Ammonium behaves chemically as an alkali metal, and the ammonium ion compares in size with alkali metal ions. Alkyl derivatives such as tetramethylammonium are similarly alkali metal-like, and the cations are generally more resistant to degradation than the ammonium ion. Stability was therefore predicted for tetraalkylammonium superoxides, and the results described below verify this prediction.

First attempts to prepare tetramethylammonium superoxide involved electrolyses of liquid ammonia solutions of tetramethylammonium chloride between a magnesium anode and an oxygen–platinum cathode. The expected electrode reactions were

$$Mg + 2Cl^- \longrightarrow MgCl_2 + 2e^-$$

$$(CH_3)_4N^+ + e^- + O_2 \longrightarrow (CH_3)_4NO_2$$

Data obtained from a limited study indicated that these reactions did occur. Insoluble magnesium chloride was formed, and the ammonia solution became yellow during electrolysis. Evaporation of solvent yielded a residue containing superoxide oxygen. The studies indicated, however, that the superoxide ion was subject to cathodic reduction, possibly to peroxide, and yields of superoxide were as a consequence low. In any event this method was unsuitable for preparation of macro quantities of product.

Two methods were found suitable for production of tetramethylammonium superoxide in macro quantities. Potassium superoxide reacted in ammonia with tetramethylammonium fluoride, giving insoluble potassium fluoride and soluble tetramethylammonium superoxide. The solid extract was only about 70–80% pure, based on active oxygen content, with tetramethylammonium fluoride being the chief contaminant. Reaction of tetramethylammonium hydroxide pentahydrate with excess potassium superoxide yielded a product separable in high purity. The pentahydrate and potassium superoxide were tumbled under vacuum in a Rinco evaporator at room temperature for 3–4 days. The solid–solid reaction yielded potassium hydroxide, oxygen, and tetramethylammonium superoxide in accordance with the equation

$$11KO_2 + (CH_3)_4NOH \cdot 5H_2O \longrightarrow (CH_3)_4NO_2 + 11KOH + {}^{15}/_{2}O_2$$

Rapid extractions with liquid ammonia (200 ml. of ammonia, $-33°$, 70 g. crude) gave 35–40% yields (based on $(CH_3)_4N^+$) of pure tetramethylammonium superoxide. Exhaustive extractions resulted in 90% yields of 85–90% pure products. Analytical data of a high purity product [C, 44.5; H, 11.4; N, 13.0; O_2 by acetic acid–diethyl phthalate[1] hydrolysis, 106 cc./g.; O_2 by water–manganese dioxide hydrolysis, 158 cc./g.] compare favorably with theoretical values [C, 45.3; H, 11.4; N, 13.2; O_2 by acetic acid–diethyl phthalate hydrolysis, 105 cc./g.; O_2 by water–manganese dioxide hydrolysis, 157.5 cc./g.].

Good yields of tetramethylammonium superoxide were obtained only when potassium superoxide was charged in quantities equal to or in excess of that required by the above equation. The excess potassium superoxide converts water of hydration to hydroxide, which is unreactive with superoxide and insoluble in liquid ammonia.

Tetramethylammonium superoxide is a pale yellow crystalline solid. Its X-ray powder diffraction pattern indicates the absence of likely impurities. The density, as determined by displacement of *n*-decane, is 1.11 g./cc. The compound is quite hygroscopic and dissolves readily in water with evolution of oxygen. It melts sharply at 97° and decomposes at about 100°. It dissolves readily in ammonia and is qualitatively quite soluble; no quantitative solubility data are available.

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Iodyl Fluorosulfate

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Only a few inorganic compounds are known which contain the IO_2 group. Muir[1] prepared an addition compound, $I_2O_5 \cdot 2SO_3$, which was later formulated as $(IO_2)_2S_2O_7$[2] and presumed to contain the cation IO_2^+. However, recent work of Gillespie and Senior[3] on solutions of HIO_3 in H_2SO_4 gave no evidence for IO_2^+ cations. Conductometric and cryoscopic measurements indicated that IO_2HSO_4 was present in a solvated and polymeric form. Iodyl fluoride[4,5] has been reported[6] not to combine with sulfur trioxide to form iodyl fluorosulfate.

Peroxydisulfuryl difluoride,[7] a substance known to be a good reagent for preparing fluorosulfates,[8,9] has now been used to prepare iodyl fluorosulfate from iodine pentoxide. The iodine pentoxide was first dried at 150°, pulverized, and placed in a flat-bottom reaction flask containing a Teflon-coated stirring bar. The flask had a side arm ending at a break-seal and a neck ending at a ground joint by which it could be attached to a vacuum

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line. A large excess of peroxydisulfuryl difluoride, $S_2O_6F_2$, was transferred to the flask by distillation, then the neck of the flask was sealed shut while the vessel was cold and evacuated. The flask was then allowed to stand at room temperature for 1 week. During the first part of this period the formation of bubbles of a gas (later shown to be oxygen) was observed. After the formation of bubbles had stopped, the vessel was held at 65° for 2 hr. while stirring. As the reaction occurred, the white I_2O_5 disappeared and was replaced by a solid powder having a light yellow color. Finally the reactor was attached to the vacuum line through the side arm and the excess of $S_2O_6F_2$ was distilled away through the break-seal into an evacuated cold trap. From 1.1056 g. of I_2O_5 the weight of the solid product obtained was 1.6995 g. (theoretical for IO_2SO_3F, 1.7080 g.). The oxidation state of iodine in the compound was found to be +5 (5.04 observed) as shown by a Volhard determination of iodine and an iodometric determination of the oxidizing capacity. *Anal.* Calcd. for IO_2SO_3F: I, 49.19; S, 12.43. Found: I, 48.9; S, 12.8.

The reaction involved in the preparation was

$$I_2O_5 + S_2O_6F_2 = 2IO_2SO_3F + {}^1/{}_2O_2$$

The IO_2SO_3F was a pale yellow, very hygroscopic powder which was stable up to 100°. At 120° it reacted slowly with the glass container producing SiF_4, SO_3, and a colorless oil (probably $IF_3(SO_3F)_2$) containing 32.6% I (theoretical for $IF_3(SO_3F)_2$, 32.2%.) The above products distilled away under vacuum as the reaction occurred. A bright yellow material remained behind in the reactor.

Iodyl fluorosulfate reacted with the solvent when dissolved in $CFCl_3$, $CHCl_3$, or CCl_4. Chlorine was produced even at room temperature and the color changed from yellow to orange to red. The resulting solution had absorption maxima at 4600 and 3300 Å. corresponding to ICl and Cl_2. An infrared spectrum of the volatile products indicated $S_2O_5F_2$, $COCl_2$, and CO_2. This behavior with the above solvents resembles that of ISO_3F and $I(SO_3F)_3$.[10] Iodyl fluorosulfate was substantially insoluble in fluorosulfuric acid but it dissolved readily with hydrolysis in water, the iodine remaining in the +5 oxidation state.

Finely crushed IO_2SO_3F was packed into a 0.5-mm. Lindemann glass capillary inside a drybox. The tube was sealed with Halcarbon wax and after removal from the drybox was mounted in a large standard Philips powder camera (radius 57.2956 mm.) having the conventional Straumanis arrangement. After a 12-hr. exposure using nickel-filtered copper X-radiation ($\lambda_{K\alpha}$ 1.54178 Å.), over 49 lines were observed and measured to within 0.05 mm. A second exposure of 2 hr. was also made. The camera was calibrated with a 30-min. exposure of a standard (sodium chloride, a = 5.63874 Å.). Calculations showed the camera to have an effective radius of 57.208 ± 0.027 mm. Using the now calibrated IO_2SO_3F intense lines in the 2-hr. exposure, the 12-hr. exposure powder spectrum was measured and the radius correction applied. The results are listed in Table I. A sample of solid I_2O_5 gave a different powder spectrum and agreed with ASTM Inorganic X-Ray Powder File 1962, p. 99, No. 1-0692.

TABLE I

d SPACINGS FROM LINES IN X-RAY POWDER PHOTOGRAPH

Å.	Intensity[a]	Å.	Intensity[a]	Å.	Intensity[a]	Å.	Intensity[a]
8.031	m	2.596	l	1.785	m	1.351	l
6.501	h	2.532	l	1.737	l	1.331	l
5.238	m	2.376	l	1.710	l	1.296	l
4.108	l	2.335	l	1.673	l	1.268	l
4.016	m	2.256	l	1.629	l	1.248	l
3.556	h	2.153	l	1.593	l	1.218	l
3.262	l	2.124	m	1.566	l	1.205	l
3.127	l	2.064	l	1.561	l	1.190	l
2.917	l	1.974	l	1.528	l	1.163	l
2.827	l	1.934	l	1.482	l	1.141	l
2.694	m	1.893	l	1.457	l	1.134	l
2.663	l	1.815	l	1.423	l	1.128	l
						1.078	l

[a] h, high intensity; m, medium intensity; l, light intensity.

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Preparation of Bis(triphenylphosphine oxide) Complexes of Nickelous and Cobaltous Halides

BY W. E. DANIELS

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In this laboratory, it has been found that a useful method for the preparation of complexes of the type $MX_2 \cdot 2(C_6H_5)_3PO$[1] consists of oxidation of the corresponding phosphine complex, $MX_2 \cdot 2(C_6H_5)_3P$, with hydrogen peroxide.

To the writer's knowledge, no such simple oxidation has been reported as a synthetic method.

Experimental

Materials.—Bis(triphenylphosphine)nickel(II) bromide and iodide were prepared by the method of Venanzi.[2] Bis(triphenylphosphine)cobalt(II) bromide was prepared by the method of Chatt and Shaw.[3] Hydrogen peroxide was J. T. Baker's Reagent Grade 30% H_2O_2. Melting points are uncorrected.

Preparation of Bis(triphenylphenylphosphine oxide)nickel(II) Bromide.—A refluxing solution of $NiBr_2 \cdot 2(C_6H_5)_3P$ (7.4 g., 0.01 mole) in absolute ethanol (250 ml.) was treated with 30% hydrogen peroxide solution (2.5 ml., 0.024 mole) for 1 hr. The dark green solution became pale yellow after this time. The solution

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