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Preparation and Properties of Lithium Ozonide and the Use of Ammonia in the Preparation of Ozonides[1]

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The tetraammoniate of lithium ozonide has been prepared and characterized. The ammoniated compound decomposes when the ammonia is removed. Lithium ozonide is the most soluble of the alkali metal ozonides in liquid ammonia. The density of a solution containing 89% by weight of $LiO_3 \cdot (NH_3)_4$ in liquid ammonia at −74° is 0.997 g./cc. The compound shows a visible spectrum characteristic of the other alkali metal ozonides, with a maximum near 450 mμ. The heat of formation of the tetraammoniate was found to be -135 ± 5 kcal./mole.

Introduction

The ozonides of sodium,[2–5] potassium,[2,4,6] rubidium,[7] cesium,[2,7,9] tetramethylammonium,[8,9] and ammonium[10,11] have been prepared. The ozonides of Na^+, K^+, Rb^+, Cs^+, and $(CH_3)_4N^+$ are prepared by the reaction of the respective hydroxide with gaseous ozone, and they are isolated by extraction with liquid ammonia. Ammonium ozonide is prepared by the reaction of ozone and ammonia at −100°.

All previous attempts to prepare lithium ozonide have been unsuccessful. Nikolskii, Bagdassaryan, and Kazarnovskii[7] proposed a mechanism for the reaction of ozone with hydroxides and stated that thermodynamic considerations prevented the preparation of lithium ozonide from the hydroxide. Observations in this Laboratory confirmed their prediction when lithium hydroxide was used as the starting material.

Results and Discussion

The tetraammoniate of lithium ozonide was prepared by the reaction of dilute gaseous ozone (3.5% ozone in oxygen) with anhydrous powdered lithium hydroxide which had ammonia adsorbed on the surface. Subsequent experiments showed that the new ozonide formed was $Li(NH_3)_4O_3$.

Lithium hydroxide was allowed to react with an excess of ozone in the presence of 1 mmole of ammonia. In two reactions the amount of ozonide formed was 0.20 and 0.22 mmole, indicating either a tetra- or a pentaammoniate. Because it was not possible to obtain the solid ozonide by evaporating the solvent from the liquid ammonia solution, a method was developed in which the ammonia solution was added to fluoroform to precipitate the ozonide. The sample then was maintained at −78° while the ammonia was distilled away. The larger amount of ammonia that distilled away in a short time was assumed to be absorbed and not coördinated. Oxygen was not formed while this ammonia was removed. The remaining ammonia then distilled away at a slow, steady rate, along with the oxygen that formed as a decomposition product. From the amount of decomposition products formed, it was calculated that the ozonide in question was the tetraammoniate. The ratio of NH_3 to Li^+ was found to be 4.17 to 1.00. A repeat run gave a ratio of 4.32 to 1.00.

The visible spectrum of the ozonide group is very characteristic and relatively independent of the cation.[5] The spectra in Fig. 1 show unambiguously that the lithium compound is an ozonide.

The solubilities of lithium and potassium ozonides in liquid ammonia at −63° were determined by observing the change in vapor pressure with concentration of these solutions, Table I. If it is

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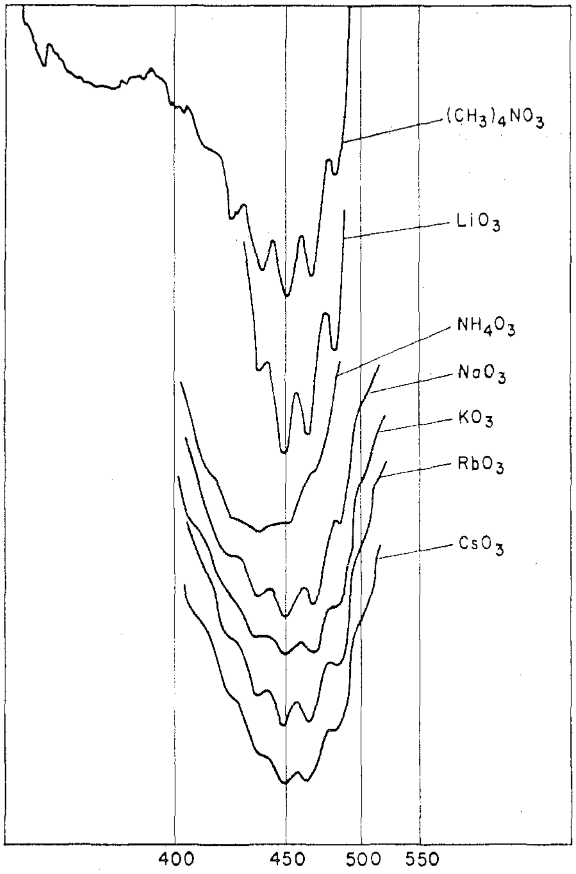

Fig. 1.—Visible spectra of ozonide compounds.

Table I

Vapor Pressure of Liquid Ammonia Solutions of Ozonides at −63.5°[a]

Lithium ozonide		Potassium ozonide	
Concn., g./100 g. NH_3	Vapor pressure, mm.	Concn., g./100 g. NH_3	Vapor pressure, mm.
7.5	120.0	6.0	123.8
12.5	116.2	9.1	122.9
16.6	111.0	12.0	122.4
24.9	101.4	15.0	122.3
33.2	92.3	26.0	122.3
49.9	71.5	39.0	122.3
66.3	31.6		

[a] Vapor pressure of pure NH_3 is 134.8 mm. at −63° and 125.9 mm. at −64°.

assumed that the constant vapor pressure of ammonia above 12% potassium ozonide indicates a saturated solution, the solubility of potassium ozonide in liquid ammonia at −63° is 12 g./100 g. of ammonia. In contrast, the lithium ozonide system did not exhibit a constant vapor pressure; it decomposed when the ratio of ammonia to ozonide became less than four.

The heat of formation of lithium ozonide tetraammoniate was determined by observing the heat of reactions 1 and 2. In this method a sintered glass disk containing the ozonide cooled to −78° was dropped into a dilute sulfuric acid solution that was kept at 25°. The heat of formation was found to be −135 ± 5 kcal./mole.

$$LiO_3\cdot(NH_3)_4 + {}^5/_2H_2SO_4 \longrightarrow {}^1/_2Li_2SO_4 + 2(NH_4)_2SO_4 + {}^1/_2H_2O + {}^5/_4O_2 \quad (1)$$

$$\text{Adsorbed } NH_3 + {}^1/_2H_2SO_4 \longrightarrow {}^1/_2(NH_4)_2SO_4 \quad (2)$$

In several attempts to prepare lithium ozonide by metathetical reactions, no isolatable new compound was obtained.

$$LiX + KO_3 \longrightarrow LiO_3 + KX \quad (3)$$

Because of solubility considerations, the X in eq. 3 represents chloride, chlorate, and cyanide.

Prior to this work, most of the known ozonides were produced from a reaction between the hydroxide and dilute gaseous ozone (about 3–5% ozone in oxygen). For example, potassium ozonide was prepared as shown in eq. 4.

$$2KOH \xrightarrow[25^\circ]{O_3} KO_3 + KOH\cdot H_2O + O_2 \quad (4)$$

However, the yields were small, probably because the product was simultaneously decomposing as shown in eq. 5.

$$KO_3 \longrightarrow KO_2 + {}^1/_2O_2 \quad (5)$$

Attempts to prevent decomposition of the product by lowering the temperature of the reaction resulted in a drastic reduction in the reaction rate; but when a small amount of ammonia was added to the potassium hydroxide, a reaction occurred even at temperatures as low as −126°. Therefore, a study was made to evaluate the effect of ammonia as a catalyst in the preparation of ozonides. The relative yield of ozonide (based on either the hydroxide or ozone charged) increased at least tenfold when the reaction was run in the presence of ammonia. This effect was shown to be general in that the yields of sodium and tetramethylammonium ozonides were greatly increased when the respective hydroxide was ozonized in the presence of ammonia.

Experimental

Preparation of Lithium Ozonide.—The apparatus used in these experiments has been described previously.[5] In a typical run, 5 g. of lithium hydroxide was coated with 0.2 g. of ammonia. (The ammonia was distilled onto the solid hydroxide, which was maintained at −196°.) Dilute gaseous ozone (~3% in oxygen) was passed through the reaction bed for 15 min. at −112°. The ozonide was extracted from the insoluble hydroxide with about 10 ml. of liquid ammonia. In order to precipitate the ozonide, the ammonia solution then was added to about 20 ml. of fluoroform maintained at −112°. The resulting red solid was washed several times with fluoroform to remove the excess ammonia. This method resulted in 5–10% conversions, based on the lithium hydroxide charged.

Calculation of Degree of Ammoniation of Lithium Ozonide.—After fluoroform had been distilled from the solid ozonide at −126°, the temperature was raised to −78° to allow the ammonia to distil. Some ammonia came off very quickly, but the remainder distilled at a slow steady rate. No oxygen was evolved while the first amount of ammonia was removed. The oxygen that was evolved in the second process was separated from the ammonia, transferred into a calibrated volume, and measured. The solid residue was analyzed for Li^+, NO_3^-, and NO_2^-.

The Li^+ was determined by flame photometry; Li^+ standards having the same acidity as the sample were used.

TABLE II

SPECIES FOUND IN THE DECOMPOSITION OF LITHIUM OZONIDE TETRAAMMONIATE

Specie	Amount, mmoles or g.-atoms
O_2	5.25
NH_3	34.65
NO_3^-	4.22
NO_2^-	0.44
Li^+	9.42

The nitrite was determined colorimetrically by means of the sulfanilic acid and α-naphthylamine method. The total nitrate and nitrite was found by means of the standard DeVarda method; the nitrate was calculated by difference.

The total nitrogen was calculated from the amounts of the various species given in Table II. The ratio of NH_3 to Li^+ was found to be 4.17. A repeat run gave a ratio of 4.32.

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Hexafluorides of Molybdenum, Tungsten, and Uranium. I. Reactions with Nitrous and Nitric Oxides[1,2]

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Reaction of nitric oxide with molybdenum and uranium hexafluorides gives the solid ionic compounds $NO^+[MoF_6]^-$ and $NO^+[UF_6]^-$. These same compounds result when molybdenum and uranium pentafluorides are allowed to react with nitrosyl fluoride. No reaction occurs between nitric oxide and tungsten hexafluoride, while nitrous oxide does not react with tungsten, molybdenum, or uranium hexafluorides.

Introduction

The properties and structure of nitrosyl compounds have been reviewed by Moeller.[3,4] Recently, nitrosyl complex fluorides of vanadium, niobium, tantalum,[5] gold, phosphorus, germanium, and tin[6] have been obtained by the reaction of the metal fluoride or oxide either directly with nitrosyl fluoride or with nitrosyl chloride in bromine trifluoride. Also, nitrosyl hexafluoroiridate(IV) has been prepared by the reaction of nitric oxide with iridium hexafluoride.[7] In this reaction, the formation of nitrosyl fluoride and iridium tetrafluoride was not detected. Simple electron transfer from nitric oxide to the hexafluoride was postulated as the mechanism of reaction.

An investigation was carried out in this Laboratory to characterize the reactions of the gaseous hexafluorides of molybdenum, tungsten, and uranium with nitrous and nitric oxides. The absorption spectra of the solids produced in these reactions were determined using samples prepared in the infrared gas cell. Work also was done to determine the mechanism of the reactions.

Experimental

Equipment, Procedure, and Materials.—A metal vacuum system was used for experimental manipulations. Pres-

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