electronegativity grounds assuming that the moment of a second quantum level sp^3 lone-pair orbital on oxygen is smaller than that of a similar but third quantum level orbital on sulfur. It would appear that appreciable sp^2 character resides in the oxygen with concomitant back-donation of oxygen electron density into the available phosphorus d orbitals and a consequent raising of the P–O moment in the direction of phosphorus. The lone-pair moment contribution of an sp^2 oxygen can be shown from simple geometrical considerations in these molecules to be 25% less than that of two sp^3 oxygens assuming similar density distributions. Thus the P–O moment in the direction of oxygen should be increased somewhat instead of decreased by such a change in hybridization. We conclude, therefore, that the abnormal P–O moment is due to an overriding electron drift from the p_z orbital on each largely sp^2 oxygen back to the bridgehead phosphorus in a π bond. These arguments are made plausible by the observation of appreciable bond shortening in the P–O links and of an average POC bond angle of 115° in $OP(OCH_2)_3CCH_3$.[15] From the evidence now available, substantially less if any π bonding apparently occurs in the P–S links of I.

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Time and Temperature Variations in the Hydrolytic Behavior of Hafnium(IV) in Aqueous Chloride Media

BY D. B. COPLEY AND S. Y. TYREE, JR.[1]

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Among the many studies of aqueous metal ion and metalate ion hydrolytic phenomena which have been reported in the scientific literature during the past 15 years, a number of comments have appeared which lead to the hypothesis that many of the solutions studied were not at equilibrium, but rather approaching equilibrium with some very long half-time. Examples of such reports are to be found for the solution chemistry of gallium(III),[2] tungsten(VI),[3] antimony(V),[4] aluminum(III),[5] and molybdenum(VI),[6] among others. Several years ago, in this laboratory, it was found that the turbidities of aqueous solutions of $ZrOCl_2 \cdot 8H_2O$ at 25° increase by as much as 25% in 1 year. Thus it was decided to study in some detail the effects of time and temperature on hydrolysis in a selected case. Hafnium was selected because (a) its chemistry is similar to that of zirconium in which the preliminary observations were made and (b) it is a heavy element and its solute ion turbidities are larger relative to the background turbidities of the solvent and supporting electrolyte.

Neither the precision of light-scattering data nor the present means of interpreting the data[7] permits the calculation of hydrolytic equilibrium constants. However, in combination with pH titration data, it has proved very useful in determining degrees of aggregation of solute ion hydrolysis products. It is an excellent technique also for following slow-time effects which result in changes in the degree of aggregation among solute ion hydrolysis products.

Previous work on hafnium(IV) solutions in the macroscopic concentration region is sparse but in general agreement. Johnson and Kraus[8] found a degree of aggregation of 3–4 in 0.50–2.00 *M* HCl by the ultracentrifugation technique. The X-ray diffraction data of Muha and Vaughn[9] on 2 *M* solutions of $HfOCl_2$ were interpreted in terms of a tetrameric solute cation.

Experimental Section

Preparation of Solutions.—Hafnium oxide dichloride octahydrate was prepared by dissolving 25–30 g of hafnium tetrachloride, prepared by the method of Hummers, *et al.*,[10] in 75–100 ml of demineralized water, and by diluting the solution with an equal volume of 12 *M* HCl. The crystals separated upon cooling. They were recrystallized from similar solutions of hydrochloric acid several times, until they gave solutions which exhibited no test for iron(III) with thiocyanate. In the course of the experiment, four batches of hafnium oxide dichloride octahydrate were prepared. Stock solutions were prepared by dissolving the crystals in demineralized water such that the Hf molarity was *ca.* 0.30. Each stock solution was analyzed for both chlorine and hafnium.

Stock sodium chloride solution was prepared by dissolving J. T. Baker sodium chloride in demineralized water.

Stock hydrochloric acid solutions were prepared from J. T. Baker reagent grade acid.

Experimental solutions were prepared from the stock solutions within 3 days after the stock solution had been prepared. Four series of solutions were prepared—series a–d; in each series the Hf(IV) concentration was varied over the range of *ca.* 0.01–0.10 *M*, in six steps. Each solution was made up in a 100-ml volumetric flask by adding from calibrated volumetric burets calculated volumes of (1) stock hafnium solution, (2) stock NaCl solution, and (3) stock HCl solutions and then diluting to the mark with water. The flask was shaken and allowed to stand several days at 25° before the first measurement was taken. In series a 280 mmol of hydrochloric acid was added and the NaCl concentration was varied such that total $[Cl^-]$ (from $HfOCl_2$, HCl, and NaCl) = 3.00 *M*. In series b and c, the HCl concentration was kept at 0.75 and 0.14 *M*, respectively, while the total chloride concentration was maintained at 1.00 *M* by the additions of calculated volumes of stock NaCl. In series d no

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acid was added and the total chloride was kept at 1.00 *M* by appropriate addition of stock NaCl.

For each series turbidities, refractive index gradients, densities, and pH values were measured at room temperature over time intervals up to several hundred hours. In series a and b the pH readings were meaningless, as was expected. Aliquots of each solution in series a and b were held at 75° for many hours, cooled to room temperature, and remeasured. In series c and d, after learning that more rapid changes were taking place, the solutions were actually thermostated in the photometric and refractometric cells while measuring the values as a function of time.

Analyses.—Stock HCl solutions were standardized against a standard NaOH solution, which, in turn, had been standardized against General Chemical Co. potassium hydrogen phthalate as a gravimetric standard. Stock solutions of Hf(IV) were analyzed for hafnium by precipitating hydrous hafnium oxide with dilute ammonia, filtering, washing, igniting, and weighing as HfO_2. Original samples of HfO_2 used in this work contained 2.2% Zr. Thus an atomic weight of 175.0 was used for Hf in all stoichiometric calculations. Chloride was determined in the Hf(IV) solutions gravimetrically as AgCl.

Densities and pH Measurements.—Densities were determined pycnometrically at 25° only. The pH of each solution in series c and d was measured several times at 25° using a Leeds and Northrup pH meter. Since the values are all in the very low pH range, the meter was standardized frequently with known solutions of HCl made with NaCl to total $[Cl^-] = 1.00$ *M*.

Turbidity and Refractive Index Measurements.—Turbidity measurements were made as previously described[11] at 25°, using dry, thiophene-free benzene as the secondary standard. The value of 7.71×10^{-4} cm^{-1} was used as the value for the absolute turbidity of benzene.[12] All measurements were made at 4358 Å. Each solution was clarified by filtration through ultrafine-fritted glass filters at a nitrogen pressure of 10 lb. For measurements at temperatures above 25°, the Brice-Phoenix Model 1974 photometer was modified by replacing the standard cell holder with the hollow cell holder furnished by the Phoenix Precision Instrument Co. Carbowax-water solutions were circulated from a temperature-controlled bath through the cell holder. Since contact is made between the cell holder and the cell only on the bottom surface of the cell, a considerable temperature difference was observed between the thermostating fluid and the experimental solution. However, no temperature gradient could be detected between the top and bottom of the experimental solution. Evaporation losses were minimized by placing a well-fitting glass cover over the top of the scattering cell.

Refractive index increments were determined at 4358 Å using a Brice-Phoenix differential refractometer calibrated with sucrose solutions. For the measurements at higher temperatures, a carbowax–water bath was substituted for the usual water circulation system of maintaining the cell at constant temperature. It was assumed that the cell physical constants determined at 25° are applicable in the range 25–75°.

Results and Discussion

The data have been treated in every way as was done in the earlier zirconium work,[13] assuming a four-component system. The background turbidity due to water, acid, and salt in a series was obtained by plotting the gross turbidities in each series *vs.* hafnium concentration and reading the intercept at zero concentration. The excess turbidities, τ^*, due to the hafnium-containing solute species, were obtained by subtracting the background turbidity from each gross value. The pH data on series c and d indicated degrees of hydrolysis of *ca.* 25 and 100%, respectively: $Hf(OH)_2^{2+} + HOH \rightarrow Hf(OH)_3^+ + H^+$. Accordingly, the gross refractive index increments measured on these two latter series were corrected for the Δn due to the HCl present from "hydrolysis."

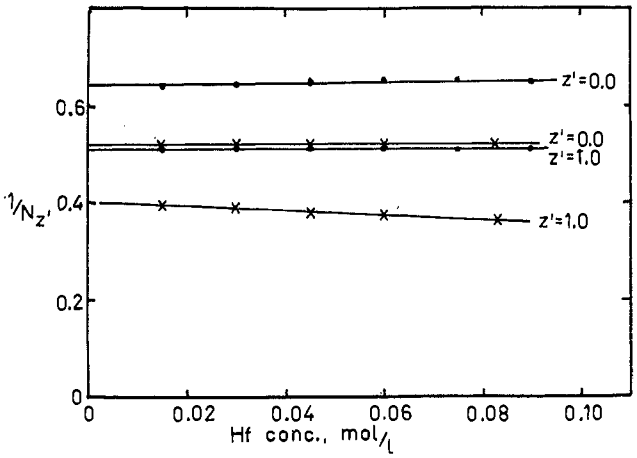

Figure 1.—Reciprocal of degree of aggregation *vs.* concentration of hafnium: series a, —●—●—; series b, —×—×—.

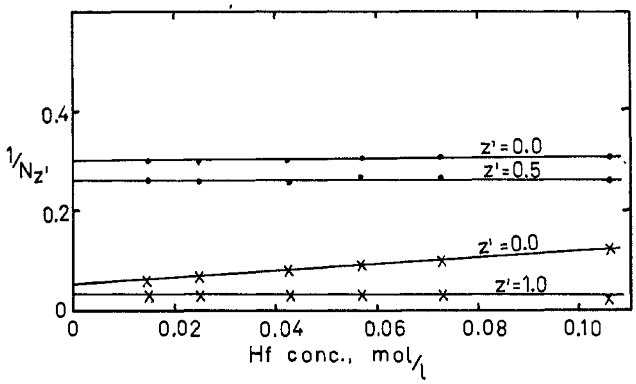

Figure 2.—Reciprocal of degree of aggregation *vs.* concentration of hafnium: series c, —●—●—; series d, —×—×—.

The results of the room-temperature experiments are shown in Figures 1 and 2. Only two values of *z'*, the parameter, are plotted and the datum itself is not given, because the main purpose of this paper is to show we do not believe these solutions are at equilibrium nor, indeed, even at a readily reproduced distance from equilibrium. For the case of series a both $\partial n/\partial M'$ and τ^* change slightly on heating at 75° for 100 hr but the $^1/N_{z'}$ plot remains unchanged. However it must be understood that it is just series a for which the average degree of hydroxylation is most uncertain. Thus *z'* is most uncertain and has also the largest possible variation, from 4 + to 0. Since the degree of aggregation in this series is a very strong function of *z'*, we do not feel justified in drawing more than two conclusions: (1) the degree of aggregation is no more than 4, probably less, in agreement with earlier findings[8]; (2) at least a steady state, if not actual thermodynamic equilibrium, was reached in series a at 75°. For the same time–temperature treatment, series b exhibited small changes in

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both $\partial n/\partial M'$ and τ^*, and the calculated $N_{z'}$ increased from *ca.* 2.0 to *ca.* 2.7.

The room-temperature data confirm the hypothesis[13] that hafnium (or zirconium) is more extensively aggregated as hydrolysis progresses, such that the possibility of monomers exists only at very high acidity.

The changes in series c and d upon heating were much larger and are best seen in Figures 3 and 4 where $1/N_{z'}$ values are plotted for solutions 0.05 M in total hafnium *vs.* time for each of four temperatures. For the plots shown z' was arbitrarily taken to be 0.50. The solutions of series c and d were returned to room temperature in order to see if they would exhibit any slight tendency to return to the room-temperature values of turbidity. No such tendency was observed. Perhaps a better test would have been to take the 75° solutions back to 60° and look for a reduction in turbidity. Such an experiment was not performed.

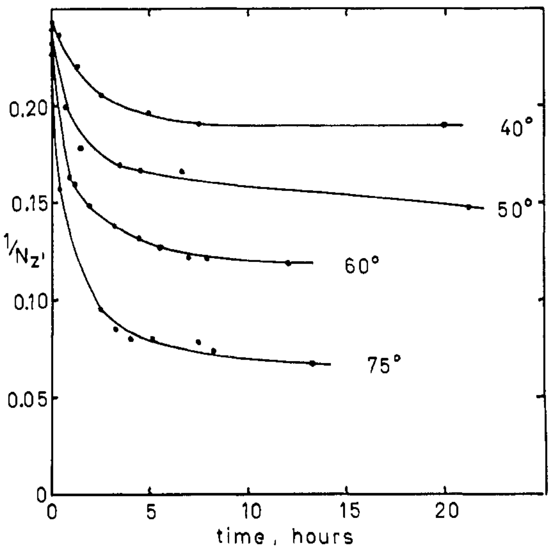

Figure 3.—Reciprocal of degree of aggregation *vs.* time for series c; [Hf] = 0.05 M.

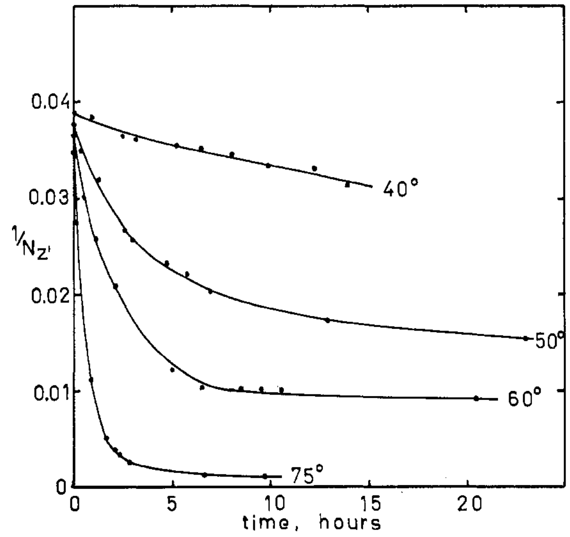

Figure 4.—Reciprocal of degree of aggregation *vs.* time for series d; [Hf] = 0.05 M.

It would be tempting to state unequivocally that solutions of $HfOCl_2$ in NaCl-supporting electrolyte exhibit an average degree of aggregation of 20; see Figure 2. However it is clear from Figures 3 and 4 that the degrees of aggregation of such solutions are strong functions of both time and temperature of storage, even though it is not possible to say whether or not the equilibrium itself is a function of temperature. As a tentative hypothesis we propose that such solutions are tending toward a single equilibrium which consists of hafnium oxide as a heterogeneous phase and a small residual concentration of monomeric hafnium solute cation in very strong acid, which acid is built up as the oxide precipitates: $Hf(OH)_2^{2+} + 2H_2O \rightleftarrows Hf(OH)_4 + 2H^+$.

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A Magnetic Study of a Chlorapatite of Manganese, $Ba_5(MnO_4)_3Cl$

By L. H. Brixner and J. F. Weiher

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Despite the fact that there is evidence of the existence of manganates(V) in the literature as early as 1864 by Rosenstiehl[1] and later by Auger[2] and Sackur,[3] it was not until 1946 when Lux[4] recognized the presence of manganese in its pentavalent state and correctly formulated the first pure manganate(V) as $Na_3MnO_4 \cdot 10H_2O$. Although many other manganates(V) have since been prepared by Scholder[5] and Klemm,[6] the pentavalent state of Mn is still considered an "unusual" valence state which should be well supported by experimental evidence. An analytical determination of the oxidation state of manganese would be arbitrary since an equimolar mixture of Mn^{4+} and Mn^{6+} would indicate the same results as Mn^{5+}. In the present note, we wish to give magnetic measurements as evidence for the existence of Mn^{5+} in the new compound $Ba_5(MnO_4)_3Cl$.

Experimental Section

$Ba_5(MnO_4)_3Cl$ was prepared by the "flux-reaction technique" (where the flux serves both as such and as the constituent com-

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