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Kinetics and Mechanism of Oxidation of Acetone, Ethyl Methyl Ketone and Diethyl Ketone With Chloramine-T in Hydrochloric Acid Medium

By

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The kinetics of oxidation of aliphatic ketones (acetone, ethyl methyl ketone and diethyl ketone) by chloramine-T in presence of hydrochloric acid (0.1 to 0.3*M*) have been investigated at 30 °C. The rate of disappearance of chloramine-T has been found to be first order each with respect to oxidant, ketone and $[H^+]$, in the range of the acid concentrations studied. The thermodynamic and kinetic parameters have been evaluated by determining the rate constants at different temperatures. The products of the reaction have been identified as chloroketones by their NMR spectra. The solvent isotope effect has been studied in the case of the oxidation of acetone and ethyl methyl ketone. A mechanism has been proposed.

Kinetic investigations of the oxidation of ketones have been carried out by several groups of workers using oxidants such as potassium permanganate[1], chromic acid[2], cerium(IV)[3], cobalt(III)[4], thallium(III)[5], manganese(III)[6], and potassium persulphate[7]. Although chloramine-T (*CAT*) is a well-known volumetric reagent, very few kinetic studies have been made with this oxidant. The *CAT*/sulphonamide system shows a pH dependent oxidation potential[8] which decreases with decreasing acidity. It is therefore to be expected that *CAT* functions as a stronger oxidising agent in acid medium. Oxidation of a few ketones by *CAT* in alkaline medium has been reported by *Mushran* and co-workers[9–12]. As a part of our investigations on the oxidation of organic substrates by *CAT* in acid medium[13, 14], the present paper describes the kinetics and mechanism of oxidation of acetone, ethyl methyl ketone and diethyl ketone by *CAT* in presence of HCl.

Experimental

All solutions were prepared in triply distilled water. BDH AnalaR acetone (corrected B.P. 56.2 °C) was used without further purification. BDH ethyl

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methyl ketone (corrected B.P. 79.6 °C) was purified by redistillation. Diethyl ketone (Fluka) was redistilled (corrected B.P. 101 °C). Approximately 1.0*M* solutions of acetone and ethyl methyl ketone in water and diethyl ketone in 50% (*V*/*V*) ethanol—water mixture were prepared and standardised by the procedure of *Messinger*[15]. Chloramine-T (E. Merck) was purified by the method of *Morris* et al.[16]. An approximately decimolar solution of this compound was prepared and standardised by the iodometric method. All other reagents were of accepted grades of purity. The ionic strength of the system was kept constant at a high value by using a concentrated solution of $NaClO_4$. Heavy water (D_2O, 99.2%) supplied by Bhabha Atomic Research Centre, India, was used to investigate the solvent isotope effect. NMR spectra of the reaction products were recorded on a Varian model spectrometer (60 and 100 MHz). IR spectra (Nujol mull) were obtained on a Perkin-Elmer Model 700 IR spectrophotometer.

Table 1. *Effect of the Concentration of the Reactants on the Reaction Rate.* $[H^+] = 0.1M$, $\mu = 1.0M$, Temp. 30 ± 0.1 °C

$[CAT]_0$	$[\text{ketone}]_0$	$k_1 \cdot 10^4\ \text{sec}^{-1}$ Acetone	Ethyl methyl ketone	Diethyl ketone
0.005	0.10	1.790	2.542	2.750
0.005	0.15	2.713	3.203	4.063
0.005	0.20	3.276	5.044	5.538
0.005	0.25	4.557	6.076	6.266
0.005	0.30	5.311	7.588	8.132
0.006	0.10	1.681	2.455	2.757
0.007	0.10	1.582	2.451	2.790
0.008	0.10	1.596	2.260	2.781
0.005*	0.10	1.858	2.540	2.716
0.005**	0.10	1.830	2.514	2.820
0.005***	0.10	2.000	2.586	—

* At ionic strength of 0.5*M*.
** In presence of excess p-toluenesulphonamide.
*** In heavy water as solvent.

The reaction was carried out in a glass stoppered pyrex boiling tube. Requisite amounts of ketone, HCl, $NaClO_4$, a constant amount of glacial acetic acid (to make the medium 10% aqueous acetic acid and keep the medium homogeneous) and water (50% ethanol—water mixture in the case of diethyl ketone) to maintain the total volume constant for all runs were taken in the tube and were thermostated at 30 °C. A measured volume of *CAT* solution at the same temperature was added to the mixture in the boiling tube. At different time intervals, aliquots of the reaction mixture were withdrawn and added to a quenching mixture of 0.005*M* ascorbic acid and 4*N*-HCl. The excess ascorbic acid was back titrated with standard *CAT* solution using starch—KI as an indicator.

Stoichiometry

Reaction mixtures containing excess chloramine-T over the ketone were kept at room temperature (28 ± 2 °C) in presence of HCl (over-all concentration 0.5*M*) for 24 hours. Iodometric estimation of unconsumed *CAT* revealed that one mole of ketone consumed one mole of *CAT*. The reaction can be represented as:

$$CH_3COCH_3 + MeC_6H_4SO_2NClNa + HCl \rightarrow$$

$$MeC_6H_4SO_2NH_2 + ClCH_2COCH_3 + NaCl \qquad (1)$$

$$CH_3COC_2H_5 + MeC_6H_4SO_2NClNa + HCl \rightarrow$$

$$MeC_6H_4SO_2NH_2 + ClCH_2COC_2H_5 + NaCl \qquad (2)$$

$$C_2H_5COC_2H_5 + MeC_6H_4SO_2NClNa + HCl \rightarrow$$

$$MeC_6H_4SO_2NH_2 + CH_3ClCH\ COCH_2CH_3 + NaCl \qquad (3)$$

The chloroketones formed were separated by *t.l.c.* technique and were identified by (i) their 2,4-dinitrophenyl-hydrazone and (ii) IR spectra and (iii) NMR spectra.

Chloroacetone: A sharp singlet at 2.2 δ for $\mathbf{ClCH_2}$ and the singlet at 2.1 δ due to $\mathbf{CH_3CO}$.

Chloromethyl ethyl ketone: A triplet centred around 1.0 δ corresponding to —CH_2CH_3, a singlet at 2.4 δ due to —$ClCH_2$. The CH_3CH_2 shows a quartet centred around 3.0 δ.

Table 2. *Effect of Hydrogen Ion Concentration on Reaction Rate.* $[CAT]_0 = 0.005M$, $[\text{Ketone}]_0 = 0.1M$, $\mu = 1.0M$, Temp. 30 °C

$[H^+]$, M	Acetone $k_1 \cdot 10^4$ sec^{-1}	Acetone $\frac{k_1}{[H^+]} \cdot 10^3$	Ethyl methyl ketone $k_1 \cdot 10^4$ sec^{-1}	Ethyl methyl ketone $\frac{k_1}{[H^+]} \cdot 10^3$	Diethyl ketone $k_1 \cdot 10^4$ sec^{-1}	Diethyl ketone $\frac{k_1}{[H^+]} \cdot 10^3$
0.10	1.790	1.790	2.542	2.542	2.750	2.750
0.15	2.898	1.932	3.867	2.578	2.264	2.843
0.20	3.842	1.921	5.040	2.520	5.204	2.603
0.25	4.509	1.804	6.282	2.514	6.857	2.745
0.30	5.380	1.794	7.021	2.341	7.773	2.591

Chlorodiethyl ketone: A triplet centred around 1.2 δ corresponding to —$CH_2\mathbf{CH_3}$, a doublet at 1.8 δ assigned to ClCH $\mathbf{CH_3}$ and the two quartets at 2.7 δ and 4.4 δ correspond to CH_3CH_2 and CH_3CHCl respectively.

Further, in the case of acetone, it was observed that the infra-red spectrum of the reaction product and that of a synthetic sample of chloroacetone are superimposable.

Results and Discussion

The kinetics of oxidation of ketones by *CAT* was investigated at different initial concentrations of the reactants. When the ketone is in

Table 3. *Effect of Temperature on the Reaction Rate.* [Ketone]$_0$ = $0.1M$,

Temp., K	$k_1 \cdot 10^4$ sec^{-1}	$k \cdot 10^2$ m^{-2} lit^{+2} sec^{-1}
Acetone		
303.0	1.790	1.790
308.2	3.262	3.262
312.5	5.297	5.297
315.0	6.643	6.643
317.5	8.686	8.686
Ethyl methyl ketone		
303.0	2.542	2.542
309.0	4.537	4.537
314.6	7.739	7.739
317.0	11.140	11.140
323.0	15.520	15.520
Diethyl ketone		
300.3	2.258	2.258
303.0	2.750	2.750
310.6	4.577	4.577
316.0	6.764	6.764

large excess, plots of log $(a/a—x)$ vs. time are found to be linear. The pseudo first order rate constants k_1 calculated are almost constant at different initial concentrations of *CAT* (Table 1). Hence, the rate of disappearance of *CAT* obeys first order kinetics. It is seen that value of k_1 increases with increase in concentration of the substrate and a plot of log k_1 vs. log [ketone]$_0$ is linear with slope equal to unity. Hence the reaction is first order with respect to the ketone. Table 2 shows that at constant $[CAT]_0$ and [ketone]$_0$, k_1 is a function of $[H^+]$ and $k_1/[H^+]$ is a constant showing first order dependence of rate on $[H^+]$. The reaction was carried out at different temperatures (Table 2). The kinetic and thermodynamic parameters calculated from a plot of log k_1 vs. $1/T$ are shown in Table 3. The pseudo first order rate constants are not very much affected by a change in the ionic strength of the medium or by the presence of excess of p-toluenesulphonamide in the reaction mixture (Table 1).

Typical kinetic data for ascertaining the solvent isotope effect on the oxidation of acetone and ethyl methyl ketone by *CAT* are given in Table 1. The values of k_{D_2O}/k_{H_2O} are 1.12 and 1.02 respectively.

The energy of activation for the oxidation of acetone, ethyl methyl ketone and diethyl ketone by *CAT* has been found to be 78.48, 74.30 and

$[CAT]_0 = 0.005M$, $[H^+] = 0.1M$, $\mu = 1.0M$

A, sec^{-1}	$\Delta S^{\neq}$, e.u.	$\Delta H^{\neq}$, kcal $mole^{-1}$	$\Delta G^{\neq}$, kcal $mole^{-1}$
$2.20 \pm 0.035 \cdot 10^{13}$	1.587 ± 0.032	20.31	19.82
$3.232 \pm 0.03 \cdot 10^{11}$	-6.830 ± 0.031	17.57	19.73
$1.195 \pm 0.019 \cdot 10^{8}$	-22.52 ± 0.047	12.76	19.69

55.9 kJ $mole^{-1}$ respectively. The values of the *Arrhenius* frequency factor and other thermodynamic parameters have been shown in table 3.

The results indicate that the kinetic behaviour of oxidation of these aliphatic ketones by *CAT* in HCl medium is similar. Hence, it may be assumed that a common mechanism is operative in these oxidations.

In general, enolization of ketones could be catalysed both by acids and bases as shown below:

$$S + OH^- \rightleftharpoons S' + OH^-$$
$$S + H^+ \rightleftharpoons S' + H^+$$

where S' represents the enolic form.

Soper[17], *Morris* et al.[16], and *Bishop* and *Jennings*[18] have shown that the following equilibria are present in acidified solutions of *CAT*:

$$RNClNa \rightleftharpoons RNCl^- + Na^+ \qquad (1)$$

where R is p-$MeC_6H_4SO_2$.

$$RNCl^- + H^+ \rightleftharpoons RNHCl \qquad (2)$$
$$2\ RNHCl \rightleftharpoons RNCl_2 + RNH_2 \qquad (3)$$
$$RNCl_2 + H_2O \rightleftharpoons RNHCl + HOCl \qquad (4)$$
$$RNHCl + H_2O \rightleftharpoons RNH_2 + HOCl \qquad (5)$$

In an acidified solution of *CAT*, the possible oxidizing species are therefore RNHCl, $RNCl_2$, and HOCl. Under the present experimental conditions dichloramine-T ($RNCl_2$) was not precipitated. Further a second order dependence of rate on *CAT* is predicted if $RNCl_2$ is assumed to be the reactive species. So, its influence on the oxidation of ketones can be ignored.

Mechanistic Steps Assuming HOCl *as the Reactive Species Lead to*

$$-\frac{\mathrm{d}[CAT]}{\mathrm{d}t} = k_3\,[S]\,[CAT]$$

The above rate expression however predicts the rate independence of the acid concentration, which is contrary to experimental observations.

Mechanistic Steps Assuming RNHCl *as the Reactive Species*

The following scheme for the reaction can be envisaged:

$$S + H^+ \rightleftharpoons SH^+ \rightleftharpoons S' + H^+; \ldots \text{fast}$$

$$RNCl^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNHCl \ \ldots \ \text{slow}$$

$$RNHCl + S' \xrightarrow{k_2} X \ \ldots \ \text{slowest and rate determining}$$

where X is the reaction intermediate.

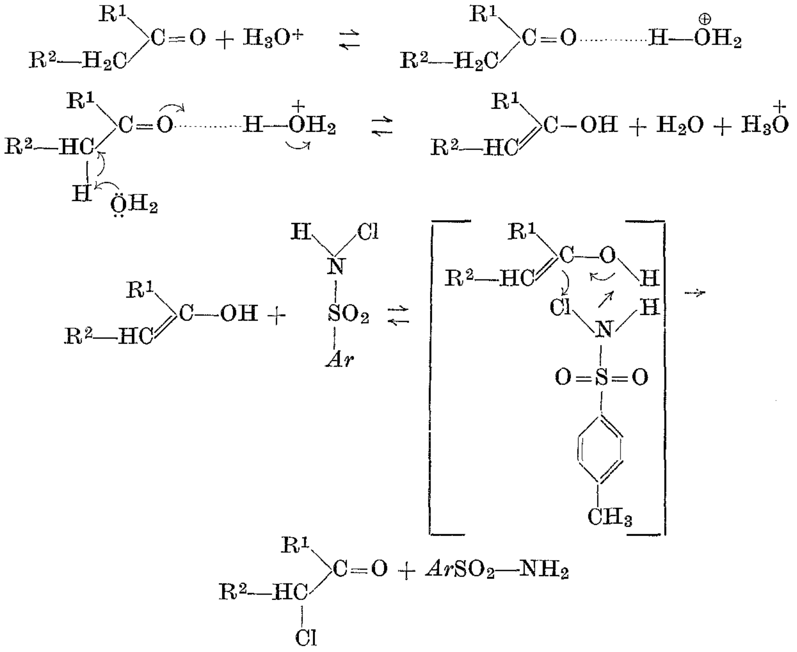
$$X \xrightarrow{k_3} \text{products} \ \ldots \ \text{fast}$$

Assuming steady state conditions for RNHCl and taking $k_{-1} \gg k_2[S']$ the rate of reaction can be shown to be

$$-\frac{\mathrm{d}[CAT]}{\mathrm{d}t} = \frac{k_1 k_2}{k_{-1}}\,[CAT]\,[S]\,[H^+]$$

The rate expression is in agreement with the experimental observations. The fairly high value of the energy of activation and the increasingly negative entropy of activation lend support for the formation of an intermediate X as shown in the mechanistic steps. The insignificant effect of varying the ionic strength of medium on the rate clearly shows that neutral molecules are present in the rate determining step. The negligible influence of toluenesulphonamide on the rate rules out the possibility of its involvement in the slow step of the reaction. Absence of any significant solvent isotope effect on the rate of reaction ($k_{D_2O}/k_{H_2O} \approx 1$) indicates that the reaction does not involve the breaking of a

C—H bond. The mechanism is further supported by the stoichiometry of the reaction. A detailed mechanism of oxidation of ketones by *CAT* is shown in scheme I.



Scheme I

a) $R^1 = CH_3$, $R^2 = H$ (Acetone).
b) $R^1 = CH_2CH_3$, $R^2 = H$ (Ethyl methyl ketone).
c) $R^1 = CH_2CH_3$, $R^2 = CH_3$ (Diethyl ketone).

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