Asian Journal of Chemistry Vol. 4, No. 3 (1992), 438–443

Kinetics and Mechanism of Oxidation of *Iso*propanol by Chloramine-T

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Kinetic studies on the oxidation of *iso*propanol have been made using chloramine-T as an oxidising agent in acidic medium. The reaction showed first order dependence with respect to chloramine-T and hydrogen ion concentration and the rate was found to be independent of the *iso*propanol concentration. No effect of ionic strength was evident. A plausible mechanism consistent with the experimental results has been proposed. The various Arrhenius parameters have also been computed.

INTRODUCTION

The study of oxidation mechanism of alcohols has been a subject of considerable interest since long[1–5]. The chloramine-T/toluenesulphonamide system has a very high value of redox potential[6] both in acidic (1.139 V at pH = 0.65) and alkaline media (0.499 at pH = 12) and this powerful oxidising agent has been widely used for the estimation of several organic and inorganic compounds[7]. Work on kinetics and mechanism of the oxidation processes involving chloramine-T was reported by several workers[8–10]. Investigations on kinetics and mechanism of chloraminometric processes involving various reducing substrates both in acidic and alkaline media have also been made[11–21].

The work described here relates to the kinetic studies on the oxidation of *iso*propanol by chloramine-T in acidic medium and a suitable mechanism of reaction has been proposed on the basis of results obtained.

EXPERIMENTAL

Aqueous solution of chloramine-T was prepared using E. Merck, proanalysis sample of the reagent which was stored in dark bottles to avoid any photochemical decomposition. Aqueous solution of E. Merck grade sample of *iso*propanol was used throughout the investigations. All other chemicals used were of analytical reagent grade and their solutions were prepared in double-distilled water. Stills were all made up of corning glass and the reactions were carried out in reaction bottles darkened black from outside. Kinetics of the oxidation of *iso*propanol was monitored by estimating chloramine-T, using iodometric method in a measured aliquot of the reaction mixture at various time intervals.

Stoichiometry

The stoichiometry of the reaction mixture was ascertained by taking a known excess of chloramine-T over *iso*propanol to interact at pH = 4.0 and at 50°C. The unconsumed chloramine-T was titrated iodometrically and it was noticed that one mole of chloramine-T (CAT) was consumed for each mole of *iso*propanol. The stoichiometry of the reaction may thus be illustrated as follows:

$$CH_3C_6H_4SO_2NCl^- + (CH_3)_2CHOH + H^+ = CH_3C_6H_4SO_2NH_2 + (CH_3)_2CO + HCl \quad (1)$$

Acetone obtained as one of the products in the above reaction was also confirmed by positive spot tests[22].

RESULTS AND DISCUSSION

Kinetics of oxidation of *iso*propanol by chloramine-T was investigated at several initial concentrations of the reactants. The reaction followed a first order dependence in chloramine-T at all concentrations of the reactants. Pseudo first order rate constants (k_1) calculated from the slope of the linear log.time plots, were independent of *iso*propanol concentration (Table 1), establishing a zero order dependence of the reaction rate with respect to the reducing substrate.

TABLE 1

EFFECT OF REACTANTS AT pH = 4.4

10^4 [Chloramine-T]	10^2 [*iso*dropanol]	$k_1 \times 10^5$ sec^{-1} at		
		45°	50°	55°
5.0	2.0	4.30	4.84	6.58
10.0	2.0	4.30	4.84	6.58
15.0	2.0	4.24	4.80	6.38
20.0	2.0	4.15	4.29	6.26
10.0	1.0	4.30	4.84	6.58
10.0	3.0	4.30	4.84	6.58
10.0	4.0	4.30	4.84	6.58

The rate of oxidation of *iso*propanol by chloramine-T was highly susceptible to the change in the pH of the reaction mixture. Kinetic investigations were carried out at different pH values and the results are being shown here by a linear plot of k_1 *vs* pH (Fig. 1). The slope of the straight line was found to be −1, establishing a first order dependence with respect to hydrogen ion concentration.

The change in ionic strength of the media by addition of $NaClO_4$ (0.1M–0.8M), KCl (0.1M–0.4M) and K_2SO_4 (0.1M–0.4M) showed practically no significant effect on the rate of oxidation.

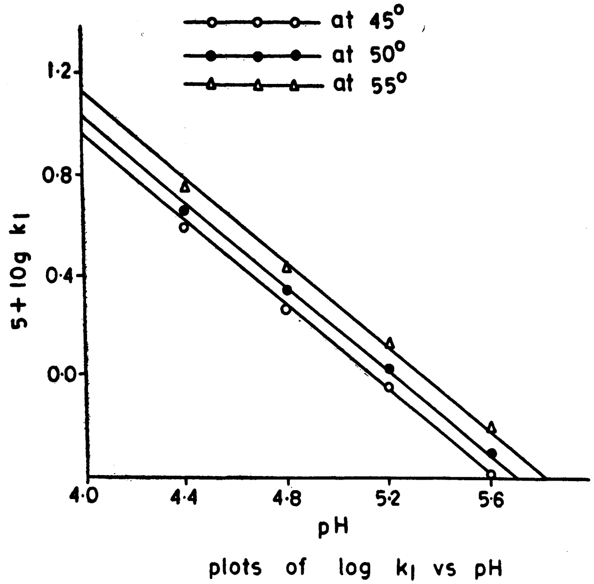

Fig. 1 Plots of log k_1 *vs* pH at 45°, 50° and 55°

The influence of the temperature on the first order rate constants was investigated in the temperature range of 45°–60°. The values of various activation parameters, *viz.* energy of activation (E_{act}), frequency factor (A) and entropy of activation (ΔS) were computed as 10.6 kcal $mole^{-1}$, 1.61×10^7 $mole^{-1}$ sec^{-1} and -26.8 e.u. respectively.

In aqueous media the sodium salt of N-chloro-p-toluene sulphonamide ($CH_3C_6H_4SO_2N.NaCl$) commonly known as chloramine-T (CAT), behave like a strong electrolyte and its ionization may be represented as follows[23].

$$\underset{\text{CAT}}{CH_3C_6H_4SO_2N{\cdot}NaCl} \rightleftharpoons \underset{\text{CAT}^-}{CH_3C_6H_4SO_2NCl^-} + Na^+ \text{ (fast)} \qquad (2)$$

In acidic medium, the anion of chloramine-T (CAT^-) readily accepts a proton and forms the free acid, N-chloro-p-toluenesulphonamide[11,23] (CAT′):

$$CH_3C_6H_4SO_2NCl^- + H^+ \rightleftharpoons CH_3C_6H_4SO_2NHCl \text{ (fast)} \qquad (3)$$

N-Chloro-p-toluenesulphonamide (CAT′) on hydrolysis gives p-toluenesulphonamide (TSA) and hypochlorous acid :

$$\underset{\text{(CAT}')}{CH_3C_6H_4SO_2NHCl} + H_2O \rightleftharpoons \underset{\text{(TSA)}}{CH_3C_6H_4SO_2NH_2} + HOCl \text{ (slow)} \qquad (4)$$

Thus an acidic solution of chloramine-T, as in the present study, contains CAT^-, CAT′ and HOCl and any one of these species may react with *iso*propanol to give the products. CAT^- is easily protonated[11, 23] in acidic media to yield CAT′, which hydrolyses[23–25] in a slow step to give HOCl. The possibility of anion of chloramine-T, CAT^-, reacting with the substrate is, therefore, ruled out. Soper *et al.*[26,27] showed that the direct interaction of N-chloro-p-toluenesulphonamide, CAT′, with the substrates could be slow, while HOCl formed by the hydrolysis of CAT′ would attack at a faster rate. It is, therefore, reasonable to neglect the direct interaction of CAT′ with *iso*propanol because of the faster rate of interaction of HOCl with the substrate. The first order dependence of the reaction rate on chloramine-T and hydrogen ion concentration undoubtedly suggests that the slowest step would be the hydrolysis of CAT′ producing HOCl (step 4) and since the rate is independent of *iso*propanol concentration, the disappearance of *iso*propanol(S) takes place through the fast reaction with hypochlorous acid.

On the basis of the above facts and the observed kinetics, the mechanism of the oxidation of *iso*propanol may be represented as follows:

$$\underset{(CAT^-)}{CH_3C_6H_4SO_2NCl^-} + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(CAT')}{CH_3C_6H_4SO_2NHCl} \quad \text{(fast)} \tag{5}$$

$$\underset{(CAT)}{CH_3C_6H_4SO_2NHCl} + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(TSA)}{CH_3C_6H_4SO_2NH_2} + HOCl \text{ (slowest the R.D.)} \tag{6}$$

$$(CH_3)_2CHOH + HOCl \xrightarrow{k_4} (CH_3)_2CO + H_2O + HCl \quad \text{(fast)} \tag{7}$$

After applying steady state treatment with respect to CAT′ and HOCl, the following rate law equation is obtained:

$$-\frac{d}{dt}[CAT^-] = [CAT^-][H^+]\left[k_2 - \frac{k_2k_{-2}\{k_{-3}[TSA] + k_4[S]\}}{k_{-2}k_{-3}[TSA] + k_3[S]\{k_{-2} + k_3[H_2O]\}}\right] \tag{8}$$

In view of the justifiable approximation, $k_4[S]\{k_{-2} + k_3[H_2O]\} \gg k_{-2}k_{-3}[TSA]$, the above equation may be simplified to the following form:

$$-\frac{d}{dt}[CAT^-] = \frac{k_2k_3[H_2O]}{k_{-2} + k_3[H_2O]}[CAT^-][H^+] \tag{9}$$

In acidic medium, CAT^- may be taken as CAT, whereby equation 9 may be transformed to:

$$-\frac{d}{dt}[CAT] = k[CAT][H^+] \tag{10}$$

where $$k = \frac{k_2k_3[H_2O]}{k_{-2} + k_3[H_2O]} = \text{constant}$$

The derived rate law equation satisfactorily abides by the observed experimental results.

The slight decrease in pseudo first order rate constants with the increasing concentration of the oxidant (Table 1) may be satisfactorily explained on the basis of (*i*) the well-known retarding action of p-toluenesulphonamide on the reaction rates[17,28,29] and (*ii*) the deactivation[30] of the oxidant by chlorate ions produced in a side reaction[11] (steps 11 and 12):

$$CH_3C_6H_4SO_2NCl^- + H_2O \rightleftharpoons CH_3C_6H_4SO_2NH_2 + ClO^- \qquad (11)$$

$$3ClO^- \rightleftharpoons ClO_3 + 2Cl^- \qquad (12)$$

As such acetone has been found out to be the end product of the reaction. The above mechanism evidently shows a two electron transfer resulting in the conversion of : CH(OH) to : CO which is in agreement with the observation of Waters and coworkers[31]. The rate determining step as proposed in the above mechanism involves neutral molecules, a fact which is supported experimentally by the observed no effect of change in ionic strength on the reaction rate.

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[*Received*: 20 August 1990; *Accepted*: 1 March 1991) AJC—295

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June, 21-26, 1992

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