The Rate of Nitronium Ion Formation from Nitric Acid in Aqueous Sulphuric Acid

By John W. Chapman and Alec N. Strachan*

(*Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire*)

Summary The rate of nitronium ion formation is the rate-determining step in the nitration of toluene with mixed acid under certain conditions, and values of the rate constant have been determined for the first time.

In organic solvents the rate of nitration of reactive aromatic substances such as toluene is, under certain conditions, observed to be independent of the concentration of the substrate.[1] This is attributed to the rate-determining step being the formation of nitronium ions [equation (1)]

$$HNO_3 + H^+ \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} NO_2^+ + H_2O \qquad (1)$$

instead of their attack on the substrate [equation (2)].

$$NO_2^+ + ArH \xrightarrow{k_2'} \text{products} \qquad (2)$$

In aqueous sulphuric acid, however, the rate is invariably first-order with respect to the aromatic substrate and (2) has always been assumed to be the rate-determining step.

Recently,[2] lower than expected rates have been observed in the two phase nitration of toluene at strengths of sulphuric acid *ca.* 75%, and the conclusion has been drawn that (1) rather than (2) is the rate-limiting kinetic step under such conditions.

Table. Values of k_1 and k_2 at 25°

% H_2SO_4	k_1/s^{-1}	k_2/l mol^{-1} s^{-1}	k_2/l mol^{-1} s^{-1} (ref. 3)
74·70	0·8	230	170
76·35	1·1	850	680
77·00	1·8	1700	1200
78·15	4·0	3400	3300
78·95	5·0	8300	6600
80·10	6·4		
81·45	8·3		

We now report confirmation of this conclusion from direct observation of a change from first- to zero-order kinetics with respect to the aromatic substrate in the homogeneous nitration of toluene at strengths of sulphuric acid between 74 and 82%. A Nortech SF-3A stopped-flow spectrometer was used at 350 nm. The nitric acid concentration and the initial toluene concentration after mixing were $1{\cdot}88 \times 10^{-2}$ and $1{\cdot}41 \times 10^{-3}$ mol l^{-1} respectively. As the sulphuric acid strength was increased, the absorbance versus time traces changed from exponential curves (first-order kinetics) to straight lines (zero-order kinetics). In the transition region the trace was linear at the start and exponential at the end, allowing both $k_1 = R_0/[HNO_3] = k_1'a_{H+}$ and $k_2 = R_1/[HNO_3][T] = k_2'k_1'a_{H+}/k_{-1}\,a_{H_2O}$ to be obtained, where R_0 and R_1 are the zero- and first-order nitration rates, [HNO_3] and [T] are the nitric acid and toluene concentrations, and a_{H+} and a_{H_2O} are the hydrogen ion and water activities respectively.

The values of k_1 and k_2 obtained are shown in the Table with values of k_2 interpolated from previous data,[3] using lower toluene concentrations of between 10^{-4} and 10^{-5} mol l^{-1} which favour first-order kinetics, and claiming no better than ±25% accuracy for some of the determinations. There is reasonable agreement between the two sets of k_2 values. We thank the S.R.C. for a grant towards the purchase of the stopped-flow spectrometer and Hickson and Welch Ltd., Castleford, for a research scholarship (J.W.C.).

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