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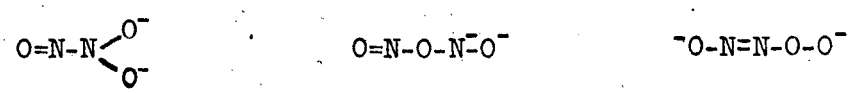
The Structure of the Oxyhyponitrite Ion

By David N. Hendrickson and William L. Jolly

The structure of the anion of Angeli's salt[1] ($Na_2N_2O_3$) has never been unequivocally determined. Three structures have been considered:



I II III

The ultraviolet spectrum,[2] the infrared spectrum,[3] the heat of formation,[4] and the pK values[5] have all been interpreted as favoring structure I. In this study, we have obtained further evidence for structure I by asymmetrically labelling the $N_2O_3^{2-}$ ion with ^{15}N, and by then isotopically analyzing the products of an asymmetric decomposition of the ion.

We prepared ^{15}N-labelled $Na_2N_2O_3$ by the reaction of labelled ethyl nitrate with ordinary hydroxylamine:[1,2]

$$EtO^{15}NO_2 + NH_2OH + 2OH^- \rightarrow O_2{}^{15}NNO^{2-} + EtOH + 2H_2O \qquad (1)$$

The salt was decomposed by treatment with aqueous silver ion:

$$O_2{}^{15}NNO^{2-} + Ag^+ \rightarrow NO + {}^{15}NO_2{}^- + Ag \qquad (2)$$

Essentially all the ^{15}N ended up in the nitrite. The lack of scrambling of the nitrogen atoms during the synthesis and decomposition proves that the two nitrogen atoms in $N_2O_3{}^{2-}$ are structurally distinguishable. Therefore structure II is unequivocally eliminated. The fact that the ^{15}N was introduced in the form of an $-NO_2$ group and finally appeared in the form of an $NO_2{}^-$ ion is persuasive evidence that the ^{15}N atom in the $N_2O_3{}^{2-}$ ion was attached to at least two oxygen atoms. Therefore we eliminate structure III.

Plausible mechanisms for the synthesis and decomposition reactions, based on structure I, can be written.

$$NHOH^- + EtO^{15}NO_2 \rightarrow EtO^- + HONH^{15}NO_2 \xrightarrow{-2H^+} ON\text{-}{}^{15}NO_2{}^{2-} \qquad (3)$$

$$ON\text{-}{}^{15}NO_2{}^{2-} + Ag^+ \rightarrow {}^{15}NO_2{}^- + [AgNO] \rightarrow Ag + NO \qquad (4)$$

Experimental Section

Syntheses.- Sodium oxyhyponitrite was prepared by the reaction of hydroxylamine with ethyl nitrate, as described by Addison *et al.*[2] The compound was labelled asymmetrically with ^{15}N in a reduced-scale synthesis

by using ^{15}N-labelled ethyl nitrate which had been synthesized by the following procedure. An aqueous solution of 2.47 g. of ordinary potassium nitrate and 0.511 g. of 95% ^{15}N potassium nitrate[6] (a total of 2.94 mmoles) was passed through a column of AG 50W-X8 cation exchange resin[6] (200-400 mesh) to give, upon evaporation of the eluate, 4.94 g. (2.91 mmoles) of labelled silver nitrate. This $AgNO_3$ was treated with 3.4 mmole of ethyl iodide in 10 ml. of absolute ethanol at room temperature for 30 minutes. The resulting ethanol solution of labelled ethyl nitrate was then vacuum-distilled at room temperature from the silver iodide precipitate and was treated with an ethoxide-ethanol solution of 4.30 mmole of hydroxylamine, as per Addison et al. The ^{15}N-labelled $Na_2N_2O_3$ was twice recrystallized by dissolving in a minimum of water and adding an excess of absolute ethanol, and was then washed with ether and vacuum-dried. A yield of 0.224 g. (6.2%, based on KNO_3) was obtained.

The unlabelled and labelled products were characterized by hydrogen and nitrogen analyses and by the u.v. spectra of their aqueous solutions. These data indicated that the samples were hydrated mixtures containing approximately 85% $Na_2N_2O_3$ and 5% $NaNO_2$.[7] (Sodium oxyhyponitrite is known to be very hygroscopic and is usually contaminated with sodium nitrite.[2]) Unlabelled material: Anal. Calcd. for $Na_2N_2O_3$: N, 22.98. Found: H, 0.67; N, 20.04. Labelled material: Anal. Calcd. for $Na_2N_2O_3$: N, 23.08. Found: H, 0.65; N, 19.22. The nitrite impurity explains why more nitrite than nitric oxide was obtained from the reactions with silver ion (see below). Its presence did not affect the validity of the results; the lack of appreciable labelling of the nitric oxide in reaction 2 is the principal evidence for an asymmetric $N_2O_3^{2-}$ ion.

Decomposition Reaction.- Reaction 2 was effected by tipping 0.3-0.4 mmole of $Na_2N_2O_3$ from a side-arm during 5 min. into excess of a degassed aqueous $AgClO_4$ solution maintained at 0° while Toepler-pumping the evolved gas through a -112° trap into a gas buret. The gas was measured and then analyzed mass-spectrometrically. The remaining solution was then frozen at -78°; 1 ml. of 60% H_2SO_4 was added, and the mixture was warmed and held at 70° for 12 hr. This procedure converted the nitrite to nitric oxide, which was pumped off and analyzed as described above.

$$2H^+ + NO_2^- + Ag \rightarrow NO + Ag^+ + H_2O \qquad (5)$$

Four samples of the unlabelled compound and three samples of the labelled compound were decomposed and analyzed by the above procedures. The total nitric oxide[8] formed in reactions 2 and 5 corresponded within 5% to the nitrogen contents of the samples. The amount of nitric oxide[8] from reaction 5 was generally 5-15% greater than that from reaction 2.

Isotopic Analysis.- The nitric oxide samples were analyzed with a Consolidated Engineering Corp. mass spectrometer (Model 21-620). The samples were found to contain 0-5% nitrous oxide. In the runs with labelled $Na_2N_2O_3$, the NO from reaction 2 was found to contain 1.1-1.5% atom % ^{15}N,[9] and the NO from reaction 5 was found to contain 14.2-15.0 atom % ^{15}N.

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(6) Bio-Rad Laboratories, Richmond, Calif.

(7) Based on the reported[2] extinction coefficients for $N_2O_3^{2-}$ and NO_2^- at 250 and 365 mμ.

(8) Corrected for the presence of N_2O.

(9) Ordinary nitrogen contains 0.36 atom % ^{15}N.

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