

Bromination of *p*-Acetotoluidide in Aqueous Medium: Substituent Effect

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The kinetics of bromination of *p*-acetotoluidide in aqueous solution has been studied using a rotating platinum electrode. The specific reaction rate and the energy of activation for the reaction at 25.4°C are $319 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and 40.2 kJ mol^{-1} , respectively. These results have been compared with those reported earlier for the brominations of acetanilide, *o*-acetotoluidide and *m*-acetotoluidide under identical conditions to provide quantitative verification for the reactivities of these substrates.

The kinetics of bromination of acetanilide, *o*-acetotoluidide and *m*-acetotoluidide have been reported by Rao and Mali¹. Presently we have studied the kinetics of bromination of *p*-acetotoluidide under parallel conditions, using the rotating platinum electrode (RPE)¹⁻³, in order to elucidate the influence of the relative positions of the $-\text{NHCOCH}_3$ and $-\text{CH}_3$ groups upon the reactivity of the ring substrate undergoing the electrophilic attack.

The main bromo product has been identified as 3-bromo-4-acetaminotoluene while the other isomers are formed in traces⁴. Among the reactants and the products, only bromine is reducible at the RPE. Hence the reaction was followed by measuring the diffusion current due to bromine at various intervals of time, using a moving coil mirror galvanometer with a sensitivity of $5.0 \times 10^{-9} \text{ amp mm}^{-1}$ with lamp and scale arrangement and a shunt. The galvanometer readings were calibrated by recording the deflections for various bromine solutions in the concentration range $0.1 \times 10^{-4} \text{ mol dm}^{-3}$ to $0.8 \times 10^{-4} \text{ mol dm}^{-3}$ in $8 \times 10^{-3} \text{ mol dm}^{-3}$ potassium chloride.

Analytical grade chemicals were used to prepare stock solutions of $1.6 \times 10^{-4} \text{ mol dm}^{-3}$ bromine (A) and $1.6 \times 10^{-4} \text{ mol dm}^{-3}$ *p*-acetotoluidide (B), both containing $8 \times 10^{-3} \text{ mol dm}^{-3}$ potassium chloride as the supporting electrolyte.

Solutions (50 ml each) of (A) and (B) were quickly poured into a beaker containing the RPE and the saturated calomel electrode (SCE). A stop-clock was simultaneously started and the galvanometer readings were recorded at 10s intervals upto 80s. The calibration plot of deflection versus concentration was linear from which the concentrations of unreacted

bromine at various instants in the reaction were evaluated.

The diffusion current measurements were reproducible within $\pm 0.3 \text{ cm}$ of deflection of the light spot and hence the specific reaction rates have less than 2.5% error.

The experiment was carried out at five different temperatures and the energy of activation, entropy of activation and frequency factor for the reaction were evaluated as 40.2 kJ mol^{-1} , $-30.6 \text{ J mol}^{-1} \text{ K}^{-1}$ and $3.41 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25.4°C respectively.

The reaction follows the generally accepted mechanism for the bromination of aromatic compounds suggested by Berliner⁵. The rate of the electrophilic substitution reaction is given by Eq.(1).

$$\text{Rate} = k [\text{Br}_2] [\textit{p}\text{-acetotoluidide}] \quad \dots (1)$$

This implies that the reaction is of the second order. This is indeed found to be the case. The plot of $[\text{Br}_2]^{-1}$ versus time was linear (Fig. 1) and the slope of this plot gave a specific rate = $319 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 25.4°C.

The above mechanism is envisaged in spite of the HOBr present in aqueous bromine solutions due to the equilibrium,



The forward and reverse specific rates of this hydrolysis being $1.1 \times 10^2 \text{ s}^{-1}$ and $10^{11} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

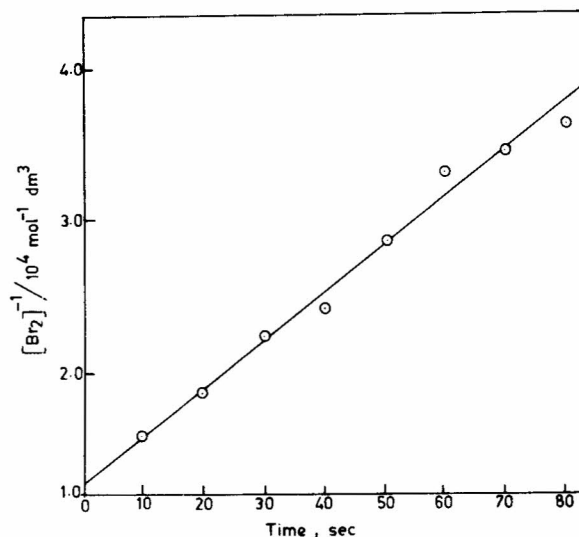


Fig. 1—Variation of $[\text{Br}_2]^{-1}$ with time for the bromination of *p*-acetotoluidide at 25.4°C

respectively⁶ and since aromatic substrates are known to react very slowly with hypohalous acids as compared to molecular halogens⁵, all the HOBr at equilibrium is converted into molecular bromine and Br₂ has been assumed to be the sole brominating species.

The specific reaction rate obtained for the bromination of *p*-acetotoluidide in this study may be compared with those obtained earlier for the bromination of acetanilide, *o*-acetotoluidide and *m*-acetotoluidide under identical conditions. The specific reaction rate (at 25.0°C) for the bromination of *m*-acetotoluidide (1510 dm³ mol⁻¹ s⁻¹) is the highest followed by acetanilide (440 dm³ mol⁻¹ s⁻¹) and *p*-acetotoluidide (315 dm³ mol⁻¹ s⁻¹) while that for *o*-acetotoluidide is the lowest (85 dm³ mol⁻¹ s⁻¹).

In the event of an electrophilic attack, -CH₃ is known to predominantly activate the *ortho* positions relative to it while the -NHCOCH₃ group strongly activates the *para* and weakly the *ortho* positions⁷. In *m*-acetotoluidide the strong *para* directing effect of the -NHCOCH₃ group and the *ortho* directing effect of the -CH₃ group are operative in unison and hence its bromination has the highest specific rate, the -Br entering the position *para* to the -NHCOCH₃. In the case of acetanilide the absence of the -CH₃ group reduces the degree of activation of the position *para* to the -NHCOCH₃ group and a lower specific rate of bromination is observed.

The *para* position with respect to the -NHCOCH₃ group is occupied by the -CH₃ group in *p*-acetotoluidide and the 3-bromo-4-acetaminotoluene formed in the bromination reaction at the specific rate of 315 dm³ mol⁻¹ s⁻¹ confirms the weaker *ortho* orienting influence of the -NHCOCH₃ as compared to its *para* directing influence. The *ortho* orienting influence of -CH₃ group is insignificant in this case as

this position being *meta* to -NHCOCH₃, the corresponding carbonium ion formed would not be stable⁷.

In *o*-acetotoluidide, the spatial proximity of the -CH₃ group to the bulky -NHCOCH₃ group results in the lack of coplanarity of the latter with the benzene ring. Consequently, the stabilization of the positive charge on the nitrogen is considerably hindered and the formation of the carbonium ion, which is the rate-determining step, is the slowest resulting in the relatively lowest specific rate of bromination of *o*-acetotoluidide. The role of the -CH₃ group as an *ortho* orienting group is again insignificant as in the case of *p*-acetotoluidide.

The reactivities of the different aromatic substrates considered here have been qualitatively speculated on the basis of substituent group characteristics and stereochemical principles, but direct kinetic measurements for a quantitative assessment of the speculated reactivities in aqueous solution were lacking. The present studies have thus provided a direct quantitative verification for the reactivities of various substrates.

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