Resolution Studies.—Both fractional crystallization and fractional precipitation techniques were employed. No resolution was noted under any circumstance with the strychnine compound. With the quinine derivative, however, slow cooling of a solution of the quinine salt with periodic removal of the crystallized product, dissolution of the latter, and examination with the polarimeter gave the data listed under series 1 in Table I. Correspondingly, addition of fractional equivalents of quinine oxalate solution to a solution of the oxalato acid, removal of the precipitates, and treatment of the latter in a similar fashion gave the data listed under series 2 in Table I.

TABLE I

OPTICAL PROPERTIES OF SOLUTIONS OF THE QUININE SALT

Series	Sample	Rotation, deg. Obsd.	Specific, $[\alpha]^{30}\text{D}$
1[a]	1-1	−0.40	−200
	1-2	− .31	−152
	1-3	− .28	−140
	1-4	− .20	−100
2[b]	2-1	−1.45	−145
	2-2	−1.21	−121
	2-3	−1.18	−118
	2-4	−1.15	−115

[a] Concentration = 0.100 g./100 ml. [b] Concentration = 0.125 g./100 ml.

Removal of quinine from fractions 1-2, 2-1, and 2-4 was effected by grinding each with slightly more than the calculated quantity of solid potassium iodide and extracting the oxalato germanate(IV) species from the insoluble quinine iodide with water. After dilution of the resulting solutions to the stated concentrations, the rotations given in Table II were obtained. That these fractions contained no quinine was shown by the complete racemization at room temperature of the solution of sample 1-1 in 21 hr. and of solutions of samples 2-1 and 2-4 in 40 hr.

TABLE II

OPTICAL PROPERTIES OF QUININE-FREE SPECIES

Sample	Concn., g./50 ml.	Rotation, deg. Obsd.	Specific, $[\alpha]^{30}\text{D}$
1-2	0.0185	−0.06	−81
2-1	.125	− .42	−84
2-4	.125	− .37	−74

X-Ray Diffraction Measurements.—Powder patterns taken for samples of the quinine salt were complicated by the presence of quinine, which gave obscuring halos, and could not be compared exactly with patterns for tris-(oxalato)-cobaltate(III), -chromate(III) and -ferrate(III) compounds. Qualitative similarities, however, and d-spacings of 1.17 and 1.30 Å., as compared with values of 1.14 and 1.27 Å. for potassium tris-(oxalato)-cobaltate (III), do give added support to the presence of the $[Ge(C_2O_4)_3]^=$ ion.

Discussion

The data in Table II indicate clearly that at least a partial resolution of the tris-(oxalato)-germanate(IV) ion has been effected. The nearly identical $[\alpha]^{30}\text{D}$ values for the first two samples are in accord with expectation since these two samples represent equivalent fractions in the two series. The lower value for the third sample is in agreement with the general decreases noted in Table I as fractionation proceeded and is probably due to the appearance of an increased quantity of the dextrorotatory form of the complex.

The existence of optical isomerism in the tris-(oxalato)-germanate(IV) ion shows clearly the predominantly covalent character of the bonding involved and suggests the existence of the stable outer orbital hybridization 4s $4p^3$ $4d^2$. It would be of particular interest to study the exchange between bound oxalate and oxalate ion by Long's technique[7] as a further test of Taube's views.[1]

(7) F. A. Long, THIS JOURNAL, **61**, 570 (1939); **63**, 1353 (1941).

URBANA, ILLINOIS

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

The Preparation and Properties of Zirconium and Hafnium Chelates of Certain β-Diketones[1]

BY EDWIN M. LARSEN, GLENN TERRY AND JAMES LEDDY

RECEIVED JUNE 12, 1953

Compounds of zirconium and hafnium with the composition MK_4 have been prepared with the following diketones: acetylacetone, trifluoroacetylacetone, 2-furoylacetone, 2-furoyltrifluoroacetone, 2-thenoylacetone, 2-thenoyltrifluoroacetone and 2-pyrroyltrifluoroacetone. The densities of the chelate compounds were determined by the standard pycnometric method using water or petroleum ether saturated with the chelate as the immersion liquid. The molecular volumes calculated, in all cases, were greater for the hafnium compound than the zirconium compound except for acetylacetone and 2-pyrroyltrifluoroacetone derivatives where the molecular volumes were almost identical. The ultraviolet absorption spectra for the non-fluorine containing chelate compounds in cyclohexane are similar to the parent diketones. For the metal derivatives of the fluorinated diketones, the λ_{max} associated with the enol ring is shifted to longer wave lengths, as compared to the λ_{max} of the free diketone. The λ_{max} for the zirconium chelates shifted to slightly longer wave lengths than for the corresponding hafnium compound.

Although certain diketones have been used for the fractional separation[2] of zirconium and hafnium, little is known about the properties of the solid metal chelates themselves. It was of interest therefore to isolate some of the solid products and examine their properties. Chelates of the following diketones were prepared: acetylacetone (HCCA), trifluoroacetylacetone (HCTA), 2-furoylacetone (HFCA), 2-furoyltrifluoroacetone (HFTA), 2-pyrroyltrifluoroacetone (HPTA), 2-thenoylacetone (HTCA) and 2-thenoyltrifluoroacetone (HTTA). Attempts to synthesize 2-pyrroylacetone were unsuccessful.

Densities, Molecular Volumes.—One of the properties studied was the molecular volume of the solid chelate, since it has been suggested[3] that molecular volume data may shed some light on the

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[1] Based on a thesis submitted by Glenn Terry 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 in part at the September 15, 1952, Atlantic City Meeting of the American Chemical Society before the Physical and Inorganic Division.

[2] E. M. Larsen and G. Terry, THIS JOURNAL, **75**, 1560 (1953).

[3] W. Biltz, *Z. anorg. Chem.*, **164**, 245 (1927).

metal ligand bonding in the chelate. However, in considering these data it must also be kept in mind that, as shown by Parry,[4] these data will be misleading if the compounds do not have the same crystal structure. Although no detailed determinations of crystal structure have been made, powder patterns have been run on all the compounds concerned here. The products are all crystalline, and the patterns indicate that the structures are all similar.

Hevesy[5] has shown that the molecular volumes of the zirconium and hafnium acetylacetone derivatives were essentially identical. Our density data for these derivatives, from which the molecular volumes (Table I) were calculated, agree very well with Hevesy's, 1.415 for the zirconium compound, and 1.67 for the hafnium compound. The similarity in molecular volumes, and consequent similarity in zirconium and hafnium radii, are consistent with the ionic radii quoted: namely, for Zr^{+4} 0.74 Å., and Hf^{+4} 0.75 Å.[6] However, it is only in the cases of acetylacetone and 2-pyrroyltrifluoroacetone derivatives that we obtained almost identical molecular volumes. In all other cases, the molecular volume for the hafnium compound was greater than that of the zirconium compound for a given diketone. This would seem to indicate that the hafnium had an effectively larger radius than the zirconium under these conditions. Perhaps these data could better be explained using the covalent radii rather than the ionic radii. Unfortunately there are no such data available for the elements with coördination number eight, except for the elements in the metallic state. In this instance the zirconium radius is given as 1.54 Å. and the hafnium radius[7] as 1.57 Å. The question next arises, will a difference of 0.03 Å. in radii account for the observed differences in molecular volumes? To check this, differences in the effective zirconium and hafnium radii, ΔR, in a given chelate, were calculated from the molecular volumes. To do this, the molecular volume was divided by the Avogadro number to obtain the effective volume of a single molecule, and then the radius calculated on the assumption that the molecule was spherical. These radii (Table I) are of the same order of magnitude as the radii arrived at using Fisher–Taylor–Hirschfelder models. These differences in effective radii represent differences in the zirconium–hafnium radii as long as it can be assumed that the rest of the chelate molecule has retained its dimensions. To test this assumption one can calculate the $4(CF_3-CH_3)$ volume differences in these compounds by subtracting the molecular volume of the non-fluorinated species from the molecular volume of the corresponding fluorinated derivative. For zirconium and hafnium derivatives of HFCA, HFTA, HTCA and HTTA, the differences were quite constant, being 74, 74, 75 and 76, respectively. For HCCA and HCTA, however, the $4(CF_3-CH_3)$ differences for the zirconium and hafnium derivatives were 63 and 84, respectively. This results from the fact that the molecular volumes of the metal derivatives of HCCA are almost identical, while the molecular volumes of the derivatives of the HCTA are different for zirconium and hafnium. Thus, in this case a constant difference would not be expected. The constancy of the $4(CF_3-CH_3)$ volume difference lends support to the conclusion that in these molecules the effective hafnium radius is on the average 0.05 Å. larger than the effective zirconium radius. This difference is not compatible with the small difference in the ionic radii, but is more comparable to the difference of 0.03 Å. in the metallic covalent radii.

Table I

Chelate	Density, g./cc.[a] Zr	Hf	Mol. vol., cc. Zr	Hf	Molecular radii, Å. Zr	Hf	ΔR, Hf–Zr
HCCA	1.416	1.691	344	340	5.15	5.13	−0.02
HCTA	1.729	1.863	407	424	5.43	5.52	.09
HFCA	1.506	1.659	462	473	5.68	5.72	.04
HFTA	1.701	1.826	536	547	5.97	6.01	.04
HPTA	1.548	1.703	585	584	6.15	6.14	− .01
HTCA	1.513	1.639	502	517	5.84	5.90	.06
HTTA	1.693	1.793	577	593	6.11	6.17	.06

[a] Average values of at least four separate determinations; average deviation ±0.005.

Melting Points.—The fact that the presence of the trifluoro group in the diketone has a greater effect on the properties of the metal derivatives of trifluoroacetylacetone than on the derivatives of diketones containing a heterocyclic group, is shown by the melting points (Table III). Whereas the metal derivatives of HCCA have melting points in the region of 190°, the derivatives of HCTA have melting points near 128°. In no other case is the difference as large. The hafnium compounds in general all melt at lower temperatures than the zirconium compounds except in the case of the HPTA and HFCA derivatives, for which the melting points are about the same. The HPTA derivatives always showed a definite shrinkage at 165°, but did not actually melt until about 185°.

Ultraviolet Spectra of the Diketones.—Another property studied was the ultraviolet absorption spectra of solutions of the chelate compounds in benzene and cyclohexane. The spectra for these compounds in benzene have essentially the same general shape, but all the λ_{max} values are shifted to longer wave lengths, and an intensification of the ϵ_{max} is noted in the case of the furoyl derivative. The absorption spectrum of acetylacetone had been studied as early as 1904.[8] In terms of the present day theories, the single absorption maximum can be related to the enol form of the molecule with the acid hydrogen completing a six-membered ring by means of a hydrogen bond. The enol ring is stabilized both by the hydrogen bond formation and the enol resonance.[9] The keto form can be ignored for it is known that the enol form of the diketones predominates in the solvents used. For instance, acetylacetone in benzene is at least 85% enol[10] and

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[4] R. W. Parry, *Chem. Revs.*, **46**, 507 (1950).

[5] G. von Hevesy and M. Logstrup, *Ber.*, **59B**, 1890 (1926).

[6] W. Zachariasen, MDDC 1151, June 11, 1947.

[7] L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, N. Y., 1948, p. 410.

[8] E. C. Baly and C. H. Desch, *Trans. Chem. Soc.*, **85**, 189 (1904).

[9] L. N. Ferguson, "Electronic Structures of Organic Molecules," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 217–218.

[10] R. H. Meyer, *Ber.*, **47**, 826 (1914).

TABLE II

	Diketone				ZrK_4				HfK_4			
	Cyclohexane		Benzene		Cyclohexane		Benzene		Cyclohexane		Benzene	
	λ_{max}	ϵ_{max} (4×10^{-3})	λ_{max}	ϵ_{max} (4×10^{-3})	λ_{max}	ϵ_{max} $\times 10^{-3}$	λ_{max}	ϵ_{max} $\times 10^{-3}$	λ_{max}	ϵ_{max} $\times 10^{-3}$	λ_{max}	ϵ_{max} $\times 10^{-3}$
HCCA	272	34.3	274	33.1	272	33.6	275	34.9	272	32.5	274	27.4
HCTA	283	24.1	285	33.0	287	25.4	290	30.7	286	28.8	289	30.6
HFCA	311	59.2	317	66.8	311	55.3	317	83.5	311	58.1	317	70.5
HFTA	320	58.8	329	64.0	340	58.8	351	99.9	338	58.4	348	92.7
HPTA	327	75.6	333	68.4	348	74.8	358	77.9	344	68.2	356	84.4
HTCA	317	65.2	321	61.6	317	65.2	321	59.9	317	66.9	321	50.9
HTTA	317	59.2	326	50.1	341	56.7	348	64.0	340	57.6	345	64.0

trifluoroacetylacetone and 2-thenoyltrifluoroacetone are 97 and 94.5%[11] enol, respectively, in dry benzene. It is assumed that this high enol content prevails in all the other cases.

There are few published data on the effect on the absorption spectra of fluorine substitutions in the diketone molecule. The absorption spectrum for trifluoroacetylacetone (Fig. 1a) has the same general shape as that of acetylacetone, but the λ_{max} has been shifted from 272 to 283 mμ (Table II) upon the substitution of the trifluoro group for the methyl group. This shift can be accounted for by assuming that the introduction of the electronegative fluorines caused an increase in the contribution of the ionic resonance forms in the excited state thus stabilizing this state and reducing the energy difference between the excited and ground states with a corresponding shift of the absorption maximum to the red. The substitution of a heterocyclic unit for a methyl group in acetylacetone had the same effect as the introduction of the CF_3 group, although the shift to the red was still greater, with the λ_{max} for 2-thenoylacetone (Fig. 2a) and 2-furoylacetone (Fig. 1b) appearing at 317 and 311 mμ, respectively. This shift probably is related to an increase in the length of the conjugated system as a whole, as compared to the enol resonance alone in the simple acetylacetone. In addition, the absorption spectra of these two compounds show a shoulder at wave lengths shorter than the λ_{max} which is probably related to the heterocyclic component itself. The substitution of a trifluoromethyl group for the remaining methyl group in the diketones containing a heterocyclic group complicates the ultraviolet spectra considerably. In each case, a third maximum appears at the long wave length side of the λ_{max}. The intensity of this third maximum increases from HPTA < HTTA < HFTA and, in this later case, the third maximum has about the same intensity as the second maximum. An explanation of this complication in spectra is lacking at the moment. If it is due to the presence of another molecular species, it is not known what this species might be. It is interesting to note that the λ_{max} for the HTCA and HTTA are both 317 mμ, while the λ_{max} for the HFCA is 311 mμ and for the HFTA it is 320 mμ, assuming that it is the second maximum in this case which is related to the enol form of the molecule. The assignment of the second maximum to the enol ring was made on the basis of the following facts: the second maximum has molar extinction coefficient approximately four times the ϵ of the diketone itself, which would follow from the composition of the chelate MK_4; and, secondly, by analogy to HCTA and its derivatives, it is assumed that a shift of the λ_{max} to the red occurs upon chelation. Since in the case of HFTA, the two maxima are of about the same intensity, the last factor cited was the determining one here.

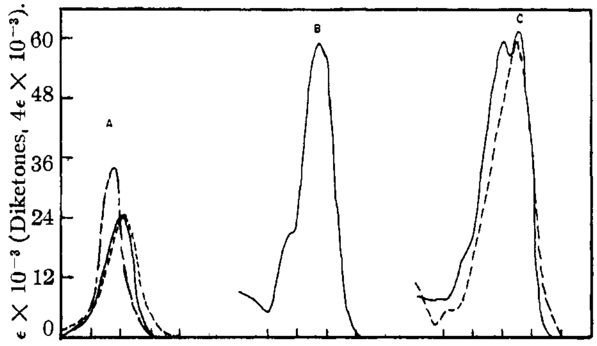

Fig. 1.—Spectra of: A, — — —, HCCA-M(CCA)$_4$; —, HCTA; - - - -, M(CTA)$_4$. B, —, HFCA-M(FCA)$_4$. C, —, HFTA; - - - -, M(FTA)$_4$.

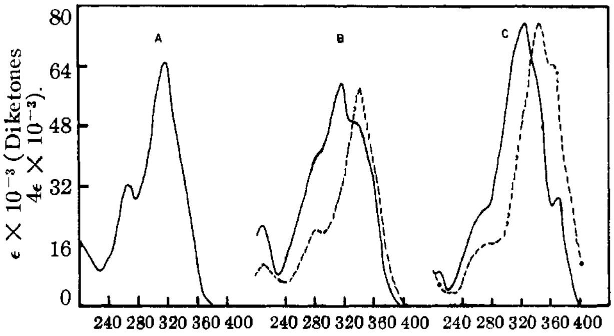

Fig. 2.—Spectra of: A, —, HTCA-M(TCA)$_4$; B, —, HTTA; - - - -, M(TTA)$_4$; C, —, HPTA; - - - -, M(PTA)$_4$.

Ultraviolet Absorption Spectra of Chelates.—It had been found early in the study of metal chelate compounds, that the spectra of the metal derivatives of acetylacetone differed little from the spectrum of the diketone itself[8,12] except in the intensity of the λ_{max} which was, however, proportional to the number of acetylacetone residues around the metal atom. This is indeed found to be the case for the zirconium and hafnium derivatives of acetylacetone (Fig. 1a), 2-furoylacetone (Fig. 1b) and 2-thenoylacetone (Fig. 2a). How-

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(11) J. C. Reid and M. Calvin, THIS JOURNAL, **73**, 2948 (1950).

(12) G. T. Morgan and H. W. Moss, *J. Chem. Soc.*, **105**, 189 (1914).

ever, the metal derivatives of trifluoroacetylacetone had λ_{max} values which were definitely shifted to longer wave lengths (Table II). In addition to these shifts, another pronounced difference upon chelation was observed between the spectra of HTTA, HFTA and their metal derivatives in that the metal derivatives showed only one major maximum instead of two as with the free diketones. The HPTA metal derivatives still showed the shoulder to the right of the λ_{max} but at considerably higher intensity than in the diketone itself. It should be noted that the pyrroyl derivative behaved differently than the other heterocyclic compounds in almost all the properties examined.

In those cases where the λ_{max} is shifted to longer wave lengths upon chelate formation, the λ_{max} for the zirconium is always shifted slightly further to the red than the λ_{max} for the hafnium compound, thus making the zirconium enol ring slightly more stable than the corresponding hafnium structure.

It appears then that in each case of a fluorinated diketone, the values of the λ_{max} of the metal derivative are shifted to longer wave lengths than the λ_{max} values for the diketones themselves. It is not easy at the present time to rationalize this fact. It has been postulated that when the metal chelate and chelating agent spectra are alike the bond is ionic, since the chelate part of the molecule is in the same condition as in the diketone itself.[13] It would appear that in the diketones containing the trifluoro group the bond should be more ionic in character than in those not containing the trifluoro group, since the presence of the electronegative CF_3 group would have a restrictive effect on the participation of the oxygen donor electrons in the bonding. Thus, greater participation of the donor electrons in the metal's orbitals cannot be used to rationalize this shift to the red.[13] In fact, one would expect the donor electrons of acetylacetone to participate to greater extent in the metal chelate bond formation, than the donor electrons of trifluoroacetylacetone yet, in this case, and in the case of the other non-fluorinated diketones, no shift to the red is observed upon chelation.

It also has been suggested[13] that the shift to the red upon chelation is due to the participation of metal electrons in double bond formation with the oxygens of the diketone. However, in the case of zirconium and hafnium there are no metal electrons available to do this, and therefore some other process must be operative. This leads us to use the same explanation for the red shift in the metal chelate spectra as was used to explain the red shift of the HCTA spectra, namely, the stabilization of the excited state by the increased contribution of ionic resonance forms, but there seems no logical reason for assuming that this is the case. The only other alternative is to assume that the ground state of the metal chelate in these trifluoro derivatives is actually higher than the ground state of the metal derivatives of the non-fluoro derivatives, then with similar energy levels for the first excited states the metal derivatives would show this shift to the red.

It is concluded from these data on molecular volumes and ultraviolet absorption spectra that it is hard to fit the observed facts in terms of present day interpretations of similar data. Only for the derivatives of acetylacetone, in which case identical molecular volumes are obtained and the spectra of chelates and diketones are the same, do the facts fit.

Experimental

Materials.—Eastman Kodak Co. acetylacetone was redistilled with the fractions coming over at 139° and 740 mm. used. The 2-furoylacetone and 2-thenoylacetone were secured from Professor R. A. Levine of the University of Pittsburgh and redistilled *in vacuo*. The other β-diketones were synthesized in this Laboratory according to published procedures[11,14,15] and purified by vacuum distillation.

Cyclohexane used as a solvent in the ultraviolet absorption spectra measurements was purified by passing it through a silica gel column[16] and by distillation.

The zirconium and hafnium oxychlorides were recrystallized from aqueous 9 *N* HCl solution. The zirconium contained only 0.04% hafnium, and the hafnium 0.75% zirconium. All the molecular weight data were corrected for these impurities.

Preparation of the Chelate Compounds.—Two general methods of preparation were used: (1) the direct addition of the diketone to the solution of the metal, (2) a two-phase extraction procedure.

In the preparation of the derivatives of HCCA, HCTA, HFCA a 25% excess of the theoretical amount of the chelating agent was added dropwise with rapid stirring to a cold 0.1 *M* solution of the metal oxychloride. The *p*H of the reaction mixture was maintained at all times at 1.45 by the addition of a dilute sodium carbonate solution. The precipitate normally formed immediately upon the addition of the diketone. The hafnium HCCA product did not precipitate immediately but began to crystallize after several hours at 0°. The conditions used for the preparation of the HTCA derivatives differed slightly, since this diketone is a solid at room temperature and is very insoluble in water. The reaction is best carried out by warming the reaction mixture to 40° at which temperature the HTCA is liquid. The resulting reaction mixture was a colloidal dispersion which was coagulated by the addition of a few drops of 0.01 *M* HCl.

In the two-phase extraction method used for HTTA, HFTA and HPTA derivatives, the aqueous solution was 0.1 *M* in HCl, and 0.01 *M* in M^{+4}; the diketone concentration of the benzene solution was 10% in excess of the theoretical requirement suitably corrected for the distribution of the diketone in the aqueous phase.[2] After shaking for 24 hours the phases were separated, the aqueous phase shaken with fresh benzene, the benzene phases combined and evaporated in a stream of filtered air at a slightly elevated temperature. The HFTA derivatives were quite insoluble in benzene as well as the aqueous phase and separated out as a large globule which was recovered by filtration.

The crude chelate product produced by either method was extracted repeatedly with warm petroleum ether (60–68° fraction) in which the unreacted diketone was soluble and the chelates were relatively insoluble. The chelate was then dissolved in sufficient benzene to give complete solution, and the chelate reprecipitated by the addition of petroleum ether. The metal chelates were finally recrystallized from hot petroleum ether solution. The products were dried and the last traces of solvent were removed *in vacuo* at 70°. The yields are given in Table III. The metal chelates of HCCA and HCTA were white crystalline compounds, while the others were creamy colored powders, with the HPTA derivatives being more yellow than the rest.

Analyses.—All the chelates were analyzed for their metal content. The samples in platinum crucibles were placed in crushed ice, a few milliliters of water added and red fuming nitric acid added dropwise until a clear solution was ob-

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[13] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 220–221.

[14] A. Henne, M. Newman, L. L. Quill and R. Staniforth, THIS JOURNAL, **69**, 1819 (1947).

[15] E. M. Larsen and G. Terry, *ibid.*, **73**, 500 (1951).

[16] M. M. Graff, R. T. O'Connor and E. L. Skau, *Ind. Eng. Chem., Anal. Ed.*, **16**, 556 (1944).

TABLE III

Compound	Yield, %	Metal, % Calcd.	Metal, % Found	Melting point, °C.
Zr(CCA)$_4$	75	18.7	18.9	190–193
Hf(CCA)$_4$	76	31.0	31.2	188–190
Zr(CTA)$_4$	97	13.0	13.2	128–130
Hf(CTA)$_4$	80	22.5	22.3	125–128
Zr(FCA)$_4$	81	13.1	13.1	198–201
Hf(FCA)$_4$	80	22.7	22.6	200–202
Zr(FTA)$_4$	95	10.0	10.0	199–201
Hf(FTA)$_4$	82	17.8	17.4	195–197
Zr(PTA)$_4$	93	10.1	10.0	184–185
Hf(PTA)$_4$	83	17.9	17.8	185–186
Zr(TCA)$_4$	81	12.0	11.95	244–245
Hf(TCA)$_4$	82	21.0	21.1	239–242
Zr(TTA)$_4$	80	9.3	9.3	225–226
Hf(TTA)$_4$	96	16.7	16.6	220–223

tained. This was evaporated to near dryness on a steam-bath, a few drops of concentrated H_2SO_4 along with a few ml. of concentrated nitric acid was added to the residue, again evaporated to near dryness, and the sulfuric acid fumed off. The charred samples were then ignited to constant weight over a Meker burner. The data in Table III represent average values of at least duplicate samples. The hafnium was assumed to have the corrected atomic weight of 177.94.

Melting Points (Table III).—The melting points were determined in a capillary melting point tube with a thermometer calibrated to an accuracy of 0.5°.

Densities and Molecular Volumes.—The densities of all the chelates were determined by the standard pycnometric method in which the volume of immersion liquid displaced by a known weight of a solid sample is measured. The immersion liquid here was boiled distilled water or petroleum ether (100–140°) saturated with the chelate. The HCCA derivatives were all run in petroleum ether. The measurements were all made at 25 ± 0.02° and the samples were degassed in a vacuum desiccator before weighing in the immersion liquid. The results along with the calculated molecular volumes are given in Table I. The molecular volume is simply the molecular weight of the compound divided by the density.

Absorption Spectra.—The ultraviolet absorption spectra were determined for each of the β-diketones and their corresponding zirconium and hafnium chelate compounds both in purified dry cyclohexane and in dry benzene. The data for the benzene solutions were determined using a Beckman DU quartz spectrophotometer, and the data for the cyclohexane solutions were obtained on a Carey model 11 recording quartz spectrophotometer. One-cm. cells were used in each case. Several of the solutions were run on both instruments with essentially identical results. The solutions were all about 10^{-5} M and were always run within a few hours of preparation. The diketones used were freshly distilled.

MADISON, WISC.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF SOUTH CAROLINA]

Activity Coefficient Ratios of Nitric Acid and Mercurous Nitrate and the Standard Potential of the Mercury, Mercurous Ion Electrode at 25°

BY OSCAR D. BONNER AND FRANCIS A. UNIETIS[1]

RECEIVED MAY 21, 1953

Electromotive force measurements on cells of the type Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $Hg_2(NO_3)_2(m_2)$, Hg have been used for the calculation of the ratios of activity coefficients at 25° of nitric acid and mercurous nitrate. From extrapolations to infinite dilution, the standard potential of the mercury, mercurous ion electrode has been found to be −0.7961 v.

Introduction

Activity coefficient ratios of nitric acid and silver nitrate have previously been determined[2] from measurements of the electromotive force of the cell without liquid junction

Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $AgNO_3(m_2)$, Ag

Similarly, activity coefficient ratios of nitric acid and mercurous nitrate may be determined from measurements of the electromotive force of the cell

Ag, AgCl, HCl(0.2 m)/glass/$HNO_3(m_1)$, $Hg_2(NO_3)_2(m_2)$, Hg

In this instance also, the glass electrode must be used instead of the hydrogen electrode as the mercurous ion is reduced by hydrogen in the presence of platinum. For this cell the equation

$$E = E^0{}_{\text{glass}} - E^0{}_{\text{Hg.Hg}_2{}^{++}} - \frac{RT}{2F}\ln\frac{a^2{}_{\text{HNO}_3}}{a_{\text{Hg}_2(\text{NO}_3)_2}} =$$

$$E^0 - \frac{RT}{2F}\ln\frac{m^2{}_{\text{HNO}_3}}{m_{\text{Hg}_2(\text{NO}_3)_2}} - \frac{RT}{2F}\ln\frac{\gamma^4{}_{\text{HNO}_3}}{\gamma^3{}_{\text{Hg}_2(\text{NO}_3)_2}} \quad (1)$$

is applicable where $E^0 = E^0{}_{\text{glass}} - E^0{}_{\text{Hg.Hg}_2{}^{++}}$.

The standard potential of the glass electrode was determined from measurements of the e.m.f. of the cell Ag, AgCl, HCl(0.2 m)/glass/HCl(m), AgCl, Ag, since the activity coefficients of the standardizing hydrochloric acid solutions are known. This standard potential varied slightly with acid concentration, and in each subsequent calculation the potential corresponding to that of an acid solution of equal concentration was used.

Experimental

Electrodes and Auxiliary Apparatus.—The glass electrodes were prepared and calibrated, and the silver chloride electrodes were prepared in the manner described previously.[2] Triply distilled mercury was used for the mercury electrode. A galvanometer having a sensitivity of 5 × 10^{-4} microampere per mm. was used for the potentiometric measurements. Due to the high resistance of the glass electrode, a Leeds and Northrup thermionic amplifier was included in the circuit.

Standardization of Solutions.—Since mercurous nitrate is only slightly soluble in pure water, it was necessary to prepare those solutions having higher concentrations of mercurous ion by dissolving solid mercurous nitrate in nitric acid solutions. These stock solutions were then diluted to the desired ionic strength and kept in contact with metallic mercury.

The mercurous nitrate concentration was determined potentiometrically by titration with standard potassium chloride. The nitric acid concentration was determined potentiometrically with standard base after the mercurous ion had been removed by precipitation. Specific gravity measurements were then made in order to convert these concentrations to a molal basis. As the concentrations of these

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(1) From a thesis submitted by Francis A. Unietis in partial fulfillment of the requirements for the degree of Master of Science, University of South Carolina.

(2) O. D. Bonner, A. W. Davidson and W. J. Argersinger, Jr., THIS JOURNAL, **74**, 1047 (1952).