Contribution from the Department of Chemistry,
The University of Wisconsin, Madison, Wisconsin

The Kinetics of the Ligand Exchange between Zirconium, Hafnium, and Thorium Chelates and Free β-Diketones Measured by Nuclear Magnetic Resonance

By A. C. ADAMS[1] and EDWIN M. LARSEN

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The exchange reactions of zirconium and hafnium trifluoroacetylacetonates with the free ligand in benzene and chlorobenzene and of the metal acetylacetonates with the free ligand in chlorobenzene are first order in both metal complex and free ligand. The acetylacetone exchange in benzene has a different rate law. The order with respect to the metal complex is one; however, the order with respect to the free ligand increases as the acetylacetone concentration increases. Rates for acetylacetone exchange in benzene and chlorobenzene are faster for zirconium than for hafnium; however, for the trifluoroacetylacetone ligands, the exchange rates are essentially the same for both metals. The exchange for thorium is faster than for zirconium or hafnium. The activation parameters are similar for all of the systems studied except for the exchange of acetylacetone in benzene. A mechanism for the ligand exchange is proposed.

Neither the kinetics of the ligand exchange between coordinated and free β-diketones nor the kinetics of the ligand exchange reactions in compounds with a coordination number of eight have been extensively studied. Johnson and Larsen[2] used C^{14}-labeled oxalate to show that oxalate exchange in the tetraoxalato complexes of uranium, zirconium, and hafnium was complete within a few minutes. The kinetics of the exchange was not studied because the reactions were too rapid. Except for the oxalate exchange, the kinetic data for octacoordinate complexes is confined to the octacyano complexes of molybdenum and tungsten.[3–5] Apparently, kinetic studies of the ligand exchange between coordinated and free β-diketones have not been previously reported. The present paper describes such a study. The compounds used are the acetylacetone and trifluoroacetylacetone complexes of zirconium, hafnium, and thorium. For the zirconium and hafnium compounds the rate of exchange is such that the reaction can be followed by using high-resolution nmr techniques. The exchange has been studied in benzene and chlorobenzene solutions as a function of temperature and concentration.

Experimental Section

Materials.—Tetrakis(2,4-pentanediono) and tetrakis(1,1,1-trifluoro-2,4-pentanediono) complexes were prepared by the method of Larsen, Terry, and Leddy.[6] (Hereafter, the common names and symbols of the ligands, *i.e.*, acetylacetone, acac, and trifluoroacetylacetone, tfac, will be used.) The purity of the compounds was checked by metal analyses and melting points.[6] The infrared and nmr spectra of the acetylacetone (Eastman Organic Chemicals) and trifluoroacetylacetone (Columbia Organic Chemicals Co., Inc.) had only the expected absorptions. The solvents were distilled and stored over drying agents (sodium metal or calcium hydride) prior to being used. All of the chemicals used were colorless.

Measurement of Nmr Spectra.—The nmr spectra were obtained with a Varian Associates Model A-60 spectrometer using standard Varian accessories. The temperature scale was calibrated using the manufacturer's recommended procedure. The spectra were recorded at least twice and usually three or more times. Saturation effects were avoided by using a low radiofrequency field. Also, the spectra were recorded at a low sweep rate (0.1 cps/sec). The chemical shifts of the metal complexes have been reported.[7]

Keto–Enol Equilibria.—Acetylacetone and trifluoroacetylacetone exist as keto and enol isomers. The kinetic studies show that only the exchange of the enol isomer is important. This is apparent from the keto methyl proton resonance of acetylacetone. This resonance (at −1.71 ppm downfield from tetramethylsilane) is a triplet with a splitting of 0.008 ppm. The triplet structure, which results from spin coupling with the two methylene protons, is preserved in all of the kinetic studies (for example, see Figure 1). If the keto isomer was exchanging at an appreciable rate, the spin coupling would be destroyed and the triplet would collapse to a single resonance. Since this is not observed, it is concluded that any exchange of the keto isomer is very slow.

The fraction of the β-diketone in the enol isomer has been measured from the areas of the keto and enol methyl resonances. This fraction is 0.90 for benzene solutions at 34° which are 0.04 to 1.30 *M* in acetylacetone, and it is 0.91 for a 0.88 *M* solution of acetylacetone in chlorobenzene. In benzene, the fraction of the enol isomer increases to 0.92 at 10°; at 70°, the fraction decreases to 0.86. The values 0.90 and 0.91 are used in the calculations. The error introduced by this approximation is small. It is assumed that all of the trifluoroacetylacetone is present as the enol isomer. This assumption is supported by nmr studies of pure trifluoroacetylacetone[8] and by bromine titrations of benzene solutions[9] which show that at least 97% of the trifluoroacetylacetone is in the enol isomer.

Preparation of Samples.—To determine the form of the rate law, two series of samples were prepared for each system studied. In one series the concentration of the metal complex was varied, and the concentration of the free ligand remained constant. In the other series the metal chelate concentration remained constant and the free ligand concentration varied. Each series contained at least eight nmr samples. Usually the concentration of the free ligand ranged from 0.05 to 0.80 *M*, and the concentration of the metal chelate ranged from 0.02 to 0.15 *M*. A par-

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(1) Predoctoral National Science Foundation Fellow, Sept 1961 to Jan 1965. This article is based on a dissertation submitted by A. C. Adams in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

(2) F. A. Johnson and E. M. Larsen, *Inorg. Chem.*, **1**, 159 (1962).

(3) A. W. Adamson, J. P. Welker, and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).

(4) H. Baadsgaard and W. D. Treadwell, *Helv. Chim. Acta*, **38**, 1669 (1955).

(5) V. Carassiti, A. M. Marinangeli, and V. Balzani, *Ann. Chim.* (Rome), **50**, 790 (1960).

(6) E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).

(7) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).

(8) J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

(9) J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950).

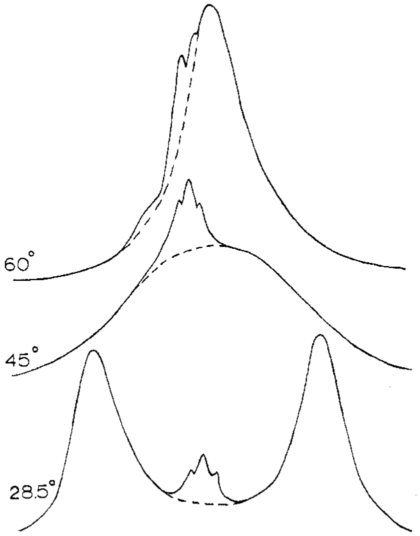

Figure 1.—The methyl resonances of a benzene solution of $Hf(acac)_4$ and acetylacetone; $[HL]_{enol} = 0.792$ *M*. The dashed line shows the resonances after subtracting the keto acetylacetone resonance.

ticular series of samples was prepared by accurately measuring the amounts of the variable reactant (the metal complexes were weighed and the free ligands were measured with micropipets). Each sample in the series was dissolved in 0.996 ml of a freshly prepared stock solution containing a known concentration of the other reactant. The samples were made up to a constant volume by adding pure solvent. The constant volume was found by summing the volumes of the individual components of the solution. The densities used in calculating the sample volume were taken from the literature.[10] Independent experiments show that the assumption of additive volumes introduces less than 1% error in the concentrations.

In the initial experiments with the chlorobenzene solutions of $Zr(acac)_4$, it was observed that the methyl resonance broadened as the temperature decreased. At about 10° two separate resonances, whose chemical shifts were the same as those of $Zr(acac)_4$ and acetylacetone, could be resolved. When the solutions were prepared in a dry atmosphere, the acetylacetone resonance was not observed. It was assumed that small amounts of water in the chlorobenzene reacted with $Zr(acac)_4$ to produce acetylacetone. Consequently, all subsequent samples containing chlorobenzene were prepared in a dry atmosphere. Similar effects were observed for benzene solutions if the benzene was not dried over sodium metal. After drying the benzene, no difference was detected between solutions prepared in a dry atmosphere and in the open air. Apparently, the rate at which benzene absorbs water from the atmosphere is slow compared to the time required to prepare and run the samples.

In addition to running the eight samples in a particular series, spectra of solutions of the pure metal complex and pure ligand were also obtained. These samples were run before and after running each sample in a given series. This procedure ensured the detection of any change in the magnetic field during the course of a run. Samples for studies on the temperature dependence of the exchange rate were prepared so that the concentration of the enol isomer of the free ligand was four times the concentration of the metal complex.

Results and Discussion

Tabulation of Data.—The reciprocal of the average lifetimes of the coordinated and the free ligands, $(\tau_{ML_4})^{-1}$ and $(\tau_{HL})^{-1}$, are given in Tables I and II. The values have been calculated from the nmr spectra by using the slow-exchange approximation[11-13]

$$(\tau_{HL})^{-1} = (T_2'_{HL})^{-1} - (T_{2,HL})^{-1} \tag{1}$$

$$(\tau_{ML_4})^{-1} = (T_2'_{ML_4})^{-1} - (T_{2,ML_4})^{-1} \tag{2}$$

where $(T_2'_{HL})^{-1}$ is the observed half-width at half-maximum of the free-ligand resonance, and $(T_{2,HL})^{-1}$ is the corresponding width for a solution of pure free ligand where exchange is not possible. Similar definitions are used for the quantities in eq 2. The values of the average lifetime have been calculated from the width of the methyl resonance of the reactant whose concentration remained constant. The width of the resonance of the varying reactant was not measured because of the large uncertainty at low concentrations.

TABLE I

RATE OF EXCHANGE FOR ZIRCONIUM COMPLEXES AT 34°

$10^3[ML_4]$, *M*	$(\tau_{HL})^{-1}$, sec^{-1}	$10^3[HL]_T$, *M*	$(\tau_{ML_4})^{-1}$, sec^{-1}
Ligand, tfac; Solvent, C_6H_5Cl			
$[HL]_T = 0.360$ *M*		$[ML_4] = 0.077$ *M*	
23	0.6	37	0.3
39	1.6	75	0.3
58	2.8	149	1.0
60	2.8	187	1.3
81	3.8	298	2.9
95	4.1	373	3.5
113	5.0	448	3.2
137	5.0	634	4.7
Ligand, tfac; Solvent, C_6H_6			
$[HL]_T = 0.371$ *M*		$[ML_4] = 0.076$ *M*	
25	0.6	75	0.8
51	1.3	149	1.3
69	1.9	187	1.6
95	2.5	298	3.8
113	2.8	373	4.1
126	3.0	448	4.7
136	3.5	634	6.6
156	3.8	746	7.9
Ligand, acac; Solvent. C_6H_6			
$[HL]_T = 0.439$ *M*		$[ML_4] = 0.056$ *M*	
20	0.6	89	2.8
60	2.2	178	3.5
85	3.5	222	3.5
105	4.3	356	3.6
119	5.0	445	3.8
142	6.3	534	3.6
160	6.3	756	5.4
177	7.6	890	5.5

Ligand, acac; Solvent, C_6H_5Cl

$10^3[ML_4]$, *M*	$10^3[HL]_T$, *M*	τ^{-1}, sec^{-1}
21	92	21.4
42	184	36.8
60	266	43.6
81	358	66.2

The nmr spectra of chlorobenzene solutions at 34° containing $M(acac)_4$ and acetylacetone have a single

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[10] The densities in g/ml are: $Zr(acac)_4$, 1.416; $Hf(acac)_4$, 1.691; $Zr(tfac)_4$, 1.729; and $Hf(tfac)_4$, 1.863; taken from ref 6. Acetylacetone, 0.976; benzene, 0.879; and chlorobenzene, 1.107; taken from the "Handbook of Chemistry and Physics," 36th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1955. Trifluoroacetylacetone, 1.26; measured in this laboratory; ref 9 gives 1.27.

[11] A. Loewenstein and T. M. Conner, *Ber. Bunsenges. Physik. Chem.*, **67**, 280 (1963).

[12] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 218–230.

[13] R. E. Richards, *Advan. Spectry.*, **2**, 101 (1961).

Table II

Rate of Exchange for Hafnium Complexes at 34°

$10^3[ML_4]$, *M*	$(\tau_{HL})^{-1}$, sec^{-1}	$10^3[HL]_T$, *M*	$(\tau_{ML_4})^{-1}$, sec^{-1}
Ligand, tfac; Solvent, C_6H_5Cl			
$[HL]_T = 0.387$ *M*		$[ML_4] = 0.067$ *M*	
12	0.5	75	1.6
27	1.7	149	1.4
38	1.9	187	2.5
53	3.2	298	3.1
63	3.2	373	4.6
79	3.6	447	6.0
85	3.6	634	6.4
98	4.7	745	9.1
Ligand, tfac; Solvent, C_6H_6			
$[HL]_T = 0.387$ *M*		$[ML_4] = 0.066$ *M*	
25	1.1	75	0.9
37	1.4	149	1.6
46	1.9	187	1.9
60	2.2	298	3.3
72	2.5	373	4.1
84	2.7	448	5.0
100	3.1	634	5.5
111	3.8	747	6.3
Ligand, acac; Solvent, C_6H_6			
$[HL]_T = 0.439$ *M*		$[ML_4] = 0.067$ *M*	
22	0.6	89	1.7
44	1.1	163	1.7
68	2.1	178	1.7
92	2.7	222	1.7
105	3.3	326	1.7
123	4.2	356	1.9
137	4.2	408	1.9
152	5.2	408	1.9
		445	1.7
		489	1.7
		489	2.1
		534	2.1
		693	2.5
		693	2.8
		756	2.7
		815	2.7
		979	2.7
		979	3.1
		1142	3.3
		1305	3.6

Ligand, acac; Solvent, C_6H_5Cl

$10^3[ML_4]$, *M*	$10^3[HL]_T$, *M*	τ^{-1}, sec^{-}
35	151	14.9
51	223	19.5
69	305	25.4

broad methyl resonance formed by the coalescence of the methyl resonances of the metal complex and the enol isomer of acetylacetone. The rate of exchange in this case is calculated from the width of the resonance by using the fast-exchange approximation[12]

$$(T_2')^{-1} = (p_{HL}/T_{2,HL}) + (p_{ML_4}/T_{2,ML_4}) + (p_{HL}p_{ML_4})^2(\delta\omega)^2(\tau_{HL} + \tau_{ML_4}) \quad (3)$$

In this equation, $(T_2')^{-1}$ is the half-width at half-maximum of the coalesced resonance. The fractional populations of the free ligand and the metal complex are p_{HL} and p_{ML_4}. The separation of the resonances when exchange is not occurring is $\delta\omega$. The value of $\delta\omega$, measured at $-1°$, is 14.45 radians/sec. It is convenient to define a new average lifetime as

$$\tau^{-1} = (\tau_{HL})^{-1} + (\tau_{ML_4})^{-1} \quad (4)$$

The values of τ^{-1} for the acetylacetone exchange in chlorobenzene are given in Tables I and II.

When temperature is a variable, the average lifetimes, τ, have been obtained from the nmr spectra by comparing the experimental spectra with spectra calculated using assumed values of τ^{11}. The proper value of τ is obtained when two curves with the same shape are found. It is convenient to have some means of interpolating between the calculated curves. For curves with two resonances, the ratio of the intensity at the signal maximum to the intensity at the central minimum is measured from the calculated curves and is plotted *vs.* τ. The experimental value of τ is obtained from the graph by using the experimental value of the intensity ratio. For the calculated curves with a single resonance, a similar procedure is used by plotting the full width at half-maximum *vs.* τ. The shapes of the spectra have been calculated from the equations of Rogers and Woodbrey.[14] The values of τ as a function of temperature are given in Table III.

Table III

Values of τ^a at Different Temperatures

Ligand, tfac; Solvent, C_6H_5Cl; $[HL]_{enol} = 0.392$ *M*; $[ML_4] = 0.0981$ *M*							
T, °K	313	318	323	328	333	343	353
$10^2\tau$ (Zr)	4.92	2.66	2.49	1.53	1.23	0.76	...
$10^2\tau$ (Hf)	4.75	3.04	2.39	...	1.45	0.82	0.46
Ligand, tfac; Solvent, C_6H_6; $[HL]_{enol} = 0.392$ *M*; $[ML_4] = 0.0981$ *M*							
T, °K	313	318	323	328	333	343	
$10^2\tau$ (Zr)	7.05	4.45	3.89	2.80	2.22	1.24	
10^2 (Hf)	6.88	5.37	4.22	3.05	2.32	1.26	
Ligand, acac; Solvent, C_6H_5Cl; $[HL]_{enol} = 0.161$ *M*; $[ML_4] = 0.0353$ *M*							
T, °K	269	272	282	292	296		
$10^2\tau$ (Zr)	106.5	75.4	42.2	22.9	16.8		
$10^2\tau$ (Hf)	...	127.5	48.6	27.0	18.8		
Ligand, acac; Solvent, C_6H_6; $[HL]_{enol} = 0.250$ *M*; $[ML_4] = 0.0611$ *M*							
T, °K	313	318	323	328	333	343	
$10^2\tau$ (Zr)	6.78	4.33	3.50	2.45	1.52	0.89	
$10^2\tau$ (Hf)	11.25	8.95	6.08	4.57	3.18	1.61	
Ligand, acac; Solvent, C_6H_6; $[HL]_{enol} = 0.792$ *M*; $[ML_4] = 0.199$ *M*							
T, °K	293	298	302	313	318	323	333
$10^2\tau$ (Zr)	12.75	8.15	5.80	1.68	1.15	0.75	0.32
$10^2\tau$ (Hf)	19.20	13.22	9.68	3.23	2.02	1.48	0.74

[a] The units of τ: seconds.

In benzene solution, the methyl resonance of M$(acac)_4$ and the enol methyl resonance of acetylacetone collapse at the higher temperatures to give a broad peak which coincides with the keto resonance. This is shown in Figure 1. Since the keto resonance can be easily subtracted, it does not interfere with the determination of τ.

Treatment of Data.—The order of the exchange reac-

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(14) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

tions has been obtained by fitting the data in Tables I and II to eq 5

$$4[\mathrm{ML_4}](\tau_{\mathrm{ML_4}})^{-1} = [\mathrm{HL}]_{\mathrm{enol}}(\tau_{\mathrm{HL}})^{-1} = k[\mathrm{ML_4}]^{n_{\mathrm{ML_4}}}[\mathrm{HL}]_{\mathrm{enol}}^{n_{\mathrm{HL}}} \quad (5)$$

where $[\mathrm{HL}]_{\mathrm{enol}}$ and $[\mathrm{ML_4}]$ are the molar concentrations of the enol isomer of the free ligand and the metal complex. Equation 5 is discussed in detail by Loewenstein and Connor.[11] The order of the exchange is obtained from the slope of the straight line formed by plotting the logarithm of $(\tau_{\mathrm{ML_4}})^{-1}$ or $(\tau_{\mathrm{HL}})^{-1}$ *vs.* the logarithm of [HL] or $[\mathrm{ML_4}]$. Except for the acetylacetone exchange, straight lines with a slope of approximately 1 were obtained. For acetylacetone in chlorobenzene only the over-all order of the exchange can be determined because the concentrations of the coordinated and the free ligands are equal. The over-all order, $n_{\mathrm{ML_4}} + n_{\mathrm{HL}}$, is calculated from the slope of the line formed by plotting the logarithm of τ^{-1} *vs.* the logarithm of $[\mathrm{HL}]_{\mathrm{enol}}$. The values of $n_{\mathrm{ML_4}}$ and n_{HL} are listed in Table IV. The exchange reactions for the trifluoroacetylacetone ligand are first order with respect to the metal chelate and the free ligand. For the acetylacetone exchange in chlorobenzene, the over-all order is nearly 2; it seems reasonable to conclude that this reaction is first order with respect to both the metal complex and the free ligand.

TABLE IV

RESULTS OF THE KINETIC STUDIES AT 25°

Metal	Ligand	Solvent	$n_{\mathrm{ML_4}}$[a]	n_{HL}[a]	k[b]	ΔH^*[c]	ΔS^*[d]
Zr	tfac	C_6H_5Cl	1.1	1.1	49	11.4	−13
Hf	tfac	C_6H_5Cl	1.0	0.8	38	11.7	−12
Zr	tfac	C_6H_6	1.0	1.1	31	11.1	−15
Hf	tfac	C_6H_6	0.8	0.9	25	11.9	−13
Zr	acac	C_6H_5Cl	$n_T = 1.8$[e]		87	9.7	−17
Hf	acac	C_6H_5Cl	$n_T = 1.8$		78	11.3	−12
Zr[g]	acac	C_6H_6	1.1		10[f]	14.0	−7
Zr[h]	acac	C_6H_6	1.1		18[b]	18.4	+9
Hf[g]	acac	C_6H_6	1.1		6[f]	13.5	−10
Hf[h]	acac	C_6H_6	1.1		13[b]	17.7	+6

[a] ±0.2. [b] In M^{-1} sec^{-1}; ±15%. [c] In kcal/mole; ±10%. [d] In cal/mole deg; ±6. [e] $n_T = n_{\mathrm{ML_4}} + n_{\mathrm{HL}}$. [f] In sec^{-1}. [g] The values on this line are for the first-order term. [h] The values on this line are for the second-order term.

The data for the acetylacetone exchange in benzene, plotted in Figure 2, are satisfactorily described by the rate equation

$$4[\mathrm{ML_4}](\tau_{\mathrm{ML_4}})^{-1} = [\mathrm{HL}]_{\mathrm{enol}}(\tau_{\mathrm{HL}})^{-1} = k_1[\mathrm{ML_4}] + k_2[\mathrm{ML_4}][\mathrm{HL}]_{\mathrm{enol}} \quad (6)$$

As indicated in Figure 2, three different series of samples, each using a different preparation of the metal complex, were run for the Hf(acac)$_4$–H(acac) system. In one series (indicated by the solid circle) the samples were prepared in a dry atmosphere to exclude the possibility of the benzene absorbing small amounts of water. Since all three of the series gave the same curve, the different rate law for this system is not caused by small amounts of water in the samples.

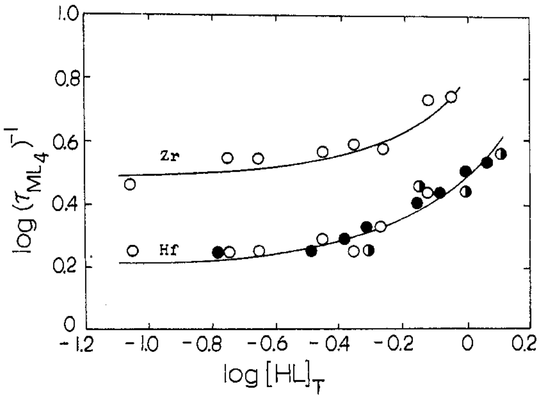

Figure 2.—Log $(\tau_{\mathrm{ML4}})^{-1}$ *vs.* log $[\mathrm{HL}]_{\mathrm{T}}$ for acetylacetone exchange in benzene at 34°. The different symbols for the hafnium curve represent kinetic runs using different preparations of Hf(acac)$_4$.

In principle, the data in Tables I and II can be used to calculate values of the rate constant. However, these values would have a very large uncertainty. In particular there are: (1) the errors introduced by using an approximation to obtain the lifetimes, (2) experimental error in the measurement of the line widths, and (3) error caused by obtaining the average lifetime by difference. Since more accurate values of τ can be calculated from the temperature dependence of the exchange rate, the data in Tables I and II have not been used to calculate k. The values of the rate constant at 25° (listed in Table IV) have been obtained from plots of the log (k/T) *vs.* $1/T$ by interpolation or short linear extrapolations. The enthalpies and entropies of activation have also been found by plotting log (k/T) *vs.* $1/T$. The activation parameters for the first-order term in eq 6 have been obtained by studying the exchange at $[\mathrm{HL}]_{\mathrm{enol}} = 0.250$ M. Figure 2 shows that at this concentration the exchange is essentially zero order with respect to free ligand; however, a calculation using the rate constants shows that 25–35% of the exchange still occurs through the second-order path. The error in these activation parameters is large because the reaction could not be studied at a concentration where exchange did not occur through the second-order path. The activation parameters for the second-order path have been found by studying the exchange at $[\mathrm{HL}]_{\mathrm{enol}} = 0.792$ M. The contribution due to the first-order term has been subtracted.

The uncertainties in the values of the activation parameters and the rate constants have been calculated from the deviation of the points about the lines in the log (k/T) *vs.* $1/T$ plots. It has been shown that, in addition to random errors, the high-resolution techniques may be subject to systematic errors.[15] The most important systematic error is the temperature dependence of the separation between the resonances. It has been assumed that this separation is independent of temperature although chemical shift data indicate that a 60° change in temperature may change the

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(15) A. Allerhand and H. S. Gutowsky, *J. Chem. Phys.*, **41**, 2115 (1964).

separation by 0.08 ppm.[16] To determine the effect of this change on the values of ΔH^*, the data for the acetylacetone exchange in benzene (at $[\mathrm{HL}]_{\mathrm{enol}} = 0.250$ M) have been recalculated after decreasing the value of the separation from 0.207 to 0.155 ppm. The value of ΔH^* decreased to 12.3 kcal/mole. This deviation of 12% from the value given in Table IV probably represents the maximum error in ΔH^* since in reality the separation should change gradually as the temperature changes. The error caused by the above assumption would seem to be within the experimental error quoted in Table IV.

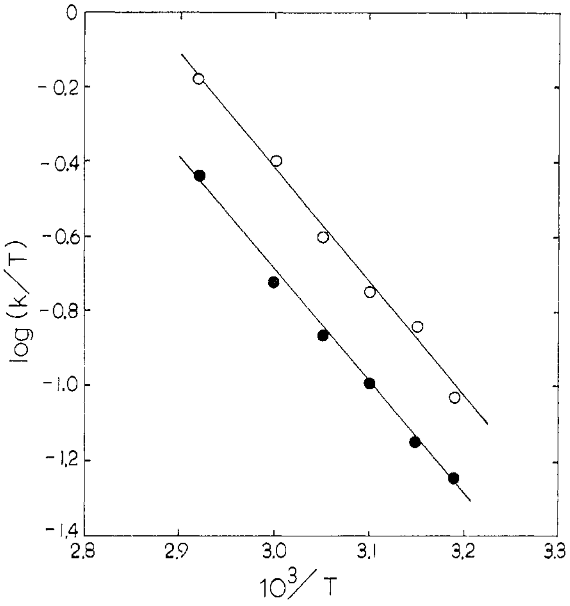

Figure 3.—Log (k/T) *vs.* $1/T$ for acetylacetone exchange in benzene; $[\mathrm{HL}]_{\mathrm{enol}} = 0.250$ M: ○, Zr; ●, Hf.

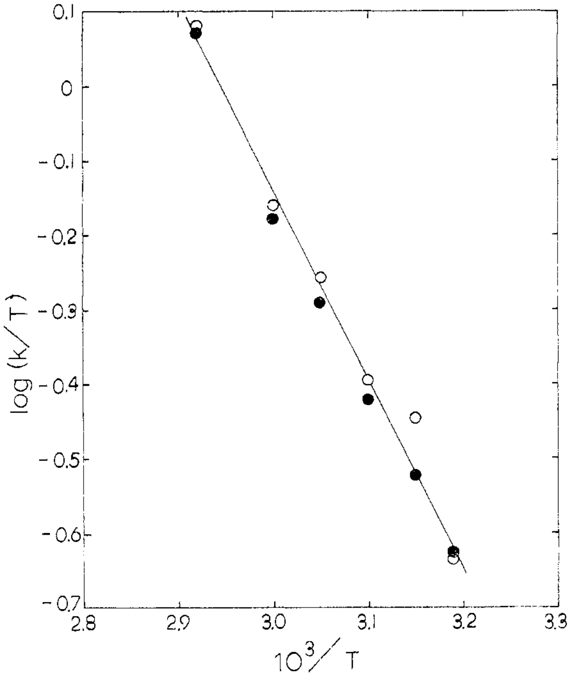

Figure 4.—Log (k/T) *vs.* $1/T$ for trifluoroacetylacetone exchange in benzene: ○, Zr; ●, Hf.

Exchange in the Th(acac)$_4$–Acetylactone System.—The spectrum of a benzene solution of Th(acac)$_4$ and acetylacetone contains two resonances at -5.16 and -1.71 ppm. These resonances represent the average environment of the CH and the methyl protons. The resonance at -1.71 ppm also contains the methyl resonance of the keto isomer of acetylacetone. Since the peak widths do not vary within the concentration range studied, the rate law for this system has not been determined. However, a lower limit for the rate constant has been calculated by using the inequality[12]

$$\tau(\delta\omega) < 0.5 \qquad (7)$$

For the CH protons, $\delta\omega$ is 81.8 radians/sec. Therefore, τ is less than 0.00611 sec. The concentrations at which the reaction has been studied are $[\mathrm{ML}_4] = 0.25[\mathrm{HL}]_{\mathrm{enol}} = 0.125$ M. If the over-all order of the exchange is 1 (first order in metal complex), then k is greater than 325 sec^{-1}. However, if the exchange is first order in metal complex and in free ligand, then k is greater than 650 M^{-1} sec^{-1}.

Comparison of the Exchange Rates.—It is interesting to compare the exchange rates for the different metal complexes. Obviously, the exchange is faster for thorium than for zirconium or hafnium. The rates for the zirconium and hafnium compounds are similar; however, the data in Table III and Figure 3 show that for acetylacetone exchange in benzene the rate is faster for zirconium than for hafnium. Figure 3 shows that at a given temperature the value of log (k/T) is less for hafnium than for zirconium. Therefore, the rate of exchange is faster for zirconium. The data for the acetylacetone exchange in benzene at $[\mathrm{HL}]_{\mathrm{enol}} = 0.792$ M lead to the same conclusion. The trifluoroacetylacetone ligands exchange at the same rate for the zirconium and hafnium compounds. This is illustrated in Figure 4 in which the values of log (k/T) at a given temperature are the same for zirconium and hafnium.

Exchange Mechanism.—A possible mechanism for the exchange path which is first order in both metal complex and free ligand is shown in Figure 5. It does not seem reasonable to speculate on the more complex situation found for the acetylacetone exchange in benzene. The first step, the rapid breaking and re-forming of one of the metal–oxygen bonds, has been proposed by other workers to explain the intramolecular ligand exchange in tris-β-diketone complexes.[17] In the present case, the rapid equilibrium explains the fact that geometric isomers of the compounds are not observed. The remaining steps in the exchange are: the reaction of the seven-coordinate species with the free ligand; the exchange of a hydrogen atom; the loss of a ligand to give again a seven-coordinate species; and the formation of a metal–oxygen bond to give the eight-coordinate complex. In this mechanism the proton exchange

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[16] The chemical shifts of the methyl resonances of H(acac) and Zr(acac)$_4$ in benzene are -1.61 and -1.82 at 10° and -1.68 and -1.81 at 70° (the chemical shifts are in ppm relative to tetramethylsilane). This system has the maximum change in the separation.

[17] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

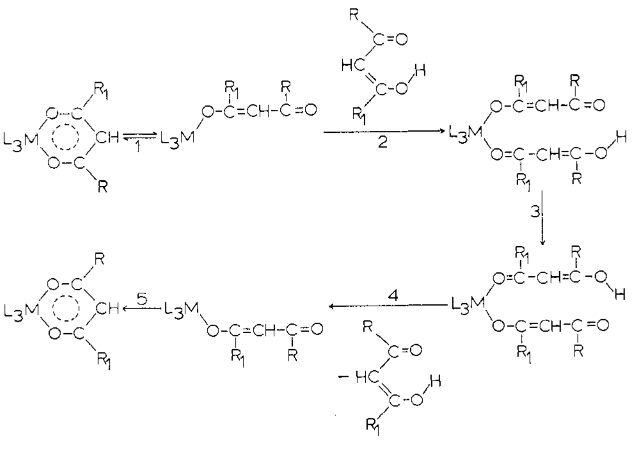

Figure 5.—Exchange mechanism, where L represents either acetylacetone or trifluoroacetylacetone.

occurs while the hydrogen is bonded to an oxygen and while both the entering and the leaving ligands are bonded to the metal. Previous work indicates that the proton exchange takes place while the hydrogen is bonded to an oxygen atom rather than to a carbon atom.[18] Because of the large mass difference between zirconium and hafnium, it is expected that the exchange should be faster for zirconium provided that the rate-determining step is the breaking of a metal–oxygen bond (as in step 4). The nmr data show that the acetylacetone exchange is faster for zirconium; therefore, it seems likely that step 4 is the rate-determining step for the acetylacetone exchange. There is no detectable difference in the exchange rate of trifluoroacetylacetone with the zirconium or hafnium complexes. For this ligand the rate-determining step must be 2 or 3. Apparently the highly electronegative CF_3 group increases the rate at which the metal–oxygen bonds are broken. It has recently been reported that electronegative groups on the β-diketone ring increase the rate of metal–oxygen bond breaking.[19] It is also possible that the exchange proceeds through a bimolecular attack on the eight-coordinate complex to give a nine-coordinate species. The breaking of a metal–oxygen bond in one of the chelate rings would give the eight-coordinate intermediate shown in Figure 5.

In order for the keto isomer of acetylacetone to exchange rapidly with the metal complex, either the exchange of a proton while it is bonded to a carbon atom or the isomerization of the keto and enol isomers would have to be rapid. Both processes are known to be slow;[20] therefore, it is not surprising that exchange with the keto isomer is not observed.

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[18] A. N. Nesmeyanov, D. N. Kursanov, T. A. Smolina, and Z. N. Parnes, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 598 (1949); *Chem. Abstr.*, **44**, 3917 (1950).

[19] J. P. Collman and J. Y. Sun, *Inorg. Chem.*, **4**, 1273 (1965).

[20] Reference 18 shows that the first process is slow. The fraction of the enol isomer of β-diketones is often measured by bromine titration; consequently, the isomerization must be slow.

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA

The Successive Stabilities and Proposed Models of the Rare Earth 1-Hydroxycyclopentanecarboxylic Acid Chelates[1]

BY J. E. POWELL AND D. L. G. ROWLANDS

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The formation constants of the first three chelate species of the tripositive rare earth cations with the 1-hydroxycyclopentanecarboxylic acid ligand (HCPC) have been determined. Some values of K_4 have also been reported where calculable. Measurement was by a potentiometric method at 25°, and the ionic medium was maintained at $\mu = 0.1$ by the supporting electrolyte, sodium perchlorate. The ionization constant of the acid was also determined over the same ligand concentration range. From the stability constant ratios and hydration data of solid species, obtained using a thermobalance technique, an effort has been made to postulate the coordination number in the complex and the dentate character of the ligand, based on the nine-coordinate, trigonal prism +3 model.

Introduction

Recently, many rare earth monocarboxylate complexes have been studied by a potentiometric method.[2-9] In this investigation a cyclic acid was chosen in order to investigate any steric effect arising from the presence of an alicyclic ring as compared to

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1832.

[2] (a) A. Sonesson, *Acta Chem. Scand.*, **12**, 165, 1937 (1958); **13**, 998 (1959); **14**, 1495 (1960); (b) R. H. Karraker, "Stability Constants of Some Rare Earth Metal Chelates," Ph.D. Thesis, Library, Iowa State University of Science and Technology, Ames, Iowa, 1961.

[3] G. R. Choppin and J. A. Chopoorian, *J. Inorg. Nucl. Chem.*, **22**, 97 (1961).

[4] J. Grenthe, *Acta Chem. Scand.*, **16**, 1695 (1962).

[5] N. Cefola, A. S. Tompa, A. V. Celiano, and P. S. Gentile, *Inorg. Chem.*, **1**, 290 (1962).

[6] R. W. Kolat and J. E. Powell, *ibid.*, **2**, 293, (1962).

[7] H. Deelstra, W. Vanderleen, and F. Verbeek, *Bull. Soc. Chim. Belges*, **72**, 632 (1963).

[8] W. R. Stagg and J. E. Powell, *Inorg. Chem.*, **3**, 242 (1964).

[9] J. E. Powell, R. S. Kolat, and G. S. Paul, *ibid.*, **3**, 518 (1964).