which is close to the value reported in the gas phase,[5] 2.010. The measured $N^{14}$ and $F^{19}$ couplings are 16 and 56 gauss, respectively.

### Experimental

The sieves used in these experiments were Linde[6] Molecular Sieves in powdered form. They were heated to 300° and then evacuated at $10^{-5}$ atm. prior to the introduction of $N_2F_4 \rightleftarrows 2NF_2$. The e.p.r. spectra reported herein were obtained with a Varian V-4502 e.p.r. spectrometer system employing 100-kc./sec. modulation and detection. The n.m.r. spectra reported were obtained with a Varian Associates V4300 40-Mc./sec. spectrometer. The sample cells were 5-mm. o.d. and 7 in. long capped by side arms and a Fischer-Porter[7] pressure valve for loading the cells with gas.

*Caution.*—$N_2F_4$ reacts with Linde Molecular Sieve 10X at room temperature and pressures greater than 0.5 atm. Occasionally we have had samples explode with both 10X and 13X sieves. It is our belief, however, that by vigorous outgassing at 300° and by vigorous exclusion of air these systems may be handled safely.

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(5) L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

(6) Linde Company, Tonawanda, N. Y.

(7) Fischer-Porter Company, Hatboro, Penna.

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## New Dioxygenyl Compounds(1)

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Interesting new compounds containing a dioxygenyl cation ($O_2^+$) have been prepared by the reaction of dioxygen difluoride with boron trifluoride and phosphorus pentafluoride.

$$O_2F_2 + BF_3 \longrightarrow O_2BF_4 + {}^1/_2F_2 \qquad (1)$$

$$O_2F_2 + PF_5 \longrightarrow O_2PF_6 + {}^1/_2F_2 \qquad (2)$$

The idea of a compound containing the $O_2^+$ species is not unfounded, in that $O_2^+(PtF_6)^-$ has been reported.[2] This compound was prepared by the reaction of platinum hexafluoride and oxygen.

Equations 3 and 4 show the thermal decomposition of $O_2BF_4$ and $O_2PF_6$.

$$O_2BF_4 \longrightarrow O_2 + {}^1/_2F_2 + BF_3 \qquad (3)$$

$$O_2PF_6 \longrightarrow O_2 + {}^1/_2F_2 + PF_5 \qquad (4)$$

The rate of decomposition is slow at 0° but rapid at room temperature. Although the decomposition rate drops as the pressure increases, a constant pressure plateau is not reached. The hydrolysis of these compounds is interesting in that a considerable amount of ozone is formed. The fact that $O_2BF_4$ reacts with dinitrogen tetroxide to produce nitronium fluoroborate is further proof that the original compound contains fluoroborate ions.

$$O_2BF_4 + {}^1/_2N_2O_4 \longrightarrow NO_2BF_4 + O_2 \qquad (5)$$

The infrared and electron paramagnetic resonance (e.p.r.) spectra are also consistent with the structure $O_2BF_4$. The infrared spectrum shows a broad absorption in the B–F region, which is not unusual in that the spectrum was run on the solid because a suitable solvent had not been found. The e.p.r. spectrum consists of a single, asymmetric, broad line centered at $g = 1.97 \pm 0.10$. The width between inflection points, measured at 77°K., is 500 oersteds.

### Experimental

The $O_2BF_4$ and $O_2PF_6$ were prepared by the reactions of boron trifluoride and phosphorus pentafluoride, respectively, with dioxygen difluoride at $-126°$. The empirical formula of the fluoroborate compound was determined from the reaction of a known excess amount of boron trifluoride with dioxygen difluoride. The unreacted boron trifluoride was pumped off while the product was maintained at $-78°$. It was found that 7.17 mmoles of boron trifluoride had been consumed and 3.14 mmoles of fluorine had been formed. According to eq. 1, 0.5 mole of fluorine should be formed per mole of $O_2BF_4$ ($0.5 \times 7.17 = 3.58$ mmoles). If $O_2BF_4$ decomposes as shown in eq. 3, the amounts of boron trifluoride, oxygen, and fluorine produced should be 7.17, 7.17, and 3.58 mmoles, respectively. The amounts found were 6.80, 7.21, and 3.40 mmoles.

The stoichiometry of eq. 5 was determined in a similar fashion. The reaction of 4.45 mmoles of $O_2BF_4$ produced 4.65 mmoles of oxygen.

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(2) N. Bartlett and K. H. Lohman, *Proc. Chem. Soc.*, 115 (1962).