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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NOTES

The Addition Reaction between Trichlorogermane and an Olefin

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

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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

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

would proceed.

Experimental.—A mixture of 80% $\mathrm{GeHCl_3}$ and 20% $\mathrm{GeCl_4}$ was prepared according to the procedure described by Delwaulle and Francois.[3] The components are difficult to separate because an azeotrope of 70% $\mathrm{GeHCl_3}$ and 30% $\mathrm{GeCl_4}$ distils, but since $\mathrm{SiCl_4}$ does not add to olefins it was expected that $\mathrm{GeCl_4}$ 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: $\mathrm{GeHCl_3}$, 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 $n^{25}\mathrm{D}$ 1.4719.

Anal. Calcd. for $\mathrm{C_6H_{13}GeCl_3}$: 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 $\mathrm{GeHCl_3}$.

Discussion.—The results show that the Ge–H bond of $\mathrm{GeHCl_3}$ acts like the Si–H bond of $\mathrm{SiHCl_3}$ in adding to the double bond of an olefin to produce an organogermanium compound. The position of addition of the $\mathrm{GeHCl_3}$ 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 ($\mathrm{R\underset{\cdot}{C}H{-}CH_2GeCl_3}$) is more stable and longer-lived than the radical which would be formed if the Ge were to bond to the 2-position ($\mathrm{RCH(GeCl_3)CH_2\cdot}$).

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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

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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.

ration of high-purity oxides by means of a recrystallization process employing sulfuric acid had been proposed by Clabaugh and Gilchrist.[6] This is perhaps the best method published for obtaining very high-purity zirconium compounds. It involves the formation of zirconium sulfate tetrahydrate ($Zr(SO_4)_2 \cdot 4H_2O$) by the addition of concentrated sulfuric acid to a fairly concentrated aqueous solution of zirconium sulfate or zirconium chloride. Small amounts of hydrochloric acid are required in the sulfate solution to insure the removal of iron. A 70% recovery of zirconium is claimed after five recrystallization steps.

Preparation of the Oxychloride

During the course of preparing large amounts of high-purity zirconium oxide for the analytical laboratory, it became evident that, by modifying the basic method of Herzfield, it was possible to recover at least 90% of the valuable metals (even after losses occasioned by several recrystallization steps). A curdy precipitate forms upon the addition of a saturated aqueous solution of zirconyl chloride to an acetone–hydrochloric acid mixture. Readily filterable, these crystals have been identified by X-ray diffraction to be zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$). To effect further recrystallization, the product can be dissolved readily in half its weight of water, then added to the acetone–hydrochloric acid mixture. The purified crystals form immediately and may be collected on a buchner funnel and washed with acetone. The recrystallization procedure may be repeated until the desired purity is obtained. The final oxychloride is ignited to the oxide by heating to 1000° for one hour. The spectrographic analysis of the zirconium samples produced indicated the presence of 20 p.p.m. each of aluminum, iron, copper, and silicon and less than 0.5 p.p.m. boron. No other elements except hafnium were detected. The average starting material contained the following impurities: 0.3% iron, 0.1% silicon, 100–1000 p.p.m. titanium and aluminum, and less than 100 p.p.m. copper. Comparable samples of high-purity hafnium have been analyzed with similar results. No heat is required in any phase of the process. The solutions are comparatively safe to handle and do not present a filtration or recovery problem.

The effect of the presence of acetone in the system is to decrease the solubility of the oxychloride in hydrochloric acid, thereby increasing the yield. However, enough acid must be added to provide a minimum normality of 4.5 to assure the high recovery.

The normality is based upon the acid entering the system in the acetone–acid mixture and the total volume of water in the zirconyl chloride solution. Figure 1 shows the effect of acidity upon the percentage of metal recovered for two ratios of acetone to zirconyl chloride. A third line is plotted to show the recovery expected without the use of acetone in the addition agent. The data for this curve were taken from the solubility curve of zirconyl chloride as found by Spink and Wilhelm.[5] The graph indicates that a higher percentage recovery of zirconyl chloride results as the ratio of acetone to metal increases. The presence of the acetone in this system greatly increases the filterability of the zirconyl chloride formed.

The optimum proportions for satisfactory recrystallization appear to be 1 ml. of saturated zirconyl chloride solution of 5 ml. of acetone and 1 ml. of concentrated hydrochloric acid. The crystals are collected in a buchner funnel, using a No. 7 Whatman filter paper. The cake is then washed a number of times with acetone and air-dried in the funnel. Using the procedure described above, 200 g. of zirconium tetrachloride, or 276 g. of zirconium oxychloride, was dissolved in water and recrystallized five times, producing 246.5 g. of high-purity material. The stepwise efficiency was 96–99% for an over-all recovery of 89.0%. Additional experimentation performed upon hafnium starting solutions have indicated that the same high purification will result for this metal also.

The equipment employed in analyzing this material was a Baird 3-meter spectrograph. Each sample was burned individually with high-purity graphite electrodes. The ignition area was thoroughly cleaned after each sample was burned. A sample of the product obtained by the sulfuric acid method of Clabaugh and Gilchrist was analyzed along with the oxides formed in this method. Each of the two products was as pure as was obtainable within the limits of detection of the method employed.

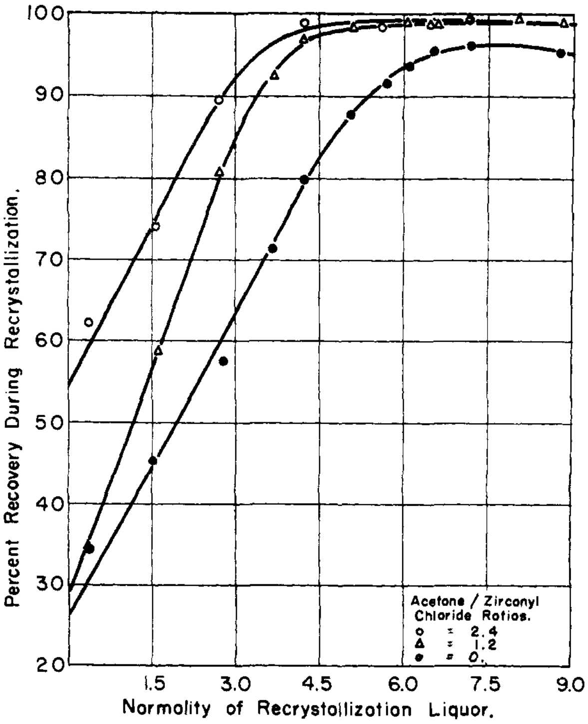

Fig. 1.—Recrystallization yield for the system zirconyl chloride–acetone–HCl.

This simple purification method is believed to be suitable for laboratory preparation of either pure zirconium oxide or hafnium oxide. Metal recoveries of 96 to 99% per crystallization step are obtainable. This system can be employed in making superpure compounds from the oxides. The high metal recovery, as compared to that obtainable by the present methods, increases the possibility of expanding the process to pilot-plant or production-plant size. Recovery of the only expensive chemical, acetone, is feasible. The rapid manipulation of the process steps, the ease of filtration of the crystals, the absence of heating and cooling periods for crystallization, and the relative safety in handling chemicals are some of the many advantages of this system. The purity developed equals or exceeds that detectable by the usual spectrographic methods employed for analyzing zirconium oxides.

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[6] W. S. Clabaugh and R. Gilchrist, THIS JOURNAL, 74, 2104 (1952).

Titration of Polyacrylic Acid with Quaternary Ammonium Bases

BY HARRY P. GREGOR, LIONEL B. LUTTINGER AND ERNST M. LOEBL

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In general, the titration behavior of acids (bases) is expected to be independent of the nature of the base (acid) with which it is titrated; this certainly holds for simple mono- and polybasic acids (bases). However, in the case of highly polyfunctional substances specific effects seem to play a role. Thus Steinhardt[1] and Tanford[2] observed that the titra-

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[1] J. Steinhardt, *Ann. N. Y. Acad. Sci.*, **41**, 287 (1941).

[2] C. Tanford, THIS JOURNAL, **72**, 441 (1950).