starting material had been distilled, the brown solid residue was sublimed *in vacuo* at 240°. The white solid which collected on the cold finger had an infrared spectrum superimposable with that reported[4] and melted at 330–331°.

Bis(2,2′-diphenylenedioxy)germane. To 0.092 mole of 2,2′-diphenylenedioxydimethylsilane was added 0.045 mole of germanium tetrachloride with constant stirring in a nitrogen atmosphere. The tan solid that had formed was sublimed *in vacuo* after excess starting material was distilled. The infrared spectrum of the product which sublimed at 270° *in vacuo* was superimposable with that reported for bis(2,2′-diphenylenedioxy)germane.[5]

Acknowledgment. The investigation was supported by Public Health Service Research Grant CA-07064-02 from the National Cancer Institute.

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Received September 10, 1965

Two New Fluorides of Oxygen, O_5F_2 and O_6F_2[1,2]

Sir:

In our paper describing the preparation of O_4F_2[3] the likely existence of two new oxygen fluorides, *i.e.*, O_5F_2 and O_6F_2, was postulated.

We wish to describe the preparation of these two fluorides, which at present are characterized mainly by their empirical formulas.

Table I

Experimental conditions	Preparation of O_5F_2 Run no. 1	2	3	Preparation of O_6F_2 Run no. 1	2	3	4
Feed rate of the $5O_2 + 2F_2$ and $6O_2 + 2F_2$ gas mixtures, cm³/hr, at NTP	8.5	8	6	22.5	20.3	15.0	15.0
Pressure in the reaction vessel, mm (±0.1)	8	4	6	2	1	1	0.5
Bath temp, °K (±1°)	70	60–70	77	70	60–61	60	60
Electric power, w (±0.2)	5.3	5.3	4.0	4–6	2	2	1.6
Duration of the expt, hr	3.5	3.0	5.0	0.75	1.5	0.83	1.25
Amount of product obtained, mg	45.0	35.1	45.9	17.3	44.9	17.6	28.0
Empirical formula of reaction product	$O_{4.94}F_{2.00}$	$O_{4.96}F_{2.00}$[a] $O_{5.06}F_{2.00}$	$O_{4.90}F_{2.00}$	$O_{6.00\pm0.15}F_{2.00}$	$O_{5.96\pm0.04}F_{2.00}$	$O_{5.88\pm0.30}F_{2.00}$	$O_{5.89\pm0.25}F_{2.00}$

[a] Analyzed by F_2 absorption with Hg!

They were prepared in the same type of electrical-discharge apparatus as described previously,[4,5] only under much milder conditions as suggested above,[3] that is, (a) in a smaller reaction vessel (9 cm high, 3 cm i.d., 1 cm in diameter, copper electrodes 2.5 cm apart), (b) using less power (only ≃6–2 w), (c) more cooling, *i.e.*, down to a bath temperature of 60°K (using a mixture of liquid O_2–N_2 and pumping), and (d) lower gas discharge pressure (*i.e.*, down to 1 and even 0.5 mm). A gas mixture of the composition $5O_2 + 2F_2$ and $6O_2 + 2F_2$, respectively, was admitted to the discharge vessel at such a rate that the pressure in it remained practically constant. All pertinent details of seven preparations are given in Table I.

The method of analysis is simple and unambiguous. On warming, the two new fluorides—like O_4F_2, O_3F_2, and O_2F_2—finally decompose to O_2 and F_2; infrared spectra established the absence of any O_3 or OF_2. Fluorine was quantitatively determined by treating it with dry KI and determining the I_2 liberated iodometrically; O_2 was determined gas volumetrically in a vacuum system by absorption with alkaline pyrogallol. Any unreacted O_2 or F_2 can be pumped off from the reaction product at 60–70°K. The only possible known oxygen compound which could falsify our analysis is *ozone*. However, it can be extracted from our product by condensing liquid O_2 or N_2; amounts of 0.3 mg of O_3 in 0.3 cc of liquid O_2 or N_2 can be detected easily. However, no ozone was formed.

Thus, for example, if 50 mg of O_6F_2 were to contain 0.3 mg of O_3, the accuracy of the empirical formula would be affected to the extent of only $O_{6.00\pm0.05}F_{2.00}$!

SiF_4 was present in our product in amounts of ≃10 wt % and is due to the action of activated fluorine on glass.

The analyses give only the empirical formulas and do not exclude a mixture of lower oxygen fluorides with higher ones, such as O_7F_2 or O_8F_2. However, we consider such a possibility very unlikely (see experiments with $5O_2 + F_2$ mixtures). Since O_3F_2 and O_4F_2 have been characterized by their epr spectra and found to contain the radical $\cdot OOF$,[6,7] *it is likely* that our new

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[1] This paper describes a part of work sponsored by the Office of Naval Research, Contract Nonr 3085(01).

[2] Presented at the 3rd International Fluorine Symposium, Munich, Germany, Aug 31, 1965.

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fluorides do contain substantial amounts of radical species.

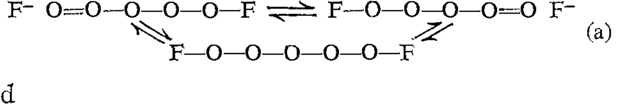
Properties. O_5F_2 is a reddish brown liquid at 90°K, similar to O_4F_2. Whereas O_4F_2 forms clusters of long needle-like crystals at 77°K,[3] O_5F_2 appears to be an oil at 77°K. It is thermally stable at 77°K; at least it decomposed to less than 0.1 mole% during 4 hr. At 90°K it decomposed readily, the final products being O_2 and F_2. At 77°K, it is practically insoluble in liquid N_2 and may be soluble to the extent of $\simeq$0.02 mole % in liquid oxygen. It is soluble at least to 0.1 wt % in CF_4 (+ $\simeq$3 wt % O_2) at 77°K. In liquid OF_2 at 65°K it is soluble in amounts of about 5 wt %. It has been characterized by its epr spectrum;[8] the spectrum is substantially different from that of O_4F_2.

O_6F_2 is dark brown in color and is a crystalline solid at 60°K; the crystal faces show a distinct *metallic* luster. At 60°K there is no noticeable thermal decomposition (*i.e.*, below 0.1 mole %) during 4.0 hr. On slow warming (*i.e.*, at a rate of $\simeq$10°K/hr) to 90°K, it decomposes quietly, forming lower oxygen fluorides and *ozone!* On fast warming to 90°K (for example, by changing the cooling bath), it explodes to O_2 and F_2. The compound is very sensitive. If quantities of over $\simeq$20 mg accumulate in the reaction vessel during preparation, it often explodes but does not *detonate* (*i.e.*, the reaction vessel is not shattered). (If similar quantities of O_3 are condensed with it they detonate, shattering the vessel as soon as the last traces of O_2 are pumped off!) O_6F_2 also explodes from the discharge of a Tesla high-frequency coil and in some cases when illuminated with a flashlight.

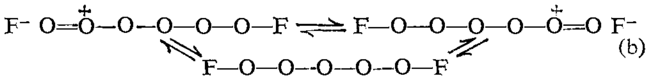
O_6F_2 is insoluble at 60°K in a liquid mixture of 95 vol % N_2–5 vol % O_2. In liquid oxygen at 60°K perhaps traces, *i.e.*, $\simeq$0.01 mole %, are soluble. In liquid OF_2 at 60°K it is soluble in amounts of about 5 wt %.

Attempts to produce *still higher* oxygen fluorides, under the same mild conditions (see Table I), but using a $5O_2 + F_2$ gas mixture, produced only the known oxygen fluorides and ozone; this would indicate that oxygen fluorides higher than O_6F_2 are not stable under the above conditions. This is not to say that they may not form and be sufficiently stable at 4°K.

The recent infrared studies of Arkell[9] suggest that the valence bond notation for O_5F_2 and O_6F_2 be, respectively

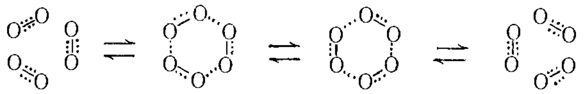


and



We have suggested[3] that by abstracting the two F atoms (for example, with atomic hydrogen at low temperatures), the interesting cyclic O_5 and O_6 molecules, *i.e.*, new modifications of oxygen, may be produced.

According to Arkell[10] it is probable that O_6 might have a resonance, involving three electron bonds of the Pauling type, as shown below.



Jackson's[11] interatomic distances in oxygen fluorides and Arkell's force constants indicate that significant differences exist between the bond energies of the O–F and the O–O bonds. Thus, it would be of interest to determine the heats of formation of O_4F_2, O_5F_2, and O_6F_2.

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Received October 11, 1965

A Memory Effect in the Generation of 2-Bicyclo[3.2.1]octyl Cation. On the Mechanism of Racemization of 2-Bicyclo[2.2.2]octyl Cation[1]

Sir:

The genetic memory effects previously observed in the ring expansions of *endo*- and *exo*-2-norbornylcarbinyl[2] and *syn*- and *anti*-2-norbornene-7-carbinyl[3] derivatives also occur in the ring expansion of 7-norbornylcarbinyl derivatives (**1**).

Rearrangements in the acetolysis of 7-norbornylcarbinyl *p*-bromobenzenesulfonate at 120° (10 mole % excess sodium acetate as buffer) produce 18.0% 2-*exo*-bicyclo[3.2.1]octyl acetate (**2**), 25.8% 2-bicyclo-[2.2.2]octyl acetate (**3**), 0.84% 2-*endo*-bicyclo[3.2.1]-octyl acetate (**4**) (all with Z = OAc), and 5.2% 7-methyl-7-norbornyl acetate (**7**). Also, 49.8% of unrearranged acetate is formed. The proportions of products **2**, **3**, and **4** (40.3:57.7:1.9) are very similar to if not identical with those observed in solvolyses (at lower temperatures) of either of the Wagner–Meerwein related pair of 2-bicyclooctyl *p*-bromobenzenesulfonates[4] or of 3-cyclohexenylethyl *p*-bromobenzenesulfonate.[5] Nitrosation of 7-norbornylcarbinylamine (aqueous acetic acid, room temperature) gives virtually the same ratio of products **2** and **3** as alcohols, Z = OH (40.9:59.1). These constitute 79% of the product mixture, the remainder being 2% acetates, 10% unrearranged alcohol, and 9% an unidentified component.

Specifically labeled *syn*- and *anti*-2,3-dideuterio-7-norbornylcarbinyl *p*-bromobenzenesulfonates (**1a** and **1b**, X = OBs) and the corresponding amines (**1a** and **1b**, X = NH_2) are prepared from the alcohols (**1a** and **1b**, X = OH), which are obtained by the action of

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[1] The support of this work by grants from the National Science Foundation (GP-1608) and from the National Institute of Arthritis and Metabolic Diseases (AM07505) is gratefully acknowledged.

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