April, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1047—1050 (1978) 1047

Kinetics of Oxidation of 4-Hydroxy-4-methyl-2-pentanone by Sodium *N*-Chloro-*p*-toluenesulfonamide

K. V. Uma and S. M. Mayanna
Department of Chemistry, Central College, Bangalore University, Bangalore 560001, India

(Received May 6, 1977)

The kinetics of oxidation of 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol) by sodium *N*-chloro-*p*-toluenesulfonamide (Chloramine-T, RNClNa) in presence of hydrochloric acid (0.05—0.6 M) has been studied at 30 °C. The reaction follows first order kinetics with respect to chloramine-T. The reaction rate depends on the square of the $[H^+]$ and independent of the alcohol concentration. The energy and entropy of activation have been found to be 65.56 kJ mol^{-1} and -73.81 JK^{-1} respectively. The rate of reaction has been affected by the addition of potassium chloride and dioxane to the reaction mixture. A mechanism has been proposed involving diacetone alcohol and H_2OCl^+ formed by the hydrolysis of chloramine-T. Applying steady state condition to RNHCl, a rate expression has been given to account for the observed results. Kinetic data have been used in the analytical estimation of diacetone alcohol in acidic medium.

Sodium *N*-chloro-*p*-toluenesulfonamide (chloramine-T) acts as an oxidising agent in both acidic and alkaline media with two electron change per mole. The oxidative properties of chloramine-T have been recently applied in the analytical estimations of variety of organic compounds in relatively low acidic and basic media.[1-3] Chloramine-T decomposes slightly in concentrated mineral acid solutions.[4] Kinetics of oxidations of α-hydroxy acids,[5] ketones[6] and allyl alcohol[7,8] have been studied. 4-Hydroxy-4-methyl-2-pentanone (diacetone alcohol) as a lacquer solvent finds a number of industrial applications. Kinetics of oxidation of diacetone alcohol by Co^{3+} and H_2O_2 have been reported.[9,10] A review of literature shows that diacetone alcohol can be estimated by brominating agent,[11] colorimetric,[12] gas[13] and column[14] chromatographic techniques. However, these methods are indirect and less accurate. The present paper deals with the kinetics of oxidation and analytical estimation of diacetone alcohol by chloramine-T.

Experimental

Chloramine-T (E. Merck) was purified according to the method of Morris *et al.*[15] Diacetone alcohol (BDH, bp 164 °C, $\eta_D-1.4300$) and all acids (AR) except perchloric acid were distilled and used. Dioxane (BDH) was purified by Riche and Milas' method,[16] potassium chloride was of analytical grade. All solutions were prepared from freshly distilled water. KCl–HCl buffers were used for the pH range 1—2. An approximately decinormal solution of chloramine-T was prepared and standardized by iodometric method.[17] The required quantity of the alcohol was accurately weighed and dissolved in the proper solvent to give nearly 0.2 M solution. Several samples were made up for each run in iodine flasks, from stock solutions prepared at reaction temperature (30± 0.1 °C). Reactions were timed from the addition of diacetone alcohol. Samples were analyzed for chloramine-T by iodometric method. The reaction was studied up to 90%. Duplicate runs agreed with each other within 3%.

Stoichiometry

Reaction mixture containing excess chloramine-T over diacetone alcohol were kept at 30 °C in presence of 0.2 M HCl for 24 h. Estimation of the unchanged chloramine-T showed that one mole of diacetone alcohol consumed one mole of chloramine-T.

$$(CH_3)_2C(OH)CH_2COCH_3+RNClNa+H_2O \longrightarrow CH_3COCH_2COCH_3+CH_3OH+RNH_2+NaCl$$

2,4-Pentanedione and methanol in the reaction mixture were identified by dimethyldiacetylpyridinediol and formaldehyde tests[18] respectively.

Results

Kinetic Data. Oxidation of diacetone alcohol (DAA) by chloramine-T (CAT) was carried out at different initial concentrations of the reactants in presence of 0.2 M HCl at 30 °C. In presence of excess of alcohol, plot of $\log[CAT]_0/[CAT]_t$ against time was

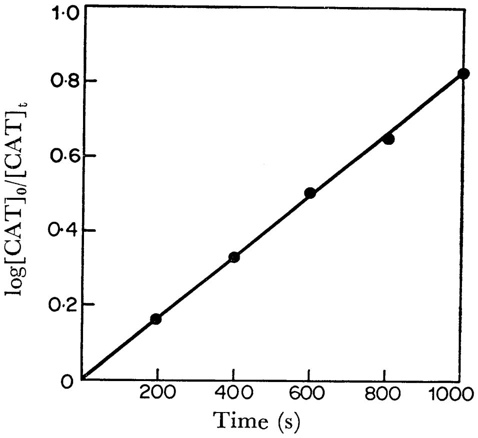


Fig. 1. Variation of the concentration of chloramine-T with time.

Table 1. Kinetics of oxidation of 4-hydroxy-4-methyl-2-pentanone by sodium *N*-chloro-*p*-toluenesulfonamide
Temp 30±0.1 °C. $[H^+]=0.2$ M.

$[CAT]_0$	$[DAA]_0$	$10^3 K$ (s^{-1})	$[CAT]_0$	$[DAA]_0$	$10^3 K$ (s^{-1})
0.005	0.100	6.70	0.0025	0.100	6.78
0.005	0.200	6.73	0.0050	0.100	6.73
0.005	0.300	6.74	0.0065	0.100	6.75
0.005	0.500	6.71	0.0050[a]	0.100	6.70

a) In presence of excess of *p*-toluenesulfonamide.

Table 2. Effect of $[H^+]$ on the reaction rates
$[CAT]_0=0.005M$, $[DAA]_0=0.1M$
Temp$=30\pm0.1$ °C.

$[H^+]$	0.05	0.1	0.2	0.3	0.4	0.5	0.6
$10^2 K$ (s^{-1})	0.0387	0.153	0.675	1.380	2.530	3.915	5.555
$\frac{10\,K}{[H^+]^2}$	1.550	1.530	1.543	1.588	1.581	1.565	1.543

linear (Fig. 1) passing through the origin showing that the order with respect to chloramine-T was unity. The first order rate constant was found to be independent of [DAA] (Table 1).

The kinetics of oxidation was studied at different concentrations of HCl (0.05—0.6 M). The rate constant increased with increase in $[H^+]$ (Table 2). A plot of log *k vs.* log $[H^+]$ gave a straight line with slope of two.

Table 3. Effect of temperature on the reaction rate
$[CAT]_0=0.005M$, $[DAA]_0=0.10M$,
$[H^+]=0.2M$

Temperature (K)	293	303	313	323
$10K$ (s^{-1})	2.787×10^{-3}	6.75×10^{-3}	1.635×10^{-2}	3.846×10^{-2}

Oxidation was also carried out at different temperatures (20—50 °C) in presence of 0.2 M HCl. From the corresponding data (Table 3) at 20, 30, 40, and 50 °C, the Arrhenius activation energy and entropy of activation were found to be 65.26 kJ mol^{-1} and -73.81 J K^{-1} respectively.

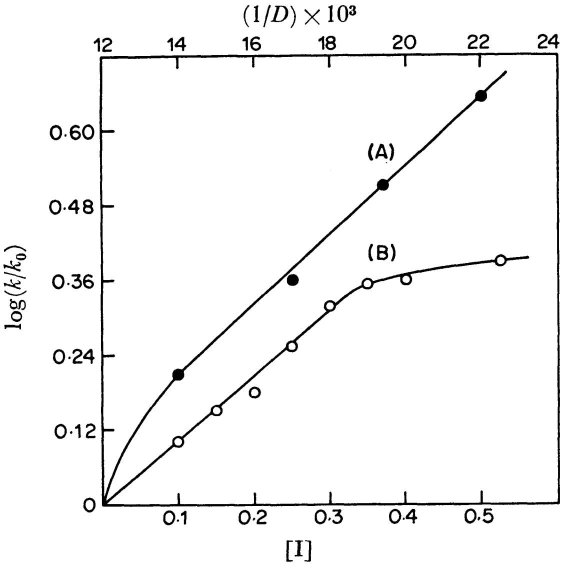


Fig. 2. Variation of rate constant with deilectric constant of the medium (B) and concentration of potassium chloride (A).

In presence of 0.2 M HCl, the effect of potassium chloride on the reaction rate at 30 °C up to ionic strength (*I*) 0.5 was investigated, the results of which are shown in Fig. 2. The line A shows the variation of log k/k_0 (k and k_0 are the rate constants with and without salt) with *I* for potassium chloride. The reaction rate was accelarated by the addition of potassium chloride.

Solvent effect on the reaction rate was studied. A series of kinetic runs were made in water–dioxane mixture of various compositions (10—40% dioxane by volume) at 30 °C in presence of 0.2 M HCl. Even in the mixture of dioxane and water, the reaction follows first order kinetics. The line B (Fig. 2) gives the variation of log k/k_0 (k and k_0 are the constants with and without dioxane respectively) with $1/D$ (D, the dielectric constant of the medium). The rate constant increased on increasing the amount of dioxane in the mixture. However, the variation is linear up to 30% dioxane in the mixture.

Analytical Data. *Preliminary Studies*: Known amounts of diacetone alcohol solution in the proper solvent were added to a known excessive volume (10—20%) of chloramine-T in an iodine flask placed in a thermostat at 30 °C. The reaction mixture was set aside for various intervals of time with occasional shaking. Then the excess of chloramine-T was determined by back titration.

Table 4 gives a typical set of results for the extent of oxidation of diacetone alcohol in 30 min at 30 °C by an excess of chloramine-T. It is seen that oxidation is slow in media other than hydrochloric acid. The rate of oxidation increases gradually as the concentra-

Table 4. Extent of oxidation of 4-hydroxy-4-methyl-2-pentanone by sodium *N*-chloro-*p*-toluenesulfonamide

Medium	CAT used (mol) / Alcohol taken (mol)	Medium	CAT used (mol) / Alcohol taken (mol)
pH 2.0[a]	0.164	0.5N HCl	0.202
pH 1.0[a]	0.170	1.0N HCl	0.216
0.2N HCl	0.185	1.0N CH_3COOH	0.124
0.2N H_2SO_4	0.160	2.0N HCl	0.230
0.2N $HClO_4$	0.170	2.5N HCl	0.320
0.3N HCl	0.185	3.0N HCl	0.504
0.4N HCl	0.188	4.0N HCl	0.765

a) KCl–HCl buffer. Alcohol taken, 5 mmol; CAT taken, 10 mmol; Time, 30 min; Temp, 30 °C.

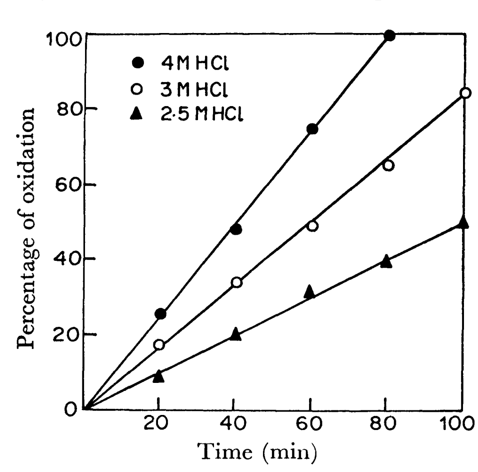


Fig. 3. Percentage of oxidation of diacetone alcohol by chloramine-T at 30 °C, at different time intervals with various concentrations of hydrochloric acid.

tion of hydrochloric acid increases, but the increase become rapid at or above 4 N acid. The extent of oxidation above 2 N hydrochloric acid is a function of time interval. Figure 3 shows the variation of extent of oxidation of diacetone alcohol with time at different concentrations of hydrochloric acid.

Recommended Procedure. Prepare an aqueous solution of diacetone alcohol (0.1 M). Add an aliquot containing 0.1—2.5 mM to a measured excessive (10—20%) volume of 0.1 N chloramine-T containing enough hydrochloric acid to make the overall acid concentration 4 N. Shake the mixture and keep it in a thermostat at 30 °C for 2 h. Add 20 ml of 10% potassium iodide solution and 10 ml of 2 N sulfuric acid and titrate with 0.1 N sodium thiosulfate. Run a blank with chloramine-T solution containing 4 N acid keeping for 2 h. The amount (mgs) of diacetone alcohol in the experimental solution is given by

$$X = 58Y(V_1 - V_2),$$

where Y is the normality of the thiosulfate, V_1 is the blank titration and V_2 the volume of thiosulfate used to titrate the excess of chloramine-T after oxidation of diacetone alcohol.

Detailed study of diacetone alcohol has brought out the following facts; (i) Foreign ions such as NO_3^-, ClO_4^-, and SO_4^{2-} have no influence up to ionic strength 0.25. (ii) Potassium chloride has slight effect on the rate of oxidation. (iii) The stoichiometry is unaffected by a reversal of the order of addition of oxidant and diacetone alcohol. (iv) The reaction rate is slightly retarded in sulfuric acid and perchloric acid (*cf.* Table 4).

Some typical results of analysis of diacetone alcohol in aqueous solutions are given in Table 5. The values obtained are accurate within 1.5%.

Table 5. ESTIMATION OF 4-HYDROXY-4-METHYL-2-PENTANONE BY SODIUM *N*-CHLORO-*p*-TOLUENESULFONAMIDE

Alcohol taken (mg)	Alcohol found (mg)	Alcohol taken (mg)	Alcohol found (mg)
2.90	2.94	26.10	26.23
5.80	5.87	31.90	32.14
8.70	8.78	37.70	37.93
11.60	11.71	41.70	42.12
14.50	14.64	47.70	48.05
20.30	20.46	53.50	53.76

Discussion

Chloramine-T in aqueous solution undergoes dissociation[19]

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

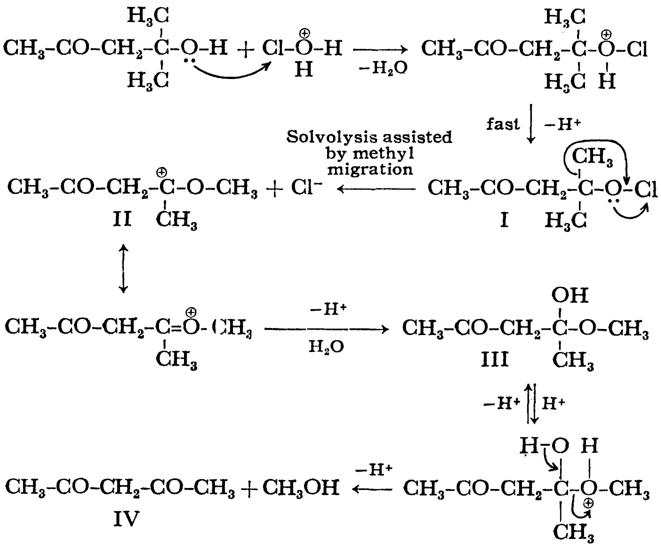
$RNCl^-$ in acidic solution gives chloronium ion (Cl^+) which reacts with water to give H_2OCl^+. The following consecutive steps have been proposed[8] for the formation of H_2OCl^+ from $RNCl^-$:

$$\mathrm{H^+} + \mathrm{RNCl^-} \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \mathrm{RNHCl} \quad \text{slow} \qquad (2)$$

$$\mathrm{RNHCl} + \mathrm{H^+} \xrightarrow{k_2} \mathrm{RNH_2} + \mathrm{Cl^+} \quad \text{still slower(rds)} \qquad (3)$$

$$\mathrm{Cl^+} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{H_2OCl^+} \quad \text{fast} \qquad (4)$$

H_2OCl^+ attacks diacetone alcohol in a fast step as follows:



The attack of the electrophile Cl^+ on an unshared pair of electros on the oxygen of the alcohol and the elimination of H^+ produces the alkyl hypochlorite (I) in a fast step. The weak O–Cl bond may be expected to break readily by solvolytic attack by water is assisted by methyl migration to produce a stabilized carbonium ion. The attack by water produces a hemiacetal (III) which is readily hydrolysed to the diketone (VI). The key step of methyl migration to electron deficient oxygen is similar to Baeyer-Villiger oxidation of ketones.[20] In this case also, formation of a discrete oxene is unlikely and the departure of Cl^- ion and migration of methyl group is concerted.

Applying steady state conditions for RNHCl, one could derive the rate equation

$$\frac{-\mathrm{d[CAT]}}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{CAT}][\mathrm{H^+}]^2}{k_1+k_2[\mathrm{H^+}]},$$

when $k_{-1} \gg k_2[H^+]$ the above equation reduces to

$$\frac{-\mathrm{d[CAT]}}{\mathrm{d}t} = \frac{k_1k_3}{k_{-1}}[\mathrm{CAT}][\mathrm{H^+}]^2.$$

This is in agreement with the experimental results. The increase of rate constant by the presence of potassium chloride and in dioxane-water mixture (Fig. 2) is in support of the rate determining step involving an ion and a neutral molecule[21,22] step (3).

Negative entropy of activation perhaps indicate the complex nature of the oxidation of diacetone alcohol by chloramine-T.

The authors are grateful to Dr. D. S. Mahadevappa, Professor of Chemistry, University of Mysore and Dr. V. R. Dani, of our department, for helpful discussions. One of us (K.V.U.) thanks Professor M. Shadaksharaswamy, Head of the Dept. of Chemistry, Central College, Bangalore University, Bangalore and Professor

P. S. Ambikadevi, Principal, Maharanis Science College, Bangalore, for their kind encouragement.

References

1) A. Berka, J. Vulterin, and J. Zyka, "Newer Redox Titrants," Pergamon press, New York (1965), p. 37.

2) G. Aravamudan and D. Venkappayya, *Talanta*, **15**, 704 (1968).

3) D. S. Mahadevappa and N. M. Madegowda, *Talanta*, **22**, 771 (1975).

4) V. R. S. Rao, D. Venkappayya, and G. Aravamudan, *Talanta*, **17**, 772 (1970).

5) S. P. Mushran, M. C. Agarwal, and B. Prasan, *J. Chem. Soc., B*, **1971**, 1712.

6) S. P. Mushran, R. Sanahi, and M. C. Agarwal., *Z. Naturforsch, Teil B*, **27**, 1161 (1972).

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

8) D. S. Mahadevappa and H. M. K. Naidu, *Aust. J. Chem.*, **28**, 899 (1975).

9) A. Meenakshi and M. Santappa, *Indian J. Chem.*, **8**, 467 (1970).

10) Devtschi Akademie der Wissenschaften zu Berlin, Brit. Pat. 937.165, 18 September (1963).

11) N. G. Polyankie, V. S. Markavich, and N. E. Shitvel, *Zh. Anal. Khim.*, **19**, 1132 (1964).

12) T. Bota, D. Sireteanu, M. Panaitesu, and J. Herscovici, *Rev. Chim.*, **16**, 337 (1965).

13) P. Fore sara and H. P. Dupay, *J. Gas Chromatogr.*, **6**, 522 (1968).

14) Holybecher, Zavis, and Praze, *Anal. Chem.*, **5**, 45 (1969),

15) J. C. Morris, J. A. Salazan, and M. A. Wineman, *J. Am. Chem. Soc.*, **70**, 2036 (1948).

16) Weissberger, "Techniques of Organic Chemistry," Vol. VII, Interscience Publishers, Inc. New York (1955), p. 372.

17) K. Bottger and W. Bottger, *Z. Anal. Chem.*, **70**, 225 (1927).

18) F. Fiegal, "Spot Tests in Organic analysis," VII, Elsevier, New York (1966), pp. 413, 446.

19) E. Bishop and V. F. Jennings, *Talanta*, **1**, 197 (1958).

20) C. M. Hassal in "Organic Reactions," ed by Adams *et al.* Vol. IX, John Wiley and Sons, Inc., New York (1957), p. 73.

21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley Eastern PVT Ltd., New Delhi (1970), p. 152.

22) K. J. Laidler and Eyring, *Ann. N, Y. Acad Sci.*, **39**, 303 (1940).