Nitrogen Tracer Evidence for a Cyclic Azide Species

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Summary Tracer experiments on the reaction of ^{15}N-enriched hydrazine with excess of nitrous acid indicate a scrambling of tracer between the nitrogens of equimolar amounts of hydrazine and nitrous acid; a cyclic azide species is suggested as an intermediate.

WE have investigated the mechanism of the reaction of hydrazine with *excess* of nitrous acid by using hydrazine doubly labelled with ^{15}N (>97 atom %) and analysing mass-spectrometrically the evolved dinitrogen and dinitrogen monoxide. The distribution of tracer followed a clear pattern: the dinitrogen showed a ratio of $^{15}N^{14}N$ to $^{15}N^{15}N$ of 2 : 1, while the dinitrogen monoxide showed a ratio of $^{15}N^{14}NO$ to $^{14}N^{14}NO$ of 2 : 1. Typical results are given in the Table, including examples which do not fit the pattern. We think these deviant results are caused by mixing problems, and we do not discuss them further in this paper. Mechanistic considerations suggest that some scrambling of the nitrogen atoms has occurred. Hydrazine and nitrous acid react[1] to form hydrazoic acid by a mechanism involving a rate-determining nitrosation, equation (1), while nitrous acid and hydrazoic acid react[2] *via* nitrosyl azide as an intermediate, equation (2). Reaction of nitrous acid with

$$H^+ + HNO_2 + N_2H_5^+ \xrightarrow[\text{slow}]{} H_3O^+ + [NH_2NHNO] \xrightarrow[\text{fast}]{} HN_3 + H_2O \quad (1)$$

$$H^+ + HNO_2 + HN_3 \xrightarrow[\text{slow}]{} H_3O^+ + [NNNNO] \xrightarrow[\text{fast}]{} N_2 + N_2O \quad (2)$$

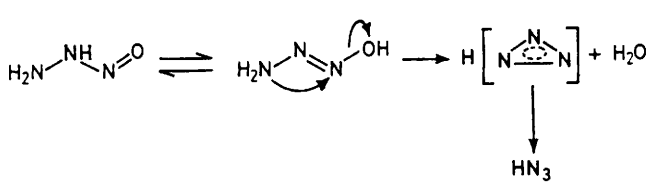
labelled hydrazine would thus be expected to produce $H[^{15}N^{15}N^{14}N]$ in the absence of any rearrangement, and when this in turn reacts with a further molecule of nitrous acid the products should be $\frac{1}{2}\,^{14}N^{14}NO + \frac{1}{2}\,^{15}N^{14}NO + \frac{1}{2}\,^{15}N^{15}N + \frac{1}{2}\,^{15}N^{14}N$. This does not fit the observed pattern of distribution of tracer.

Another possible reaction mechanism, one that is analogous to mechanisms claimed for the reaction of methylhydrazine[3] and phenylhydrazine[4] with excess of nitrous acid, is a double nitrosation of hydrazine. This would produce $^{15}N^{14}NO + {}^{15}N^{14}N$, again a distribution that

$$N_2H_5^+ + HNO_2 \longrightarrow H_3O^+ + [NH_2NHNO] \xrightarrow{HNO_2} [ONNHNHNO] + H_3O^+ \longrightarrow N_2 + N_2O + H_2O \quad (3)$$

does not correspond to that observed. A combination of these two pathways, 66·6% of reactions (1) + (2) and 33·3% of reaction (3) would fit the observed tracer distribution, but it seems improbable that the relative rates of these processes would remain fixed over as wide a range of conditions as we have studied.

A more plausible explanation is complete scrambling of the nitrogen atoms in hydrazoic acid. The work of Clusius[5] shows that scrambling does not occur during the reaction of nitrous acid with hydrazoic acid, so we consider the possibility of scrambling occurring during the formation of hydrazoic acid from the primary nitrosation product, NH_2NHNO. It has been suggested[1] that a species such as $NH_2N{=}NOH$ might be involved, and the Scheme shows how



SCHEME

TABLE. Tracer studies of the reaction of hydrazine enriched in ^{15}N (99 atom %) with excess of nitrous acid at 22 °C.[a,d]

$[H^+]$ /mol dm^{-3}	[nitrite] /mol dm^{-3}	[hydrazine] /mol dm^{-3}	N_2, 29[b]	m/e 30[b]	N_2O, 44[c]	m/e 45[c]
0·0002	0·20	0·05	68·1	31·9	36·0	64·0
0·035	0·04	0·02	69·4	30·6	47·5	52·5
0·059	0·30	0·10	55·1	44·9	35·5	64·5
0·43	0·04	0·02	66·3	33·7	36·1	63·9
0·95	0·04	0·02	66·3	33·7	39·7	60·3
3·42	0·0225	0·0075	69·2	30·8	37·1	62·9
8·43	0·0225	0·0075	66·8	33·2		

[a] Samples of N_2 and N_2O were separated from the mixture of gaseous products and were separately analysed mass-spectrometrically. [b] Some samples were undoubtedly contaminated by air leaks, and for the dinitrogen analyses we report here only the percentage intensities of peaks $m/e = 29$ and 30. [c] The samples of N_2O were stored over alkali to avoid contamination by CO_2. The peak at $m/e = 46$ was less than 0·3% and we report the percentages for the peaks of m/e 44 and 45. [d] The NO^+ from N_2O gave essentially 100% of peak $m/e = 30$.

such a scrambling mechanism might occur. The hydroxyl ion is not a good leaving group, and it seems more likely that protonation would occur so that water is the leaving group. This might involve acid catalysis and proton donation from the solvent, or it could involve a tautomer $^-NHN{=}NOH_2^+$ as the ring-closing species. We note in passing that a pathway of this type could also be written for the dehydration of *trans*-hyponitrous acid (HO–N=N–OH) to $N_2O + H_2O$ as an alternative to the inversion or double bond rotation mechanisms of isomerisation to the unstable *cis* isomer previously suggested.[6] Attack by HNO_2 and H^+ on the scrambled HN_3 (or on the postulated cyclic intermediate) would give a tracer distribution identical to that observed.

Cyclic structures were postulated for azides in the early days of azide chemistry, but the linear structure has been long established. One objection to our proposal is that a cyclic azide ion such as we suggest would have 4π electrons and be anti-aromatic, and thus might be a species of too high an energy to be an acceptable intermediate. Spectroscopic evidence indicates that a species with D_{3h} symmetry, possibly cyclic N_3, is formed when alkali metal azides are photochemically irradiated.[7]

An alternative explanation, for which we are indebted to a referee, is that in the decomposition of nitrosyl azide some scrambling might occur by the homolytic fission of the N_3–NO bond, and the reversible formation of a cyclic six-nitrogen species [reactions (4) and (5)]. If reaction occurred by this pathway we would expect that there would be some decomposition of N_6 to $3N_2$ giving an overall stoicheiometry (6). This is not known to occur. It seems improbable that

$$N_3NO \rightleftharpoons N_3^{\bullet} + NO^{\bullet} \quad (4)$$

$$2N_3^{\bullet} \rightleftharpoons N_6 \quad (5)$$

$$2N_3NO \rightarrow 3N_2 + 2NO \quad (6)$$

after the formation of N_6, this species should redissociate to $2N_3^{\bullet}$ and these radicals should diffuse back and recombine with $NO^{\bullet}$. Another possible explanation is that homolytic fission took place, and that *within the solvent cage* the azide radical formed a cyclic radical (which would lead to scrambling). If such a cyclic radical either reacted with nitrogen monoxide or else reverted to a scrambled linear species which then recombined with NO to reform N_3NO one could account for the isotopic results. The cyclic azide species reported in reference 7 is the product of a high-energy photolytic process, and this seems much less likely for a thermal reaction at ambient temperatures. We do not, furthermore, see any obvious reason why this type of behaviour was not observed by Clusius and Effenberger[5] in their original investigation.

We thank A.E.R.E. Harwell for financial support and for mass-spectrometric analyses, and we acknowledge helpful discussions with Dr. R. K. Webster, Dr. J. H. Miles, Professor F. T. Bonner, and Mr. J. Calfa.

(*Received, 22nd December* 1980; *Com.* 1360.)

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