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Kinetics of Chlorination of *o*-Acetotoludide in Aqueous Solution by Molecular Chlorine

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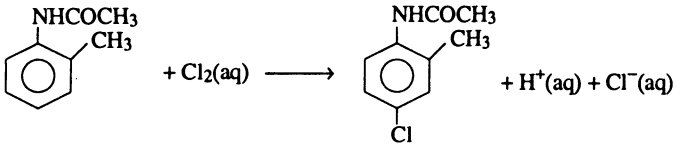
Kinetics of chlorination of *o*-acetotoludide by molecular chlorine in aqueous medium has been studied by employing the conventional technique. The specific reaction rate has been evaluated and found to be 1.88 m^{-1} s^{-1} at 25°C. Similar reaction rate determinations have been carried out at temperatures 30°, 35° and 40°C. The energy of activation, frequency factor and entropy of activation for the reaction has been evaluated and found to be 47.86 kJ mol^{-1}, 4.91×10^8 m^{-1} s^{-1} and –87.0 kJ mol^{-1} respectively.

Key Words: Kinetics, Chlorination of *o*-acetotoludide, Molecular chlorine.

INTRODUCTION

The halogenation of aromatic substrates and their derivatives are usually very rapid reactions in solution. Their kinetics have been studied only by indirect methods[1]. Since these reactions follow second order kinetics, their half lives can be extended by making the solution dilute enough such that convenient kinetic measurements are possible. The rotating platinum electrode[2] can measure very low concentrations of halogens and hence can be used to follow the course of such reactions. But the reaction under study is less rapid to study by rotating platinum electrode technique. Thus the kinetics of this reaction has been studied here by conventional technique. The equation for this reaction is:



The main product of the reaction is *p*-derivative, while other isomers are found to occur in traces[3]. From the start of the reaction definite aliquots of the reaction mixture are pipetted into a flask containing excess potassium iodide, at various time intervals whereby iodine is liberated and is a measure of the extent of the reaction by titration with standard sodium thiosulphate solution.

EXPERIMENTAL

The aqueous chlorine was prepared by dropping concentrated hydrochloric acid over bleaching powder and passing the gas through a little distilled water.

Then the gas was dissolved in another container of distilled water and the concentration was determined iodometrically. From this 12.0×10^{-4} M chlorine solution (**A**) was prepared. Analytical grade chemicals were used to prepare stock solutions of 12.0×10^{-4} M *o*-acetotoludide (**B**) and $6. \times 10^{-3}$ M potassium chloride (**C**) in double distilled water. Both (**A**) and (**B**) also contain 6.0×10^{-2} M potassium chloride.

In the thermostat 100 mL each of (**A**) and (**B**) were kept and maintained at 25°C for 0.5 h. Then (**A**) and (**B**) were quickly mixed and the stopwatch was simultaneously started. 25.0 mL aliquots of the reaction mixture was withdrawn at intervals of 1, 3, 8, 15, 25 and 40 min and added to flasks containing excess potassium iodide. The iodine liberated was titrated with 0.25 M sodium thiosulphate using starch as an indicator. A plot of reciprocal concentration of chlorine *vs.* time is found to be linear and hence the reaction is of second order.

The specific reaction rates are reproducible to within ±4% by considering the errors in the various measurements. The experiment was repeated at temperatures 25, 30, 35 and 40°C and hence the energy of activation for reaction was evaluated (Table-2 and Fig. 2).

RESULTS AND DISCUSSION

A typical set of results of the study are presented in Table-1 and Fig. 1. The specific reaction rate for chlorination of *o*-acetotoludide is found to be 1.88 m^{-1} s^{-1} at 25°C, the energy of activation is 47.86 kJ mol^{-1}. The frequency factor A for the reaction is evaluated and is found to be 4.91×10^8 m^{-1} s^{-1} . The entropy of activation for the reaction is found to be –87.0 J K^{-1} mol^{-1}.

TABLE- 1
KINETICS OF CHLORINATION OF *o*-ACETOTOLUDIDE AT 25°C

Time t (min)	Burette reading (mL)	Concentration of Cl_2 remaining, $[Cl_2]/10^{-4}$ M	$\frac{1/[Cl_2]}{10^3\ M^{-1}}$
1	10.5	5.25	1.90
3	10.0	5.00	2.00
8	7.5	3.75	2.67
15	5.7	2.85	3.51
25	4.4	2.20	4.50
40	3.2	1.60	6.25

Slope of the curve $[Cl_2]$ *vs.* time = specific reaction rate = 1.88 m^{-1} s^{-1}

A significant observation in the study is that chlorination reaction follows second order kinetics. Presumably, in the rate determining step of the reaction a molecule each of chlorine and *o*-acetotoludide react, to yield the activated complex. In aqueous solution chlorine is known to undergo hydrolysis[4] according to the equation

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \quad (1)$$

However, molecular chlorine can be considered to be the sole chlorinating agent in spite of hydrolysis in view of the fact that the specific rates for the forward and

reverse reactions in this hydrolysis are 115.0 s^{-1} and 1.4×10^{-4} m^{-1} s^{-1} respectively. Besides hypochlorous acid is a very slow chlorinating agent as compared to molecular chlorine in case of aromatic substrate. Hence the equilibrium concentration of chlorine falls due to progress of the reaction.

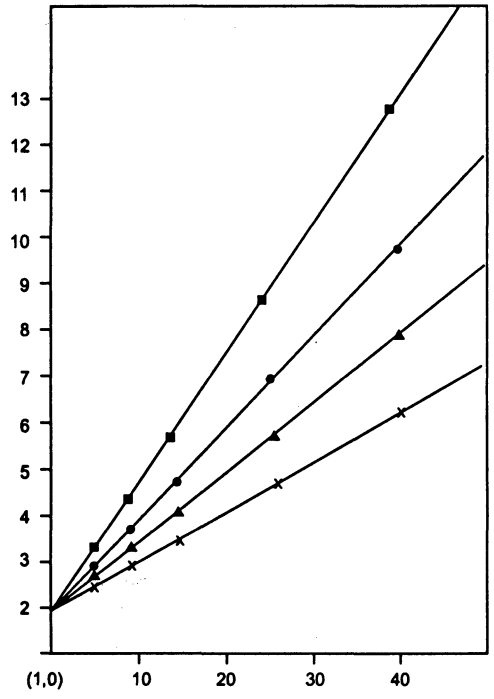


Fig. 1. Kinetics of chlorination of *o*-acetotoludide at various temperatures

TABLE-2
VARIATION OF THE SPECIFIC RATE OF CHLORINATION OF *o*-ACETOTOLUDIDE WITH TEMPERATURE

Temperature, t (°C)	Specific reaction rate, k_2 (m^{-1} s^{-1})
25	1.88
30	2.72
35	3.47
40	4.72

Slope of the curve, log k_2 *vs.* $T^{-1} = -2.50 \times 10^3$
Energy of activation, $E_a = 47.86$ kJ mol^{-1}
Frequency factor, $A = 4.91 \times 10^{-8}$ m^{-1} s^{-1}
Entropy of activation, $S^* = -87.0$ J K^{-1} mol^{-1}

Equilibrium (1) causes conversion of the existing hypochlorous acid to molecular chlorine. This conversion being rapid, the entire chlorination could be attributed to molecular chlorine.

In view of the mechanism of the halogenation of aromatic compounds[5], the reaction under study could be thought to occur by electrophilic substitution. The

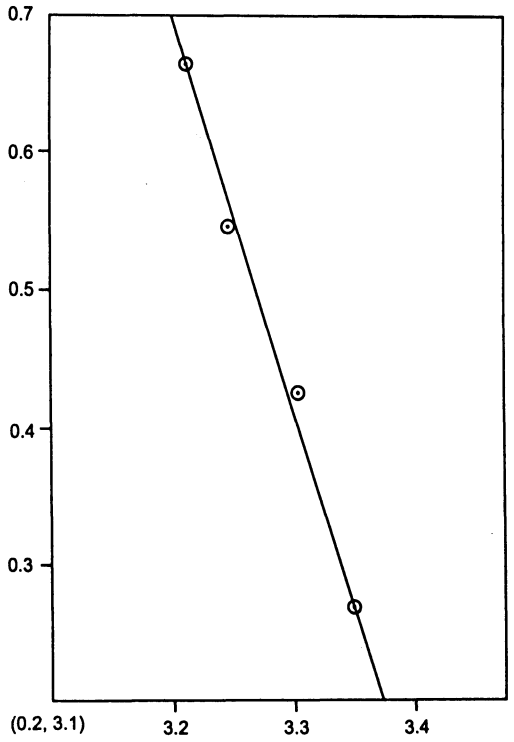
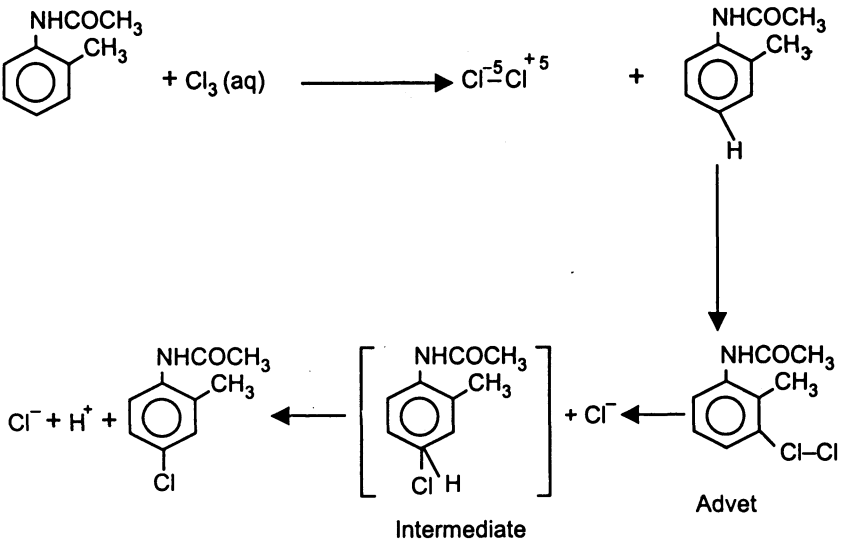


Fig. 2. Variation of specific reaction rate of chlorination of *o*-acetotoludide

chlorine molecule is first polarized by an inductive effect of the aromatic ring of *o*-acetotoludide.

The π-electrons of the ring react with the polarized chlorine molecule to form



an adduct. This yields which is the intermediate in the rate determining step, while the removal of proton is very fast[6,7]. Therefore the rate of reaction by this mechanism would be Rate = $k[Cl_2][o\text{-acetotoludide}]$ which implies that the reaction is of the second order.

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