6. Base Adducts.—Stannous fluoride was dissolved in a minimum amount of dimethyl sulfoxide at 90°, and on cooling, colorless crystals formed; m.p. 85° with decomposition.

Anal. Calcd. for $SnF_2 \cdot OS(CH_3)_2$: Sn, 50.6; S, 13.6. Found: Sn, 50.4; S, 13.7.

Germanium difluoride (5 g.) was dissolved in 15 ml. of dimethyl sulfoxide. Excess sulfoxide was removed under high vacuum to give an oil which, when ether washed and dried, gave a white solid which begins to decompose above 240°.

Anal. Calcd. for $GeF_2 \cdot OS(CH_3)_2$: F, 20.3; S, 17.0. Found: F, 20.7; S, 17.3.

A referee correctly pointed out that the data initially presented did not preclude the possibility that oxygen is abstracted from dimethyl sulfoxide and that the isolated complexes might be $MF_2 \cdot S(CH_3)_2$. The infrared data, which had not been included initially, clearly showed absorption in the region ($\sim$1020 cm.$^{-1}$) characteristic of S–O stretching vibration.

Germanium difluoride (5 g.) was dissolved in 25 ml. of dioxane and filtered. On cooling, colorless needles formed; m.p. 74–78° with decomposition. These needles, after a brief (0.5 hr.) vacuum drying, consistently analyzed for $GeF_2 \cdot X$dioxane with X ranging from 0.92 to 0.95. Extended vacuum drying led to lower values of X, indicating dissociation of the complex at 25°.

All of the tin and germanium complexes, in solution, absorbed oxygen as shown by tensimetric measurements.

Analytical.—The compounds to be analyzed for Ge, Sn, or F were decomposed by peroxide fusion. Germanium was determined by a tannic acid procedure,[12] tin by a modified hydrolysis and ashing procedure,[13] and fluorine by distillation (Willard and Winter) and titration with standard thorium nitrate.

Acknowledgment.—The assistance of Mr. A. F. Biddle in the X-ray analyses is gratefully acknowledged.

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[12] W. R. Schoeler and A. R. Powell, "Analysis of Minerals and Ores of the Rare Elements," Charles Griffin and Co. Limited, London, 1955, p. 170.

[13] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, New York, N. Y., 1953, p. 288.

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The Hydrolysis of Lanthanum and Cerium Carbides[1]

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The hydrolysis of lanthanum and cerium carbides at various temperatures was investigated. The complex hydrocarbon mixtures resulting from the hydrolysis were analyzed by gas chromatography. The production of acetylene at room temperature was approximately 65 mole %, but no acetylene was produced at 200°.

Introduction

The hydrolytic reactions of rare earth dicarbides have been studied by Moissan,[2,3] by Damiens,[4] by Zambonini,[5] by Villelume,[6] and recently by Greenwood and Osborn.[7] Damiens and Moissan found the major product of the reactions to be acetylene, but differed markedly as to the constitution of the remainder of the gaseous products. The more recent work of Villelume conflicts with the earlier studies. Damiens also hydrolyzed a carbide, supposedly cerium tricarbide, which he reported to give 98% acetylene. The existence of this tricarbide and the products from the hydrolysis reaction have never been confirmed.

Greenwood and Osborn studied the reactions of lanthanum dicarbide and sesquicarbide with sulfuric, nitric, and chlorosulfonic acids and molten iodine. The reactions of the carbides with the above reagents are complicated by various side reactions which obscure the nature of the hydrolysis products. The present hydrolysis study was conducted under conditions which restrict the effect of the hydrolysis medium and the highly exothermic nature of the reaction in influencing the final products.

This study of the hydrolysis of lanthanum and cerium carbides was undertaken as part of a

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[1] This work was supported by the Office of Ordnance Research. It is based in part on a dissertation submitted by G. Palenik to the Graduate School of the University of Southern California in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1960.

[2] H. Moissan and A. Etard, *Compt. rend.*, **122**, 576 (1896); *ibid.*, **123**, 148 (1896).

[3] H. Moissan, "The Electric Furnace," Chemical Publ. Co., Easton, Pa., 1920.

[4] A. Damiens, *Compt. rend.*, **157**, 214 (1913); *Ann. Chim.*, **10**, 137, 330 (1918).

[5] F. Zambonini, *Atti accad. naz. Lincei*, (v) **33**, 16 (1924).

[6] J. Villelume, Doctoral Thesis, University of Paris, 1952; *Compt. rend.*, **232**, 235 (1951); *Ann. chim.*, **7**, 265 (1952).

[7] N. N. Greenwood and A. J. Osborn, *J. Chem. Soc.*, 1775 (1961).

general investigation of the rare earth–carbon system. Shortly after the completion of the experimental work on this system, Atoji, *et al.*,[8] Spedding, *et al.*,[9] and Vickery, *et al.*,[10] reported similar investigations on the rare earth–carbon systems. The present investigation, while corroborating the composition and structures recently reported, is primarily concerned with the hydrolysis of these carbides.

Experimental

Preparation of the Carbide Samples.—The carbide samples were prepared by heating a mixture of the metal hydride and graphite to 1700° *in vacuo* as described below. The metal hydride is brittle and can be powdered easily, facilitating the preparation of intimate mixtures of the metal hydride and graphite. The above method is very well suited to the preparation of small quantities of the carbides.

The high purity rare earth metals, supplied by Dr. F. H. Spedding,[11] were cut into small cubes, using a water-cooled abrasive saw. The metal samples then were filed under mineral oil to obtain a bright surface, washed with solvent, and quickly dried and weighed. The graphite, obtained by powdering spectrographic grade rods, then was weighed to give the desired stoichiometry. A slight (5–10%) excess of graphite was used in some preparations to compensate for loss due to reaction with the crucible. The metal cube, the graphite, and a glass rod hammer were placed in a Pyrex reaction tube which could be attached through two sets of ball joints to a vacuum line.

The hydrogen used to convert the pure metal to the hydride was supplied by the thermal decomposition of uranium hydride. Once the rare earth metal had been converted to the hydride by heating, the reaction tube was removed and mechanically shaken until an intimate mixture with the graphite was produced.

The reaction tube containing the powdered metal hydride–graphite mixture was transferred to the glove box in which the induction furnace was mounted. All transfers to and from the furnace were made in the glove box in an atmosphere of dry carbon dioxide. The furnace was loaded, sealed, and evacuated without disturbing the inert atmosphere in the box. The samples then were heated in tantalum crucibles, in successive stages to 1700° *in vacuo* and maintained at this temperature for 0.5 hr. to ensure complete reaction of the metal and graphite. The samples were allowed to cool in the furnace under vacuum.[12]

Characterization of the Carbide Samples.—Both X-ray powder diffraction patterns and standard combustion analysis were used to characterize the carbide samples. The existence of the dicarbides previously reported by Moissan[3] and by von Stackelberg[13] thus was confirmed.

In addition to the dicarbides, which were electrically conducting and golden in appearance, silvery lower carbides also were observed. These compounds could not be obtained free of the dicarbide or of the metal, but the cell constants indicated sesquicarbides isostructural with plutonium sesquicarbide. The cell constants determined for these body-centered tetragonal dicarbides and body-centered cubic sesquicarbides are summarized in Table I; they are in agreement with recent values found by others.[7-10]

Table I

Cell Constants for the Dicarbide and Sesquicarbide Phases

Metal	Dicarbides RC_2 a_0 (Å.)	Dicarbides RC_2 c_0 (Å.)	Sesquicarbides R_2C_3 a_0 (Å.)
La	3.93 ± 0.01	6.56 ± 0.01	8.80 ± 0.01
Ce	3.87	6.47	8.58
Pr	3.83	6.42	8.34
Nd	3.81	6.38	...

In all cases where a dicarbide sample was hydrolyzed, care was taken to ensure that only the dicarbide phase was present. If either the results of the combustion analysis or the X-ray powder pattern indicated a deviation from ideal stoichiometry, the sample was not used.

Hydrolysis of the Carbide Samples.—The apparatus used to study the hydrolysis reaction at various temperatures is illustrated in Fig. 1. The gaseous product was analyzed by means of a Perkin-Elmer gas chromatograph. A few preliminary analyses were made mass spectrographically; the results of the two methods agreed satisfactorily.

In a typical hydrolysis reaction, a sealed sample tube containing the carbide was broken and the carbide poured into the holder. The sample holder was lowered into the reaction tube which then was attached to the manifold and evacuated. The above operations were carried out quickly

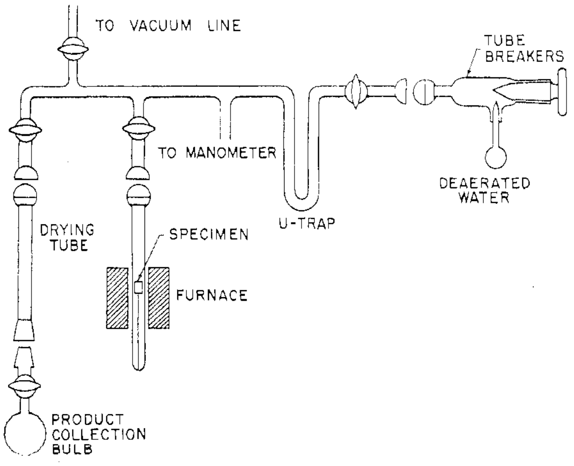

Fig. 1.—Apparatus for hydrolysis of carbides.

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[8] M. Atoji, K. Gscheidner, Jr., A. H. Daane, R. E. Rundle, and F. H. Spedding, *J. Am. Chem. Soc.*, **80**, 1804 (1958).

[9] F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, *ibid.*, **80**, 4498 (1958); *Trans. Met. Soc. AIME*, **215**, 192 (1959).

[10] R. C. Vickery, R. Sedlacek, and Ardys Ruben, *J. Chem. Soc.*, 498, 503, 505 (1959).

[11] Institute for Atomic Research, Iowa State University, Ames, Iowa.

[12] A more complete description of the furnace and experimental techniques can be found in the dissertation.

[13] M. von Stackelberg, *Z. physik. Chem.*, **9B**, 437 (1930); *Z. Elektrochem.*, **37**, 542 (1931).

TABLE II

COMPOSITION OF HYDROCARBONS FROM HYDROLYSIS OF RARE EARTH CARBIDES

Substance	Relative response per mole[a]	LaC_2, 25° mole %	CeC_2, 25° mole %	CeC_2, 100° mole %	CeC_2, 200° mole %	$CeC_{1.10}$, 25° mole %
Ethane	51	24.3	19.7	16.3	11.2	26.8[b]
Ethylene	48	8.45	6.56	4.96	39.6	...
Propane	65	0.21	0.03	1.03	13.5	1.10
Propylene	63	.03	.05	0.53	12.4	0.48
n-Butane	85	.51	.83	2.32	1.96	3.18
Acetylene	(48)	61.5	67.3	63.9	0.00	58.0
1-Butene	81	1.13	1.39	1.20	1.76	1.89
Isobutene	82	0.00	0.00	0.00	0.58	0.00
Unknown I	(80)	.00	.00	0.37	0.89	0.00
trans-2-Butene	85	.66	.84	1.49	3.64	1.41
cis-2-Butene	87	.72	.87	1.84	3.74	1.28
n-Pentane	105	.05	.00	0.00	3.17	0.07
Unknown II	(80)	.03	.03	0.37	0.00	1.51
1,3-Butadiene	80	.05	.07	2.70	3.56	0.00
Unknown III	(80)	.00	.00	0.00	2.38	0.00
1,2-Butadiene	(80)	.26	.22	0.42	1.48	0.24
Unknown IV	(80)	2.14	2.10	2.51	0.00	3.95

[a] These values were taken from ref. 14, except for those assumed values shown in parentheses. [b] The value represents the combined mole percentages of both ethane and ethylene.

to avoid undue decomposition of the sample by atmospheric moisture.

If the hydrolysis was to be carried out at an elevated temperature, the furnace was positioned and allowed to reach thermal equilibrium. In any case the system was evacuated for at least an hour. The hydrolysis reaction was initiated, after the Anhydrone-filled drying column and sample bulb were isolated from the system, by breaking the tube of boiled water. Under the above conditions the reaction proceeded slowly, and formation of local hot spots on the carbide surface was minimized. There was a large volume expansion on reaction of the dense carbide sample with the water vapor. This volume increase caused the reacted material to overflow the sample holder and fall to the bottom of the reaction tube. A slight tapping of the tube facilitated this process, exposing more unreacted surface.

The reaction was considered to be complete when no appreciable pressure increase was observed over a 24-hr. period. The water tube was isolated from the system and the drying tube and sample bulb opened. The gas, after being drawn through the drying column, was condensed in the sample bulb by means of liquid nitrogen.

Results

Runs were made with $LaC_{2.0}$, $CeC_{2.0}$, and $CeC_{1.10}$ at room temperature and with $CeC_{2.0}$ at 100 and 200°. The gas samples were analyzed by gas chromatography, the area under the chromatographic peaks being measured with a Keuffel-Esser planimeter. The peaks were measured several times and the results averaged. The area under each peak was converted to mole fractions using the data of Messner, Rosie, and Argabright.[14] The mole fractions converted into percentages are given in Table II. Where a component is labeled as unknown, the calibration of the instrument did not cover a peak with that emergence time. Since the instrument was used for analytical purposes in an oil refinery laboratory, the calibration covered the most common hydrocarbons. Except for the peak at the end, the unknown peaks represented minor components.

Since the samples were condensed with liquid nitrogen, non-condensables such as hydrogen, methane, and carbon monoxide were not collected in the sample bulb. An estimate of the amount of non-condensables was made by observing the manometer before and after condensation with liquid nitrogen. In the room temperature runs this difference amounted to about 5%, while at 200° it was approximately 15%.

Discussion

Lanthanum and cerium dicarbides yielded closely similar gaseous products on hydrolysis, indicating that the final oxidation states in both cases are the same. If the oxidation states were different, the proportion of hydrogen or hydrogenated products would be expected to differ considerably. The behavior of the residue from the cerium dicarbide hydrolysis supports the belief that the final oxidation number of cerium was three. The residue was a light gray material which turned greenish-yellow on exposure to the

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(14) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

atmosphere. The above color change can be explained on the basis of the oxidation of cerium(III) to the plus four state. The materials appeared to be amorphous hydroxides, and no X-ray powder diffraction patterns could be obtained from either. No carbon was found in the hydrolysis residues, in contrast to the results of Greenwood and Osborn.[7]

The stoichiometry provides little information regarding the mechanism of the hydrolysis reaction; however there are several features which should be noted. The presence of a large proportion of acetylene and even-numbered hydrocarbons in the gaseous products is not unexpected. Atoji[8] showed that C_2^{-2} units with a C–C distance of 1.28 Å. are present in the crystal of lanthanum dicarbide. The retention of the C_2 unit during the hydrolysis at room temperature is not unreasonable. However, the fact that no acetylene was found at elevated temperatures is surprising. The absence of acetylene at the higher temperature, together with an increase in the odd-numbered hydrocarbons produced, indicates that a large proportion of the C–C bonds initially present must be broken. The intermediate species in the reaction must have a highly increased reactivity at 200°.

One of the most interesting features of the hydrolysis reaction is the production of nearly equal amounts of *cis*- and *trans*-2-butene. Equilibrium constants for the isomerization of *cis* to *trans*, calculated using the thermodynamic data of Rossini,[15] were 3.2 at 298°K. and 1.8 at 500°K. The formation of equimolar amounts of the two 2-butenes does not represent thermal equilibrium and therefore must be a consequence of the mechanism by which the two were formed.

A number of mechanisms in harmony with these observations can be visualized, probably but not necessarily involving formation of adsorbed C_2–H entities on the surface. Such C_2–H radicals are considered to be the precursors of the various C_2- and C_4- hydrocarbons. The mobility of the radicals on the surface increases with temperature, favoring radical combination over acquisition of a second hydrogen. The proportion of acetylene thus would decrease and the proportion of odd-numbered hydrocarbons resulting from bond splitting would increase.

The hydrolysis of the sesquicarbide is more complicated since this substance was not obtained in a pure state. In the hydrolysis of the R_2C_3 phase, two metal atoms can be considered as undergoing a three-electron oxidation, resulting in more hydrogenated hydrocarbons and less acetylene. The room temperature hydrolysis of the sample with the stoichiometry $CeC_{1.10}$ is in agreement with this hypothesis. The mechanism is expected to be similar to that postulated for the dicarbide phase.

A quantitative comparison of our results with the results of Greenwood and Osborn[7] is not possible. Both studies indicate that the final products are a function of the reaction temperature. Because of the highly exothermic nature of the reaction, the direct addition of the carbide sample into the hydrolysis medium should be avoided. If such an addition is made, it could result in small areas of high temperature which would affect the results, an effect not considered by Greenwood and Osborn.

The use of sulfuric and nitric acids by Greenwood and Osborn for the hydrolysis medium might have caused secondary changes in hydrocarbon composition. It is well known that sulfuric acid can act as an isomerization catalyst and therefore might influence the results of the reaction. The inversion of the ratio of the 2-butene isomers in the nitric *vs.* the sulfuric acid experiments could be explained on the basis of isomerization by sulfuric acid. It is evident from their results with calcium carbide that side reactions occur when nitric acid is used as the hydrolysis medium. Furthermore, it has been reported that nitrates of the rare earths catalyze the oxidizing power of nitric acid with regard to organic compounds.[16]

Unfortunately, data in the literature on the hydrolysis of other carbides are sparse and often contradictory. One of the major difficulties inherent in these studies is obtaining samples of a single phase. The earlier work probably suffers most in this regard. The results of the hydrolysis of thorium[2,17,18] and uranium[3,17,19] dicarbides are typical. Three studies of the hydrolysis of thorium dicarbide reported to date do not even agree on the major product of the reaction. Two of the three studies carried out on the hy-

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[15] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," comprising the Tables of the American Petroleum Institute Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

[16] H. W. Lohse, "Catalytic Chemistry," Chemical Publishing Co., New York, N. Y., 1945, p. 188.

[17] P. Lebeau and A. Damiens, *Compt. rend.*, **156**, 1987 (1913).

[18] F. J. Modic, private communication to E. B. Hunt and R. E. Rundle, appearing in *J. Am. Chem. Soc.*, **73**, 4777 (1951).

[19] L. M. Litz, Doctoral Dissertation, Ohio State University, 1948.

drolysis of uranium dicarbide agree as to the major product, even though the two studies were carried out at widely different temperatures.

In the case of the thorium and uranium carbides, the final oxidation state is plus four. 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. The hypothesis given above can be tested only when additional data are available on the thorium and uranium carbide hydrolyses.

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Dimethylaminomethylchloroborane and Related Compounds[1]

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The dimerization of $(CH_3)_2NBCl_2$ and non-dimerization of $(CH_3)_2NB(CH_3)_2$ have been investigated by preparing $(CH_3)_2NBCH_3Cl$. It is made in high yield by heating $(CH_3)_2NBCl_2$ and $(CH_3)_2NB(CH_3)_2$ together at 170°. It is very stable to disproportionation. It slowly forms a solid dimer like that of $(CH_3)_2NBCl_2$. The dimerization is shown to be a non-equilibrium process resembling freezing which occurs at a higher temperature than the true melting point. This can be located by observation of the kinetics of freezing and by finding the intersection of vapor pressure curves. Solid adducts $[(CH_3)_2NBCl_2][(CH_3)_2NB(CH_3)_2]$ and $[(CH_3)_2NBCl_2][(CH_3)_2NBCH_3Cl]$ also are described.

This study arose from the observation in the literature that two apparently similar boron amines have dramatically different properties. Dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, is a mobile, fuming liquid that deposits a solid on standing, referred to as a "dimer" because of the molecular weight of its solutions in benzene.[2] This substance has remarkable resistance to hydrolysis by water. Dimethylaminodimethylborane, $(CH_3)_2NB(CH_3)_2$, on the other hand, is a mobile, oxidizable liquid that does not deposit a solid or undergo any detectable changes in properties, no matter how long it stands in the absence of oxygen.

In an attempt to determine the reason for this behavior, we prepared the compound intermediate between these two, dimethylaminomethylchloroborane, $(CH_3)_2NBCH_3Cl$, observed some of its physical and chemical properties, and compared the properties of all three compounds.

In this paper the term "dimer" will be used for the solids that deposit from pure, monomeric liquids, and the term "adduct" for solids that deposit from mixtures of monomers. The solids may be more complex than "dimer" implies.

Experimental

(1) Preparation and General Properties.—All monomeric aminoboranes were handled in dry nitrogen atmospheres. Samples for analysis were subjected to basic peroxidation at 100°. After neutralization, boric acid was determined by titration in the presence of mannitol, and chlorine was determined by the Mohr titration. Molecular weights were measured cryoscopically in *p*-xylene.

(a) $\mathbf{(CH_3)_3NBCl_2}$ was prepared by using a slight modification of the method of Goubeau.[3] The separation of $[(CH_3)_2N]_3B$ and $[(CH_3)_2N]_2BCl$ was found to be unnecessary, since both reacted readily with BCl_3 to give the desired product. Each sample was purified by fractional distillation through a 45.8-cm., wire-spiral column at 30–40 mm., collected in a receiver chilled to −25°, and stored at −25° until used. Yields ranged up to 75%.

(b) $\mathbf{(CH_3)_2NB(CH_3)_2}$ was prepared by the action of methyl Grignard reagent on $(CH_3)_2NBCl_2$, as described elsewhere.[4]

(c) $\mathbf{[(CH_3)_2NBCl_2][(CH_3)_2NB(CH_3)_2]}$ was prepared by mixing approximately equimolar amounts of the monomers at −25° and allowing the mixture to stand for 4–8 hr. at this temperature. The reaction at room temperature was too violent. Unreacted starting materials then were removed *in vacuo*, and the crystals were washed with water and dried in a vacuum desiccator for several hours. Yields

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[1] Based in part on a thesis submitted by Frank Gunderloy in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Rutgers, the State University, September, 1957. Presented at the 135th National Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1959.

[2] E. Wiberg and K. Schuster, *Z. anorg. u. allgem. Chem.*, **213**, 89 (1933).

[3] J. Goubeau, M. Rabtz, and H. J. Becher, *ibid.*, **275**, 162 (1954).

[4] F. C. Gunderloy, Jr., and C. E. Erickson, *J. Org. Chem.*, **24**, 1161 (1959).