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EXTRACTION OF ZIRCONIUM AND HAFNIUM WITH VARIOUS FLUORINATED β-DIKETONES

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ABSTRACT

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.

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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

(1) E. H. Huffman and L. J. Beaufait, J. Am. Chem. Soc., 71, 3179 (1949).

(2) B. G. Schultz and E. M. Larsen, J. Am. Chem. Soc., 72, 3610 (1950).

(3) E. M. Larsen and G. Terry, J. Am. Chem. Soc., 75, 1560 (1953).

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

(4) R. E. Connick and W. H. Reas, J. Am. Chem. Soc., 73, 1171 (1951).

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 is 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 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-naphthyltrifluoroacetone 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, n-hexane, stated by the manufacturer (Phillips Petroleum) to be 99 mole percent 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 acid to precipitate $Zr(Hf)OCl_2 \cdot 8H_2O$. Weighed amounts of 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.

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

(5) H. Liebhafsky and E. Winslow, J. Am. Chem. Soc., 60, 1776 (1938).

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-

(6) W. H. Reas, Thesis, University of California, 1948.

dichlorobenzene,[7] 0.979; HBTA-benzene,[7] >0.995.

(7) T. E. Hicks, California Research and Development Corp., Livermore, California, private communication.

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 the diketone. The mixtures were then 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 data obtained and the values calculated for the distribution ratios and equilibrium constants are given in Tables I and II. 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 in the tables were assumed to be equal to those given by King and Reas[8] for HTTA. This

(8) E. L. King and W. H. Reas, J. Am. Chem. Soc., 73, 1804 (1951).

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.

The data of Tables I and II are plotted in Figures 1, 2 and 3. The straight lines are drawn with a slope of four and corresponding to the average values found for the equilibrium constants. In only one case, that for zirconium extraction with HTTA in o-dichlorobenzene (Figure 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 tables, is 25. This is comparable to the factor previously found using 2 M perchloric acid.[1,3] The corresponding values 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.

This work was done under the auspices of the U. S. Atomic Energy Commission.

Table I

Zirconium

Diketone-Solvent	$(HK)_o$ moles/ℓ.	(M^{+4}) moles/ℓ.	(MK_4) moles/ℓ.	[HK] γ(moles/ℓ.)	R γ$(MK_4)/(M^{+4})$	K'
HTTA-benzene	0.0500	0.0352	0.00955	0.0115	0.269	1.6×10^7
	.0750	.0291	.0153	.0134	.521	1.6
	.100	.0212	.0204	.0177	.950	0.96
	.150	.00910	.0322	.0205	3.44	1.94
	.175	.00711	.0372	.0251	5.13	1.3
	.225	.00175	.0466	.0363	25.8	1.5
	.250	.000348	.0480	.0542	131	1.5
	.250	.000150	.0435	.0702	300	1.2
						1.5 Ave.
HTTA-o-$CL_2\Phi$	0.0500	0.0280	0.00650	0.0231	0.228	0.80×10^6
	.100	.0183	.0162	.0335	.859	0.68
	.150	.00819	.0260	.0433	3.05	0.87
	.200	.00149	.0328	.0637	20.8	1.3
	.225	.000500	.0344	.0800	64.3	1.6
	.250	.000132	.0346	.103	242	2.2
						1.2 Ave.
HBTA-benzene	0.0493	0.0371	0.00515	0.0280	0.136	2.2×10^5
	.100	.0284	.0143	.0413	.486	1.7
	.140	.0184	.0234	.0445	1.22	3.1
	.197	.00709	.0324	.0637	4.32	2.6
	.240	.00201	.0387	.0797	18.0	4.5
	.300	.000504	.0408	.124	73.5	3.1
	.340	.000154	.0415	.156	241	4.1
						3.0 Ave.

Table I, cont.

Diketone-Solvent	$(HK)_o$ moles/ℓ.	(M^{+4}) moles/ℓ.	(MK_4) moles/ℓ.	[HK] γ(moles/ℓ.)	R γ(MK_4)/(M^{+4})	K'
HITA-benzene	0.0579	0.0316	0.00481	0.0371	0.147	0.78×10^5
	.116	.0218	.0165	.0474	.725	1.4
	.186	.00978	.0292	.0647	2.82	1.6
	.278	.00117	.0382	.113	29.8	1.8
	.348	.000285	.0383	.171	119	1.4
						1.4 Ave.
HITA-n-hexane	0.0600	0.0285	0.00761	0.0282	0.261	4.1×10^5
	.120	.0159	.0198	.0384	1.21	5.5
	.180	.00530	.0303	.0547	5.45	6.1
	.180	.00580	.0309	.0526	5.10	6.7
	.240	.000983	.0360	.0871	34.1	5.9
	.300	.000240	.0360	.137	135	3.9
	.300	.000271	.0373	.133	124	4.0
						5.2 Ave.

Table II

Hafnium

Diketone-Solvent	$(HK)_o$ moles/ℓ.	(M^{+4}) moles/ℓ.	(MK_4) moles/ℓ.	[HK] γ(moles/ℓ.)	R γ$(MK_4)/(M^{+4})$	K'
HTTA-benzene	0.0400	0.0379	0.00405	0.0229	0.105	3.8×10^5
	.0700	.0337	.0104	.0272	.302	5.5
	.140	.0158	.0246	.0392	1.51	6.4
	.170	.00950	.0300	.0470	3.03	6.2
	.180	.00825	.0315	.0506	3.65	5.6
	.190	.00660	.0330	.0541	4.76	5.6
	.200	.00482	.0335	.0612	6.59	4.7
	.230	.00206	.0390	.0675	17.8	8.6
	.250	.00104	.0375	.0908	33.6	4.9
	.300	.000255	.0417	.119	150	7.5
						5.9 Ave.
HTTA-o-$Cl_2\Phi$	0.0500	0.0366	0.00400	0.0324	0.106	9.6×10^4
	.100	.0291	.0115	.0506	.378	5.8
	.125	.0251	.0170	.0532	.646	8.1
	.150	.0198	.0214	.0598	1.02	8.0
	.200	.0106	.0272	.0833	2.40	5.0
	.250	.00398	.0346	.101	8.02	7.7
	.400	.000240	.0401	.206	147	8.2
						7.5 Ave.
HBTA-benzene	0.100	0.0347	0.00766	0.0656	0.209	1.1×10^4
	.200	.0174	.0246	.0942	1.31	1.7
	.250	.0106	.0314	.114	2.71	1.6

Table II, cont.

Diketone-Solvent	$(HK)_o$ moles/ℓ.	(M^{+4}) moles/ℓ.	(MK_4) moles/ℓ.	[HK] γ(moles/ℓ.)	R γ$(MK_4)/(M^{+4})$	K'
HBTA-benzene (cont.)	0.340	0.00248	0.0392	0.163	14.1	2.0×10^4
	.400	.000978	.0403	.209	36.0	1.9
	.440	.000672	.0393	.244	50.5	1.4
	.500	.000277	.0432	.279	133	2.2
						1.7 Ave.
HITA-benzene	0.116	0.0300	0.00952	0.0717	0.298	1.1×10^4
	.232	.0135	.0272	.112	1.84	1.2
	.348	.00310	.0370	.175	10.6	1.1
	.579	.000245	.0405	.344	138	0.99
						1.1 Ave.
HITA-n-hexane	0.0600	0.0348	0.00348	0.0432	0.0961	2.8×10^4
	.104	.0306	.0115	.0539	.358	4.3
	.156	.0240	.0201	.0695	.789	3.4
	.180	.0167	.0264	.0677	1.48	7.0
	.240	.00845	.0345	.0922	3.78	5.2
	.300	.00382	.0394	.126	9.37	3.7
	.364	.00133	.0435	.165	29.1	3.9
	.416	.000615	.0432	.207	61.5	3.3
	.520	.000190	.0440	.286	197	3.0
						4.1 Ave.

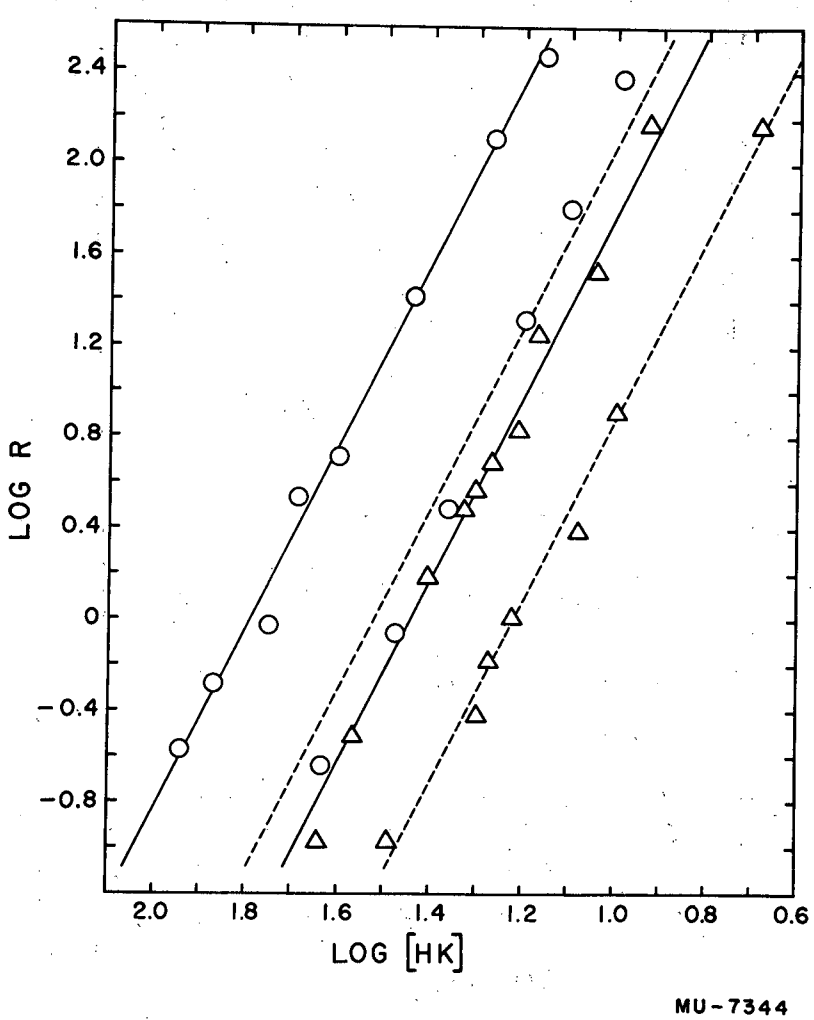

Figure 1. Dependence of distribution ratios on 2-thenoyltrifluoroacetone activities: O, zirconium; Δ, hafnium; solid lines, benzene; broken lines, o-dichlorobenzene.

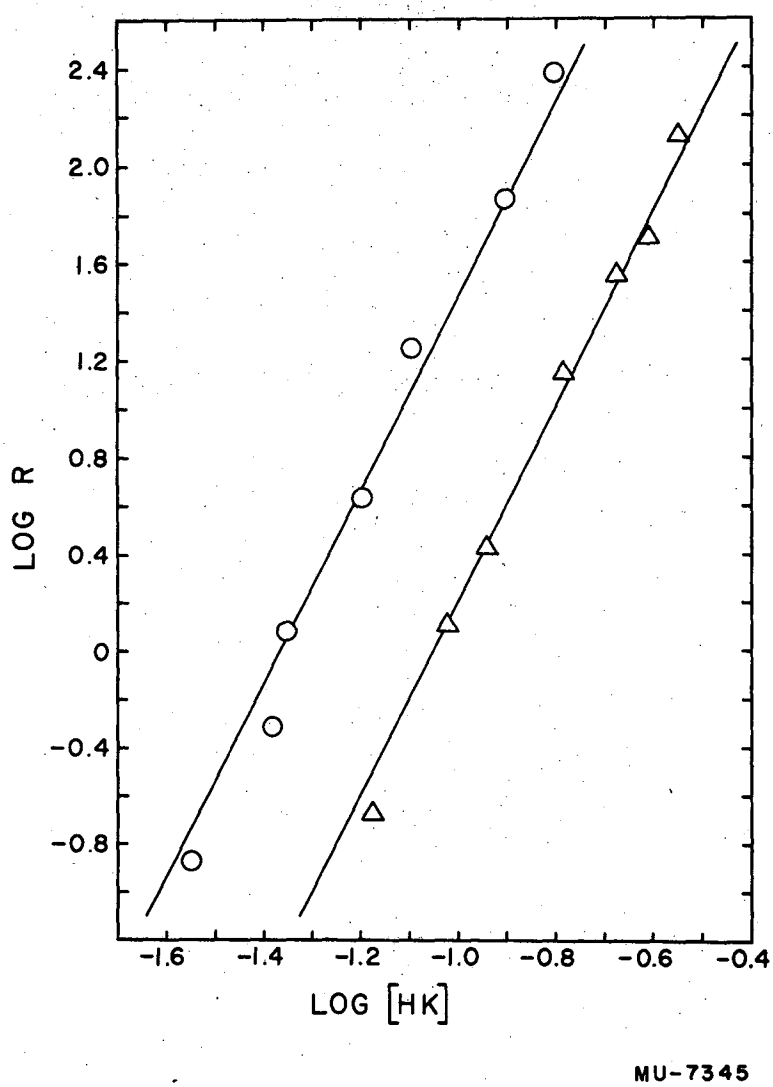

Figure 2. Dependence of distribution ratios on benzoyltrifluoroacetone activities in benzene: O, zirconium; △, hafnium.

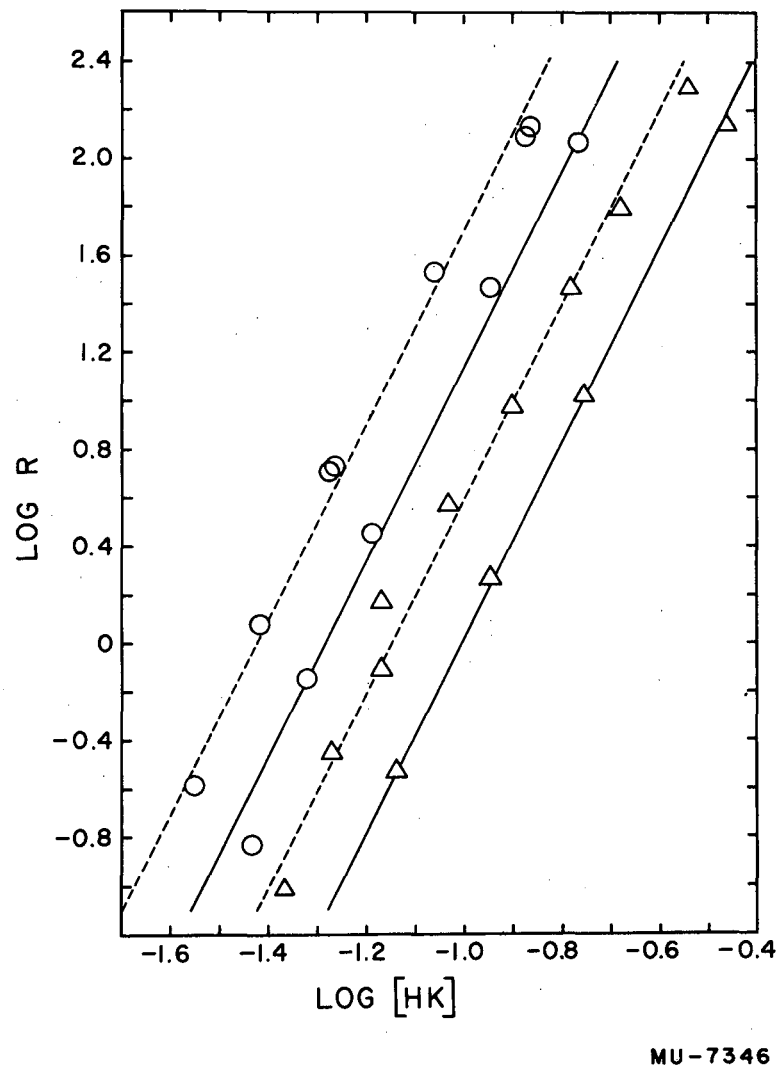

Figure 3. Dependence of distribution ratios on isovaleroyltrifluoroacetone activities: O, zirconium; Δ, hafnium; solid lines, benzene; broken lines, n-hexane.