amino)boranes and boron trihalides has been reported by Greenwood, Hooton, and Walker (eq 11).[15] Intermediate formation of a di(alkylamino)boron halide was suggested.

$$2B(HNR)_3 + 4BX_3 \longrightarrow 3RNH_2BX_3 + [RNBX]_3 \quad (11)$$
$$R = CH_3C_2H_5,\ n\text{-}C_3H_7,\ sec\text{-}C_4H_9$$
$$X = Cl, F$$

Reactions of B_2H_6 with $LiNH_2$ and $LiP(CH_3)_2$. The reaction between diborane and lithium amide in diethyl ether (eq 2) is unique.[2] The precipitation of polymeric aminoborane probably eliminates the possibility of further reaction with diborane. In comparison, all intermediates in the *N*-alkylamide systems are ether soluble and labile, allowing ultimate formation of μ-aminodiboranes *via* reactions 4–6.

In complete contrast, the phosphorus analog of the amides, lithium dimethylphosphide, reacts quantitatively with diborane in diethyl ether without the formation of detectable intermediates to produce lithium bis(borane)dimethylphosphide(1−) (eq 1).[1] The crucial difference between the nitrogen and phosphorus systems is the π stabilization of all three-coordinate boron–nitrogen intermediates. Since boron–phosphorus π bonding is either very weak or nonexistent,[16] boron must remain four-coordinate in reaction 1 and give the bis(borane) adduct. The phosphorus analogs of the intermediates and products of reactions 4–6, monomeric phosphinoborane R_2PBH_2, di(phosphino)borane $(R_2P)_2BH$, and tri(phosphino)borane $(R_2P)_3B$ are unknown.[16]

In view of the low reactivity of polymeric dimethylphosphinoboranes,[17] it is at first surprising that no evidence for reaction 12 has been found. If this process

$$LiP(CH_3)_2 + B_2H_6 \longrightarrow (1/n)[(CH_3)_2PBH_2]_n + LiBH_4 \quad (12)$$
$$n = 3, 4$$

requires the intermediate formation of monomeric dimethylphosphinoborane, it will be less favorable under mild conditions than simple adduct formation. The great resistance to ring opening and dissociation of dialkylphosphinoboranes may, in large part, result from the instability of the monomer.

Acknowledgment. Support for this work was provided by a grant from the National Science Foundation and by a traineeship from the National Aeronautics and Space Administration held by L. D. S.

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Reaction of Xenon with Dioxygenyl Tetrafluoroborate. Preparation of $FXe–BF_2$

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Contribution from the Shell Development Company,
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Abstract: A reaction between xenon and O_2BF_4 has been observed to liberate oxygen and fluorine at temperatures near 173°K. A white solid was produced which decomposed at 243°K into an equimolar mixture of Xe and BF_3. On the basis of analytical and vibrational spectroscopic data, it is believed that the structure of this solid is $FXe–BF_2$. This structure is novel in that a covalent xenon–boron bond is assumed.

The structure of dioxygenyl tetrafluoroborate was reported to be $O_2^+BF_4^-$ on the basis of isotopic tracer studies and kinetic data.[2] This structure recently has been confirmed[3] by a detailed infrared study.

Solomon, *et al.*,[4] reported that O_2BF_4 reacted with nitrogen dioxide to give NO_2BF_4 and oxygen. This reaction demonstrated that the dioxygenyl cation, in O_2BF_4, could react by a simple electron-transfer mechanism with compounds of lower ionization potential than oxygen. This suggested that a similar reaction might occur between xenon and O_2BF_4, since the ionization potential[5] of xenon (12.13 eV) is very close to that of oxygen (12.2 eV). In addition, it has been predicted[6] that the expected product, $Xe^+BF_4^-$, should be stable up to about 150°.

For these reasons, it seemed reasonable that a reaction between xenon and O_2BF_4 might occur if proper reaction conditions were met. The reaction of xenon with dioxygenyl cations has not been reported, and demonstration of this reaction would introduce into xenon chemistry a new method of preparing selected xenon salts. This paper describes the reaction between xenon and dioxygenyl tetrafluoroborate along with spectroscopic evidence for the structure of the product.

Experimental Section

O_2BF_4 was prepared by liquid phase radiolysis of a mixture of fluorine, oxygen, and boron trifluoride as described previously.[7]

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All samples were handled on a stainless-steel vacuum system using stainless-steel or sapphire vessels. Sampling operations were carried out in a hydrocarbon-free drybox under a nitrogen atmosphere.

The vacuum system was equipped with three U-tube traps for low-temperature distillation, calibrated volumes (600, 110, and 25 ml), a stainless steel Bourdon gauge (0–800 mm), and bellows-type Hoke valves with Teflon seats. The manifold for connecting reaction vessels to this system was equipped with a nitrogen flush to minimize atmospheric attack on passivated surfaces. Connections made made by means of Cajon fittings with flat copper washers. Waste fluorine was vented or pumped from the system through a 500° chamber packed with carbon.

The sapphire reaction vessel was described in detail previously.[7] Briefly, it comprised a short test tube (24 × 8 mm i.d.) made of optical-grade sapphire, silver soldered to a stainless-steel tube[8] and fitted with a bellows-type stainless steel valve, Hoke No. 4112-G4Y. The stainless steel reactor was a solenoid activated stirred reactor consisting of a stainless steel tube (20 cm × 2 cm i.d.) which mated to a bellows-type Hoke valve with a large Cajon fitting. The stirrer was constructed such that it scraped the walls of the reactor.

Reaction studies were carried out using both a static system and a recirculating reaction system. In a static system, a typical experiment consisted of cooling a 0.3-mmol sample of O_2BF_4 in a sapphire reaction tube to 195°K and pumping down to 10^{-3} Torr. After further cooling to 77°K, 1.0 mmol of xenon was condensed over the sample. The sapphire tube was then isolated from the vacuum system and warmed by removing the liquid nitrogen bath surrounding the tube. By carefully raising and lowering the liquid nitrogen bath, the xenon was alternately vaporized and condensed around the solid. After completion of the reaction (no further release of oxygen gas), the volatiles, at 77°K, were expanded into a calibrated volume for pressure measurement. A quadrupole mass spectrometer[9] was used to analyze these volatile products and others generated in subsequent steps. After pumping away these gases, the sample was warmed to 195°K; volatile gases were measured and analyzed as before. The white solid product that remained was used directly in subsequent spectroscopic studies to determine its composition and structure.

The quadrupole mass spectrometer, though excellent for qualitative and quantitative identification of O_2, Xe, and BF_3, was relatively insensitive to small amounts of fluorine because of wall reactions in the inlet system and within the spectrometer. To analyze for fluorine, the procedure described by Keith, *et al.*,[2] was used. This involved cooling the gases to 77°K to condense any Xe or BF_3, passing the volatile gases through a heated tube containing sodium chloride, then condensing and measuring the volume of chlorine produced.

In order to study the effect of temperature on the reaction of xenon with O_2BF_4, a recirculating reaction system was constructed (Figure 1). In this system, a precooled mixture of xenon and nitrogen was pumped through the O_2BF_4 sample. Any oxygen or fluorine produced was removed from the system by reaction with copper at 300°. Consequently, the uptake of xenon was directly related to the pressure drop of the system.

Infrared spectra were obtained using Beckman IR4 and IR4P spectrometers. Samples were studied at 77°K using a specially constructed low-temperature cell.[3] Raman spectra were obtained with a Spectra Physics 125 He–Ne laser and a Jarrell-Ash 25-300 spectrometer.

Results

Reaction of Xenon with O_2BF_4. No reaction occurred when liquid xenon was condensed over O_2BF_4 at 163°K even after several hours. However, if the temperature was raised somewhat, by alternately vaporizing and condensing xenon around the O_2BF_4, a visible reaction was observed; the color of the reaction mixture changed from white to purple to white again with a concomitant release of oxygen and fluorine. Following the stoichiometric release of oxygen gas from O_2BF_4 the transient purple color disappeared.

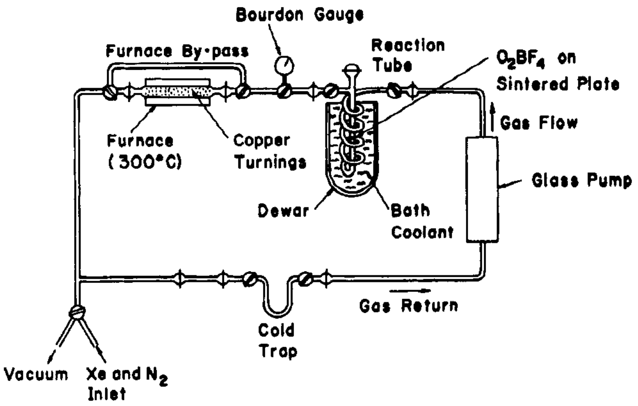

Figure 1. Recirculation system for the reaction of Xe with O_2BF_4.

The only volatile gases produced during this reaction were oxygen and fluorine; no boron trifluoride was observed. A white solid (A) remained after pumping away all the residual gases at 195°K. This solid decomposed about 243°K into xenon and boron trifluoride; no fluorine was observed. In some cases, a very small quantity of xenon difluoride remained after the decomposition of A.

The effect of temperature on the reaction of xenon with O_2BF_4 was studied in the apparatus described in Figure 1. It was found that the optimum reaction temperature was about 173°K. Below this temperature the reaction was very slow; at higher temperatures, *e.g.*, 195°K, boron trifluoride was released. The remaining white solid then decomposed about 220°K into xenon, oxygen, and fluorine. No further identification was made of this compound.

Analytical Data. The ratio of O_2/F_2 produced during the reaction of xenon with O_2BF_4 varied between 2.0 and 2.3, but never dropped below 2.0. When this ratio was greater than 2, a small amount of XeF_2 was produced which accounted for the lower fluorine yield. This is illustrated in an example where the O_2/F_2 ratio was 2.3. In this case, 0.30 mmol of O_2 and 0.13 mmol of F_2 were obtained along with 3.2 mg (0.02 mmol) of XeF_2.

Volumetric measurements indicated that 1 mol of xenon reacted for each mole of oxygen gas released. If some XeF_2 was produced, a corresponding increase in the xenon consumption resulted.

The mass spectrum of the thermal decomposition products of A was very clean, showing only fragments derived from xenon and boron trifluoride, with no evidence for oxygen containing species of any kind. The molar ration of Xe/BF_3 in the decomposition products was unity as determined by a calibration of the mass spectrometer; this is consistent with a composition for A of F_3XeB.

Spectroscopic Observations. The infrared spectrum of the reaction product A is shown in Figure 2. The observed spectrum did not change with time and no reaction with the AgCl sample plates was observed. Comparison with the spectrum of O_2BF_4[3] indicates that the BF_4 is not present in A; the strong bending modes at 532 and 518 cm^{-1} in BF_4^- are absent in the spectrum of A, and the BF stretching modes occur at lower frequencies than is the case for BF_4^-. This is consistent with the analytical data and eliminates $Xe^+BF_4^-$ as a possible structure for A. The observed

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[8] Eitel-McCullough Inc., San Carlos, Calif., a division of Varian Associates.

[9] Quad 200 mass spectrometer, Electronic Associates Inc., Palo Alto, Calif.

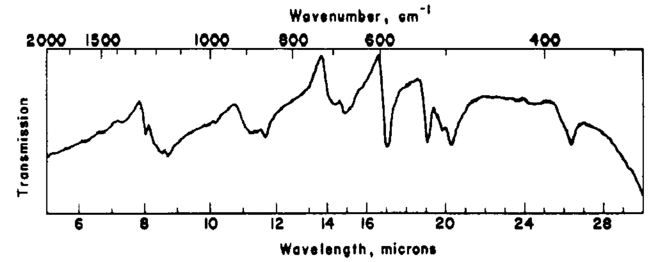


Figure 2. Infrared spectrum of FXe–BF_2 at 77°K.

bands for the BF stretching modes at ~1180 and ~800 cm^{-1} occur in a region characteristic of BF_3 which is bonded to another element in a Lewis acid complex, such as H_3NBF_3.[10] Initially[11] we favored a structure $XeBF_3$ for A, in spite of the relatively numerous bands observed in the infrared spectrum above 350 cm^{-1}.

Reconsideration of the infrared data in the light of the results of Bartlett and his coworkers[12] for a series of $XeF^+MF_6^-$ salts, in which a strong doublet at 612–610 cm^{-1} in the infrared was attributed to the XeF^+ cation, cast further uncertainty on our earlier conclusion and led us to obtain the Raman spectrum. Raman spectra were obtained of the sample in a sapphire tube cooled to 150°K by a stream of cold nitrogen gas. The spectrum consisted of two bands, a relatively strong band at 590 cm^{-1} and a weaker one near 370 cm^{-1}. We believe the stronger band to be an XeF vibration and the weaker one the XeB vibration. No evidence was found for any BF stretching bands, which are expected to be weak due to the low polarizability of the BF bond. Since stretching modes are generally more intense than bending modes in the Raman spectrum, we feel reasonably confident in making these assignments. On the basis of these results, we now believe the structure of A is best described as covalently bonded FXe–BF_2.

The observed infrared and Raman bands together with proposed assignments are listed in Table I. Although the infrared spectrum is perhaps more complex than would initially be expected from a molecule of FXe–BF_2, which presumably has C_{2v} symmetry, such complexity could well be the result of crystal effects. The absence of any change in the spectrum with the passage of time and no reaction with the window material was noted.

Table I. Vibrational Spectrum of FXe–BF_2

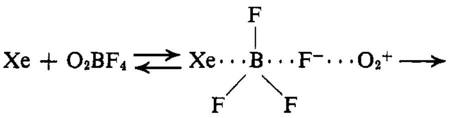
Frequencies, cm^{-1}			Suggested assignment
Infrared	Raman		
1250 (w)			
1180 1149 (s)		BF_2	Antisym str
885 857 (m)		BF_2	Sym str
694 672 (s)		BF_2	Sym def
588 (s)	~590 (m)	XeF	Str
524 504 (m) 492		BF_2	Sym def
379 (w)	~370 (w)	XeB	Str

Discussion

The reaction of xenon with O_2BF_4 appears to be more complex than first expected. An electron-transfer mechanism to produce $XeBF_4$ does not occur, nor is it likely that $XeBF_4$ is formed as an unstable intermediate, decomposing to $FXeBF_2$ and a fluorine atom. For one thing, such a mechanism would not account for the unstable oxygen-containing xenon compound which has been observed at reaction temperatures near 195°K. Also, there is no evidence that BF_4^- salts decompose by release of fluorine atoms. In fact, Keith, *et al.*,[2] have evidence that O_2BF_4 decomposes *via* the following equilibrium.

$$O_2BF_4 \longleftarrow \cdot O_2F + BF_3$$

To account for the observed products, the following series of reactions is proposed.



$$\mathrm{Xe} + O_2BF_4 \rightleftharpoons \mathrm{Xe}\cdots BF_3\cdots F^-\cdots O_2^+ \longrightarrow \mathrm{FXe{-}BF_2} + \cdot O_2F \quad (1)$$

$$2\cdot O_2F \longrightarrow F_2 + 2O_2 \quad (2)$$

$$2\cdot O_2F \rightleftharpoons O_4F_2 \longrightarrow O_2F_2 + O_2 \quad (3)$$

$$O_2F_2 \longrightarrow O_2 + F_2 \quad (4)$$

$$O_2F_2 + \mathrm{Xe} \longrightarrow \mathrm{XeF_2} + O_2 \quad (5)$$

The transient purple color, described earlier, is suggestive of a charge-transfer complex such as B. This complex is similar to that proposed earlier[2] for the reaction of O_2F_2 with BF_3, *i.e.*, $FO_2^+\cdots F\cdots BF_3$. In our case, we suggest that the $\cdot O_2F$ radical is displaced from O_2BF_4 by xenon. The decomposition of $\cdot O_2F$ and its reaction with xenon are well documented[7,13] and would account for the oxygen, fluorine, and xenon difluoride produced. It is interesting to note that Morrow and Young[13] found evidence for an unstable oxygen-containing compound of xenon when a sample of O_2F_2 and xenon was held at 195°K. This may be similar to the oxygen-containing xenon compound we observed when reacting xenon with O_2BF_4 at 195°K.

The requirement that a B–F bond in BF_3 be sacrificed in making the FXe–BF_2 molecule is difficult to rationalize thermodynamically. For this reason, we initially favored the structure Xe–BF_3 involving the pyramidal BF_3 associated with xenon. Although the vibrational spectroscopic data support the structure FXe–BF_2, we looked for chemical evidence that might differentiate between the two structures. One approach was to determine if xenon and boron trifluoride would combine to form Xe–BF_3. Attempts to cause reaction of xenon and boron trifluoride in their ground states were unsuccessful, so the possibility of an excited-state BF_3 combining with xenon was considered. To examine this possibility, two irradiation experiments were performed. First, a mixture of xenon and boron trifluoride was irradiated

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at 77°K for 1 hr with 3-MeV bremsstrahlung of up to 100 Mrads/hr intensity. Second, boron trifluoride was irradiated in a similar manner, then xenon added to the excited BF_3 at 77°K. In neither case was a reaction between xenon and boron trifluoride observed. Interestingly, however, a reaction did occur by irradiating a mixture of xenon and boron trifluoride containing 1–2% fluorine at 77°K to produce largely compound A and some XeF_2. In this case, the catalytic effect of fluorine can be explained by assuming that $\cdot XeF$ was produced which then reacted with BF_3.

Meinert, *et al.*,[14,15] have shown that a $XeF_2 \cdot BF_3$ adduct is formed by combining XeF_2 and BF_3. The possibility that this was an intermediate in our work was discounted when we found that the complex $XeF_2 \cdot BF_3$ would not yield compound A. We suggest that in our studies[16] an adduct $FXe \cdot BF_3$ is present in an excited state capable of reacting further with xenon to yield compound A and $\cdot XeF$. A possible reaction path for this reaction could be as follows

$$XeF \cdot BF_3 + Xe \rightleftharpoons FXe \cdots BF_2 \cdots F \cdots Xe \longrightarrow FXe\text{–}BF_2 + \cdot XeF$$

The proposed structure, $FXe\text{–}BF_2$, certainly has not been proven beyond the shadow of a doubt; however, we believe our experimental evidence favors this structure over the structure $Xe\text{–}BF_3$. Further experiments on this system, such as F^{19} magnetic resonance and X-ray defraction studies, would be desirable to establish the structural parameters of this intriguing molecule more firmly.

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Reactions of Transition Metal Compounds with Macrocyclic Alkadiynes. I. Intramolecular Transannular Cyclizations with Cyclopentadienyldicarbonylcobalt[1]

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30601. *Received July 19, 1971*

Abstract: The macrocyclic alkadiynes 1,7-cyclododecadiyne, 1,7-cyclotridecadiyne, 1,7- and 1,8-cyclotetradecadiyne, and 1,8-cyclopentadecadiyne react with $C_5H_5Co(CO)_2$ or, in some cases, $C_5H_5Co(1,5\text{-}C_8H_{12})$ in boiling octane or cyclooctane to give yellow to orange volatile compounds of the composition C_5H_5Co(alkadiyne) in which the macrocyclic alkadiyne has undergone an intramolecular transannular cyclization to form a tricyclic cyclobutadiene derivative. The reaction of 1,8-cyclotetradecadiyne with $C_5H_5Co(CO)_2$ also gives the black trimetallic derivative $(C_5H_5)_3Co_3(CO)(C_{14}H_{20})$. The infrared, proton nmr, and mass spectra of these new cyclopentadienylcobalt derivatives are discussed.

Since 1958 extensive studies have been carried out on reactions of numerous types of transition metal derivatives with diverse alkynes.[3] This work has resulted in the preparation of many unusual transition metal organometallic compounds including metal complexes of monodentate monometallic, bidentate bimetallic, and bidentate monometallic alkynes,[4] as well as cyclobutadienes, cyclopentadienones, benzenes, tropones, metallacyclopentadienes, metallacyclohexadienones, etc. This rich variety of interesting transition metal organometallic compounds that can be obtained from reactions of transition metal carbonyls, halides, etc., with alkynes containing one carbon–carbon triple bond suggested that analogous reactions of similar transition metal derivatives with acetylenic derivatives containing two or more carbon–carbon triple bonds might provide useful synthetic routes to novel transition metal organometallic derivatives.

The reported studies on reactions of transition metal derivatives with alkadiynes have been mainly confined to acyclic 1,3-alkadiynes.[5–7] In most cases, the carbon–carbon triple bonds of such acyclic 1,3-alkadiynes interact individually with transition metal atoms. Thus, acyclic 1,3-alkadiynes react with $Co_2(CO)_8$ to give complexes of the type (alkadiyne)$[Co_2(CO)_6]_2$ which correspond to two (alkyne)$Co_2(CO)_6$ units linked by carbon–carbon bonds.[5,7] The limited amount of work on reactions of iron carbonyls with acyclic 1,3-alkadiynes suggests that only one of the two carbon–carbon triple bonds interacts with iron atoms to give ultimately com-

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(2) Postdoctoral research associate, 1968–1971.

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