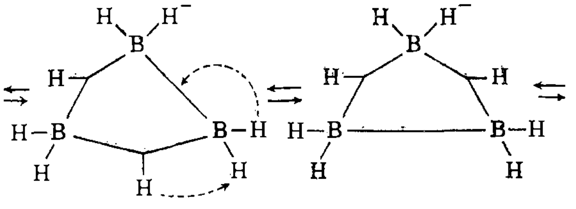
mechanism accounts for alkylborane isomerization more satisfactorily than the previously suggested dissociation–association mechanism.

Hydrogen tautomerism and intramolecular rearrangement have been observed to take place in many electron-deficient boron containing compounds. Examples are: $Al(BH_4)_3$,[2] $B_3H_8^-$,[3] $B_3H_7:O(C_2H_5)_2$,[3] B_6H_{10},[3,4] $B_2H_7^-$,[4,5] $B_4H_6:N(CH_3)_3$,[5] and $B_{10}H_{14}$:cineole[5,6]; the B^{11} n.m.r. spectra of $B_{10}H_{13}^-$[7] and $(CH_3)_2NB_2H_5$.[8]

We suggest that the bridge hydrogen tautomerism mechanism in $B_3H_8^-$ and $(CH_3)_2NB_2H_5$ is relevant to alkylborane isomerization.

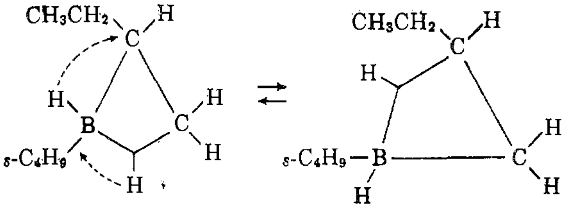
The hydrogens in $B_3H_8^-$ may be considered to migrate about the molecule ion in the following manner



I

The B^{11} n.m.r. spectra of μ-dimethylaminodiborane at several temperatures are compatible with the bridge hydrogen tautomerism mechanism about the boron–boron–nitrogen skeleton although other processes also have been suggested.[8]

One might speculate that an electron-deficient (and isoelectronic) system of boron, carbon, and hydrogen atoms also could tautomerize. For example, di-2-butylborane could rearrange *via* a tautomeric process.



This intermediate structure was suggested previously to account for the *cis* addition of BH_3 groups to the double bond in the hydroboration of olefins.[9] However, the dissociation–association mechanism was considered to account for the alkylisomerization.[10]

The bridge hydrogen tautomerism mechanism explains several observations with respect to alkylborane isomerization which are not satisfactorily explained by the dissociation–association mechanism.

(1) The bridge hydrogen tautomerism mechanism requires that R_2BH be present. Unusually rapid isomerization has been reported[11] in cases where the olefin is too bulky to allow the formation of the trialkylborane.

(2) The addition of a small amount of diborane should increase (*via* rapid alkyl-hydrogen exchange[12]) the concentration of R_2BH present in the system. Subsequent rapid alkyl-hydrogen exchange would allow *all* alkyl groups to exist "part time" in R_2BH molecules and alkylborane isomerization consequently should be speeded up. Such an effect for diborane has been reported.[13]

(3) Alkylborane isomerization proceeds at 160° (*ca.* 1 hr.) in diglyme, whereas 215° (20–50 hr.) is necessary[14] in the absence of diglyme. Diborane and diglyme react reversibly to form diglyme:BH_2^+ and $B_2H_7^-$.[5,15]

It is probable that the diglyme–diborane equilibrium is such that the last traces of diborane are not easily removed, therefore a small amount of diborane is retained which catalyzed the isomerization reaction as in (2), above.

It is probable that alkylaluminane isomerization[16,17] and certain rearrangements and hydrogen migration in carbonium ions also take place *via* a bridge hydrogen tautomerism mechanism.

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(2) R. A. Ogg and J. D. Ray, *Discussions Faraday Soc.*, **19**, 239 (1955).

(3) W. N. Lipscomb, *Advan. Inorg. Chem.*, **1**, 132 (1959).

(4) R. E. Williams, *J. Inorg. Nucl. Chem.*, **20**, 198 (1961).

(5) R. E. Williams, 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1960.

(6) R. J. F. Palchak, J. H. Norman, and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961).

(7) This conclusion also was made independently by Dr. R. L. Williams, Admiralty Materials Laboratory, Dorset, England.

(8) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(9) H. C. Brown and G. Zweifel, *ibid.*, **81**, 247 (1959).

(10) H. C. Brown and B. C. Suba Rao, *ibid.*, **81**, 6434 (1959).

(11) H. C. Brown and G. Zweifel, *ibid.*, **82**, 4708 (1960).

(12) H. I. Schlesinger and A. A. Walker, *ibid.*, **57**, 621 (1935).

(13) G. Zweifel, *Tetrahedron*, **2**, 117 (1961).

(14) G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowsky, *J. Am. Chem. Soc.*, **79**, 5190 (1957).

(15) H. C. Brown and P. E. Tierney, *ibid.*, **80**, 1552 (1958).

(16) K. Ziegler, *Brennstoff-Chem.*, **35**, 321 (1954).

(17) K. Ziegler, "Metal-Organic Syntheses," in "Perspectives in Organic Chemistry," A. Todd, ed., Interscience Publ., New York, N. Y., 1956.

SPACE-GENERAL CORPORATION ROBERT E. WILLIAMS
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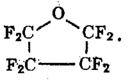
RECEIVED FEBRUARY 23, 1962

The Reaction of Dioxygen Difluoride with Tetrafluoroethylene

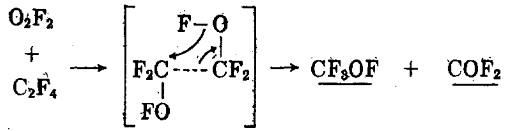
Sir:

Dioxygen difluoride, O_2F_2, discovered by Ruff and Menzel,[1] melts at −163.5° to a red liquid; it decomposes rapidly to O_2 and F_2 close to its normal boiling point of −57°. Little is published concerning the chemistry of this compound and we wish to report here its reaction with tetrafluoroethylene.

Dioxygen difluoride was prepared in an electrical discharge by a method described by Kirshenbaum and Grosse.[2] The method yields O_2F_2 when the proportions of oxygen and fluorine are 1:1. The discharge tube, which also was used as the reactor, was maintained at −196° during the preparation and was warmed and cooled slightly several times with pumping to remove any dissolved oxygen.

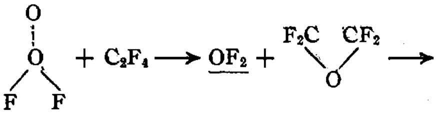
The reactions were conducted by allowing tetrafluoroethylene to condense into the reactor containing the solid O_2F_2 at −196°, maintained with a liquid nitrogen-filled dewar. Upon contact, flashes were observed even at this temperature and these continued with gradual lowering of the liquid nitrogen level. The products from the reaction were COF_2 and CF_4 with lesser amounts of C_2F_6, SiF_4, and CF_3OOCF_3. All products were isolated by conventional vacuum line fractional condensation and chromatographic techniques and were identified by their reported infrared and mass spectra. In an additional experiment, several liquid cc. of diluent argon (vapor pressure at −196° = 200 mm.) were condensed into the reactor containing the O_2F_2. The C_2F_4 was allowed to diffuse to the cold zone. A single small flash was observed. In addition to the above products, CF_3OF, OF_2, and C_4F_{10} also were produced. Finally, the C_2F_4 was highly diluted with helium before being passed through the reactor at −196° and 2–4 mm. No flashes were noticed during addition, but on warming a few were again observed. Most of the condensable material was volatile at −160° and the products included the above (with the exception of OF_2) along with CO_2, $C_2F_5OCF_3$, and . No C_2F_4 or O_2F_2 was recovered from any of these experiments. These results were generally reproducible if similar conditions were employed.

Most of the steps necessary to give the products isolated (underlined) can be explained by known reactions (eq. 3, 4, and 5). Equations 1 and 2 may offer an explanation for the primary reactions.



(1)

or



$$COF_2 + (CF_2)_{n=1-4} \qquad (2)$$

$$CF_3OF + C_2F_4 \longrightarrow \underline{C_2F_5OCF_3}\ ^{3,4} \qquad (3)$$

$$2CF_3OF \xrightarrow{\Delta} \underline{CF_4} + \underline{CO_2} + [F_2^-]\ ^{3} \qquad (4)$$

$$CF_3OF + COF_2 \longrightarrow \underline{CF_3OOCF_3}\ ^{3b} \qquad (5)$$

The great reactivity of CF_3OF at ignition temperature no doubt explains its isolation in low yield. It is suggested that this reaction under the proper conditions probably would give a higher yield of CF_3OF.

Grateful acknowledgment is made to Mr. L. Adlum for interpretation of the infrared data.

(3) (a) When the authors in ref. 3b attempted this reaction, addition did not occur; instead Teflon-like polymers or CF_4 and CO were produced. However, the authors in ref. 4 did effect addition of CF_3OF to ethylene to give $CF_3OC_2H_4F$ and the conditions used in the current work may explain the results. (b) R. S. Porter and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 5625, 5628 (1957).

(4) J. A. C. Allison and G. H. Cady, *ibid.*, **81**, 1089 (1959).

(5) Office of the Secretary of Defense, Advanced Research Projects Agency, Washington 25, D. C.

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MURRAY S. COHEN

RECEIVED SEPTEMBER 5, 1961

Comment Concerning the Effect on the Diborane–Pentaborane Exchange Reaction of the Reported Deuterium Isotope Effect in the Decomposition of Diborane[1]

Sir:

In a recent paper[2] calculation of the ratio of equilibrium constants for dissociation of B_2D_6 and B_2H_6 was reported to lead to the conclusion that under identical conditions the BD_3 concentration will be about twice as large as the BH_3 concentration. This is significant in view of the fact that diborane–pentaborane isotopic exchange reactions which Professor Koski and the author

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(1) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

(2) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

[1] This work was supported in part by the Office of Naval Research.

[2] R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).