indicated by the stoichiometric data, it appears that the electron which enters the chloroerythro ion in the redox step never reaches the pentaammine chromium, although the pentaammine chromium(III) must be connected by means of a hydroxo bridge to a chromium(II), *i.e.*, to the reduced tetraammine fragment, for *ca.* 10^{-9} sec, the lifetime of a ligand in the first coordination sphere of chromium(II).[7] A possible interpretation of these results is that the existence of a bridged complex is not sufficient to ensure electron transfer between the two metal ions involved.[8] It is also possible, however, that the reduction of the pentaammine fragment is thermodynamically less favorable than reduction of the tetraammine fragment.

It is interesting to compare the reaction of the chloroerythro ion with chromium(II) to reactions of some similar chromium(III) complexes with Cr(II) also. There is very good evidence[9] that the chloroerythro ion has the *trans* configuration, *i.e.*, that the chloride ligand is located *trans* to the bridging oxygen atom. The chloroerythro ion is then formally a derivative of the *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion, derived by the replacement of an H atom on the water molecule of the chloroaquo complex by the $Cr(NH_3)_5$ fragment. At 25° and in 1 M $HClO_4$, the second-order rate constant for the reaction of the chloroerythro ion with Cr^{2+} is 3.0 M^{-1} sec^{-1}, whereas k for the reaction of the *trans*-chloroaquo complex with Cr^{2+} is only 1.1 M^{-1} sec^{-1} under the same conditions.[10] Thus the binuclear complex reacts more rapidly with Cr^{2+} than does the mononuclear complex, although the activated complex bears a charge of +6 in the case of the binuclear complex and only +4 for the mononuclear ion. It has been shown recently[10] that the Cr–O bond of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ must be stretched substantially in forming the activated complex for reaction with Cr^{2+}. It may be that the character of the Cr–O bond is changed sufficiently by the substitution of the $Cr(NH_3)_5$ fragment for an H atom to account for the increased rate of reaction.

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[7] C. W. Meredith, Thesis; Lawrence Radiation Laboratory Report UCRL-11704, University of California, Berkeley, Calif., 1965.

[8] A considerable energy mismatch between the pentaammine and tetraammine fragment probably is produced during the formation of the activated complex for the transfer of the electron to the tetraammine fragment. However, this mismatch is probably not as great as that between ground-state chromium(II) and chromium(III) ions. In attemping to answer why the electron does not reach the pentaammine fragment, it should be noted that analogous binuclear chromium(III) complexes have magnetic moments only slightly lower than predicted by the spin-only formula (A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961)), indicating little electronic interaction between the metal ions. However, the electrons responsible for the paramagnetism are located primarily in T_{2g} orbitals, whereas the electron transfer is presumably between E_g orbitals.

[9] For example, acid cleavage of the chloroerythro ion yields *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ as the almost exclusive tetraammine product.

[10] Sr. M. J. DeChant and J. B. Hunt, *J. Am. Chem. Soc.*, **89**, 5988 (1967).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Polycyclic Group V Ligands. IV. 2,6,7-Trithia-4-methyl-1-phosphabicyclo[2.2.2]octane and Derivatives

BY A. C. VANDENBROUCKE, JR., E. J. BOROS,
AND J. G. VERKADE[1]

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Bicyclic phosphorus compounds of the type $P(YZ)_3CCH_3$, where YZ = OCH_2,[2] CH_2O,[3] and $N(CH_3)CH_2$,[4] and some of their ligand properties have been reported in previous communications from our laboratories. In order to facilitate our study of phosphorus ligands having approximately constant steric requirements while varying the electronegativity of the YZ group, the compound $P(SCH_2)_3CCH_3$ (I) and its 1-sulfo (II) and 1-oxo (III) derivatives, as well as the arsenic analog of I (IV), are described. The measurement of the dipole moments of I, of IV, and of the oxa analogs $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$ allow for the first time a calculation of an approximate value for the P–S, P–O, As–S, and As–O bond moments from structural considerations. The infrared and H^1 nmr spectral properties of I–IV are contrasted with those of their trioxa analogs.

Experimental Section

A Varian A-60 spectrometer was used to obtain the H^1 nmr spectra. Molecular weights were determined by observing the position of the ion of highest mass on an Atlas CH4 single-focusing mass spectrometer at 70 eV. Infrared spectra were measured in KBr pellets on a Perkin-Elmer Model 21 spectrophotometer. Analyses were carried out by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Dipole moments were measured with a heterodyne-beat apparatus described elsewhere.[5] Melting points are uncorrected.

Starting Materials.—The trimercaptan $(HSCH_2)_3CCH_3$ was prepared as described elsewhere[6] with the modification that, at the end of the distillation of the benzene–water azeotrope, enough dry tetrahydrofuran was added to make a slush of the product after the benzene was completely removed. The sodium–liquid ammonia reduction was then carried out on this slush which permitted good mixing rather than on the hard mass that resulted otherwise. Tris(dimethylamino)phosphine was prepared as previously described[7] and the arsenic analog was synthesized in 45% yield in a similar manner.

$P(SCH_2)_3CCH_3$ (I).—To 3.00 g (17.9 mmol) of the trimercaptan stirred at 70° under nitrogen was added dropwise over a period of 15 min 3.00 g (18.4 mmol) of $P(N(CH_3)_2)_3$. After the evolution of dimethylamine subsided, the temperature was raised to 160° and held there for 30 min. The solid which formed on cooling was treated with 5 ml of benzene and filtered. The white solid

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[1] Alfred P. Sloan Fellow.

[2] K. J. Coskran, T. J. Huttemann, and J. G. Verkade in Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966, p 590.

[3] E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968).

[4] Part III: B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *ibid.*, **6**, 173 (1967).

[5] A. C. Vandenbroucke, R. W. King, and J. G. Verkade, *Rev. Sci. Instr.*, **39**, 558 (1968).

[6] W. von E. Doering and L. K. Levy, *J. Am. Chem. Soc.*, **77**, 509 (1955).

[7] A. Burg and P. J. Slota, *ibid.*, **80**, 1107 (1958).

was sublimed at 110° under vacuum to give white needles in 60% yield, mp 187–189°.

Anal. Calcd for $C_5H_9S_3P$: C, 30.60; H, 4.62; P, 15.78; S, 49.00; mol wt, 196. Found: C, 30.58; H, 4.62; P, 15.78; S, 49.06; mol wt, 196.

Attempts to synthesize I by routes analogous to those used earlier to synthesize $P(OCH_2)_3CCH_3$[8,9] were only partially successful. Thus addition of PCl_3 to a 3:1 mole ratio of pyridine to trimercaptan afforded only a very small amount of product. Transesterification of $P(OCH_3)_3$ with the trimercaptan afforded no detectable product with the properties of I.

$SP(SCH_2)_3CCH_3$ (II).—A mixture of 2.00 g (1.02 mmol) of I and 0.0333 g (1.02 g-atom) of sulfur was placed in a sealed tube. After heating the tube at 120° for 2 hr and cooling, the pale yellow solid was removed, ground to a fine powder, and shaken with 20 ml of CS_2 for 2 hr to remove any unreacted sulfur. After filtering and washing with *n*-pentane, the white solid was sublimed at 180° under vacuum to give the product in 90% yield, mp 286–290°.

Anal. Calcd for $C_5H_9S_4P$: C, 26.30; H, 3.97; P, 13.55; S, 56.20; mol wt, 228. Found: C, 26.33; H, 4.05; P, 13.52; S, 56.47; mol wt, 228.

$OP(SCH_2)_3CCH_3$ (III).—Following the method of Poshkus, *et al.*,[10] 7.2 g (5.3 mmol) of SO_2Cl_2 was added to 0.5 g (2.6 mmol) of I in 25 ml of stirred benzene (previously dried over sodium) under nitrogen. A precipitate formed immediately, and after stirring for 5 min the reaction mixture was filtered and washed with pentane. The solid which fumed in moist air was treated with 8 ml of water and filtered. The resulting yellow solid after drying under vacuum was shaken with 5 ml of CS_2 for 5 min. After filtering the mixture, the white solid was washed with *n*-pentane and sublimed under vacuum at 130° to give a 20% yield of III, mp 236–239°.

Anal. Calcd for $C_5H_9S_3OP$: C, 28.29; H, 4.27; P, 14.59; S, 45.31; mol wt, 212. Found: C, 28.41; H, 4.34; P, 14.46; S, 45.15; mol wt, 212.

Several attempts at oxidizing I to III proved unsuccessful before the SO_2Cl_2 method was tried. The procedure given by Lippert and Reid[11] for the oxidation of $P(SCH_3)_3$ using 3% H_2O_2 in glacial acetic acid yielded only a small amount of starting material. Similar results were obtained using 30% H_2O_2 in glacial acetic acid which was used to oxidize $HC(SCH_2)_3CCH_3$ to $HC(S(O)_2CH_2)_3CCH_3$.[6] Bubbling N_2O_4, O_2, and O_3 through a solution of I in $CHCl_3$, C_2H_5OH, and CH_2Cl_2, respectively, produced no characterizable solid.

$As(SCH_2)_3CCH_3$ (IV).—The reaction of 5.0 g (29 mmol) of the trimercaptan with 6.0 g (29 mmol) of $As(N(CH_3)_2)_3$ was carried out in a manner similar to that described for I. After the evolution of dimethylamine subsided, the temperature was raised to 100° for 30 min. A white solid formed on cooling which sublimed at 110° under vacuum from a yellow oil. Two additional sublimations were necessary to remove all traces of the yellow oil which tended to accompany the sublimate. A yield of 66% of IV was realized, mp 118–120°.

Anal. Calcd for $C_5H_9S_3As$: C, 25.00; H, 3.78; As, 31.19; S, 40.04; mol wt, 240. Found: C, 24.86; H, 3.73; As, 31.36; S, 39.79; mol wt, 240.

Discussion

The trimercaptan does not undergo transesterification with $P(OCH_3)_3$ nor metathesis with PCl_3 in the presence of pyridine to form I although the analogous triol reacts easily to produce $P(OCH_2)_3CCH_3$.[8,9] The reaction involving $P(N(CH_3)_2)_3$ is quite suitable, however, for synthesizing I as well as $P(OCH_2)_3CCH_3$[12] and $P(N(CH_3)CH_2)_3CCH_3$.[4] The P–S bond energies in I are undoubtedly smaller than P–O and P–Cl energies by about 40 and 20 kcal/mol, respectively[13] although P–N bonds are about 10 kcal/mole stronger than P–S links.[13] The formation of volatile $NH(CH_3)_2$ in the formation of I facilitates the reaction. It is also peculiar that I did not form the 1-oxo derivative II upon reaction with 3% H_2O_2 in glacial acetic acid since $P(SCH_3)_3$ oxidizes readily to $OP(SCH_3)_3$[11] with this reagent. Furthermore $P(OCH_2)_3CCH_3$[8] and $P(N(CH_3)CH_2)_3CCH_3$[4] also oxidize quite readily with H_2O_2.

The infrared spectra of these compounds are consistent with the assigned structures. The P=O stretching region in III consists of a very strong band at 1202 cm^{-1} with a shoulder at 1214 cm^{-1} which is in good agreement with the assignment of this mode at 1200 cm^{-1} in $OP(SC_2H_5)_3$.[14] In contrast, the appearance of this band in $OP(OCH_2)_3CCH_3$ is some 45 cm^{-1} higher than in $OP(OC_2H_5)_3$.[15] The P=S stretching frequency of II is assigned to an intense band at 672 cm^{-1} which compares favorably with 685 cm^{-1} reported for $SP(SCH_3)_3$.[16]

The H^1 nmr spectral data for the new compounds are collected in Table I along with those of the oxa analogs for comparison. The proton chemical shifts of I–III in pyridine progress toward lower applied fields reflecting the increase in electronegativity of the terminal chalcogens bonded to phosphorus. The same trend although not as pronounced holds for the oxa analogs. The rise in PSCH coupling in I (2.1 Hz) upon oxidation to II (10.0 Hz) and III (11.6 Hz) is significantly larger than in the oxa analogs and may be indicative of a larger increase in s character of the P–S bonds upon oxidation of I. Examination of the structures of the polycyclic phosphorus sulfides[17] shows that in general the PSP bond angles in $P(SP-)_3$ groups widen from 100–103 to 108–109° upon oxidation to $SP(SP-)_3$ groups whereas the bridgehead SPS angles and P–S bond lengths within the cage are relatively constant (102–103° and 2.08–2.09 Å, respectively). This would indicate that the primary change in the cage structure of I upon oxidation to II or III is a widening of the PSC bond angles to include more s character in the P–S and S–C bonds. Moreover the structural observations in the phosphorus sulfides imply that π bonding in the internal P–S links in II and III is expected to be smaller than in the internal P–O bonds in $OP(OCH_2)_3CCH_3$, for instance, since the per cent shortening over the sum of the single-bond covalent radii in a P–S bond would be only 3% whereas that of the P–O bond in $OP(OCH_2)_3CCH_3$ was recently found to be 11%.[15] Although the increase in J_{PSCH} from II to III is in accord with electronegativity considerations, the magnitudes of the J_{POCH}

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TABLE I

PROTON NMR CHEMICAL SHIFTS (PPM)[a] AND COUPLING CONSTANTS (Hz)

Compound	δ_{CH_2}	J_{PYCH} (Y = O or S)	δ_{CH_3}	Solvent
$P(SCH_2)_3CCH_3$ (I)	2.87	2.1	1.11	CH_2Cl_2
	2.82	2.1	0.88	C_5H_5N
$SP(SCH_2)_3CCH_3$ (II)	3.32	10.0	1.04	C_5H_5N[d]
$OP(SCH_2)_3CCH_3$ (III)	3.38	11.6	1.05	C_5H_5N[d]
$As(SCH_2)_3CCH_3$ (IV)	2.94	...	1.09	CH_2Cl_2
$P(OCH_2)_3CCH_3$[b]	3.93	1.8	0.72	$CDCl_3$
$SP(OCH_2)_3CCH_3$[b]	4.48	7	0.87	$CDCl_3$
$OP(OCH_2)_3CCH_3$[b]	4.48	6	0.90	$CDCl_3$
$As(OCH_2)_3CCH_3$[c]	4.04	...	0.65	$CDCl_3$

[a] Tetramethylsilane was used as an internal standard. [b] See ref 3. [c] J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964). [d] Insufficiently soluble for a good spectrum to be obtained in less polar solvents.

values are reversed in the analogous oxa compounds as well as in several open-chain systems in spite of the assignment of both these couplings as positive in sign.[3]

TABLE II

DIPOLE MOMENT DATA[a]

Compound	Dielectric constant	Mole fraction, $X \times 10^3$	$\delta\epsilon/\delta X$[c]	$\delta n_D/\delta X$	P_0
$P(SCH_2)_3CCH_3$[b]	2.611	15.67	21.30	0.178	310.7
	2.446	7.884			
	2.364	3.493			
	2.326	2.202			
	2.276	0.0			
$P(SCH_3)_3$	2.429	47.66	3.181	0.204	37.70
	2.358	25.07			
	2.321	13.22			
	2.302	7.375			
	2.276	0.0			
$As(SCH_2)_3CCH_3$	2.381	7.510	13.96	0.106	200.0
	2.364	6.356			
	2.340	4.624			
	2.315	2.820			
	2.277	0.0			

[a] Measured in benzene solution at 25.00 ± 0.05°. [b] Insolubility of the 1-oxo and 1-sulfo derivatives prevented obtaining data on these compounds. [c] A least-squares plot of ϵ *vs.* X for $P(SCH_2)_3CCH_3$ follows the equation $\epsilon = 21.30X + 2.280$; for $P(SCH_3)_3$, $\epsilon = 3.181X + 2.277$; and for $As(SCH_2)_3CCH_3$, $\epsilon = 13.96X + 2.276$.

TABLE III

DIPOLE MOMENTS, MY_3 GROUP MOMENTS, AND MY BOND MOMENTS

Compound	μ,[a] D	MY_3 group moment, D[c,d]	MY bond moment, D[d]	MY electronegativity differences Mulliken	MY electronegativity differences Pauling
$As(OCH_2)_3CCH_3$	2.68	$\overset{\rightarrow}{0.65}$	$\overset{\rightarrow}{0.5}$	1.42	1.26
$P(OCH_2)_3CCH_3$	4.13	$\overset{\leftarrow}{0.8}$	$\overset{\leftarrow}{0.6}$	1.36	1.25
$As(SCH_2)_3CCH_3$ (IV)	3.13	$\overset{\rightarrow}{0.2}$	$\overset{\rightarrow}{0.15}$	0.66	0.40
$P(SCH_2)_3CCH_3$ (I)	3.86[b]	$\overset{\leftarrow}{0.5}$	$\overset{\leftarrow}{0.4}$	0.60	0.39

[a] All moments were measured at 25.0° in benzene and are precise to 0.02 D (see ref 5). [b] The dipole moment of $P(SCH_3)_3$ in benzene by comparison is 1.36 D. [c] See ref 19. [d] Arrows indicate the direction of + to − charge separation in the MY_3 and MY moieties.

Dipole moment data for I, IV, and $P(SCH_3)_3$ are summarized in Table II. The dipole moments for the compounds, their oxa analogs, and some open-chain derivatives are given in Table III. As was noted previously,[18] orientation of the chalcogen lone-pair electrons in the bicyclic structures substantially enhances the over-all moment. The moment of the PS_3, AsS_3, PO_3, and AsO_3 moieties in the bicyclics can be evaluated from simple geometrical considerations[19] since rotations of the $(-CH_2)_3CCH_3$ moiety and chalcogen lone pairs are eliminated. Since the C–O and C–S bond moments calculated from the known dipole moments and geometries of $(CH_3)_2O$ and $(CH_3)_2S$ include half the density of the chalcogen lone-pair electrons, vectorial subtraction of these contributions in the caged molecules along with the C–H moments from the total moment leaves the moment of the MY_3 portion (M = P or As and Y = O or S). This group moment includes the lone-pair electrons on M and half the lone-pair density on each Y atom. The rather large apparent moment of the PO_3 group in the opposite direction expected on electronegativity grounds can then in part be ascribed to the considerable contribution of lone-pair components toward the phosphorus which in the case of the PS_3 group does not seem as pronounced. Assuming that the H–C, C–O, C–S, and C–C bond moments used in the calculations are valid in these bicyclics, the approximate but useful values for the P–S, P–O, As–S, and As–O links (Table III) can be obtained for the first time from the relationship $(^1/_3)\cdot(MY_3 \text{ group moment})/\cos\theta$ where θ is the angle between the C_3 axis in the molecule and the MY bond. These values clearly show that neither the Pauling nor the Mulliken electronegativity differences in the bonded atoms are dominant in determining the trends of the moments. In both scales the P–O and P–S bonds are abnormally high in the "wrong" direction.

If the anomalous P–O and P–S moments were due primarily to the directionality of the chalcogen lone pairs, their magnitudes would be expected to be reversed on

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(18) T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

(19) The H–C moment was assumed to be 0.4 D in the direction of carbon and the C–C bond moments were taken to be zero. (See C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, for further discussion of these assumptions.) The C–O and C–S moments of 0.71 and 0.72 D, respectively, were then calculated from the known bond angles in $(CH_3)_2O$ (L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 2684 (1935)) and $(CH_3)_2S$ (L. Pierce and M. Hayasaki, *J. Chem. Phys.*, **35**, 479 (1961)) and the dipole moments in benzene of $(CH_3)_2O$ (1.25 D, A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963) and $(CH_3)_2S$ (1.45 D, C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J. Chem. Soc.*, 5323 (1965)). In the case of I, a typical value of 103° for the SPS bond angle was used and the PSC bond angle was assumed to be near 103° as are typical PSP angles.[17] Even if the PSC angle were tetrahedral, the results are not significantly affected since they are only approximate estimates. The same structure was assumed for IV. Bond lengths used were sums of the appropriate covalent radii. For $P(OCH_2)_3CCH_3$ and $As(OCH_2)_3CCH_3$, the appropriate bond angles from the structure[15] of $OP(OCH_2)_3CCH_3$ were used: OPO angle = 104° and POC angle = 115°. Again the assumption of tetrahedral POC angles does not change the results significantly. The slight deviation of the O–C bonds from colinearity with the three-fold axis in the structure of $OP(OCH_2)_3CCH_3$ does not significantly influence the moments. Substitution of arsenic at the bridgehead was assumed not to alter the structure enough to affect the bond moments. In all cases the angle θ (that is the angle between the MY bond and the C_3 axis of the molecules) was near 65°. If the YMY bond angles were tetrahedral, the moment of the MY bonds by symmetry would be those of the MY_3 group (see Table III).

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$_2$)$_3$CCH$_3$.[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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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA

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$_2$·8H$_2$O 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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(1) College of William and Mary, Williamsburg, Va.

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