

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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