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Dynamic NMR Study of Ligand Exchange Reactions in U(VI)−Phosphonic Acid Systems

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The rates of hydrogen ion exchange on phosphonic acid ligands and that of phosphonate ligand exchange on selected uranyl−phosphonate complexes have been investigated by dynamic NMR spectroscopy. The spin−spin relaxation time ($\ln(1/T_2)$) for H^+ exchange on the free ligands exhibits a parabolic dependence on reciprocal temperature ($1/T$ (K^{-1})). The empirical fit parameters are correlated with the activation parameters (ΔH^*, ΔS^*, ΔC_p^*) by adapting the statistical mechanical framework developed by Braibanti et al. to the Eyring activated complex theory. The correlation of the apparent activation enthalpy with temperature indicates that 6−11 water molecules participate in the transition from reactants to activated complex for ligand proton exchange reactions, depending on the ligand. Mechanistic details of ligand exchange reactions of phosphonic acid complexants onto the corresponding uranium(VI) complexes are not fully developed, but the negative values for ΔS^* imply increased order in the transition to the activated complex. Though ΔH^* for ligand exchange covers a range of 15 kJ/mol, the free energy of activation (ΔG^*) is nearly constant for the series of ligands, implying substantial entropy compensation in the activation process. Application of the Marcus relationship defines a correlation between ΔG^* and the thermodynamic stability ($\Delta G°$) for the 1:2 uranyl complexes with methanediphosphonic acid and 1-hydroxyethane-1,1-diphosphonic acid.

Introduction

Over the past several years, we have studied the kinetics of ligand exchange reactions of actinide complexes with several phosphonic and carboxylic acid chelating agents.[1−6] The pentavalent and hexavalent actinide ions NpO_2^+ and UO_2^{2+} have been investigated in the greatest detail. These metal ions are unique in the periodic table as the only linear dioxo cations of adequate redox stability for studies of this type (each of the actinides between uranium and americium can exist in these oxidation states, however, several are strong oxidants and the pentavalent state is generally prone to disproportionation). The bound oxygen ions (O^{2-}) are substitution inert in acidic solutions, thus, ligand exchange reactions are generally restricted to the equatorial plane of the ions.

The rates of ligand exchange of actinyl complexes are amenable for investigation by stopped-flow spectrophotometry, that is, they have half-lives on the order of milliseconds to seconds. In several systems we have investigated, the reaction conditions were such that the ligand exchange reactions were best fit as a first-order approach to equilibrium. In this case, the experimental results allow the determination of both complex formation and dissociation in the same series of experiments. Comparisons of the relative rates of complexation of NpO_2^+ and UO_2^{2+} and the respective activation parameters (ΔH^*, ΔS^*) have led us to postulate that the rate of exchange of coordinated water molecules in the precursor complexes governs the relative rates of ligand exchange.

Dynamic NMR studies probe a significantly different aspect of the coordination dynamics of these systems. Whereas in the stopped flow study the kinetic observations are based on spectrophotometric detection of the metal ion and so are metal-centered, the application of DNMR methods probing either ^{31}P or ^{13}C as the sensitive species more directly address the exchange reaction from a ligand-centered perspective. It is expected that experiments of this type will probe more explicitly changes occurring in the ligand as bound and free ligands are exchanged in the complex. The results of a DNMR investigation of both H^+ exchange on the ligands and of ligand exchange in the uranyl complexes are described herein.

Experimental Section

Reagents. The preparation and standardization of the dioxouranium(VI) (as the perchlorate salt), methanediphosphonic acid (MDPA), and 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) solutions have been previously described.[2] Hydroxymethanephosphonic acid (HMPA) and methylphosphonic acid (MPA) were purchased from Aldrich and used as received. The ^{13}C-labeled acetic acid also was purchased from Aldrich. *N*-piperidinylmethanediphosphonic acid (PMDPA) was prepared and purified in our laboratories as described previously.[7] The ionic strength of the media ranged between 0.1 and 0.4 M but was not explicitly controlled by the addition of supporting electrolyte. Most experiments were conducted in 0.1 M $HClO_4$. Total ligand concentrations ranged between 0.025 and 0.2 M. In the uranyl ligand exchange reactions, the total uranium concentration was 0.03−0.06 M.

Procedures. *NMR Measurements.* All NMR experiments were performed on a Bruker model DMX 500 NMR spectrometer (11.7 T). The ^{13}C 90° pulse was 12.25 μs. The ^{31}P 90° pulse was 16.75 μs. The variable temperature was calibrated by ^1H NMR spectroscopy of ethylene glycol (295−330 K) and methanol (270−295 K) at the same gas flow rate as the experiments. With the use of the nitrogen precooler, heater coil, and the variable temperature controller, the temperature was stable to within ±0.1 K. We used a two-channel 10 mm broadband detection, variable temperature probe with proton decoupling and ^2H lock at 76.773 MHz.

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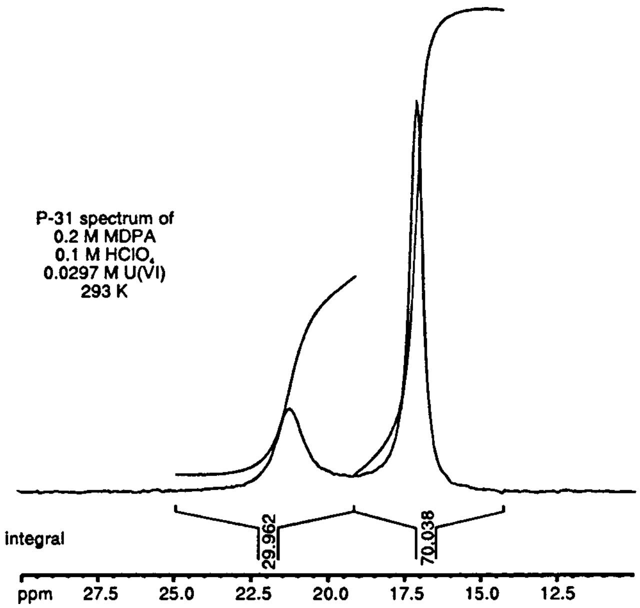

Figure 1. Example of ^{31}P NMR spectrum for the uranyl−MDPA complex at 0.2 M MDPA, 0.1 M $HClO_4$, 0.0297 M $UO_2(ClO_4)_2$ at T = 293.0 K.

The spin−lattice relaxation time (T_1) was determined by the inversion recovery with power gated decoupling pulse sequence. The spin−spin relaxation time (T_2) was determined by the Carr−Purcell−Meiboom−Gill (CPMG) pulse sequence.[8] For experiments with the ligands only, in which there was only one resonance for the ^{31}P nucleus, we used a modified version of the CPMG sequence. A single point was digitized at the top of each echo between 180° pulses. The T_2 was then calculated from the dwell and resulting exponential decay. This method has an 8-fold time advantage and produced results in excellent agreement with the standard CPMG procedure.

Results and Discussion

Our principal objective in this investigation was to examine the rate of the ligand exchange reactions

$$\mathrm{U(VI)}\cdot\mathrm{L}_n + \mathrm{L}^* \rightleftharpoons \mathrm{U(VI)}\cdot\mathrm{L}_{n-1}\mathrm{L}^* + \mathrm{L} \qquad (1)$$

where L represents the series of alkyl mono- and diphosphonic acids. There are no thermodynamic data available in the literature to allow prediction of the value of n for the monophosphonates or for PMDPA under these conditions. The thermodynamic data for the uranyl complexes with HEDPA and MDPA are available[9] and indicate that the dominant complexes under the conditions of these experiments are the 1:2 complexes between UO_2^{2+} and H_3L^- ($UO_2(H_3MDP)_2$ and $UO_2(H_3HEDP)_2$). Thermodynamic data strongly suggest that both phosphonate groups on each ligand are bound to the uranyl cation in the stable complexes.

The room-temperature NMR spectra for those systems in which uranyl is complexed by the phosphonate ligands were characterized by two distinct ^{31}P resonances corresponding to the free and complexed ligand species. The approximate chemical shifts for the free and bound ligands (in 0.1 M $HClO_4$) are 16.8 and 21.0 ppm for MDPA, 18.9 and 21.7 ppm for HEDPA, 5.8 and 9.7 ppm for PMDPA, and 21.2 and 22.8 ppm for HMPA. The ^{31}P chemical shift for free MPA (in 0.1 M $HClO_4$) is a quartet centered at 29.5 ppm (the uranyl complexes of MPA were not investigated). A sample spectrum for uranyl−MDPA is shown in Figure 1. The integrated areas of the two peaks in the NMR spectrum confirm that the dominant metal−ligand stoichiometry is 1:2 for the diphosphonates (MDPA, HEDPA, PMDPA) but only 1:1 for the complexes with HMPA. The exchange rate between free and coordinated ligand was calculated from DNMR measurements of T_2 as a function of concentrations of reactants and temperature variation of the solutions. The T_2 at a given temperature was the same for both the free ligand and the metal complex resonances in these experiments, indicating that the process being monitored was that described in eq 1.

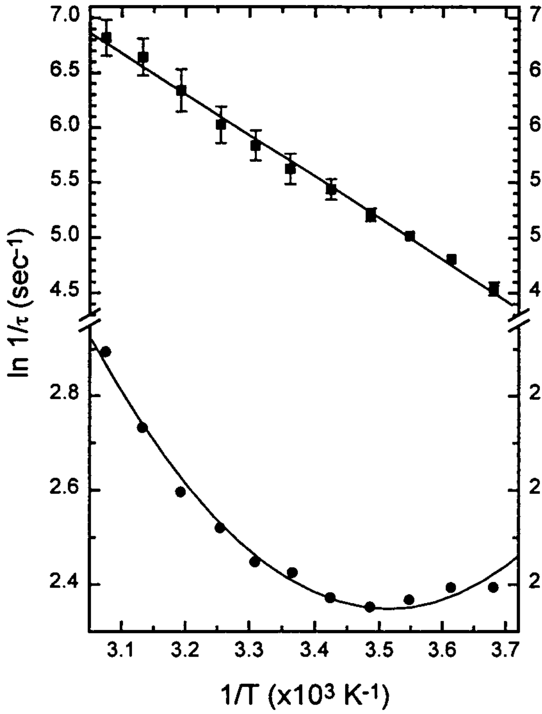

Figure 2. Relaxation time (τ) as a function of temperature for 0.025 M PMDPA, 0.1 M $HClO_4$ (●), and 0.025 M PMDPA, 0.0066 M UO_2^{2+}, 0.1 M $HClO_4$ (■)

The calculation of the rate of ligand exchange in the uranyl complexes necessitated a determination of the T_2 values for the free ligands as a function of temperature. Measurements of T_2 provide chemical kinetic information about a process in which the ^{31}P nucleus exchanges between two environments. We interpret the protonation/deprotonation of the phosphonic acids as providing the two different environments in the ligand-only experiments. The postulated general reaction is

$$(\mathrm{H_2O})_x\mathrm{L}^- + (\mathrm{H_2O})_y\mathrm{H}^+ \rightleftharpoons [(\mathrm{H_2O})_{x+y}\mathrm{L}^-\mathrm{H}^+]^* \rightleftharpoons (\mathrm{H_2O})_{x+y-z}\mathrm{LH} + z\mathrm{H_2O} \qquad (2)$$

In the acidity range of these experiments, the diphosphonate/phosphonate protonation reactions correspond to the exchange of a second H^+ on the monoanion ($L^- = R{-}PO_3H^-$ for the monophosphonates or $R(PO_3H_2)(PO_3H^-)$ for the diphosphonates).

We have determined the temperature-dependent values of T_2 for MDPA, HEDPA, HMPA, MPA, and PMDPA. A plot of the temperature-dependent relaxation rates for H^+ exchange on PMDPA and for PMDPA ligand exchange on the uranyl complex is shown in Figure 2. The data plotted for the ligand exchange experiments are the mean of the values determined at the free ligand and complexed ligand resonances, weighted for the relative integrated areas of bound and free ligands in the NMR spectrum. The result shown for PMDPA are repre-

TABLE 1: Quadratic Fit Parameters for Spin−Spin Relaxation Time as a Function of Temperature for the H^+ Exchange Reactions of the Fully Protonated Ligands[a]

	$A(\times 10^1)$	$B\ (\times 10^4)$	$C\ (\times 10^6)$
[MDPA]	5.58(0.51)	−3.18(0.30)	4.52(0.44)
[HEDPA]	2.64(0.21)	−1.55(0.12)	2.33(0.18)
[PMDPA][b]	3.86(0.25)	−2.07(0.15)	2.96(0.22)
[HMPA]	2.78(0.27)	−1.66(0.16)	2.43(0.24)
[MPA]	5.07(0.18)	−2.98(0.10)	4.26(0.16)
[$CH_3{}^{13}COOH$][c]	2.61(0.53)	−1.85(0.32)	2.90(0.50)

[a] 0.1 M in organic acids, 0.1 M perchloric acid. Values in parentheses represent $\pm 1\sigma$ uncertainty limit. Fit function/parameters are defined by $\ln k = A + B/T\ (K^{-1}) + C/(T\ (K^{-1}))^2$. [b] 0.025 M in PMDPA. [c] pH = 3.0.

sentative of those obtained in each of the ligand systems investigated.

For the H^+ exchange reactions of all ligand systems, the nonlinear relationship between $\ln 1/T_2$ and inverse temperature is observed. A quadratic function was found to adequately reproduce the observed data. Attempts to apply higher order fits did not result in improved agreement between observed and calculated data. The quadratic fit parameters are listed in Table 1. These parameters for the phosphonates carry uncertainty estimates between 4% and 10% in each term of the quadratic. The uncertainties are greater for acetate (about 20%).

The power series representation of the experimental data is a useful empirical correlation but not intellectually satisfying. For an interpretation of these parameters in physically significant terms, we need an additional postulate. Braibanti et al.[10−12] have developed a statistical mechanical model to describe equilibria in solution. This formalism models solution equilibria in terms of Boltzmann probability functions which can be transformed into “affinity thermodynamic space” to relate free energy, enthalpy, and entropy terms of thermodynamic quantities that describe solution equilibria. They define an “excess” partition function (Z_M) for a set of complexes formed between a receptor M and a ligand L to form successive complexes ML_i as:

$$Z_M = \sum_{i=0}^{t} \beta_i [L]^i = \sum_{i=0}^{t} \exp(-\Delta G_i/RT) = \sum_{i=0}^{t} \exp(-\Delta H_i/RT)\exp(\Delta S_i/R) \quad (3)$$

where β_i is the cumulative complex formation (or protonation) constant $[ML_i]/[M][L]^i$. The temperature variation (as $1/T$) of the partition function is related to the apparent equilibrium constant as

$$\ln \beta_{app} = \ln \beta_\theta + (-\Delta H_{app}/R)(1/T) + (1/2)\Delta C_{p,app}\ (1/T)^2 \quad (4)$$

The apparent enthalpy is related to the intrinsic enthalpy (i.e., the strength of the interation between reactants) according to

$$-\Delta H_{app}/R = -\Delta H°/R - (n_w C_{p,w}/R)T \qquad (5)$$

where n_w is the number of water molecules involved in the equilibrium and $C_{p,w}$ is the heat capacity of water. Thus, a plot of $-\Delta H_{app}/R$ vs T will yield a straight line defining the intrinsic enthalpy from the intercept and the number of water molecules associated with the process from the slope. As a test of their model development, Braibanti et al.[12] completed an analysis of the protonation equilibria of carboxylic acids as a function of temperature and concluded that two water molecules are involved in the protonation equilibrium of low molecular weight monocarboxylic acids.

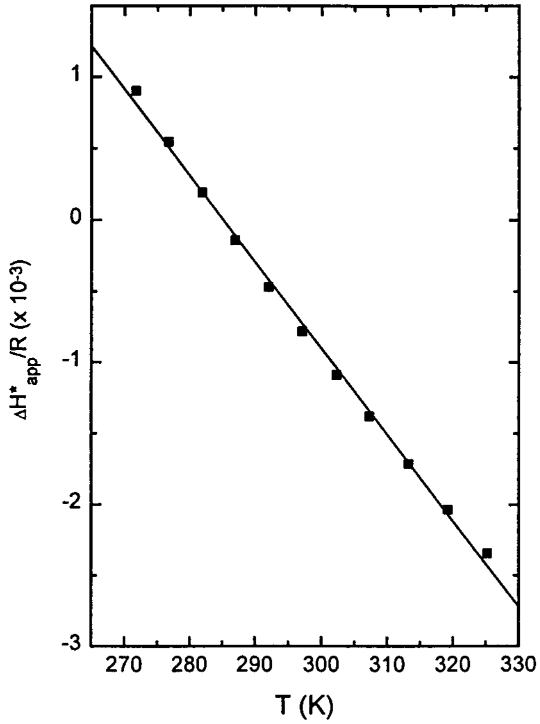

Figure 3. $\Delta H^*_{app}/R$ as a function of temperature for 0.025 M PMDPA, 0.0066 M $UO_2{}^{2+}$.

TABLE 2: Linear Fit of $\partial(\ln k_{app})/\partial(1/T\ (K^{-1})) = -\Delta H^*_{app}/R = (-\Delta H^*/R) - (n_w C_{p,w}/R)T$[a]

	$-\Delta H^*/R\ (\times 10^3)$	ΔH^* (kJ/mol)	$n_w C_{p,w}/R$	n_w
[MDPA]	−29.57(0.53)	+246(4)	−103.7(1.8)	11
[HEDPA]	−15.88(0.25)	+132(2)	−52.5(0.9)	6
[PMDPA]	−17.27(0.31)	+144(3)	−60.6(1.0)	7
[HMPA]	−16.05(0.26)	+133(2)	−54.8(0.9)	6
[MPA]	−27.46(0.46)	+228(4)	−96.1(1.6)	11
[$CH_3{}^{13}COOH$]	−19.98(0.38)	+166(3)	−63.2(1.2)	7

[a] Values in parentheses represent $\pm 1\sigma$ uncertainty limit.

To interpret the temperature dependence of the rate data in the present systems, we make the explicit assumption that the formalism can be applied to the Eyring activated complex theory. In this case, the coefficients of the quadratic fit are $A = \ln k_{app}$, $B = -(\Delta H^*_{app}/R)$, and $C = -(\Delta C_p{}^*{}_{app}/R)$. The rate and activation parameters are the measured apparent values and are not corrected for the changes in concentration of the water molecules, which depend on changes in the hydration of the reactants and the activated complex. If we calculate the values for the derivatives of the function $\ln k_{app}$ with respect to $1/T$ at each temperature, we find

$$\partial(\ln k_{app})/\partial(1/T\ (K^{-1})) = -\Delta H^*_{app}/R = (-\Delta H^*/R) - n_w C_{p,w} T/R \quad (6)$$

From the slope of the straight line of $\Delta H_{app}{}^*/R$ vs T, one calculates a value of n_w, where n_w is now the number of water molecules associated with the transition from reactants to the activated complex. A plot of $\Delta H^*_{app}/R$ vs T for the PMDPA protonation data is shown in Figure 3. We use the value of 75.378 J/mol K for $C_{p,w}$. The results of the calculations for all ligand systems are summarized in Table 2. The phosphonate ligands having hydrophilic groups on the α-carbon (HEDPA,

TABLE 3: Relaxation Time for Free and Bound MDPA Ligands in the Presence of Uranyl Ion[a]

T°A	τ(s) (bound)	τ(s) (free)
275	282.8	270.0
278	368.4	375.5
283	542.2	564.0
288	721.2	668.6
293	1055	1012
298	1506	1556

[a] 0.194 M MDPA, 0.0577 M U(VI), 0.1M $HClO_4$. Mole fraction free ligand/mole fraction bound ligand measured = 2.24 compared to 2.41 calculated. Values in parentheses represent ±1σ uncertainty limit.

TABLE 4: Relaxation Rates for the Uranyl−MDPA System at Variable Concentrations of Reagents[a]

[MDPA], M	[$HClO_4$], M	[U(VI)], M	k (s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J/m K)
0.l94	0.10	0.0577	381(38)	40.2(1.2)	−54(8)
0.201	0.10	0.0297	309(31)	39.3(1.2)	−59(8)
0.200	0.20	0.0297	309(31)	42.7(2.4)	−50(8)
0.103	0.10	0.0297	328(33)	45.2(1.2)	−38(12)

[a] k interpolated from plot of ln k vs 1/T plot at 273.16 K. Values in parentheses represent ±1σ uncertainty limit.

TABLE 5: Ligand Exchange Rate Constant and Activation Parameters[a]

	MDPA	HEDPA	HMPA	PMDPA
k (s^{-1})	1224(120)	391(39)	950(95)	305(30)
ΔG^* kJ/mol	55.6(3.4)	58.0(5.3)	56.1(5.7)	58.8(3.9)
ΔH^* kJ/mol	44.0(l.3)	32.1(2.3)	33.7(3.9)	28.7(1.2)
ΔS^* J/mol K	−39(7)	−87(10)	−75(6)	−101(9)

[a] 0.1 M $HClO_4$, 0.0297 M U(VI), 0.194 M ligands. k at 298.16 interpolated from ln k vs 1/T plot. The respective ratios of mole fraction free ligand/mole fraction bound ligand measured and calculated (in parentheses): HMPA 0.77(0.70); PMDPA 0.71(0.81); HEDPA 0.34(0.35). Another small unidentified signal of bound HEDPA of 7% was observed. Values in parentheses represent ±1σ uncertainty limit.

PMDPA, HMPA) involve 6−7 water molecules in the proton exchange reaction, while MPA and MDPA require a substantially greater number. A molecular scale rationale for this observation is not immediately apparent.

The results of the $CH_3{}^{13}COOH$ observations are of significance since such results demonstrate that the parabolic temperature dependence of the exchange reaction is not solely characteristic of ^{31}P in phosphonic acids. An additional point of interest is that we calculate a value of $n_w = 1$ if we treat the equilibrium data presented in ref 12 in the formalism described above. This is to be compared to a value of 2 calculated by Braibanti et al. using the full series expansion approach. We consider the agreement to be within the uncertainty limits of the calculation (±1 water molecule).

Ligand Exchange Reactions. As the dominant thermodynamically stable species for the uranyl diphosphonates are the 1:2 complexes, the generalized equation for the ligand exchange reaction is (omitting charges and the ligand protons for simplicity)

$$UO_2L_2 + L^* \rightleftharpoons UO_2L^*L + L \quad (7)$$

The T_2 values were measured for both bound and free ligands, divided by their respective mole fractions. The agreement between calculated values of 1/τ for the two sites may be evaluated from the data presented in Table 3. Since there is no apparent systematic difference between the values of τ measured for the free or bound ligand, the data were pooled for calculation of E_a, as was shown in Figure 2. Note that the parabolic temperature dependence is not observed for the ligand exchange reaction.

The verification of the rate as a function of ligand and U(VI) concentrations as well as the independence of the rate on [H^+] is demonstrated by the data in Table 4. The rate constant for the ligand exchange process is (under the conditions of 3−7-fold excess ligand) independent of [MDPA], [$HClO_4$], and [$UO_2{}^{2+}$].

The rates of exchange of bound and free ligands were also studied for HEDPA, HMPA, and PMDPA at fixed concentrations of (excess) ligand. The first-order rate constants along with activation parameters that were obtained are presented in Table 5. The relative rates are $k_{MDPA} > k_{HMPA} > k_{HEDPA} \geq k_{PMDPA}$. Activation enthalpies (ΔH^*) decrease in the same relative order while the activation entropy (ΔS^*) becomes more negative. The negative activation entropies of these reactions imply an increase in order upon traversing the reaction coordinate. Negative values for ΔS^* have also been reported for carbonate ion exchange on actinyl triscarbonato complexes.[13−15] The present data are not sufficient to distinguish between an outer-sphere preequilibrium between the replacement ligand and the metal complex or the existence of a true intermediate species in which the uranyl ion has a higher coordination number than the thermodynamically stable complex, as was suggested in the carbonate system.[13] It is surprising and unexpected that the rates of exchange of the free and bound ligands do not differ by more than a factor of about 4, despite the varied structures of the ligands.

One feature worth exploring is determination of the kinetic role of the ligand in the exchange reactions. The observed differences in the rates of exchange between the complexes can be rationalized qualitatively within the framework of the Marcus relations as demonstrated by Albery.[16] For the exchange reactions of U(VI) with the phosphonic acids, the relevant equation is

$$(\Delta G^*_{L,U} - \Delta G^*_{L',U}) = 1/2(\Delta G^*_{L} - \Delta G^*_{L'}) + \delta(\Delta G^\circ_{L,U} - \Delta G^\circ_{L'U}) \quad (8)$$

where L and L′ are the ligands under consideration. This equation shows the functional relation between the kinetic parameters for ligand exchange reactions and the corresponding thermodynamic equilibrium constants for the association reactions. In this case, the ΔG° values are taken as the stepwise equilibrium constants for addition of the second ligand to the 1:1 complex according to

$$UO_2(H_3L)^+ + H_4L \rightleftharpoons UO_2(H_3L)_2 + H^+ \quad (9)$$

which represents the dominant thermodynamic equilibrium under the conditions of these experiments. The equilibrium constants calculated from data in ref 9 (log $K_2(UO_2{-}MDPA) = 2.47$, log $K_2(UO_2{-}HEDPA) = 2.55$) give the corresponding free energy values $\Delta G_{UO_2MDPA} = -14.1$ kJ/mol and $\Delta G_{UO_2HEDPA} = -14.6$ kJ/mol. The term δ (in eq 5) generally has a value of about 0.5 for this type of reaction. We consider the ΔG^*_L to be the free energy of activation that describes the change in solvation and geometry of the ligand to form the activated complex. This is not the same reorganization that is necessary for the protonation−deprotonation reaction of the free ligand that we have reported above.

For the U(VI) systems with the ligands HEDPA and MDPA (where the respective rate constants differ by a factor of 3) eq 5 becomes (based on the thermodynamic data reported

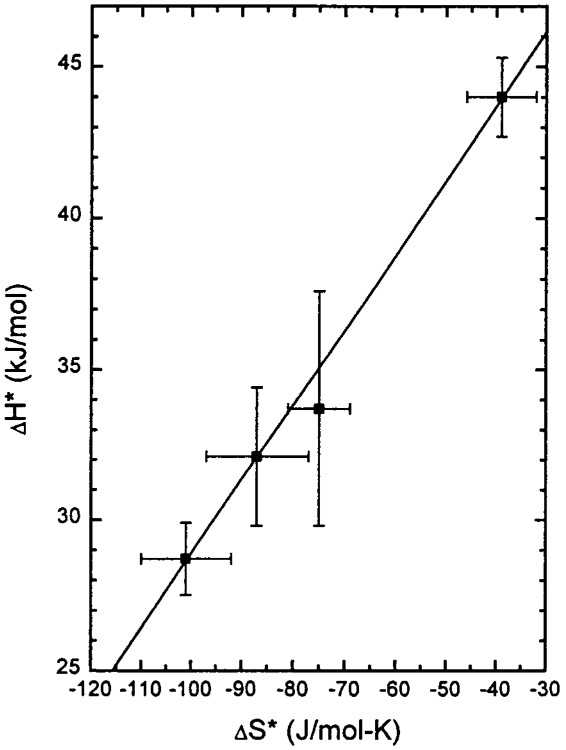

Figure 4. Isokinetic plot for phosphonate ligand exchange reactions in uranyl phosphonate complexes.

previously[9] and the ΔG^* values in Table 5)

$$(\Delta G^*_{\mathrm{HEDPA,U}} - \Delta G^*_{\mathrm{MDPA,U}}) = 1/2(\Delta G^*_{\mathrm{HEDPA}} - \Delta G^*_{\mathrm{MDPA}}) + \delta(\Delta G^\circ_{\mathrm{HEDPA,U}} - \Delta G^\circ_{\mathrm{MDPA,U}}) \quad (10)$$

$$(58.0 - 55.6) = 2.4 = (\Delta G^*_{\mathrm{HEDPA}} - \Delta G^*_{\mathrm{MDPA}}) + (-0.5)$$

Though the ΔG^* values for ligand exchange carry some uncertainty, this analysis demonstrates that changes in the geometry and hydration spheres of the ligands are more responsible for the difference in the rates of ligand exchange than is the difference in the thermodynamic stability of the respective uranyl complexes. Due to the absence of thermodynamic data, we unfortunately cannot extend this analysis to include the other ligands studied. However, we previously concluded that the relative rates of ligand exchange for uranyl complexes with ethane-1,2-diphosphonic acid and oxydiacetic acid were similarly determined by differences in ligand solvation and structural properties.[6]

The complex kinetic behavior of the phosphonic acids, as reflected in the temperature-dependent T_2 measurements, makes an interpretation of the activation parameters for the ligand exchange reactions as a criteria of the mechanism complicated. The importance of hydration effects is, however, demonstrated by noting that the number of water molecules participating in hydrogen ion exchange (calculated from the ligand T_2 temperature-dependent measurements) is greatest for MDPA, which also has the least negative value of ΔS^* for the ligand exchange reactions.

An examination of the $\Delta H^* - \Delta S^*$ values for the exchange reactions also is instructive. A linear relation between ΔH^* and ΔS^* for the ligand exchange reactions is apparent (Figure 4). This $\Delta H^* - \Delta S^*$ compensation can be interpreted to imply that not only does the compensation hold for the $\Delta(\Delta G^\circ)$ term but also for the $\Delta(\Delta G^*)$ term. In addition, if we extend the intuitive reasoning advanced by Levy et al.[17] to the Eyring formalism, the $\Delta H^* - \Delta S^*$ compensation provides a reasonable rationalization of our kinetic observations. A stronger interaction between the molecular constituents of the activated complexes will result in a reduction of the entropy and a weaker interaction will produce an increase in the value of ΔS^*. The theoretical basis for these results, however, still remains a point of conjecture.

Conclusions

The following general comments are offered to summarize the results of these experiments.

(1) The parabolic temperature dependence of $1/T_2$ for the free ligands was interpreted to indicate a significant change in solvation of the free ligand in the formation of the activated complex for H^+ exchange. For acetate, the present data indicate that the number of waters involved in the activation process is substantially greater than that for the overall (thermodynamic) reaction, as reported by Braibanti et al.[12] This implies that additional readjustment of solvent molecules around the ligand occurs as the activated complex relaxes into the thermodynamically stable species.

(2) There have been numerous studies of ligand exchange reactions on actinyl ions with carbonate.[13−15] This is the first example of exchange studies with bidentate phosphonic acid ligands. The results are consistent with an associative mechanism for the ligand exchange reactions.

(3) The difference in ΔG^* for the exchange reactions of the HEDPA and MDPA uranyl complexes with the respective free ligands is shown to be dominated by the $\Delta(\Delta G^*)$ values of the ligands.

(4) The $\Delta H^* - \Delta S^*$ compensation provides a reasonable explanation of the small changes in the rate of exchange noted with the ligands of markedly different properties.

To elucidate greater details of such reactions, further investigations of actinide−ligand exchange rates using this technique are planned.

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