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Photochemical Synthesis of Dioxygenyl Salts

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The dioxygenyl salts of arsenic and antimony hexafluoride were synthesized by a photochemical reaction by exposure of a mixture of oxygen, fluorine and the appropriate pentafluoride to daylight. The resulting solids have been analysed and identified. The presence of O_2^+ cation is suggested by the E.S.R. spectrum.

Introduction

In recent years several dioxygenyl compounds have been prepared, the first being $O_2^+PtF_6^-$ [2]. Later some more salts of the general formula $O_2^+MF_6^-$ (M = P, As, Sb)[3] and $O_2^+BF_4^-$ [4] were prepared. Only the antimony and arsenic dioxygenyl compounds are stable at room temperature, whereas the phosphorus and boron salts decompose at even lower temperatures.

We found it possible to synthesize the arsenic and antimony dioxygenyl compounds using a photochemical reaction—exposure of a mixture of oxygen, fluorine, and the appropriate pentafluoride to daylight.

Experimental Section

Chemicals. Fluorine and oxygen were purchased from the Matheson Co., Inc. Arsenic and antimony pentafluorides were purchased from Ozark-Mahoning Co.

The fluorine and oxygen were freed from less volatile impurities by passing the gases through a liquid air cooled trap prior to use. The pentafluorides of arsenic and antimony were subjected to low temperature distillations.

Preparation. A mixture of the appropriate pentafluoride, excess fluorine and oxygen was prepared in a transparent vessel, in Pyrex or KEL-F. All the operations were performed and the materials handled in an all-metal vacuum line, apart from the reaction vessel itself. The vessel containing the reaction mixture was then detached from the line and exposed to daylight. A reaction took place, and in a short time a white solid formed. If placed in direct sunlight, the reaction was complete in a matter of minutes. On the other hand, if the reaction vessel was covered with black paper, no reaction at all was noticed even after several days, and no solid was observed.

The reaction took place in a 180 ml Pyrex flask fitted with a ground joint and glass vacuum stopcock, and lubricated with KEL-F grease. The total pressure was therefore limited to not more than 1 atm.

The composition of the resulting solids was determined by material balance and by analysing the hydrolytic products of the solids. 181 mg (1.06 m*M*) of AsF_5 yielded 230 mg solid, equalling 1.04 m*M* based on the formula O_2AsF_6. 146 mg (0.67 m*M*) of SbF_5 yielded 195 mg solid, which equal 0.72 m*M* based on the formula O_2SbF_6.

Weighed samples of the products were hydrolysed with water. The gas evolved was collected in a calibrated volume and its pressure determined with a mercury manometer after a steady reading had been reached. A layer of KEL-F oil over the mercury prevented chemical reaction of the mercury. This whole reaction was performed in a glass vacuum line. The gas phase was also analysed in a mass spectrometer and was found to consist of oxygen only.

Amount of Sample	Amount of Gas
O_2AsF_6 – 0.67 m*M*	0.82 m*M*
– 0.46 m*M*	0.58 m*M*
O_2SbF_6 – 0.50 m*M*	0.56 m*M*
– 0.51 m*M*	0.63 m*M*

In the antimony complex, both fluorine and antimony were determined in a solution resulting from a basic hydrolysis using a sodium hydroxide solution. Fluorine was determined by titrating an aliquot of the solution with thorium nitrate. In another aliquot, antimony was determined by titration with iodine after reduction of the antimony to the trivalent state.

Anal. Calcd. for O_2SbF_6: Sb, 45.47; F, 42.58. Found: Sb, 48.11; F, 44.58%.

X-Rays. X-ray diffraction patterns were obtained for O_2AsF_6 and O_2SbF_6 powders, filled into KEL-F and Pyrex capillaries and sealed off. The diffraction pattern of O_2AsF_6 is very similar to that described by Young *et al.*,[3] and may be correlated on the basis of a cubic unit cell with a_o = 8.10 Å as compared to a_o = 8.00 Å obtained by Young. We succeeded in obtaining quite sharp and clear diffraction patterns of O_2SbF_6 as well. Its pattern may be correlated on the basis of a cubic unit cell with a_o = 10.30 Å; by way of comparison,

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(1) In partial fulfillment of the requirements for a Ph. D. thesis to be submitted to the Senate of the Hebrew University by J. B.

(2) N. Bartlett and D. H. Lehmann, (a) *Proc. Chem. Soc.*, 115 (1962); (b) *J. Chem. Soc* , 5253 (1962).

(3) A. P. Young II, T. Hirata and S. I. Morrow, *J. Am. Chem. Soc.*, 86, 20 (1964).

(4) I. H. Solomon *et al.*, *Inorg. Chem.*, 3, 457 (1964).

Young obtained $a_o = 10.71$ Å, which resulted from a composite of two fairly sharp patterns.

Infrared. The I.R. spectra were recorded on a Berkin-Elmer 21, equipped with a sodium chloride prism. The powder sample was pressed between two silver chloride windows. The AsF_6^- absorption band was observed at 705 cm^{-1}.

E.S.R. An E.S.R. spectrum was recorded on an O_2AsF_6 sample and a single line was observed. The width of the line varied from 66 gauss at room temperature to 24 gauss at –80°C. The g-value at –80°C is 1.9980 ± 0.0002, which corresponds to one free electron.

Results and Discussion

The experiments performed on the above solids prove that these materials correspond to the formula O_2MF_6, and are in general agreement with the data described by Young.[3] These highly oxidizing solids are therefore easily preparable by this novel and simple photochemical reaction method. The solids obtained were white, and only when some excess pentafluoride was distilled on to the solids did violet colored areas appear.

The hydrolysis follows the equation:

$$2O_2MF_6 + H_2O \longrightarrow O_2 + O_3 + 2HMF_6$$

and accordingly the amount of gas evolved is equimolar to the sample hydrolysed. In our results the amount of gas is 1.25 larger than the amount of hydrolysed sample. These high results can be explained by assuming that the ozone is decomposed to molecular oxygen:

$$O_2 + O_3 \longrightarrow O_2 + O_2 + \tfrac{1}{2}O_2 = 2\tfrac{1}{2}O_2$$

i.e. 1.25 moles per mole sample. Ozone is indeed known to undergo self-decomposition, accelerated by the presence of molecular oxygen.

The absorption band of fluorine shows a tail in the visible; owing to its low dissociation energy, atomic fluorine can be formed by light absorption. This could provide an explanation for the following mechanism of the reaction:

$$F_2 \xrightarrow{h\nu} F\cdot + F\cdot \qquad (1)$$

$$O_2 + F\cdot \longrightarrow O_2F\cdot \qquad (2)$$

$$O_2F\cdot + F_2 \longrightarrow O_2F_2 + F\cdot \qquad (3)$$

$$O_2F_2 \longrightarrow O_2F\cdot + F\cdot \qquad (4)$$

$$O_2F\cdot + MF_5 \longrightarrow O_2F\cdot MF_5 \longrightarrow O_2^+MF_6^- \qquad (5)$$

The fluorine atoms react with molecular O_2 to form the radical $O_2F\cdot$. The second step can be terminated by reacting directly with the pentafluoride as in step (5), or it may cause a chain reaction as in steps (3) and (4) and then terminate as in step (5). This chain mechanism can explain the fast rate of the reaction, in spite of the low absorption of F_2 in the visible region.

The existence of a radical $O_2F\cdot$ has been proved by A. Arkell[5] and Malone and McGee.[6] This proposed mechanism can be further supported by the synthesis of the dioxygenyl compounds by reacting the pentafluoride with the thermally unstable O_2F_2. The mechanism for the decomposition of O_2F_2 proposed by Grosse and Kirshenbaum[7] includes the following as the first step:

$$O_2F_2 \longrightarrow O_2F\cdot + F\cdot$$

which would then react with the pentafluoride.

The O_2^+ cation has an odd electron which is detectable in the E.S.R. spectrum with the appropriate g-value for an unpaired electron.

The evidence for the AsF_6^- anion can be derived from the I.R. spectrum. It seems therefore that good proof is provided for the ionic structure. We are now exploring the use of this photochemical reaction for other preparations.

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(5) A. Arkell, *J. Am. Chem. Soc.*, *87*, 4057 (1965).

(6) T. J. Malone and H. A. McGee Jr., *J. Phys. Chem.*, *69*, 4338 (1965); *ibid.*, *70*, 316 (1966).

(7) A. V. Grosse and A. D. Kirshenbaum, Production, isolation and identification of the OF, O_2F and O_3F radicals. 2nd Quarterly Report, Air Force Contract AF-04(611)-9555, The Research Institute of Temple University, March 31, 1964.