Kinetics and Mechanism of Oxidation of Diethyl Ether by Chloramine-T in Acidic Medium

Y. I. HASSAN* and N. H. M. SAEED

Department of Chemistry
College of Education, University of Mosul, Iraq
youhassan51@yahoo.com

Received 7 July 2011; Accepted 20 September 2011

Abstract: The kinetics of oxidation of diethyl ether (DE) with sodium N-chloro-p-toluenesulphonamide (CAT) in hydrochloric acid solution has been studied at (313°K). The reaction rate shows a first order dependence on [CAT] and fractional order dependence on each [DE] and [H⁺]. The variation of ionic strength of the medium has no significant effect on the reaction rate, addition of p-toluenesulphonamide (p-TSA) affects the reaction rate marginally; the rate increased with decreasing dielectric constant of the medium, the stoichiometry of the reaction was found to be 1:2 and oxidation products were identified. A Michaelis – Menten type mechanism has been suggested to explain the results. The equilibrium and the decomposition constants of CAT – diethyl ether complex have been evaluated. Thermodynamic parameters were computed by studying reaction at temperatures range (308 – 323°K) for the rate limiting step and for the observed first order constants by the linear Arrhenius plot. The mechanism proposed and the derived rate law are consistent with observed kinetics.

Keywords: Oxidation kinetic, Diethyl ether, Chloramine-T, Acidic medium.

Introduction

The versatile nature of aromatic sulphonyl haloamines is due to their ability to act as sources of halonium cations, hypohalite species and nitrogen anion which act as both bases and nucleophiles. Sodium-N-chloro-P-toluenesulphonamide (p-CH₃-C₆H₄SO₂NCINa.3H₂O), well known as chloramine-T (CAT, R⁺NCINa), is a very important member of this class of compounds and has received a considerable attention as an oxidizing agent for a wide range of functional groups in both acidic and alkaline media. Generally, Chloramine-T undergoes a two-electrons change in its reactions, the products being p-toluenesulphonamide (p-TSA) and sodium chloride. The redox potential of CAT/RNH₂ is pH dependent and decreases with an increase in pH dependent and decreases with an increase in the pH of the medium, having the values of 1.14 at pH 0.65 and 0.5 at pH 12^{1,2}. Depending on the pH of the medium CAT

furnishes different types of reactive species in solution, such as N-chloro-p-toluenesulphonamide (R'NHCl , monochloramine-T, where $\text{R}=\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2$), dichloramine-T (R'NCl_2), HOCl and possibly $\text{H}_2\text{O}^+\text{Cl}$ and RNH_2^+Cl in acid solution and R'NCl^- and OCl^- in alkaline medium. Free chlorine has also been detected in medium in the presence of chloride ion³. Although this reagent has been widely utilized for the quantitative determination of a large number of inorganic and organic compounds in solution^{4,5}, only a few kinetic studies have been carried out. Mention may be made about the oxidation of hydrogen peroxide⁶, P-cresols^{7,8}, phenols⁹, aldehyde¹⁰, ketones¹¹, aldoses^{12,13}, primary¹⁴ and secondary alcohols¹⁵, α -hydroxy acid¹⁶, formic acid¹⁷, furan-2-carboxic acid¹⁸, amino acid^{19,20}, aniline²¹, toluene²², acetanilide²³, catecholamines²⁴, sulphoxides^{25,26}, cyanide²⁷ and thiocyanate²⁸ by CAT.

Diethyl ether is widely used as a solvent, a reaction medium and to a very low extent as reactant. It can be oxidized to acetic acid with sodium bromate²⁹. The present work is an attempt to find out the nature of reacting species and to explore the mechanistic pathway involved in the oxidation of diethyl ether, since, such study has not previously been (fully) explored.

Experimental

Diethyl ethers (fluka) of spectrophotoscopic grade used as received. Chloramine-T was prepared as reported in the literature⁽³⁰⁾ and purified by the method of Morris *et al*³¹. An aqueous solution of CAT was standardized by iodometric method and preserved in brown bottles to prevent its photochemical deterioration. All other reagents were of Analar grade and used as supplied. The ionic strength of the system was kept at a high value by using sodium perchlorate.

Kinetic measurements

The reaction was carried out in glass stoppered pyrex boiling tubes, under pseudo-first order condition by keeping diethyl ether concentration large in comparison with $[\text{CAT}]$. Appropriate amounts of diethyl ether, hydrochloric acid, sodium perchlorate solutions, and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 40°C for the thermal equilibrium. A desired amount of thermostated CAT at the same temperature was rapidly added to the mixture in the boiling tube. The progress of the reaction was followed by withdrawing measured samples at various time intervals to the quenched solution (5% potassium iodide, 2M sulphuric acid) and water in a volumetric acid. The liberated iodine was estimated spectrophotometrically at 353 nm. The course of reaction was studied for at least two half-lives. The pseudo-first order rate constant calculated from the slope of the plots of $[\text{CAT}]$ vs. time, were reproducible within $\pm 3\%$.

Stoichiometry

Varying ratios of CAT to diethyl ether in the presence of 0.2M HCl, ethanol and water were equilibrated at 313K° for 24 h. Estimation of residual oxidant showed that 2 mole of CAT is consumed per mole of diethyl ether. The stoichiometry obtained can be represented as:

p-Toluenesulphonamide among the reaction products was detected by paper chromatography. Benzyl alcohol saturated with water was used as the solvent with 0.5% vaniline in 1% HCl solution in ethanol as spray reagent ($R_F=0.905$)^{32,33}. The acetic

acid produced was identified by conversion to hydro –oximic acid derivative³⁴ which give violate color with ferric ion .or formation of deep-red coloration on reaction with practically neutral or basic solution of ferric chloride³⁵.

Results and Discussion

The kinetics of oxidation of diethyl ether (DE), by chloramine-T was investigated at several initial concentration of reactants in acid medium.

Effect of varying reactant concentration

At constant acid concentration with the substrate in excess ,plots of $\log [\text{CAT}]$ vs. time were linear ($r > 0.9954$), indicating a first –order rate dependence of rate on $[\text{CAT}]$.The pseudo – first-order rate constant (k') are given in Table 1. The values of k' increase with substrate concentration . Plot of $\log k'$ vs. $\log [\text{DE}]$ gives a straight line ($r=0.9931$) with slope of (0.52) indicating a fractional –order dependence on the substrate concentration .

Effect of varying $[\text{H}^+]$

The reaction rate will increase with increase in $[\text{H}^+]$, Table 1. A plot of $\log k'$ vs. $\log [\text{H}^+]$ was linear ($r=0.9960\%$) with slope of (0.53), thus indicating a fractional –order dependence on the $[\text{H}^+]$

*Effect of varying ionic strength on *p*-Toluenesulphonamide*

Variation of ionic strength of the medium (0.125-0.625 M) by adding concentrated solution of sodium perchlorate, has no significant effect on the reaction rate. Also addition of *p*-toluenesulphonamide (*p*-TSA) affected the reaction rate marginally Table 2.

Effect of changing the solvent composition

The first-order rate constant k' was affected by variation of methanol in the methanol-water content or the reaction mixture with $[\text{methanol}]=20,30,40,50,\text{and }60\%$, $10^4 k' \text{ sec}^{-1}$ values were 3.071 ,5.374, 8.061, 9.212 and 13.434 respectively. A plot of $\log k'$ vs. $1/D$ (dielectric constant values were taken from literature³⁵) gives a straight line ($r=0.9884$) with a positive slope.

Effect of temperature

Kinetics were studied at different temperatures (308-323K^o) under varying substrate concentrations (0.48-2.41M). Plots of $\log k'$ versus $\log [\text{DE}]$ were linear ($r>0.9570$) with slopes (0.563,0.528, 0.503,0.503 and 0.511) at 308,313,318,323, and 328 K^o for each of $[\text{DE}]$,respectively ,indicating fractional –order dependence on substrate .The rate constant of the slow step (k_3) was obtained from the intercept of the linear plot $1/k'$ versus $1/[\text{DE}]$. ($r=0.9852$). From the linear Arrhenius plot of $\log k'$ versus $1/T$ ($r=0.9980$) the activation energy and other thermodynamic parameters for composite and reaction for the rate limiting step were evaluated. These values are given in Table 3.

Table 1. Effect of varying of chloramine-T, diethyl ether, and hydrogen ion concentration on the reaction rate.

$10^3[\text{CAT}] \text{ M}$	$[\text{DE}] \text{ M}$	$10[\text{H}^+] \text{ M}$	$10^4 k' \text{ Sec}^{-1}$	$10^4 k^a$
1.50	0.96	3.0	3.071	
1.75	0.96	3.0	3.070	
2.00	0.96	3.0	2.986	
2.25	0.96	3.0	2.986	
2.50	0.96	3.0	3.081	
1.50	0.48	3.0	2.303	3.393
1.50	0.96	3.0	3.071	3.138
1.50	1.45	3.0	3.455	2.839
1.50	1.93	3.0	3.838	3.154
1.50	2.41	3.0	4.606	2.895
1.50	0.96	2	2.508	5.848
1.50	0.96	2.5	2.850	5.909
1.50	0.96	3	3.071	5.785
1.50	0.96	3.5	3.372	5.857
1.50	0.96	4	3.629	5.876

$T = 313 \text{ K}^0$ in (1:5) ethanol: water(v/v), $\mu = 0.5 \text{ M}$. Note. $a = k'/[\text{DE} \text{ or } \text{H}^+]^n$, where n is slope of the plot $\log k' \text{ vs } \log [\text{DE} \text{ or } \text{H}^+]$ k has the units of $\text{L}^h \text{ mol}^n \text{ sec}^{-1}$.

Table 2. Effect of varying ionic strength and [P-TSA] on the reaction rate.

$[\text{NaClO}_4] \text{ M}$	$10^4 k' \text{ Sec}^{-1}$	$10^3 [\text{P-TSA}] \text{ M}$	$10^4 k' \text{ Sec}^{-1}$
0.125	3.071	1.25	3.000
0.250	3.062	2.50	2.851
0.375	3.079	3.75	2.590
0.500	3.075	5.00	2.412
0.625	3.071	6.25	2.374

$T = 313 \text{ K}$, $[\text{DE}] = 0.96 \text{ M}$, $[\text{CAT}] = 0.001 \text{ M}$ in (1:5) ethanol :water (v/v) and $\mu = 0.25 \text{ M}$ while varying $[\text{P-TSA}]$.

Table 3. Effect of temperature on the reaction rate and activation parameters.

Temperature K^0	$10^4 k' \text{ Sec}^{-1}$	$10^4 k_3 \text{ Sec}^{-1}$	Activation Parameters
308	2.00	(6.83)	E_a , KJ mol^{-1} 84.955 (77.22)
313	3.07	(7.89)	$\Delta H^\ddagger$, KJ mol^{-1} 82.309 $\pm$ 0.084 (74.575 $\pm$ 0.083)
318	3.84	(15.15)	$\Delta S^\ddagger$, $\text{JK}^{-1} \text{ mol}^{-1}$ -47.766 $\pm$ 1.844 (-65.156 $\pm$ 178)
323	4.61	(19.60)	$\Delta G^\ddagger$, K J mol^{-1} -197.509 $\pm$ 0.884 (95.305 $\pm$ 1.07)
328	5.20	(43.48)	$10^{-10} \text{ A, sec}^{-1}$ 5.822 $\pm$ 1.275 (0.7205 $\pm$ 0.1301)

$\mu = 0.25 \text{ M}$, (1:5) ethanol :water(v/v), $[\text{CAT}] = 0.001 \text{ M}$, $[\text{DE}] = 0.96 \text{ M}$, $[\text{H}^+] = 0.3 \text{ M}$ and Note. values in parenthesis are the decomposition constant and activation parameters limiting step.

Chloramine-T behaves like a strong electrolyte in aqueous solution and dissociates according to equation (2). The anion picks up a proton in acid solutions to give the free acid has not been isolated there is an experimental evidence for its formation in acid solution .It undergoes disproportionation giving rise to *p*-toluenesulphonamide and dichloramine-T ,equation(4). Dichloramine-T and the free acid hydrolyse to give hypochlorous acid , HOCl ,[equation (5) and (6)]. Hypochlorous acid produce can be ionize according to equation (7).

hypochlorous acidinium ion ($\text{H}_2\text{O}^+\text{Cl}$) and protonated monochloramine-T ($\text{R}'\text{NH}_2\text{Cl}$) have also been detected in acid medium through equation (8) and equation (9), respectively.

$$\text{rate} = d[\text{CAT}]/dt = k_3[\text{X}] \quad (10)$$

Therefore the possible reactive species in acidified chloramine-T solutions are $\text{R}'\text{NHCl}$, $\text{R}'\text{NCl}_2$, HOCl , Cl_2 , and probably (RNH^+Cl and $\text{H}_2\text{O}^+\text{Cl}$). If RNCl_2 were to be the reactive species then the rate predicts a second –order dependence of rate on CAT but experimentally clear first –order plots were obtained for disappearance of CAT. Equation (6) indicates that the hydrolysis is slight and if HOCl is involved a first –order retardation of rate by the added *P*-toluenesulphonamide is expected. However, no such effect was observed. First –approximation calculations by Bishop and Jennings⁽³⁶⁾ on 0.05 M solution of CAT have shown that the concentration of RNHCl and HOCl are 10^{-2} and 10^{-7}M , respectively; at $\text{PH} < 3$. Under the present experimental conditions ($0.2\text{--}0.4 \text{ M H}^+$), it is quite likely that $\text{R}'\text{NHCl}$ is the oxidizing species variation of ionic strength of medium or addition of the reaction product. *P*-toluenesulphonamide, have virtually no effect on the rate. Bearing these facts in mind, the following scheme 1 has been proposed;

Scheme 1

In scheme 1, DE represent the substrate, X and X' represents the complex intermediate species whose structures are shown in scheme 2, where a details plausible mechanism of oxidation of DE with CAT in HCl medium is illustrated.

From the slow step of scheme 1,

$$\text{rate} = \frac{d[\text{CAT}]}{dt} = k_3[\text{X}] \quad (10)$$

If $[\text{CAT}]_t$ is the total effective concentration of CAT, then

$$[\text{CAT}]_t = [\text{R}'\text{NCl}] + [\text{R}'\text{NHCl}] + [\text{X}] \quad (11)$$

By substituting for $[\text{R}'\text{NCl}]$ and $[\text{R}'\text{NHCl}]$ from step (i) and (ii) in scheme 1, respectively, in to equation (11) and solving for $[\text{X}]$, one obtains;

$$[\text{CAT}]_t = \frac{[\text{X}]}{K_1 K_2 [\text{DE}][\text{H}^+]} + \frac{[\text{X}]}{K_2 [\text{DE}]} + [\text{X}] \quad (12)$$

$$[\text{X}] = \frac{K_1 K_2 [\text{DE}][\text{H}^+][\text{CAT}]_t}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{DE}][\text{H}^+]} \quad (13)$$

Substituting equation (13) in equation (10), the following , rate law can be obtained;

$$\text{rate} = \frac{d[\text{CAT}]}{dt} = \frac{K_1 K_2 k_3 [\text{DE}][\text{H}^+][\text{CAT}]_t}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{DE}][\text{H}^+]} \quad (14)$$

Rate law (14) is in good agreement with the experimental results ,where in a first –order dependence of rate on $[\text{CAT}]$, a fractional order dependence on both $[\text{DE}]$ and $[\text{H}^+]$ have been observed .Since $\text{rate} = k_1 [\text{CAT}]_t$, equation (14) can be transformed in to equations (15-17)

$$k' k' = \frac{K_1 K_2 k_3 [\text{DE}][\text{H}^+]}{1 + K_1 [\text{H}^+] + K_1 K_2 [\text{DE}][\text{H}^+]} \quad (15)$$

$$\frac{1}{k} = \frac{1}{K_1 K_2 k_3 [\text{DE}][\text{H}^+]} + \frac{1}{K_2 k_3 [\text{DE}]} + \frac{1}{k_3} \quad (16)$$

$$\frac{1}{k} = \frac{1}{K_2 k_3 [\text{DE}]} \left\{ \frac{1}{K_1 [\text{H}^+]} + 1 \right\} + \frac{1}{k_3} \quad (17)$$

Based on equations (16) and (17), plots of $1/k'$ versus $1/[\text{DE}]$ and $1/k'$ versus $1/[\text{H}^+]$ were linear ($r > 0.9910$) (Figure 1) .from the intercepts and slopes of these plots values of formation constant k_3 calculated and found to be $K_1 = 1.34 \text{ mol.dm}^{-3}$, $K_2 = 2.06 \text{ dm.mol}^{-1}$ and $k_3 = 7.886 \times 10^{-3} \text{ sec}^{-1}$ at 313 K° respectively. Since the rate was fractional –order in $[\text{DE}]_0$, Michaelis –Menten³⁷ kinetics were adopted to study the effect of $[\text{DE}]_0$ on the rate at different temperatures ($308\text{--}343^\circ\text{K}$) by plotting $1/k'$ versus $1/[\text{DE}]_0$.Using the calculated k_3 and the observed rate constants k' values, activation parameters were evaluated from linear Arrhenius plot of $1/k'$ versus $1/T$. the values are recorded in Table 3.

Figure 1. plot of $1/k'$ versus $1/[\text{H}^+]$ and $1/[\text{DE}]$; $[\text{CAT}] = 0.001 \text{ M}$; $\mu = 0.25 \text{ M}$; Temperature = 313 K° .

Scheme 2

The proposed mechanism and the derived rate law are supported by the experimental data and findings; there is a good agreement between them indicating the consistency and the correctness of the proposed Schemes and the derived rate law, except that for (K_1) value, which may be due to variation of experimental condition. The reaction rate is unaltered by the variation of ionic strength of the medium. Addition of the reaction product P-TSA affects the reaction rate marginally showing that it is not involved in a pre-equilibrium. A change in the solvent composition by varying the methanol content in methanol-water affects the reaction rate which has been described in detail by Frost and Pearson³⁸, Laidler³⁹ and Amis⁴⁰. For the limiting case of zero angle of approach between two dipoles or an ion-dipole system, Amis⁽⁴⁰⁾ has shown that a plot of $\log k$ versus $1/D$ gives a straight line, with a negative ion and a dipole or between two dipoles, while a positive result for a positive ion-dipole interaction. The latter concept agrees with the present investigation where a positive ion may be involved in the rate-determining step (which extended to the transition-state) of the proposed mechanism. The proposed mechanism is also supported by the moderate $\Delta H^\ddagger$ and $\Delta G^\ddagger$ values and by the high negative value of $\Delta S^\ddagger$ which indicate that the transition state is more ordered than the reactants.

Conclusion

Oxidation of diethyl ether with chloramine-T in HCl medium has been studied. The stoichiometry of oxidation of diethyl ether with CAT in acid medium is found to be 1:2. The oxidation product identified was ethyl acetate. The active oxidizing species involved in acid medium is $CH_3C_6H_4SO_2NHCl$. Activation parameters calculated from Arrhenius plot of the observed results supported the proposed mechanism and derived rate law.

References

1. Murthy.A R V and Rao.V R S, *Proc Indian Acad Sci.*, 1952, **69**, 35.
2. Cambell M M and Johnson.G, *Chem Rev.*, 1978, **78**, 65.
3. Rao.V.R.S, Venkappayya.D and Aravamudan.G, *Talanta*, 1970, **17**, 770.
4. Kolthoff.I.M and Belcher R, "Volumetric Analysis" Vol.3, Interscience, New York, 1975, P639.
5. Jennings V J, *CRC Crit Rev Anal Chem.*, 1964, 407.
6. Coull J, Hope H B and Gouguell.B, *J Am Chem Soc.*, 1935, **57**, 1489.
7. Pryde L R and Soper F G, *J Chem Soc.*, 1931, 1510.
8. Higuchi T and Hussain A, *J Chem Soc.*, 1967, B, 549.
9. Balasubramania.V and Thiagarajain.V, *Int J Chem Kinet.*, 1975, **7**, 605.
10. Agrawal M C and Mushran S P, *Naturfrosch.*, 1972, **B27**, 401.
11. Bose A K, Sanehi R and Mushran S P, *J Indian Chem Soc.*, 1973, **50**,197 .
12. Agrawal M C and Mushran S P, *J Chem Soc Perken Trans II*, 1973, 762.
13. Rangappa K S, Manjunathaswamy H, Ragharendra M P and Gowda D C, *Carbohydrate Reseach.*, 1998,307,253.
14. Mahadevappa D S and Naidu H M K, *Aust J Chem.*, 1974, **27**, 1203; 1975, **28**, 899.
15. Natarajam M M and Thiagarajan V, *J Chem Soc Perken Trans.*, 1975, II, 1590.
16. Mushran S P, Agrawal M C and Prased B, *J Chem Soc.*, 1971, 1712 .
17. Hassan Y I, Aziz L A and AL-Joraycee A A, *J Edec.and Sci.*, 1989, **9**, 73.
18. Hassan Y I and AL-Hatim A A, *Mutah J Res Stud.*, 1995, **5**, 19.
19. Bose A K, Mehrotra R M and Mushran S P, *Indian J Chem.*, II,1973,896.
20. Mahadevappa D S, Rangappa K S, Gowda M M and Gowda B T, *J Phys Chem.*, 1981, **85**,3 651, *Int.J.Chem.Kinet.*1981, 14,1183, *J Chem Soc Perkin Trans II*,39, (1985) and Ref. (13) there in.
21. Ramanujam V M S and Trieff N M, *J Chem Soc Perken Trans.*, II, 1975, 1590.
22. Radhakrishnaamurti P S, Pati S C and Dev B R, *Int J Chem Kinet.*, 1982, 14.
- 23.. Hassan Y I and Saeed N H M, *J Educt Scince*, 2008, 21,9, Saeed N H M, M.Sc.Thesis, University of Mosul ,Mosul,Iraq, (2006).
24. Puttaswamy, Jadadeesh R V and Vaz N, *Europ J Chem.*,2005, **3**, 326.
25. Mahadevappa D S, Jadhav M B and Naidu H M K, *Int J Chem Kinet.*, 1979, 11.261.
26. Jadhav M B, Naidu H M K and Mahadevappa D S, *J Indian Chem Soc.*, 1980, **57**, 693.
27. Mahadevappa D S and Gowda B T, *Indian J Chem.*, 1979, **17**, 484.
28. Ahmed M S, Gowda B T and Mahadevappa D S, *Indain J Chem.*, 1980, **19**, 650.
29. Metsger L and Bittner S, *Tetrahedron*, 2000, **51**, 1905.
30. Vogel A I, "Text Book of practical organic chemistry" 4th ed. Longman press, London, U.K.P, 1978, 651.
31. Morris J C, Salazar J A and Wineman M A, *Am Chem Soc.*, 1948, **70**, 2036.
32. Soloway S and Lipshits A, *Anal Chem.*, 1952, **24**, 898.
33. Gowda N M M and Mahadevappa D S, *Talanta*, 1970, **24**, 470.
34. Cheronis N D and Entrikim J B, "Identification of organic compounds" See Ed., 1966, John Wikey and Sons ,New York ,U.S.A.
35. Vogel A I, "A Text-Book of Macro and Semimicro qualitative Inorganic Analysis" 4th Ed., Longmans, London, U.K, 1965.
36. Gkerlof A and Amer J, *Chem Soc.*, 1932, **54**, 4125.
37. Bishop E and Jennings V J, *Talanta*, 1958, **1**, 197.
38. Forst A A and Pearson R G "Kinetics and mechanism" 2nd Ed., Wiley, New York U.S.A, 1961.
39. Laidler K J, "Reaction Kinetics"Progamon, 1962, New York, U.S.A, 1962.
40. Amis E S, *Anal Chem.*, 1955, **27**, 1672.