talline pattern, although indicating poor structure, was found for a hydrated oxide approximating to the composition $Ta_2O_5 \cdot 4.28H_2O$. The structure observed for the oxide heated between 650° and 1300° is identical with that obtained for the commercial oxide, and was found to be isomorphous with the low temperature modification of Cb_2O_5 reported by Brauer.[6] When heated to higher temperatures, the pentoxide was found to transform, and the pattern obtained was that observed previously for the "reduced" oxide. The low temperature structure persisted up to 1300°, the high temperature structure having been obtained after heating to 1350°, in agreement with the findings of Lagergren and Magneli.[3]

The transition of the pentoxide appeared to involve considerable structural changes, judging from the diffraction patterns. The high temperature structure remained unchanged after heating at 1300° for 48 hours. Neither of the diffraction patterns obtained corresponded to that given in the A.S.T.M. Index,[2] and the attempts at growing single crystals of the oxide, suitable for rotation photographs, were unsuccessful.

Discussion of Results

The discrepancies in the values reported for the tantalum lattice parameter previously are thought to have been due to oxygen present in the metal used. Andrews[9] and Myers[10] have observed the increase of the metal lattice parameter on addition of oxygen. While it has been stated,[11] that hydrogen also causes a lattice expansion, a slight expansion only was found by Burgers and Basart[12] in the metal prepared under conditions facilitating the solution of hydrogen. During the author's experiments the expansion was found to be small, a far more marked effect of the absorption having been the widening of the diffraction lines, consistent with high stresses being set up in the metal lattice.

The solubility of oxygen in the metal appears to be higher at temperatures of the order of 2000°, as found during an investigation of a sintered metal bar, showing considerable surface oxidation. Both the suboxide and the body-centered cubic metal patterns were obtained from this specimen, the parameter of the latter, however, was found to be 3.340 Å.; *i.e.*, considerably higher than that found for the maximum oxygen content at 1050°. This solubility must, however, decrease with further temperature increase, since the oxygen or the oxide is expelled by heating above about 2200° *in vacuo*.[9,10,13]

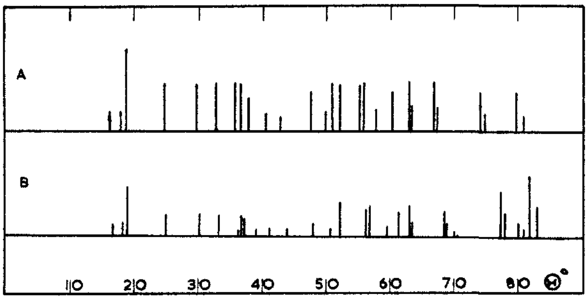

Fig. 1.—Debyograms of Cb_2O (A), from Kubaschewski[5,14] and tantalum suboxide (B). The relative intensities were estimated visually (A), and by means of a microphotometer (B).

The photogram of the pattern obtained with tantalum containing 4.2% oxygen was compared with that given by Kubaschewski for Cb_2O.[14] Figure 1 shows the similarity of the patterns, and consequently the structure is thought to correspond to the composition Ta_2O. An attempt was made to determine the symmetry of the unit cell, following the method of Jacob and Warren.[15] It was found that an orthorhombic cell of a = 5.29, b = 4.92 and c = 3.05 Å. would account for all the lines present. The experimental density being 15.52 g. cm.$^{-3}$, the cell contains two formula units of Ta_2O, the corresponding X-ray density being 15.8 g. cm.$^{-3}$.

It is evident that no confirmation of the existence of the dioxide has been found, and it is doubtful whether, in fact, any structure intermediate between Ta_2O and Ta_2O_5 exists, since the first new pattern obtained on the reduction of the pentoxide is that of the suboxide. Thus the "dioxide" appears to be a mixture $Ta_2O \cdot 3Ta_2O_5$, obtained by partial reduction of the pentoxide.

The reaction of the pentoxide with tantalum metal appears to be very rapid in the temperature range 1700–2200°. This indicates that the diffusion of oxygen through the metal must be rapid, which would account for the difficulty in obtaining oxygen-free metal, if it is cooled slowly through this critical range after sintering.

The author wishes to express his thanks to the Board of Directors of MUREX, Ltd., Rainham, Essex, Eng., for their permission to publish the results of the experimental work described above.

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[9] M. R. Andrews, This Journal, **54**, 1845 (1932).

[10] R. H. Myers, *Metallurgia*, **41**, 301 (1950).

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[12] W. G. Burgers and J. C. M. Basart, *Z. anorg. allgem. Chem.*, **216**, 223 (1934).

[13] "Tantalum, The Metal," Fansteel Metal Corporation, 1939.

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The Partial Hydrolysis of Chlorosilanes

By Robert West

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Schumb and Stevens have shown that hexachlorodisiloxane can be prepared in fair yield by the partial hydrolysis at −78° of silicon tetrachloride dissolved in ether.[1] We have extended this work by studying the partial hydrolysis of trichlorosilane,[2] dichlorosilane and methyltrichlorosilane, under similar conditions. With trichlorosilane, 5 to 10% yields of 1,1,3,3-tetrachlorodisiloxane (a new compound) are obtained, but with dichlorosilane and methyltrichlorosilane only traces of partially-hydrolyzed products could be isolated. The reason for the diminished yields is not known; however, recent unpublished work in this Laboratory indicates that among these chlorosilanes the tendency toward the formation of addition compounds with amines[3] falls off in the same order.

In the titration of 1,1,3,3-tetrachlorodisiloxane (in acetone solution) with standard alcoholic sodium

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[1] W. C. Schumb and A. J. Stevens, This Journal, **69**, 726 (1947); **72**, 3178 (1950).

[2] The complete hydrolysis of trichlorosilane has been studied recently; see G. H. Wagner and A. N. Pines, *Ind. Eng. Chem.*, **44**, 321 (1952).

[3] W. R. Trost, *Can. J. Chem.*, **29**, 877, 1075 (1951).

hydroxide, an indicator with a color change above *p*H 7 cannot be used, because of the lability of the silane hydrogen in the presence of excess base. Satisfactory titrations were obtained using brom thymol blue (*p*H 6.0–7.6). However, equally good results were obtained without an added indicator; the first appearance of bubbles of hydrogen in the solution gave an accurate end-point.

Experimental

1,1,3,3-Tetrachlorodisiloxane.—To 70 ml. of anhydrous ethyl ether was added 47 g. (0.35 mole) of trichlorosilane (Anderson Laboratories). This solution was cooled to −78° in a Dry Ice–acetone-bath and stirred vigorously while 3.4 g. (0.19 mole) of water was added from a buret over a period of 30 minutes. The mixture was then stirred for several hours while it warmed to room temperature. Fractional distillation of the solution was carried out using a 50-cm. column packed with stainless steel helices. The product distilled at 99–100° (763 mm.); a trace of chlorine-containing material boiling at 145° was also found (probably hexachlorotrisiloxane). The yield was 3.2 g., or 8.5%. Yields from similar runs varied from 5 to 10%. The product was a colorless mobile liquid with $n^{25}{}_{D}$ 1.4075 and $d^{25}{}_{4}$ 1.347. The molecular weight by the vapor-density method was 222 (calcd. 216).

Anal. Calcd. for $H_2Si_2OCl_4$: Cl, 65.67. Found: Cl, 65.6, 65.7.

The infrared absorption spectrum of tetrachlorodisiloxane vapor was obtained using a cell of 3-cm. path length with KBr windows. The spectrum in the sodium chloride region was measured with a Baird automatic recording infrared spectrophotometer (Fig. 1); the region from 450 to 650 cm.$^{-1}$ was studied with a Perkin–Elmer spectrophotometer using a KBr prism. Strong absorption bands in this region were found centered at 533 and 604 cm.$^{-1}$. For most of the absorption bands, analogies are found in the spectrum of $HSiCl_3$.[4,5] However, the bands at 871, 912 and 1128 cm.$^{-1}$ have no counterparts in the $HSiCl_3$ spectrum.

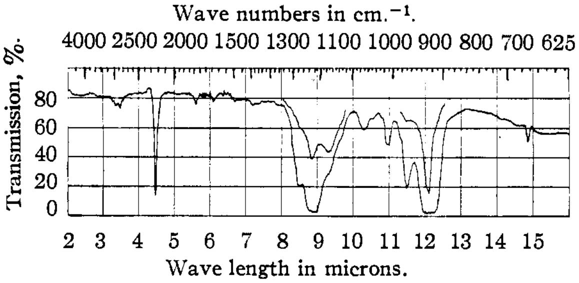

Fig. 1.—Infrared absorption spectrum of 1,1,3,3-tetrachlorodisiloxane. The lower line is at 40 mm., while the upper line is at 4 mm.

Partial Hydrolysis of Dichlorosilane.—The hydrolysis was carried out in the same way as that of trichlorosilane, except that *n*-propyl ether was used in place of ethyl ether. From 35 g. of dichlorosilane,[6] about 1 g. (4%) of product was obtained boiling over the range 70–81%. This material probably contained some *n*-propyl ether. Analysis gave 42.9% Cl; dichlorodisiloxane requires 48.2%.

In the course of this and other experiments with dichlorosilane, it was found that when a large quantity of the gas is vented in air, it inflames spontaneously and explosively. This is contrary to the findings of Stock,[7] who was working only with very small quantities. The liquid could be handled with relative safety if kept at −78°.

Partial Hydrolysis of Methyltrichlorosilanes.—The hydrolysis was performed in the same way as that of trichlorosilane. Only a trace of chlorine-containing material, boiling near 110°, was found.

Acknowledgment.—The author wishes to thank Dr. Eugene G. Rochow for his help and encouragement during the course of this work.

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[4] T. C. Gibian and D. S. McKinney, THIS JOURNAL, **73**, 1431 (1951).

[5] C. A. Bradley, *Phys. Rev.*, **40**, 908 (1932).

[6] The dichlorosilane was a gift from the Linde Air Products Co., of Tonawanda, N. Y.

[7] A. Stock and C. Somieski, *Ber.*, **52**, 718 (1919).

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COMMUNICATIONS TO THE EDITOR

THERMODYNAMIC AND KINETIC CONSTANTS FOR THE DIBORANE-BORINE EQUILIBRIUM

Sir:

We have succeeded in making a reliable estimate of the equilibrium constant for the dissociation of diborane into borine groups. The method is an indirect one. It is now clear why physical experiments designed to detect directly borine in diborane[1] have failed; at 155° and one atmosphere, the degree of dissociation of diborane as computed from the equilibrium constant given below is 1.63×10^{-5}, and at that temperature its general pyrolysis is fairly rapid.

The enthalpy change for the association reaction $2BH_3 = B_2H_6$ was deduced as follows. We measured the heats of reaction of trimethylamine with diborane and tetramethyldiborane, to produce the solid and liquid association products, respectively, using a precision vacuum ice calorimeter. These were corrected to the gas phase reactions and combined with the value given by Brown[2] for the heat of reaction of trimethylamine with boron trimethyl. Thus the three values (−17.3, −11.0, −17.6 kcal./mole of amine) demonstrate the effect of methyl substitution on the acidity of the boron unit, as well as on the strength of the (BH_2B) bridge. By making suitable corrections for inductive, steric and mesomeric contributions from the methyl groups as deduced from other data, we arrived at $\Delta H^{\circ}_{273} = -32 {}^{+1}_{-2}$ kcal. per mole of diborane, for the above reaction.

The entropy change for the association of two borines was computed. Based on the structure of diborane as reported by Hedberg and Schomaker,[3] its translational plus rotational entropy is 53.70 ±

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[1] A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923); G. C. Pimentel and K. S. Pitzer, *J. Chem. Phys.*, **17**, 882 (1949).

[2] H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944).

[3] K. Hedberg and V. Schomaker, *ibid.*, **73**, 1482 (1951).