

A Comparative Study of the Kinetics of Electrophilic Substitution in Aromatic Substrates by Iodine Monochloride and Iodine in Potassium Iodide

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Electrophilic substitution in aromatic substrates by iodine monochloride is about 10^5 times faster than by iodine in potassium iodide. This is due to the permanent dipole in the iodine monochloride, with iodine as the positive end, which greatly facilitates electrophilic attack.

Introduction

Electrophilic substitution in aromatic substrates by iodine in aqueous potassium iodide solutions is a slow reaction because iodine here exists mostly as I_3^- , which is a poor electrophile because of its negative charge, and I_2 must first be polarized by the substrate to enable electrophilic attack by its positive end [1]. Any reagent in which iodine is at the positive end of a dipole would be a faster iodinating agent. This has been assessed in the present work by comparing the specific rates of electrophilic substitution in two typical aromatic substrates, namely salicylic acid and aniline, by ICl and I_2 in potassium iodide.

Since iodinations by iodine monochloride are too rapid to be studied by conventional techniques, they have been studied with the rotating platinum electrode (RPE) [2–4]. At suitable applied potentials (-0.1 V) versus the saturated calomel electrode (SCE), the diffusion current generated at the RPE is linearly proportional to the concentration of ICl . Since iodine monochloride is the only electroactive species in the system, the course of the reaction can be followed by measuring the diffusion current. This current is separately calibrated with respect to the concentration of iodine monochloride.

Experimental

A saturated solution of iodine and a concentrated solution of chlorine in water were prepared and

standardised [5]. The two halogen solutions were mixed in equimolar amounts. Absorption spectrophotometric measurements showed that the two halogens had completely reacted to yield ICl whose concentration was 2.38×10^{-3} M. That this solution functions solely as an iodinating agent was confirmed by the following tests.

Equimolar amounts of the substrate and iodine monochloride were mixed. After complete reaction, the derivative and the supernatant solution were analysed. The purified derivative contained only iodine and no chlorine. Its m.p. was 197 °C in the case of salicylic acid and 67 °C in the case of aniline. Therefore the derivatives were 5-iodo salicylic acid [6] and 4-iodo aniline [7], respectively. The supernatant solution, on quantitative analysis by potentiometric titration against standard silver nitrate, was found to contain only the chloride ion, precisely equivalent to the initial iodine monochloride. This confirms that an equimolar mixture of aqueous iodine and chlorine quantitatively iodinates these substrates releasing an equivalent amount of the chloride.

For the kinetic runs, 50 cm^3 aliquots of salicylic acid and iodine monochloride, each 2.0×10^{-4} M and containing 1.0×10^{-2} M potassium nitrate as supporting electrolyte, were kept in a thermostat. The RPE and SCE were placed in an empty beaker in the same thermostat. The two solutions were simultaneously poured into the beaker and the reaction was followed by noting the evolution of the diffusion current. The concentrations of the unreacted iodine monochloride were evaluated on the basis of the calibration curve. The reciprocals of these concentrations, when plotted versus time, yielded a straight line whose slope gave the specific rate of the second order reaction.

The experimental error in the determination of the specific rate was $\pm 2\%$.

The study was repeated at various temperatures in the range of 15.0 to 35.0 °C for the iodination of salicylic acid, from the results of which the energy of activation for the reaction was evaluated. In the case of aniline the kinetics were similarly studied in the temperature range of 5.0 to 25.0 °C, but in a 0.05 M potassium hydrogen phthalate buffer of pH 4.0. The pH was controlled in this case, as the

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reaction was sensitive to hydrogen ion concentration [8].

The kinetics of iodination of these substrates by I_2 in potassium iodide were studied by the classical technique of mixing the reactants in equimolar amounts and estimating the unreacted iodine by titration against standard sodium thiosulphate.

Results and Discussion

The results of these studies, presented in Table 1, clearly show that iodine monochloride brings about iodinations of aromatic substrates approximately 10^5 times faster than does iodine in potassium iodide. This enormously higher rate with iodine monochloride is obviously due to the permanent dipole in the molecule with iodine as the positive end as compared to the infinitesimally small dipole induced in the molecular iodine by the aromatic substrate.

Table 1. Kinetics of iodination of aromatic substrates by iodine monochloride and iodine in potassium iodide at 25.0 °C.

Iodinating agent	Specific rate, k $M^{-1} s^{-1}$		Energy of activation $kJ mol^{-1}$		$\frac{k_{ICl}}{k_{I_2}}$
	ICl	I_2	ICl	I_2	
Salicyclic acid	13.6	1.13×10^{-4}	26.0	80.1	1.20×10^5
Aniline	3930	1.10×10^{-2}	50.5	93.6	3.57×10^5

Considering the generally accepted mechanism of electrophilic substitution in aromatic substrates by halogens [8], the mechanisms of the present iodinations would involve an electrophilic attack by the positive end of the dipole in the halogenating agent on the electron rich site of the aromatic substrate. The formation of an adduct and the subsequent deprotonation lead to the products.

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