Reduction of Nitroamine (NH_2NO_2) by Vanadium(II) and Chromium(II) in Acid Solution

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Reaction of nitroamine with vanadium(II) involves a two-electron reduction to dinitrogen, $NH_2{}^{15}NO_2$ giving $^{14}N-^{15}N$. Reduction of nitroamine by chromium(II) gives dinitrogen and ammonia, with an overall stoicheiometry of $\Delta[Cr^{II}] : \Delta[NH_2NO_2]$ *ca.* 6 : 1. Hydrazine could not be detected in the nitroamine–Cr^{II} reaction. A possible mechanism for this reaction is discussed, in which a hydrazido-complex of chromium is postulated to be an intermediate.

WHILST the base-catalysed decomposition of nitroamine has been much investigated in studies of classical significance,[1] other aspects of its solution chemistry are only poorly characterised. An exception to this is its reaction with nitrous acid.[2] We now report details of the reduction of nitroamine by chromium(II) and vanadium(II).

EXPERIMENTAL

Nitroamine was prepared by a modification [2] of a literature method [3] involving the reaction of nitric acid with sulphamic acid. Nitrogen-15-labelled nitroamine, $NH_2{}^{15}NO_2$, was prepared from $H^{15}NO_2$ supplied by Prochem (98.6% ^{15}N). All other chemicals were of AnalaR grade. Solutions of chromium(II) were prepared by passing an acidified solution of 0.1 mol dm^{-3} chromium(III) chloride down a Jones-reductor column. The resulting solutions of chromium(II) were standardised before use.[4] Solutions of vanadium(II) were prepared by reducing solutions of ammonium vanadate with zinc amalgam. Ammonium vanadate solutions were prepared by dissolving the solid in alkali and then acidifying with dilute sulphuric acid solution.

The stoicheiometry of the reduction of nitroamine by vanadium(II) was determined by adding a known volume of standard vanadium(II) solution to a weighed amount of nitroamine under an inert atmosphere. After the reaction was complete, excess of ammonium vanadate solution was added to convert unreacted V^{II} and any intermediate oxidation states into the air-stable vanadyl ion. The resultant solution was then titrated with a standard solution of potassium permanganate. By comparing this result with the amount of vanadium(II) originally present it was possible to calculate the number of electrons involved in the reduction of nitroamine. The stoicheiometry of the chromium(II)-nitroamine reaction was determined by adding an excess of chromium(II) to nitroamine. When the reaction was complete, the excess of chromium(II) was estimated by adding a known amount of copper(II) sulphate solution and back-titrating for excess of copper(II) with the solution of chromium(II). All end-points were determined potentiometrically under an oxygen-free atmosphere.

The gaseous products were analysed using an AEI MS20 mass spectrometer. Solutions of the reducing agent were placed in one arm of a Y tube and solid nitroamine in the other. The system was degassed thoroughly and the reactants mixed, the gas produced being analysed. Yields of dinitrogen were estimated manometrically.

Yields of ammonia were determined by making alkaline the final reaction solution and distilling off all ammonia into a known volume of standard acid, which was subsequently titrated with standard alkali. The presence of hydrazine was tested for with Ehrlich's reagent (4-dimethylaminobenzaldehyde in hydrochloric acid solution).

RESULTS

Reduction with Vanadium(II).—The reaction between nitroamine and vanadium(II) in acid solution occurred rapidly at room temperature with a vigorous evolution of gas. Mass spectroscopic studies indicated that the only gaseous product was dinitrogen. The product from the reduction of $NH_2{}^{15}NO_2$ was $^{14}N-^{15}N$, while no species of mass number 30 was detected. In these experiments with labelled nitroamine, *ca.* 2% of the total dinitrogen was $^{14}N-^{14}N$, in accord with the original ^{15}N enrichment. Manometric studies indicated that the production of dinitrogen from the vanadium(II) reduction of nitroamine corresponded to over 90% of the reaction. No other products could be detected in solution, so it is assumed that nitroamine is reduced quantitatively to dinitrogen. The data in Table 1 show that for a range of $[V^{II}]/[NH_2NO_2]$ values, two electrons are transferred for each molecule of nitroamine reduced [equation (1)].

TABLE 1

Reduction of nitroamine with V^{II} * in sulphuric acid solution

$[H_2SO_4]$/ mol dm^{-3}	$10^{-4}[NH_2NO_2]$/ mol dm^{-3}	Electrons per NH_2NO_2
0.405	1.07	1.95
0.405	0.947	2.17
0.405	0.881	1.97
0.405	0.715	1.97
0.405	0.654	1.94
0.405	0.601	2.17
0.405	0.535	2.16
0.405	0.476	2.31
1.335	0.788	2.05
1.335	0.690	1.80
1.335	0.510	2.10
1.335	0.443	2.12

* $[V^{II}] = 2.14 \times 10^{-4}$ mol dm^{-3}.

$$NH_2NO_2 \xrightarrow[2e]{2H^+} N_2 + 2H_2O \qquad (1)$$

Under the conditions used in these experiments, the reaction is over in a few seconds. An attempt was made to study the kinetics of the reaction using stopped-flow techniques and using an excess of nitroamine over vanadium(II). However, there was interference from the production of bubbles of dinitrogen and accurate rate constants could not be determined.

Reduction with Chromium(II).—Addition of nitroamine to an acidic solution of chromium(II) at room temperature resulted in an evolution of dinitrogen, as shown mass spectroscopically. Quantitative measurements suggest that up to 25% of the nitroamine was converted into dinitrogen. No evidence could be found for the formation of hydrazine, but ammonia could be detected on alkaline distillation of the product solution. The production of ammonia is shown in Table 2, where it can be seen that 71—79% of the nitroamine is reduced to ammonia. The stoicheiometry of the Cr^{II}–nitroamine reaction is shown in Table 3 and is approximately 6 : 1. This value reflects the relative contributions of the two-electron and eight-electron reductions of nitroamine to dinitrogen and ammonia.

TABLE 2

Production of ammonia in the Cr^{II}–NH_2NO_2 reaction

$[H_2SO_4]$/ mol dm^{-3}	$10^3[Cr^{II}]$/ mol dm^{-3}	$10^4[NH_2NO_2]$/ mol dm^{-3}	$10^4[NH_3]$/ mol dm^{-3}	$\frac{10^2\Delta[NH_3]}{2\Delta[NH_2NO_2]}$
0.05	7.90	7.66	11.7	76
0.20	7.50	12.3	19.5	79
0.20	8.63	7.82	11.0	71
1.00	7.20	11.8	18.8	79
1.00	7.50	7.16	11.0	76

TABLE 3

Reduction of nitroamine by Cr^{II} in sulphuric acid solutions

$[H_2SO_4]$/ mol dm^{-3}	$10^3[Cr^{II}]$/ mol dm^{-3}	$10^4[NH_2NO_2]$/ mol dm^{-3}	$\frac{\Delta[Cr^{II}]}{\Delta[NH_2NO_2]}$
0.05	3.95	3.79	5.88
0.20	4.12	4.32	5.93
0.20	4.33	4.26	5.90
0.20	3.00	3.90	5.92
1.00	3.71	3.40	6.46

Nitroamine is stable with respect to hydrolysis under the conditions of all the experiments described above. This is confirmed by the absence of dinitrogen monoxide in the gaseous products.

DISCUSSION

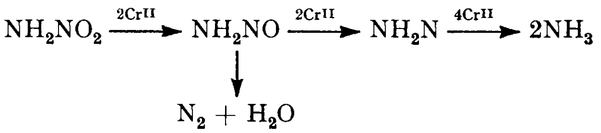
It seems reasonable that the initial steps in the reduction of nitroamine by V^{II} and Cr^{II} are similar, the differences arising at a later stage and probably reflecting the binding of intermediates to the inert Cr^{III}. The simplest mechanism for reduction by V^{II} involves the formation of NH_2NO in a two-electron reduction, NH_2NO then undergoing loss of water to give dinitrogen. The production of ^{14}N–^{15}N from $NH_2{}^{15}NO_2$ suggests that N–N bond fission does not occur. The two-electron reduction by V^{II} could involve inner-sphere oxygen-atom transfer from nitroamine to give VO^{2+} [equations (2) and (3)].

$$V^{II} + NH_2NO_2 \longrightarrow NH_2NO + VO^{2+} \qquad (2)$$

$$NH_2NO \longrightarrow N_2 + H_2O \qquad (3)$$

Reduction with Cr^{II} yields dinitrogen and ammonia, the stoicheiometry of 6 : 1 reflecting the balance between these two products. It should be noted, however, that the stoicheiometric ratio $[Cr^{2+}]:[NH_2NO_2]$ should be greater than the quoted value in order to accommodate the production of some 76% NH_3 and 24% N_2 (based upon the mean value in Table 2), namely $[Cr^{2+}]:[NH_2NO_2] = 6.56:1$. It is probable that this difference is not significant.

Hydrazine could not be detected as a product of the reaction by using Ehrlich's reagent, although added trace amounts of hydrazine could be detected quantitatively. It is also well known that Cr^{II} cannot reduce hydrazine, so it seems clear that hydrazine cannot lie on the reaction pathway to ammonia, a point of some interest. The following scheme is suggested; intermediates will be bound to Cr^{III}. Support for this



$$\begin{tikzcd} NH_2NO_2 \arrow[r, "2Cr^{II}"] & NH_2NO \arrow[r, "2Cr^{II}"] \arrow[d] & NH_2N \arrow[r, "4Cr^{II}"] & 2NH_3 \\ & N_2 + H_2O & & \end{tikzcd}$$

scheme comes from a consideration of the reduction of dinitrogen to ammonia in the complexes $[M(N_2)_2(PMe_2Ph)_4]$, where M = Mo or W. Chatt *et al.*[5] suggest that reduction occurs *via* the co-ordinated hydrazido-group, and that hydrazine does not lie on the main reaction pathway. This provides excellent evidence for the pathway suggested above for the reduction of nitroamine. The reduction of the Cr^{III}-bound hydrazide group probably involves steps (4) and (5).

$$CrNNH_2 \xrightarrow[H^+]{Cr^{II}} CrN + NH_3 \qquad (4)$$

$$CrN \xrightarrow[3H^+]{3Cr^{II}} Cr^{III} + NH_3 \qquad (5)$$

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