vious work.[4] Therefore, some polymerization of the complexes is indicated.

It is possible to explain the data qualitatively by postulating that: (i) there exists an equilibrium between two types of polynuclear beryllium–citrate complexes; (ii) both contain the same number of beryllium atoms; (iii) but one complex contains one more citrate group than does the other; (iv) only the complex containing the least citrate is adsorbed by the resin to a significant extent; (v) the adsorbable complex has a smaller distribution coefficient than have beryllium ions.

For such a system, the application of equation 10 would give curves similar to those from *p*H 4.35 to 4.65 in Fig. 1; *i.e.*, linear plots extrapolating to a $1/K^\circ_*$ value higher than $1/K^\circ_d$. To illustrate, the following equilibrium could satisfy the requirements

$$\{Be_2(HCit)_2\}^0 \rightleftarrows \{Be_2HCit\}^{+2} + HCit^{-2}$$

Other possibilities may be deduced by altering the number of hydrogens in the citrate groups or by adding BeO groups to both complexes.

It seems unlikely that complexes having a Be/citrate molar ratio less than unity (*e.g.*, $Be(HCit)_2^{-2}$ or $BeCit_2^{-4}$) are present to a significant extent in these experiments below *p*H 4.6, because such complexes would introduce a $(T{\cdot}Cit)^2$ term which would prevent linearity of the $1/K_d$ *versus* (T·Cit) plot. Furthermore, the adsorption of beryllium by the anion-exchange resin (Table I) was not detected at *p*H 4.6 or below.

However, near *p*H 7 some beryllium was adsorbed by the anion-exchange resin, whereas none was taken up by the cation exchanger. This is shown by the data in rows 9–13 of Table I. A beryllium–citrate anionic complex having a charge more negative than −1 is, therefore, present above *p*H 7.

The poor reproducibility in the *p*H 4.15 region would be expected if the transition from mononuclear to polynuclear complexes were occurring. In this region significant quantities of all complexes would be present and the system would not be expected to follow the mathematics for any one type.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

Extraction of Zirconium and Hafnium with Various Fluorinated β-Diketones

BY E. H. HUFFMAN, G. M. IDDINGS, R. N. OSBORNE AND G. V. SHALIMOFF

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The distribution ratios and equilibrium constants for the extraction of zirconium and hafnium from 4 *M* perchloric acid with various combinations of fluorinated β-diketones and organic solvents have been determined. The separation factors, K'_{Zr}/K'_{Hf}, found for this acidity were: 2-thenoyltrifluoroacetone in benzene, 25; 2-thenoyltrifluoroacetone in *o*-dichlorobenzene, 16; benzoyltrifluoroacetone in benzene, 18; isovaleroyltrifluoroacetone in benzene, 13; isovaleroyltrifluoroacetone in *n*-hexane, 13.

The fractional separation of zirconium and hafnium by chelation–extraction with benzene solutions of various β-diketones has been reported previously.[1–3] These studies have been extended in the present work to other fluorinated β-diketones and to other solvents. In order to use more concentrated solutions of zirconium and hafnium, and hence to increase the usefulness of the fractionation method, 4 *M* perchloric acid has been used in these studies instead of 2 *M* acid, as in the previous studies. The concentration of zirconium or of hafnium may be as high as 0.04 *M* in 4 *M* perchloric acid and still be completely extracted, showing that the metal ion is either monomeric or that the monomer and any polymer establish equilibrium rapidly. Attempts were also made, in the case of 2-thenoyltrifluoroacetone, to extract 0.09 *M* zirconium from 5 *M* perchloric acid, a condition which also allows complete removal of zirconium from the aqueous phase, but precipitates formed at the organic–aqueous interfaces for the higher concentrations of diketone and consistent data could not be obtained.

The metal ion species for zirconium and hafnium is mainly M^{+4} for the monomers in 2 *M*, or stronger, perchloric acid,[4] and the extraction reaction may be expressed as

$$M^{+4} + 4HK = MK_4 + 4H^+ \qquad (1)$$

At constant acid concentration the equilibrium constant is then

$$\log K' = \log R - 4 \log [HK] \qquad (2)$$

where R is the extraction coefficient, $[MK_4]/(M^{+4})$, and [HK] is the diketone activity. The equilibrium constants obtained using 4 *M* perchloric acid cannot be compared directly to those[1–3] obtained using 2 *M* perchloric acid because the activity coefficients of the metal ion species at the two different ionic strengths are not known.

The diketones and solvents for which extraction data were obtained were 2-thenoyltrifluoroacetone (HTTA) in benzene and in *o*-dichlorobenzene, benzoyltrifluoroacetone (HBTA) in benzene and isovaleroyltrifluoroacetone (HITA) in benzene and in *n*-hexane. Interference in the form of precipitation at the organic–aqueous interface was encountered when extractions were tried with HTTA in hexone (4-methyl, 2-pentanone) and with 2-naphthoyltrifluoroacetone (HNTA) in benzene. It is probable that satisfactory data for these combinations of reagent and solvent could be obtained at

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(1) E. H. Huffman and L. J. Beaufait, THIS JOURNAL, 71, 3179 (1949).

(2) B. G. Schultz and E. M. Larsen, *ibid.*, 72, 3610 (1950).

(3) E. M. Larsen and G. Terry, *ibid.*, 75, 1560 (1953).

(4) R. E. Connick and W. H. Reas, *ibid.*, 73, 1171 (1951).

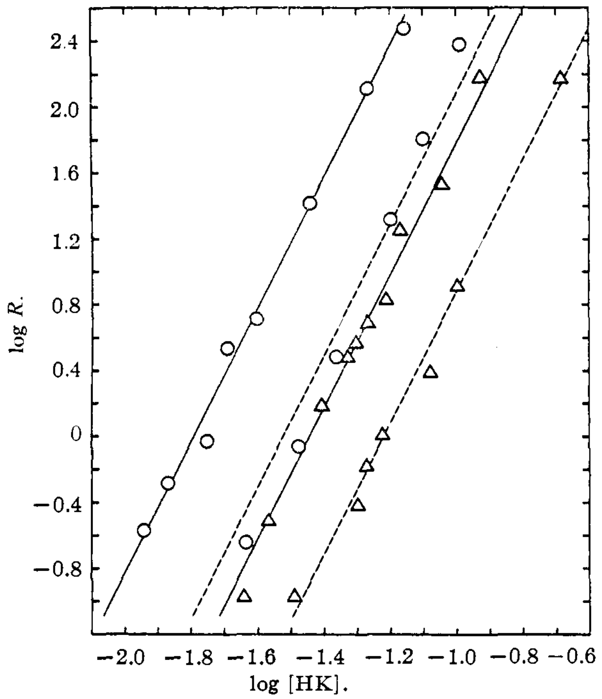

Fig. 1.—Dependence of distribution ratios on 2-thenoyltrifluoroacetone activities: O, zirconium; △, hafnium; solid lines, benzene; broken lines, *o*-dichlorobenzene.

either a higher temperature or with lower concentrations of zirconium. The highly fluorinated β-diketone 1-(3,4-dichlorophenyl)-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione exhibited no appreciable extraction of zirconium from 4 *M* perchloric acid into a 0.250 *M* solution of the reagent in benzene.

Experimental

Materials.—The 2-thenoyltrifluoroacetone, 2-naphthoyltrifluoroacetone and 1-(3,4-dichlorophenyl)-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione were obtained from the Dow Chemical Company and the benzoyltrifluoroacetone and isovaleroyltrifluoroacetone were obtained from M. Calvin of this Laboratory.

The thenoyltrifluoroacetone was recrystallized twice from benzene to obtain a product of 99.3% purity, the 2-naphthoyltrifluoroacetone was recrystallized twice from ethanol to obtain 99.0% purity and the isovaleroyltrifluoroacetone was distilled at a pressure of 62 mm. to obtain a fraction boiling at 78–80° and having a purity of 99.2%. The benzoyltrifluoroacetone, 98.7% pure, and the substituted hexanedione, 99.2% pure, were used without further purification. Weighed amounts of these reagents were dissolved in the selected solvents to make known volumes of stock solutions. The purities were determined by potentiometric titration of aliquots added to 50% ethanol, using 0.1 *M* sodium hydroxide (carbonate-free) and a nitrogen blanket to keep out carbon dioxide.

The solvents used were reagent grade thiophene-free benzene (Baker and Adamson), *n*-hexane, stated by the manufacturer (Phillips Petroleum) to be 99 mole % minimum and *o*-dichlorobenzene, stated by the manufacturer (Eastman Kodak) to be 96+%.

Zirconium and hafnium solutions were prepared from their oxides. These were warmed with about 1 ml. of concentrated sulfuric acid and a little hydrofluoric acid and then fumed until clear solutions were obtained. After dilution the hydroxides were precipitated with ammonium hydroxide, the precipitates dissolved in hydrochloric acid and the hydroxides again precipitated to remove sulfate. Concentrated hydrochloric acid was then used to dissolve the hydroxides and this solution was diluted to 6–7 *M* hydrochloric cid to precipitate $Zr(Hf)OCl_2 \cdot 8H_2O$. Weighed amounts f these salts were dissolved in 4 *M* perchloric acid to obtain stock solutions approximately 0.04 *M* in metal ion. Spectrographic analyses showed the zirconium to contain 0.6% hafnium and the hafnium to contain 0.3% zirconium.

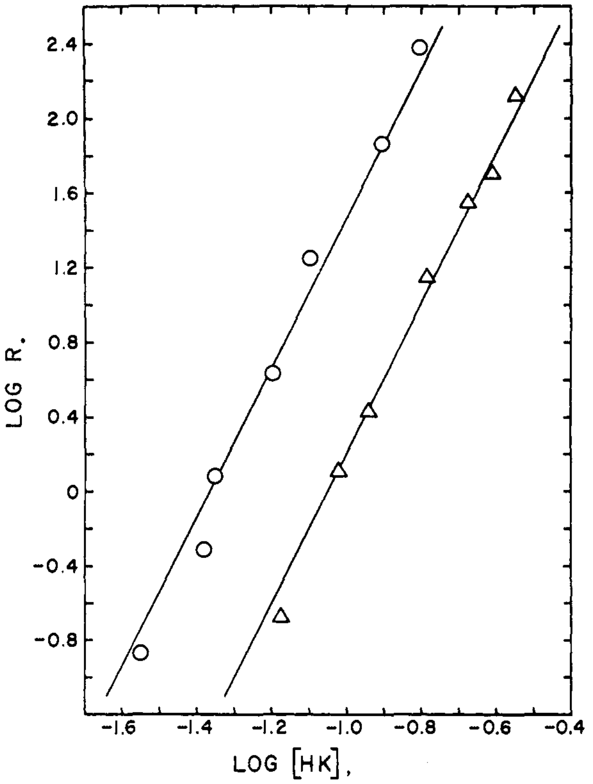

Fig. 2.—Dependence of distribution ratios on benzoyltrifluoroacetone activities in benzene: O, zirconium; △, hafnium.

Analyses.—Both the organic and aqueous phases were analyzed for metal content after extraction. Colorimetric analyses were made with a Beckman Model DU spectrophotometer using the alizarin method of Liebhafsky and Winslow[5] as modified[1] to correct for the effects of the organic substances and perchloric acid present, and using the appropriate β-diketone where thenoyltrifluoroacetone is called for in the modification.

Extractions.—The distribution coefficients between the organic solvents and 4 *M* perchloric acid for HITA were obtained by equilibrating a solution of known concentration of the diketone in organic solvent with an equal volume of acid. The concentration of diketone in the aqueous phase was then determined by the absorption at 284 mμ, the peak in its absorption curve. The molar extinction coefficient at this wave length is 280. The distribution coefficients found, expressed as proportion in the organic phase, were 0.990 for benzene and 0.976 for *n*-hexane.

The corresponding values for the other diketones had been obtained in a similar manner and found to be: HTTA–benzene,[6] 0.979; HTTA–*o*-dichlorobenzene,[7] 0.979; HBTA–benzene,[7] >0.995.

The chelation–extraction equilibrations were carried out by mixing 5 ml. of the perchloric acid phase containing the zirconium or hafnium with 5 ml. of the organic phase containing diketone. The mixtures were shaken for at least 90 minutes, as equilibrium was found to be reached in not more than 60 minutes for any diketone–solvent combination. Aliquots of the organic and aqueous phases were then analyzed.

Results

The values found for the equilibrium constants for the various combinations of element, diketone

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[5] H. Liebhafsky and E. Winslow, This Journal, **60**, 1776 (1938).

[6] W. H. Reas, Thesis, University of California, 1948.

[7] T. E. Hicks, California Research and Development Corp., Livermore, California, private communication.

and solvent are shown in Table I, together with their average deviations. These values were determined from the results obtained for the distribution ratios at different diketone activities,[8] according to equation 2. The calculations were made as previously reported,[1] allowing for the solubilities of the free diketones in 4 *M* perchloric acid, as given above. The activity coefficients used in determining [HK] and *R* were assumed to be equal to those given by King and Reas[9] for HTTA. This approximation probably involves a small error. The greatest error in this respect would be expected at the highest concentrations of diketone for the hafnium extractions using HITA in *n*-hexane, where both the reagent and solvent differ from those used in obtaining the activity coefficients. Even here the results are in good agreement with the expected straight line.

TABLE I

Diketone	Solvent	K'(Zr)	K'(Hf)
HTTA	C_6H_6	$1.5 \pm 0.2 \times 10^7$	$5.9 \pm 1.0 \times 10^5$
	o-$C_6H_6Cl_2$	$1.2 \pm .4 \times 10^6$	$7.5 \pm 1.2 \times 10^4$
HBTA	C_6H_6	$3.0 \pm .8 \times 10^5$	$1.7 \pm 0.3 \times 10^4$
HITA	C_6H_6	$1.4 \pm .2 \times 10^5$	$1.1 \pm .1 \times 10^4$
	n-C_6H_{14}	$5.2 \pm 1.0 \times 10^5$	$4.1 \pm 1.0 \times 10^4$

The data for [HK] and *R* are plotted in Figs. 1, 2 and 3. The straight lines are drawn with a slope of four and correspond to the average values found for the equilibrium constants. In only one case, that for zirconium extraction with HTTA in *o*-dichlorobenzene (Fig. 1), does the slope of the plotted data appear to be other than four. In this instance the slope appears to be greater than four, but since the corresponding data for hafnium extraction are in agreement with the expected slope it is likely that chance experimental deviations account for the result.

The separation factor (K'_{Zr}/K'_{Hf}) for HTTA-benzene, calculated from the average values given in the table, is 25. This is comparable to the factor previously found using 2 *M* perchloric acid.[1,3]

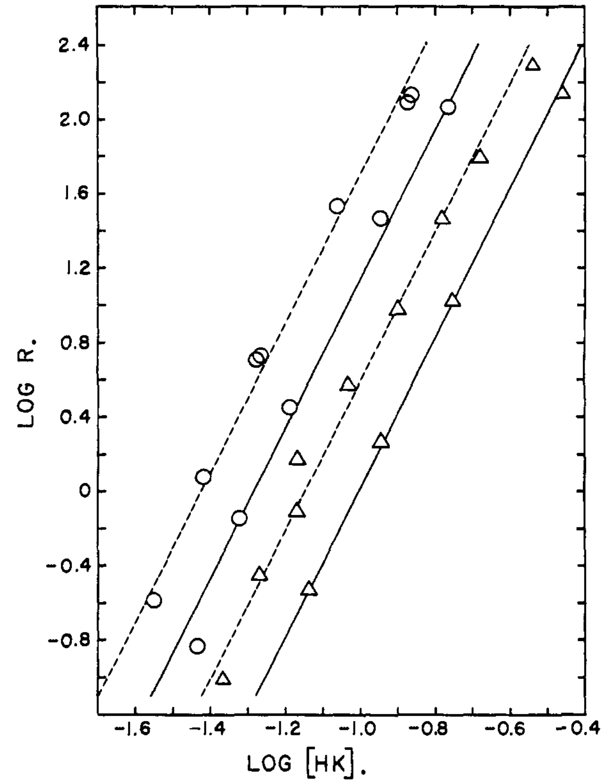

Fig. 3.—Dependence of distribution ratios on isovaleroyltrifluoroacetone activities: ○, zirconium; △, hafnium; solid lines, benzene; broken lines, *n*-hexane.

The separation factors for the other diketone–solvent pairs are all lower, being 16 for HTTA–*o*-dichlorobenzene, 18 for HBTA–benzene, 13 for HITA–benzene and 13 for HITA–*n*-hexane The distribution ratios for the extraction of the metal–ITA chelates into *n*-hexane are higher than those for extraction into benzene, though the reverse situation was found to hold for the diketones themselves. It has been shown[1] that these separation factors, obtained by extractions of the individual elements, can be used to determine the degree of separation when these elements are present together.

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[8] The complete data for calculating the equilibrium constants and for plotting the curves in the three figures are contained in Report UCRL 2536, obtainable from the Information Division, Radiation Laboratory, University of California, Berkeley. These data include the initial concentrations of diketone, the concentrations of the metal species in the aqueous and organic phases at equilibrium and the calculated values for the distribution ratios and diketone activities.

[9] E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1804 (1951).