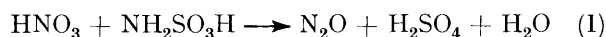


Kinetics and Mechanism of the Sulphamic Acid–Nitric Acid Reaction: Evidence for Consecutive Reactions

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The title reaction occurs in three stages. The first and fast step probably involves attack of $[\text{NO}_2]^+$ on sulphamic acid, while the subsequent steps involve rearrangement and elimination. The direct displacement of $[\text{SO}_3\text{H}]^+$ by $[\text{NO}_2]^+$ can be excluded. Dinitrogen oxide and sulphate are produced in the third (and slowest) stage, for which the kinetics have been studied over the range $[\text{HNO}_3] = 0.274\text{--}14.8 \text{ mol dm}^{-3}$. This third stage is first order in both $[\text{NH}_2\text{SO}_3\text{H}]$ and $[\text{NO}_3^-]$, and approximately second order with respect to the acidity function H_0 , indicative of involvement of a $[\text{NO}_2]^+$ group in the transition state. The second stage of the reaction is retarded by HNO_3 . Several alternative mechanisms are discussed.

NITRIC ACID and sulphamic acid react¹ in aqueous solution giving dinitrogen oxide and sulphuric acid [equation (1)]. Nitroamine, NH_2NO_2 , may be isolated²



when the reaction is carried out at -50°C , implying that it may be an intermediate. We have studied the kinetics of reaction of sulphamic acid with nitric acid, and the reaction of sulphamic acid with sodium nitrate in perchloric acid, as an extension of earlier work on the nitrosation of sulphamate.³ In view of the possible build-up of intermediates, we attempted to follow the course of the reaction by measuring the loss of $\text{NH}_2\text{SO}_3\text{H}$ and the production of N_2O and sulphate. As necessary background work we have extended earlier studies on the hydrolysis of sulphamate⁴ and the decomposition of nitroamine⁵ to cover the temperature and acidity range used in the present study. In the concluding stages of this work it was discovered that this reaction was being studied elsewhere, but in less detail. These

results have now been published⁶ and the suggestion made that the mechanism involves rate-determining displacement of $[\text{SO}_3\text{H}]^+$ by the nitryl cation $[\text{NO}_2]^+$ giving nitroamine which then decomposes to N_2O and water. Attwood and Stedman⁶ pointed out that other possibilities existed but stated that 'in the absence of any compelling evidence we prefer the alternative of a direct displacement reaction.' We have obtained additional kinetic evidence⁷ that proves that there must be several steps involved in the mechanism and it is now possible to exclude the one-stage displacement mechanism.

EXPERIMENTAL

All the chemicals were the best grade available. 'Organic Analytical Standard' sulphamic acid was used, the use of other grades leading to some irreproducibility of results. Kinetic runs were started by the addition of a sulphamic acid solution to an otherwise complete reaction

¹ K. W. C. Burton and G. Nickless, 'Inorganic Sulphur Chemistry, Elsevier, Amsterdam, 1968, p. 607.

² S. Tellier-Pollon and J. Henbal, *Rev. Chim. minérale*, 1967, **4**, 413.

³ M. N. Hughes, *J. Chem. Soc. (A)*, 1967, 902.

⁴ J. P. Candlin and R. G. Wilkins, *J. Chem. Soc.*, 1960, 4236.

⁵ C. A. Marlies and V. K. La Mer, *J. Amer. Chem. Soc.*, 1935, **57**, 1812.

⁶ D. Attwood and G. Stedman, *J.C.S. Dalton*, 1976, 508.

⁷ M. N. Hughes and J. R. Lusty, *Inorg. Nuclear Chem. Letters*, 1977, **13**, 37.

solution thermostatted at appropriate temperatures in an oil thermostat. In cases where the production of N_2O was followed, the reaction was carried out in a Warburg flask, with the sulphamic acid solution stored in the side arm. For other kinetic runs, samples were withdrawn at appropriate time intervals and analysed for NH_2SO_3H or sulphate as appropriate.

Analysis for Sulphamate using Sodium Nitrite Solutions.—Known volumes of the reaction mixture (usually 1 cm³) were pipetted into a known amount of dilute sodium nitrite solution at 0 °C, the total concentration of nitrite being greater than that of sulphamate at zero time of reaction. The sulphamic acid reacts rapidly with the nitrous acid in 1 : 1 mol ratio, so the concentration of the former could be determined knowing the initial amount of nitrite and the amount present after reaction. The latter quantity was determined by measurement of the nitrous acid absorption at 372 nm using 40 mm silica cells and a Unicam SP 500 spectrometer. Rate constants were obtained from plots of $\log(A_\infty - A_t)$ where A_∞ and A_t are the absorptions due to HNO_2 at infinity and time t respectively. This method was independently devised by Attwood and Stedman⁶ and was the only one used in their work.

Analysis for Sulphate.—The production of sulphate was measured by the use of a standard method⁸ modified to allow for the concentrated acids present in the reaction mixture. This worked satisfactorily. Rate constants were obtained from plots of $\log(c_\infty - c_t)$ against time, where c_∞ and c_t are concentrations of sulphate at infinity and time t respectively.

RESULTS

A possible complication in this reaction system is the hydrolysis of sulphamic acid to ammonium and sulphate ions. This has only been measured previously⁴ up to 2.6 mol dm⁻³ $HClO_4$. Accordingly, we have studied⁹ the kinetics of hydrolysis of NH_2SO_3H at several temperatures up to $[H^+] = 10.0$ mol dm⁻³. This shows that the rate of hydrolysis decreases with increasing acidity beyond 2.6 mol dm⁻³. At lower acidities the hydrolysis reaction becomes relatively more important and allowance had to be made for this on the few occasions when such acidities were studied.

Studies on the $NH_2SO_3H-HNO_3$ reaction utilising HNO_2 as an analytical reagent for sulphamic acid gave unexpected results of considerable interest. It was anticipated that at the early stages of the reaction the sulphamic acid concentration would still be high and so the residual $[HNO_2]$ in the analytical solution would be low. For successive reaction samples the residual $[HNO_2]$ in the analysis should increase as the $[NH_2SO_3H]$ decreases. Such a situation was apparently observed by Attwood and Stedman, who obtained excellent plots of $\log(A_\infty - A)$ against time, where A is the absorbance at 372 nm. However, we observed quite different behaviour from this in the early stages of the reaction. Typical results are shown in Figure 1 where it may be seen that the reaction occurs in three stages. Figure 1 shows the variation of the unconsumed $[HNO_2]$ in the analytical reaction with the time of sampling for repeat runs under the same conditions. At zero time,

the extrapolated value of $[HNO_2]$ corresponds exactly to the excess of nitrous acid over sulphamic acid for the analysis conditions. Values of $[HNO_2]$ then increase for successive samples, giving a maximum value at *ca.* 1–2 min reaction time which is equal to the total amount of nitrous acid present in the analytical process, *i.e.* NH_2SO_3H had been completely converted into a compound that did not react with HNO_2 . However, further samples, instead of also giving this high nitrous acid level, then showed a decrease in residual $[HNO_2]$ so that under these conditions at *ca.* 15–20 min the nitrous acid concentration equalled that found at zero time of reaction, *i.e.* NH_2SO_3H has now been completely converted into a second intermediate that could

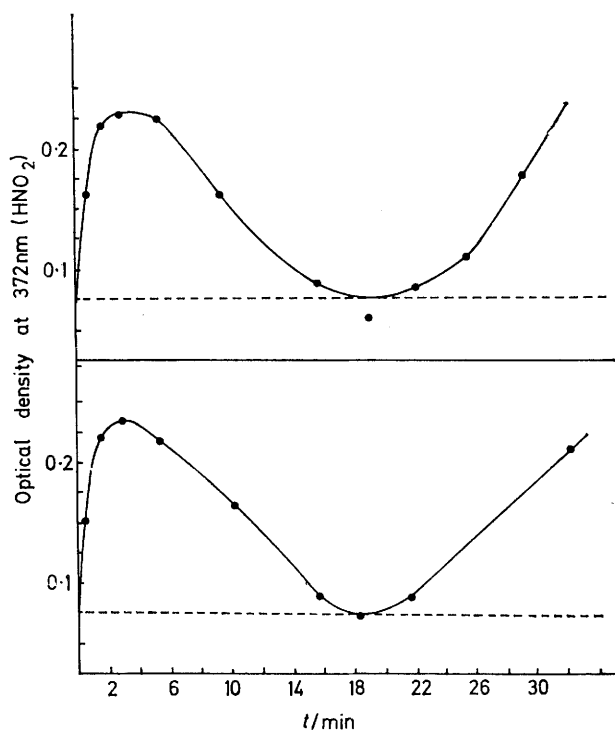


FIGURE 1 Variation in $[HNO_2]$ in the analytical reaction with time of sampling at 70 °C, $[HNO_3] = 8.6$ mol dm⁻³, and $[NH_2SO_3H] = 0.018$ mol dm⁻³.

react with HNO_2 . Finally, in the third and slow stage of the reaction, successive reaction samples leave increasing amounts of unchanged HNO_2 . This effect appears not to have been observed by Attwood and Stedman, whose results correspond to the third stage of our results.* Nevertheless it seems certain that the reaction proceeds in three consecutive stages, which under certain conditions appear to be largely independent of each other. Our kinetic results relate to the third stage of the reaction, and so describe the reaction of some intermediate species, and not the electrophilic displacement of $[SO_3H]^+$ by $[NO_2]^+$. The first stage of our reaction probably reflects the attack of $[NO_2]^+$ on NH_2SO_3H to give a nitro-derivative which subsequently decomposes.

The numerical data of Attwood and Stedman agree well with our own kinetic results for the third stage of the

* These workers accept this observation; G. Stedman, personal communication.

⁸ E. E. Archer, *Analyst*, 1957, **82**, 308.

⁹ M. N. Hughes and J. R. Lusty, *J.C.S. Dalton*, 1977, 509.

reaction. Values of their rate constants fall exactly on our plot of k_1 against H_0 . Our results obtained by measuring the production of sulphate also fall exactly on this plot, so it is clear that sulphate is produced in this third stage. The sulphate-analysis method could not be used in the early stages of the reaction as the amount of sulphate present is too small to be analysed. It was not possible to check precisely, therefore, that sulphate was not produced in the first stages of the reaction, but this fact is suggested indirectly by the failure to extrapolate a graph of sulphate production against time to zero time. Gas-evolution studies were carried out at a lower temperature (50 °C), but parallel runs followed by sulphate production for comparison purposes gave very similar rate constants (Table 1).

TABLE 1

Measured first-order rate constants for the sulphamic acid-nitric acid reaction in nitric acid solutions

(a) Followed by sulphate analysis at 70 °C				
[HNO ₃]/mol dm ⁻³	0.274	0.548	1.10	2.74
10 ⁵ k ₁ /s ⁻¹	1.27	1.28	1.31	1.53
[HNO ₃]/mol dm ⁻³	5.48	6.57	8.21	10.95
10 ⁵ k ₁ /s ⁻¹	2.26	3.10	5.45	32.6
[HNO ₃]/mol dm ⁻³	12.05	12.6	12.87	13.14
10 ⁵ k ₁ /s ⁻¹	60.4	82.7	91.4	137
[HNO ₃]/mol dm ⁻³	13.69	14.24	14.51	14.79
10 ⁵ k ₁ /s ⁻¹	221	367	471	635

(b) Followed by nitrous acid technique

θ _c /°C	[HNO ₃]/mol dm ⁻³	10 ⁵ k ₁ /s ⁻¹
65	11.52	13.5
	12.44	21.9
	12.96	34.3
	13.52	55.7
	14.81	188
75	11.52	37.8
	14.14	302
	14.81	550

(c) Followed by N₂O analysis at 51 °C

[HNO ₃]/mol dm ⁻³	10 ⁵ k ₁ /s ⁻¹	
	N ₂ O	[SO ₄] ²⁻
12.60	8.82	8.20
13.69	28.8	28.8

If N₂O is produced from the decomposition of NH₂NO₂ then this must be a fast step, in accord with studies that we have carried out¹⁰ on the decomposition of this molecule at high acidity and temperature, which show that the rate of decomposition of nitroamine is some hundred times faster than the rate of the third stage of the NH₂SO₃H-HNO₃ reaction under the same conditions. Values of k_1 determined by all the three methods are given in Table 1; most measurements have been made with the sulphate-determination method. Most values of k_1 are the means from several determinations over a five-fold range of sulphamic acid concentration (0.02–0.10 mol dm⁻³).

The third stage of the reaction is first order in [NH₂SO₃H], excellent plots of log(optical density) against time being obtained, while values of the measured first-order rate constants (k_1) are independent of [NH₂SO₃H]. Values of k_1 increase with nitric acid concentration. A plot of log k_1 against the acidity function H_0 gives a good straight line of gradient 1.80, thus suggesting a mechanism involving the nitryl cation since the rates of such reactions are known to depend on the acidity function H_R , and $H_R \sim 2H_0$. The plot

of log k_1 against H_R is a good straight line with a gradient of ca. 0.7. The results at low [HNO₃] do not fit into this picture since the competing hydrolysis reaction is important, the rate constant at low [HNO₃] being close to that determined independently⁹ for the hydrolysis of NH₂SO₃H in HClO₄.

In order to investigate the dependence of the rate on [NO₃⁻], the reaction was studied in perchloric acid solutions with various amounts of sodium nitrate present. The results are shown in Table 2. The constancy of the values

TABLE 2

First-order rate constants for the reaction^a in nitrate-perchloric acid at 70 °C

(a) [HClO ₄] = 6.78 mol dm ⁻³					
[NO ₃ ⁻]/mol dm ⁻³	0.457	0.686	0.914	1.142	1.486
10 ⁵ k ₁ /s ⁻¹	7.58	11.3	14.0	17.9	24.2
10 ⁵ k ₂ /dm ³ mol ⁻¹ s ⁻¹	1.66	1.65	1.53	1.56	1.63
(b) [HClO ₄] = 5.09 mol dm ⁻³					
[NO ₃ ⁻]/mol dm ⁻³	0.570	0.686	0.914	1.143	
10 ⁵ k ₁ /s ⁻¹	1.55	2.05	2.30	2.73	
10 ⁵ k ₂ /dm ³ mol ⁻¹ s ⁻¹	2.72	2.99	2.51	2.40	
(c) [HClO ₄] ^b = 2.71 mol dm ⁻³					
[NO ₃ ⁻]/mol dm ⁻³	0.457	0.685	1.03	1.37	1.71
10 ⁵ k ₁ /s ⁻¹	1.25	1.35	1.45	1.68	1.87
10 ⁵ (k ₁ - k ₀)/s ⁻¹	0.23	0.33	0.43	0.66	0.85
10 ⁵ k ₂ /dm ³ mol ⁻¹ s ⁻¹	0.503	0.482	0.418	0.482	0.497

^a Followed by sulphate analysis. ^b k₀ = 1.02 × 10⁻⁵ s⁻¹.

of k_1 /[NO₃⁻] = k_2 at [HClO₄] = 6.78 and 5.09 mol dm⁻³ confirms that the reaction is first order with respect to [NO₃⁻]. Results at [HClO₄] = 2.71 mol dm⁻³ gave a rather different picture, a plot of k_1 against [NO₃⁻] giving an intercept (k_0) of 1.02 × 10⁻⁵ s⁻¹ on the k_1 axis. This corresponds to the first-order rate constant for the hydrolysis of sulphamic acid. The rate constant for reaction with nitrate is given by ($k_1 - k_0$). Values of ($k_1 - k_0$)/[NO₃⁻] are constant. This first-order dependence on [NO₃⁻] was independently observed by Attwood and Stedman.⁸

The reaction in nitric acid (of 12.6 and 13.69 mol dm⁻³) has been studied over the range 41–79 °C (Table 3) and

TABLE 3

Temperature dependence

[HNO ₃] = 12.60 mol dm ⁻³		[HNO ₃] = 13.69 mol dm ⁻³	
θ _c /°C	10 ⁵ k ₁ /s ⁻¹	θ _c /°C	10 ⁵ k ₁ /s ⁻¹
41.5	2.04	41.5	6.95
51.0	8.15	52.0	28.8
55.5	18.0	55.5	46.0
65.0	24.2*	65.0	63.3*
70.0	82.7	70.0	222
79.0	266	79.0	771

* Followed by the nitrous acid technique; the value falls on the Arrhenius plot. All other runs were followed by the sulphate technique.

gives a value for the activation energy of 121 kJ mol⁻¹ compared with that of Attwood and Stedman of 106 kJ mol⁻¹.

It is important that additional studies be carried out on the first two stages of the reaction. We have done little

¹⁰ M. N. Hughes and J. R. Lusty, in preparation.

on the first stage other than to establish its existence, but the effect of $[\text{HNO}_3]$ on the second stage is shown in Figure 2. This reaction is clearly retarded by high $[\text{HNO}_3]$, values of $k'[\text{HNO}_3]$ being approximately constant, where k' is the measured first-order rate constant for the second stage.

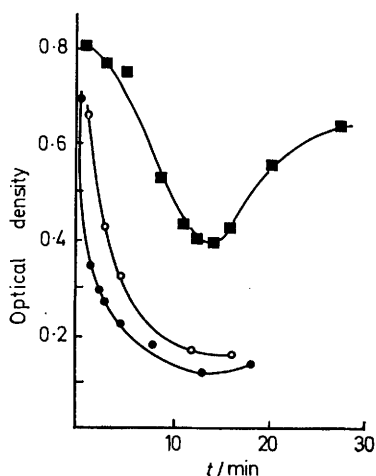


FIGURE 2 Effect of $[\text{HNO}_3]$ on the stages of the reaction at 75 °C: $[\text{HNO}_3] = 6.57$ (●), 9.20 (○), and 13.8 mol dm⁻³ (■)

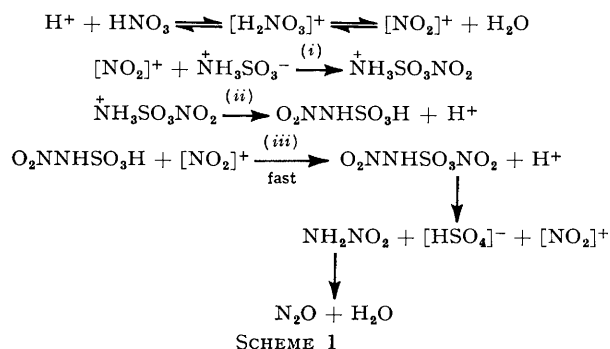
Values of k' at $[\text{HNO}_3] = 13.8, 9.20,$ and 6.57 mol dm⁻³ are $1.8 \times 10^{-2}, 2.2 \times 10^{-2},$ and 2.2×10^{-2} dm³ mol⁻¹ s⁻¹ respectively.

DISCUSSION

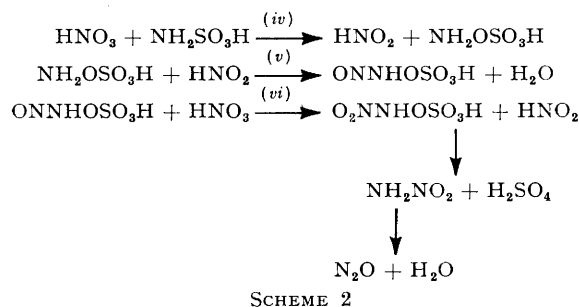
The results show that the nitric acid–sulphamic acid reaction involves an addition of a $[\text{NO}_2]^+$ group followed by rearrangement and elimination, rather than a direct displacement of $[\text{SO}_3\text{H}]^+$. The fact that sulphate and N_2O production occur at the same rate indicates that if nitroamine is an intermediate then it must occur as a rapidly decomposing species at the end of the reaction sequence, in accord with its known instability under those conditions.

Any reaction scheme must postulate intermediates that will react or not react with nitrous acid in accord with the results obtained using HNO_2 as an analytical reagent. In addition it must account for the dependence on $[\text{NO}_3^-]$ of the rate of the third stage of the reaction by either invoking the direct involvement of $[\text{NO}_2]^+$ in this stage or by postulating species which are related to $[\text{NO}_2]^+$ by a series of equilibria. The former possibility is accommodated by a second nitration reaction in the third stage, provided that the stoichiometry of the reaction is unaffected. An additional complication lies in deciding whether sulphamic acid reacts as the zwitterion $\overset{+}{\text{N}}\text{H}_3\text{SO}_3^-$ or the uncharged species $\text{NH}_2\text{SO}_3\text{H}$. Initial *O*-nitration of the zwitterion will give a mixed acid anhydride which could still rearrange to the *N*-nitro-species. A possible reaction sequence is illustrated in Scheme 1 which involves an initial *O*-nitration. The product of reaction (i) on dilution in the nitrous acid analytical medium will give $\text{NH}_2\text{SO}_3\text{NO}_2$, which must

not be able to react with HNO_2 . The product of reaction (ii) on dilution will be $[\text{O}_2\text{NNHSO}_3]^-$ which must either react with nitrous acid or decompose to give a species (nitroamine) that will react¹¹ with HNO_2 . Nevertheless, in the concentrated acid medium it must survive long enough to undergo further nitration to give an unstable species that breaks down to NH_2NO_2 , sulphate, and $[\text{NO}_2]^+$.



Reaction schemes not involving initial nitration should also be considered. An example could involve oxygen-atom transfer from nitric acid to sulphamic acid generating HNO_2 and $\text{NH}_2\text{OSO}_3\text{H}$. This would account for the decrease in consumption of nitrous acid on analysis of successive samples in the first stage of reaction, provided that HNO_2 and $\text{NH}_2\text{OSO}_3\text{H}$ react readily on dilution so that there is no compensating overall production of HNO_2 in the parent reaction. A possible second stage in this scheme could be reaction between the $\text{NH}_2\text{OSO}_3\text{H}$ and the HNO_2 produced during the first stage giving an *N*-nitroso-species $\text{ONNHOSO}_3\text{H}$, which decomposes on dilution giving a species capable of reacting with HNO_2 and which on further standing in the concentrated nitric acid solution reacts with $[\text{NO}_2]^+$ to give NH_2NO_2 and sulphate (Scheme 2). An attractive



alternative would be to postulate the hydrolysis of $\text{NH}_2\text{OSO}_3\text{H}$ in the nitric acid medium in the second stage to give hydroxylamine, which would then react with the nitrous acid produced in step (iv) to give N_2O . However, this does not accommodate the dependence of rate on $[\text{NO}_2]^+$ or the sulphate production in the third stage of the reaction.

¹¹ M. N. Hughes and J. R. Lusty, *J.C.S. Dalton*, 1976, 1175.

Attempts to confirm the validity of such schemes by noting the production of HNO_2 in the reaction mixture in the first stage of the reaction were unsuccessful. All attempts to identify intermediates by u.v. difference spectroscopy and by chemical tests were unsuccessful. It is hoped in the near future to carry out stopped-flow

studies on the early stage of the reaction and to make further attempts to identify intermediates.

We thank the S.R.C. for the award of a studentship (to J. R. L.).

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