most stable. However, a structure described in terms of octahedra sharing faces would force the titanium atoms so close together, 2.3 Å, if normal Ti–O bond distances are maintained, that there is no doubt that such a structure would be one of very high energy. Bringing titanium atoms close enough together to actually touch would mean increasing the repulsion energies of such like-charged atoms greatly. It is probably due to such interactions that isopolyacids of groups IV, V, and VI adopt structures best represented by octahedra sharing edges rather than faces. It is probable also that the degree of polymerization of this alkoxide in solution is three for steric reasons. That polymerization of titanium alkoxides is affected by the bulk of the alkoxide group is known from previous work.[1]

The findings of the present study tend to be entirely consistent with the general structural theory of Bradley, which predicts that metal alkoxides will form stable polymeric species having the minimum degree of polymerization consistent with the achievement of a maximum characteristic coordination number for the metal "ion." To be sure the maximum coordination number of titanium in such compounds appears to be six, and it is reasonable to assert that the tetramer appears in the solid state because it is the lowest molecular weight molecule, with reasonable Ti–O and Ti–Ti atom distances, which can be constructed with titanium of coordination number six. Upon melting, however, and in solution it is suggested that the additional degrees of freedom allowed due the ethoxide group rotations result in the stabilization of the trimeric molecule with respect to the tetramer.

The likelihood of substantial error in the Ti–O longitudinal bond polarizability value used is readily acknowledged, since bond lengths used were taken from the solid state study of Ibers, which involved only six-coordinate titanium. If the calculated molecular anisotropies of the three structures were not substantially different from one another the correct structural assignment might have been difficult. However, the calculated anisotropy of structure III is clearly so much larger than that of the other two and so close to the measured value that huge errors in the Ti–O bond polarizability would have to be invoked to result in a mistaken assignment. It appears rather certain that the structure in solution is structure III. It should be noted that the measurement of the optical anisotropy, γ^2, alone allowed the unambiguous selection of the proper structure. It is anticipated that many other structures of practical or theoretical interest presently inaccessible to determination in solution will be studied successfully using the method discussed.

Acknowledgment. Thanks are due to Research Inc., for generous support during the early stages of this study. Much appreciated help also has been received from the National Science Foundation through GP-5880. Valuable advice concerning construction of the photometer was generously given by Dr. J. L. Lundberg.

A Phase Investigation of the Ytterbium–Carbon System

John M. Haschke and Harry A. Eick[1]

Contribution from the Department of Chemistry,
Michigan State University, East Lansing, Michigan 48823.

Received September 15, 1969

Abstract: The ytterbium–carbon system, YbC_x, has been investigated over the composition range $0.33 \leq x \leq 2.00$; samples were prepared by direct reaction of the elements in sealed tantalum bombs. Four phases have been identified by X-ray diffraction and elemental analysis: tetragonal $YbC_{2.00}$ ($a = 3.639 \pm 0.003$, $c = 6.110 \pm 0.008$ Å), monoclinic $YbC_{1.25+y}$ with $0 \leq y \leq 0.16$ ($a = 7.070 \pm 0.005$, $b = 7.850 \pm 0.004$, $c = 5.623 \pm 0.005$ Å, $\beta = 90.99 \pm 0.09°$, for samples quenched from 1450°K), $YbC_{0.95}$, and dimorphic $YbC_{0.50\pm z}$ (fcc, $a = 5.001 \pm 0.003$ Å and rhombohedral, $a = 6.167$ Å, $\alpha = 33.33°$). A linear variation of both the carbon-rich $YbC_{1.25+y}$ phase boundary and the monoclinic b parameter with temperature has been observed. A partial phase diagram for the Yb–C system is proposed, and the variation of composition and lattice parameter of the $YbC_{1.25+y}$ phase is discussed.

From a structural investigation of the lanthanide carbides Spedding, *et al.*,[2] reported for ytterbium the dicarbide, a trimetal monocarbide, and "an intermediate carbide" of undetermined composition. More recent studies on this system have been concerned with the carbon-rich phases. Krikorian, *et al.*,[3] investigated the dicarbide–carbon eutectic and searched for a tetragonal-cubic dicarbide transition. Haschke and Eick[4] presented evidence for a two-phase region between $YbC_{1.5}$ and YbC_2, and consequently for the existence of a sesquicarbide. The present investigation was initiated to examine the metal-rich portion of the ytterbium–carbon system and, in particular, to characterize the phase diagram near the sesquicarbide composition.

---

(1) To whom inquiries should be addressed.

(2) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, *J. Amer. Chem. Soc.*, 80, 4499 (1958).

(3) N. H. Krikorian, T. C. Wallace, and M. G. Bowman, Proceedings, Colloque International Sur les Derives Semimetallique du Centre National de la Recherche Scientifique et Universite du Paris, Orsay, 1965.

(4) J. M. Haschke and H. A. Eick, *J. Phys. Chem.*, **72**, 1697 (1968).

Experimental Section

Preparative Methods. Ytterbium metal (Research Chemicals Phoenix, Ariz., 99.9%, impurities: Ca, Mg, and Cu each <0.01%) and CP graphite (Fisher Scientific Co., Pittsburgh, Pa.) which had been degassed under vacuum at 1800° were combined in the desired stoichiometric ratio and sealed into tantalum ampoules by arc welding in an argon atmosphere. The ampoules, which were fashioned from 6.35-mm o.d. seamless tantalum tubing, were thoroughly outgassed under vacuum prior to use. Mixtures of the stoichiometry YbC$_x$, $0.33 \leq x \leq 2.00$, were heated at 1400–1500° by induction for 2–3 hr at 10^{-6}–10^{-7} Torr pressure. The samples were then annealed at 800–1100° for approximately 1 hr before being quenched. The surface temperature of the ampoules was measured with a NBS-calibrated Leeds and Northrup disappearing filament pyrometer, and was corrected for transmission losses from the vacuum system viewing port and for the emissivity of tantalum[5] (0.49). A series of preparations with $x = 1.50$ was treated at the higher temperature, and then annealed for 1 hr at a carefully measured lower temperature (817–1457°) prior to quenching. The reaction products were removed from the ampoules and manipulated in a glove box, in which the recirculated argon atmosphere was purged of oxygen (BASAF catalyst, Badische Anilin u. Soda Fabrik, A.G.) and water (activated alumina and phosphorus pentoxide).

Analytical Methods. The products were analyzed microchemically for both metal and carbon content by conversion to sesquioxide and carbon dioxide. Samples were weighed into quartz boats in the glove box, and transferred under argon in polyethylene bags to the analysis line. There they were ignited at 850–950° under a stream of high purity oxygen. A cupric oxide–ceria catalyst was employed for conversion of carbon monoxide to the dioxide, which was determined gravimetrically by collection on Ascarite. Analyses were run in triplicate, whenever possible, and the error reported is the standard deviation of the measurements. Samples were also examined by X-ray fluorescence for possible tantalum contamination.

X-Ray Methods. X-Ray powder diffraction patterns of the polycrystalline phases were obtained with an 80-mm radius Haegg-type Guinier camera. The samples, which were prepared in the glove box, were coated with a thin layer of paraffin oil to prevent hydrolysis during transfer and exposure. Both annealed KCl (a = 6.29300 ± 0.00009 Å) and Pt (a = 3.9237 ± 0.0003 Å) were employed as internal standards. The diffraction data were refined on a CDC-3600 computer by the method of least regressions with a computer program written by Lindquist and Wengelin.[6] The errors reported for lattice parameters are the standard deviations.

Results

Four ytterbium carbide phases were observed by analytical and X-ray diffraction techniques: YbC$_2$, YbC$_{1.25+y}$, YbC$_{0.95}$, and YbC$_{0.50\pm z}$. The phases observed at various reacted C/Yb ratios, x (hereafter x is defined as the bulk C/Yb ratio), are presented in Table I, and are considered in detail below.

Table I. Ytterbium Carbide Phases Observed at Various Bulk C/Yb Ratios

x in YbC$_x$	Observed phase(s)
0.33	Yb + YbC$_{0.43}$
0.50	YbC$_{0.50\pm z}$
0.75	YbC$_{0.50\pm z}$ + YbC$_{0.95}$
0.90	YbC$_{0.95}$
1.00	YbC$_{0.95}$ + YbC$_{1.25}$
1.15	YbC$_{0.95}$ + YbC$_{1.25}$
1.50	YbC$_{1.25+y}$ + YbC$_2$
1.65	YbC$_{1.25+y}$ + YbC$_2$
2.00	YbC$_2$

YbC$_{2.00}$. The golden-colored dicarbide was present in all reaction products in which $1.50 \leq x \leq 2.00$, but a mixture of the dicarbide and a silver-gray phase was always present for $x \leq 2.00$. Because of their color difference, these phases could often be separated physically for elemental analysis. Segregation of the two phases was enhanced if the reactants were not mixed thoroughly; the metal-rich gray phase and the dicarbide were found in the product in regions which were initially metal- and graphite-rich, respectively. After equilibrium compositions had been attained, ytterbium migration apparently ceased. Although all preparations appeared to be sintered well, no evidence of melting was observed. Samples with $x = 1.50$, which were quenched from various temperatures, were also mixtures of dicarbide and gray phase. The composition of a crystallographically pure sample of dicarbide, which was separated from an $x = 1.50$ mixture quenched from 1475°, was YbC$_{2.003\pm0.005}$. The tetragonal lattice parameters (a = 3.639 ± 0.003, c = 6.110 ± 0.008 Å) remained invariant; neither quenching temperature nor bulk stoichiometry altered them.

YbC$_{1.25+y}$. The composition of the previously mentioned silver-gray phase varied from YbC$_{1.25}$ to YbC$_{1.41}$ (55.5–58.5 atom % C). The interplanar d spacings of a preparation quenched from 1450°K were indexed on monoclinic symmetry (a = 7.070 ± 0.005, b = 7.850 ± 0.004, c = 5.623 ± 0.005 Å, and β = 90.99 ± 0.09°), and the first 34 values and their relative intensities are presented in Table II.

Table II. Observed Interplanar d Values and Relative Intensities of YbC$_{1.25+y}$ Quenched from 1450°K

Rel int	hkl	d value, Å	Rel int	hkl	d value, Å
w–m	010	7.849	w	$\bar{1}31$	2.252
w	100	7.058	w	$\bar{3}01$	2.186
vw	001	5.588	w	301	2.158
vw	$\bar{1}10$	5.306	vw	230	2.102
w	011	4.554	w	320	2.015
vw	101	4.366	w	041	1.852
w	020	3.927	m	103	1.807
m	200	3.533	w	$\bar{1}41$	1.795
m–s	210	3.220	m	400	1.766
vs	$\bar{1}21$	2.928	m	113	1.753
w	002	2.798	m	331	1.669
w	211	2.787	w	241	1.634
s	$\bar{1}02$, $\bar{2}20$	2.625	w	042	1.606
w–m	030	2.617	w–m	142	1.565
m–s	$\bar{1}12$	2.498	m–s	051	1.513
m–s	112	2.464	m	430	1.465
w	300	2.350	w–m	250	1.436

Both the composition and the monoclinic b parameter varied linearly with quench temperature (Figure 1). The refined cell parameters and compositions of crystallographically pure YbC$_{1.25+y}$ samples are listed in Table III. Analytical data were not collected on each of the samples prepared at a different temperature because the diphasic mixtures could not always be separated. When mixtures of YbC$_{1.25+y}$ ($y < 0.16$) and YbC$_2$ were crushed, reheated to 1300–1400°, and quenched, no indication of melting or phase separation was apparent, but shifts in the b parameter corresponding to the quenching temperature were observed. In the YbC$_{1.25+y}$–YbC$_{0.95}$ two-phase region, the b parameter

---

(5) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 45th ed, The Chemical Publishing Co., Cleveland, Ohio, 1964, p E110.

(6) O. Lindquist and F. Wengelin, *Ark. Kemi*, **28**, 179 (1967).

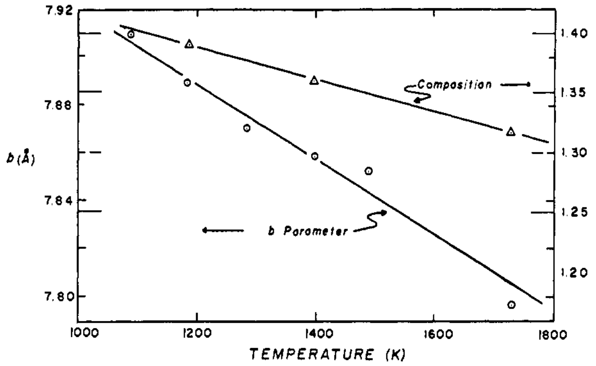

Figure 1. Variation of the *b* parameter and the composition of $YbC_{1.25+y}$ with temperature.

was invariant at 7.75 ± 0.01 Å (estimated error). Since this parameter also varies linearly across the variable composition region, the intersection of a graph of this parameter *vs.* composition with the $b = 7.75$ line indicates the lower phase boundary to be $YbC_{1.25\pm0.01}$.

Table III. Lattice Constants and Composition of $YbC_{1.25+y}$ Samples Quenched from Various Temperatures

Quench temp, °K	*a*, Å	*b*, Å	*c*, Å	*β*, deg	Cell volume, Å^3	Yb/C ratio
1091	7.067[a]	7.91_0[b]	5.621[a]	90.88	314.37	
1183	7.070	7.88_9	5.621	90.88	313.54	1.389 ± 0.015
1285	7.065	7.86_9	5.620	90.88	312.41	
1398	7.065	7.85_8	5.621	90.97	312.06	1.360 ± 0.015
1490	7.070	7.85_4	5.624	90.94	312.25	
1730	7.073	7.80_1	5.624	91.18	310.28	1.319 ± 0.006

[a] Estimated error ±0.005 Å. [b] Estimated error ±0.01 Å.

$YbC_{0.95}$. A second intermediate carbide, also colored silver-gray, has been observed near the monocarbide composition. The X-ray diffraction data indicate a complex structure which we could not index on either orthogonal or trigonal symmetry. The interplanar *d* values and relative intensities of the first 20 observed reflections are listed in Table IV. The X-ray diffraction pattern is independent of both annealing temperature and bulk composition of mixtures containing the phase. Analysis of the product from the $x = 0.90$ stoichiometry, which appeared to be a pure phase, indicated a composition of $YbC_{0.95\pm0.02}$ (6.07 ± 0.11 wt % C, 93.99 ± 0.09 wt % Yb).

Table IV. Observed *d* Values and Relative Intensities of $YbC_{0.95}$

Rel int	Interplanar *d* value,[a] Å	Rel int	Interplanar *d* value, Å
w-m	9.460	s	2.822
w-m	6.529	s	2.744
w-m	4.742	s	2.609
w	3.893	m	2.596
w	3.859	w	2.504
w-m	3.524	s	2.491
w	3.295	w	2.465
m-s	3.091	w-m	2.436
m	2.990	w	2.382
s	2.978	m-s	2.342

[a] Estimated error ±0.001 Å.

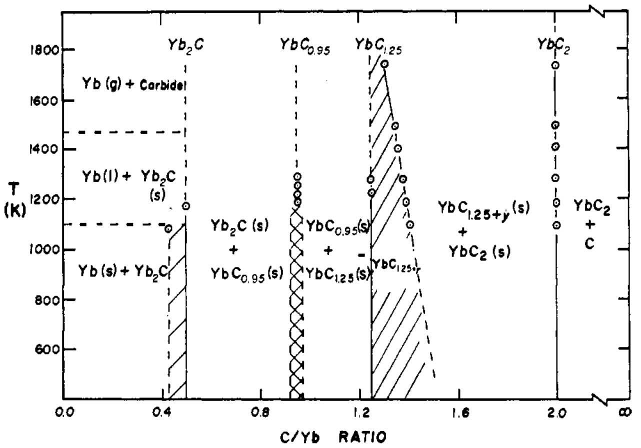

Figure 2. The ytterbium–carbon phase diagram.

$YbC_{0.50\pm z}$. The lowest observed carbide possesses a metallic luster and appears in a region at the diytterbium monocarbide (hypocarbide) composition. The X-ray diffraction data were interpreted on the basis of a diphasic mixture of fcc ($a = 5.001 \pm 0.003$ Å) and hexagonal ($a = 3.541 \pm 0.004$, $c = 17.46 \pm 0.02$ Å) structures. When the latter structure is refined on rhombohedral symmetry, it yields $a = 6.167$ Å and $\alpha = 33.33°$ ($\alpha = 33.56°$ for fluorite expressed on rhombohedral symmetry). Both phases were observed in all mixtures containing the hypocarbide. The composition range ($\pm z$) of the hypocarbide was not determined, but a crystallographically pure sample from the $x = 0.33$ reaction mixture quenched from 1080°K indicated C/Yb = 0.43 ± 0.02 ($-z = 0.07$).

The Yb–C Phase Diagram. The results of the phase investigation can be presented graphically in a temperature–composition phase diagram (Figure 2). Whereas the cross-hatched regions about Yb_2C and $YbC_{1.25+y}$ demonstrate variable composition, that about $YbC_{0.95}$ is only indicative of the uncertainty in the composition of the phase. The experimental data points, designated by open circles, represent the analytically determined composition of a specimen quenched from these temperatures. The data for the solid, liquid, and gaseous regions of ytterbium metal are from Hultgren.[7]

Discussion

The ytterbium–carbon system is very different from those of lighter lanthanide elements which exhibit well-defined dicarbides, Pu_2C_3-type sequicarbides, and fcc hypocarbides.[2] Only the tetragonal dicarbide has been observed across the entire lanthanide series,[2,3,8] and for ytterbium, appears to occupy a narrow composition range up to 1750°K.

As Spedding, *et al.*,[2] have noted, ytterbium forms an intermediate carbide, but apparently not at the Yb_2C_3 composition. The $YbC_{1.25+y}$ phase occurs in the same region as the 55–58 atom % solid solution reported for the yttrium–carbon system.[9] However, the yttrium

---

(7) R. Hultgren, "Supplement to the Selected Values of Thermodynamic Properties of Metals and Alloys," private communication.

(8) R. E. Gebelt and H. A. Eick, *Inorg. Chem.*, **3**, 335 (1964).

(9) O. N. Carlson and W. M. Paulson, *Trans. Met. Soc. AIME*, (*Amer. Inst. Mining, Met., Eng.*), **242**, 846 (1968).

carbide phase apparently does not exhibit a composition variation with temperature, and its X-ray diffraction data suggest that it is not isostructural with $YbC_{1.25+y}$. Previous analytical results from this laboratory[4] indicated that the sesquicarbide composition had been attained; however, these data were based on metal analysis by oxalate precipitation. Since X-ray diffraction data for the samples were collected using the Debye–Scherrer technique, undetected dicarbide probably accounts for the high carbon content of the specimen. From Figure 2 it is apparent that the $YbC_{1.50}$ composition should be obtained by annealing the proper stoichiometry at approximately 275°, but at this temperature, attainment of equilibrium would be very slow. Perhaps Yb_2C_3 could also be prepared by a high-pressure technique similar to that employed for the preparation of Pu_2C_3-type Y_2C_3.[10]

An intriguing feature of the Yb–C system is the apparent regular variation of the monoclinic b parameter and of the composition of the $YbC_{1.25+y}$ phase with annealing temperature. It is interesting to speculate about this behavior. Structural[2] and hydrolysis[11] studies of the lanthanide sesquicarbides reveal that the heavy lanthanides (Er–Lu) and yttrium neither exhibit the bcc structures of the lighter lanthanides nor have the same hydrolysis products. While the light Ln_2C_3 phases hydrolyze to produce principally ethyne and ethane, the heavier lanthanides (Tm and Lu) evolve approximately equimolar percentages of methane and propyne, and essentially no C_2 hydrocarbons. Although no hydrolysis data are available for the $YbC_{1.25+y}$ phase, it would be expected to behave like those of Tm and Lu. The hydrolysis results suggest that the carbon is present in the lattice as C^{4-} and $C_3{}^{4-}$ ions. Although the propyne might arise from association of methanide and acetylide ions during hydrolysis, relatively large amounts of ethyne should also be observed. With trivalent ytterbium present in the lattice, the sesquicarbide composition could be attained by either an equimolar ratio of methanide and acetylide or of methanide and propynide ions. If the alkyne bond ($C\equiv C$) of either $C_2{}^{2-}$ or $C_3{}^{4-}$ is collinear with the b axis of the monoclinic cell, replacement of the polyatomic group with a methanide ion ($C_2{}^{2-}$ replaced by C^{4-} in one case, and $C_3{}^{4-}$ replaced by $2C^{4-}$ in the other) would account for the variation of both composition and lattice parameter. An increase in the fraction of C^{4-} groups requires both that the stoichiometry shift to a more metal-rich composition and that the b parameter decrease. The variation of the methanide to alkynide ratio with temperature could easily arise from a shift in thermodynamic stability of carbide anions. This interpretation is also consistent with the observed composition invariance of a, c, and β. Investigations which might verify these hypotheses include examination of the $YbC_{1.25+y}$ hydrolysis products as a function of y, and determination of the crystal structure. However, attempts to obtain a single crystal of the phase have thus far been unsuccessful.

Since quenching techniques were employed in the investigation of the carbon-rich $YbC_{1.25+y}$ phase boundary, the validity of these data may be questioned. In our experimental design the ampoules cooled to <600° in 15–20 sec. For the temperature range investigated, a very low carbon mobility is anticipated, and the principal mechanism for composition change is metal diffusion. The equilibrium partial pressure of ytterbium in the $YbC_{1.25+y}$–YbC_2 two-phase region has been measured by the Knudsen effusion technique[12] and found to vary from 10^{-6} to 10^{-3} atm in the temperature range 1056–1337°K. Since these measurements indicate that about 5 min is required for the equilibrium composition to be attained after a 25–50° temperature excursion, the results of the quenching experiments are believed accurate. Interestingly, an anomalously rapid increase in ytterbium pressure with temperature has been observed in the Knudsen experiments and has reconfirmed the corresponding decrease observed in the C:Yb ratio.

The unique feature of the Yb–C system is the existence of a phase near the monocarbide composition. Analytical results and preparative data suggest that the phase has a C:Yb ratio <1.00. Since the stoichiometric 1:1 phase would be expected to exhibit the fcc lattice characteristic of other monocarbides,[13] the $YbC_{0.95}$ composition is reasonable. It is possible that the phase is either an oxide carbide or an ytterbium tantalum carbide; but, in all cases, the sum of ytterbium and carbon percentages is $\geq 99.85\%$ and tantalum could not be detected by X-ray fluorescence.

The diphasic mixture observed at the hypocarbide composition indicates the ytterbium phase is dimorphic, and is consistent with results reported for corresponding yttrium[14] and holmium[15] phases. As Atoji and Kikuchi[14] have noted for the yttrium system, the cubic and rhombohedral forms of Y_2C always appear to coexist. The lattice parameter for the NaCl-type phase agrees with the value reported for Yb_3C;[2] however, the composition appears more consistent with the data reported for Y_2C.[16] The composition of ytterbium hypocarbide in equilibrium with the metal at 1080°K ($YbC_{0.43}$) agrees well with the value observed at the Y_2C boundary.[16] The rhombohedral anti-$CdCl_2$-type structure is also consistent with the interpretation of the data for the M_2C phases of other heavy lanthanides (Gd, Dy, Ho, Er), yttrium, and scandium.[14] No evidence was observed for the cubic YbC_{1-x} ($4.85 \leq a \leq 4.97$ Å) phases reported recently by Laplace and Lorrenzelli.[17] Since these workers prepared their samples by allowing YbH_2 at 600° to react with $(1 - x)$ mol of carbon, their cubic phase is probably an ytterbium carbide hydride.

Although numerous questions about the ytterbium–carbon system remain unanswered, this investigation has indicated clearly that the behavior of ytterbium is

---

[10] M. C. Krupka, A. L. Giorgi, N. H. Krikorian, and E. G. Szklarz, *J. Less-Common Metals.*, **17**, 91 (1969).

[11] H. J. Svec, J. Capellen, and F. E. Saalfeld, *J. Inorg. Nucl. Chem.*, **26**, 721 (1964).

[12] J. M. Haschke and H. A. Eick, *Inorg. Chem.*, **9**, 851 (1970).

[13] E. K. Storms, "The Refractory Carbides," Academic Press, New York, N. Y., 1967.

[14] M. Atoji and M. Kikuchi, U. S. Atomic Energy Commission Report, ANL-7441, Argonne, Ill., May 1968.

[15] G. L. Bacchella, P. Meriel, M. Pinot, and R. Lallement, *Bull. Soc. Fr. Mineral. Cristallogr.*, **89**, 226 (1966).

[16] R. Lallement, Centre d'Etude Nucleaires de Fontenay-Aux-Roses Rapport, CEA-R 3043 (1966).

[17] A. Laplace and R. Lorrenzelli, Colloques Internationaux du Centre National de la Recherche Scientifique, Centre National de la Recherche Scientifique, No. 180, Paris–Grenoble, May 1969.

markedly different from that of the light lanthanides. The results obtained for the intermediate carbide phases should facilitate interpretation of analogous data collected for other heavy lanthanides.

Acknowledgment. Support of the U. S. Atomic Energy Commission (AT(11-1)-716) and a National Science Foundation Fellowship (to J. M. H.) are gratefully acknowledged.

Silicon–Fluorine Chemistry. IX. The Reactions of Silicon Difluoride and Silicon Tetrafluoride with Water and Some Reactions of Tetrafluorodisiloxane

J. L. Margrave, K. G. Sharp, and P. W. Wilson

Contribution from the Chemistry Department, Rice University,
Houston, Texas 77001. *Received September 9, 1969*

Abstract: The reactions of silicon difluoride and silicon tetrafluoride with water have been investigated. The compound 1,1,1′,1′-tetrafluorodisiloxane has been isolated from the reaction of silicon difluoride with water. The mass spectrum, infrared spectrum, nmr spectrum, and some of the chemical properties of this compound are reported.

Although a large number of the reactions of silicon difluoride has been investigated,[1] the reaction of silicon difluoride with water has not been previously described. When most silicon halides are hydrolyzed polymeric oxides are formed. It is possible that silicon difluoride also would react in this manner to give Si–O–F polymers. Such polymers were produced in the reaction of silicon difluoride with oxygen.[2] The methanolysis reaction of silicon difluoride was reported recently and two new compounds were isolated from the reaction products.[3] It thus seemed possible that the controlled hydrolysis of silicon difluoride would also produce nonpolymeric products.

Since a considerable quantity of silicon tetrafluoride is always present in silicon difluoride reactions, there will necessarily be a simultaneous reaction between the silicon tetrafluoride and water when the hydrolysis of silicon difluoride is carried out. When silicon tetrafluoride reacts with an excess of water, silicon dioxide and fluorosilicic acid are produced.[4] However, Chaigneau has reported that silicon tetrafluoride reacts with wet magnesium sulfate to give fluorosiloxanes.[5] It therefore seemed advisable to study the reaction of silicon tetrafluoride with water to determine what products would be formed under the conditions used in this investigation.

Experimental Section

The silicon difluoride was produced as described previously by passing silicon tetrafluoride over a column of silicon heated to 1250°.[6] Water vapor was introduced into the stream of silicon difluoride and silicon tetrafluoride leaving the furnace and the resultant mixture was condensed. The apparatus was designed to minimize the time between mixing and condensation. By means of ballast bulbs fitted with needle valves the ratio of silicon difluoride to water could be adjusted to any selected value. In any particular experimental run the value of this ratio was held constant, but it was varied over a number of runs from 1:1 to 7:1.

After the reaction was completed the resultant condensate was warmed to room temperature and any volatile products were collected. The products were purified by either trap-to-trap distillation or by the Cady codistillation method.[7] The Cady method was particularly valuable in these experiments since the various reaction products were eluted as well-separated peaks.

A reaction between water and silicon tetrafluoride was, as expected, observed in the experiments described above. This reaction was further investigated by mixing silicon tetrafluoride and water in the gas phase, condensing and revaporizing the mixture several times, and examining the products. Silicon tetrafluoride was always present in excess as this limited the amount of polymer formed.

The reactions of tetrafluorodisiloxane reported were studied by condensing the tetrafluorodisiloxane and the second reagent into a 20-cc glass ampoule and allowing the mixture to stand at room temperature until products were formed.

The infrared spectra were obtained using the Beckman spectrophotometers IR-8 and IR-11. The mass spectra were obtained on a Bendix Time-of-Flight Model 14-107 mass spectrometer, and the nmr spectra were taken on a Varian Model A-56/60A nmr spectrometer.

Results and Discussion

A. Reaction of Silicon Fluorides with Water. A multicolored polymer was produced by cocondensing water and silicon difluoride at −196°; when the water and silicon difluoride were present in approximately equimolar amounts the condensate was white, when silicon difluoride was in slight excess the condensate was green, and when silicon difluoride was in large excess the condensate was yellow. In most experiments bands of all three colors were seen.

When the condensate was warmed to room temperature, it gradually turned white and evolved volatile compounds. A considerable quantity of white polymer always remained after removal of volatile products. This polymer differed from those obtained in other reactions of silicon difluoride studied in that it was not

---

(1) J. C. Thompson and J. L. Margrave, *Science*, **155**, 669 (1967).

(2) G. Besenbruch and J. L. Margrave, unpublished work.

(3) J. L. Margrave, K. G. Sharp, and P. W. Wilson, in press.

(4) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1966, p 467.

(5) M. Chaigneau, *C. R. Acad. Sci., Paris, Ser. C*, **266**, 1053 (1969).

(6) P. L. Timms, R. A. Kent, T. C. Ehlert, and J. L. Margrave, *J. Amer. Chem. Soc.*, **87**, 2824 (1965).

(7) G. H. Cady and D. P. Siegworth, *Anal. Chem.*, **31**, 618 (1959).