Kinetics of iodination of aniline & anthranilic acid by iodine in aqueous medium

V T Dangat*, S L Bonde, A S Gayakhe & B S Ghorpade

Department of Chemistry, Nowrosjee Wadia College,
Pune 411 001, India

The title reactions are fast and follow overall second order kinetics. The two reactions have been studied at pH 4.7 using a rotating platinum electrode. The ratge constants and the energies of activation for the two reactions at 24.5°C are : 136 dm^3 mol^{-1} s^{-1}, 115 dm^3 mol^{-1} s^{-1}; and 82.1 kJ mol^{-1}, 82.2 kJ mol^{-1}, respectively.

Presently, we have studied the kinetics of iodination of aniline and anthranilic acid using aqueous iodine in the absence of iodide ions. Aqueous iodine is far more reactive than the triiodide anion formed in the presence of iodide. The kinetics were followed by measuring the extent of reduction of iodine at a rotating platinum electrode[1] (RPE).

The main iodo product in these reactions is the *para*-isomer, the other isomers being formed in traces[2]. The reactions being second order, their half-lives were prolonged by diluting the solutions.

AR grade chemicals were used to prepare aqueous solutions of 2.0×10^{-4} mol dm^{-3} each of iodine, aniline and anthranilic acid, all containing the required buffer components for maintaining pH 4.7 in 0.01 mol dm^{-3} KNO$_3$. Dilute aqueous iodine solution was prepared without adding iodide ions and its concentration was measured during the course of the reaction at RPE at which only iodine is reducible among the reactants and products at an applied voltage of $+0.25$ V (versus the SCE). At this applied potential, the shift in reduction potential of iodine with decrease in concentration was almost negligible. Hence the reactions were followed by measuring the diffusion current due to iodine at RPE at various intervals of time, using a moving coil mirror galvanometer with a lamp and scale arangement and shunt. The galvanometer readings were calibrated by recording the deflections for iodine solutions in the range of 2.0×10^{-5} mol dm$^{-3}$ to 10.0×10^{-5} mol dm^{-3} in 0.01 mol dm^{-3} KNO$_3$. These deflections remained constant for time periods much longer than those for the kinetic sets. Lead acetate was added to the reaction mixtures for scavenging any iodide ion produced during the reaction.

Fixed volumes (50 ml) of iodine and aniline solutions were quickly poured into a beaker containing the RPE and a saturated calomel electrode. The RPE had an inverted T-shape for effecting mixing while rotating. It was cleaned with concentrated nitric acid between every two sets of readings. A stop-clock was started simultaneously and the galvanometer readings were recorded at 10s intervals upto 90s. This procedure was repeated for the reaction of aqueous iodine with anthranilic acid also. The concentration of unreacted iodine at varying instants in the two reactions was found from the calibration plot of the deflections versus [I$_2$]. The plots of [I$_2$]$^{-1}$ versus time were linear and the rate constants were found to be 136 dm^3 mol^{-1} s^{-1} and 115 dm^3 mol^{-1} s^{-1} at 24.5°C for the iodination of aniline and anthranilic acid respectively, under the conditions, [HOAC] = [NaOAC] = 3.0×10^{-3} mol dm^{-3}, [Pb(OAc)$_2$], [I$_2$], (C$_6$H$_5$NH$_2$) and [anthranilic acid] = 1.0×10^{-4} mol dm^{-3} each. The second order observed experimentally for these reactions is in accord with the generally accepted mechanism of Berliner[3] for halogenation of aromatic substrates who gave the rate law

$$\text{Rate} = k[\text{I}_2][\text{aromatic substrate}] \qquad \ldots (1)$$

The diffusion current measurement were reproducible within ± 0.3 cm deflection of the galvanometer. Hence the error in the rate constant was $< 2.5\%$. The study was carried out at five different temperatures and the energies of activation for the iodination of aniline and anthranilic acid were evaluated as 82.1 kJ mol^{-1} and 82.2 kJ mol^{-1} respectively.

The hypoiodous acid present in these reaction mixtures due to the equilibrium (2), because of the low hydrolysis constant (2.0×10^{-13}), does not have any significant influence on these substitution reactions.

$$\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HOI} + \text{H}^+_{aq} + \text{I}^-_{aq} \qquad \ldots (2)$$
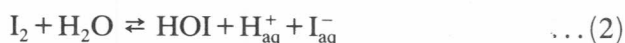
Besides, aromatic substrates are known to react much slowly with hypohalous acids than with halogens[3].

The ionized and unionized forms of the substrates used have different reactivities and their relative proportions are pH dependent. Hence the reactions were studied at pH 4.7 using sodium acetate-acetic acid buffer system. The increase in $[CH_3COO^-]$ due to the addition of lead acetate is only 1/30th of that already existing therein and hence does not cause any pH change. This has been verified experimentally.

References

1 Rao T S & Mali S I, *Z. Naturforsch.*, 31a (1976) 1735.
2 De La Mare & Ridd J H, *Aromatic substitution* (Butterworths, London) 1959.
3 Berliner E, *J chem Educ.*, 43 (1966) 124.
4 Cotton F A & Wilkinson G, *Advanced inorganic chemistry* (Wiley Eastern, New Delhi (1972) 569.