Notes

Nitrogen Tracer Studies on the Decomposition of Hydroxylamine in Nitric Acid

Michael S. Garley, Kieran G. Phelan, and Geoffrey Stedman *
Chemistry Department, University College of Swansea, Singleton Park, Swansea SA2 8PP

The reaction of low concentrations of $[^{15}NH_3OH]^+$ with isotopically normal nitric acid produces singly labelled N_2O with equal amounts of ^{15}NNO and $N^{15}NO$ and very little $^{15}N_2O$, but as $[^{15}NH_3OH^+]$ increases there is an increasing amount of $^{15}N_2O$ formed, the highest observed yield being $[^{15}N_2O]/[N_2O]_{total} = 0.23$. This increase occurs as the system changes from one in which there is a net increase in nitrous acid due to oxidation of hydroxylamine to one in which hydroxylamine acts as a net scavenger of nitrous acid.

During a study of the oxidation of hydroxylamine by nitric acid to form dinitrogen monoxide + nitrous acid, tracer experiments were carried out[1] using $[^{15}NH_3OH]^+$ reacting with isotopically normal HNO_3. Mass-spectrometric analysis of the N_2O showed it to be singly labelled with ^{15}N, the tracer being distributed equally between the two nitrogens, with only a small percentage of doubly labelled N_2O. This distribution of tracer was very similar to that observed in the N_2O formed in the reaction between HNO_2 and $[^{15}NH_3OH]^+$ and clearly indicated that the N_2O was formed by reaction (1). The small proportion of $^{15}N_2O$ enabled us to reject mechanisms involving the dimerisation of nitroxyl (HNO) of the type often postulated as a pathway for the formation of N_2O such as those shown in equations (2) and (3). However in two experiments some 20% of $^{15}N_2O$ was observed, and this has now been investigated in more detail to see if it required the presence of a nitroxyl dimerisation pathway. Recent work[2] has placed emphasis on pathways of this type.

$$HNO_2 + [NH_3OH]^+ \longrightarrow N_2O + H_2O + [H_3O]^+ \quad (1)$$

$$[NH_3OH]^+ - 2e \longrightarrow HNO + 3H^+ \quad (2)$$

$$2HNO \longrightarrow N_2O + H_2O \quad (3)$$

Experimental

Hydroxylamine hydrochloride, labelled with ^{15}N to 97 atom % (Prochem), was used without further purification. The procedures used were identical to those described previously.[1] For some experiments at high $[^{15}NH_3OH^+]$ the amount of N_2O liberated was rather small, and this reduced the accuracy of the mass-spectrometric analyses. Experiments were carried out at ambient temperature, 20 ± 2 °C.

Computer simulations used a standard Runge–Kutta numerical integration program to integrate the differential equations corresponding to our published mechanism for this reaction. This program has already been used to simulate aspects of the kinetic behaviour of the hydroxylamine–nitric acid–nitrous acid system and the results have been published.[3] It was modified to distinguish between nitrogen atoms derived from $[^{15}NH_3OH]^+$, assumed 100% isotopic purity, and from the nitric acid and nitrous acid which were assumed to be 100% ^{14}N at the start of reaction. The calculations were made for the same system studied previously, 4.28 mol dm^{-3} nitric acid containing initially 8×10^{-4} mol dm^{-3} nitrous acid at 25 °C, with a range of different initial hydroxylamine concentrations. The rate constants used were the same as those used previously and gave the following expressions for the rate of reactions (4)—(6) and (9): $V(4) = 2.28\ [HNO_2]$ mol dm^{-3} s^{-1}; $V(9) = 20.6\ [HNO_2][NH_3OH^+]$ mol dm^{-3} s^{-1}; $V(6)/V(5) = 0.187\ [NH_3OH^+]^{-1}$.

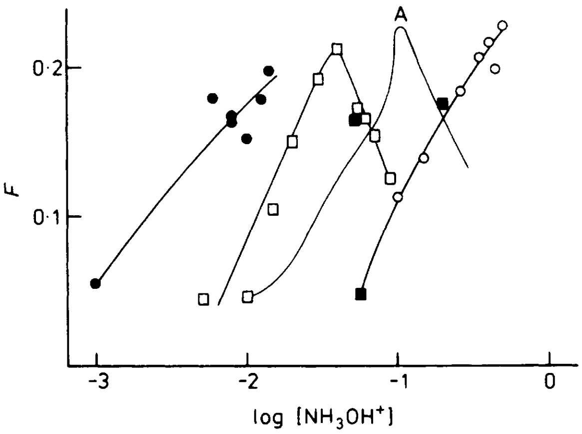

Figure. Plot of the fraction of doubly labelled dinitrogen monoxide, *F*, as a function of log $[NH_3OH^+]$. $[HNO_3]$/mol dm^{-3} = 2.5 (●), 3.5 (□), and 5.0 (○). ■, Earlier measurements described in ref. 1; A, curve calculated for reaction in 4.28 mol dm^{-3} nitric acid

Results and Discussion

The most complete set of experiments covered the range $[^{15}NH_3OH^+] = 0.005$—0.5 mol dm^{-3} in 3.5 mol dm^{-3} nitric acid, and are shown in the Figure. At low $[^{15}NH_3OH^+]$ there is only a small amount of $^{15}N_2O$, but as the hydroxylamine concentration increased the ratio of the ion-current peaks $F = 46/(44 + 45 + 46)$ rises, reaches a maximum, and then decreases. Less extensive measurements in 5.0 mol dm^{-3} nitric acid showed a similar rise in *F* with $[^{15}NH_3OH^+]$, but over the more limited concentration range studied there was no evidence for a maximum. The results for 2.5 mol dm^{-3} nitric acid are clustered, and the line drawn through them is only justified by analogy with the results for the other two acidities. Included in the Figure are the earlier observations that stimul-

Table. Computer simulation of the decomposition of $[^{15}NH_3OH]^+$ in 4.28 mol dm^{-3} nitric acid at 25 °C

$10^2[^{15}NH_3OH^+]_0$/mol dm^{-3}	1	2	4	7	7.5	10	15	20	25	30
100 F	4.5	7.9	12.5	16.5	17.9	22.7	20.0	17.4	15.2	13.5
$10[HNO_2]_\infty/[^{15}NH_3OH^+]_0$	5.19	4.35	3.34	2.30	1.86	0	0	0	0	0
$10[N_2O]_\infty/[^{15}NH_3OH^+]_0$	6.39	6.51	6.70	6.95	7.06	0.65	0.17	0.093	0.062	0.046
$10^2[^{15}NH_3OH^+]_\infty$/mol dm^{-3}	0.0	0.0	0.0	0.0	0.0	9.2	14.7	19.8	24.8	29.8

ated the present work. The results show some scatter, and this may reflect problems in obtaining reproducible mixing. Solutions of nitric acid and of the hydroxylamine salt were in separate legs of a two-legged vessel. As reaction was sometimes very rapid, it is doubtful if reproducible mixing conditions were attained.

We base our discussion on the mechanism in equations (1) and (4)—(8), discussed in detail in previous papers.[1,3]

$$H^+ + HNO_2 + [NO_3]^- \longrightarrow N_2O_4 + H_2O \quad (4)$$

$$N_2O_4 + H_2O \longrightarrow H^+ + HNO_2 + [NO_3]^- \quad (5)$$

$$N_2O_4 + NH_2OH \longrightarrow N_2O_3 + HNO + H_2O \quad (6)$$

$$N_2O_4 + HNO \longrightarrow N_2O_3 + HNO_2 \quad (7)$$

$$N_2O_3 + H_2O \longrightarrow 2HNO_2 \quad (8)$$

For low $[NH_3OH^+]$, $V(6) \gg V(5)$ and most of the N_2O_4 formed in (4) is hydrolysed back as shown in (5). The rapid formation and hydrolysis of N_2O_4 by (4) and (5) provides a pathway by which labelled nitrogen in HNO_2 is rapidly exchanged with the large excess of isotopically normal nitric acid. Thus although labelled HNO_2 is formed by oxidation of $^{15}NH_2OH$, the exchange reaction ensures that all the N_2O formed in (1) is derived from normal HNO_2 and $[^{15}NH_3OH]^+$, giving rise to equal amounts of ^{15}NNO and $N^{15}NO$.

As the concentration of hydroxylamine increases, an increasing proportion of the N_2O_4 is trapped by hydroxylamine, and $V(6) \gg V(5)$. Thus the route by which $H^{15}NO_2$ is exchanged with the large excess of nitric acid is removed, and the nitrous acid that reacts with $[^{15}NH_3OH]^+$ in (1) is a mixture of isotopically normal HNO_2 and $H^{15}NO_2$ derived from the route (6) and (7), $^{15}NH_2OH \longrightarrow H^{15}NO \longrightarrow H^{15}NO_2$. Thus the N_2O will be a mixture of $^{15}N^{15}NO$, ^{15}NNO, and $N^{15}NO$. If there were no exchange of nitrogen between HNO_2 and nitric acid, then a simple calculation shows that one should get 33.3% of doubly labelled N_2O and 66.6% of singly labelled N_2O. This will be an overestimate, because even if $[NH_3OH^+]$ was sufficiently high to ensure complete trapping of N_2O_4 at the start of the reaction, as the reaction proceeds hydroxylamine will be consumed and $V(6)/V(5)$ must fall. In the last stages of reaction the value of $[NH_2OH]$ will be low and the exchange reaction (4) + (5) will proceed.

Further insight can be obtained by use of a computer program to integrate numerically the differential equations corresponding to (1) and (4)—(8), distinguishing between nitrogen atoms derived from $[^{15}NH_3OH]^+$ and those from HNO_2 and HNO_3. The integration was initially carried out using a set of rate constants for 4.28 mol dm^{-3} nitric acid that were used in calculations previously reported. This gave curve A in the Figure. The maximum in the plot of F against log $[NH_3OH^+]$ is reproduced satisfactorily, and the curve falls almost midway between the points measured for 3.5 and 5.0 mol dm^{-3}. The calculations show that the maximum in F is associated with a change in chemistry. At low values of $[NH_3OH^+]$ the nitrite-generating reactions (6)—(8) dominate the nitrite-scavenging process (1) and reaction involves a net formation of the catalytic species HNO_2. All the hydroxylamine is destroyed, $[HNO_2]_\infty$ has a finite value, and $[NH_3OH^+]_\infty = 0$. At higher values of $[NH_3OH^+]_0$ the nitrite-scavenging process dominates, and all the HNO_2 is consumed before the $[NH_3OH]^+$ has completely reacted, *i.e.* $[HNO_2]_\infty = 0$ and $[NH_3OH^+]_\infty$ has a finite value. At these higher concentrations of $[^{15}NH_3OH]^+$ only a small amount of the hydroxylamine is oxidised to $H^{15}NO_2$ and the relative amounts of doubly and singly labelled N_2O depend on the amount of isotopically normal HNO_2 present initially and the amount of $H^{15}NO_2$ generated by the oxidation of $[^{15}NH_3OH]^+$. The yield of N_2O formed in the reaction with high concentrations of hydroxylamine is calculated to be quite low, and this probably accounts for the small amounts found in some of our experiments.

Although this approach enables us to understand the shape of the curve of F against log $[NH_3OH^+]$, and the occurrence of a maximum, its quantitative success depends upon the values assigned to the rate constants. The curve for 4.28 mol dm^{-3} nitric acid fits well into the pattern of experimental results, but attempts to extend the calculation to 2.5, 3.5, and 5.0 mol dm^{-3} were less successful. The shapes of the calculated curves were similar to that of A, and were in the expected sequence along the abscissa, but agreement with the experimental points was not good. Agreement can be improved by changing the values assigned to the rate constants, but we were not able to predict accurately the appropriate value on a chemical basis. The value for the rate constant for reaction (1) in nitric acid was predicted from measurements on this reaction in perchloric acid, and at a mineral acid concentration of several mol dm^{-3} there could well be substantial specific salt effects. It has been shown[4] that there are marked differences between perchloric and sulphuric acids. In predicting the variation of $V(5)/V(6)$ with $[HNO_3]$ we needed an acidity function to describe the protonation of NH_2OH. We used the H_0 acidity function, but recognise that it may not adequately describe the protonation of NH_2OH, as it uses indicator bases with a very different structure. With these uncertainties, and the limitations of the isotopic results, we do not think it worth pursuing these calculations further.

We conclude that the appearance of a substantial proportion of doubly labelled N_2O is a sign that the hydroxylamine–nitric acid–nitrous acid system is near the borderline where the chemical role of hydroxylamine changes from an autocatalytic decomposition that forms nitrous acid to a process whereby it scavenges nitrous acid. Although the dimerisation of nitroxyl is a well established route for the formation of N_2O in many reactions there is no compelling evidence to include it in the mechanism for the decomposition of hydroxylamine in nitric acid.

Acknowledgements

The present work was carried out with support from a C.A.S.E. award from A.E.R.E., Harwell, and British Nuclear Fuels Ltd. The mass-spectrometric analyses were carried out at Harwell.

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Received 13th September 1983; *Paper* 3/1609