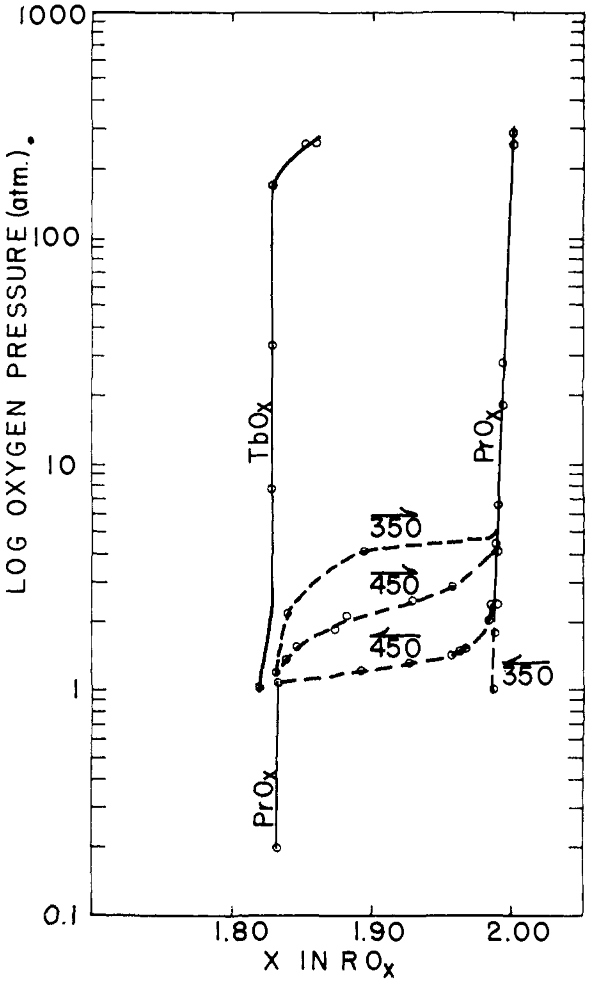

Fig. 1.—Pressure–composition diagram: oxygen–TbO_x, PrO_x systems.

tions are those corresponding to the final cold product determined by weight increase determinations.

It will be observed that samples of composition PrO_2 are obtained only at very high pressures, but that samples treated at 350° and five atmospheres are oxidized almost all the way to PrO_2.

At pressures below five atmospheres and 450° the lack of reproducibility of the points on oxidation and reduction implies that the samples are not really at equilibrium during the soak period at these temperatures.

Terbium oxidizes to a lesser degree than praseodymium at moderate to high oxygen pressures. For example, at 282 atmospheres and 400° the two oxides obtained are $TbO_{1.86}$ and $PrO_{2.00}$. One run with terbium designed to take advantage of any slow uptake of oxygen at lower temperatures was cooled from 400° to room temperature over a period of five days. The final composition was $TbO_{1.86}$.

Some experiments not shown in Fig. 1 are tabulated in Table II. It might be noted that the precise composition of $TbO_{1.75}$, which has long been reported as the brown product obtained when terbium oxides are ignited in air and cooled to room temperature, is not easily realized.

Table II

Experiments on Terbium Oxide

Treatment, hr.	Temp., °C.	Pressure, atm.	Compn. (x in TbO_x)	Remarks
12	400	1	1.82	Removed to desiccator while still hot
24	300	1	1.83	Cooled rapidly
14	600	1	1.81	Cooled very rapidly
4	700	1	1.75	N_2 admitted while hot then cooled very rapidly
6	600	0.2	1.80	Cooled slowly
5	900	0.2	1.73	Cooled slowly to 150°, desiccated
5	900	0.2	1.73	Cooled slowly to 200°, desiccated
120	400–25	252–160	1.86	Cooled slowly over 5 days

[Contribution from the Department of Chemistry at the University of Washington]

The Iron(II) Chloride–Iron(II) Bromide System[1]

By Richard O. MacLaren and N. W. Gregory

Received June 14, 1954

The arrangement of layers of halogen atoms in mixtures of $FeCl_2$(CCP) and $FeBr_2$(HCP) annealed to 400° has been studied by X-ray powder pattern analysis. Coexistence of CCP and HCP phases with the same composition is observed between 40 and 80 mole per cent. chloride. Solid solutions prepared by mixing the pure components and by halogen exchange reaction of the solid phases with HCl and HBr were found to have the same structural characteristics and to be nearly ideal.

Crystals of $FeCl_2$ and $FeBr_2$ have layer structures with the halogen atoms cubic close packed (CCP) in $FeCl_2$ ($CdCl_2$ type, $R\bar{3}m$) and hexagonal close packed (HCP) in $FeBr_2$ ($Cd(OH)_2$ type, $C\bar{3}m$).[2] These structures are also characteristic of $CdBr_2$ and CdI_2. An intermediate phase in the $CdBr_2$–CdI_2 system, with bulk composition near CdIBr, has been reported by Hägg and Linden[3] to have a unique packing with a layer repeat unit ABCBCA-BABCAC-. We have made a study of intermediate phases in the $FeCl_2$–$FeBr_2$ system. The halogen exchange equilibrium between the solid iron halide phases and HCl and HBr has been investigated at 400°. An X-ray powder pattern study of solid solutions formed in this way and of those obtained by heating various mixtures of the two simple

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[1] Presented at the Northwest Regional Meeting of the American Chemical Society at Richland, Washington, June 11, 1954.

[2] A. Ferrari, A. Celeri and F. Giorgi, *Atti accad. nasl. Lincei*, **9**, 782, 1134 (1929).

[3] G. Hägg and E. Linden, *Arkiv Kemi, Mineral. Geol.*, **B16**, No. 5, 1 (1942).

halides (annealed to 400°) has been made. Two modifications of the structure of pure $FeCl_2$ have also been discovered.

Exchange Equilibrium.—The reaction

$$FeCl_2 + 2HBr(g) = FeBr_2 + 2HCl(g)$$

established apparent equilibrium in 24 hours at 400°; results are summarized in Fig. 1. The initial reactants were HCl and $FeBr_2$ in experiment 1 (open circles) and HBr and $FeCl_2$ in experiment 2 (solid circles). Both hydrogen halides were added to $FeBr_2$ in experiment 3 (half-closed circles) to keep the solid composition near pure $FeBr_2$.

The absence of any apparent regions of immiscibility suggests that a complete series of solid solutions is formed. However, a continuous series of iso-structural solid solutions is obviously impossible in view of the structural difference of the pure components. Two possible explanations may be suggested. Continuous solid solutions could occur by formation of random packed structures, which would then resemble neither of the pure components; or the co-existence of two phases, each isostructural with one of the pure halides, over a range of composition could exhibit the behavior observed.[4] However, the latter would require that the free energies of the two phases be identical over an appreciable concentration range if the system is in true thermodynamic equilibrium.

The correlation of results on the basis of a complete series of ideal solid solutions is remarkably good. The broken curve in Fig. 1 was calculated from an equilibrium constant $K = N_{FeBr_2}N^2_{HCl}/N_{FeCl_2}N^2_{HBr}$ equal to 57.4 at 400°. This value is based on accepted thermodynamic properties of HCl and HBr,[5] standard entropies of 28.19 and 33.62 e.u., and molal heat capacities of 18.35 and 19.06 cal./deg. for $FeCl_2$ and $FeBr_2$, respectively,[6] and standard heats of formation of −81.5 kcal. for $FeCl_2$ and −67.36 kcal. for $FeBr_2$ (ref. Br_2 gas).[6] The latter has been redetermined in this Laboratory to be −66.0 kcal.[7]; with this value the equilibrium constant is 20.6, which gives the solid curve in Fig. 1. The heat capacity change for the exchange reaction at 25° (0.71 cal./deg.) has been assumed not to change with temperature.

Structural Properties.—Interplanar spacings in crystals of $FeCl_2$, $FeBr_2$ and twelve annealed $FeCl_2$–$FeBr_2$ mixtures are shown in Fig. 2. The 003 plane (with spacings between 5.863 for $FeCl_2$ and 6.204 for $FeBr_2$) has been omitted for graphical convenience. Patterns have been indexed on the basis of the smallest cell common to both iron(II) halides. While the unit cell for $FeCl_2$ is rhombohedral and contains one molecule, it can be represented by a hexagonal pseudo-unit cell which contains three molecules with a base analogous to the true $FeBr_2$ hexagonal unit cell (a = 3.780 Å.) but a "c" dimension three times as large (c = 18.612 Å.).

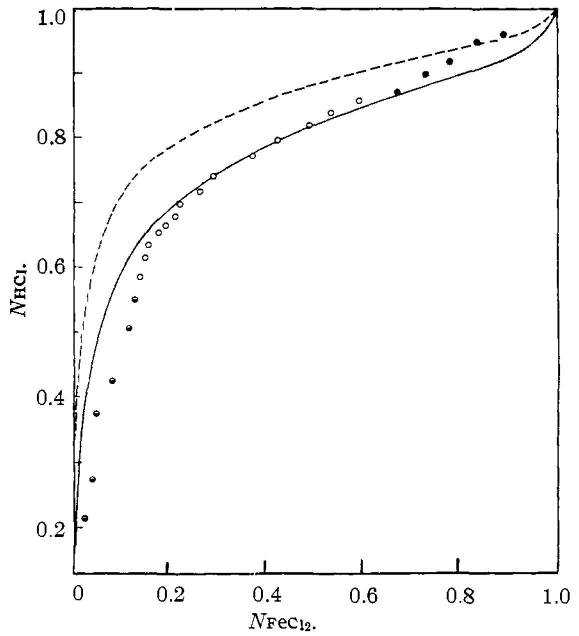

Fig. 1.—Compositions of HCl–HBr mixtures in equilibrium with $FeCl_2$–$FeBr_2$ solid at 400°.

Comparison of observed planes for $FeCl_2$ and $FeBr_2$ clearly shows the dissimilarity arising from the difference in packing. For the non-primitive cells used, only those planes with "l" divisible by three are observed for the bromide while those for $FeCl_2$ have indices such that $2h + k + l$, $-h + k + l$ and $-h - 2k + l$ are divisible by three. Seven observed diffraction lines are common to both: 003, 006, 110, 113, 0012, 1 1 12 and 300.

A given spacing can be seen to vary continuously with composition (Fig. 2); hence a series of substitutional solid solutions must occur. The change from one type of packing to the other is necessarily discontinuous. The HCP structure can be detected in mixtures containing as much as 80 mole per cent. chloride (note 103, 106 and 109). The CCP structure can be detected to 30 or 40 mole per cent. chloride, as shown by the 101 spacing in particular, and 104, 107(009) and 211.

The unit cell parameters, calculated for the best fit with the observed spacings, are shown in Fig. 3. The change in "a" (shaded circles) with composition follows Vegard's rule[8]; however, two different values of "c" are apparent in the center of the system. The doubling is particularly obvious for 006, 0012, and 1112, Fig. 2. Unit cells with the larger "c" are HCP while the smaller cells are CCP. The variation in "c" cannot be ascribed to a difference in composition of the structurally different phases since only one "a" can be derived from each pattern.

Unit cell parameters of solid phases formed in the exchange studies are shown by the squares in Fig. 3. (Experiment 1: 0.589 (sublimed portion) and 0.608; 2: 0.646; and 3: 0.034 mole fraction chloride). In all exchange equilibrium experiments a portion of the solid collected on the cooler regions of the vessel (*ca.* 398°), the amount dependent on the experiment time. Powder patterns of the sub-

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[4] R. W. G. Wyckoff, "The Structure of Crystals," The Chemical Catalog Co., Inc., New York, N. Y., 1924, pp. 404–405.

[5] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circ. 500, Series I, U. S. Government Printing Office, Washington, D. C., 1950.

[6] Private communication from Professor E. F. Westrum, Jr., University of Michigan, Department of Chemistry.

[7] J. C. M. Li and N. W. Gregory, THIS JOURNAL, **74**, 4670 (1952).

[8] L. Vegard, *Z. physik.*, **5**, 17 (1921).

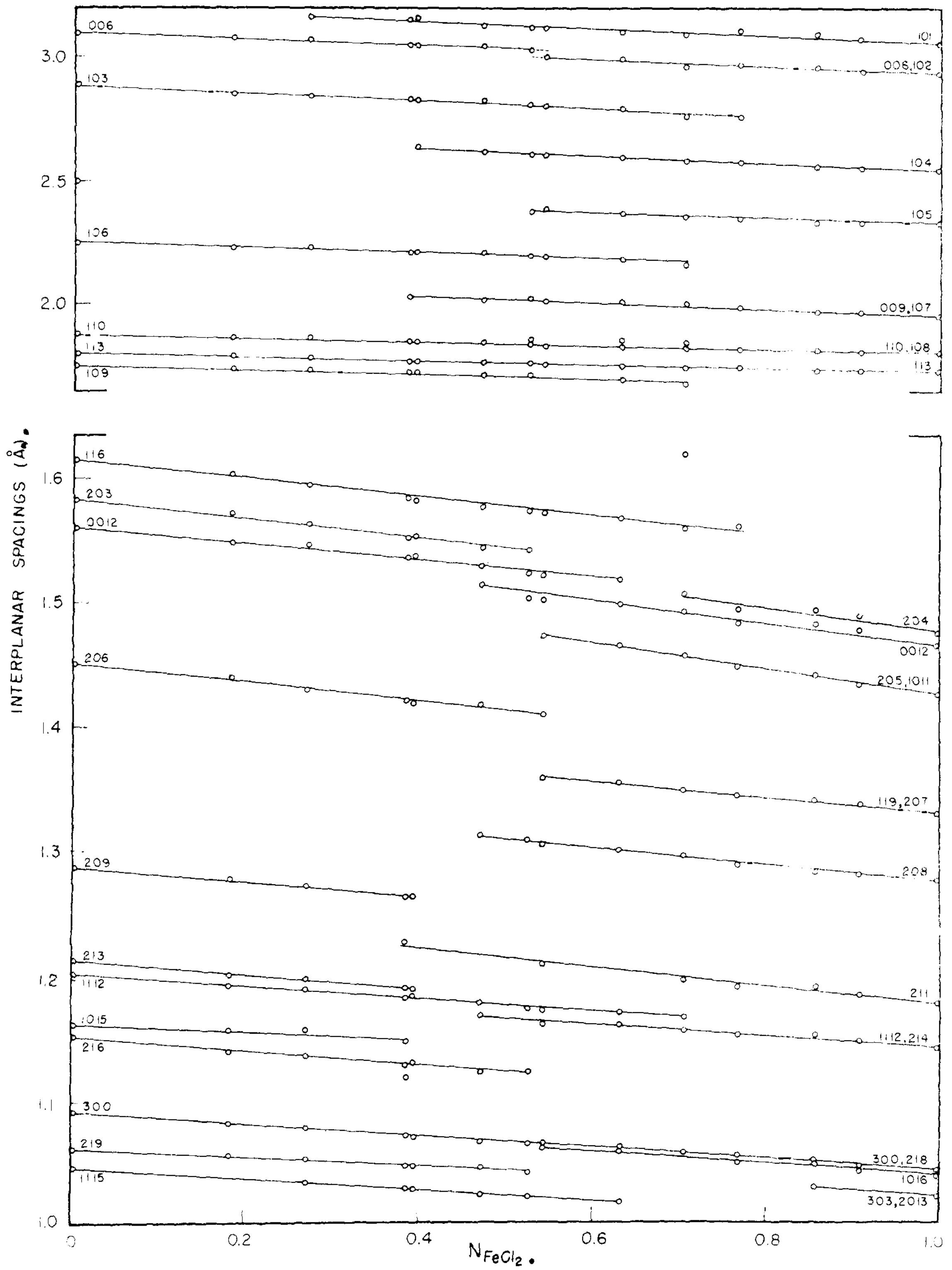

Fig. 2.—Powder pattern spacings for annealed $FeCl_2$–$FeBr_2$ mixtures.

limate were identical with those of the bulk of the solid except in the first experiment where nearly a fourth of the solid had sublimed during a three-month period. In this case, patterns show the same two structures but with a decided difference in the predominant phase as evidenced by relative intensities of the lines. The predominant phase could not be associated with retention of the packing in the starting material since the bulk solid showed principally a CCP arrangement, while the sublimate had primarily the structure of the reactant, $FeBr_2$.

This variation in two samples of essentially the same composition, observed to a much lesser degree in independent patterns of a given annealed mixture, implies that the relative amounts of each phase is largely a matter of chance in the intermediate concentration range. The lack of specific line broadening representing random faults[9] and the absence of extra lines or extinctions due to combination HCP–CCP or random packings in any mixture suggests that each single crystal has one or the other arrangement. The relative intensities of the various diffraction lines in each phase were the same in mixtures as in the pure components.

The concurrence of two crystal types (body-centered cubic and CCP) with the same composition over a 10 mole per cent. range has been reported in annealed iron–nickel mixtures.[10] Cobalt is the only substance in which CCP and HCP structures have been reported to co-exist,[9] even though it appears that the two packings should have the same lattice energy in elementary substances.[11]

The co-existence of two phases with the same composition over a considerable concentration range is not expected in an equilibrium system (Gibbs Phase Rule) unless the free energies of the phases remain identical. Hence it appears that true equilibrium has not been established at all concentrations in our systems, even though the exchange reaction was allowed to stand for three weeks (expt. 1) before the final measurement and removal of powder samples. The free energy difference between the two solid phases throughout the intermediate region must be so slight that no appreciable thermodynamic driving force exists which would stabilize a particular phase. The equilibrium constant obtained may thus be assumed to characterize either phase within the experimental error. A close similarity of the lattice energy for the two types of packing is also indicated by the behavior of $FeCl_2$ discussed in the next section.

Although there is only a subtle difference between HCP and CCP structures for elementary substances, a more definite distinction may be noted in the iron halides. In the CCP arrangement, the halogens of the 3rd layer are in better positions for interaction with the cations between the first two layers. In HCP structures, the alternate positions for the halogens of the 3rd layer favor stronger interactions of halogens between the 2nd and 3rd layers, since van der Waals forces are enhanced by polarization. In intermediate $FeCl_2$–$FeBr_2$ mixtures, either position appears to give the crystal essentially the same stability, as long as the stacking is orderly; surprisingly, random packing of layers is not observed.

Structural Variations of $FeCl_2$.[12]—Although the halogen atoms in the stable structure of $FeCl_2$ are CCP, one of three patterns of separately sublimed $FeCl_2$ (rapid condensation) exhibited additional lines which indexed as strong lines of a HCP structure. Comparison of observed intensities with those calculated for a mixture of $^2/_3$ CCP and $^1/_3$ HCP gave good agreement and accounted for the presence of 103, 106, 109 and 203. The average deviation of all observed spacings from those calculated from the unit cell parameters of the normal CCP structure was 0.15%, while the deviation of the four HCP lines was 0.07%. Hence in this case, the unit cell size is apparently identical for both packings.

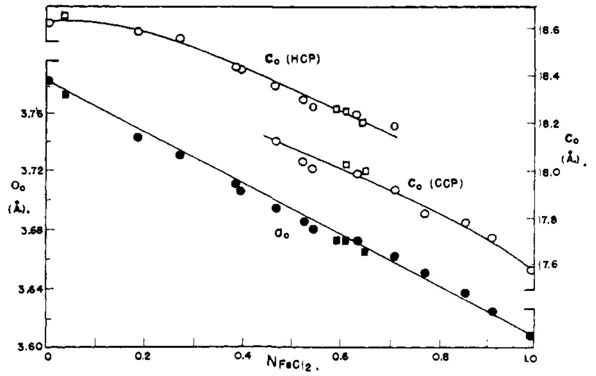

Fig. 3.—Unit cell parameters for annealed $FeCl_2$–$FeBr_2$ mixtures.

A third variation of the crystal structure of $FeCl_2$ was obtained by low temperature dehydration of the tetrahydrate, a procedure reported to produce a random packed structure for $CdBr_2$.[3] Commercial $FeCl_2 \cdot 4H_2O$ was recrystallized and dried over 95% H_2SO_4 *in vacuo* for two weeks. The resulting dihydrate was heated *in vacuo* at not over 110° for 48 hours to complete the dehydration. The pattern of this sample (purity 99.76 ± 0.5%) agreed very well with that predicted for a random structure with the normal unit cell dimensions of the CCP structure, except for the presence of a weak line which appeared to be the 101. Conversion to the CCP structure occurred when the sample was heated at 500° for several hours; at this temperature, sublimation facilitates rearrangement.

Experimental

Exchange Equilibria.—A known weight of anhydrous iron-II) halide was sublimed in high vacuum into the Pyrex equilibrium vessel (862-ml. volume) which was connected to the vacuum system by a 2-mm. capillary tube and a stopcock. After the sublimation tube was sealed-off, the appropriate hydrogen halide was introduced at a measured pressure (between 450 and 600 mm.) and the system allowed to equilibrate at 400 ± 2°. Twelve hours was found sufficient with the exception of three measurements with the solid phase near pure $FeBr_2$ which required several days. At 300°, equilibrium is not established in periods as long as 20 days.

The composition of the equilibrium gas phase was determined by measurement of the vapor pressure of the condensed sample at −78.51°.[13] In the majority of experiments the gas mixture was returned to the equilibrium vessel and measurements checked after at least 20 hours of additional equilibration. The solid composition was followed from the amount of gas reacted. At the end of the series of experiments the final composition of the solid was checked

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[9] O. S. Edwards and H. Lipson, *Proc. Roy. Soc.* (*London*), **180A**, 268 (1942).

[10] L. W. McKeehan, *Phys. Rev.*, **2**, 402 (1923).

[11] G. Kane and M. Goeppert-Mayer, *J. Chem. Phys.*, **8**, 642 (1940).

[12] A table showing the observed spacings and intensities and a comparison with calculated values for the various $FeCl_2$ structures has been deposited as Document number 4310 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

[13] J. D. Corbett and N. W. Gregory, THIS JOURNAL, **75**, 5238 (1953).

by analysis. The total deviation from the value calculated by gas analysis was −2.1, 1.5 and 0.1 mole per cent., respectively, for the three independent samples.

Annealed Mixtures.—Mixtures of the iron(II) halides were prepared by grinding together weighed samples of the pure components in a dry carbon dioxide atmosphere. The powder was transferred to Pyrex tubes of 10-ml. volume which were evacuated and baked out at 400° prior to sealing. The tubes were heated at 510° for two to fourteen days, cooled slowly over a two-hour period to 400°, then removed from the furnace. The composition of the resulting solid solutions was then checked by analysis.

Powder Patterns.—Pyrex capillaries 0.4 mm. i.d. were prepared, filled with the ground sample in the dry-box and subsequently sealed with a flame. X-Ray diffraction patterns were obtained using Cu Kα radiation (nickel-filtered; North American Phillips unit; 30 kv., 20 ma.) in a cylindrical camera of 11.49 cm. radius (calibrated with sodium chloride). Exposures varied from 15 to 48 hours.

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SEATTLE, WASHINGTON

NOTES

The Addition Reaction between Trichlorogermane and an Olefin

BY ALBERT K. FISCHER, ROBERT C. WEST AND E. G. ROCHOW

RECEIVED JUNE 11, 1954

Sommer, Pietrusza and Whitmore have described the addition reaction between an olefin and trichlorosilane,[1] for which an applicable free-radical mechanism has been discussed by Kharasch, Jensen and Urry.[2] It was desired to determine whether the analogous reaction

$$RCH{=}CH_2 + GeHCl_3 \xrightarrow[\text{catalyst}]{\text{peroxide}} RCH_2CH_2GeCl_3$$

would proceed.

Experimental.—A mixture of 80% $GeHCl_3$ and 20% $GeCl_4$ was prepared according to the procedure described by Delwaulle and Francois.[3] The components are difficult to separate because an azeotrope of 70% $GeHCl_3$ and 30% $GeCl_4$ distils, but since $SiCl_4$ does not add to olefins it was expected that $GeCl_4$ would not interfere. Therefore the direct product was used in these experiments. Benzoyl peroxide was chosen as catalyst, and the olefin which was used was 1-hexene (Phillips Research Grade). Amounts of materials taken were: $GeHCl_3$, 18.9 g. (actual), 0.10 mole; 1-hexene, 18.5 g., 0.22 mole; benzoyl peroxide, 0.7 g., 0.003 mole.

The reactants were refluxed under a pressure about 5 cm. above one atmosphere at 62–64° for 35 hours in a flask fitted with two water-cooled condensers in series connected to a mercury seal to keep out air.

The product was distilled at a pressure of 40–50 mm. A fraction boiling at 122–125° and weighing 5.5 g. was obtained. This product was redistilled at 14 mm. with a constant boiling point of 97°, and yielded a clear and colorless liquid with a refractive index of $n^{25}D$ 1.4719.

Anal. Calcd. for $C_6H_{13}GeCl_3$: Cl, 40.27; H, 4.96; C, 27.28; Ge, 27.49. Found: Cl, 39.65; H, 4.81; C, 27.34; Ge, 28.20 (by difference).

The 5.5 g. of product represents a 22% yield of hexyltrichlorogermane, calculated on the basis of $GeHCl_3$.

Discussion.—The results show that the Ge–H bond of $GeHCl_3$ acts like the Si–H bond of $SiHCl_3$ in adding to the double bond of an olefin to produce an organogermanium compound. The position of addition of the $GeHCl_3$ to the olefin is not certain, but it seems reasonable that the Ge adds to the 1-position in accordance with experience with Si–H compounds, and because the radical which is formed in this manner ($R\underset{\cdot}{C}H{-}CH_2GeCl_3$) is more stable and longer-lived than the radical which would be formed if the Ge were to bond to the 2-position ($RCH(GeCl_3)CH_2\cdot$).

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(1) L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, THIS JOURNAL, **69**, 188 (1947).

(2) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945).

(3) M. L. Delwaulle and F. Francois, *Compt. rend.*, **228**, 1007 (1949).

An Improved Method for Obtaining High-Purity Zirconium and Hafnium Oxides

BY A. W. HENDERSON AND K. B. HIGBIE

RECEIVED JUNE 9, 1954

The need for high-purity zirconium and hafnium compounds for use as spectrographic standards is becoming more important as the knowledge of the uses for these metals increases. Because of the complex nature of the chemistry of these elements, the present purifying procedures mainly involve formation of oxychloride or sulfate compounds. Herzfield,[1] in 1914, patented the process of crystallizing zirconium oxychloride octahydrate from a concentrated solution of hydrochloric acid to remove large amounts of silica. A second recrystallization step was possible by dissolving the readily soluble crystals in water, adding concentrated hydrochloric acid, and boiling. The oxychloride octahydrate again crystallized out upon cooling. Venable,[2] Brauer,[3] and Spink and Wilhelm[4] have published variations of this basic method. The application of the method in large-scale production of zirconium metal has been summarized by Kalish.[5] The prepa-

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(1) H. Herzfield, German Patent 290,878 (May 29, 1914); *J. Soc. Chem. Ind.*, **35**, 634 (1916).

(2) F. P. Venable, "Zirconium and its Compounds," The Chemical Catalog Company, New York, N. Y., 1922.

(3) G. Brauer, "Handbuch den Preparativen Anorganischen Chemie," Enke Verlag, Stuttgart, 1952, p. 908.

(4) D. R. Spink and H. A. Wilhelm, U. S. Atomic Energy Commission Report I.S.C. 217, March, 1952.

(5) H. S. Kalish, "The Preparation of Zirconium Powder," a paper presented before the Eighth Western Metal Congress and Exposition, Los Angeles, California, March 23, 1953.