287. *The Oxidation of Hydrazine in Aqueous Solution. Part II.* The Use of ^{15}N as a Tracer in the Oxidation of Hydrazine.*

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The isotopic composition of nitrogen evolved in the oxidation of hydrazine containing 33 atom % of ^{15}N in the presence of a large excess of ordinary hydrazine has yielded information as to the extent of N–N bond fission in oxidation. As suggested in the preceding paper, oxidation by 1-electron-transfer oxidising agents and complex oxidising agents involves the simultaneous occurrence of two limiting reactions :

$$N_2H_4 \xrightarrow{-(e)} \tfrac{1}{2}N_2 + NH_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$N_2H_4 \xrightarrow{-4(e)} N_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In (1) the nitrogen atoms in half the evolved nitrogen molecules are derived from the same hydrazine molecule; in the other half the nitrogen atoms come from separate hydrazine molecules. In (2), which is also the sole reaction for 2-electron-transfer oxidation and for all oxidations in alkaline solution, no N–N fission occurs and no new N–N bonds are formed.

The nature of some of the radical intermediates is discussed.

THE reaction schemes for the oxidation of hydrazine in acid, aqueous solution discussed in Part I* can be confirmed to some extent by a study of the isotopic composition of the nitrogen formed in the oxidation of hydrazine enriched in ^{15}N. We have synthesised hydrazine from ammonia containing 33·4 atom % of ^{15}N. This hydrazine was assumed to contain the statistical proportions of $^{15}N_2H_4$, $^{15}NH_2{\cdot}^{14}NH_2$, and $^{14}N_2H_4$ in accordance with the expression $[^{15}NH_2{\cdot}^{14}NH_2]^2/([^{15}N_2H_4][^{14}N_2H_4]) = 4$. In dilute sulphuric acid this hydrazine was diluted with ordinary hydrazine sulphate (N_2H_4,H_2SO_4), the molar ratio of ^{15}N-enriched : ordinary hydrazine being 1 : 92·0. In this mixture the proportions of $^{15}N_2H_4$, $^{15}NH_2{\cdot}^{14}H_2$, and $^{14}N_2H_4$ no longer correspond to those of statistical equilibrium. The hydrazine sulphate mixture was then oxidised by an excess of various oxidising agents and the evolved nitrogen collected in each case and submitted to mass-spectroscopic analysis for the 28, 29, and 30 mass-number abundances (measured as the ratios 30 : 29 and 29 : 28). These abundance ratios for those reagents which react according to the equation $N_2H_4 \xrightarrow{-4(e)} N_2$ are recorded in Table 1. The abundance ratios

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and observed consumption of oxidising agent in equivalents per hydrazine molecule oxidised are recorded in Table 2 for other oxidising agents.

TABLE 1.

Reagent	Conditions	Isotope abundance ratios 30 : 29	29 : 28	^{15}N (%)
IO_3^-	0·1N-H_2SO_4	0·1022 ± 0·0003	0·01192 ± 0·00004	0·708
		0·1036 ± 0·0005	0·01197 ± 0·00002	0·714
Tl(III)	0·7N-$HClO_4$	0·1025 ± 0·0006	0·01208 ± 0·00005	0·718
$Fe(CN)_6^{3-}$	0·1N-NaOH	0·1026 ± 0·0005	0·01252 ± 0·00004	0·744
		0·1016 ± 0·0006	0·01196 ± 0·00007	0·710

If on quantitative oxidation of hydrazine to nitrogen, no fission of the N–N bonds occurs, the abundance ratios should be equal to those calculated for the hydrazine mixture, *i.e.*, 30 : 29 = 0·0987, 29 : 28 = 0·01247, ^{15}N = 0·736 atom %. If all the N–N bonds are broken in the oxidation, the statistical proportions of $^{15}N_2$, $^{15}N^{14}N$, and $^{14}N_2$ will be formed, and the abundance ratios can be calculated from the proportion of ^{15}N present (0·736 atom % as before) as 30 : 29 = 0·00371, 29 : 28 = 0·01482. Comparison shows that there is fairly good agreement between the experimental values and those calculated on the assumption that no N–N bond fission occurs. Exact agreement is not to be expected since isotope fractionation is likely to occur during the synthesis of the ^{15}N-enriched hydrazine; analysis of the nitrogen formed as by-product during the synthesis showed 32·85 atom % of ^{15}N instead of the 33·4 atom % of the ammonia used. Further, we have assumed that the nitrogen isotopes are distributed in ordinary hydrazine in exactly the statistical equilibrium proportions and that the amount of ^{15}N present is the same as in atmospheric nitrogen, 0·38 atom % (Vaughan, Williams, and Tate, *Phys. Review*, 1934, **46**, 327). We therefore feel justified in assuming that, under conditions where elementary nitrogen is the sole nitrogenous oxidation product, no fission of the N–N bond occurs.

In the experiments listed in Table 2, comparison with Table 1 shows that the proportion of $^{15}N_2$ has decreased while that of $^{15}N^{14}N$ has increased, the differences being more marked the lower the stoicheiometry. This suggests that whenever less than four equivalents of oxidising agent are consumed per N_2H_4 molecule oxidised, that is, whenever ammonia is formed, some of the nitrogen is formed by a mechanism involving the union of nitrogen-containing radicals from two different hydrazine molecules. By linear extrapolation of plots of the 30 : 29 and 29 : 28 abundance ratios against the corresponding stoicheiometry for the experiments with Ce(IV) and Fe(III), the 30 : 29 and 29 : 28 ratios at 1 equivalent of oxidising agent consumed per N_2H_4 molecule may be estimated as 0·0490 and 0·01331 respectively. These values do not correspond to complete fission of the N–N bonds in hydrazine. We have therefore assumed that a part of the nitrogen produced under the conditions of the limiting equation $N_2H_4 \xrightarrow{-(e)} \frac{1}{2}N_2 + NH_3$ involves no N–N fission and therefore has the same distribution of ^{15}N isotopes as the hydrazine mixture. The other part is assumed to involve complete N–N fission, and the nitrogen isotope distribution will be statistical. Calculation based on the ^{15}N-isotope distribution in the hydrazine mixture and in the nitrogen produced at a stoicheiometry of 1 equivalent of oxidising agent per N_2H_4 molecule consumed then shows that 0·508 of the total nitrogen

TABLE 2.

Reagent	Conditions	Equivs. per N_2H_4	Isotope abundance ratios 30 : 29	29 : 28	^{15}N (%)
Ce(IV)	0·5N-H_2SO_4	1·06	0·0499 ± 0·0007	0·01327 ± 0·00003	0·738
Ce(IV)	0·5N-H_2SO_4	1·38	0·0580 ± 0·0004	0·01298 ± 0·00004	0·729
Fe(III)	N-H_2SO_4; 4 hr. at 80°	1·49	0·0607 ± 0·0004	0·01293 ± 0·00004	0·723
Fe(III)	N-H_2SO_4; 4 hr. at 80°	1·76	0·0685 ± 0·0006	0·01271 ± 0·00007	0·725
V(V)	N-H_2SO_4	3·66	0·1009 ± 0·0011	0·01134 ± 0·00006	0·673
V(V)	N-H_2SO_4	3·92	0·1018 ± 0·0006	0·01189 ± 0·00004	0·706
$KMnO_4$	0·05N-H_2SO_4	2·11	0·0742 ± 0·0029	0·01200 ± 0·00010	0·680
$K_2Cr_2O_7$	0·1N-H_2SO_4	3·82	0·0970 ± 0·0003	0·01140 ± 0·00004	0·672

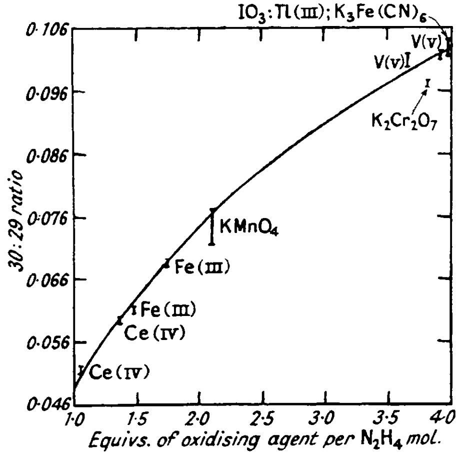
is formed, molecule for molecule, from a single hydrazine molecule, while the remaining part derives one nitrogen atom from each of two hydrazine molecules. Within the errors of the quantities used in the calculation this corresponds to the formation of half the total nitrogen from a single hydrazine molecule and half from two hydrazine molecules.

In the actual cases studied the stoicheiometry lay between 1 and 4, and, as suggested in the preceding paper, even for complex oxidising agents such as potassium permanganate, this can be ascribed to the simultaneous occurrence of the two reactions :

$$N_2H_4 \xrightarrow{-(e)} \tfrac{1}{2}N_2 + NH_3$$

$$N_2H_4 \xrightarrow{-4(e)} N_2$$

From the consumption of oxidising agent, the proportion of each reaction can be determined. The isotopic composition of the nitrogen evolved for any stoicheiometry between 1 and 4 can thus be calculated as our results have already shown the connection between the isotopic composition of the evolved nitrogen and of the parent hydrazine in each of the two limiting reactions above. For this purpose we have assumed that the isotopic abundance ratios in the hydrazine mixture are given by the average of the first three experiments listed in Table 1, *i.e.*, 30 : 29 = 0·1028, 29 : 28 = 0·01199, ^{15}N = 0·713 atom %. The calculated 30 : 29 abundance ratio, plotted as a curve against the equivalents of oxidising agent consumed per hydrazine molecule (see Figure), holds only when an excess of oxidising agent is used so that isotope fractionation effects are minimised. The figure also shows the experimental values for the reagents in Table 2. Agreement is reasonably good and thus the validity of regarding the oxidation at a consumption of oxidising agent of less than four equivalents per hydrazine molecule as involving two distinct series of reactions seems confirmed. The series giving nitrogen only will, as with the 2-electron-transfer mechanism, involve the intermediate formation of N_2H_2, though here two steps are necessary :



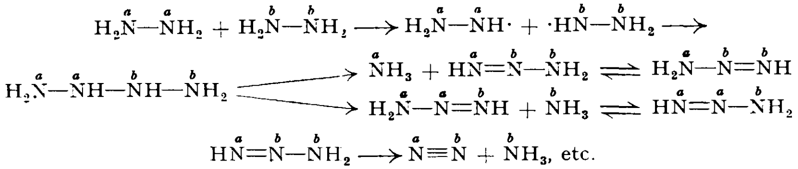
$$N_2H_4 \xrightarrow{-(e)} N_2H_3 \xrightarrow{-(e)} N_2H_2 \dashrightarrow N_2$$

In alkaline solution 1-electron-transfer reagents presumably react solely according to this scheme. In the case of complex oxidising agents such as potassium permanganate and dichromate 2-electron-transfer steps leading directly to N_2H_2 may also occur.

The second series of reactions has, we have suggested, the same initial step as the first series for 1-electron-transfer reagents, and then the N_2H_4 radicals formed dimerise and eventually break down to nitrogen and ammonia. This step seems to occur in acid solution only :

$$N_2H_4 \xrightarrow{-(e)} N_2H_3 \longrightarrow \tfrac{1}{2}N_4H_6 \dashrightarrow \tfrac{1}{2}N_2 + NH_3$$

The observation that half of the nitrogen evolved in this series of reactions is formed from two hydrazine molecules and half from one hydrazine molecule suggests that the above schemes can be written in greater detail :



$$H_2\overset{a}{N}-\overset{a}{N}H_2 + H_2\overset{b}{N}-\overset{b}{N}H_2 \longrightarrow H_2\overset{a}{N}-\overset{a}{N}H\cdot + \cdot H\overset{b}{N}-\overset{b}{N}H_2 \longrightarrow$$

$$H_2\overset{a}{N}-\overset{a}{N}H-\overset{b}{N}H-\overset{b}{N}H_2 \begin{array}{l} \nearrow \overset{a}{N}H_3 + H\overset{a}{N}=\overset{b}{N}-\overset{b}{N}H_2 \rightleftharpoons H_2\overset{a}{N}-\overset{b}{N}=\overset{b}{N}H \\ \searrow H_2\overset{a}{N}-\overset{a}{N}=\overset{b}{N}H + \overset{b}{N}H_3 \rightleftharpoons H\overset{a}{N}=\overset{a}{N}-\overset{b}{N}H_2 \end{array}$$

$$H\overset{a}{N}=\overset{b}{N}-\overset{b}{N}H_2 \longrightarrow \overset{a}{N}\equiv\overset{b}{N} + \overset{b}{N}H_3\text{, etc.}$$

Here *a* and *b* are merely used to identify the particular hydrazine molecule from which the atoms so marked originate. Thus the intermediate $H_2N\cdot N{:}NH$, as formed, has a nitrogen atom from one hydrazine molecule joined by a double bond to a nitrogen atom from another hydrazine molecule. Loss of ammonia would be expected always to involve loss of the NH_2-group, and the doubly bound nitrogen atoms would remain joined together. Nitrogen molecules so formed, possessing a nitrogen atom from each of two hydrazine molecules, must, it can be shown, exhibit the statistical distribution of the nitrogen isotopes. However if there is an equal possibility of losing either of the terminal nitrogen atoms as ammonia the experimental findings can be explained. We suggest that there can be rapid interconversion by proton transfer, $H_2\overset{a}{N}\cdot\overset{b}{N}{:}\overset{b}{N}H \rightleftharpoons H\overset{a}{N}{:}\overset{b}{N}\cdot\overset{b}{N}H_2$. Possibly the intermediate form $\overset{+}{\overbrace{H_2N\text{---}N\text{---}NH_2}}$ is relatively stable in acid solution, though it is necessary only that the interconversion of the unsymmetrical forms should be rapid compared with the rate of loss of ammonia to account for the experimental findings.

N_3H_3 has been postulated previously in discussions of the oxidation of hydrazine (see, *e.g.*, Audrieth and Ogg, " The Chemistry of Hydrazine," John Wiley and Sons, New York, 1951, p. 127). Dimroth and Pfister (*Ber.*, 1910, **43**, 2757) also suggested that this compound may exist as an unstable intermediate in the reduction of hydrazoic acid, though their evidence appeared inconclusive.

EXPERIMENTAL

Synthesis of Hydrazine from Ammonia Rich in ^{15}N.—Koenig and Brings' synthesis (*Z. phys. Chem.*, Bodenstein-Festband, 1931, 541) was used, in which a silent discharge is passed through ammonia gas which is continually condensed to liquid, removing any hydrazine formed from the discharge zone (see also Sutton, Thesis, Manchester, 1952). The source of enriched ammonia was ammonium nitrate, enriched to 33·4 mole % of ^{15}N in the ammonium-nitrogen only, obtained from A.E.R.E., Harwell. 0·9 G. of ammonia was used and about one-quarter of this was decomposed. The yield of hydrazine was 0·071 g.

Preparation of the Hydrazine Sulphate Mixture.—The ^{15}N-rich hydrazine was dissolved in excess of 0·1N-sulphuric acid, to give a 0·02125M-solution (titration against potassium iodate solution under Andrews' conditions). In this way the yield was found to be 0·0694 g. A portion of this solution of ^{15}N-enriched hydrazine was diluted with a solution in 0·1N-sulphuric acid of " AnalaR " hydrazine hydrogen sulphate (standardised as above), in proportions of one mole of enriched hydrazine to 92·0 moles of ordinary hydrazine. The final hydrazine solution was 0·01973M.

Preparation of Samples of Nitrogen for Mass-spectroscopic Analysis.—A two-bulb reaction vessel was used for the production of nitrogen samples. Each bulb was of 50-ml. capacity, and up to 25 ml. of the hydrazine sulphate mixture or of oxidising agent could be placed in each. The vessel was connected by a flexible stainless steel tube to a Töpler pump whence evolved gas could be compressed into calibrated bulbs for measurement of the volume, and thence into a 5-ml. sample tube for subsequent transference to a mass-spectrometer.

Hydrazine sulphate mixture and excess of oxidising agent were measured by pipette into separate bulbs, acid or alkali was added if required, the solutions were frozen in liquid air, and the vessel evacuated by a mercury-vapour pump. The vessel was then isolated from the pump and immersed in water at 70°, with avoidance of splashing. It was then again immersed in liquid air, and the air which had boiled out of the solution was pumped off. This procedure was repeated, after which the reactants were melted and mixed. Generally the temperature of mixing was about 18°, but was 80° for oxidation by ferric perchlorate (4 hours to ensure complete reaction). For Fe(III), Ce(IV), and V(V) the stoicheiometry was altered in successive experiments by keeping in one experiment the oxidising agent, and in the other the hydrazine in excess during the initial mixing. Preliminary experiments were necessary in some cases to determine the appropriate time of reaction. After reaction, the whole was cooled in liquid air, and connected with the Töpler pump; one stroke removed about half of the evolved nitrogen which was then compressed into the calibrated measuring bulbs, and the pressure was noted. The gas was next transferred into a sample tube and sealed off for mass-spectroscopic analysis. In most of the experiments at a stoicheiometry of less than 4 the remainder of the evolved nitrogen was pumped off and measured.

The amount of oxidising agent consumed was determined by titration of the excess with an appropriate reducing agent or titration of the amount reduced with an appropriate oxidising agent. In experiments with Ce(IV) and Fe(III) a fairly large amount of ammonia was produced and as a further check on the stoicheiometry this was determined (Kjeldahl) after the consumption of oxidising agent had been found. Comparison between amounts of nitrogen predicted from the stoicheiometry and measured showed fair agreement, the latter being approx. 1·5% low. We estimate that the observed stoicheiometry is accurate within ±0·005 for oxidation by Ce(IV), ± 0·01 for Fe(III) and $KMnO_4$, and ±0·02 for other reagents.

0·1—0·5 Millimole of hydrazine was used, with about a 50% excess of oxidising agent (generally about 0·1M), except for the slow reaction with ferric perchlorate where a 40-fold excess was used. The amounts of nitrogen produced varied from 0·1 to 0·5 millimole, and the samples for analysis from 1 to 2 ml. at N.T.P.

Mass-spectrometric Analysis.—The samples were analysed in a Metropolitan-Vickers Type M.S.2 mass-spectrometer. We are grateful to Messrs. Metropolitan-Vickers Electrical Company Ltd. for their kind co-operation and especially to Dr. Waldron (of their Research Department) for making the measurements and for advice. In addition to the 30 : 29 and 29 : 28 abundance ratios, the proportion of oxygen in most of the samples was determined—several samples contained about 0·6% of oxygen; a few contained over 1% and these results were discarded. We cannot suggest a reason for the presence of this oxygen; the amounts of evolved gas calculated and measured were in sufficiently good agreement to make unlikely the leak of an amount of air necessary to cause the observed oxygen content. On the other hand, the presence or absence of oxygen seemed to bear no relation to the reagent used and we do not think that it can be a by-product of reaction. We therefore assumed a leak of air and corrected the 30 : 29 and 29 : 28 abundance ratios where necessary: the corrections are small—the 30 : 29 ratio is increased by about 1·5% on average—and none of the conclusions drawn would be altered if they were not made.

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