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Reaction of Nitric Oxide with Alkaline Hydroxylamine

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The stoichiometry of the title reaction was determined by gas analysis to be $2NO + 2NH_2OH \rightarrow N_2O + N_2 + 3H_2O$. A tracer study with nitrogen-15 showed that, for both the N_2O and the N_2, one nitrogen atom arises from NO and the other from NH_2OH and that the two nitrogen atoms of the N_2O are isotopically equivalent.

Although nitric oxide and aqueous hydroxylamine do not react noticeably in acidic solution, they do so readily in alkaline solution. So far as we are aware, this reaction was first noted by Benson, *et al.*,[2] and was first examined systematically by J. E. C.[3] We report here its stoichiometry and an isotopic tracer experiment using nitrogen-15.

Experimental Part

Apparatus and Procedure.—All reactions were carried out in standard vacuum-line apparatus. Gases were transferred by Toepler pump or by trap-to-trap distillation. Aqueous solutions were added by tip-over side-arm flasks. All aqueous solutions were degassed before use by several cycles of freezing and pumping. Reacting mixtures were stirred by magnetic stir bars.

Reagents.—For the stoichiometric experiments, tank nitric oxide (Matheson) was used. For the isotopic experiments, nitric oxide of 10.0 atom % ^{15}N was prepared by treating sodium nitrite of 10.0 atom % ^{15}N (Stohler Isotope Chemicals) with a slight excess of acidified sodium iodide. In either case, the nitric oxide was subjected to several trap-to-trap distillations. All other reagents were reagent grade, used without further purification. The purity of the hydroxylamine salt used was verified by analysis. According to the literature,[4] alkaline hydroxylamine, although very subject to air oxidation, is stable in the absence of air, and we verified that degassed solutions of alkaline hydroxylamine did not decompose detectably upon storage at room temperature for as much as 1 week.

Analysis.—Gas compositions reported here were determined by gas chromatography (Aerograph A-90-P). N_2 was separated from NO on a column of Linde 13X molecular sieve at room temperature, and N_2O was separated from N_2 and NO on a column of activated charcoal at 125°. Isotopic analyses were made on a Consolidated Model 130 mass spectrometer.

Results and Discussion

Stoichiometry.—In our earliest examination of the reaction, gases were separated by fractional distillation and determined volumetrically.[3] However, the data reported here, which are in good agreement with the earlier data, were obtained by gas chromatography.[5] The data are collected in Table I. The results can be summarized as follows. Within the accuracy of our analyses, the products of reaction are equimolar quantities of N_2O and N_2, each in half the molar quantity of the initial NH_2OH or NO, whichever is less. Thus the reaction is $2NO + 2NH_2OH \rightarrow N_2O + N_2 + 3H_2O$. The stoichiometry is the same at 0° as at 20°. The observation of the same product composition at about half-reaction as at complete reaction (*cf.* first and fifth entries of Table I) indicates that soluble intermediates, if any are formed, have a half-life short compared to the half-life of the reaction, which in these solutions is about 20 min. Hyponitrite was not spectrophotometrically detectable in the solution.

TABLE I

STOICHIOMETRY OF REACTION[a]

Initial NH_2OH, mmol	Initial NO, mmol	Temp, °C	Time, min	Final NO, mmol	Final N_2O, mmol	Final N_2, mmol
2.80	1.55	20	30	0.55	0.48	0.57
2.80	2.08	20	50	0.00	0.94	1.14
0.56	2.09	20	180	1.57	0.21	0.25
2.80	2.29	20	180	0.00	1.14	1.12
2.75	1.76	0	40	0.58	0.59	0.56
2.75	1.80	0	120	0.05	0.87	0.82
2.75	1.80	0	240	0.00	0.87	0.89
0.55	1.78	0	120	1.16	0.23	0.27

[a] Reaction medium was 20 ml of 0.5 *M* NaOH.

Isotopic Tracer Study.—The reaction was carried out using 1 mmol of NO of 10.0 atom % ^{15}N and an excess (4 mmol) of hydroxylamine salt of ordinary isotopic composition, in 20 ml of 0.5 *M* NaOH at room temperature. The reaction was allowed to proceed for at least 6 hr (*viz.*, at least 18 half-lives) so as to use up essentially all the NO. The products N_2 and N_2O were then collected separately and their mass spectra were determined.

The product N_2O consisted of molecules of mass 44, 45, and 46 in the ratio 89.4%:10.3%:0.3% (duplicate run, 89.1%:10.6%:0.3%). This composition indicates unequivocally that one nitrogen atom derives from NO; the other, from NH_2OH (theoretical 89.5%:10.3%:0.2%; the 0.2% arises from the natural abundance of ^{18}O). The product N_2 consisted of molecules of mass 28, 29, and 30 in the ratio 89.9%:10.1%:0.0% (duplicate run 89.6%:10.4%:0.0%). Here also, one nitrogen atom derives from NO, the other from NH_2OH (theoretical 89.7%:10.3%:0.0%). The isotopic compositions of N_2O and N_2 are, of course, not independent; given the stoichiometry, one of them implies the other.

The fragmentation of N_2O in the mass spectrometer

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(1) To whom enquiries should be directed.

(2) R. E. Benson, T. L. Cairns, and G. M. Whitman, *J. Amer. Chem. Soc.*, **78**, 4202 (1956).

(3) J. E. Chilton, Jr., Dissertation, University of California, Berkeley, Calif., Jan 1960.

(4) (a) H. Holzapfel, *Z. Anorg. Allg. Chem.*, **288**, 28 (1956); (b) P. Moews, Jr., and L. Audrieth, *J. Inorg. Nucl. Chem.*, **11**, 242 (1959); (c) M. N. Hughes and H. G. Nicklin, *Chem. Ind. (London)*, 2176 (1967).

(5) J. N. Cooper, Dissertation, University of California, Berkeley, Calif., Sept 1964.

gave rise to NO of mass 30 and 31 in the ratio 94.6%: 5.4% (duplicate run, 94.6%:5.4%). This composition is consistent with the complete, or nearly complete, randomization of the nitrogen atoms of N_2O (theoretical for complete randomization, 94.8%:5.2%). Inasmuch as the mass spectrometric process itself causes only about a 7% randomization of the nitrogen atoms of N_2O,[6] we may infer that N_2O arises in this reaction from a precursor that is either symmetrical or capable of rapid tautomerization.

Reaction Scheme.—A sequence of elementary reactions consistent with our observed stoichiometry and isotopic results begins with a one-hydrogen transfer from NH_2OH to NO

$$NO + NH_2OH \longrightarrow NOH \text{ (or HNO)} + NHOH \text{ (or } NH_2O)$$

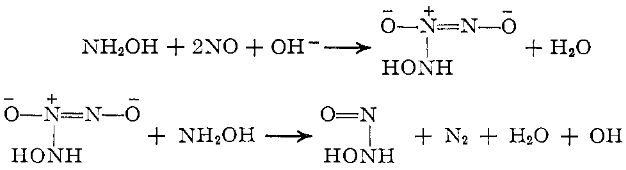
The nitroxyl molecule, NOH or HNO, presumably exists mostly as its conjugate base, NO^-, in these alkaline solutions. These two primary products are then conjectured to react rapidly, the radical species NHOH with another molecule of NO and the species NO^- with another molecule of NH_2OH, *viz.*

$$NHOH + NO \longrightarrow ON\text{-}NHOH \longrightarrow N_2O + H_2O$$

$$NO^- + NH_2OH \longrightarrow N_2 + H_2O + OH^-$$

We have written the precursor of N_2O as nitrosohydroxylamine. It cannot be hyponitrite, which under these reaction conditions has a half-life of 11 days.[7] Three groups of prior investigators[8-10] have reported mass spectrometric studies on the N_2O which results from the reaction of nitrous acid with hydroxylamine. All agree that when the N_2O arises in weakly acidic or neutral solution, its two nitrogen atoms are completely randomized, although when it arises in distinctly acidic solution there is some preference for the central atom of nitrogen to have derived from the HNO_2. There appears to be no firm evidence as to the role of nitrosohydroxylamine in the formation of randomized N_2O. Bothner-By and Friedman[8] conjectured that unsymmetrical N_2O arose from ON–NHOH; symmetrical, from hyponitrite; but with the advantage of subsequent kinetic data, it is clear that their conjecture is in error, since the half-life of hyponitrite is much longer than the half-life of the reaction.[7,10c] Hussain, *et al.*,[10c] conjectured that unsymmetrical N_2O arose from ON–NHOH; symmetrical, from the hypothetical species *cis*-hyponitrite, which they postulated to form N_2O rapidly. Perhaps a simpler hypothesis than either of these is that nitrosohydroxylamine itself, which plausibly exists as its conjugate base $ON\text{–}NHO^-$ in alkaline solutions, is capable of intramolecular nitrogen-to-nitrogen tautomerization at a rate which is comparable to, and somewhat faster than, its rate of loss of OH^- to form N_2O. Our data reported here do not go very far toward resolving this nitrosohydroxylamine problem but do indicate that the randomization takes place rapidly in alkaline solution.

Alternative Reaction Scheme.—A referee has suggested an alternative to the foregoing free-radical scheme. He postulates that the first step is the formation of N-hydroxylaminonitrosohydroxylamine and that the second step is the reaction of this intermediate with a further molecule of hydroxylamine



$$NH_2OH + 2NO + OH^- \longrightarrow \overset{-}{O}-\underset{\substack{|\\ HONH}}{\overset{+}{N}}=N-\overset{-}{O} + H_2O$$

$$\overset{-}{O}-\underset{\substack{|\\ HONH}}{\overset{+}{N}}=N-\overset{-}{O} + NH_2OH \longrightarrow \underset{\substack{|\\ HONH}}{O=N} + N_2 + H_2O + OH^-$$

This mechanism does account for the stoichiometry and, provided that the unsubstituted NO group is the one to react with the second molecule of hydroxylamine, accounts also for the isotopic tracer results. The first postulated reaction is not implausible, having its parallel in the well-known formation of N-substituted nitrosohydroxylamines by reaction of NO with such nucleophiles as sulfite, secondary amines, Grignard reagents, and various active-hydrogen species in alkaline solution. The second postulated reaction, which requires the transfer of the unsubstituted NO group to hydroxylamine either as a potential NO^+ moiety or potential NO^- moiety, must be viewed with more reservation, inasmuch as no such reaction of a nitrosohydroxylamine appears to have been observed heretofore.

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[7] J. R. Buchholz and R. E. Powell, *J. Amer. Chem. Soc.*, **85**, 509 (1963).

[8] A. Bothner-By and L. Friedman, *J. Chem. Phys.*, **20**, 459 (1952).

[9] K. Clusius and E. Effenberger, *Helv. Chim. Acta*, **38**, 1834 (1955).

[10] (a) M. N. Hughes and G. Stedman, *J. Chem. Soc.*, 2824 (1953); (b) T. D. B. Morgan, G. Stedman, and M. N. Hughes, *ibid.*, *B*, 344 (1968); (c) M. A. Hussain, G. Stedman, and M. N. Hughes, *ibid.*, *B*, 597 (1968).