

decomposes rapidly to  $O_2$  and  $F_2$  close to its normal boiling point of  $-57^\circ$ . 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.<sup>2</sup> 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  $-196^\circ$  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  $-196^\circ$ , 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  $-196^\circ = 200$  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  $-196^\circ$  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  $-160^\circ$  and the products included the above (with the exception of  $OF_2$ ) along with  $CO_2$ ,

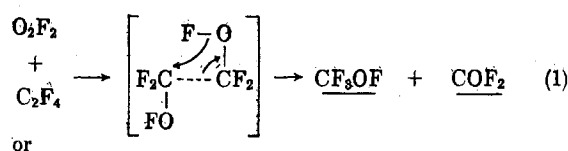
$C_2F_6OCF_3$ , and  $\begin{matrix} F_2C & O & CF_2 \\ | & / \quad \backslash & | \\ F_2C & & CF_2 \end{matrix}$ . No  $C_2F_4$  or  $O_2F_2$  was

recovered from any of these experiments. These results were generally reproducible if similar conditions were employed.

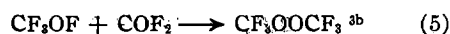
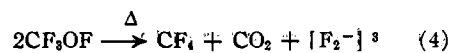
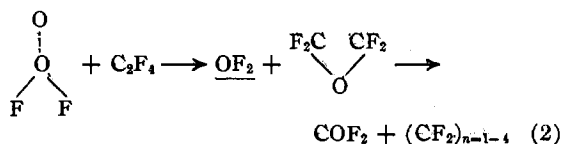
Most of the steps necessary to give the products isolated (underlined) can be explained by known reactions (eq. 3, 4, and 5). Equations 1 and 2 may offer an explanation for the primary reactions.

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

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



or



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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### Comment Concerning the Effect on the Diborane-Pentaborane Exchange Reaction of the Reported Deuterium Isotope Effect in the Decomposition of Diborane<sup>1</sup>

Sir:

In a recent paper<sup>2</sup> 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

(1) This work was supported in part by the Office of Naval Research.

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

ran some years ago showed the rate of exchange of  $B_2D_6$ - $B_5H_9$  to be faster than that of the reverse exchange  $B_2H_6$ - $B_5D_9$ .<sup>3</sup> This can be seen from Fig. 3 of reference 3, the distribution of partially deuterated pentaboranes from (a)  $B_2D_6$ - $B_5H_9$  and (b)  $B_2H_6$ - $B_5H_9$  exchange reactions run under identical conditions, where the species due to exchange are greater in (a). A larger concentration of  $BD_3$  than of  $BH_3$  in a comparable reaction would lead to this result.

Also, the decomposition rate of  $B_2H_6$  appeared to be *five* times faster than that of  $B_2D_6$ <sup>2</sup> if one follows the rate of hydrogen evolution assuming the rate-determining step to be



This result also is pertinent to the diborane-pentaborane exchange because a complication in this exchange is the synthesis of some partially deuterated (or partially hydrogenated) pentaborane from the diborane during the course of the exchange reaction at 80°. A larger amount of pentaborane was synthesized from the diborane in the  $B_2H_6$ - $B_5D_9$  exchange than was synthesized in the reverse exchange  $B_2D_6$ - $B_5H_9$ ; this is entirely in accord with the observed deuterium isotope effect reported in the decomposition of diborane.

There is further experimental evidence from the exchange studies which relates to this observed isotope effect in diborane decomposition. For calibration of both infrared and mass spectrometric experiments, samples of partially deuterated penta- and decaboranes with random distribution of deuteriums were prepared by pyrolysis of partially deuterated diborane samples under appropriate conditions.<sup>4</sup> The original partially deuterated diboranes were made by mixing  $B_2H_6$  and  $B_2D_6$  in the proper proportions, equilibrating the mixture by self-exchange to random H-D distribution, and checking for deuterium content by thermal conductivity<sup>5</sup>; then the diboranes were pyrolyzed. The deuterium contents of the final penta- or decaboranes prepared this way were always several per cent higher than those of the starting diboranes themselves.<sup>6</sup> Since  $B_3X_9$  (X = H or D) probably also is the intermediate

in the rate-controlling step of the pyrolysis to form the higher boron hydrides, the observed five-times faster rate of  $H_2$  evolution than of  $D_2$  evolution would indeed favor a product with a higher deuterium content than the starting material.

There is another experimental datum which might conceivably be related to the greater concentration of  $BD_3$  relative to  $BH_3$ . In a mass spectrometric appearance potential study of isotopically labeled diboranes,<sup>7</sup> the apparently anomalous experimental observation was made that the appearance potential of  $BH_3^+$  from  $B_2H_6$  was about 0.4 e.v. higher than that of  $BD_3^+$  from  $B_2D_6$ . The relationship that, from a molecule  $R_1-R_2$

$$A(R_1^+) = I(R_1) + D(R_1-R_2)$$

[where  $A(R_1^+)$  is the appearance potential of  $R_1^+$ ,  $I(R_1)$  is the ionization potential of  $R_1$ , and  $D(R_1-R_2)$  is the bond dissociation energy], would lead one to the conclusion that either  $I(BD_3)$  or  $D(BD_3-BD_3)$  must be unusually low compared to the hydrogenated compound. A recent measurement of the heat of formation of deuterated diborane shows the heat of dissociation of  $B_2D_6$  to be what one normally would expect from the differences in zero point energies.<sup>8</sup> There appears little reason to believe that  $I(BD_3)$  is 0.4 e.v. lower than  $I(BH_3)$ . However, there now seems to be an alternative explanation for this observed discrepancy in the appearance potentials. Appearance potentials are pressure dependent. A combination of the higher concentration of  $BD_3$  originally present together with the  $BD_3$  formed from  $B_2D_6$  upon electron impact would raise the effective pressure of  $BD_3$  relative to  $BH_3$  (from  $B_2H_6$ ). This quite possibly would lead to a lower observed appearance potential for  $BD_3^+$  than for  $BH_3^+$ .

One last comment might be added here. The calculations<sup>2</sup> were performed assuming molecular parameters for  $B_2H_6$  and  $B_2D_6$  to be the same. However, the author has had some question as to the validity of this assumption for the past several years and has proposed instead the following structure: Terminal B-D bonds in  $B_2D_6$  are presumed to be shorter than terminal B-H bonds by approximately the same amount as

(3) W. S. Koski, J. J. Kaufman, L. Friedman, and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

(4) (a) J. J. Kaufman and W. S. Koski, *J. Chem. Phys.*, **24**, 403 (1956); (b) *J. Am. Chem. Soc.*, **78**, 5774 (1956).

(5) W. S. Koski, P. C. Maybury, and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

(6) J. J. Kaufman and W. S. Koski, unpublished experimental results.

(7) W. S. Koski, J. J. Kaufman, C. F. Pachucki, and F. J. Shipko, *J. Am. Chem. Soc.*, **80**, 3202 (1958).

(8) S. R. Gunn and L. G. Greene, *J. Chem. Phys.*, **36**, 1118 (1962).

normal C-D bonds are shorter than normal C-H bonds; on the other hand, bridge B-D bonds are postulated to be longer than bridge B-H bonds. While there is no direct experimental evidence to confirm this hypothesis, a recent preliminary electron diffraction study of deuterated diborane reports that the average of B-H terminal and bridge distances in  $B_2H_6$  and the average of B-D terminal and bridge distances in  $B_2D_6$  are almost the same.<sup>9</sup> Since it seems very likely that the terminal B-D distance in  $B_2D_6$  is shorter than the terminal B-H distance in  $B_2H_6$ , it is quite probable that the bridge B-D distance is longer than the bridge B-H distance. However, this point awaits experimental confirmation, possibly by differential neutron diffraction of  $B_2^{11}H_6$  and  $B_2^{11}D_6$ .

(9) L. S. Bartell, paper presented before the Division of Chemical Physics, American Physical Society Meeting, March, 1962.

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### Observations on the Hydrolysis Product Distributions for Some Inner Transition Metal Carbides

Sir:

In a recent article, Palenik and Warf<sup>1</sup> reported on the hydrolysis of lanthanum and cerium carbides. The purpose of this communication is to point out some similarities in the hydrolysis product distributions of the rare earth carbides  $LaC_2$  and  $CeC_2$  and the actinide carbides  $ThC_2$  and  $UC_2$ , and to show that the prediction of Palenik and Warf<sup>1</sup> concerning the nature of the  $ThC_2$  and  $UC_2$  hydrolysis products is indeed correct.

In recent investigations in this Laboratory, Kempter and Krikorian<sup>2</sup> and Kempter<sup>3</sup> studied the hydrolysis of  $ThC$  and  $ThC_2$  and  $UC$  and  $UC_2$ , respectively. Although the hydrolysis product distributions from the homotypic carbides  $ThC_2$  and  $UC_2$  appeared to be dissimilar, it was found<sup>3</sup> that both consisted of about two-thirds

even-numbered carbon atom hydrocarbons, about three-tenths hydrogen plus methane, and a small fraction of catenated odd-numbered carbon atom hydrocarbons. In examining the composition of hydrocarbons, excluding methane, from the 25° hydrolysis<sup>1</sup> of the isomorphous carbides  $LaC_2$  and  $CeC_2$ , one sees a semiquantitative agreement between individual species and between total alkanes, total alkenes, and total alkynes. However, if one sums the even-numbered carbon atom hydrocarbons, the catenated odd-numbered hydrocarbons, and the unidentified components, the agreement is much better. The various summations of hydrolysis products for  $LaC_2$ ,  $CeC_2$ ,  $ThC_2$ , and  $UC_2$  are shown for comparison in Table I. Hydrogen and methane are not included in any of the totals because Palenik and Warf<sup>1</sup> used liquid nitrogen to condense their samples; in the room temperature runs they obtained about 5 mole % non-condensables. The mole percentages of hydrogen and methane not included in the  $ThC_2$  and  $UC_2$  hydrolysis product totals are 27.2%  $H_2$ , 2.35%  $CH_4$  and 14.1%  $H_2$ , 17.3%  $CH_4$ , respectively. Methane is of course the only non-catenated odd-numbered carbon atom hydrocarbon.

TABLE I  
DISTRIBUTION OF HYDROCARBON HYDROLYSIS PRODUCTS OF SOME INNER TRANSITION METAL DICARBIDES

Species <sup>a</sup>	$LaC_2$	$CeC_2$	$ThC_2$	$UC_2$
Alkanes	25.07	20.56	49.8	68.9
Alkenes	11.30	10.00	19.5	28.3
Alkynes	61.5	67.3	27.8	2.8
Unidentified	2.2	2.1	2.8 <sup>b</sup>	..
Even-no. C	97.6	97.8	92.9	93.6
Odd-no. C	0.3	0.1	4.3	6.4

<sup>a</sup> All totals expressed in mole % of total catenated hydrocarbons produced in room temperature hydrolysis.  
<sup>b</sup> Hydrocarbons above  $C_4H_x$ .

It also is apparent that the prediction of Palenik and Warf<sup>1</sup> that in the case of thorium and uranium carbides "the two-electron oxidation in the hydrolysis reaction is expected to produce more hydrogen and hydrogenated hydrocarbons than in the case of the rare earth dicarbides" is consistent with the hydrolysis product data for  $ThC_2$  and  $UC_2$ .

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(1) G. J. Palenik and J. C. Warf, *Inorg. Chem.*, **1**, 345 (1962).

(2) C. P. Kempter and N. H. Krikorian, *J. Less-Common Metals*, **4**, 244 (1962).

(3) C. P. Kempter, *ibid.*, in press.

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