explosion temperature with increasing pressure, up to the very high pressure range, has been reported for a number of solid explosives.[5]

The fact that for the systems under investigation the rates of both the normal and of the explosive reactions are decreased by a pressure increase could be interpreted on the assumption that, whatever the activated complex may be, the activation volume[6] is positive for both the normal and the explosive reactions.

Acknowledgments.—The authors are pleased to acknowledge the support of this research by the Advanced Research Projects Agency and the Army Research Office (Durham). E. M. was supported by the National Research Council of Italy.

(5) F. B. Bowden and A. D. Yoffe in "Fast Reactions in Solids," Academic Press, New York, N. Y., 1958, p. 38.

(6) D. Lazarus and N. H. Nachtrieb in "Solids under Pressure," W. Paul and D. M. Warshauer, Ed., McGraw-Hill Book Co., New York, N. Y., 1963, p. 43; R. W. Keyes, *ibid.*, p. 71.

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The Infrared Spectrum of Sodium α-Oxyhyponitrite[1]

BY ROBERT D. FELTHAM

Received November 26, 1963

The α-oxyhyponitrite ion has been assigned the structure  $\left[{}^{O}_{O}{>}N\text{-}N\text{-}O\right]^{2-}$ on the basis of recent calorimetric measurements.[2] Addison, *et al.*,[3] had previously come to the same conclusions by comparing the ultraviolet spectra of NO_3^-, NO_2^-, and $N_2O_2^{2-}$ with that of $N_2O_3^{2-}$. While investigating some reactions of nitric oxide, the author had occasion to prepare this compound and measure its infrared spectrum. The details of this infrared spectrum and a partial Raman spectrum presented here are also consistent with the above structure.

Experimental

The white compound, $Na_2N_2O_3$, was prepared according to the procedure described by Addison.

Anal.[4] Calcd.: N, 22.91; Na, 37.65; O, 39.34. Found: N, 22.36; Na, 35.40; O, 40.00.

The infrared spectra were obtained as Nujol and hexachlorobutadiene mulls using a Beckman IR-4 spectrophotometer with NaCl and CsBr optics. The Raman spectrum was obtained using a Cary Model 81 recording Raman spectrophotometer.

Results and Discussion

A typical infrared spectrum of $Na_2N_2O_3$ is shown in Fig. 1. Samples from several different preparations were identical except for the occasional appearance of impurity bands due to $NaHCO_3$ and water. A partial Raman spectrum was obtained from a saturated aqueous solution of $Na_2N_2O_3$ at room temperature. Unfortunately, the solution decomposed too rapidly to obtain reliable Raman spectra. When it decomposed, the compound liberated oxides of nitrogen which were evolved as tiny bubbles of gas. These appear as "noise" on the recorded Raman spectrum. For the very intense Raman bands the "noise" presents few difficulties, but it is a serious problem for the weak Raman bands. The results of the partial Raman spectrum are presented in Table I, along with the observed infrared frequencies. The facts that the bands at 1100 and 980 cm.$^{-1}$ are only single bands in solution and that at least nine other strong bands are observed in the infrared spectrum of the solid indicate that the two bands at 1100 and the two at 980 cm.$^{-1}$ represent a total of only two fundamentals.

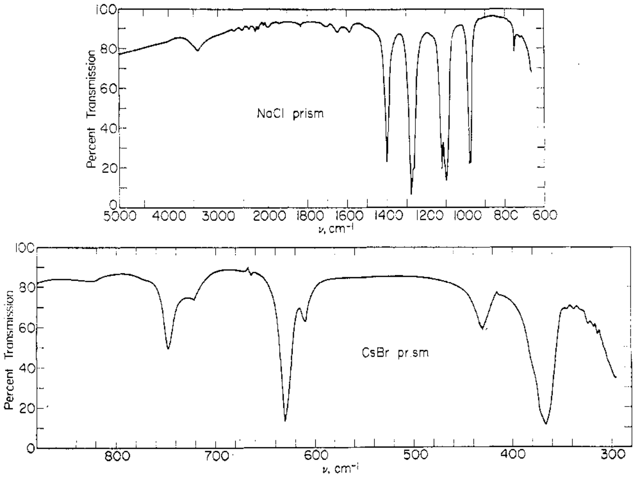

Figure 1.

TABLE I

THE RAMAN AND INFRARED FREQUENCIES (CM.$^{-1}$) OF $N_2O_3^{2-}$

Raman	Infrared	Assignment
1380 s[a]	1400 s[a]	Antisymmetric NO_2 stretch
1240 w	1280 s	Symmetric NO_2 stretch
1110 m	1120 s	N–N stretch
	1100 s	
975 s	980 s	N–O stretch
	970 s	
745 w	747 w	NO_2 bending
	630 m ?	N–NO bending
605 m	610 w	N–NO bending
425 w	430 w	ON–NO_2 out-of-plane bending
	367 m	ON–NO_2 out-of-plane bending

[a] s, strong; m, medium; w, weak.

There are two types of configurations which will be considered for the $N_2O_3^{2-}$ ion. One is O–N–NO_2^{2-} and the other is O–N–O–N–O^{2-}. Both of these arrangements have at least two possible types of symmetry, C_s and C_{2v}. These configurations cannot be distinguished from one another by the number of infrared-active fundamentals or by the number of frequencies coincident in the infrared and Raman spectra.

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(1) This work was sponsored by The International Nickel Company, Inc.

(2) H. R. Hunt, J. R. Cox, and J. D. Ray, *Inorg. Chem.*, **1**, 938 (1962).

(3) C. C. Addison, G. A. Gamlen, and R. Thompson, *J. Chem. Soc.*, 338 (1952).

(4) The analyses were carried out by Huffman Microanalytical Laboratories, Wheatridge, Colo.

Therefore it is necessary to make comparisons of the infrared spectrum with compounds whose structure is known.

The bands at 1400, 1280, and 747 cm.$^{-1}$ are typical of compounds with the R-NO_2 group.[5] These frequencies are only slightly lower than those found in alkyl or aryl nitro compounds. Although the frequencies involved are somewhat higher, the two arrangements for N_2O_3 may be characterized by the presence of the NO_2 group frequencies in $ONNO_2$ and the absence of such frequencies in ONONO.[6] The absorptions at 1100 and 970 cm.$^{-1}$ are then assigned to the N-N and N-O bonds, respectively. The assignments made in Table I are compatible with previous assignments for other nitrogen oxides and strongly suggest $[ON-NO_2]^{2-}$ as the structure of $N_2O_3{}^{2-}$.

Acknowledgments.—The author is indebted to Dr. Wm. Baer for obtaining the Raman spectrum, to Dr. F. A. Miller for the use of the Raman spectrophotometer, and to Mr. Earle Hewitt for his experimental assistance.

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[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 298–300.

[6] W. G. Fateley, H. A. Bent, and B. Crawford, *J. Chem. Phys.*, **31**, 204 (1959).

CONTRIBUTION FROM THE RADIOCHEMISTRY DEPARTMENT,
SOREQ RESEARCH ESTABLISHMENT, ISRAEL ATOMIC
ENERGY COMMISSION, YAVNE, ISRAEL

Praseodymium(IV) Nitrate

BY J. SORIANO AND Y. MARCUS

Received November 18, 1963

Preparation of anhydrous lanthanide nitrates by nitration of the oxides in nitromethane has been reported by us.[1] We wish to report here some experimental results proving the existence of praseodymium(IV) nitrate.

Anhydrous neodymium nitrate was prepared by allowing dinitrogen tetroxide to react at room temperature with a suspension of neodymium oxide in nitromethane.[1] The success of the nitration probably depends on the ionization of N_2O_4 to $NO^+NO_3^-$ in the solvent. A light blue precipitate, shown to be $Nd(NO_3)_3$ by analysis, and which is completely soluble in water, is obtained with 100% yield.

Applying the same method on Pr_6O_{11} gave only a 10% yield. Using dinitrogen pentoxide, instead of the tetroxide, increased the yield of praseodymium(III) nitrate 20% at room temperature. Raising the temperature to 70° increased the yield to complete nitration. Dissolution of the nitromethane-washed precipitate in water gave a clear pale green solution, showing the characteristic praseodymium(III) spectrum. Analysis of aqueous solutions obtained in this way showed, however, a nitrate-to-praseodymium ratio always greater than three. The solution also showed considerable acidity, an effect not found in parallel experiments with neodymium. It is suggested that these results are due to the presence of some praseodymium(IV) in the preparation which decomposes on dissolution in water to produce acid and the extra nitrate. The oxidizing power of the preparations was measured with iodide, and the results agreed with the nitrate-to-praseodymium ratio, indicating 6–7% praseodymium in the tetravalent state.

Ozonization of the reaction mixture, to prevent the presence of dinitrogen tetroxide in the pentoxide, increased the yield of praseodymium(IV) to 12%. In an effort to increase the yield of the tetravalent state still further, Pr_6O_{11} was replaced by PrO_2. The dioxide was prepared[2] by refluxing a suspension of Pr_6O_{11} in 5% acetic acid for a few hours and drying the precipitate at 160° for 24 hr. Analysis showed the product to be pure praseodymium dioxide. The yield on nitration with ozonized dinitrogen pentoxide increased indeed to 50% Pr(IV), the ratio of nitrate to praseodymium reaching 3.5.

To prove that the oxidizing power is actually due to tetravalent praseodymium, and not to some adduct of dinitrogen tetroxide with Pr(III) nitrate, the following experiment was made. Tetrabase (*p,p'*-dimethylaminodiphenylmethane) is known[3] to be oxidizable by cerium(IV), but not by nitrite, nitrate, or nitrogen oxides. The praseodymium(IV) preparation was found to oxidize tetrabase to the blue quinoide from, whereas the blank nitration mixture, not containing praseodymium, did not. On reaction with water, the praseodymium preparation yielded the expected amount of oxygen gas, after catalytic decomposition of the hydrogen peroxide also formed on dissolution.

Anhydrous praseodymium(IV) nitrate (mixed with the trivalent compound) is a white powder, insoluble in nitromethane, acetonitrile, diethyl ether, butyl acetate, and acetic acid and soluble with reduction in water and in butanol. Addition of tetrabutylammonium nitrate to a suspension of the preparation in nitromethane causes some solubilization of the praseodymium nitrate. In a few successful experiments, examination of the absorption spectrum showed the bands of praseodymium(III), which is always present, to grow with time, and especially on reduction with hydrazine nitrate. The absorption of the nitrate ion in the ultraviolet precluded finding bands due to praseodymium(IV), which presumably occur at similar wave lengths to those of isoelectronic cerium(III). The soluble species is assumed to be $[(C_4H_9)_4N]_2Pr(NO_3)_6$. A slight solubility of the praseodymium in warm nitromethane, containing dinitrogen pentoxide, may be due to formation of analogous $(NO_2)_2Pr(NO_3)_6$.

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[1] J. Padova and J. Soriano, Israel A.E.C. Semiannual Report IA 775, p. 71 (1962); *ibid.*, IA 822, p. 72 (1962); J. Soriano and Y. Marcus, *ibid.*, IA 900, p. 63 (1963).

[2] W. Prandtl and K. Huttner, *Z. anorg. allgem. Chem.*, **149**, 235 (1925).

[3] F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., Amsterdam, 1958, p. 293.