

[A CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

## The Nature of the Addition Compounds of Zirconium and Hafnium Tetrachloride with Phosphorus Oxychloride<sup>1</sup>

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Cryoscopic measurements were made in nitrobenzene on the  $(\text{Zr,Hf})\text{Cl}_4 \cdot 2\text{POCl}_3$  and  $(\text{Zr,Hf})\text{:POCl}_3$  addition compounds. The 1:1 compounds are monomers, and the 1:2 compounds dissociate presumably to the 1:1 compound and  $\text{POCl}_3$ . The zirconium compound is slightly more dissociated than the hafnium compound. X-Ray powder patterns show that the symmetries of the addition compounds are lower than those of the metal tetrahalides, and that the structures of the zirconium and hafnium compounds are the same.

In a previous publication<sup>2</sup> syntheses for the compounds  $\text{Zr(Hf)Cl}_4 \cdot \text{POCl}_3$  and  $\text{Zr(Hf)Cl}_4 \cdot 2\text{POCl}_3$  were described. In this work, cryoscopic measurements and X-ray powder patterns were obtained for these compounds.

For the cryoscopic work, nitrobenzene was chosen as the solvent after a few preliminary solubility measurements had been made. At 25°, the  $\text{ZrCl}_4 \cdot 2\text{POCl}_3$  compound, insoluble in carbon tetrachloride and benzene had a solubility of 1.25 *m* in nitrobenzene. It was shown that the 1:2 compound could be recovered unchanged from the nitrobenzene solution, by analyzing the product crystallized at 0° from the supernatant of the saturated solution of  $\text{ZrCl}_4 \cdot 2\text{POCl}_3$ . After the crystals were isolated, washed free of nitrobenzene with benzene, and the latter removed completely in a stream of dry air, the analysis gave a P/Zr ratio of 2.1 and a Cl/Zr ratio of 9.9. For the pure  $\text{ZrCl}_4 \cdot 2\text{POCl}_3$  compound these ratios are 2.00 and 10.0, respectively. In agreement with these data was also the fact that an X-ray diffraction powder pattern of these crystals agreed exactly with other patterns for the 1:2 compound prepared by other means.

The molal freezing point lowering constant ( $K_f$ ) for the nitrobenzene purified here was determined using resublimed naphthalene as the solute. The naphthalene, which is known to be a monomer in this solvent,<sup>3</sup> was studied over the concentration range of 0.2 to 0.04 *m*. From the nine results obtained over this range of concentrations, the best result was determined by calculating the weighted mean assuming that the probable error in the determination of  $\Delta T$  was about  $\pm 0.01$ , and that it would remain constant at all temperatures. This value was 6.79 with a probable error of  $\pm 0.02$ .

Roberts and Bury<sup>3</sup> found  $K_f$  to be 6.89, a value which is in very good agreement with the value calculated using the heat of fusion of nitrobenzene of 22.46 cal./g., as determined by Meyer,<sup>4</sup> and our melting point of 5.785°. The slightly low value obtained here is probably due to something inherent in our method. It would mean that the observed temperature rise was not as rapid as it should

have been. This condition would indicate a time delay between the change in the temperature of the solution, and the corresponding change in the thermometer reading. This may have resulted from inefficient thermal transfer and the slowness of response of the Beckmann thermometer. However, since the experimentally determined values for  $K_f$  were consistent over a fivefold concentration range it was decided that for our purposes the procedure could be used without further refinement.

The results for the 1:1 addition compounds appear in Table I. The zirconium studies were always made first, the hafnium studies in limited number after the procedure had been worked out because of the small supply of hafnium stock available. The mole fraction of the addition compound in the nitrobenzene was calculated as if it were a monomer. Since the ratio  $K_f \text{ detd.}/6.79$ , is one within the limits of random error, it was concluded that both the zirconium and hafnium 1:1 addition compounds behave as undissociated monomers in nitrobenzene over the composition range 0.24–0.04 mol fraction.

TABLE I

ZrCl <sub>4</sub> :POCl <sub>3</sub> , mole fraction	$\Delta T \pm 0.01^\circ$	$K_f$	$K_f/6.79$
0.235	1.580	6.72	0.99 $\pm$ 0.01
.112	0.770	6.88	1.01 $\pm$ .01
.110	.750	6.82	1.00 $\pm$ .01
.110	.760	6.91	1.02 $\pm$ .01
.0944	.615	6.52	0.96 $\pm$ .02
.0913	.630	6.90	1.02 $\pm$ .02
.0674	.460	6.83	1.00 $\pm$ .02
.0614	.410	6.68	0.98 $\pm$ .02
.0605	.400	6.61	0.97 $\pm$ .03
.0577	.380	6.59	0.97 $\pm$ .03
.0459	.295	6.43	0.95 $\pm$ .03
.0452	.290	6.42	0.94 $\pm$ .03
.0392	.260	6.63	0.98 $\pm$ .04
.0377	.230	6.83	1.00 $\pm$ .04
HfCl <sub>4</sub> :POCl <sub>3</sub>			
0.154	1.055	6.85	1.01 $\pm$ 0.01
.0802	0.535	6.67	0.98 $\pm$ .02
.0438	.290	6.62	.97 $\pm$ .03

The  $\text{MCl}_4 \cdot 2\text{POCl}_3$  compounds on the other hand behave as though dissociation was occurring upon dilution. In Table II are given the cryoscopic data for both the zirconium and hafnium compounds in nitrobenzene. Again the concentrations of the compounds were calculated on a monomer basis. The  $K_f$  values increase with increasing dilution which can be best interpreted on the basis of a two par-

(1) Based on a thesis submitted by Layton J. Wittenberg in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and carried out under Task Order 4 of Contract N7onr-28504 between the Office of Naval Research and the University of Wisconsin. Presented at the September, 1954, New York Meeting of the American Chemical Society before the Physical and Inorganic Division.

(2) E. M. Larsen, J. Howatson, A. Gammill and L. J. Wittenberg, *THIS JOURNAL*, **74**, 3489 (1952).

(3) H. M. Roberts and C. R. Bury, *J. Chem. Soc.*, **123**, 2037 (1923).

(4) J. Meyer, *Z. physik. Chem.*, **72**, 245 (1910).

title rather than three particle dissociation. This was determined by calculating equilibrium quotients on the basis of two and three particle dissociation. Whereas the constants obtained for two particle dissociation are reasonably constant, the values obtained for three particle dissociation show a steady decrease. The dissociation can be simply described as

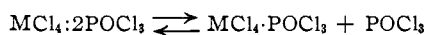


TABLE II

ZrCl <sub>4</sub> : 2POCl <sub>3</sub> , mole fraction	ΔT ± 0.01°	K <sub>f</sub>	Equilibrium quotients	
			Two Particle 10 <sup>3</sup>	Three 10 <sup>5</sup>
0.434	3.225	7.43	4.26	8.27
.235	1.825	7.77	5.72	8.92
.226	1.725	7.63	3.95	5.01
.150	1.205	8.03	6.12	7.75
.118	0.945	8.01	4.60	4.44
.0671	.565	8.42	5.09	3.55
.0458	.400	8.73	5.25	2.85
Av.			5.0 ± 0.5	
HfCl <sub>4</sub> : 2POCl <sub>3</sub>				
0.208	1.595	7.67	4.01	5.04
0.193	1.465	7.59	3.04	3.24
.164	1.245	7.59	2.58	2.34
.110	.865	7.86	3.24	2.56
.0657	.535	8.14	3.25	1.88
.0413	.345	8.35	2.83	1.16
Av.			3.2 ± 0.3	

An average for the two particle dissociation constant with probable error was calculated for both the zirconium and hafnium compounds for the purpose of comparing the extent to which both dissociated. Taking an average is not strictly legitimate since a temperature variation is involved, but since this is only a matter of 2-3 degrees the error due to this factor probably is small compared to the probable error of the experiment as a whole. The equilibrium quotient for the HfCl<sub>4</sub>:2POCl<sub>3</sub> is only about 2/3 the value for the corresponding zirconium compound, which would indicate that the hafnium tetrachloride was a very slightly better Lewis acid than the zirconium tetrachloride.

**X-Ray Data.**<sup>5</sup>—X-Ray powder patterns of the tetrahalides and all of the addition compounds were taken, in an attempt to correlate structural changes taking place upon addition compound formation. The powder diffraction patterns for zirconium tetrachloride had previously been reported by Hansen.<sup>6</sup> Of the thirteen lines reported by Hansen, all but two matched quite closely, and for the zirconium tetrachloride six additional lines were obtained. The assignment of intensities, however, did differ considerably, although as he noted, the relative intensities seemed to be a function of sample preparation. We were able to index all the observed lines on the basis a cubic symmetry. The

(5) The X-ray data referred to in this paper have been deposited as Document number 4636 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 in advance \$1.25 for photoprints or \$1.25 for 35 mm. microfilm payable to: Chief, Photoduplication Service, Library of Congress.

(6) H. Hansen, *Z. physik. Chem.*, **B8**, 19 (1930).

*a* values for zirconium and hafnium tetrachlorides calculated on the basis of the best value for the quantity  $\lambda^2/4a^2$ , and the weighted mean of the Cu-K $\alpha_{1,2}$  radiation, 1.5418 Å., were  $10.43 \pm 0.03$  and  $10.41 \pm 0.06$ , respectively. This is slightly higher than the Hansen value of  $10.36 \pm 0.01$  Å.

For the addition compounds, the powder patterns were different than those of the tetrachlorides. The lines did not fit cubic symmetry, and did not appear to fit either tetragonal or hexagonal symmetry. It was concluded that a single crystal study would have to be made to satisfactorily elucidate the symmetry. There was some similarity in the patterns to the extent that the most intense lines in both patterns had similar *d* values.

### Experimental

**Materials.**—Zirconium and hafnium tetrachloride were prepared by mixing the corresponding dioxides with charcoal and passing chlorine gas over the mixture at 600°. The zirconium dioxide contained only 0.04% hafnium and the hafnium dioxide only 0.75% zirconium. The crude tetrachloride was purified by first subliming in an atmosphere of hydrogen and then resubliming several times *in vacuo*.

The 1 MCl<sub>4</sub>:2POCl<sub>3</sub> compounds were prepared<sup>2</sup> in the cell used in the cryoscopic measurements. When the 1:2 compound was thermally decomposed to the 1:1 compound there was always a small amount of sublimate which collected on the walls of the cooler part of the tube. This necessitated the transfer of the bulb of the 1:1 compound to another cell in order to determine the weight of sample actually in solution. The composition of the samples was checked by gain or loss in weight during the synthesis, with only those samples used which checked within one per cent. of the desired ratio.

Reagent grade naphthalene was resublimed *in vacuo*.

**Dry Nitrobenzene.**—It was necessary to be very careful in the preparation of pure dry nitrobenzene in order to obtain batches which had reproducible melting points. The method finally used was similar to that described by Roberts and Bury.<sup>3</sup> To reagent nitrobenzene was added phosphoric anhydride, this resulted in a mixture which soon turned brown. This mixture was then fractionally distilled, and the middle fraction saved. To this was added more phosphoric anhydride. After 24 hours, if the liquid was only slightly discolored, usually a very light green, it was distilled under vacuum in a dry all glass apparatus. At 10 mm. pressure the boiling point was 65°. The product was stored in a dry box. The freezing point of the product was  $5.785 \pm 0.005^\circ$ .

**Apparatus.**—Since the addition compounds are easily hydrolyzed, it was necessary to use an all glass cell for the freezing point determinations. The cell was essentially a test tube 15 cm. in length and 25 mm. in internal diameter with a 24/40 outside joint at the top, into which was placed a thermometer well with an inner 24/40 joint. The length of the thermometer well was such that it extended well into the solution contained in the cell. Its internal dimensions were such that a Beckmann thermometer fit in it very snugly. The cell was fitted at the joint with a rubber stopper of a size such that the cell could be held inside of an empty 1.5 inch × 8 inch test-tube. The entire assembly was mounted in a rubber stopper which fit the mouth of a one-quart Dewar flask. The apparatus was assembled in this fashion so that the cell and well alone could be easily weighed. Thus samples could be removed or more solvent added, without being concerned about the entrance of moisture or the loss of sample during such manipulations. All such transfers were made in a dry box.

The Beckmann thermometer used was set at 1° against another Beckmann thermometer which had been set at the ice point. This was necessary since the scale on the Beckmann was not long enough to extend from the ice point to the melting point of nitrobenzene, 5.785°. The thermometer was handled in a manner identical with that used in the freezing point determinations. With the aid of a magnifying glass the temperature could be read to  $\pm 0.003^\circ$ .

**Determination of Freezing and Melting Points.**—The cell containing the sample was placed in the Dewar flask which

contained a water-ice mixture. The whole apparatus was shaken in a steady up and down motion, and the temperature was observed to decrease slowly to  $0^{\circ}$ . Neither pure nitrobenzene nor the solutions of the addition compounds froze at this temperature as they had a great tendency to supercool. To induce freezing, the cell was removed from the Dewar, and a piece of Dry Ice was touched to the outside of the cell. Freezing was observed immediately, the cell was returned to the Dewar, shaken well and the temperature was recorded every thirty seconds.

To determine the melting points, the ice-water in the Dewar flask was replaced with water at a temperature of about  $8^{\circ}$ . The cell containing the frozen nitrobenzene or solution was placed in the Dewar and the temperature of the system read every 30 seconds as the solid melted. With pure solvent the temperature remained constant for a long

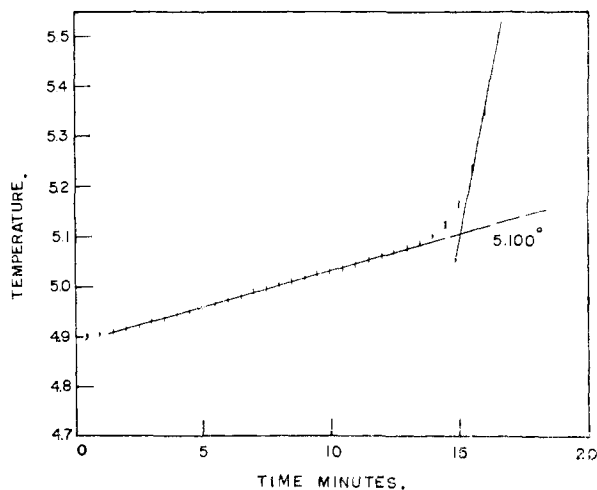


Fig. 1.—Typical melting curve— $\text{HfCl}_4 \cdot 2\text{POCl}_3$  in nitrobenzene.

period of time, and then increased rapidly when the solid had melted. The freezing and melting temperatures for the purified nitrobenzene agreed to within  $0.005^{\circ}$ . Apparently, the method of mixing and the procedure in general were satisfactory.

When a solute was dissolved in the nitrobenzene, both the freezing and the melting curves were determined. In either case however the true freezing point of the solution had to be determined by extrapolation to zero time, the time of initial freezing, in order to correct for the change in freezing point as the concentration of the solution changed with the amount of solvent crystallized out. It was concluded that the true freezing point of the solutions could be best determined from the melting point curves, since the extrapolation was shorter and more precisely made (Fig. 1).

**Procedure of X-Ray Diffraction Samples.**—A Debye-Scherrer type powder camera was used which had a diameter of 114.59 mm. The radiation used was  $\text{Cu K}\alpha_{1,2}$  with a Ni filter. The tube was run at 37 kilovolts and 20 millamp. Exposures of 8–9 hours were required. The lines obtained with these samples were rather broad, and it was difficult to locate the centers to an accuracy of better than 0.1 mm. The maximum error in  $\theta$  would be then  $6'$  of a degree.

The tetrachloride patterns were taken on freshly sublimed samples contained in a Pyrex capillary. The addition compound specimens were prepared in the following manner. In a dry box, an aliquot of a saturated solution of the metal tetrachloride in phosphorus oxychloride was transferred by means of a capillary eye dropper into thin-walled capillary tubes bent in the shape of a U. It was necessary to have the liquid in the tubes unbroken by air bubbles. The filled capillaries were transferred to a container which was then attached to a vacuum manifold. The excess phosphorus oxychloride was removed under 30 mm. pressure of dry air at room temperature to leave a deposit of  $\text{MCl}_4 \cdot 2\text{POCl}_3$ . The  $\text{MCl}_4 \cdot \text{POCl}_3$  specimens were prepared by heating the vessel containing the capillaries *in vacuo* at  $110^{\circ}$  for eight hours. The final trace of solvent was removed by pumping on the system directly. The portion of the capillary tube which contained a heavy solid deposit was cut into one inch lengths and sealed with beeswax.

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## NOTES

### Peroxide Yield in the $\gamma$ -Irradiation of Air-saturated Water<sup>1</sup>

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The formation of peroxide in air-saturated water, irradiated with X- or  $\gamma$ -rays, is one of the oldest and most frequently studied reactions in radiation chemistry. The first detailed study of this reaction was made by Risse<sup>2</sup> in 1929. A careful study was published by Fricke<sup>3</sup> in 1935, and many more studies have appeared.<sup>4</sup> The rate of peroxide formation is found in general to decrease as the peroxide accumulates and eventually to become zero as the

peroxide reaches a steady-state level. Published values of the initial yield range from 1.1 to 2.0. This yield is of interest in connection with studies of the mechanism of water decomposition under irradiation.<sup>5</sup> Discrepancies in the reported initial yields occur in part because of ambiguity in the interpretation of what is meant by initial values. Some of the data, particularly of Hochanadel<sup>4a</sup> and of Hart and co-workers,<sup>4b</sup> appear to indicate a very short initial period of relatively rapid peroxide formation extending up to no more than a very few  $\mu\text{moles}$  per liter of peroxide, followed by a longer period at a nearly constant rate extending up to 30–100  $\mu\text{M}$  with gradually decreasing rate at higher concentrations. Hochanadel and others have regarded the constant rate appearing after the short initial portion as being the correct yield, or have ignored the existence of the very short initial period, but Hart and co-workers have regarded the higher figure of the initial period as the true yield.

Sworski<sup>4c</sup> recently has shown that the peroxide yield decreases on the addition of bromide ion at  $p\text{H}$

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) O. Risse, *Z. physik. Chem.*, **A140**, 133 (1929).

(3) H. Fricke, *J. Chem. Phys.*, **3**, 556 (1935).

(4) (a) C. J. Hochanadel, *J. Phys. Chem.*, **66**, 587 (1952); (b) E. J. Hart, S. Gordon and D. A. Hutchison, Abstracts, American Chemical Society Meeting, Los Angeles, March, 1953; (c) T. J. Sworski, *This Journal*, **76**, 4687 (1954); (d) T. Alper, M. Ebert, L. H. Gray, M. Lefort, H. C. Sutton and F. S. Dainton, *Discs. Faraday Soc.*, **12**, 296 (1952).

(5) A. O. Allen, *Radiation Research*, **1**, 85 (1954).