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MECHANISM OF CHLORAMINE-T OXIDATION OF METHYL VINYL KETONE AND ISOPROPYL METHYL KETONE IN AQUEOUS ALKALINE MEDIA

BHARAT SINGH,* A. K. SAMANT and B. B. L. SAXENA
Department of Chemistry, University of Allahabad, Allahabad-2, India

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Abstract—The oxidation kinetics of methyl vinyl ketone and isopropyl methyl ketone by chloramine-T in aqueous alkaline solutions show first-order dependence on chloramine-T, both substrates and alkali. No effect of p-toluenesulphonamide was evident. Observed stoichiometry, negligible effect of ionic strength and a positive dielectric effect point to a mechanism involving interaction of enolate anions with chloramine-T in the rate determining step. Activation parameters and the isolation of the product formaldehyde are in agreement with the proposed mechanism.

Less widely used but potent oxidant chloramine-T with high redox potential ($E_{red} = 1.138$ V at pH 0.65) has recently been used in kinetic studies involving it as an oxidant, both in acidic as well as in alkaline media.[1-9] Oxidation kinetics of VMK and IMK by ceric sulphate in sulphuric acid solutions has already been reported by Singh[10,11] *et al.* The present communication summarizes the results of an investigation on the kinetics and mechanism of the oxidation of VMK and IMK by aqueous alkaline solutions of chloramine-T.

MATERIALS AND METHODS

The materials employed were of highest purity available. Substrates and chloramine-T were E. Merck samples. Koch-Light (England) sample of p-toluene sulphonamide was used. All other reagents were of Analar grade. Chloramine-T solutions were stored in black coated bottles to prevent photochemical deterioration. The reaction stills were blackened from outside and doubly-distilled water was used throughout the experiments.

The reaction was initiated by rapid addition of chloramine-T to already equilibrated alkali-ketone mixture with vigorous shaking. The kinetics were followed by examining aliquot portions of the reaction mixture for unconsumed chloramine-T iodometrically.

RESULTS AND DISCUSSION

Different sets of experiments carried out with varying ratios of chloramine-T to each ketone i.e. methyl vinyl ketone and isopropyl methyl ketone in presence of 0.2M-NaOH at 45° for 48 h showed that two moles of chloramine-T were consumed for oxidation of molar concentration of each ketone according to the following stoichiometric equations yielding formaldehyde as the product which was tested by conventional method.[12]

$$\mathrm{CH_3COCH{=}CH_2 + 2CH_3C_6H_4SO_2NNaCl + OH^- + 2H_2O = 2CH_3C_6H_4SO_2NH_2 + CH_3COO^- + 2HCHO + 2NaCl} \qquad (1)$$

$$\mathrm{CH_3COCH(CH_3)_2 + 2CH_3C_6H_4SO_2NNaCl + OH^- + H_2O = 2CH_3C_6H_4SO_2NH_2 + (CH_3)_2CHCOO^- + HCHO + 2NaCl.} \qquad (2)$$

The oxidation was studied over a wide range of concentrations of reactants at constant alkali concentration. The rate data indicate first order kinetics in chloramine-T, methyl vinyl ketone and isopropyl methyl ketone.

At constant ionic strength, an increase in alkali concentration increases the pseudo-first order rate constant linearly, thus showing strong dependence of oxidation of methyl vinyl ketone and isopropyl ketone on alkali concentration. The plots of $\log k_1'$ against $\log [\mathrm{O\bar{H}}]$ gave straight lines (Fig. 1) with slopes 0.96 (methyl vinyl ketone) and 1.00 (isopropyl methyl ketone) establishing first-order dependence of both oxidation processes on hydroxide ion concentration.

Ionic strength variation (affected by KCl) in both cases has an insignificant effect (Table 1) on the rate constants, while addition of methanol has negative effect (Table 2). p-Toluenesulphonamide, the reduction product of chloramine-T, however, had no effect on the reaction rates.

Average values of energy of activation (ΔE) and entropy of activation (ΔS) were calculated from rate study measurements carried out at four temperatures (30–45°) and were found to be 11.05 K.cal/mole and −27.77 e.u. respectively (methyl vinyl ketone) and

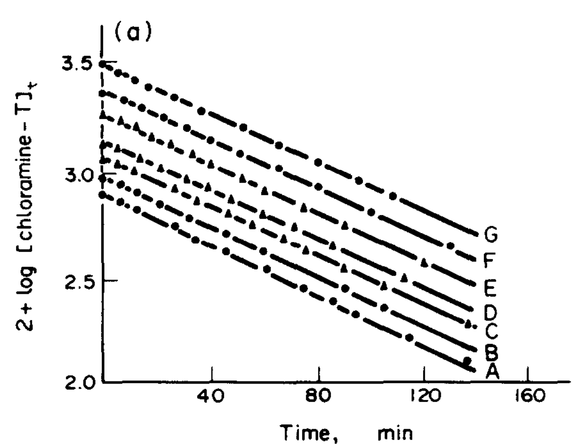


Fig. 1(a). First-order rate plots at 35°C, (isopropyl methyl ketone) = 4.00×10^{-2} M, $\mu = 0.3$ M, (NaOH) = 0.2 M and (chloramine-T) = 0.84, 1.00, 1.25, 1.44, 2.00, 2.50 and 3.34×10^{-3} M in A, B, C, D, E, F and G respectively.

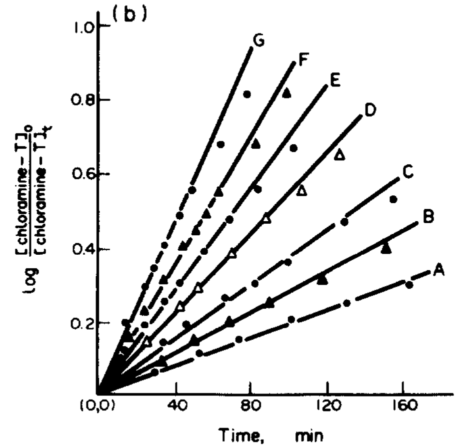


Fig. 1(b). First-order rate plots at 35°C (chloramine-T) = 2.10×10^{-3} M, (NaOH) = 4.00×10^{-2} M, $\mu = 0.2$ M and (vinyl methyl ketone) = 1.00, 1.32, 1.67, 2.50, 3.32, 4.00 and 5.00×10^{-2} M A, B, C, D, E, F and G respectively.

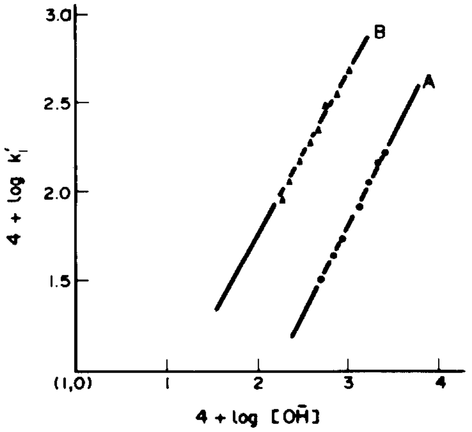
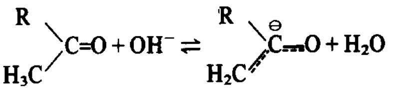


Fig. 2. Plot of log k_1' against log (OH^-) at 35°, A, (chloramine-T) = 2.00×10^{-3} M, $\mu = 0.3$ M, (isopropyl methyl ketone) = 4.00×10^{-2} M; B, (chloramine-T) = 2.00×10^{-3} M, $\mu = 0.2$ M (vinyl methyl ketone) = 4.00×10^{-2} M.

8.50 K cal/mole and −40.81 e.u. respectively (isopropyl methyl ketone).

Base catalysed oxidation is only consistent with the enolate anion mechanism.



$$\mathrm{R(H_3C)C{=}O + OH^- \rightleftharpoons R(H_2C{\cdots})\overset{\ominus}{C}{\cdots}O + H_2O} \qquad (3)$$

where R = $-CH{=}CH_2$ or $-CH(CH_3)_2$.

The oxidising property of chloramine-T is due to its four oxidising species, viz. chloramine-T itself, p-toluenesulphochloramide, dichloramine-T and hypochlorite ion. In an acidic medium, dichloramine-T predominates over the rest of the species and any amount of it formed is converted to p-toluenesulphochloramide and hypochlorite ion. Thus in our case, possibility of dichloramine-T acting as oxidising species is ruled out.

In aqueous alkaline solutions, chloramine-T (CAT) hydrolyses[13] to p-toluenesulphochloroamide (CAT′) and p-toluenesulphonamide (TSA) as follows:

The relative amounts of CAT′ and ClO⁻ depend upon the pH of the solution.[14] it is, therefore, clear that one of the three oxidising species of CAT, viz. CAT itself, CAT′ and ClO⁻ ion may react with enolic anion of the ketones used here in the slow and rate determining step. If ClO⁻ is assumed to be the main oxidising species, the reactions would involve an interaction between two similarly charged ions and thus would correspond to a positive ionic strength effect which is contrary to our experimental observations. Thus the possibility of ClO⁻ acting as main oxidising species is completely ruled out.

The insignificant effect of ionic strength on the rate constant in both reactions clearly indicates the involvement of at least one neutral molecule in the rate determining step. Interaction of a neutral molecule with a negatively charged ion is, further, indicated by observed positive dielectric constant effect. These observations indicate that enolic anion of the ketones will interact with neutral molecule viz. either CAT or CAT′.[15] The rate law deduced by assuming CAT′ as the oxidising

$$\underset{}{\mathrm{CH_3C_6H_4SO_2N{\cdot}NaCl + H_2O}} \rightleftharpoons \underset{\mathrm{CAT'}}{\mathrm{CH_3C_6H_4SO_2N{\cdot}HCl}} + \mathrm{NaOH} \qquad (4)$$

$$\mathrm{CH_3C_6H_4SO_2N{\cdot}HCl + NaOH} \rightleftharpoons \underset{\mathrm{TSA}}{\mathrm{CH_3C_6H_4SO_2NH_2}} + \mathrm{NaClO.} \qquad (5)$$

Table 1. Effect of ionic strength on the reaction rate at 35°

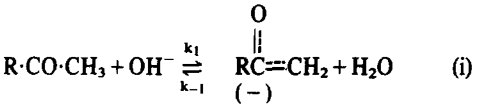
[Chloramine-T] = 2.00×10^{-3}M		[Chloramine-T] = 2.10×10^{-3}M	
[Isopropyl methyl ketone] = 4.00×10^{-2}M		[Vinyl methyl ketone] = 4.00×10^{-2}M	
[NaOH] = 8.3×10^{-2}M		[NaOH] = 2.00×10^{-2}	
μ*(M)	$k'_1 \times 10^2 \mathrm{min}^{-1}$	μ*(M)	$k'_1 \times 10^2 \mathrm{min}^{-1}$
0.10	0.50	0.10	1.08
0.15	0.48	0.15	1.05
0.20	0.47	0.20	1.18
0.25	0.50	0.25	1.10
0.30	0.52	0.30	1.30
0.35	0.55	0.35	1.20
0.40	0.55	0.40	1.32

μ* Ionic strength adjusted by addition of KCl solution.

Table 2. Effect of solvent composition on the reaction rate

[Chloramine-T] = 2.00 x 10^{-3}M [Isopropyl methyl ketone] =4.00x10^{-2}M [NaOH] = 2.50 x 10^{-1}M μ = 0.3M and Temp. 40°		[Chloramine-T]= 2.10 x 10^{-3}M [Vinylmethyl ketone]= 4.00x10^{-2}M [NaOH] = 4.00 x 10^{-2}M μ=0.2M and Temp. 35°	
MeOH %	k'_1x10^3min^{-1}	MeOH %	k'_1 x 10^3min^{-1}
0	16.33	0	22.90
5	14.34	10	21.80
10	11.36	15	17.50
15	9.23	20	16.10
20	7.41	25	14.50
25	6.17	30	12.12

species predicts a zero-order dependence in hydroxide ion concentration which is contrary to our experimental observations. This rules out the possibility of the involvement of CAT' in the rate controlling step. Now, the only alternative left is involvement of CAT itself as possible oxidising species in the rate determining step. The following mechanism for oxidation of both ketones viz. methyl vinyl ketone and isopropyl methyl ketone may thus be schematically represented



$$R{\cdot}CO{\cdot}CH_3 + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{(-)}{R\overset{\overset{O}{\|}}{C}{=}CH_2} + H_2O \quad (i)$$

(E) enolate anion ($\bar{E}$)

where R = -CH=CH$_2$ or -CH(CH$_3$)$_2$

$$\bar{E} + CH_3C_6H_4SO_2NNaCl \underset{slow}{\overset{k_2}{\rightarrow}} \text{Intermediate (Y)} \quad (ii)$$

$$Y + CH_3C_6H_4SO_2NNaCl \underset{fast}{\overset{k_3}{\rightarrow}} \text{Products.} \quad (iii)$$

By applying the steady-state approximation to enolate anion ($\bar{E}$) and intermediate (Y) and making the assumption that $k_{-1} \gg k_2[CH_3C_6H_4SO_2N\,NaCl]$, the following rate law is obtained.

$$-\frac{d}{dt}[CH_3C_6H_4SO_2NNaCl] = \frac{2k_1k_2}{k_{-1}H_2O}[CH_3C_6H_4SO_2NNaCl][E][OH^-] \quad (6)$$

where E = methyl vinyl ketone or isopropyl methyl ketone.

The above derived rate eqn (6) shows first order dependence in chloramine-T, hydroxide ion and ketones. This also confirms that chloramine-T itself is undoubtedly oxidising species. The results indicate that the transition state contains chloramine-T, hydroxide ion and the ketone.

REFERENCES

[1] K. Weber and F. Valic, *Z. Phys. Chem.* **238**, 353 (1968).

[2] T. Hoiguchi and A. Hussain, *J. Chem. Soc.* **B**, 549 (1967).

[3] S. P. Mushran, M. C. Agrawal and B. Prasad, *Ibid.* **B**, 1712 (1971).

[4] S. P. Mushran and M. C. Agrawal, *J. Phys. Chem.* **75**, 838 (1971); *J. Chem. Soc. Perkin* **II**, 762 (1973).

[5] S. P. Mushran, M. C. Agrawal and R. Sanehi, *Ind. J. Chem.* **12**, 311 (1974).

[6] S. P. Mushran, R. M. Mehrotra and A. K. Bose, *Ibid.* **12**, 311 (1974).

[7] D. S. Mahadevappa and H. M. K. Naidu, *Austr. J. Chem.* **27**, 1203 (1974).

[8] S. P. Mushran, R. Sanehi and A. K. Bose, *Acta Chim. Acad. Sci. Hungaricae* **84**, 135 (1975).

[9] A. Kumar, A. K. Bose and S. P. Mushran, *Monatsh. Chem.* **106**, 863 (1975).

[10] Bharat Singh, P. K. Saxena and B. Krishna, Unpublished work, Chem. Dept., Allahabad University, Allahabad, India.

[11] Bharat Singh, P. K. Saxena, (Km.) M. Richards and B. Krishna, *Z. Phys. Chem.* **259**, 801 (1978).

[12] F. Feigl, *Spot Tests in Organic Analysis*, p. 441. Elsevier, Amsterdam, New York (1965).

[13] R. Dietzel and K. Taufel, *Apoth. Ztg.* **44**, 989 (1929).

[14] J. C. Morris, J. A. Salazar and M. A. Wineman, *J. Am. Chem. Soc.* **70**, 2038 (1948).

[15] P. S. Radhakrishnamurthy, *Ind. J. Chem.* **19A**, 80 (1979).