1820 *Inorg. Chem.* **1993**, *32,* 1820–1823

Kinetics of the Complexation of Dioxouranium(VI) with Selected Diphosphonic Acids in Acidic Solutions[†]

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Received October 23, 1992

The kinetics of reactions of dioxouranium(VI) with diphosphonic acid complexants (methanediphosphonic acid (MDPA), 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), and ethane-1,2-diphosphonic acid (E12DPA)) have been investigated in acidic solutions (pH 1–2) by stopped-flow spectrophotometry where arsenazo III is used as an indicator for the free uranyl ion. The complex formation reaction was acid independent at acidities above 0.03 M while the dissociation reaction had a direct dependence on the acidity over the range of hydrogen ion concentration 0.1–0.01 M. The measured first-order rate parameter is defined as $k_{obs} = k_f[UO_2^{2+}][H_3L] + k_d[UO_2H_2L][H^+]$. The rate parameters for formation and dissociation reactions at 25.0 °C are as follows. Uranyl–MDPA: $k_f = 6813$ (±320) M^{-1} s^{-1}, $k_d = 31.3$ (±2.1) s^{-1}. Uranyl–HEDPA: $k_f = 7715$ (±146) M^{-1} s^{-1}, $k_d = 27.5$ (±2.0) s^{-1}. Uranyl–E12DPA: $k_f = 216$ (±24) M^{-1} s^{-1}, $k_d = 47.4$ (±2.6) s^{-1}. The equilibrium quotient calculated from the rate parameters for the formation of uranyl–E12DPA is in agreement with the previously reported stability constant for that complex. Activation parameters for both formation and dissociation reactions are consistent with an associative mechanism. Uranyl–MDPA: $\Delta H_f^* = 38.0$ (±1.4) kJ/mol, $\Delta S_f^* = -44$ (±4) J/(mol K), $\Delta H_d^* = 44.8$ (±2.4) kJ/mol, $\Delta S_d^* = -66$ (±8) J/(mol K). Uranyl–HEDPA: $\Delta H_f^* = 38.8$ (±0.6) kJ/mol, $\Delta S_f^* = -40$ (±2) J/(mol K), $\Delta H_d^* = 57.8$ (±20.9) kJ/mol, $\Delta S_d^* = -22$ (±62) J/(mol K). Uranyl–E12DPA: $\Delta H_f^* = 46.8$ (±0.1) kJ/mol, $\Delta S_f^* = -43$ (±1) J/(mol K), $\Delta H_d^* = 44.2$ (±4.1) kJ/mol, $\Delta S_d^* = -65$ (±13) J/(mol K).

Introduction

The thermodynamics of the reactions between selected lanthanide and actinide metal ions and phosphonic acids have been the subject of several earlier reports.[1–3] These complexes exhibit unusually high stability compared with carboxylic acid ligands in acidic aqueous solutions. This result has been correlated with the presence of an extra oxygen donor atom[4] and the formation of protonated complexes by the phosphonate bearing ligands. For example, the dominant europium complexes in the pH 1–2 range for the europium–methanediphosphonic acid (MDPA) system are $Eu(H_3L)^{2+}$, $Eu(H_2L)^+$, $Eu(H_3L)_2^+$, and $Eu(H_2L)_2^-$.[2]

Most recently, the stability constants for a series of uranyl complexes with several 1,1-diphosphonates, a 1,2-diphosphonate, and a mixed carboxylate–phosphonate ligand have been reported.[3] The complexes are intermediate in stability between those of europium[1] and thorium.[2] Complex stability decreases with ring expansion (ethane-1,2-diphosphonic acid, E12DPA) and carboxylate substitution (carboxymethanephosphonic acid, CMPA). For MDPA, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), and vinylidene-1,1-diphosphonic acid (VDPA), protonated 1:2 ($UO_2(H_2L)_2^{2-}$) complexes are the dominant species even at very low total ligand concentrations.

These ligands are of interest to us because of their unusually high affinity for lanthanide and actinide elements in acidic solutions. New reagents of this type could provide more efficient isolation and purification procedures for f elements.

The present investigation reports the rates of chelation reactions for uranyl phosphonate complexes in acidic, aqueous solutions. The ligands chosen are MDPA, to study the effect of the simplest 1,1-diphosphonate, HEDPA, to explore the effect of an α-hydroxide group, and E12DPA, to examine the effect of ring expansion. Despite the structural modifications, the number and types of atoms in the ligands that coordinate with uranyl remain constant. There have been no previous reports of the rates and mechanism of metal ion complexation by phosphonic acid ligands although there have been a few studies which have addressed selected problems in uranyl complexation kinetics.[5]

Experimental Section

The dioxouranium(VI) solution was prepared from NBS grade U_3O_8 by dissolution in nitric acid. The resulting solution was fumed to dryness with perchloric acid, and the solid was then redissolved in 1.0 M $HClO_4$. The UO_2^{2+} solution was standardized by weight and isotope dilution mass spectroscopy. A working stock solution was prepared from this solution by dilution with triply distilled water. Arsenazo III (2,2′-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bis(benzenearsonic acid), AAIII) forms highly colored complexes with uranyl under these conditions, and thus serves as a probe for free UO_2^{2+}. The maximum absorbance for the uranyl–AAIII complex occurs at 650 nm and is free of interference from other absorbing species. The AAIII stock solution (1×10^{-3} M) was prepared by weight using material obtained from Aldrich Chemical Co., adjusted to total acidity of 0.1 M ($HClO_4$), and diluted to volume with triply distilled water. The preparation and purity of the diphosphonate ligands have been described previously.[1–3] The ionic strength of the ligand solutions was 0.1 M, adjusted with $NaClO_4$.

Experiments were performed as a function of both diphosphonate concentration and acidity. $[UO_2^{2+}]$ and [AAIII] were 1.0×10^{-5} M (after mixing) for the experiments reported here. The results of preliminary experiments demonstrated that for constant hydrogen ion and ligand concentrations a variation of either UO_2^{2+} or AAIII initial concentrations did not result in a change in the value calculated for the first-order rate constant. Due to potential photosensitivity, all solutions were stored out of the light when prepared in advance. Reagent solutions (uranyl–AAIII and diphosphonate ligand) were adjusted to the same acidity in a given experiment. The acid concentration was varied between 0.01 and 0.1 M.

[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38.

[‡] Participant in the Summer 1991 Student Research Participation Program from the College of Charleston, Charleston, SC.

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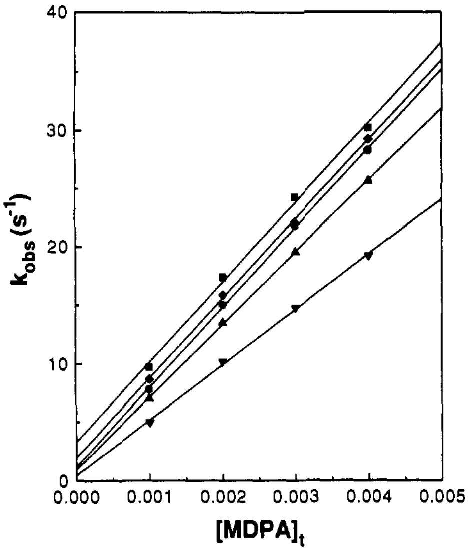


Figure 1. Observed first order rate constant (k_{obs} (s^{-1})) for the uranyl–MDPA system as a function of the total ligand concentration at 25.0 °C, $I = 0.1$ M: ■, 0.1 M acid; ◆, 0.05 M acid; ●, 0.03 M acid; ▲, 0.02 M acid; ▼, 0.01 M acid.

The experiments were performed in the Hi-Tech Scientific stopped-flow spectrophotometer described previously.[6] The mixing chamber of the spectrophotometer was thermostated to ±0.1 °C. The variations of the rate parameters as a function of temperature were used to calculate activation parameters. For each experiment, five replicate runs were made.

A DEC 11/23 computer running the RT program was used for data acquisition. The absorbance–time data were adjusted using the integrated first-order rate law

$$A = (A_0 - A_\infty)e^{-kt} + A_\infty \qquad (1)$$

The nonlinear-least-squares calculation minimizes the value of $(A_{obs} - A_{cal})^2$ by adjusting the three parameters, A_0, A_∞, and k.

Results and Discussion

A first-order rate law was found to adequately describe the experimental data under all conditions. The calculated first-order rate constants as a function of the total diphosphonate ligand concentration are plotted in Figures 1–3 for MDPA, HEDPA, and E12DPA, respectively. The finite intercepts in each system indicate that the most appropriate analysis is to assume a first-order approach to equilibrium. Within this assumption, the slope corresponds to the rate of complex formation while the intercept defines the rate constant for complex dissociation (at constant acidity).

The rate parameters for the complex formation reaction are independent of [H^+] above 0.03 M. At [H^+] = 0.01 M, the rate of formation is lower than that observed at higher acidities. The slower rate is demonstraed in Figures 1 and 2 by a decreased slope in the plot of k_{obs} as a function of total ligand concentration. We believe that this results from a change in the configuration of the uranyl–AAIII complex to a sterically hindered species. The existence of multiple complexes in the uranyl–AAIII system is well established.[7] Previous kinetic analysis of the uranyl–AAIII system supports this interpretation.[8]

The dissociation reaction exhibits a direct dependence on the hydrogen ion concentration. The plots of the k_d versus [H^+], shown in Figures 4–6 are linear with a zero intercept (within $\pm 2\sigma$) at 25.0 and 10.5 °C for all three systems. At 36.0 °C, there is a possible contribution from an acid-independent dissociation pathway for the 1,1-diphosphonates, but not for E12DPA. The major dissociation pathway under all conditions is the acid dependent.

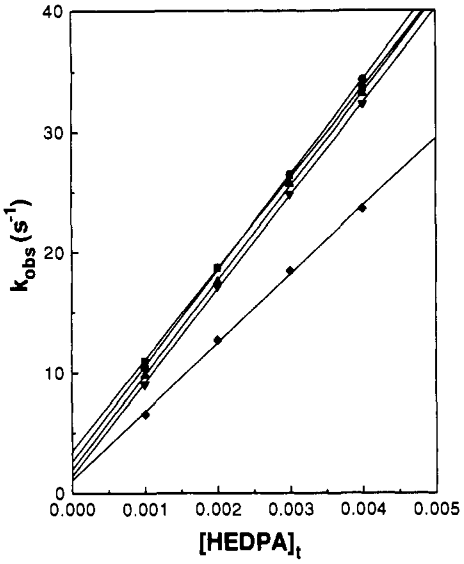
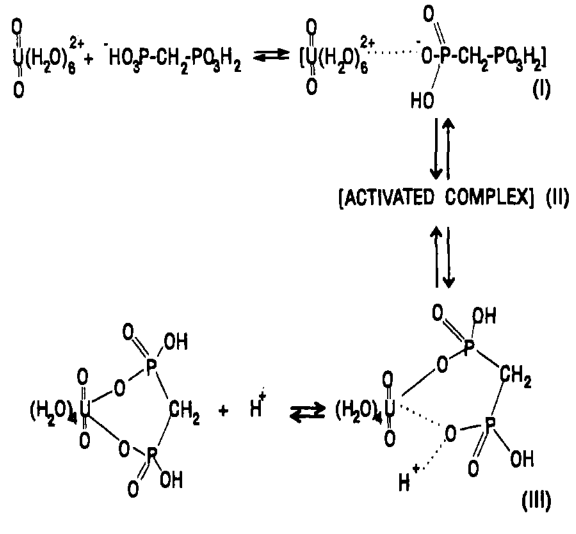


Figure 2. Observed first-order rate constant (k_{obs} (s^{-1})) for the uranyl–HEDPA system as a function of the total ligand concentration at 25.0 °C, $I = 0.1$ M; ■, 0.1 M acid; ●, 0.07 M acid; ▲, 0.05 M acid; ▼, 0.03 M acid; ◆, 0.01 M acid.

The proposed reaction scheme is



where I is the precursor complex for the forward reaction and III is the precursor complex for the reverse reaction. The first ionization constants of the H_4L ligands are as follows: MDPA, $pK_1 = 1.51$; HEDPA, $pK_1 = 1.5$; E12DPA, $pK_1 = 1.25$. The predominant ligand species in these reactions are, therefore, H_3L^-. Two major differences to be noted between the precursor complexes I and III are the number of inner-sphere water molecules coordinated to the uranyl ion and the degree of association of the metal ion with the second phosphonate group of the diphosphonic acid (i.e., the number of phosphonate groups bound).

Using the Eyring equation, $\ln k = \ln(kT/h) - \Delta G^*/RT - \ln(kT/h) - (\Delta H^*/RT - \Delta S^*/R)$, and the resolved rate constants as a function of temperature, the activation enthalpy and entropy for both formation and dissociation reactions were calculated (Table I). The activation parameters for both formation and dissociation reactions are comparable to previously reported values

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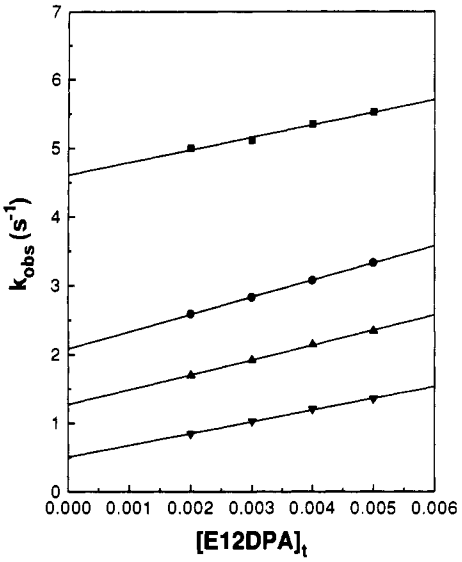

Figure 3. Observed first-order rate constant (k_{obs} (s^{-1})) for the uranyl–E12DPA system as a function of the total ligand concentration at 25.0 °C, I = 0.1 M: ■, 0.1 M acid; ●, 0.05 M acid; ▲, 0.03 M acid; ▼, 0.01 M acid.

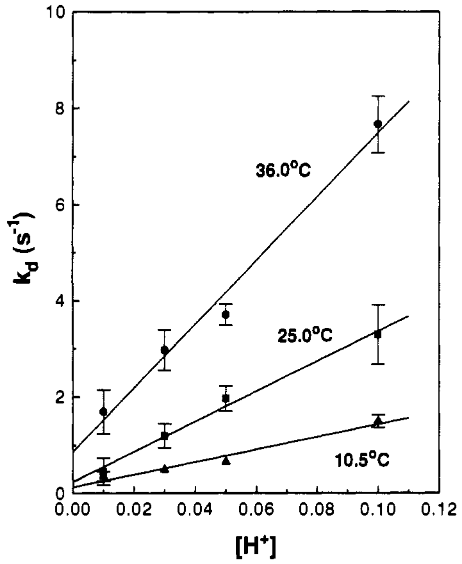

Figure 4. Rate constant of the acid-catalyzed dissociation reaction (k_d (s^{-1})) for the uranyl–MDPA system as a function of acidity and temperature.

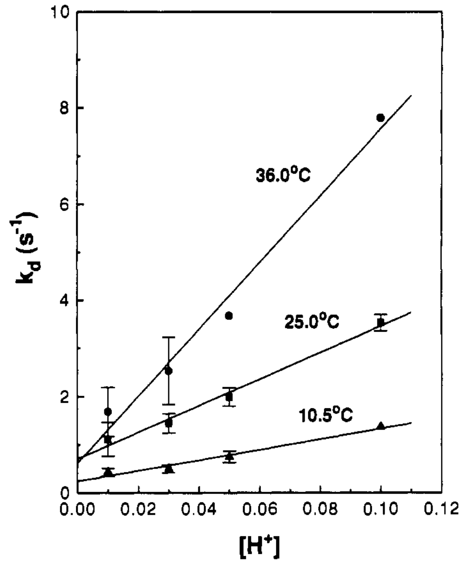

Figure 5. Rate constant of the acid-catalyzed dissociation reaction (k_d (s^{-1})) for the uranyl–HEDPA system as a function of acidity and temperature.

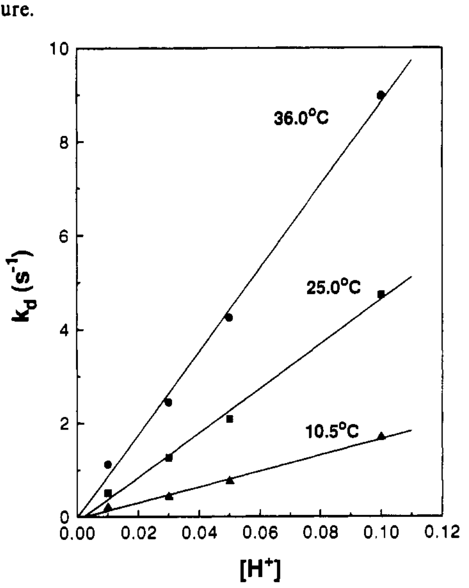

Figure 6. Rate constant of the acid-catalyzed dissociation reaction (k_d (s^{-1})) for the uranyl–E12DPA system as a function of acidity and temperature.

Table I. Experimental Average Values for the Activation Parameters ΔH^* and ΔS^* between 0.10 and 0.03 M H$^+$ (at 25 °C)

ligand	ΔH^* (kJ/mol)	ΔS^* (J/(mol K))	ref
	Formation		
MDPA	38.0 (±1.4)	−44 (±4)	present work
HEDPA	38.8 (±0.6)	−40 (±2)	present work
E12DPA	46.8 (±0.1)	−43 (±1)	present work
arsenazo III	30.1	−42	8
arsenazo III	36.6	−20	9
(pyridylazo)resorcinol	34.2	−44	10
	Dissociation		
MDPA	44.8 (±2.4)	−66 (±8)	present work
HEDPA	57.8 (±20.9)	−22 (±62)	present work
E12DPA	44.2 (±4.1)	−65 (±13)	present work
arsenazo III	48	−65	8

for uranyl complexation with both arsenazo III[8,9] and (pyridylazo)resorcinol (PAR).[10] These data are reported in Table I as well.

The lower activation enthalpy for formation of uranyl complexes with the 1,1-diphosphonate ligands is probably a result of the shorter distance between the phosphonate groups as compared with the case of the 1,2-diphosphonate ligand. It should be noted, although not readily amenable to rationalization, that the activation enthalpies for the forward and reverse reactions are nearly identical for the reaction with E12DPA but are slightly larger for the reverse reactions in the 1,1-diphosphonate reactions. The more negative activation entropy for the reverse reaction in all cases implies a greater degree of ordering between the products through precursor complex III to the activated complex II than is observed in the formation pathway of aquo cation + ligand to precursor complex I to activated complex II. This difference may reflect the rehydration–dehydration of the complex, plus the influence of chelation effects. The magnitude of the former effect on the difference between the activation entropies for the forward and reverse reactions corresponds, for example, to approximately two-thirds of a water molecule (cratic entropy contribution, $\Delta S_c = R \ln(55.5) = 33$ J/(mol K)).

For complex reaction mechanisms involving preequilibria, experimental activation enthalpies and entropies include a contribution from the thermodynamic parameters describing the

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preequilibria.[11] For example, for activation enthalpy of the association reactions, $\Delta H^* = \Delta H(\text{I–II}) + \Delta H(\text{precursor complex}) + \Delta H(\text{ligand protonation})$.

We can use the rate constants summarized in Table I, and protonation constants, enthalpies, and entropies for the free ligands reported elsewhere,[3,12] to calculate equilibrium constants for the overall complex formation reaction for each ligand system. The parameters thus calculated are, within the uncertainty of the measurements, independent of temperature, indicating small complexation heats for all reactions. The equilibrium constants are log K(MDPA) = 4.00 (±0.20), log K(HEDPA) = 4.00 (±0.15), and log K(E12DPA) = 2.32 (±0.30). The last value overlaps at the $\pm 2\sigma$ uncertainty level with the value 2.88 (±0.1) reported earlier for the formation of $UO_2(H_2E12DP)$.[3] Assuming $\Delta H \simeq 0$ for all three ligand systems, calculated values are ΔS(MDPA) = ΔS(HEDPA) = 77 (±12) J/(mol K) and ΔS(E12DPA) = 44 (±9) J/(mol K). The assumption of small complexation heats (it should be noted) is consistent with most previous reports of uranyl complexation reactions.[13]

For the 1,1-diphosphonates, stability constant data for the $UO_2(H_2L)$ 1:1 complex have not been reported. However, the data for the formation of $UO_2H_3L^+$ complexes have been determined. For uranyl–MDPA, log K = 5.22 (±0.26) for the following equilibrium:

$$UO_2^{2+} + H_3L^- = UO_2H_3L^+ \tag{2}$$

This leads to a calculated protonation constant for the complex:

$$UO_2H_2L + H^+ = UO_2H_3L^+, \quad pK_a = 1.2\ (\pm 0.3) \tag{3}$$

The protonation constant is reasonable by comparison with values reported for analogous reactions of europium ($pK(EuH_3MDP)$ = 1.95) and thorium ($pK(ThH_3VDP)$ = 0.19) complexes with diphosphonate ligands.

The effects that structural modifications have on the rates and equilibria of these complex formation reactions are manifested in the variations of the entropy values with relatively small and constant values of the enthalpies. This result emphasizes the difference between chelation reactions of the 5f elements and the d transition metals. For example, a recent study of the effect of ligand structural variation on complex strength[14] indicates that complexation heats for copper(II) complexes with minor structural variants of macrocyclic tetrathioethers are primarily responsible for differences in complex stability. For the f elements, complexation enthalpies are dominated by metal and complex hydration effects. The absence of metal–ligand covalent interactions also contributes to the relatively minor role of complexation enthalpies in f-element complex formation reactions.

It has been noted previously[5,15] that differences in lanthanide and actinide complex stabilities are most often a result of differences in complex dissociation rates. For a given ligand, the rates of formation of lanthanide complexes are more-or-less constant while the rates of dissociation of the complexes vary monotonically with shrinking radii across the series. Comparisons of different ligands with a single metal ion clearly must be made more carefully, but the present data indicate a departure from this norm in the diphosphonate ligand system. The complexes of uranyl with E12DPA are about 100 times weaker than those of the 1:1 diphosphonates studied. The difference results, primarily, from a slower rate of complex formation.

Conclusions

The kinetics of complexation uranyl with the diphosphonate ligands MDPA, HEDPA, and E12DPA, which form strong complexes with the uranyl ion, have been studied by ligand displacement procedures. The reactions, occurring in the stopped-flow time regime, proceed as a first-order approach to equilibrium under all conditions. The rate-determining step is postulated to be an intramolecular process characterized by activation parameters similar to those reported previously for other uranyl–ligand systems of different coordination geometries. Thermodynamic parameters calculated from the formation and dissociation rates result in complexation enthalpies near zero with the consequence that complex stability is derived primarily from a favorable entropy change.

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