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The Acid-catalysed Decomposition of Nitroamine ((NH_2NO_2))

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The decomposition of nitroamine (previously called nitramide) is of classical significance in the development of theories of general-base catalysis. It is probably the most studied example of a general-base catalysed reaction. Nevertheless recent studies [1] have shown that decomposition occurs by two parallel pathways, the traditional general-base catalysed reaction of the *aci*-form of nitroamine, and the general-base catalysed decomposition of the nitroamine anion. An acid catalysed decomposition has also been established [2] for hydrochloric acid solutions up to 2.0 mol dm^{-3}, with a 30% increase in rate constant over this range compared to the value in neutral or weakly acid solutions. We have studied [3] this reaction in a range of mineral acids up to about 8 mol dm^{-3} and have confirmed the presence of the acid-catalysed pathway. In this communication we report the results of experiments using oxygen-18 labelled water, which show that the dinitrogen monoxide produced by the acid-catalysed pathway contains oxygen-18.

Experimental

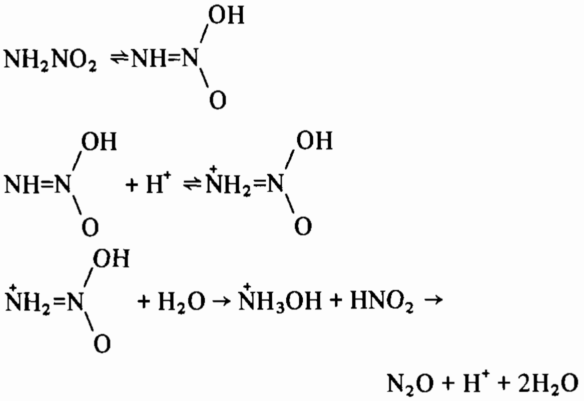
Nitroamine was prepared by the nitric acid-sulphamic acid reaction as described earlier [4] Oxygen-18 enriched water with 2.8 atom percent excess was used, allowance being made for the water added with the perchloric acid. Reactions were carried out using an inverted Y tube, with solid nitroamine in one leg and $H_2^{18}O/HClO_4$ in the other. After cycles of freezing, evacuation and degassing, the Y tube was tipped to initiate reactions. At the completion of the reaction the solution was frozen in CO_2/acetone slush and the dinitrogen monoxide transferred to storage bulbs prior to analysis for oxygen-18 on an AEI MS20 mass spectrometer on the University of London Intercollegiate Research Service at University College London.

Results and Discussion

The dinitrogen monoxide produced in neutral or weakly acid solution did not contain oxygen-18. As the acidity of the reaction is increased so the dinitrogen monoxide contains greater amounts of oxygen-18. By 7.0 mol dm^{-3} [$HClO_4$] the oxygen-18 content in the dinitrogen monoxide equalled that in the solvent water, as shown below.

[$HClO_4$]/mol dm^{-3}	4.0	4.0	7.0	9.0
[$N_2^{18}O$]/[$H_2^{18}O$]	0.70	0.75	0.99	1.00

These results eliminate earlier mechanisms [2] for the acid-catalysed reaction. We suggest a scheme in which solvent water attacks the amino nitrogen of the protonated *aci*-form of nitroamine, giving hydroxylamine and nitrous acid, which then react together to give dinitrogen monoxide *via* intermediate formation of hyponitrous acid [5].



$$NH_2NO_2 \rightleftharpoons NH{=}\overset{OH}{\underset{O}{N}}$$

$$NH{=}\overset{OH}{\underset{O}{N}} + H^+ \rightleftharpoons \overset{+}{N}H_2{=}\overset{OH}{\underset{O}{N}}$$

$$\overset{+}{N}H_2{=}\overset{OH}{\underset{O}{N}} + H_2O \rightarrow \overset{+}{N}H_3OH + HNO_2 \rightarrow N_2O + H^+ + 2H_2O$$

The hydroxylamine produced in this reaction will be labelled, while the nitrous acid will exchange oxygen with the solvent *via* the formation of N_2O_3. The hyponitrous acid will thus be labelled at both oxygen atoms, so giving at high acidity a level of oxygen-18 in the dinitrogen monoxide equal to that in the solvent water. Reaction of labelled hydroxylamine with unlabelled nitrous acid would give a maximum level of isotope in the dinitrogen monoxide equal to only half that in the water through the decomposition of $H\overset{*}{O}NNOH$.

Acid catalysed nucleophilic attack of water at the amino nitrogen is favoured by protonation of the site, while the neutral nitrous acid molecule will be a good leaving group. Other examples are known in which hydroxylamine is generated by nucleophilic attack of water or hydroxide on substituted amines, for example, $NH_2OSO_3^-$.

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