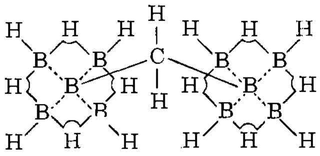
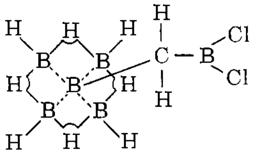
boron atom. We are now able to report that in the course of experiments with halomethanes we were able to isolate, among others, two new derivatives of B_5H_9, di(1-pentaboryl)methane, $(B_5H_8)_2CH_2$ (I), and (1-pentaboryl)dichloroborylmethane, $(B_5H_8)CH_2BCl_2$ (II).[3]


I


II

Reactions with methylene chloride, methylene bromide, and chlorobromomethane lead to rather similar results. In a typical reaction B_5H_9 (64.4 mmoles), CH_2Cl_2 (26.5 mmoles), and $AlCl_3$ (4.3 mmoles) were heated together in a sealed 500-ml. Pyrex flask at 70° for 5 hr. To guard against the consequences of possible explosions the flask was enclosed by a wire mesh protection. On vacuum fractionation 40% of the original B_5H_9 was recovered. The highly volatile portion of the reaction products consisted of H_2 (13.6 mmoles), HCl (1.1 mmoles), B_2H_6 (0.3 mmole), and a trace of BCl_3. A crystalline material and a liquid, which proved to be $(B_5H_8)_2CH_2$ (1.2 mmoles) and $B_5H_8CH_2BCl_2$ (0.3 mmole), respectively, were trapped at −36°. A considerable amount of low-volatile material remained and was not further analyzed.

Separation of the mixture, although difficult, was accomplished by a careful distillation from a simple microstill into a small fractionation train, followed by sublimation of the crystalline $(B_5H_8)_2CH_2$ fraction from room temperature to a −15° cold finger. During storage and fractionation some decomposition always occurred.

$(B_5H_8)_2CH_2$ was identified by its analysis and molecular weight. Elemental analysis was accomplished as previously described[2] after oxidation with fuming nitric acid or after hydrolysis with air-free water.

Anal. Calcd. for $(B_5H_8)_2CH_2$: C, 8.64; H (hydrolysis), 11.66; B, 78.24; mol. wt., 138.3. Found: C, 8.5; H, 11.65; B, 78.1; mol. wt. (gas density), 144; mol. wt. (cryoscopic, cyclohexane), 139. The melting point was 50.8–51.8° and the vapor pressure at 88° was 14 mm.

The infrared spectrum includes the major bands observed for B_5H_9[4] (2600, 1800, 1400, and 1100 $cm.^{-1}$). The 1800 $cm.^{-1}$ region exhibits two *well-defined* peaks which are found to be a characteristic of B_5H_9 derivatives substituted at the apex boron atom, when compared to compounds substituted at a base atom.[2,5,6]

The substance $(B_5H_8)_2CH_2$ reacts rapidly on exposure to air. Under vacuum, it decomposes very slowly at room temperature with evolution of a noncondensable gas, and the formation of liquid and a nonvolatile white solid with a B:C ratio of approximately 1:1.

The compound $(B_5H_8)CH_2BCl_2$ was more difficult to identify than $(B_5H_8)_2CH_2$ because of its lesser stability. It decomposes at room temperature and during vacuum transfers, producing HCl, a highly volatile boron compound, and a nonvolatile solid. Elemental analysis and molecular weight determination are in accord with the proposed formula.

Anal. Calcd. for $B_5H_8CH_2BCl_2$: C, 7.61; H (hydrolysis), 5.11; B, 41.11; mol. wt., 157.92. Found: C, 7.5; H, 5.2; B, 41.2; mol. wt. (cryoscopic, cyclohexane), 167. The infrared spectrum indicates the presence of C–H bonds, contains the main bands for B_5H_9 (including the twin peaks around 1800 $cm.^{-1}$ characteristic of apex substitution), and exhibits a strong broad band around 900 $cm.^{-1}$ which has been assigned to the B–Cl stretching mode.[7] These data and the method of synthesis prompt us to assign to the compound the structure II.

Both compounds, together with other substances such as CH_3BCl_2 and $B_5H_8CH_3$, were also found in low yields as products of the reaction of B_5H_9 with $CHCl_3$, $CHCl_2Br$, or CCl_4 in the presence of $AlCl_3$. In these instances, a carbon–halogen bond had been replaced by a carbon–hydrogen bond.

Acknowledgment.—This work was performed with financial support from the Olin Mathieson Chemical Corporation under a contract with the Ohio State Research Foundation during the years 1952–1957.

(3) Nomenclature in accord with the preliminary report of the Advisory Committee on the Nomenclature of Boron Compounds, American Chemical Society.

(4) H. J. Hrostowski and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

(5) G. E. Ryschkewitsch, E. J. Mezey, E. R. Altwicker, H. H. Sisler, and A. B. Garrett, *Inorg. Chem.*, **2**, 893 (1963).

(6) B. Figgis and R. L. Williams, *Spectrochim. Acta*, 331 (1959).

(7) L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

CONTRIBUTION FROM ROHM AND HAAS COMPANY,
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Isolation and Storage of Free Radicals on Molecular Sieves. II. The Electron Paramagnetic Resonance Spectrum of Nitrogen Difluoride (NF_2)

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AND FREDERIC A. JOHNSON

Received October 3, 1963

A fairly well resolved, isotropic e.p.r. spectrum of NF_2 is obtained when $N_2F_4 \rightleftarrows 2\ NF_2$ is introduced above Linde Molecular Sieves 13X, 10X, and 5A at a pressure of 650 mm. and at room temperature. The NF_2 spectrum on 5A sieve, presented in Fig. 1, appears to show even better resolution than that obtained in solution.[1]

An F^{19} n.m.r. signal from adsorbed N_2F_4 is observed on the 13X and 10X sieves (effective pore diameters,

(1) R. Ettinger and C. B. Colburn, *Inorg. Chem.*, **2**, 1311 (1963).

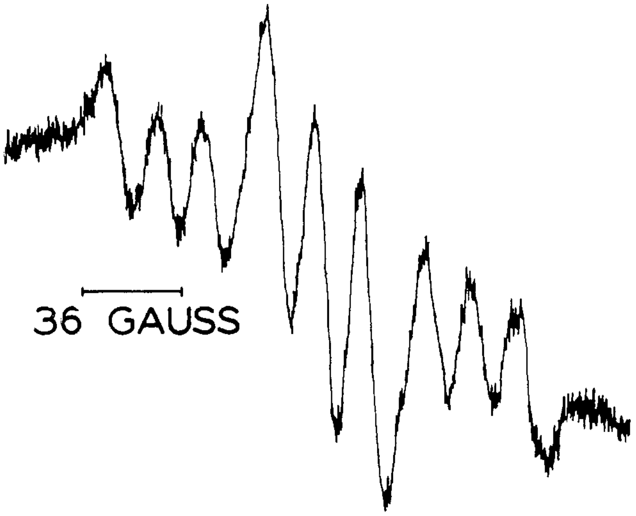

Fig. 1.—Derivative e.p.r. spectrum of NF_2 on Molecular Sieve 5A, 649 mm. N_2F_4.

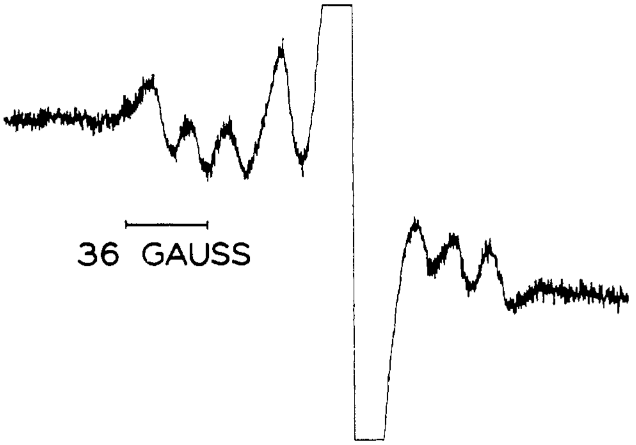

Fig. 2.—Derivative e.p.r. spectrum of NF_2 on Molecular Sieve 13X, 707 mm. N_2F_4.

9 and 8 Å., respectively) but not on 5A sieve (5 Å. effective pore diameter). These n.m.r. results are consistent with some rough adsorption isotherms we have determined, using a helical balance. Above about 0.5 atm. pressure, adsorption of N_2F_4 on 13X and 10X ranges from 0.10 to 0.20 g./g. of sieve. (This amounts to an N_2F_4 concentration of 1–2 *M*, assuming the average volume of the voids is 0.38 cc./g. of sieve and that the intracrystalline voids make up about 51% of the zeolite. All adsorption takes place in the voids.) With these methods, we were unable to detect any gross adsorption of N_2F_4 on 5A sieve (*i.e.*, adsorption was less than about 0.01 g. of N_2F_4 per g. of sieve), and apparently the N_2F_4 has been "screened out" because the adsorption characteristics are similar for very small molecules on all of these sieve materials.

Despite the widely different N_2F_4 concentrations on these three adsorbents, there appear to be similar concentrations of NF_2 radicals judging from the e.p.r. signal amplitudes. With respect to 5A sieve (average void volume 0.27 cc./g., voids 45 vol. % of zeolite), as little as 1 μg. of NF_2 adsorbed per g. of sieve would give a detectable concentration of radical. Thus we are not dealing with a case of adsorption in which the N–F species are frozen out at their equilibrium concentrations, but in which N_2F_4 and NF_2 seemingly follow relatively independent adsorption isotherms.

Neither e.p.r. nor n.m.r. signals could be derived from N_2F_4 (NF_2) on Linde Molecular Sieves 4A and 3A (effective pore diameters 4 and 3 Å., respectively). The latter observation places a limit on the critical dimensions of the radical. (We had estimated a critical diameter for NF_2 of 3.7 Å. from the estimated bond length, 1.37 Å. as in NF_3,[2] the bond angle[3] of 104°, and the van der Waals radii.) Strangely enough, an e.p.r. signal has not been obtained from NO_2 on 5A sieve, although it was observed[4] with NO_2 adsorbed on 13X and 10X sieves. From the known dimensions of the NO_2 radical, one would have expected it to possess a smaller critical diameter than NF_2.

It might be pointed out that silica gel adsorbs N_2F_4 sufficiently for F^{19} n.m.r. detection, yet no e.p.r. signal from adsorbed NF_2 has been found. These observations are summarized in Table I.

TABLE I

ADSORPTION OF $N_2F_4 \rightleftarrows 2NF_2$ ON VARIOUS SUBSTRATES

Molecular sieve	NF_2 e.p.r. signal	N_2F_4 n.m.r. signal	Bulk adsorption of $N_2F_4 \rightleftarrows 2NF_2$[a]
13X	Yes	Yes	0.10
10X	Yes	Yes	0.19[b]
5A	Yes	No	<0.01
4A	No	No	<0.01
3A	No	No	<0.01
Silica gel	No	Yes	Not measured

[a] In grams per gram of adsorbent at room temperature and 1 atm. [b] This value was obtained at 0.4 atm.

Occasionally, on 13X sieve, a second e.p.r. signal appears superimposed on the NF_2 signal as shown in Fig. 2. This signal, together with the one produced by the NF_2, can be removed from the sieve with evacuation at 10^{-5} atm., at room temperature. The species causing this absorption has not been identified to date. The appearance of this second signal is also not reproducible, and in most experiments only the NF_2 spectrum is observed.

From our experience with free radicals and these crystalline zeolites, it would appear that the molecular sieves provide a convenient "inert matrix" for observations at room temperature. Since the adsorption capacities involved are less than one radical per cavity, the radicals are fairly well isolated from one another. Some intriguing questions remain to be explored: (1) what is the nature of the adsorption of the NF_2 radical (ion–dipole interaction with a surface cation?), (2) why the presumably reactive radical species do not attack the sieves more vigorously than they do, and (3) why the e p.r. spectrum is so little affected by the adsorption process. NF_2, both in solution[1] and adsorbed on molecular sieves, has a *g* value of 2.009,

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(2) V. Shomaker and C. S. Lu, *J. Am. Chem. Soc.*, **72,** 1182 (1950).

(3) D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **31,** 1129 (1959).

(4) Paper I: C. B. Colburn, R. Ettinger, and F. A. Johnson, *Inorg. Chem.*, **2,** 1305 (1963).

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.

Acknowledgments.—This work was carried out under Contract No. DA-01-021 ORD-11878 (Z) Mod. No. 7.

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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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James N. Keith, and John M. McDonough

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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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[1] Research reported in this publication was supported by the Advanced Research Projects Agency and technically monitored by the Air Force Office of Scientific Research, Contract No. AF 49(638)-1175.

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