Lawrence Berkeley National Laboratory

Recent Work

Title

THE STRUCTURE OF THE OXYHYPONITRITE ION

Permalink

<https://escholarship.org/uc/item/71c8w0z3>

Authors

Hendrickson, David N.
Jolly, William L.

Publication Date

1968-09-01

ey. Z

THE STRUCTURE OF THE OXYHYPONITRITE ION

RECEIVED
LAWRENCE
RADIATION LABORATORY

David N. Hendrickson and William L. Jolly

September 1968

APR 7 1969

LIBRARY AND
DOCUMENTS SECTION

AEC Contract No. W-7405-eng-48

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-18750

ey. Z

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Contribution from the Department of Chemistry, University of
California, and the Inorganic Materials Research
Division, Lawrence Radiation Laboratory, Berkeley, California 94720

The Structure of the Oxyhyponitrite Ion

By David N. Hendrickson and William L. Jolly

The structure of the anion of Angeli's salt¹ ($\text{Na}_2\text{N}_2\text{O}_3$) 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 values⁵ have all been interpreted as favoring structure I. In this study, we have obtained further evidence for structure I by asymmetrically labelling the $\text{N}_2\text{O}_3^{2-}$ ion with ^{15}N , and by then isotopically analyzing the products of an asymmetric decomposition of the ion.

We prepared ^{15}N -labelled $\text{Na}_2\text{N}_2\text{O}_3$ by the reaction of labelled ethyl nitrate with ordinary hydroxylamine:^{1,2}

-2-

The salt was decomposed by treatment with aqueous silver ion:

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 $\text{N}_2\text{O}_3^{2-}$ are structurally distinguishable.

Therefore structure II is unequivocally eliminated. The fact that the ^{15}N was introduced in the form of an $-\text{NO}_2$ group and finally appeared in the form of an NO_2^- ion is persuasive evidence that the ^{15}N atom in the $\text{N}_2\text{O}_3^{2-}$ 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.

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

-3-

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 nitrate⁶ (a total of 2.94 mmoles) was passed through a column of AG 50W-X8 cation exchange resin⁶ (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 $\text{Na}_2\text{N}_2\text{O}_3$ 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% $\text{Na}_2\text{N}_2\text{O}_3$ 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 $\text{Na}_2\text{N}_2\text{O}_3$: N, 22.98. Found: H, 0.67; N, 20.04. Labelled material: Anal. Calcd. for $\text{Na}_2\text{N}_2\text{O}_3$: 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 $\text{N}_2\text{O}_3^{2-}$ ion.

-4-

Decomposition Reaction.- Reaction 2 was effected by tipping 0.3-0.4 mmole of $\text{Na}_2\text{N}_2\text{O}_3$ 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.

Four samples of the unlabelled compound and three samples of the labelled compound were decomposed and analyzed by the above procedures. The total nitric oxide⁸ formed in reactions 2 and 5 corresponded within 5% to the nitrogen contents of the samples. The amount of nitric oxide⁸ 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 $\text{Na}_2\text{N}_2\text{O}_3$, 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 .

Acknowledgement.- This research was supported by the U.S. Atomic Energy Commission.

References

- (1) A. Angeli, Ahrens Samm. Chem. Tech. Vortrage, 13, 2 (1908).
- (2) C. C. Addison, G. A. Gamlen, and R. Thompson, J. Chem. Soc., 338 (1952).
- (3) R. D. Feltham, Inorg. Chem., 3, 900 (1964).
- (4) H. R. Hunt, Jr., J. R. Cox, Jr., and J. D. Ray, Inorg. Chem., 1, 938 (1962).
- (5) P. E. Sturrock, J. D. Ray, J. McDowell, and H. R. Hunt, Jr., Inorg. Chem., 2, 649 (1963).
- (6) Bio-Rad Laboratories, Richmond, Calif.
- (7) Based on the reported² extinction coefficients for $\text{N}_2\text{O}_3^{2-}$ and NO_2^- at 250 and 365 m μ .
- (8) Corrected for the presence of N_2O .
- (9) Ordinary nitrogen contains 0.36 atom % ^{15}N .

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or*
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.*

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

TECHNICAL INFORMATION DIVISION
LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720