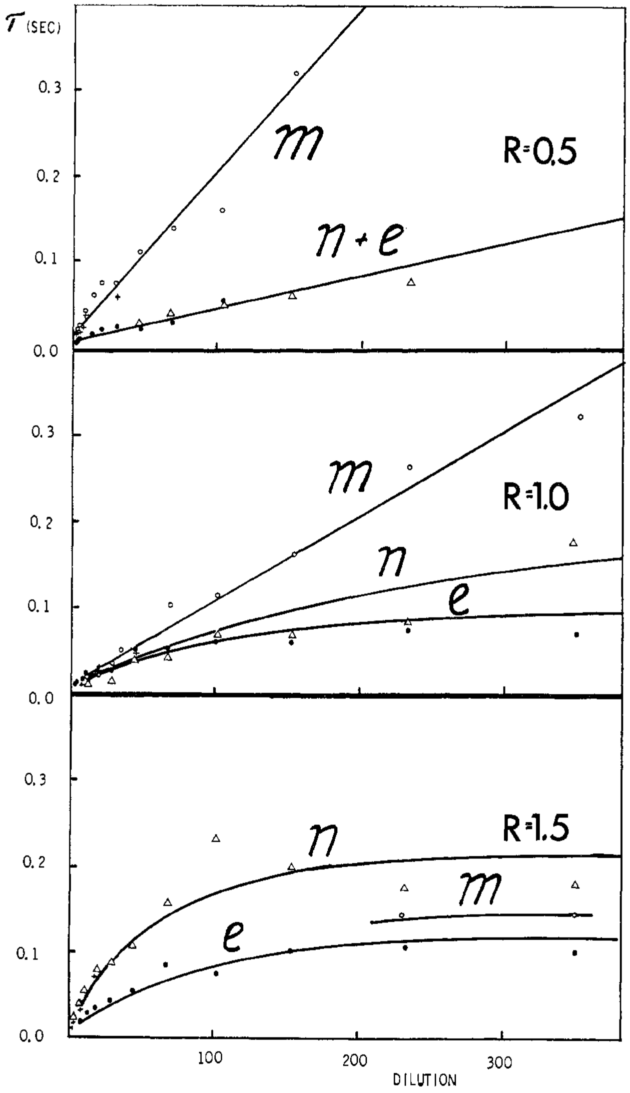

Fig. 3.—Average lifetimes, τ, in the system $(CH_3)_2SnI_2$ *vs.* $(CH_3)_2SnS$ for various dilutions with CCl_4 (vol./vol.) at 35°. The crosses represent data obtained from saddle-shaped resonances. All other points were obtained from line broadening, n = *neco*, e = end groups, m = middle groups.

dilutions, from the line width of the three separated resonances. The pre-exchange lifetimes at different dilutions are presented in Fig. 3 for the compositions R = 0.5, 1.0, and 1.5.

Linearity in Fig. 2 and 3 is consistent with a second-order rate of exchange. The observed curvature in some of the lines in these figures corresponds to a lesser decrease in rate with increasing dilution than would be expected for a second-order process. This is probably attributable to an increase with dilution in the ratio of the activity coefficients of the reactants over that of the activated complex.

The n.m.r. peak for pure dimethyltin diiodide is sharp at all concentrations (exhibiting a width of 1 c.p.s. rather than 0.5 c.p.s. due to slight quadrupole broadening by the iodine) because exchange of iodine between these like molecules does not result in a change in the chemical environment of the dimethyltin moiety. This means that the calculated pre-exchange lifetime in this case is infinite. As the value of R is decreased from 2 (corresponding to the pure dimethyltin diiodide), the calculated lifetime is found to decrease rapidly at first and then more slowly because of the continuing rise in the amount of end and middle groups with which the *neso* compound can exchange an iodine for a sulfur atom. Similar arguments apply to the lifetime of dimethyltin sulfide and middle groups.

Activation Energy of the Exchange Reactions.—From the variation in n.m.r. line width[7] with temperature, the activation energy of the exchange of halogen atoms and sulfur bridges was determined. For the 1 M solutions in CCl_4, the activation energy for the exchange process was found to be *ca.* 4 kcal. for the system in which the halogen is chlorine, *ca.* 2 kcal. for the bromine system, and also *ca.* 2 kcal. for the iodine system.

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Contribution from the Department of Chemistry, and the Inorganic Materials Research Division
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Some Properties of *n*- and Isotetrasilane

By SUDARSHAN D. GOKHALE and WILLIAM L. JOLLY

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The two isomers of tetrasilane were prepared in an ozonizer-type electric discharge and isolated by gas chromatography. The isomers were identified, consistently, by their n.m.r. spectra, their infrared spectra, and their relative volatilities.

Introduction

Stock, *et al.*,[1] obtained normal tetrasilane from the products of the reaction of magnesium silicide with hydrochloric acid, but they were unable to isolate the branched-chain isomer. Fehér, *et al.*,[2] achieved a partial separation of the two isomers by fractional distillation and reported the boiling and freezing points, densities, and refractive indices of the isomers. Borer and Phillips[3] and Fehér and Strack[4] showed that the

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(1) A. Stock, P. Stiebeler, and F. Zeidler, *Ber.*, **56**, 1695 (1923).

(2) F. Fehér, H. Keller, G. Kuhlbörsch, and H. Luhleich, *Angew. Chem.*, **70**, 402 (1958).

(3) K. Borer and C. S. G. Phillips, *Proc. Chem. Soc.*, 189 (1959).

(4) F. Fehér and H. Strack, *Naturwissenschaften*, **50**, 570 (1963).

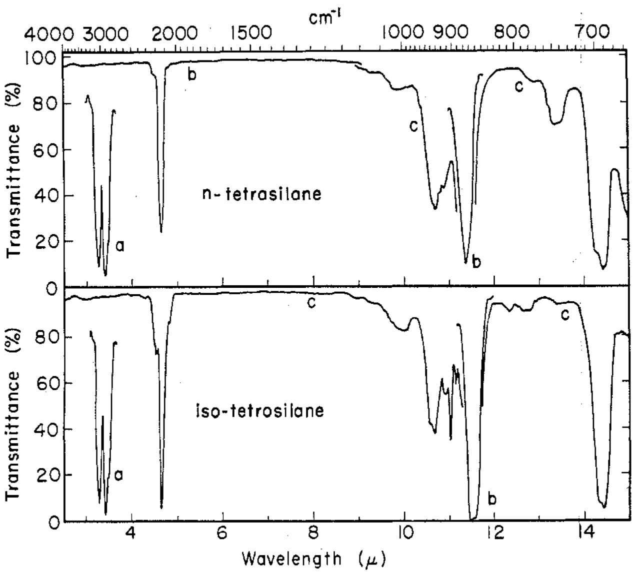

Fig. 1.—Infrared spectra of *n*- and isotetrasilane: a, polystyrene calibration; b, 5 mm. pressure in 5-cm. cell; c, 10 mm. pressure in 5-cm. cell.

mixture of silanes obtained from the reaction of magnesium silicide with aqueous acid can be separated into many components, including *n*- and isotetrasilane, by gas chromatography.

We have prepared a mixture of higher silanes by an electric discharge method similar to that used to prepare the higher germanes[5] and trisilane.[6] The isomers of tetrasilane were separated by gas chromatography and identified by their relative volatilities, by their infrared spectra, and, most unequivocally, by their n.m.r. spectra.

Experimental

The tetrasilanes were prepared from pure silane by the ozonizer-type electric discharge method,[5,6] subjecting the products higher than trisilane to gas–liquid chromatographic separation. The details of the method will be published elsewhere. Generally the ratio of *n*-tetrasilane to isotetrasilane was 5:1.

The infrared spectra were obtained with Perkin-Elmer Infracord spectrophotometers (NaCl Model 137B and KBr Model 137) using a 5-cm. NaCl cell and a 6-cm. KBr cell, respectively. The spectra are given in Fig. 1. The infrared spectrum of *n*-tetrasilane shows bands at the following frequencies (cm.$^{-1}$): 2155 (s), 1020 (s), 935 (m), 917 (w), 879 (s), 748 (w), 741 (w), 701 (sh; m), 694 (s), 662 (s), 535 (w), 470 (w). The spectrum of isotetrasilane shows bands at the frequencies (cm.$^{-1}$): 2210 (w), 2155 (s), 945 (sh; w), 935 (m), 915, 906, 898 (m), 871 (s), 866 (s), 698 (sh; m), 693 (s). Weak bands at 1000, 810, and 785 cm.$^{-1}$ may be due to impurities.

The vapor pressure of *n*-tetrasilane was found to be 10.0 ± 1.0 mm. at 0° and 29.5 ± 1.0 mm. at 25°. The vapor pressure of isotetrasilane could not be measured accurately because even our best sample contained perhaps as much as 5% impurity. However, we can state that, at 0°, the vapor pressure of isotetrasilane is more than 5 mm. higher than that of *n*-tetrasilane. In the chromatographic separation, the iso isomer preceded the normal isomer, in keeping with the vapor pressure measurements.

The mass spectrum of *n*-tetrasilane showed a fragmentation pattern of the four different types of ions with the following relative order of intensities: $Si_3^+ > Si_2^+ > Si_4^+ > Si_1^+$; this order is the same as that found for *n*-tetragermane.[7] The mass spectrum of isotetrasilane was not obtained.

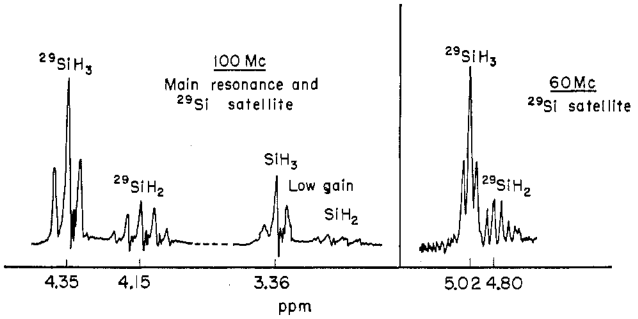

Fig. 2.—N.m.r. spectra of trisilane at 100 and 60 Mc. Satellite resonances shown are to low field of main resonances. Chemical shifts are given to low field of TMS.

The isomers of tetrasilane (and, for comparison, disilane and trisilane) were diluted with "conditioned" tetramethylsilane (TMS) for measurement of the n.m.r. spectra. "Conditioned" TMS was prepared by treating the middle fraction of a fractional distillation of TMS with silane, followed by fractional condensation on the vacuum line using traps at −78, −130, and −196°. The TMS which collected in the −130° trap was used to dilute the tetrasilanes enough to fill the n.m.r. tubes to the optimum height. It also served as an internal standard. The approximate concentrations of the silanes in TMS were: Si_2H_6, 50%; Si_3H_8, 75%; *n*-Si_4H_{10}, 30%; *i*-Si_4H_{10}, 4%. The proton magnetic resonance spectra were obtained using the A-60 and 100-Mc. Varian Associates n.m.r. spectrometers.[8] The spectra are presented in Fig. 2 to 5. H–H coupling constants were obtained from the ^{29}Si satellites except in the case of isotetrasilane, for which the H–H coupling constant could be obtained from the main resonance. Figure 2 shows the ^{29}Si satellite spectra for trisilane at 100 and 60 Mc. The p.p.m. values given are to lower field of TMS.

Discussion

The more volatile isomer of tetrasilane was assumed to be the branched-chain isomer, in analogy to the relative volatilities of the butane isomers. In our following discussions of the infrared spectra and n.m.r. spectra, it will be seen that this assignment is borne out.

Infrared Spectra.—In the infrared spectrum of isotetrasilane [$(SiH_3)_3SiH$], one expects the presence of bands due to the SiH group and the absence of bands due to the SiH_2 group. The weak absorption at 2210 cm.$^{-1}$, on the high-frequency side of the main Si–H stretching frequency band, probably corresponds to a stretching frequency of the SiH group. It is apparent from our study of the n.m.r. spectrum that the SiH proton is shielded more than the SiH_3 protons. We conclude that the SiH bond has a higher electron density, and that therefore it is stronger and has a higher stretching frequency than a corresponding bond in an SiH_3 group. In alkanes, the average of typical symmetric and antisymmetric CH_3 stretching frequencies is *higher* than the typical CH stretching frequency.[9] This difference may be explained by the

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[5] J. E. Drake and W. L. Jolly, *J. Chem. Soc.*, 2807 (1962).

[6] E. J. Spanier and A. G. MacDiarmid, *Inorg. Chem.*, **1**, 432 (1962).

[7] J. E. Drake and W. L. Jolly, *Proc. Chem. Soc.*, 379 (1961).

[8] The cooperation and help given by Varian Associates in permitting us to use their 100-Mc. spectrometer is gratefully acknowledged.

[9] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

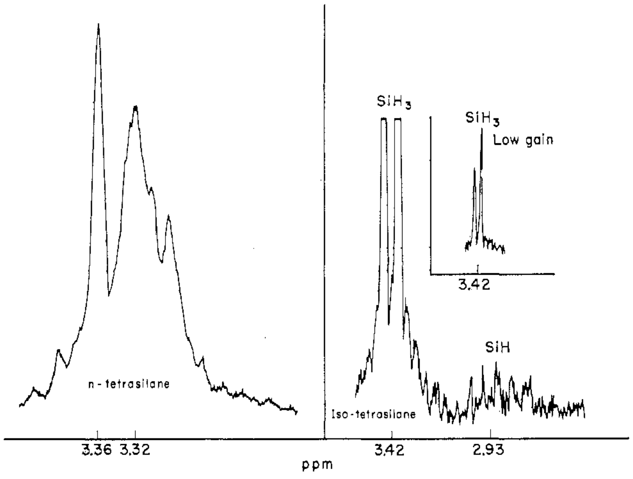

Fig. 3.—N.m.r. spectra of *n*- and isotetrasilane. Main resonances at 60 Mc. Chemical shifts are given to low field of TMS.

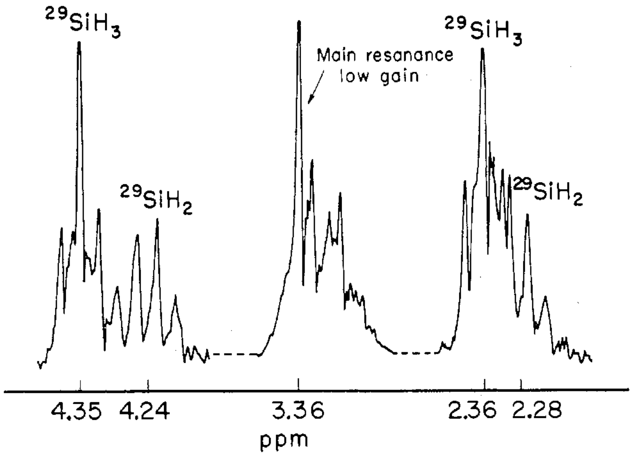

Fig. 4.—N.m.r. spectrum of *n*-tetrasilane. Main and satellite resonances at 100 Mc. Chemical shifts are given to low field of TMS.

fact that the electronegativity of hydrogen lies between the electronegativities of carbon and silicon.

There is no significant absorption in the KBr region or in the 720–830 cm.$^{-1}$ region in the case of isotetrasilane at 10 mm. pressure, whereas there is a strong absorption band at 622 cm.$^{-1}$ and a weak absorption band at 748 cm.$^{-1}$ in the case of *n*-tetrasilane. The infrared spectrum of trisilane shows similar, but much weaker, absorptions in the 740–750 and 570–590 cm.$^{-1}$ regions. It is therefore suggested that these bands are due to the SiH_2 group.

The strong absorption band near 870 cm.$^{-1}$ in both tetrasilanes, presumably due to the SiH_3 symmetrical deformation, is split in the case of isotetrasilane. The analogous type of resonance splitting of the methyl symmetrical deformation band, due to more than one methyl group on a carbon atom, is observed in the infrared spectra of alkanes.[9] We suggest that the band with distinct PQR branches centered at 906 cm.$^{-1}$ in the isotetrasilane spectrum corresponds to an Si–H bending mode. Infrared spectra of the silanes seem to be less complex than the corresponding spectra of the alkanes because the Si–Si vibration frequencies are much lower than the Si–H vibration and bending frequencies.[10]

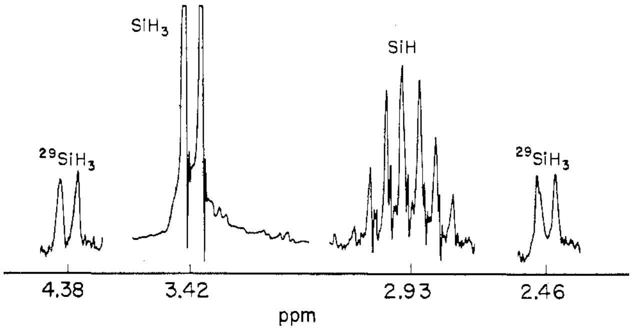

Fig. 5.—N.m.r. spectrum of isotetrasilane. Main and satellite resonances at 100 Mc. Chemical shifts are given to low field of TMS.

N.m.r. Spectra.—The n.m.r. spectrum of trisilane at 60 Mc. is complicated, just as it is at 40 Mc.,[11] because the chemical shift and coupling constant between the SiH_3 and SiH_2 protons are of the same order of magnitude. At 100 Mc., the spectrum is relatively simple, but by far the best spectra are found in the ^{29}Si satellites. The ^{29}Si satellite spectra of trisilane at both 100 and 60 Mc. are shown in Fig. 2. As expected, the $^{29}SiH_3$ resonance is split into a triplet and the $^{29}SiH_2$ resonance is split into a septet, of which only five lines are apparent in Fig. 2.

The n.m.r. spectrum of *n*-tetrasilane at 60 Mc. is shown on the left side of Fig. 3, and that at 100 Mc. is shown in Fig. 4. It will be noticed that the main resonance is complicated in each case.[12] However, the ^{29}Si satellite spectra (shown in Fig. 4 for 100 Mc.) are simple. As expected, the $^{29}SiH_3$ resonance is split into a triplet. The $^{29}SiH_2$ resonance is split into a sextet, of which only four components are apparent in Fig. 4, by the five protons which are nearby. Apparently the $\overline{H_3Si\text{–}^{29}SiH_2}\text{–}$ and $\overline{^{29}SiH_2\text{–}SiH_2}$ coupling constants are of very similar magnitude. On the low-field side of the main resonance, the $^{29}SiH_3$ and $^{29}SiH_2$ resonances are well separated. On the high-field side, the resonances overlap but are still recognizable.

The n.m.r. spectrum of isotetrasilane at both 60 (Fig. 3) and 100 Mc. (Fig. 5) is simple. The strong SiH_3 resonance is a doublet, and the weak SiH resonance is split into ten components, of which two or three are lost in the noise and cannot be seen in Fig. 5. The $^{29}SiH_3$ satellite bands are shown in Fig. 5. The ^{29}SiH satellite bands were too weak to be seen.

The chemical shifts are given in Table I. We have included our data for disilane and trisilane for comparison purposes. It is clear from the data that, as we increase the number of silicon atoms bonded to a silicon atom adjacent to a silyl group, the shielding of

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(10) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1113 (1957).

(11) J. J. Turner, "High Resolution NMR Spectroscopy," Thesis, Cambridge University, Oct., 1960.

(12) The general shape of the main resonance is similar to that of *n*-tetragermane[5] and is a mirror image of that of *n*-butane.[13]

(13) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 235.

the protons in the silyl group decreases. This effect is just the opposite of that predicted from simple electronegativity considerations and parallels the variations in chemical shifts of the CH_3 group in ethyl halides[14] and of the SiH_3 group in disilanyl halides.[15] The increase in shielding on going from the SiH_3 group to the SiH group is explicable in terms of the reduced electronegativity of silicon compared with hydrogen.

The H–H and ^{29}Si–H coupling constants are given in Table II. They are of the same order of magnitude as those reported by Abedini, *et al.*[15] Although the mechanism of the spin–spin interaction is not clearly understood, it is logical to expect that if this interaction is through the bonds it should decrease with an increase in the number of interposed bonds. The value of 3.5 to 4 c.p.s. for the coupling constant of vicinal protons in the higher silanes and the value of 2.75 c.p.s. of geminal protons in silane reported by Ebsworth and Turner[16] indicate that something other than mere "through-bond" interaction is involved. In the case of saturated hydrocarbons, vicinal proton coupling constants lie in the range of 5–8 c.p.s., and the geminal proton coupling constant in methane is 12.4 c.p.s.[17]

TABLE I

CHEMICAL SHIFTS IN P.P.M. (±0.02) TO LOW FIELD OF TMS

Compound	$-SiH_3$	$-SiH_2-$	$>$SiH
Si_2H_6	3.26		
Si_3H_8	3.36	3.18	
n-Si_4H_{10}	3.36	3.26	
i-Si_4H_{10}	3.42		2.93

TABLE II

COUPLING CONSTANTS IN C.P.S.

Compound	$H_3Si-SiH_n$ ±0.2	$^{29}Si-H_3$ ±1.0	$^{29}Si-H_2$ ±1.0
Si_2H_6	3.5	199	
Si_3H_8	4.0	199	194
n-Si_4H_{10}	3.7	199	197
i-Si_4H_{10}	4.0	192 ± 5	

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

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[14] B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955).

[15] M. Abedini, C. H. Van Dyke, and A. G. MacDiarmid, unpublished data.

[16] E. A. V. Ebsworth and J. J. Turner, *J. Chem. Phys.*, **36**, 2631 (1962).

[17] Reference 13, pp. 193, 236.

CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY,
NUCLEAR MATERIALS AND PROPULSION OPERATION, CINCINNATI, OHIO

Crystal Chemistry of the Rhombohedral $MO_3 \cdot 3R_2O_3$ Compounds[1]

BY E. A. AITKEN, S. F. BARTRAM, AND E. F. JUENKE

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Two new rhombohedral phases were found in the UO_2–UO_3–Y_2O_3 ternary system. Both of these phases exist at a fixed oxygen-to-metal atom ratio, one of which (designated rhomb 1) can be expressed by the formula $U_mY_{7-m}O_{12}$ where m = 1 to 3.4. For values of m greater than 2.8, low temperature oxidation produces the second rhombohedral structure (designated rhomb 2) of composition $U_nY_{8-n}O_{15}$ where n = 2 to 3.9. The rhombohedral 1 crystal structure is characteristic of a large family of new compounds formed between rare earth oxides and UO_3, WO_3, or MoO_3. Crystallographic data on these isostructural compounds are presented. The influence of ionic size and valence upon the formation and stability of this structure are discussed.

Introduction

Many generic families of mixed oxide compounds are well-known. Some of these are the group II–III spinels, II–IV perovskites, and III–IV pyrochlores. However, little or no information has been published on compound formation between III–VI oxides. In 1962, Chase[2a] revealed the existence of a rhombohedral phase in the U–Y–O system at the composition $UO_3 \cdot 3Y_2O_3$. Since then, a paper by Borchardt[2b] on yttrium–tungsten oxides gave data on the isostructural compound $WO_3 \cdot 3Y_2O_3$.

During a study of the phase relations in the system UO_2–UO_3–Y_2O_3,[3] it was found that a rhombohedral phase persisted over a wide range of compositions. Since the nature and behavior of the III–VI mixed oxides are unknown, this investigation was undertaken to study the crystal chemistry of this new family of compounds.

Experimental

Sample Preparation.—The metal oxides of greater than 99% purity were blended in a Mix-R-Mill (Spex Industries). To vary oxygen concentration, reactions were carried out in dry air, in hydrogen (∼ −46° dew point), and in a mixture of 10 parts CO_2 to 1 part CO at temperatures between 1000 and 1700°. Platinum or yttria-stabilized zirconia crucibles were used in the

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[1] (a) This paper originated from work sponsored by the Fuels and Materials Development Branch, Division of Reactor Development, U. S. Atomic Energy Commission, under Contract AT(40-1)-2847; (b) presented in part at the Basic Science Division Meeting, American Ceramic Society, Washington, D. C., Oct. 7–8, 1963.

[2] (a) G. A. Chase, *Acta Cryst.*, **15**, 91 (1962); (b) H. J. Borchardt, *Inorg. Chem.*, **2**, 170 (1963).

[3] S. F. Bartram, E. F. Juenke, and E. A. Aitken, *J. Am. Ceram. Soc.*, **47**, 171 (1964).