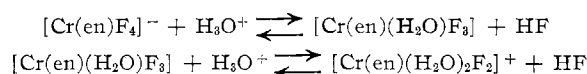Application of the solubility rules of Werner[9] to the analogous chromium and cobalt fluoro complexes indicates both of these to have the same relative generic configuration. This is further supported by the observation that both complexes have similarly shaped rotatory dispersion curves. Thus d-cis-[Cr(en)$_2$F$_2$]I, d-cis-[Co(en)$_2$F$_2$]I, and l-cis-[Co(en)$_2$Cl$_2$]Cl all have the same relative configurations.

The formation of the complex anion is probably dependent upon the following factors. First, there is a difference in the structures of solid chromium(III) fluoride and solid chromium(III) chloride. The three-dimensional structure of chromium(III) fluoride could possibly facilitate the transfer of a fluoro ligand between adjacent metal ions more easily than could a two-dimensional structure. Second, chromium(III) resembles aluminum(III) and it is known that the affinity of an aluminum(III) halide for another halogen drops off markedly with increasing atomic weight of the halogen. Anionic fluoro complexes of chromium(III) such as M$_3$[CrF$_6$] and M$_2$[CrF$_5$H$_2$O] are known, but apparently the only example of an anionic complex involving ethylenediamine similar to the one found in the study is M[Cr(en)(SCN)$_4$].[10] A similar complex involving ethylenediamine and chlorine is apparently not known.

The instability of the tetrafluoroethylenediamine-chromate(III) anion in acid solution is probably due to reactions of the type

$$[Cr(en)F_4]^- + H_3O^+ \rightleftarrows [Cr(en)(H_2O)F_3] + HF$$
$$[Cr(en)(H_2O)F_3] + H_3O^+ \rightleftarrows [Cr(en)(H_2O)_2F_2]^+ + HF$$

Such reactions would explain the observed shifts in the absorption spectra and the formation of a new cationic species as the solutions were allowed to age at room temperature.

On the basis of the limited amount of data available the 1,2-propanediamine complex of chromium(III) fluoride would appear to involve a *cis* arrangement of the fluoro ligands. Resolution of the complex cation is currently underway in this laboratory.

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 229.

(10) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green, and Co., London, 1948, p. 410.

CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION,
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Reactions of Thorium Carbides with Aqueous Sodium Hydroxide Solutions[1]

BY MILDRED J. BRADLEY, MERLE D. PATTENGILL,
AND LESLIE M. FERRIS

The reactions of thorium mono- and dicarbides with aqueous sodium hydroxide solutions were investigated

as part of a continuing program on the chemistry of the heavy metal carbides. The reactions of the thorium carbides with water were studied previously.[2] No reference to their behavior toward basic solutions could be found.

Experimental

Preparation and Characterization of Carbides.—The carbide specimens were prepared by arc melting high purity thorium metal with spectroscopic grade carbon using graphite electrodes, as described previously.[2] Only thorium monocarbide or thorium dicarbide was detected in the X-ray diffraction powder patterns. Metallographic examination of the thorium monocarbide specimens showed 5 to 8% thorium dicarbide impurity. No free metal was observed, indicating that thorium monocarbide is a carbon-deficient compound.[3] The thorium dicarbide specimen was nearly single-phase dicarbide with a small amount of graphite inhomogeneously dispersed throughout the carbide. No thorium monocarbide impurity was observed in the dicarbide specimen by metallographic examination.

Sodium Hydroxide Solutions.—The sodium hydroxide solutions were prepared by the standard method for carbonate-free base[4] using reagent grade sodium hydroxide pellets and boiled distilled water. At the conclusion of the experimental program the solutions contained an average of 0.4 mg. of CO$_3$$^{2-}$ per ml.

Procedure.—The apparatus, analytical techniques, and experimental procedures used were similar to those described previously.[2,5] When the reaction was complete, 12 M HCl was added to neutralize the sodium hydroxide and dissolve the thorium oxide.

Results

Thorium Monocarbide.—The reaction of thorium monocarbide with 0 to 18 M NaOH solutions at 80° produced thorium oxide (identified by X-ray diffraction analysis) and 90 ml. (STP) of gas per gram of carbide consisting of 83 vol. % methane and 13% hydrogen with small quantities of C$_2$ to C$_8$ hydrocarbons (Table I). The reaction with 6 M NaOH gave the same products at 40 and 80°. Of the total carbon present initially in the carbide, 79% was found as methane, 12% as gaseous C$_2$ to C$_8$ hydrocarbons, 2% in a hydrochloric acid insoluble residue, and 7% was unaccounted for. There may have been a trace of wax deposited on the surface of the reaction vessel; however, the amount was too small to recover. The thorium oxide dissolved readily in hydrochloric acid; material balances for thorium ranged from 97 to 100%.

After dissolving the thorium oxide, a small amount of an insoluble white solid remained (about 0.1 g./g. of carbide). Semiquantitative emission spectroscopy showed that it consisted mainly of sodium (10 to 100%) and silicon (10 to 100%) with a little boron (1 to 10%), indicating that it probably resulted from a reaction between the sodium hydroxide and the Pyrex reaction flask and possibly also the silicone stopcock grease.

The rate of reaction was not affected by the sodium hydroxide concentration. At 80°, 95% of the gas was evolved within the first 4 hr.; the reaction was complete in about 6 hr. The reaction with 6 M NaOH at

(2) M. J. Bradley and L. M. Ferris, *J. Inorg. Nucl. Chem.*, in press.

(3) M. J. Bradley and T. M. Kegley, manuscript in preparation.

(4) W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1944, p. 108.

(5) M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **3**, 189 (1964).

40° was much slower, requiring about 30 hr. for 95% completion.

TABLE I

GASEOUS PRODUCTS FROM THE REACTION OF THORIUM MONOCARBIDE[a] WITH NaOH SOLUTIONS

NaOH concn., M	0.0	2.0	6.1	12.2	18.0	40° 6.1
Vol. of gas evolved, ml. (STP)/g. of sample	93	90	89	90	91	89
Gas composition, vol. %						
Hydrogen	12	12	13	12	14	12
Methane	83	83	82	83	81	83
Ethane	2.8	2.7	3.0	3.0	3.0	2.9
C_3 to C_8 alkanes	0.8	0.7	0.8	0.8	1.0	0.7
Unsaturates	1.3	1.4	1.3	2.1	1.6	1.2

[a] Elemental analysis: thorium, 94.77 wt. %; total carbon, 5.06%; free carbon, 0.01%; oxygen, 0.01%; and nitrogen, 149 p.p.m. Combined-C:Th atom ratio, 1.03.

Thorium Dicarbide.—The reaction of thorium dicarbide with 0 to 18 M NaOH solutions yielded a mixture of hydrogen and gaseous hydrocarbons, a nonvolatile wax, and thorium oxide. The gaseous products consisted of about 35 vol. % hydrogen, 30% ethane, 25% unsaturated C_2 to C_8 hydrocarbons, 4% methane, and small quantities of C_3 to C_8 alkanes (Table II). In general the composition of the gas remained constant over the 0 to 18 M NaOH concentration range except the concentration of ethyne, which increased from 8 vol. % with 0-6 M NaOH to 12% with 18 M. The total volume of gas evolved also increased slightly at higher concentration: 49 ml. (STP)/g. of carbide with 0-6 M NaOH; 53 ml./g. with 12 M NaOH; and 55 ml./g. with 18 M NaOH. The reaction with 6 M NaOH gave about the same products at 40° as at 80°, although the volume was slightly lower (45 ml./g. at 40°). These changes in volume are relatively small and had little effect on the carbon distribution. Of the total carbon present initially in the carbide, 48% was found as C_2 to C_8 gaseous hydrocarbons, 14% as wax, and 1% as methane. Dissolved organic compounds were not detected in the sodium hydroxide solutions (limit of detection, 3% of the total carbon in the carbide) and no NaOH-insoluble liquid hydrocarbons were observed visually. As in the thorium monocarbide reactions, a small amount of residue (0.01 to 0.1 g./g. of carbide) remained after dissolution of the thorium oxide in hydrochloric acid and the wax in acetone and ether. This residue contained the free carbon present originally in the carbide as well as the products resulting from etching of the glass. In most experiments the amount of residue was too small to recover for analysis. Even if this residue were pure carbon, it would only account for 3% of the total carbon; thus, about one-third of the carbon is still unaccounted for (see below). Thorium balances for the system ranged from 95 to 100%.

The rate of gas evolution at 80° in the thorium dicarbide–sodium hydroxide reaction increased with increasing base concentration. About 2 hr. was required for complete reaction with water and 2 and 6 M NaOH, while only 20 min. was required with 18 M NaOH. The

TABLE II

GASEOUS PRODUCTS FROM THE REACTION OF THORIUM DICARBIDE[a] WITH NaOH SOLUTIONS

NaOH concn., M	0.0	2.0	6.1	12.2	18.0	40° 6.1
Vol. of gas evolved, ml. (STP)/g. of sample	49	48	49	53	55	45
Gas composition, vol. %						
Hydrogen	35	36	32	33	36	29
Methane	4.0	4.8	3.8	4.0	3.8	3.6
Ethane	29	29	31	30	28	35
Propane	0.7	0.6	0.8	0.8	0.4	0.8
Butanes	2.8	3.2	3.1	2.7	2.8	2.4
C_5 to C_8 alkanes	0.6	0.4	0.4	0.4	0.4	0.2
Ethene	4.5	4.6	4.4	4.3	3.9	5.1
Butenes	5.7	5.3	5.9	4.9	4.6	5.5
C_5 to C_7 alkenes	1.7	1.3	1.2	1.1	0.6	1.1
Ethyne	7.5	8.1	8.5	9.9	11.5	9.5
Propyne	1.8	1.8	2.1	2.2	2.2	1.9
Butyne	4.2	2.8	4.3	4.0	3.9	4.3
Hexynes	0.2	0.2	0.2	0.2	0.1	0.2
Unidentified	2.4	2.0	2.5	1.9	2.0	1.9

[a] Elemental analysis: thorium, 90.46 wt. %; total carbon, 9.26%; free carbon, 0.30%; oxygen, 0.02%; and nitrogen, 226 p.p.m. Combined-C:Th atom ratio, 1.91.

reaction with 6 M NaOH at 40° was much slower, taking 25 hr. for 95% completion.

Discussion

The hydrolysis of thorium carbides in 2 to 18 M NaOH at 80° was virtually the same as that in distilled water. No differences were observed with thorium monocarbide. With 12 and 18 M NaOH, thorium dicarbide produced slightly more gas and reacted more rapidly than with 0 to 6 M NaOH, but there was essentially no change in the composition of the gas, which contained over 30 different hydrocarbons from the polymerization and hydrogenation of the C_2 units in the carbide. As observed earlier in the water reaction,[2] one-third of the dicarbide carbon was not found in either the gas or the wax. Presumably this was lost as volatile species when the acetone and ether were evaporated from the wax. Much additional study of the nonvolatile hydrocarbons, particularly the isolation of the "unaccounted for" carbon, is needed. Failure to draw a complete material balance for the thorium monocarbide experiments (7% unaccounted for) is consistent with the microstructure analysis, which showed significant amounts of dicarbide impurity.

Some corrosion of the glass equipment by the NaOH solutions was encountered, but the corrosion products do not seem to have affected the carbide hydrolysis itself.

CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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## Carborane Derivatives. An Eight-Membered Exocycle of 1,2-Dicarbaclovododecaborane(12)

BY NATHAN MAYES AND JOSEPH GREEN

The syntheses of five- and seven-membered carborane[1] exocycles, in which one carborane participates in the ring, have been reported.[2,3] We wish to report now such an exocycle which has eight members. This compound, 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1'-carboranyl)-2-methylcyclooctane, is a condensation product of 1-(epoxyisopropyl)carborane[4] and 1,2-bis-(hydroxymethyl)carborane.[5] The condensation yielded, in addition to the cyclooctane, the linear ether, β-hydroxy-β-(carboran-1-yl)propyl-(1'-hydroxymethylcarboran-2'-yl)methyl ether. The linear ether is probably an intermediate of the cyclooctane; however, this was not proven by independently converting the linear compound to the cyclic compound.

The preparation and probable structures of these compounds are illustrated in the equation below.
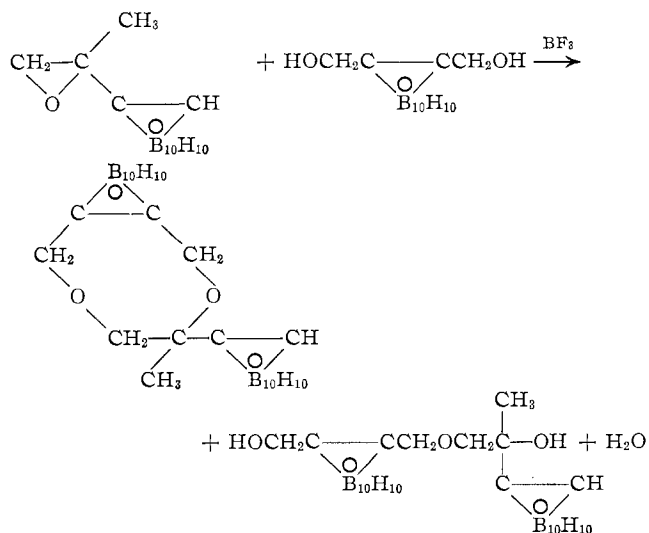
Experimental

1-(Epoxyisopropyl)carborane (26.0 g., 0.130 mole), 1,2-bis(hydroxymethyl)carborane (26.0 g., 0.127 mole), and 150 ml. of toluene were placed in a reaction flask fitted with a water condenser, a Dean–Stark distilling receiver, a Teflon-coated magnetic stirrer, and a gas inlet tube. The mixture was heated with stirring to reflux and became homogeneous. Boron trifluoride was bubbled into the solution several times during 48 hr. of refluxing, and 2.0 ml. of water was collected in the Dean–

Stark receiver. The reaction mixture was concentrated by evaporating most of the solvent and then dissolved in methanol and precipitated by addition of water. The solid precipitate weighed 19.5 g. (40% yield); a sample twice recrystallized from hexane melted at 249–251°. Infrared analysis, molecular weight determination, and elemental analysis indicated the compound to be 1,4-dioxa-6,7-(1,2-carboranylene)-2-(1'-carboranyl)-2-methylcyclooctane. The infrared spectrum contained absorptions at 3060 cm.$^{-1}$ for CH of carborane, at 2560 cm.$^{-1}$ for BH of carborane, at 1374 cm.$^{-1}$ for CCH$_3$, at 1127 cm.$^{-1}$ for COC, and at 730 cm.$^{-1}$ for BH deformation of carborane. No absorption for OH was present. The molecular weight obtained cryoscopically in benzene was 378 (calculated 386). *Anal.* Calcd. for C$_9$H$_{30}$O$_2$-B$_{20}$: C, 27.96; H, 7.82; B, 55.93. Found: C, 26.77; H, 7.92; B, 55.72.

The methanol–water mother liquor was evaporated to yield a gum from which unreacted 1,2-bis(hydroxymethyl)carborane was extracted with 5% aqueous sodium hydroxide and unreacted 1-(epoxyisopropenyl)carborane was extracted with petroleum ether. The remaining solid, weight 9.6 g. (19% yield), was identified as β-hydroxy-β-(carboran-1-yl)propyl-(1'-hydroxymethylcarboran-2'-yl)methyl ether. After three recrystallizations from heptane it melted at 196–201°. The infrared spectrum exhibited absorption bands at 3370 cm.$^{-1}$ for OH stretching and a doublet at 1170 and 1160 cm.$^{-1}$ for tertiary OH deformation. Other bands were at 3080 cm.$^{-1}$ for CH of carborane, at 2940 and 2860 cm.$^{-1}$ for aliphatic CH, at 2560 cm.$^{-1}$ for BH of carborane, at 1116 cm.$^{-1}$ for COC, and at 727 cm.$^{-1}$ for BH deformation of carborane. The molecular weight determined cryoscopically in benzene was 415 (calculated 405). The proton magnetic resonance spectrum, obtained in benzene solution with tetramethylsilane added as an internal reference, exhibited the following singlets (τ): 8.95, CH$_3$; 7.18, CH$_2$; 6.89, tertiary OH; 6.72, CH$_2$; and 6.26, –CB$_{10}$H$_{10}$CH. The CH$_2$OH group appeared as an AB$_2$ multiplet with the center of the CH$_2$ doublet at τ 6.56 and the center of the OH triplet at τ 8.01. The first-order coupling constant was 7.9 c.p.s. The error for all values, except the –CB$_{10}$H$_{10}$CH shift, is ±0.01 p.p.m. The –CB$_{10}$H$_{10}$CH shift error is greater due to its unusually broad resonance. *Anal.* Calcd. for C$_9$H$_{32}$O$_3$B$_{20}$: C, 26.71; H, 7.97; B, 53.44; OH, 8.40. Found: C, 26.95; H 8.09; B, 51.34; OH, 8.92.

(1) The term "carborane" is used here to denote 1,2-dicarbaclovododecaborane(12).

(2) S. Papetti, B. B. Schaefer, H. J. Troscianiec, and T. L. Heying, *Inorg. Chem.*, **3**, 1444 (1964).

(3) J. Green, N. Mayes, A. P. Kotloby, and M. S. Cohen, *J. Polymer Sci.*, **A2**, 3135 (1964).

(4) M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *Inorg. Chem.*, **2**, 1111 (1963).

(5) M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. S. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

CONTRIBUTION FROM INORGANIC MATERIALS DIVISION,
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Additional Observations on the Electronic Spectrum of Copper(II) Acetate Monohydrate

BY CURT W. REIMANN,[1a] GERALD F. KOKOSZKA,[1a] AND GILBERT GORDON[1b]

Copper(II) acetate monohydrate is a binuclear complex.[2] At low temperatures it is diamagnetic and

(1) (a) National Bureau of Standards; (b) University of Maryland.

(2) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953).