Research Paper

Volume : 5 | Issue : 1 | JANUARY 2016 • ISSN No 2277 - 8179

Rapid Kinetics of Chlorination of p-Acetotoluidide in Aqueous Medium Using Rotating Platinum Electrode.

Chemistry

KEYWORDS : Chlorination, Kinetics, RPE, voltametry.

ROHOKALE G. Y P.G. Department of Chemistry, Arts, Science and Commerce College, Rahuri – 413 705 (M.S.)-India

PATHARE S.A P.G. Department of Chemistry, Arts, Science and Commerce College, Rahuri – 413 705 (M.S.)-India

ROHOKALE P.G P.G. Department of Chemistry, Arts, Science and Commerce College, Rahuri – 413 705 (M.S.)-India

ABHANG A.R Department of Botany, Arts, Science and Commerce College, Rahuri – 413 705 (M.S.)-India

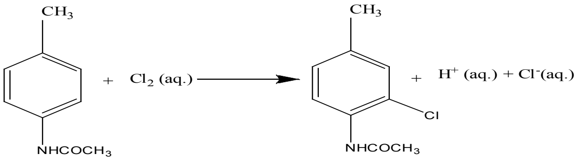
ABSTRACT

The rapid kinetics of the chlorination of p-acetotoluidide in aqueous medium by molecular chlorine at 7 pH has been studied using the rotating platinum electrode RPE. The specific reaction rate, energy of activation Ea, Entropy of Activation and the pre-exponential factor A, are evaluated. The reaction was found to be rapid and of the second order with a half life 16.3 s at 24.7°C. The rapidity of the reaction necessitated a special technique RPE to measure the unreacted chlorine which is the only electro reducible species in the reaction. The result obtained have been compared with those reported earlier for the bromination of acetanilide, o- acetotoluidide, m-acetotoluidide and p-acetotoluidide under identical conditions. Thus the present work provides the quantitative verification of the relative nucleophilicity of substrates using kinetics as an investigational tool.

INTRODUTION:

The rotating platinum electrode, RPE[1,6] although used less commonly than dropping mercury electrode in voltametric measurements, has yet proved to be a convenient device for the study of several rapid reactions in solution. Some rapid halogenations, for instance, have been studied by Rao, Mali, Dangat and Rohokale[7,8,9] using the RPE. Since such halogenation reactions are often of the second order, their half lives can be extended by diluting the solutions under identical conditions, direct kinetic measurements can be conveniently carried out using the RPE, which can be estimate very low concentrations of halogens. The kinetics of brominations of acetanilide, o-acetotoluidide, m-acetotoluidide and p- acetotoluidide has already been reported[7,9]. In comparision with these it would be interesting to study the kinetics of chlorination of p-acetotoluidide under parallel conditions. It would provide comparative results for the influence of the position of $-CH_3$ group relative to the $-NHCOCH_3$ group on the kinetics of the chlorination reaction. This attempt has been made in the present study, using the RPE technique for the kinetics measurements.

The equation for the reaction being studied is[10]



The main product of the reaction is 3-chloro-4-acetaminotoluene while the other isomers are formed in trace amounts[12]. Among the reactants and products of the reaction, only chlorine can be reduced at the RPE. Hence the kinetics of the reaction can be studied by measuring the diffusion current due to chlorine at various intervals of time from the start of reaction.

EXPERIMENTAL:

Construction of the RPE:

The RPE consists of a 0.5 mm diameter platinum wire fused to one end of an inverted 'T' shaped glass tube having 6 mm diameter, such that a centimeter of the platinum wire protrudes out. A pulley and a pair of ball bearings are mounted on this glass tube, having a total length of 32 cm. The ball bearings are fixed rigidly to a stand and the pulley is connected to a synchronous motor. The radius of the pulley is so adjusted that the electrode rotates at a speed of 600 revolutions[#] per minute. Some mercury kept inside the glass tube and the copper wire is dipped in it for electrical contact. The lower 4 cm portion of the glass tube effects a stirring action in the solution when the electrode rotates. A constant potential of +0.2 V versus the saturated calomel electrode (SCE) is applied at the RPE, using a potentiometer.

(# the limiting current is proportional to the cube root of the number of revolutions per minute above 200 r.p.m.[12])

A galvanometer with a sensitivity of 5.0 $\times 10^{-9}$ amp mm^{-1} provided with a lamp and scale arrangement is used for measurement of the diffusion current due to chlorine in terms of the deflection of the galvanometer light spot. The current passing through the galvanometer is controlled by employing a shunt so that the deflection of the light spot is within the scale limits.

Preparation of solutions :

Chlorine: For the stock solution of molecular chlorine the concentrated hydrochloric acid was added drop wise in solid leaching powder and the liberated gas was bubbled through water to free it from excess HCl. The exact concentration was determined using iodometric titration using starch as an indicator.

p-acetotoluidide : 20.0 gm of analytical grade p-toluidine are boiled with 20.0 cm^3 of analytical grade acetic anhydride in a one liter round-bottomed flask for half an hour. On cooling the solution p-acetotouidide separates as white crystals. These are recrystallized from absolute alcohol, and the melting point[10] of the needle shaped crystals found to be 146.0 ^{0}C.

Further, the reaction of p-acetotoluidide with chlorine in aqueous solution is carried out on a qualitative scale, and the precipitate obtained is confirmed to be 3-chloro,4-acetaminotoluine, as on crystallizing, and purity is checked by measuring its physical constant.

Potassium chloride: Analytical grade KCl is used to prepare a stock solution of the required strength of potassium chloride which is used as a supporting electrolyte.

Calibration of Reading:

The RPE and SCE are dipped in 100.0 cm^3 of 8 x 10^{-3} M potassium chloride solution which is the supporting electrolyte. A potential of + 0.2 V versus the SCE is applied at the RPE. The galvanometer light spot is adjusted to zero deflection on the scale. The potassium chloride solution is then replaced by 8 x10^{-5} M chlorine solution containing 8 x10^{-3} M potassium chloride. The shunt is adjusted for the deflection of the galvanometer light spot to be 35 to 40 cm. The shunt value is kept constant throughout the experiment. The diffusion currents, in terms of deflection of the light spot on the scale, are recorded for various concentrations of chlorine in the range of 8 x 10^{-5}M to 1 x 10^{-5} M. The plot of deflection observed in cm versus concentration of chlorine is found to be linear.

All the calibration readings are carried out only after the solution have attained the thermostatic temperature at which the kinetics readings are to be recorded subsequently.

Kinetic readings:

50 cm^3 of 16.0 x 10^{-5} M p-acetotoluidide containing 8.0 x 10^{-3} M potassium chloride and in 50 cm^3 of 16.0 x 10^{-5} M Cl_2 containing 8.0 x 10^{-3} M in different containers are kept in a thermostat at the desired temperature. After the solutions have acquired the temperature of the thermostat, they are quickly mixed in an empty beaker in which the SCE has been dipped and the RPE is rotating. At the moment of mixing a stop-clock is started. As the reaction proceeds, the galvanometer deflection decreases steadily. This is recorded at every ten seconds for about one and a half minute.

The above procedure of calibration and kinetics measurements is repeated thrice for checking the reproducibility of the galvanometer measurements, and these are found to be within the limits of +/- 0.3 cm.

From the observed deflections during kinetics study, the concentrations of unreacted chlorine, (a-x), at various instants obtained using the calibration curve 'x' is the concentration of chlorine reacted at time 't' and 'a' is the initial concentration of reactants. A plot of $[Cl_2]^{-1}$ i.e. 1/ (a-x) versus time't' is found to be linear and hence the reaction is the second order.

The slope of this plot gives the specific reaction rate k. These studies are carried out at various temperatures in the range 20-38 ^{0}C, from which the energy of activation 'E_a' for the reaction is evaluated. Further the frequency factor A and entropy of activation $\Delta S^{\#}$ for the reaction are also calculated.

TABLE- 1: Kinetics of chlorination of p-acetotouidide.

Calibration of diffusion current for chlorine concentration at 20.4 ^{o}C.

Concentration of chlorine /10^{-5} M	1.0	2.0	4.0	6.0	8.0
Diffusion current in scale divisions/cm	5.7	11.8	24.0	35.0	46.4

TABLE-2 : Variation of the specific rate of chlorination of p-actotoluidide with temperature.

Temp in °C	Temp T/K	T^{-1}/10^{-3}K^{-1}	Specific reaction rate k/M^{-1}s^{-1}	log k
20.4	293.4	3.408	332	2.5211
23.0	296.0	3.378	368	2.5668
25.4	298.4	3.351	397	2.5987
33.0	306.0	3.268	550	2.7403
38.0	311.0	3.215	693	2.8407

Slope of the curve log k vs T^{-1} = -2.12 x 10^3 K

Energy of activation 'Ea' = 31.592 kJ mole^{-1}

Frequency factor 'A' (at 25.4 ^{0}C) = 3.47 x 10^9 M^{-1}s^{-1}

Entropy of activation $\Delta S^{\#}$ = -30.6 Jk^{-1}mole^{-1}

TABLE-3 : Comparison of the specific rates of bromination of different substrates at 25.0 ^{0}C

Substrate	Specific reaction rate / M^{-1}s^{-1}
***o-acetotoluidide**	85
p-acetotoluidide	315
***acetananilide**	440
***m-acetotoluidide**	1510

*These specific reaction rates have been obtained by earlier workers[7].

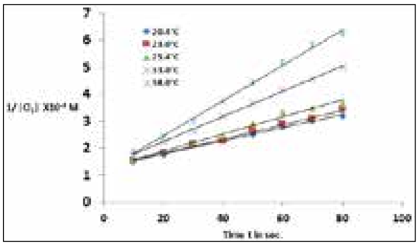


Fig. 1 : FAST KINETICS OF THE CHLORINATION OF p-ACETOTOLUDIDE AT VARIOUS TEMPERATURES.

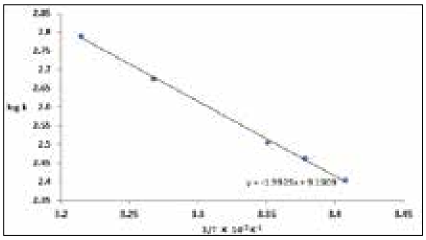
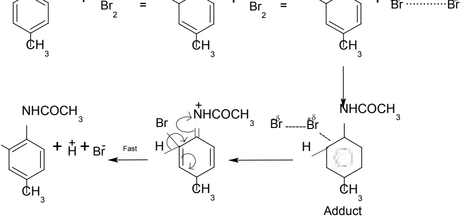


Fig. 2: EFFECT OF TEMPERATURE ON RATE CONSTANT k.

RESULTS AND DISCUSSION :

The specific reaction rate of chlorination of p-acetotoluidide in aqueous solution is found to be 419 M^{-1}s^{-1} at 25.4 ^{0}C. The energy of activation for the reaction is found to be 31.2 KJmole^{-1}. The frequency factor 'A' and entropy of activation for the reaction are found to be 1.87 x 10^9 M^{-1}s^{-1} and -39.6 Jk^{-1} mole^{-1} respectively.

The error in the specific rate determination is less than +/- 3% keeping in view the reproducibility of the diffusion current readings which have relatively the larger error among the various steps of the reaction.The results are presented in the Table 1- 2 and Figures 1-2. In view of the generally accepted mechanism of halogenations of aromatic compound[13], the probable mechanism for the chlorination of p-acetotoluidide in aqueous solution can be written as an electrophilic substitution reaction as follows:



The π electron of the ring react with the polarized bromine molecule to form an adduct which yields the intermediate in the rate determining step. The removal of proton is very fast[14,15]. The rate of reaction is hence, Rate = k[Cl_2] [p-acetotoluidide]

This implies that the reaction is of the second order. This indeed experimentally found to be the case.

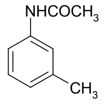
The above mechanism is envisaged even in view of the presence of hypochlorous acid in aqueous chlorin due to the following equilibrium.

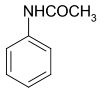
$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+_{aq} + Cl^-_{aq}$$

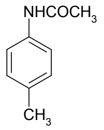
Aromatic substrates are known to react very slowly with hypohalous acids as compared to molecular halogens[13]. The forward and reverse specific rates of the above hydrolysis are 2.18 x 10^2 s^{-1} and 10^{11} M^{-2} s^{-1} respectively[16]. Thus molecular chlorine is the sole chlorinating species in the reaction mechanism as all the equilibrium HOCl concentration is converted to chlorine during the course of the reaction under study.

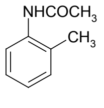
The specific reaction rate for the chlorinationof p-acetotoluidide in aqueous solution at 25.0 ^{0}C, 497 M^{-2} s^{-1}, that has been obtained in this study, may be compared with those for the bromination of acetanilide, m-acetotoluidide and o-acetotoluidide, under similar conditions at 25.0 ^{0}C, which have been obtained by earlier workers[7]. (Table-3).

It is evident that the specific rate for the bromination of m-acetotoluidide is the highest, viz- 1510 M^{-2} s^{-1}, followed by that for acetanilide and p-acetotoluidide. The specific reaction rate in the case of o-acetotoluidide in the above group of compounds is the lowest, viz, 85 M^{-2} s^{-1}. This trend of reactivates of these compounds can be looked upon as the influence of the position of the –CH_3 group relative to the –$NHCOCH_3$ group on the rapidity of the entry of the incoming –Br.


m-acetotoluidide


acetanilide


p-acetotoluidide


o-acetotoluidide

-CH_3 group is known to activate predominantly the ortho position in the event of an electrophilic attack on the aromatic ring substrate. Similarly, the –$NHCOCH_3$ group is strongly para directing and weakly ortho directing. The activating effect of both, -CH_3 and $NHCOCH_3$ groups are operative in unison in the case of the bromination of m-acetotoluidide and the –Br enters the para position with respect to the –$NHCOCH_3$ group at a very high rate, this position being highly activated. In the case of acetanilide, the absence of the –CH_3 group reduces the degree of activation of the para position of the benzene ring with respect to the –$NHCOCH_3$ group and hence a lower rate of bromination is expected. This is indeed the observation in p-acetotoluidide, the para position with respect to the –$NHCOCH_3$ group is occupied by the –CH_3 group. Hence the entry of the –Br is restricted to the ortho position with respect to the –NHCOCH3 group which is a weakly ortho directing group, and the reaction proceeds at a moderate rate. The ortho diecting effect of the –CH_3 group is not influential in this case as it is weaker than that of –$NHCOCH_3$. In o-acetotoluidide, the proximity of the –CH_3 and –$NHCOCH_3$ group's results in the lack of co planarity of the –$NHCOCH_3$ group with the benzene ring. Consequently, the stabilization of the positive charge on the carbanium ion is hindered considerably and formation of the chloro product is relatively the slowest.

The reactivities of the different aromatic substrates considered here undergoing the electrophilic attack have been predicted for long on the basis of substituent group characteristics and stereochemistry principles but direct kinetics measurements for most of these reactions and the verification of the predicted reactivities seem lacking. The specific reaction rate for the chlorination of p-acetotoluidide obtained in this study when compared with those obtained earlier for the bromination of m-acetotoluidide, acetanilide, o-acetotoluidide, and p-acetotoluidide provides this verification.

ACKNOWLEDGEMENT:
The authors are thankful to Principal, A.S.C College,Rahuri for providing laboratory facilities during the investigation. We are also thankful to Prof. T.S.Rao, Dr. V.T.Dangat and Prof. M.S. Wadia for valuable discussions.

REFERENCE

1. I.M. Kolthoff and H.A. Laitinen., 1941. J.Phys. Chem. 45,1079 2. T.Tsukamata, T.Kambara and Tachi, 1951. J.Electrochem. Soc. Japan, 19,311-313 3. I.M. Kolthoff,1950. J.Assoc. Offic. Agr.Chemists, 39,47 4. B.R.Sant and A.K.Mukharji, 1959. Anal.Chim. Acta, 20,476 5. R.C.Kapoor and K.C. Mathur,1965. J.Polarog. Soc.II 164 6. I.M. Kolthoff and J.J. Lingane, 'Polarography' second edition, 1952.Interscience Publishers New York. Vol. I P-421. 7. T.S.Rao and S.I. Mali, 1976. Z.Naturforsch. 31 a, 1735-36 8. T.S.Rao, S.I.Mali and V.T. Dangat, 1979. J.Unive. Poona, Sci. Tech. 52,111-114 9. V.T.Dangat,S.L.Bonde and G.Y.Rohokale., 1984. Indian J. of Chemistry. 23A, 237-238 10. R.T.Morrison and R.N. Boyd 'Organic Chemistry', 1977.Prentice-Hall of India PVT.Ltd, Second Edition p. 760 11. A.I. Vogel,'A textbook of Practical Organic Chemistry', 1967. Prentice-Hall of India PVT.Ltd, E.L.B.S. Third Edition p- 606. 12. K.J. Porton and A.E. Brandfield., 1927. J. Chem. Soc., 986 13. "A.I.Vogel" A Text book of Quantitative Inorganic Analysis including elementary instrumental analysis (E.L.B.S. and Longman), 1975.Third Edition p- 1049. 14. Berliner E.J.Chem. Edu., 1966. 43(3) 124 15. Wynne-Jones W.F.K., 1936.Trans, Farad. Soc. 32,1397 16. Melander L.,1950. Arkiv-kemi, 2, 211 17. M.Eigen and K.Kustin, 1962. J.Amer.Chem.Soc.82, 1355 18. Dangat V.T.,Bonde S.L., Borkar V.T. and Mhaske P.D., 2012. Research Journal of Chemical Sciences, 2(7),75-78 19. Bhore J.B.,Dangat V.T.,Bonde S.L. and Borkar V.T. 2014. Int. Res.J of Science and Engineering, 2(4), 142-144