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.

---

[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 $(NO_2)_2Pr(NO_3)_6$.

---

[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.

Acknowledgment.—The help of Dr. J. Padova in the initial phase and of Dr. E. Jungreis in the final stage of this work is gratefully acknowledged.

CONTRIBUTION NO. 201 FROM THE RESEARCH AND
DEVELOPMENT DIVISION, EASTERN LABORATORY,
EXPLOSIVES DEPARTMENT, E. I. DU PONT DE NEMOURS
AND COMPANY, GIBBSTOWN, NEW JERSEY

Interaction of Metathioboric Acid with Some Phosphines and Amines

BY S. C. MALHOTRA

Received December 2, 1963

Synthesis of metathioboric acid, $(BHS_2)_x$, was first reported by Stock[1] and later by Wiberg,[2] who obtained both the dimer and the trimer forms by bubbling hydrogen sulfide through a solution of boron tribromide in carbon disulfide. Wiberg also prepared several derivatives by the reaction of the trimer with some appropriate boron compounds, *e.g.*, tris(dimethylamino)borosulfole, $[B(N(CH_3)_2)S]_3$, from trimeric metathioboric acid, $[B(SH)S]_3$, and tris(dimethylamino)borane, $B(N(CH_3)_2)_3$.[3] He has also described an alternate route to obtain tris(dimethylamino)borosulfole from tribromoborosulfole and tris(dimethylamino)borane. With a primary amine, tribromoborosulfole gives tris(alkylamino)borosulfole.

Stock[4] has reported the formation of boron sulfide hexaammoniate by the reaction of the metathioboric acids with ammonia. The product decomposes at 105° to give $B_2(NH)_3$ and at 125° to form BN. There is, however, no report in the literature on the corresponding phosphine adducts.

Boron sulfide and hydrogen sulfide are the products of thermal decomposition of metathioboric acids.[1]

A small amount of diborane is reported to be formed upon bubbling hydrogen through a solution of the trimeric metathioboric acid in the presence of Raney Ni catalyst.[5]

Finally, the structure of trimeric metathioboric acid is discussed by Goubeau.[6]

We have synthesized a new series of complexes of the general formula $R_3P:B_2S_3$ by the interaction of substituted phosphines with metathioboric acid. The synthesis and characterization of these compounds as well as those of the corresponding amine adducts are described below.

Experimental

All materials were handled exclusively in an atmosphere of dry nitrogen.

Trimeric metathioboric acid and boron sulfide were prepared as described above.[1] Substituted phosphines were obtained from Metal & Thermit Corporation.

Boron was analyzed by fusion with sodium peroxide, followed by removal of the sodium in the hot water extract by means of a cation-exchange resin and titration with NaOH solution in the presence of mannitol. The two breaks in the titration correspond to boron and phosphorus, respectively. Standard procedures were used for all other elements.

Preparation and Properties of Triphenylphosphine–Boron Sulfide Adduct.—A sample of 2.2 g. (8.4 mmoles) of triphenylphosphine was stirred in benzene (200 ml.) with 1.3 g. (17.1 mmoles) of trimeric metathioboric acid in a 300-ml. round-bottom flask fitted with a reflux condenser. The stirring was continued for 6 hr. at 70°, after which the mass was cooled and filtered and the solid (2.8 g., 7.4 mmoles of adduct) washed twice with benzene and dried under reduced pressure; yield 87%. It is difficultly soluble in tetrahydrofuran and dibromomethane, and decomposes without melting at 180°.

Anal. Calcd. for $(C_6H_5)_3P:B_2S_3$: C, 56.9; H, 4.0; P, 8.1; B, 5.7; S, 25.3; mol. wt., 379.6. Found: C, 54.3; H, 4.0; P, 7.6; B, 5.7; S, 25.8; mol. wt., 355 (in dibromomethane by osmometer method).

Infrared spectrum (KBr, cm.$^{-1}$): 3078 (w), 1960 (w), 1888 (w), 1818 (w), 1588 (w), 1483 (m), 1430 (s), 1300 (sh), 1190 (w), 1163 (w), 1105 (s), 1070 (w), 1025 (m), 1000 (s), 980 (w), 890 (w), 848 (s), 778 (w), 752 (s), 717 (m), and 695 (s).

X-Ray diffraction data for the adduct are given in Table I.

TABLE I

X-RAY DIFFRACTION DATA

$(C_6H_5)_3P:B_2S_3$		$(n\text{-}C_4H_9)_3P:B_2S_3$		$C_5H_5N:B_2S_3$		$((C_6H_5)_2N\text{-}BS)_3$	
d, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$	*d*, Å.	*I*/*I*$_0$
9.3	0.10	11.0	0.70	8.8	0.30	11.2	1.00
8.7	0.50	9.0	1.00	7.3	0.70	9.3	0.05
8.6	1.00	7.5	0.30	5.5	0.90	7.6	0.05
8.0	0.20	7.08	0.30	4.75	0.95	6.43	0.10
6.75	0.20	4.97	0.40	4.41	0.10	5.57	0.20
5.57	0.20	4.57	0.40	4.18	0.65	4.82	0.25
4.87	0.10	4.43	0.60	3.88	0.20	4.65	0.20
4.74	0.30	4.27	0.40	3.66	1.00	4.28	0.50
4.66	0.20	4.07	0.20	3.51	0.65	4.13	0.30
4.61	0.90	3.79	0.30	3.20	0.50	3.93	0.05
4.28	0.50			2.97	0.10	3.66	0.05
4.22	0.20			2.89	0.20	3.50	0.05
4.01	0.10			2.72	0.20		
3.89	0.80			2.66	0.25		
3.64	0.10			2.58	0.20		
3.38	0.10						
3.33	0.50						
2.97	0.10						
2.76	0.10						
2.29	0.10						

Proton–N.m.r. Spectra.—$(C_6H_5)_3P:B_2S_3$: One strong peak at 7.15 p.p.m.[7] and several fine structures at between 7.05 and 7.15 p.p.m. $(C_6H_5)_3P$: One strong peak at 7.25 p.p.m. and one medium strong at 7.20 p.p.m. $(C_6H_5)_3PS$: Splitting of the above, resulting in several peaks at between 7.35 and 7.85 p.p.m.

The magnetic susceptibility of $(C_6H_5)_3P:B_2S_3$ is -0.83×10^{-6} c.g.s.

Action of Water.—A sample of 0.70 g. of triphenylphosphine–boron sulfide adduct upon treatment with 150 ml. of water at 25° gave 0.41 g. of triphenylphosphine (infrared), 0.04 g. of boron (as boric acid; calcd., 0.04 g. of boron), and 100.5 cc.[8] of hydrogen sulfide (calcd. 123.8 cc.). No hydrogen was evolved during the reaction.

Action of Pyridine.—The infrared spectrum and X-ray diffraction pattern of the insoluble product obtained from the re-

---

[1] A. Stock and O. Poppenberg, *Ber.*, **34**, 399 (1901).

[2] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 530 (1953).

[3] E. Wiberg and W. Sturm, *Angew. Chem.*, **67**, 483 (1955).

[4] A. Stock and M. Blix, *Ber.*, **34**, 3042 (1901).

[5] C. J. Barr, *et al.*, U. S. Patent 2,965,450 (to Olin Mathieson Chemical Corporation).

[6] J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **272**, 303 (1953).

[7] With reference to tetramethylsilane.

[8] It does not include the amount dissolved in water under the experimental conditions.