to those proposed for such 1:2 adducts as py·$2BF_3$ and $(C_2H_5)_3N\cdot 2BF_3$.[5]

A second, perhaps less attractive, formulation involves the possible utilization of the unshared electron pair on one selenium atom in bonding to the selenium atom of an adjacent molecule. The formation of an N→Se bond by interaction of trimethylamine with I would aid in making the unshared pair associated with the selenium atom more available for coordinate bond formation. Such an arrangement would present the rather unusual situation of simultaneous Lewis acid and Lewis base behavior by the same species in an addition compound.

In any of the formulations suggested here a total of six electron pairs, bonding plus nonbonding, are disposed about each selenium atom. In light of the existence of ions such as $SeCl_6^{2-}$ and $SeBr_6^{2-}$, structures involving seven electron pairs should not be excluded from consideration. Thus, for III, a nonionic arrangement, $\{SeCl_2(CH_3)_2[N(CH_3)_3]_2\}$, can be written, and for II a combination of the ions $[Se(CH_3)_3]^+$ and $\{SeCl_4(CH_3)[N(CH_3)_3]\}^-$ would meet the stoichiometric requirements.[6]

Acknowledgments.—The financial support of the Selenium–Tellurium Development Association, Inc., and the National Science Foundation is gratefully acknowledged by the authors.

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[6] We are grateful to a referee for this suggestion.

Contribution from the Chemicals Division,
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Some Spectral Evidence for the Dioxodifluoroiodate Group and Structure of $IO_2F\cdot AsF_6$

By James J. Pitts, S. Kongpricha, and Albert W. Jache

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The compound $IO_2F\cdot AsF_6$ was first obtained by Schmeisser and Lang[1] and formulated by them as IO_2^+-AsF_6^-. Aynsley and Sampath[2] suggested the compound was more likely $AsF_4^+IO_2F_2^-$ in view of the isolation of $K^+IO_2F_2^-$ by Helmholz and Rogers.[3] The identification of one of the ionic species involved would resolve the question.

The preparation of KIO_2F_2 and $AgIO_2F_2$ and subsequent characterization by infrared spectroscopy provided us with the necessary tool. We obtained the infrared absorption band for the $IO_2F_2^-$ group and were able to differentiate between the presence of this group or the AsF_6^- group in the compound $IO_2F\cdot AsF_6$.

The known dioxodifluoroiodate salts include those of Na, K, Rb, Cs, and NH_4 prepared by the method of Weinland, Lauenstein, and Köppen[4,5] from aqueous hydrofluoric acid. We have synthesized $AgIO_2F_2$ by the reaction of silver iodate with anhydrous liquid hydrogen fluoride. In an alternate procedure, $AgIO_2F_2$ was obtained in a double replacement reaction with KIO_2F_2 and $AgHF_2$ in anhydrous liquid hydrogen fluoride.

The reaction of KIO_2F_2 and AsF_5 in anhydrous liquid hydrogen fluoride first precipitates $KAsF_6$, leaving in effect "IO_2F dissolved in the hydrogen fluoride solvent." Further reaction between this solution and AsF_5 yielded the desired product $IO_2F\cdot AsF_5$.

Experimental

Potassium Dioxodifluoroiodate(V).—KIO_2F_2 was prepared by the method of Weinland, Lauenstein, and Köppen[4,5] by allowing a solution of 35 g. of potassium iodate dissolved in approximately 75 ml. of 48% aqueous hydrofluoric acid to evaporate over a 2-day period. The remaining few milliliters of solvent was decanted off and the white crystalline product washed with anhydrous ethyl ether to remove the last traces of solvent. Finally the product was dried in a stream of dry nitrogen.

A yield of 38 g., or 98.5% based on starting potassium iodate, was obtained. On heating, the product decomposed above 295° evolving iodine vapor.

The infrared spectrum of a Nujol mull of the product (see Figure 1) showed distinctive absorption bands at 855 (s), 847 (s), 820 (vs), and 722 (w) cm.$^{-1}$. Characteristic peaks for potassium iodate at 800 (w) and 746 (vs) cm.$^{-1}$ were completely absent.

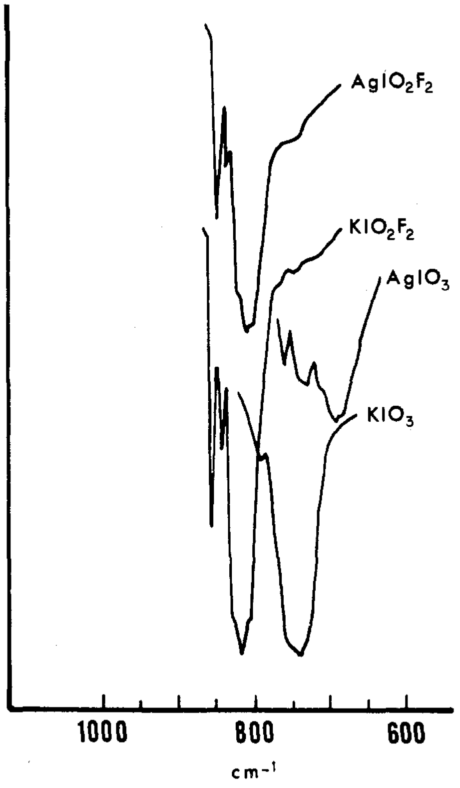

Figure 1.—Infrared absorption spectra of potassium and silver dioxodifluoroiodate compared to potassium and silver iodate.

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The X-ray pattern of the product[6] showed general agreement with the single crystal X-ray diffraction work on KIO_2F_2 of Helmholz and Rogers.[3]

Fluorine in the product was determined by titrating the acidity generated from the hydrolysis of a weighed sample.

$$KIO_2F_2 + H_2O \longrightarrow K^+ + IO_3^- + 2H^+ + 2F^-$$

Anal. Calcd. for KIO_2F_2: F, 16.1. Found: F, 16.1.

Silver Dioxodifluoroiodate(V).—Silver iodate (0.765 g.) was dissolved in anhydrous liquid hydrogen fluoride (50 ml.) condensed onto the solid at −78° in a Kel-F reaction vessel containing a Teflon-coated stirring bar. The −78° bath was removed and the liquid hydrogen fluoride allowed to distil under vacuum conditions into a monel cylinder cooled with a liquid nitrogen bath. A light gray solid precipitated from solution. When the Kel-F reactor finally reached ambient temperature the system was evacuated for 2 hr. to remove the last traces of solvent. A total of 0.706 g. of solid product was collected or 92.3% based on silver iodate. The product on heating decomposed above 285° with sublimation of iodine.

The infrared spectrum of the product in a potassium chloride pellet (see Figure 1) showed the typical absorption bands for the $IO_2F_2^-$ group at 855 (s), 844 (s), 806 (s), and 746 (w) cm.$^{-1}$. No silver iodate peaks at 769 (s), 746 (s), and 704 (vs) cm.$^{-1}$ were observed. The X-ray powder pattern of the product showed similar spacings and intensities to the KIO_2F_2 pattern and is in agreement for the $IO_2F_2^-$ group.

In an alternate procedure 4.00 g. (18.7 mmoles) of KIO_2F_2 was first dissolved in 42 ml. of anhydrous hydrogen fluoride. This solution was then poured slowly into a second solution of 2.71 g. (18.5 mmoles) of silver hydrogen difluoride dissolved in 32 ml. of hydrogen fluoride. No precipitate appeared immediately and so the mixture was cooled with a −78° bath and the reactor evacuated. The solution was then allowed to warm to ambient temperature distilling off the acid solvent at the reduced pressure. A white precipitate appeared. When the volume of solvent had been reduced to approximately 10 ml. the vacuum distillation was halted. The reactor was recooled to −78° and the remaining solvent was decanted off the solid product. The solid was replaced under vacuum and pumped on for over an hour at room temperature.

A total of 5.08 g. of white solid product was collected. Analysis established the product to be a mixture of $AgIO_2F_2$ and $KF \cdot xHF$. Hydrolysis of a weighed sample yielded silver iodate equivalent to 78% by weight $AgIO_2F_2$. A sodium tetraphenylborate solution added to the filtrate yielded potassium tetraphenylborate equivalent to 6% by weight potassium fluoride. Titration of the filtrate with base revealed acidity equivalent to 22% by weight hydrofluoric acid. This total acidity was comprised of that portion from the hydrolysis of the $AgIO_2F_2$ plus that from the $KF \cdot xHF$.

The infrared spectrum in a potassium chloride pellet of this mixture of $AgIO_2F_2$ and $KF \cdot xHF$ revealed the characteristic $IO_2F_2^-$ group absorption bands at 855 (s), 847 (s), 813 (vs), and 746 (w) cm.$^{-1}$ plus the expected potassium hydrogen difluoride bands.

Iodyl Hexafluoroarsenate(V).—Potassium dioxodifluoroiodate (0.964 g., 4.5 mmoles) was placed in a Kel-F reactor vessel equipped with a Teflon-coated stirring bar. The reactor was attached to the vacuum system and evacuated. The reactor was cooled to −78° with a trichloroethylene–Dry Ice bath and 25 ml. of anhydrous hydrogen fluoride condensed on the solid. The mixture was allowed to warm, with stirring, to ambient temperature to aid in solution of the solid. The solution was again cooled to −78° and 1 g. (5.9 mmoles) of arsenic pentafluoride condensed into the solution. On warming to room temperature, with stirring, an insoluble white solid remained.

The mixture was once more cooled to −78° and the solution decanted off into a Teflon bottle also cooled to −78°; 0.909 g. of yellowish white solid was collected. A sample of the product dissolved in distilled water showed the presence of AsF_6^- ions by the precipitate formed on addition of 10% nitron acetate solution. Addition of sodium tetraphenylborate solution yielded a precipitate of potassium tetraphenylborate equivalent to potassium needed for potassium hexafluoroarsenate(V). The yield of product based on potassium dioxodifluoroiodate was thus 97.5%.

The infrared spectrum in a potassium chloride pellet of the product showed a strong broad absorption band centered at 694 cm.$^{-1}$ for the AsF_6^- group.

The acid solvent decanted from the potassium hexafluoroarsenate was poured back into the reactor under a blanket of dry nitrogen gas and once more cooled to −78°. A total of 1 g. (5.9 mmoles) of arsenic pentafluoride was condensed into this solution of what was in effect "iodyl fluoride dissolved in anhydrous liquid hydrogen fluoride." The resulting mixture was permitted to warm to ambient temperature to ensure reaction. Finally, the acid solvent was vacuum distilled off into a monel cylinder cooled with liquid nitrogen. The white solid product obtained was pumped on under reduced pressure for a further 2-hr. period at room temperature.

A total of 1.39 g. of solid was collected. A weighed sample dissolved in distilled water showed no precipitate on addition of sodium tetraphenylborate solution, indicating the absence of potassium ions. Treatment of a second sample with 10% nitron acetate solution yielded a white precipitate, indicating the presence of AsF_6^- ions. Thus a yield of 92.7% by weight of the desired product was obtained based on KIO_2F_2.

The infrared spectrum of this product (see Figure 2) showed a strong broad absorption band centered at 704 cm.$^{-1}$ assigned to the AsF_6^- group. No other absorption peaks were observed in the product.

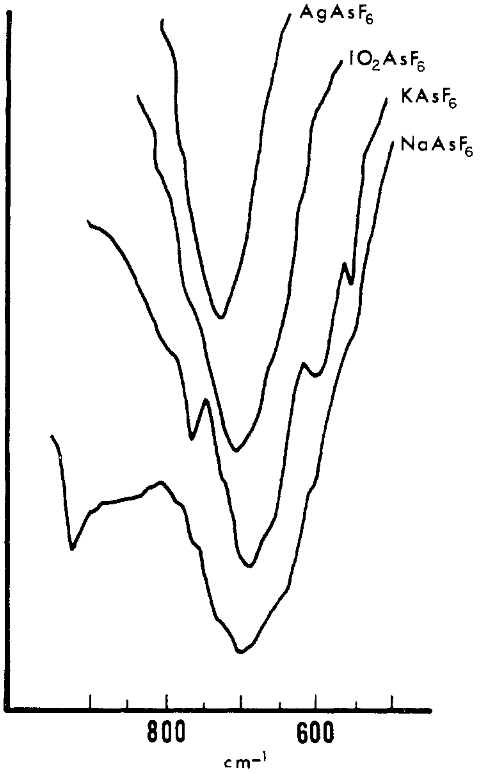

Figure 2.—Infrared absorption spectra of iodyl hexafluoroarsenate compared to silver, potassium, and sodium hexafluoroarsenate.

Infrared Absorption Spectra.—Solids were run as Nujol mulls between silver chloride plates or in potassium chloride pellets on both a standard Perkin-Elmer Infracord and a Perkin-Elmer Model 521 spectrometer.

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(6) X-Ray data submitted to J. V. Smith, Ed., A.S.T.M. X-Ray Powder Data File, Department of Geology, University of Chicago, Chicago, Ill.

X-Ray Powder Diffraction.—Powder patterns were made in Philips Electronics 114.7-mm. diameter powder cameras using filtered Cu radiation on a Philips Electronics basic X-ray unit. The samples were in 0.5-mm. soft glass capillaries and lines were measured on an N. P. Nies transparent scale, the intensities estimated visually.

Discussion

Figure 2 shows the typical AsF_6^- ion infrared absorption bands found in $KAsF_6$, $NaAsF_6$, and $AgAsF_6$.[7] The infrared spectrum of the $IO_2F \cdot AsF_5$ product revealed the same characteristic peak centered at 704 cm.$^{-1}$. Our characterization of KIO_2F_2 and $AgIO_2F_2$ demonstrated the distinctive $IO_2F_2^-$ group infrared absorption bands at 855–806 cm.$^{-1}$. The complete absence of the spectrum of $IO_2F_2^-$ ion in the spectrum of our $IO_2F \cdot AsF_5$ product proves that the structure should be represented as $IO_2^+AsF_6^-$.

Evidence for the IO_2^+ iodyl cation was not positively established although it has been postulated in the literature.[1,8–13]

Schmeisser and Brandle[14] found that in hydrogen fluoride iodyl fluoride readily reacted with various compounds which functioned as acids in this system. Iodyl fluoride was therefore thought to dissolve as a base in hydrogen fluoride. Our specific case showed as expected that AsF_5 acts as a stronger acid in the hydrogen fluoride system than IO_2F, for it formed $IO_2^+AsF_6^-$ rather than $AsF_4^+IO_2F_2^-$. However, one may think of iodyl fluoride as being amphoteric, with the nature of the species dependent upon the fluoride ion concentration of the hydrogen fluoride system in which it is dissolved.

$$IO_2F \rightleftharpoons IO_2^+ + F^-$$

$$IO_2F + F^- \rightleftharpoons IO_2F_2^-$$

Our findings were also consistent with this concept for

$$AsF_5 + IO_2F \xrightarrow{HF} AsF_6^- + IO_2^+$$

and

$$Ag^+ + F^- + IO_2F \xrightarrow{HF} AgIO_2F_2$$

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Reactions of Fluorine Nitrate

BY BARRY TITTLE AND GEORGE H. CADY

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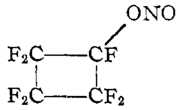
Since fluorine nitrate, NO_3F, is known to contain an OF group,[1] the substance has now been included among the various compounds under investigation to determine the chemical characteristics of the hypofluorite functional group.[2–6]

In general hypofluorites add across a carbon–carbon double bond in such a way that the F atom of the OF group combines with one carbon atom and the O atom with the other. This appears to be the case for fluorine nitrate. The substance reacts readily with ethylene at room temperature to give a liquid product which almost surely is 1-fluoro-2-nitratoethane, $FCH_2CH_2ONO_2$. A little polymeric material also is formed. The mass spectrum of the liquid product indicates the following species, listed in order of decreasing intensity: HCO^+, (NO^+ and H_2CO^+), NO_2^+, CF^+, CFH_2^+, NO^{2+}, CO^+, CH_2^+, O^+, $CH_2CH_2O^+$, CFH^+, $CFH_2CH_2^+$, F^+. On standing this compound evolves nitrogen dioxide. It can readily be distilled under vacuum. The infrared spectrum of the compound has absorption maxima (μ) at 3.45, w; C–H 6.0, vs; NO_2 asymmetric stretch 7.8, m; symmetric NO_2 stretch 9.2, w; 9.5, w; 9.7, m; 11.15, m; 11.85, ms.

Fluorine nitrate reacts almost quantitatively at room temperature with tetrafluoroethylene to form carbonyl fluoride and CF_3NO_2. It is probable that $C_2F_5ONO_2$ is formed as an intermediate and that this decomposes into COF_2 and CF_3NO_2. Although perfluoroalkyl nitrates have not been prepared, probably because of their rapid decomposition, the cyclic compound



is known. It rearranges even at 20° into $O_2N(CF_2)_3COF$.[7] A similar rearrangement of the hypothetical compound $C_2F_5ONO_2$ would give CF_3NO_2 and COF_2, the observed products of reaction.

Hypofluorites react at about 140° and above with sulfur tetrafluoride as shown in the equation[6]

$$R_fOF + SF_4 \longrightarrow R_fOSF_5$$

$$R_f = CF_3, SF_5, SO_2F$$

When the thermal reaction of fluorine nitrate with sulfur tetrafluoride occurs in a nickel vessel with slowly

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