# Kinetics of Fast Brominations by the Use of Rotating Platinum Electrode

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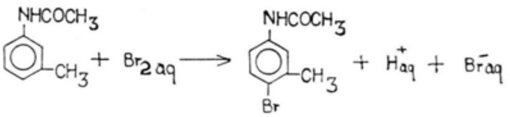
The utility of the rotating platinum electrode for the study of fast reactions has been shown by evaluating the specific reaction rates of brominations of *m*-acetotoluidide, acetanilide and *o*-acetotoluidide in aqueous solution.

The rotating platinum electrode, RPE[1] has been used much less frequently than the Dropping Mercury Electrode in voltammetric measurements. Nevertheless, it is useful for the study of the kinetics of fast reactions. The brominations of aromatic amines and their derivatives are usually very fast and their kinetics have been studied only by indirect methods[2,3]. Since these reactions follow second order kinetics, their half lives can be made long enough for convenient kinetic measurements by making the solutions dilute enough and since, by means of the RPE, it is possible to measure even very low concentrations of bromine, the course of such reactions can be directly followed. As typical instances, the kinetics of the bromination of o-acetotoluidide, acetanilide and m-acetotoluidide in aqueous solution have been studied. The equation for a typical reaction is as follows:



The main products are the p-derivatives[4], while the other isomers occur in traces[5]. In the reaction, only $Br_2$ is reducible at the RPE among the reactants and products. Hence the reaction can be conveniently followed by the use of the RPE.

## *Experimental*

The RPE consists of a piece of platinum wire, 0.5 mm diam, fused at the end of a glass tube, 10 mm diam so that 10 mm of the wire protrudes out. The electrode is fixed to a pulley and rotated at a speed of 600 r.p.m. This electrode is used in conjunction with a saturated calomel electrode (SCE), and by means of a potentiometric arrangement $+ 0.2$ V is applied at it. The diffusion current due to bromine is measured by a moving coil mirror galvanometer with lamp and scale arrangement and a shunt.

Analytical grade chemicals are used to prepare stock solutions of $3.0 \times 10^{-5}$ M bromine (A) and $3.0 \times 10^{-5}$ M m-acetotoluidide (B), both containing $1.0 \times 10^{-3}$ M potassium chloride as the supporting electrolyte, and of $1.0 \times 10^{-3}$ M KCl (C). All these solutions are maintained at 25.0 °C.

To begin with, the RPE and the SCE are dipped in 200 ml of (C) in a beaker. The galvanometer light spot is adjusted to zero. The KCl solution is now replaced by a mixture of 100 ml of (A) and 100 ml of (C). The resulting bromine solution is $1.5 \times 10^{-5}$ M. The galvanometer shunt is so adjusted that the deflection of the light spot is about 30 cm. The beaker is emptied. Now 100 ml each of (A) and (B) are quickly mixed in the beaker and a stop clock is simulaneously started. The galvanometer readings are recorded at every ten seconds for about two minutes.

The galvanometer readings are calibrated by noting the deflections for various bromine solutions in the concentration range of $0.50 - 1.50 \times 10^{-5}$ M in $1.0 \times 10^{-3}$ M KCl. The plot of the deflections versus concentrations is linear. From the observed deflections during the kinetic study the concentrations of unreacted bromine at various instants are evaluated from the calibration curve. A plot of $1/[Br_2]_{aq}$ versus time is linear and hence the reaction is of second order.

The experiment is repeated at temperatures in the range 10.0 °C – 30.0 °C and hence the energy of activation, entropy of activation and the frequency factor at 25.0 °C of the reaction are evaluated.

Table 1. Kinetics of bromination of *m*-acetotoluidide in aqueous solution at 25.0 °C. Galvanometer deflection for $1.5 \times 10^{-5}$ M Bromine = 27.0 cm.

| Time $t$ (sec) | Diffusion current (cm) * | Concentration of Bromine (M) |
|---|---|---|
| 10 | 22.8 | $1.24 \times 10^{-5}$ |
| 20 | 19.0 | 1.03 |
| 30 | 16.0 | 0.88 |
| 40 | 14.0 | 0.77 |
| 50 | 12.6 | 0.69 |
| 60 | 11.5 | 0.64 |
| 70 | 10.6 | 0.58 |
| 80 | 9.9 | 0.54 |
| 90 | 9.2 | 0.49 |
| 100 | 8.6 | 0.47 |

* (Diffusion current in deflection of galvanometer light spot in cm), Specific reaction rate = Slope of $1/[Br_2]_{aq}$ versus $t$ curve = 1510 $M^{-1}$ $sec^{-1}$.

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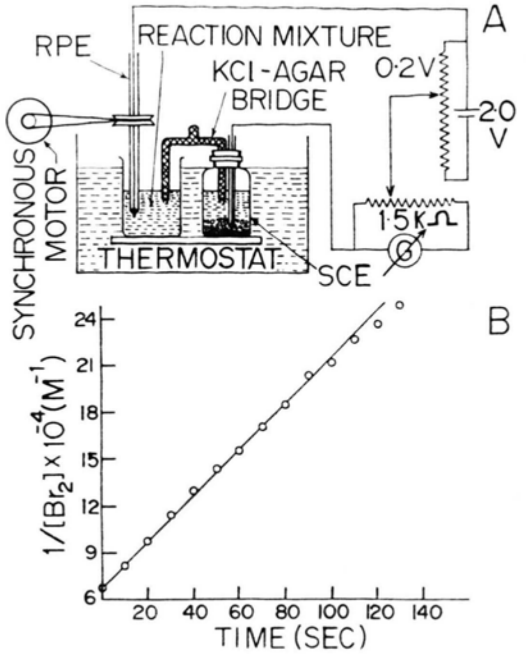

Fig. 1. A: Schematic diagram of the experimental set up. B: Kinetics of bromination of *m*-acetotoluidide at 25 °C.

The kinetics of brominations of o-acetotoluidide and acetanilide are similarly studied. In these cases the reactions are relatively slower, and hence more concentrated solutions of the reactants and a shorter platinum wire in the RPE are used.

A typical set of results for the bromination of m-acetotoluidide at 25.0 °C is presented in Fig. 1 and Table 1.

## *Results and Discussion*

The results of the study are summarized in Table 2. The technique is simple and yet its performance is good. Significantly the results for the bromination of acetanilide by this technique agree quite satisfactorily with those obtained earlier by the continuous flow technique[6]. Although the mechanism of these and similar other reactions has been postulated since long[7], in several cases its verification by direct kinetic measurement has been lacking.

Table 2. Kinetics of bromination of *m*-acetotoluidide, acetanilide and *o*-acetotoluidide.

| Compound | Specific reaction rate at 25.0 °C ($M^{-1}$ $sec^{-1}$) | Energy of activation cal $mole^{-1}$ | Frequency factor at 25.0 °C ($M^{-1}$ $sec^{-1}$) | Entropy of activation cal $mole^{-1}$ $deg^{-1}$ |
|---|---|---|---|---|
| *m*-acetotoluidide | 1510.0 | 3330 | $4.25\times10^5$ | −37.2 |
| acetanilide | 440 | 6670 | $3.56\times10^7$ | −28.5 |
| *o*-acetotoluidide | 85.0 | 13500 | $7.28\times10^{11}$ | −10.0 |

By using clean vessels and double distilled water the diffusion current measurements are reproducible within ±0.5 cm of deflection of the light spot, and hence the specific reaction rates have less than 4% error. The RPE is well suited for the study of fast bromination reactions upto a maximum limit of specific reaction rates of about $5.0\times10^{-3}\,M^{-1}\,s^{-1}$. For still faster reactions one has to use bromine solutions more dilute than $10^{-6}$ M wherein the reproducibility of results becomes poor. A further advantage of the RPE is that it can be used for the measurement of halogen concentrations even in the presence of dissolved oxygen.

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