'_1 and k_0 values (Figure 3). The k_0 value corresponding to $[Cl^-]$ 0 thus obtained (Figure 3A) was checked with and found to be the same to within ±5% of the independent k_0 value collected under similar conditions in the absence of added Cl^-. While the k'_1 component was negligible so that $k_{obs} = k_0[TCICA]^0$ for reactions with $[Cl^-]_{ad}$ 0, the k_0 component was negligible so that $k_{obs} = k'_1[TCICA]$ for reactions employing sufficiently high $[Cl^-]_{ad}$ (1×10^{-3}—50×10^{-3}M). The computed values of k'_1 and k_0 for a representative reaction are presented in Table 2.

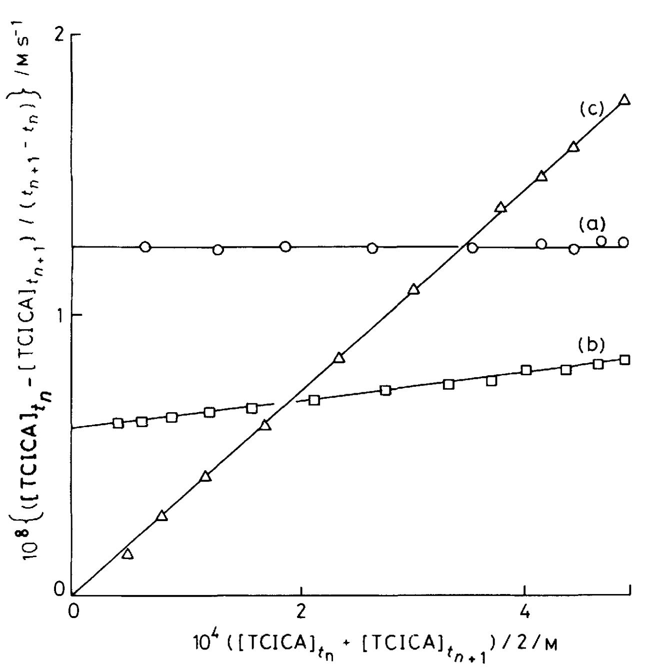


Figure 3. Representative plots showing separation of pseudo-zero-order and pseudo-first-order rate constants. $[\text{Acetone}]_0$ 1 × 10^{-2}M, $[H^+]$ 1 × 10^{-2}M, $[\text{TCICA}]_0$ 5 × 10^{-4} M. $10^4[Cl^-]_{ad}$/M: nil (a); 1 (b); 500 (c) [*cf.* equation (4)]

The k_{obs} showed a linear dependence on $[SL]_0$ in the range studied (Table 3). Increasing $[Cl^-]_{ad}$ had an accelerating effect on k_{obs}, but k_{obs} approached limiting values at higher relative $[Cl^-]_{ad}$ (Table 4). Plots of $(k_{obs})^{-1}$ *versus* $([Cl^-]_{ad})^{-1}$ were linear, furnishing slopes and intercepts which were linearly dependent on $[H^+]$. A linear k_{obs}–$[H^+]$ relationship was observed (Table 4).

Table 3. Pseudo-first-order rate constants for the reaction of ketones with TCICA in the presence of added Cl^-. $[\text{TCICA}]_0$ 5 × 10^{-4}M, $[H^+]$ 1 × 10^{-2}M, $[Cl^-]_{ad}$ 1 × 10^{-3}M

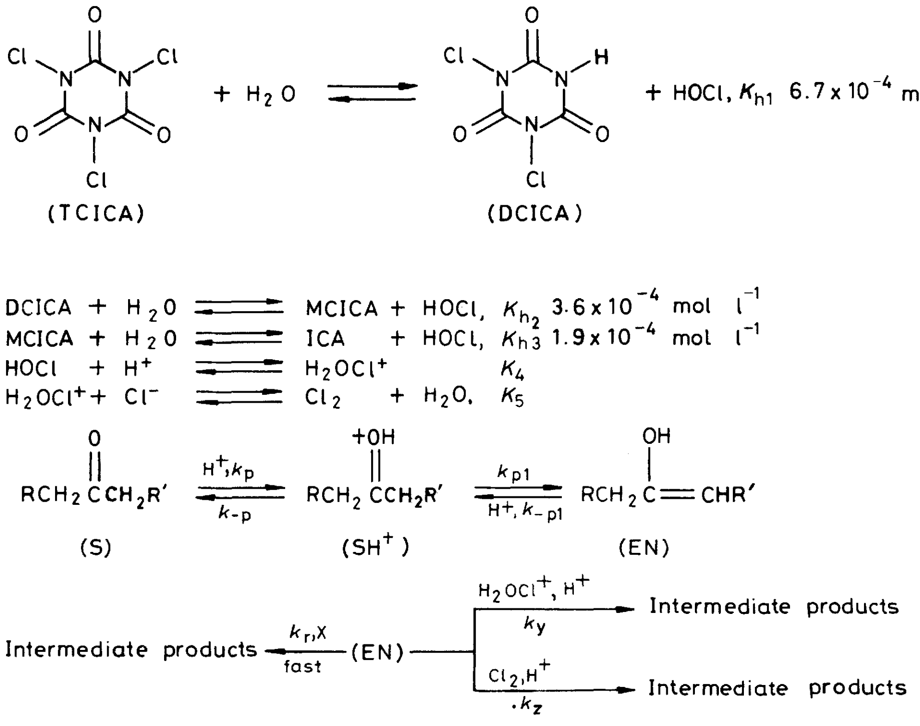
		$10^5k_{obs}/s^{-1}$			
(S)	$10^2[S]_0$/M	0.1	1	5	10
Acetone		0.2	2.4	12	25
Cyclopentanone		0.3	3.4	17	35
Cyclohexanone		0.8	8.3	42	
Acetophenone		0.1	1.1	5.5	

Reactions were found to be immeasurably slow when carried out (a) in the pH range 3.7—12.8 (at pH values of 3.7, 4.4, 4.7, 5.0, 7.6, 9.1, 9.7, 10.8, 12.2, and 12.8) in the absence of added Cl^- and (b) at pH values of 4.2, 5.0, and 7.2 in the presence of $[Cl^-]_{ad}$ 5 × 10^{-2}M; buffers used (pH range) were: acetate–acetic acid (3.7—5.0), BO_3^{3-}–H^+–OH^- (7.6—10.8), HPO_4^{2-}–OH^- (12.2—12.8). Variation of ionic strength of the medium in the range μ 1 × 10^{-2}—1.5M, using perchlorate and/or hydrogensulphate salts of sodium and/or potassium as supporting electrolytes, had no significant influence on k_{obs}.

Rate Law and Mechanism.—The important equilibria connected with the various reactant species in the present reaction are shown in the Scheme.

The pertinent steps in the Scheme suggest that the concentrations of monochloroisocyanuric acid (MCICA) and isocyanuric acid (ICA) would be negligible in acid medium as $(K_{h1}K_{h2}K_{h3})$ and $(K_{h1}K_{h2}) \ll K_{h1}$. The amount of each of Cl^+ (unhydrated),[8a] $ClOCOCH_3$,[8b] and HOCl[9] would be negligible in the predominantly aqueous acid solutions employed. At the $[Cl^-]_{ad}$ employed, $[Cl_3^-]$ would also be negligible (as $[Cl_3^-]$ $0.2[Cl_2][Cl^-]$).[1]

In the absence of added Cl^-, when the 'unmediated reaction' was found to be pseudo-zero order in the disappearing $[\text{TCICA}]_0$, enol formation from SH^+ (*i.e.* the k_{p1} step) was envisaged as rate limiting;[4] in that event the reactions of enolisable ketones could be represented by the rate law (5) when



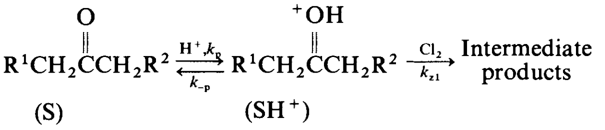
Scheme. $K_p = k_p/k_{-p}$; $K_{p1} = k_{p1}/k_{-p1}$; EN = enol; X = halogenating species TCICA, HOCl, or H_2OCl^+.

$$\mathrm{d[TCICA]}/\mathrm{d}t = k_0 = \frac{(k_{\mathrm{p1}}k_{\mathrm{p}})[\mathrm{S}][\mathrm{H}^+][\mathrm{TCICA}]^0}{k_{-\mathrm{p}} + k_{\mathrm{p1}}[\mathrm{H}^+]} \approx (k_{\mathrm{p1}}K_{\mathrm{p}})[\mathrm{S}][\mathrm{H}^+] \approx k'_0[\mathrm{S}][\mathrm{H}^+] \tag{5}$$

$$-\frac{\mathrm{d[TCICA]}/\mathrm{d}t}{[\mathrm{TCICA}]} = k_{\mathrm{obs}} = \frac{(k_{\mathrm{y}}K_{\mathrm{p}}K_{\mathrm{p1}}K_{\mathrm{h1}}K_4 + k_{\mathrm{z}}K_{\mathrm{p}}K_{\mathrm{p1}}K_{\mathrm{h1}}K_4K_5[\mathrm{Cl}^-])[\mathrm{S}][\mathrm{H}^+]^2}{\{[\mathrm{DCICA}] + K_{\mathrm{h1}} + K_{\mathrm{h1}}K_4[\mathrm{H}^+] + K_{\mathrm{h1}}K_4K_5[\mathrm{H}^+][\mathrm{Cl}^-]\}\{1 + K_{\mathrm{p}}[\mathrm{H}^+] + K_{\mathrm{p}}K_{\mathrm{p1}}\}} \tag{6}$$

$$k_{\mathrm{obs}} \approx \frac{k_{\mathrm{z}}K_{\mathrm{h1}}K_{\mathrm{p}}K_{\mathrm{p1}}K_4K_5[\mathrm{S}][\mathrm{H}^+][\mathrm{Cl}^-]}{(K_{\mathrm{h1}} + [\mathrm{DCICA}])/[\mathrm{H}^+] + K_{\mathrm{h1}}K_4 + K_{\mathrm{h1}}K_4K_5[\mathrm{Cl}^-]} \tag{7}$$

$$k_{\mathrm{obs}} \approx \frac{(k_{\mathrm{z}}K_{\mathrm{p}}K_{\mathrm{p1}})K_5[\mathrm{S}][\mathrm{H}^+][\mathrm{Cl}^-]}{1 + K_5[\mathrm{Cl}^-]} \approx \frac{k'_{\mathrm{z}}K_5[\mathrm{S}][\mathrm{H}^+][\mathrm{Cl}^-]}{1 + K_5[\mathrm{Cl}^-]} \tag{8}$$



$$\underset{(\mathrm{S})}{\mathrm{R^1CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2R^2}} \underset{k_{-\mathrm{p}}}{\overset{\mathrm{H}^+, k_{\mathrm{p}}}{\rightleftarrows}} \underset{(\mathrm{SH}^+)}{\mathrm{R^1CH_2}\overset{^+\mathrm{OH}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2R^2}} \xrightarrow[k_{\mathrm{z1}}]{\mathrm{Cl_2}} \text{Intermediate products} \tag{9}$$

$$k_{\mathrm{obs}} \approx \frac{(k_{\mathrm{z1}}K_{\mathrm{p}})K_5[\mathrm{S}][\mathrm{H}^+][\mathrm{Cl}^-]}{1 + K_5[\mathrm{Cl}^-]} \approx \frac{k''_{\mathrm{z}}K_5[\mathrm{S}][\mathrm{H}^+][\mathrm{Cl}^-]}{1 + K_5[\mathrm{Cl}^-]} \tag{10}$$

$k_{\mathrm{p1}}[\mathrm{H}^+] \ll k_{-\mathrm{p}}$ under the conditions employed. The value of the second-order rate constant (k'_0) reported for acetone, for example, was 1.23×10^{-4} l mol^{-1} s^{-1} in 15% aqueous acetic acid at 35 °C[4] and appears to be similar to that reported earlier by several workers (*e.g.*, k_1 0.29×10^{-4}[1] and 0.28×10^{-4} l mol^{-1} s^{-1}[2] in aqueous medium at 25 °C).

At appreciable $[\mathrm{Cl}^-]_{\mathrm{ad}}$, when the zero-order component of the disappearance rate of [TCICA] became negligible, the reaction proceeded through a Cl^--mediated route. Envisaging a rate-determining interaction of the enol (EN) with the active chlorine-containing species in the presence of acid, the rate law of the reaction in this situation may be given by (6) if k_{y} and $k_{\mathrm{z}} \ll k_{\mathrm{p1}}$. Under the conditions of the present study, assuming that K_{p} is a small quantity so that $(K_{\mathrm{p}}[\mathrm{H}^+] + K_{\mathrm{p}}K_{\mathrm{p1}}) \ll 1$, and that the reactivity of the $\mathrm{H_2OCl^+}$ is small and negligible by comparison with that of $\mathrm{Cl_2}$ (as the Cl^--independent component of the pseudo-first-order rate constant k_{obs} was not discernible even at very low $[\mathrm{Cl}^-]_{\mathrm{ad}}$ 5×10^{-5}M), then relationship (6) reduces to (7). The term [DCICA] in the denominator of (7), which depends on $[\mathrm{TCICA}]_0$, should show a retardation of k_{obs} at higher $[\mathrm{TCICA}]_0$; the retardation in k_{obs} at higher $[\mathrm{TCICA}]_0$ can also be qualitatively understood by the argument that at higher $[\mathrm{TCICA}]_0$, the unreactive TCICA species is relatively higher in concentration than the reactive chlorine-containing species participating in the reaction. However, the actual effect of [DCICA] on k_{obs} could not be separately found out from experiments because of the non-availability of the sample. If this small term $(K_{\mathrm{h1}} + [\mathrm{DCICA}])/[\mathrm{H}^+]$ in the denominator can be neglected, then relationship (7) becomes (8) for the pseudo-first-order disappearance of $[\mathrm{TCICA}]_0$ at low and constant $[\mathrm{TCICA}]_0$. The concentration terms in relationship (8) refer to those initially taken. Data treatment in accordance with (8) furnished the value of k'_{z} and K_5 (Table 5). The pseudo-first-order rate constants calculated using the resolved constants are in good agreement with the experimental k_{obs} values.

A similar rate law (10) can also be derived for an alternative sequence (9), which envisages a rate-determining reaction of the active chlorine-containing agent with the conjugate acid of the ketone $\mathrm{SH^+}$ (the equilibrium represented by K_{p1} being unimportant). The computed values of k''_{z} [$\equiv k'_{\mathrm{z}}$ of equation (8)] are also presented in Table 5.

Table 4. Pseudo-first-order rate constants for the reaction of ketones with TCICA in the presence of added Cl^-. $[\mathrm{S}]_0$ 1×10^{-2}M, $[\mathrm{TCICA}]_0$ 5×10^{-4}M

		$10^5k_{\mathrm{obs}}/\mathrm{s}^{-1}$				
$10^2[\mathrm{H}^+]/\mathrm{M}$	$10^2[\mathrm{Cl}^-]_{\mathrm{ad}}/\mathrm{M}$	0.1	1	5	10	20
Acetone						
0.1		0.2	0.3	0.4	0.4	0.4
1	0.3[a], 0.5[b], 1.7[c]	2.4	3.5	3.7	3.8	3.8
2		4.5	7.0	7.3	7.4	7.4
4		9.1	13	14	15	15
Cyclopentanone						
0.1		0.4	0.6	0.6	0.6	0.6
1		3.4	5.6	6.0	6.1	6.1
2		7.0	10	11	11	11
4		14	22	24	25	25
Cyclohexanone						
0.1		0.8	1.2	1.4	1.5	1.4
1		8.3	13	14	14	15
2		16	26	28	28	29
4		28	50	56	56	58
Acetophenone						
0.1					0.2	0.2
1		1.1	1.8	2.0	2.0	2.0
2		2.1	3.6	4.0	4.0	4.1
4		4.1	7.2	8.1	8.1	8.1

[a–c] Values obtained using equation (4) at $[\mathrm{Cl}^-]_{\mathrm{ad}}$ 0.5×10^{-4}, 1×10^{-4} and 5×10^{-4}M, respectively.

Discussion

Although the kinetic observations have been most plausibly explained in terms of two alternative but somewhat related schemes, several mechanistic implications of the reaction need mention.

(1) That the reactions are immeasurably slow at higher pH precludes the possibility of direct oxidation of the substrates in primary steps, for, in that event, HOCl which is predominantly formed at higher pH should have reacted faster than $\mathrm{Cl_2}$ on redox-potential considerations.[9]

(2) Under the conditions employed, the concentrations of the effective reacting species $[\mathrm{Cl_2}]$ are very small (as $[\mathrm{Cl_2}] < K_{\mathrm{h1}}K_5[\mathrm{H}^+][\mathrm{Cl}^-][\mathrm{TCICA}]_0$ so that $[\mathrm{Cl_2}]$ is of the order of *ca.* 10^{-8}—10^{-7}M at $[\mathrm{H}^+]$ 1×10^{-2}M, $[\mathrm{Cl}^-]$ 1×10^{-2}M, $[\mathrm{TCICA}]_0$ 3×10^{-4}—20×10^{-4}M) in reactions carried out in

Table 5. Average values of the observed rate constants and the resolved constants for the reaction of enolisable ketones with TCICA in the presence of added Cl^-. K_5 1.4 × 10^3 l^2 mol^{-2}

(S)	$10^5k_{obs}{}^a/s^{-1}$	$10^2k_z'{}^b$ (or $10^2k_z''$)^c/l^2 mol^{-2} s^{-1}	$-pK_a{}^d$	$10^9k_0^e$/l mol^{-1} s^{-1}
Acetone	3.5	38	7.24	12.3
Ethyl methyl ketone	3.7	40	7.2	10.3
Cyclopentanone	5.6	60	7.1	19.0
Cyclohexanone	13	140	6.8	45
Acetophenone	1.8	20	6.0	6.2
p-Methylacetophenone	3.0	32	5.5	8.5
p-Chloroacetophenone	0.8	8.6	6.42	1.8
p-Bromoacetophenone	0.6	6.4	6.6	0.9
p-Nitroacetophenone	0.1	1.1	7.92	0.8
m-Nitroacetophenone	0.13	1.4	7.72	0.83

[a] At $[S]_0$ 1 × 10^{-2}M, $[TCICA]_0$ 5 × 10^{-4}M, $[H^+]$ 1 × 10^{-2}M, $[Cl^-]_{ad}$ 1 × 10^{-2}M. [b] Calculated using equation (8). [c] Calculated using equation (10). [d] Reported in strong H_2SO_4 medium. The first four values in the column refer to those in >80% H_2SO_4 (ref. 11*a*); the rest in <70% H_2SO_4 (ref. 11*b*). [e] Values calculated using those reported at $[Cl^-]_{ad}$ 0 (ref. 4).

the presence of added Cl^-; $[Cl_2]$ would be much smaller in the absence of added Cl^-. Therefore, the earlier contention[1,2] that at very low $[Cl_2]$ (< 10^{-5}M) the reaction in general was pseudo-first order in the halogen species, and that at sufficiently high $[Cl_2]$ (> 10^{-4}M) the reaction became pseudo-zero order in halogen, does not appear valid under the conditions of the present study.

(3) The agreement of the resolved constants of the present reaction system with the values of earlier investigations is apparent from the following considerations. For example, the value of the dissociation constant ($1/K_p$) of the conjugate acid of acetone, acetoneH^+, determined from conductometric and spectrophotometric studies in aqueous acid solutions is reported[10] to lie in the range $10^{0.48}$—$10^{0.77}$M. Using an average value of $k_p \approx 10^{-0.6}$ l mol^{-1} and the reported second-order rate constant for the 'unmediated reaction' of acetone (k_0' 1.23 × 10^{-4} l mol^{-1} s^{-1})[4], the following values can be calculated for acetone: K_pK_{p1} (the keto–enol equilibrium constant) obtained from halogen–titration data[1] 2.5 × 10^{-6}, K_p 0.25 l mol^{-1}, $K_{p1} \approx 1 \times 10^{-5}$ mol l^{-1}, $k_{p1} \approx 5 \times 10^{-4}$ s^{-1}, and $k_{-p1} \approx 50$ l mol^{-1} s^{-1}. On the other hand, using a recent value[2c] of K_pK_{p1}, 3.5 × 10^{-9}, the above constants for acetone can be worked out as: $K_p \approx 0.25$ l mol^{-1} $K_{p1} \approx 1.4 \times 10^{-8}$ mol l^{-1}, k_p 2.8 × 10^{-5} l mol^{-1} s^{-1},[1,2c] $k_{-p} \approx 1.1 \times 10^{-4}$ s^{-1}, $k_{p1} \approx 5 \times 10^{-4}$ s^{-1}, and $k_{-p1} \approx 3.6 \times 10^4$ l mol^{-1} s^{-1}.

Using K_pK_{p1} 2.5 × 10^{-6} for acetone,[1] the $[H^+]$-dependent value of $k_z[H^+]$ at $[H^+]$ 1M would become: $[H^+]k_z'/(K_pK_{p1})$ 1.5 × 10^5 l mol^{-1} s^{-1} at 35 °C in 15% aqueous acetic acid medium for the 'Cl^--mediated' reaction of acetone; this value is of the same order of magnitude as the second-order rate constant for the acetone enol–Cl_2 reaction at $[H^+] \approx$ 1M and 25 °C in aqueous medium (*e.g.*, k_2 7.3 × 10^5 l mol^{-1} s^{-1}).[1] Similarly, if the more recent value[2c] of K_pK_{p1}, 3.5 × 10^{-9}, for acetone is used, $k_z[H^+] = [H^+]k_z'/(K_pK_{p1}) = 0.1 \times 10^9$ l mol^{-1} s^{-1} at $[H^+]$ 1M and 35 °C in 15% aqueous acetic acid; this value is also of the same order of magnitude as the most probable value of the second-order rate constant for the acetone enol–Cl_2 reaction (*e.g.*, 5 × 10^9 l mol^{-1} s^{-1} at 25 °C in aqueous medium and differing by one order of magnitude).[2] Considering the diversity of experimental conditions employed in the present work and in other investigations,[1,2] the agreement is satisfactory. (The apparent difference in the magnitude of the second-order rate constant for the acetone enol–Cl_2 reaction in the different sets of investigations[1,2] is only due to the use of different values of K_pK_{p1} in calculations; the values of the keto–enol equilibrium constant from different sources were listed earlier.[2c,d]) Thus our present data, if treated on the basis of the Scheme, would more or less be in agreement with those of earlier investigations[1,2] in which the enol–Cl_2 reaction has been shown as rate determining.

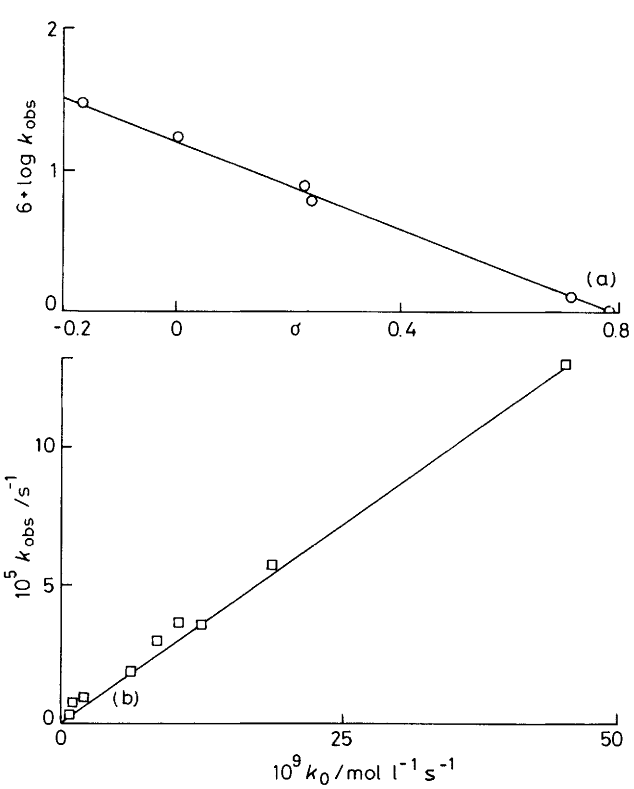


Figure 4. (a) Plot of log k_{obs} *versus* σ. (b) Plot of k_{obs} *versus* k_0 (*cf.* Table 5)

(4) However, *if* the first mechanistic sequence [*cf.* Scheme and the corresponding rate law (8)] were operative, the implication is that the interaction of the enol with the effective molecular halogen species Cl_2 (*e.g.*, the k_z step) is rate determining, *i.e.*, k_z should be $\ll k_{p1}$. Calculations for acetone, as already shown, indicate that this appears improbable. (For example, for acetone if K_pK_{p1} 2.5 × 10^{-6}, k_z 1.5 × 10^5 l^2 mol^{-2} s^{-1}, $k_{p1} \approx 5 \times 10^{-4}$ s^{-1}, and $k_{-p1} \approx 50$ l mol^{-1} s^{-1}; if K_pK_{p1} 3.5 × 10^{-9}, k_z 0.1 × 10^9 l^2 mol^{-2} s^{-1}, $k_{p1} \approx 5 \times 10^{-4}$ s^{-1}, and $k_{-p1} \approx 3.6 \times 10^4$ l mol^{-1} s^{-1}.)

(5) On the other hand, if the alternative mechanism represented by relationships (9) and (10) is more probable, then it implies that the interaction of the conjugate acid of ketone (SH^+) with the effective halogen species Cl_2 (*viz.*, the k_{z1}

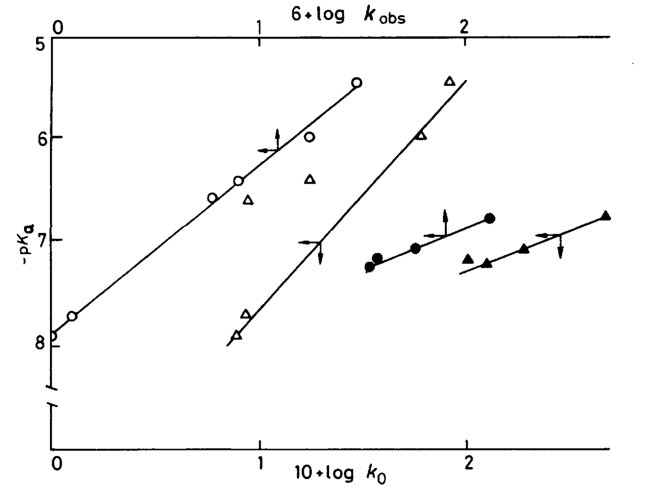


Figure 5. Plots of log k_{obs} or log k_0 *versus* pK_a. Circles and triangles refer to log k_{obs} and log k_0 values, respectively. Open and filled points refer to two sets of values of pK_a (*cf.* Table 5)

step) is rate determining in the presence of added Cl^-. In that event, the rate-limiting step in the 'unmediated' reaction (the k_{p1} step) and that in the 'Cl^--mediated' reaction involving Cl_2 (the k_{z1} step) should be parallel (the magnitude of the former being small in comparison with that of the latter Cl_2 reaction). The values computed for acetone (*e.g.*, k_{z1} 1.5 l mol^{-1} s^{-1}, k_{p1} 5 × 10^{-4} s^{-1}) do not appear to contradict this statement.

Should the rate-determining step in the 'unmediated' and the 'Cl^--mediated' reactions be parallel, the values of k_0 and k_{obs}, the measured pseudo-zero-order and pseudo-first-order rate constants for these reactions, respectively (Table 5), should bear a linear relationship. A plot of k_{obs} *versus* k_0 is excellently linear (Figure 4b). Moreover, a plot of log k_{obs} *versus* σ for various acetophenones is also linear (ρ − 1.5, Figure 4a) like that of log k_0 *versus* σ ($\rho \approx -1.1$), showing that these reactions do indeed proceed through the common activated state (the SH^+).[2c] The dissociation constants ($K_a = 1/K_p$) in aqueous acid (or aqueous acid–acetic acid) solutions of SH^+ for the substrates in the present study are not available (except for acetone[10]), but if the pK_a values reported in sulphuric acid[11] are any indication of the relative magnitudes of the acid strengths of SH^+, good linear log k_{obs} or log k_0 *versus* pK_a plots were observed (Figure 5).

This work presents similar rate data for the primary step of chlorination of enolisable ketones as those in other investigations,[1,2] although on the basis of a modified mechanistic interpretation. Our suggestion is that, under the conditions of the present study, the primary steps of the reactions of enolisable ketones with TCICA in acid medium most probably are (i) a rate-determining reaction of the conjugate acid of the ketone (SH^+) to form the enol in the absence of added Cl^-, and (ii) a rate-determining reaction of SH^+ with the most effective molecular chlorine species in the presence of added Cl^-, prior to the kinetically indistinguishable and rapid (*e.g.*, diffusion-controlled or near-encounter rate)[1,2] steps of product formation. Further probes with different halogen compounds may corroborate this.

Acknowledgements

One of us (N. K. R.) thanks the authorities of Khallikote College and Berhampur University, Berhampur for permission and facilities to carry out the work.

References

1 R. P. Bell and M. Spiro, *J. Chem. Soc.*, 1953, 429; R. P. Bell and K. Yates, *ibid.*, 1962, 1927, 2285; R. P. Bell and G. G. Davis, *ibid.*, 1964, 902.
2 (*a*) J. P. Guthrie, *Can. J. Chem.*, 1979, **57**, 240, 797, 1177; J. Hine, J. C. Kaufmann, and M. S. Cholod, *J. Am. Chem. Soc.*, 1972, **94**, 4590; (*b*) J. Toullec and J. E. Dubois, *Tetrahedron*, 1973, **29**, 2851, 2859; *J. Am. Chem. Soc.*, 1974, **96**, 3524; (*c*) J. E. Dubois, M. E. Alaoui, and J. Toullec, *ibid.*, 1981, **103**, 5393 and references cited therein; (*d*) E. Tapuhi and W. P. Jencks, *ibid.*, 1982, **104**, 5758.
3 V. Balasubramanian and V. Thiagarajan, *Aust. J. Chem.*, 1976, **29**, 1449, and references cited therein.
4 P. S. Radhakrishnamurti and N. K. Rath, *Indian J. Chem.*, 1985, **24A**, 300.
5 K. S. Vasudevan and N. Venkatasubramanian, *Indian J. Chem.*, 1985, **24A**, 304.
6 Osaka Pharmaceutical Assoc., *Osaka-Fu-Yaku Zasshi*, 1979, **30**, 39 (*Chem. Abstr.*, 1979, **91**, 157 695g).
7 S. Acharya, G. Neogi, and R. K. Panda, *Int. J. Chem. Kinet.*, 1983, **15**, 887.
8 (*a*) C. G. Swain and D. R. Christ, *J. Am. Chem. Soc.*, 1972, **94**, 3195; (*b*) P. B. D. de la Mare, I. C. Hilton, and C. A. Vernon, *J. Chem. Soc.*, 1960, 4039; P. B. D. de la Mare and J. L. Maxwell, *Chem. Ind. (London)*, 1961, 553.
9 W. M. Latimer, 'The Oxidation Potentials,' Prentice-Hall, Englewood Cliffs, 1961, 2nd edn., p. 54.
10 (*a*) A. T. Gelbstein, G. G. Stscheglova, and M. T. Temkin, *Dokl. Akad. Nauk. SSSR*, 1956, **107**, 108; (*b*) U. L. Haldna and V. A. Palm, *ibid.*, 1960, **135**, 667; U. L. Haldna, *Org. React.*, 1964, **1**, 184.
11 (*a*) H. J. Campbell and J. T. Edwards, *Can. J. Chem.*, 1960, **38**, 2109; (*b*) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, 1958, **80**, 6355.

Received 6*th January* 1986; *Paper* 6/046