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Mechanism of the Oxidation of Cycloheptanone by Chloramine-T

By

Adarsh Kumar, A. K. Bose, and S. P. Mushran

Department of Chemistry, University of Allahabad, Allahabad, India

With 2 Figures

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The oxidation kinetics of cycloheptanone by chloramine-T in alkaline media has been investigated. A mechanism involving the formation of an intermediate by the interaction between the enolic anion of cycloheptanone and chloramine-T in a slow step followed by its interaction with another molecule of chloramine-T in a fast step leading to products has been proposed. The scheme satisfactorily accords with the observed stoichiometry, negligible influence of ionic strength and a positive dielectric effect. Various rate parameters have been computed and 1.2-cycloheptanedione identified as the end product.

The high redox potential of the less familiar potent oxidant chloramine-T ($E_{\text{red.}} = 1.138\,\text{V}$ at pH 0.65) has prompted several recent kinetic studies[1–7] involving it as an oxidant, both in acidic as well as in alkaline media. The present work constitutes an investigation on the kinetics and mechanism of the oxidation of cycloheptanone by chloramine-T in alkaline media.

Material and Methods

The materials employed were of highest purity available. Fluka AG (Buchs SG) cycloheptanone and E. Merck p. a. chloramine-T were used. Chloramine-T solutions were stored in black coated bottles to prevent its photochemical deterioration[8]. Ascorbic acid solutions (G.R.S. Merck) were always prepared fresh. All other reagents viz. $NaClO_4$, NaCl and methanol were of AnalaR grade. Triple distilled water was used throughout the course of investigation. The reaction stills were blackened from outside.

Kinetic Measurements

The progress of the reaction was monitored by estimating unconsumed chloramine-T indirectly using ascorbic acid[9]. The reaction was initiated by rapid addition of chloramine-T to a cycloheptanone—alkali mixture with vigorous shaking. 5 ml aliquots of the reaction mixture were withdrawn at regular intervals of time and transferred to the titrating flasks containing an excess ascorbic acid and 5 ml 1*N*-HCl. The excess ascorbic acid was then back titrated against standard chloramine-T using the iodometric method[10].

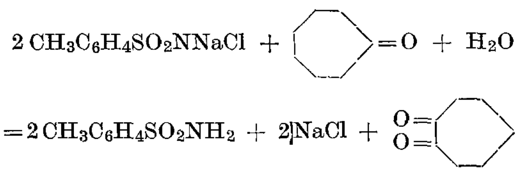
Table 1. *Effect of Reactants' Concentration on the Reaction Rate*
[NaOH] = 0.25*M*

10^3 [Chloramine-T]	10^2 [Cycloheptanone]	$k_1' \times 10^5$ $\sec^{-1}$	
M	*M*	40 °C	45 °C
0.6	1.0	10.9	14.6
0.8	1.0	11.3	14.8
1.0	1.0	11.3	15.6
1.4	1.0	11.0	15.4
2.0	1.0	11.1	16.4
3.0	1.0	11.6	15.7
1.0	0.8	7.83	12.0
1.0	1.4	14.9	21.0
1.0	2.0	20.8	26.5
1.0	2.4	26.5	31.9
1.0	3.0	32.7	38.7

Results and Discussion

Stoichiometry and Identification of Product

Different sets of experiments were carried out with varying ratios of chloramine-T to cycloheptanone in presence of 0.25*M*-NaOH at 55° for 48 hours. From the results, it was concluded that one mole of cycloheptanone consumes two moles of chloramine-T according to the following stoichiometric equation yielding-cycloheptane-1.2-dione as the product which was tested by conventional method[11].



(1)

Effect of Varying [Reactant]

The oxidation kinetics were studied over a wide range of concentrations of the reactants (Table 1). Pseudo-first order dependence in chloramine-T was followed at all initial concentrations of chloramine-T (Fig. 1). A linear increase in the pseudo-first order rate constant (k_1') in chloramine-T was observed with increase in cycloheptanone concentration, keeping other variable parameters constant. The second order rate constants calculated as $k_2' = k_1'/[\text{cycloheptanone}]$ gave concordant values (1.05 ± 0.07, $1.42 \pm 0.12 \times 10^{-4}\ \text{l} \cdot \text{mol}^{-1} \cdot \text{sec}^{-1}$ at 40°, 45°) and thus established a first order dependence in cycloheptanone concentration.

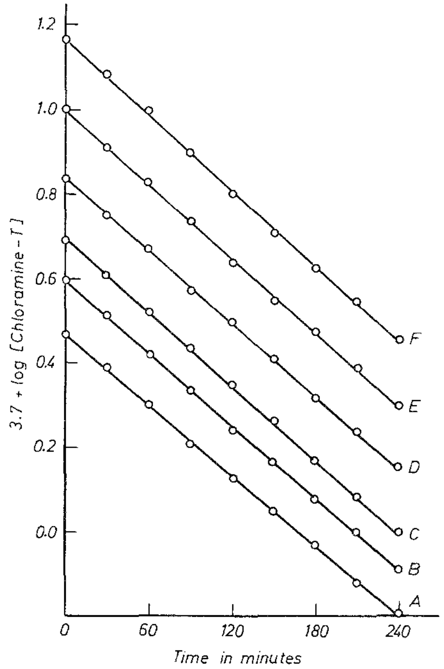


Fig. 1. First order rate plot at 40°. [Cycloheptanone] = $1.0 \times 10^{-2} M$; [NaOH] = $0.25 M$; [Chloramine-T] = 0.6, 0.8, 1.0, 1.2, 2.0 and $3.0 \times 10^{-3} M$ in A, B, C, D, E, and F

Effect of Varying [Hydroxide Ion]

A strong dependence of the rate to the hydroxide ion concentration was observed. Keeping ionic strength constant, an increase in $[\text{OH}^-]$ increased the pseudo-first order rate constant linearly. The plots of $\log k_1'$ against $\log [\text{OH}^-]$ gave straight lines (Fig. 2) with slopes 1.0, 1.1 at 40°, 45° establishing a first order dependence of the rate to $[\text{OH}^-]$.

Effect of Varying Ionic Strength

Ionic strength variations by using $NaClO_4$ and $NaCl$ were found to have negligible effect on the reaction rate (Table 2), which thereby indicated that the rate determining slow step involves at least one neutral molecule.

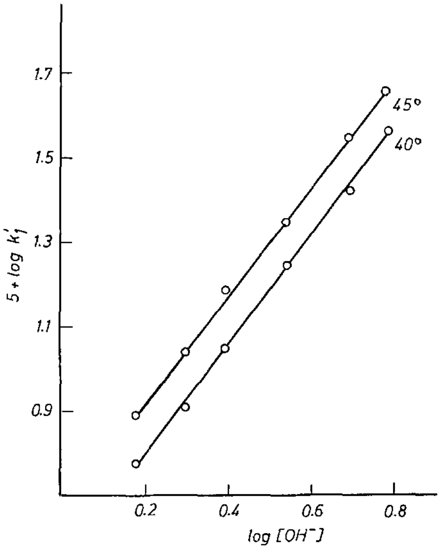


Fig. 2. Plot of log k_1' against log $[OH^-]$. [Chloramine-T] = $1.0 \times 10^{-3} M$; [Cycloheptanone] = $1.0 \times 10^{-2} M$; Ionic strength = $0.72 M$

Effect of Varying Solvent Composition

The rates were studied in different water—methanol mixtures. It was observed that an increase in methanol concentration considerably decreases the rate of the reaction (Table 3). This led to the conclusion that the rate determining slow step involves either an interaction between two similarly charged ions or a negatively charged ion and a dipole.

Effect of Varying Temperature

From the rate study measurements carried out at five temperatures (35–55°), average values of the rate parameters viz. energy of activation ($\Delta E^{\neq}$), frequency factor (A), entropy of activation ($\Delta S^{\neq}$), heat of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta F^{\neq}$) were calculated as 10.4 kcal/mole, $7.78\ l^2 \cdot mol^{-2} \cdot sec^{-1}$, —32.7 e.u., 9.76 kcal/

mole and 20.1 kcal/mole resp. The average value of the temperature coefficient was found to be 1.70.

Base catalysed oxidation of cycloheptanone points to the involvement of the enolic anion of cycloheptanone in the oxidation process.

The oxidising property of chloramine-T is due to its four oxidising species viz. chloramine-T itself, p-toluenesulphochloramide, dichloramine-T and hypochlorite ion, the last three being the hydrolytic products[12] of chloramine-T and the relative amounts of each of which depend upon the pH of the solution[13].

Table 2. *Effect of Ionic Strength on the Reaction Rate at 45°*
[Chloramine-T] = $1.0 \times 10^{-3} M$, [Cycloheptanone] = $1.0 \times 10^{-2} M$,
[NaOH] = $0.25 M$

10 [Salt]	$k_1' \times 10^5$ sec^{-1}	
M	$NaClO_4$	NaCl
0.0	15.6	15.6
2.0	15.1	15.5
2.4	15.1	15.4
2.8	15.2	15.5
3.2	15.0	15.2
4.0	15.1	15.0

Table 3. *Effect of Solvent Composition on the Reaction Rate at 45°*
[Chloramine-T] = $1.0 \times 10^{-3} M$, [Cycloheptanone] = $1.0 \times 10^{-2} M$,
[NaOH] = $0.25 M$

[*Me*OH] %	$k_1' \times 10^5$ sec^{-1}
0	15.6
10	11.1
20	10.2
30	8.90
40	7.80
50	6.67

In an acidic medium, dichloramine-T predominates over the rest of the species. But in highly alkaline media, it does not exist even in traces and any amount of it formed is converted to p-toluenesulphochloramide and hypochlorite ion. Thus dichloramine-T is excluded from the oxidising species in this case.

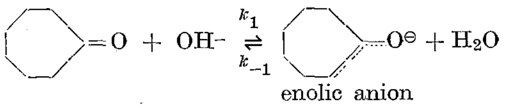
Turning to hypochlorite ion, the slow and rate determining step in the proposed mechanism would necessarily involve the interaction of two negatively charged ions (enolic anion of cycloheptanone and hypochlorite ion), which would correspond to a highly negative entropy of activation, high energy of activation and a significant positive ionic strength effect. The observed kinetic data however do not point to such a reaction path. Thus the possibility of hypochlorite ion as the oxidising species is also ruled out.

Being a fairly strong acid ($pK_a = 4.55$)[14], p-toluenesulphochloramide exists in traces only at high hydroxide ion concentration and its amount decreases with increase in [OH⁻]. However, the negligible influence of ionic strength and a positive dielectric effect accords well with its interaction with the enolic anion of cycloheptanone in the slow and rate determining step. The rate law deduced by assuming p-toluenesulphochloramide as the oxidising species is however found to show an independence to [OH⁻] which is contrary to experimental results. The possibility of p-toluenesulphochloramide being the oxidising species is therefore also ruled out.

Table 4. *Effect of Temperature on the Reaction Rate and Rate Parameters*
[Chloramine-T] = $1.0 \times 10^{-3} M$, [Cycloheptanone] = $1.0 \times 10^{-2} M$,
[NaOH] = $0.25 M$

Temp., °C	$k_1' \times 10^5$ sec^{-1}	$k \times 10^2$ $l^2 \cdot mol^{-2} \cdot sec^{-1}$	$\Delta E^{\ddagger}$ kcal/mole	$A \times 10^{-5}$ $l^2 \cdot mol^{-2} \cdot sec^{-1}$	$\Delta S^{\ddagger}$ e.u.	$\Delta H^{\ddagger}$ kcal/mole	$\Delta F^{\ddagger}$ kcal/mole
35	9.33	3.73	10.4	7.92	— 32.6	9.78	19.8
40	11.3	4.52	10.4	7.38	— 32.7	9.77	20.0
45	15.6	6.24	10.4	7.84	— 32.7	9.76	20.2
50	19.8	7.92	10.4	7.70	— 32.7	9.75	20.3
55	26.5	10.6	10.4	8.07	— 32.6	9.74	20.4

One is therefore left with the only alternative that chloramine-T itself is the possible oxidising species in this case. It is proposed that a chloramine-T molecule interacts with an enolic anion of cycloheptanone to form an intermediate in a slow and rate determining step followed by its subsequent fast interaction with another molecule of chloramine-T giving the products. The following mechanism for oxidation may thus be schematically represented.



(2)

$$\text{enolic anion} + CH_3C_6H_4SO_2NNaCl \xrightarrow[\text{slow}]{k_2} X \text{ (Intermediate)} \quad (3)$$

$$X \text{ (Intermediate)} + CH_3C_6H_4SO_2NNaCl \xrightarrow[\text{fast}]{k_2} \text{Products.} \quad (4)$$

Application of steady state treatment with the reasonable approximation that $k_{-1} \gg k_2[CH_3C_6H_4SO_2NNaCl]$, the rate law obtained is

$$-\frac{d}{dt}[CH_3C_6H_4SO_2NNaCl] =$$

$$= \frac{2\,k_1\,k_2}{k_{-1}\,[H_2O]}[CH_3C_6H_4SO_2NNaCl]\ [\text{cycloheptanone}]\ [OH^-]. \qquad (5)$$

The proposed scheme thus gives a rate law which predicts a first order dependence in chloramine-T, cycloheptanone and hydroxide ion concentration and also accords with the stoichiometry, negligible influence of ionic strength and a positive dielectric effect.

It is thus justifiable to conclude that chloramine-T itself is directly involved in the oxidation of cycloheptanone.

Acknowledgement

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Correspondence and reprints:
Prof. S. P. Mushran
Department of Chemistry
University of Allahabad
Allahabad 211002
India