Kinetics and Mechanism of the Reaction between Sulphamic and Nitric Acids

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The kinetics of the disappearance of sulphamic acid in concentrated nitric acid are first order with respect to the concentration of sulphamic acid, and the rate constant varies with $H_0^{1.74}$. Reaction occurs by an electrophilic attack of the nitryl cation, $[NO_2]^+$, on sulphamic acid to form nitroamine, NH_2NO_2, which then decomposes to dinitrogen oxide and water.

MANY reactions in which nitric acid functions as an oxidising agent are catalysed by nitrous acid. There is therefore interest in the mechanism of the well known[1] reaction (1). Sulphamic acid is a very effective nitrite scavenger,[2] and the rate of its reaction with nitrous acid increases with increasing acidity, so it is most unlikely that catalysis by nitrous acid is involved in (1). During the course of the present investigation it was discovered that an independent and more detailed study of (1) was being carried out in other laboratories.[3] We do not, therefore, intend to pursue our work beyond the point described in this paper.

$$HNO_3 + NH_2SO_3H \longrightarrow N_2O + H_2SO_4 + H_2O \quad (1)$$

RESULTS

The stoicheiometry of (1) appears to be well established, and was not further investigated. The kinetics were studied by following the disappearance of sulphamic acid, and were found to be first order with respect to the concentration of this species. This conclusion is based on the linearity of first-order plots over three half-lives, and the fact that the first-order rate constant, k(s^{-1}), was independent of the initial sulphamic acid concentration. The reaction rate increased steeply with increasing stoicheiometric nitric acid concentration over the range 53.5—67.8% w/w at 65 °C, and a plot of log k_1 against H_0† gave a good straight line. A least-squares treatment yielded equation (2).

$$\log k_1 = -1.74\, H_0 - 9.37 \quad (2)$$

Because we are working in concentrated solutions of nitric acid, these results do not give us any information about the dependence of the rate on nitrate concentration. To investigate this point the reaction was studied in 56.3% w/w perchloric acid at 78 °C in the presence of small amounts of added sodium nitrate. The results, shown below, establish that the reaction is first order with respect to nitrate concentration.

A temperature study showed that for reaction in 63.4% w/w nitric acid over the range 35—60 °C the Arrhenius activation energy was 105.9 kJ mol^{-1}.

$[NaNO_3]$/mol dm^{-3}	0.04	0.08	0.12	0.16	0.20
10^4k_1/s^{-1}	0.458	0.966	1.47	1.98	2.35

DISCUSSION

The fact that the variation in rate with acidity approximates to a second-order dependence on H_0 strongly suggests a mechanism involving the nitryl cation, $[NO_2]^+$. The rates of aromatic nitrations are known† to vary with H_R,[4] and for several acids $H_R = 2H_0$ to a good approximation.[5] Sulphamic acid is only a moderately strong acid,[2] pK_a 1.11, and over the range of nitric acid concentrations used in the present work it will exist almost totally as the neutral zwitterion form $NH_3^+SO_3^-$. There will be a small concentration of the tautomer NH_2SO_3H in equilibrium with the zwitterion,

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† H_0 is the Hammett acidity function for primary aromatic amine indicators, and H_R is the corresponding acidity function with carbinol-type indicators.

[1] 'Introduction to Advanced Inorganic Chemistry,' 2nd edn., eds. P. J. Durrant and B. Durrant, Longmans, 1970, p. 685.

[2] M. N. Hughes, *J. Chem. Soc.* (*A*), 1967, 902.

[3] M. N. Hughes, personal communication.

[4] F. H. Westheimer and M. S. Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.

[5] 'Acidity Functions,' ed. C. H. Rochester, Academic Press, p. 75; A. J. Kresge, H. J. Chen, and Y. Chiang, *J.C.S. Chem. Comm.*, 1972, 969.

and we propose a rate-determining electrophilic substitution at the amino-group of this species, with $[SO_3H]^+$ as the leaving group. Nitroamine, NH_2NO_2, is known to undergo ready decomposition to dinitrogen oxide and water. A powerful argument in favour of this mechanism is the fact that when nitric acid and sodium sulphamate are allowed to react at −50 °C it is possible[6] to isolate a substantial yield of nitroamine from the mixture. This mechanism requires the rate of formation and hydrolysis of $[NO_2]^+$ to be much greater than the rate of reaction with sulphamic acid. From the present data we calculate the rate of reaction for 0.0174 mol dm^{-3} sulphamic acid in 67.8% w/w nitric acid at 0 °C to be 6.1×10^{-9} mol dm^{-3} s^{-1}, which compares with the rate of $[NO_2]^+$ formation and hydrolysis[7] of 3.8×10^{-5} mol dm^{-3} s^{-1}. Clearly there is no inconsistency here. Other, more complex, mechanisms are also consistent with our data. Thus the reaction of $[NO_2]^+$ with sulphamic acid could be an addition process to form $O_2N{\cdot}\overset{+}{N}H_2SO_3H$ rather than a displacement reaction. The formation of an equilibrium concentration of such an adduct, followed by rate-determining breakdown of this species, could also be consistent with our data. However, in the absence of any compelling evidence, we prefer the simpler alternative of a direct displacement reaction.

$$H^+ + HNO_3 \underset{\text{fast}}{\rightleftharpoons} [H_2NO_3]^+ \underset{\text{fast}}{\rightleftharpoons} [NO_2]^+ + H_2O \qquad (3)$$

$$[NO_2]^+ + NH_2SO_3H \xrightarrow{\text{slow}} NH_2NO_2 + [SO_3H]^+ \qquad (4)$$

EXPERIMENTAL

All chemicals used were AnalaR grade materials. The reaction was followed by taking 1-ml samples from the reaction mixture and quenching them in a fixed volume of dilute sodium nitrite solution which was cooled to 0 °C. Concentrations were chosen so that at the start of a run there was a substantial excess of sodium nitrite. In the quenched solution the sulphamic acid was rapidly destroyed by the nitrous acid; the excess of nitrous acid was then determined by direct spectrophotometry at 372 nm using 4 cm cells and a Unicam SP 600 spectrophotometer. Plots of log $(A_\infty - A)$ against time gave good straight lines, where A was the absorbance at 372 nm.

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[6] S. Tellier-Pollon and J. Heubal, *Rev. Chim. minérale*, 1967, **4**, 413.

[7] C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 1958, 2420.