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Oxygen-17 NMR Study of the Uranyl Ion. V.[1] Kinetics and Mechanisms of Formation and Decomposition Reactions of Di-μ-hydroxo-bis[uranyl(VI)] Ion in Aqueous Nitrate Solutions

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The rates of formation and decomposition reactions of di-μ-hydroxo-bis[uranyl(VI)] ion, $(UO_2)_2(OH)_2^{2+}$, have been measured in aqueous nitrate solutions (ionic strength=0.5 M; M=mol dm^{-3}) by ^{17}O NMR spectroscopy. In weakly acidic solutions the reactions obey the rate law:

$$d[(UO_2)_2(OH)_2^{2+}]/dt = k_2[UO_2^{2+}][UO_2OH^+] - k_{-2}K_a[H^+][(UO_2)_2(OH)_2^{2+}]/2,$$

where $K_a=[(UO_2)_2OH^{3+}]/[H^+][(UO_2)_2(OH)_2^{2+}]$. A mechanism involving a single-bridged binuclear intermediate, $(UO_2)_2OH^{3+}$, is proposed. Rate constants (M^{-1} s^{-1}) at 25 °C and activation parameters $\Delta H^{\neq}$ (kJ mol^{-1}) and $\Delta S^{\neq}$ (J K^{-1} mol^{-1}) for the formation and decomposition are as follows: 1.52×10^5, 18.9 ± 1.5, and -82.4 ± 5.0 for k_2 and 2.10×10^5, 23.6 ± 1.3, and -64.0 ± 4.2 for $k_{-2}K_a$. The rate of the decomposition reaction is compared with that in several related systems.

Thermodynamic studies of the hydrolysis reaction of uranyl ions have been carried out extensively.[2–5] Although the equilibrium quotients (Q_{11}, Q_{22}, and Q_{35}) of the reactions differ depending on the ionic medium, the following reactions have been established as main ones:[2]

$$UO_2^{2+} + H_2O = UO_2OH^+ + H^+ \qquad Q_{11} \qquad (1)$$

$$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+ \qquad Q_{22} \qquad (2)$$

$$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+ \qquad Q_{35} \qquad (3)$$

where hereafter $(UO_2)_p(OH)_q^{(2p-q)+}$ ion will be abbreviated as (p, q) and their concentrations as $[p, q]$ for brevity. There seems to be little doubt about the existence of (2,2) and (3,5) species as major ones, the former of which has been confirmed by X-ray investigations.[6] This binuclear complex has a dihydroxo-bridged and not an oxo-bridged structure. Recently the two major species have been identified by Raman spectroscopy.[7] Our recent study[8] showed that ^{17}O NMR signals of the major hydrolysis species are resolved from the signal of the uranyl ion below room temperature and the rate of the equilibrium reaction (Eq. 2) between (1,0) and (2,2) species is within the range of ^{17}O NMR measurements. Kinetic studies of the reaction have been undertaken by several workers,[9–12] but the mechanism remains unclear. We studied the kinetics of formation and decomposition reactions of (2,2) species by the ^{17}O NMR spectroscopic method and the kinetic results are reported in this paper.

Experimental

Preparation of Sample Solutions. Uranyl complex used is uranyl(VI) nitrate hexahydrate $UO_2(NO_3)_2\cdot6H_2O$, which was prepared by the same method as described in a previous paper[1] by using ^{17}O enriched water (^{17}O=42.1% atom%). ^{17}O enrichment of uranyl oxygen atoms (henceforth called uranyl oxygens) of the stock solution was so performed that oxygen isotope effects may not occur in ^{17}O NMR spectra of uranyl oxygens.[13] Therefore, the ^{17}O signal of uranyl oxygens of the stock solution consisted of a single line of Lorentzian shape, which corresponds to $[^{16}O=U=^{17}O]^{2+}$. The sample solutions for NMR measurements were prepared by diluting the stock solution with doubly distilled deionized water and adjusting the hydrogen ion concentration with either NaOH or HNO_3 solutions. The hydrogen ion concentrations of the solutions were measured with a Toa IM-20E pH meter. The pH meter readings at each temperature were calibrated to give $-\log[H^+]$ by using standard HNO_3 solutions at 0.5 M ionic strength (1 M= 1 mol dm^{-3}), which was adjusted with KNO_3. The hydrogen ion concentrations of the sample solutions increased with increasing temperature in weakly acidic solutions, while remained almost constant irrespective of temperature in strongly acidic solutions. The total uranyl ion concentration ($[UO_2^{2+}]_t$) of all sample solutions was 0.17 M. The hydrogen ion concentrations of the solutions were calculated on the assumption that the activity coefficient of the hydrogen ion in the self media is the same as that in KNO_3 media. The rates were measured at 0.5 M ionic strength because, to our knowledge, the thermodynamic parameters of equilibrium constants for hydrolysis reactions (Eqs. 1—3) of uranyl ions are available only for this ionic strength.[3]

Measurements of NMR Spectra and Kinetic Analysis. The measurements of the ^{17}O NMR spectra were carried out by JEOL JNM-GX 500 and JEOL JNM-GX 400 FT-NMR spectrometers operating at 67.83 and 54.26 MHz, respectively equipped with a GVT-3 temperature controller which was calibrated directly by use of a digital resistance thermometer (Tsuruga Electric Work, Ltd.). The measurements were performed with a 5-mm-o.d. NMR sample tube, which was

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immersed in a 10-mm-o.d. concentric NMR tube containing D_2O as a lock solvent. Conditions for NMR measurement were: pulse width, 22 μs (corresponding to 45°); spectral width, 30 kHz; number of scans, 2000—30000. The kinetic analysis was carried out by using a computer program of two-site exchange model as described previously.[14] The ^{17}O transverse relaxation time of (2,2) species in the absence of chemical exchange was not measured directly in the temperature range studied, but was estimated to be 4.08×10^{-2} s at 5 °C by the computer simulation. This value was relatively smaller than the relaxation time (6.68×10^{-2} s) of (1,0) in the absence of chemical exchange. Owing to the quadrupole relaxation, the transverse relaxation time T_2 of ^{17}O changes with temperature. The relation between T_2 and temperature is usually reported by an Arrhenius-type function

$$1/T_2 = A\exp(-E_Q/RT)$$

where E_Q is an activation energy. In the earlier paper,[1] the activation energies for T_2 of free water and water coordinated to uranyl ion were determined to be 22.4 ± 0.1 and 24.8 ± 0.8 kJ mol^{-1}, respectively, and the activation energy for T_2 of uranyl oxygens was 24.2 ± 0.3 kJ mol^{-1} in the temperature range from 7 to 35 °C. Based on these results, it is reasonable to assume that the activation energies for T_2 of both (1,0) and (2,2) are close to 24 kJ mol^{-1}. Therefore, the correction was made for T_2 based on the above assumption.

Results and Discussion

^{17}O resonances of uranyl oxygens in strongly acidic solutions are always observed as a single Lorentzian resonance (Fig. 1A), the chemical shift of which is ca. 1118 ppm relative to pure water at room temperature. In weakly acidic solutions the line shapes of the resonances are sensitive to [H^+], i.e. to the degree of hydrolysis, as shown in Fig. 1. At 25 °C two resonances were observed (Fig. 1B-D) in the range of $-\log[H^+]$ from 3.15 to 3.38, while three resonances (Fig. 1E) at $-\log[H^+]=3.71$. The ratios of intensities of three resonances from the high field agree with [1,0]:2[2,2]:3[3,5] at 5 °C, which can be estimated on the basis of thermodynamic parameters reported by Baes and Meyer.[3] For example, the estimated ratio at $-\log[H^+]$ of 3.71 is 40.9:52.5:6.5, which agree well with the ratio of intensities in Fig. 1E. This fact supports our previous assignment[8] that the resonances at 2.0 and 6.7 ppm downfield relative to the uranyl ion correspond to (2,2) and (3,5) species, respectively.

Figure 2 shows that the resonances of (1,0) and (2,2) species tend to coalesce with increasing temperature. This indicates that there occurs a chemical exchange reaction between the two species. The τ values at each temperature were obtained from the best fit of the line shapes. The calculated lines are shown at the right-hand side in Fig. 2. In the calculations of τ we

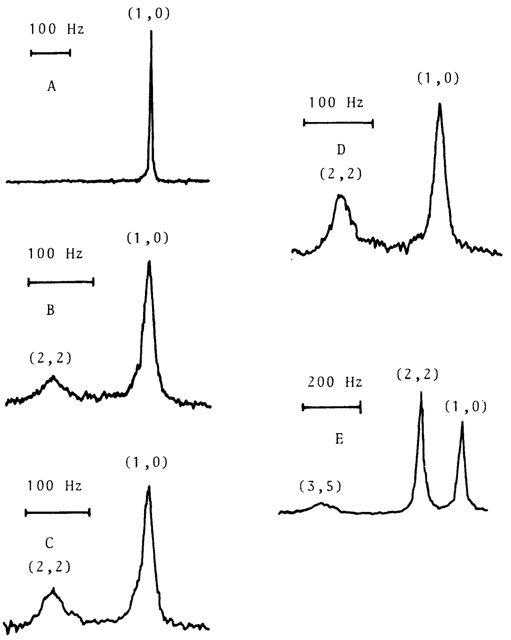

Fig. 1. ^{17}O spectra of uranyl solutions at $-\log[H^+]$ of 1.17 (A), 3.15 (B), 3.28 (C), 3.38 (D), 3.71 (E); $[UO_2^{2+}]_t=0.17$ M. The NMR spectra were recorded on a JEOL GX-500 at 25 °C except for (E), which was measured with a JEOL GX-400 at 5 °C.

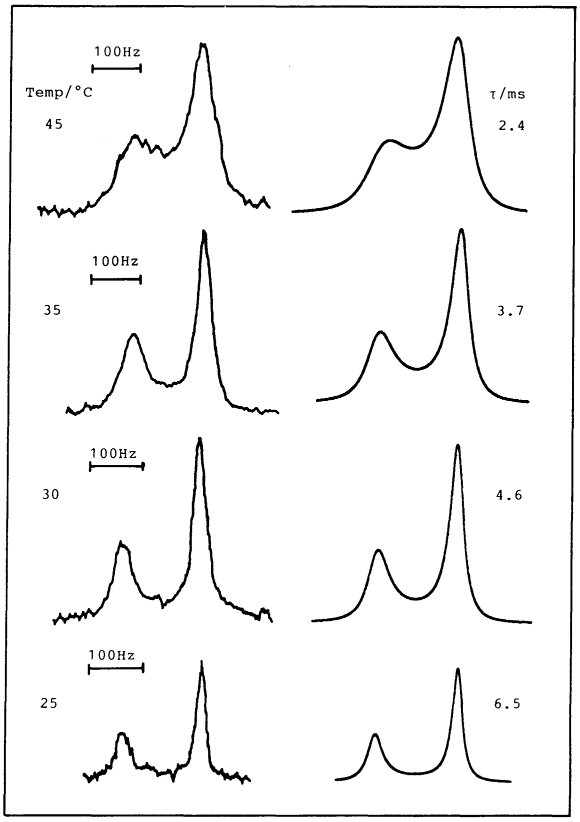

Fig. 2. Experimental (left side) and best-fit calculated ^{17}O NMR lineshapes of uranyl solutions which were recorded on a JEOL GX-500; $[UO_2^{2+}]_t=0.17$ M and $-\log[H^+]=3.38$ at 20 °C. Temperatures and best-fit τ values are shown at left and right sides in the figure, respectively.

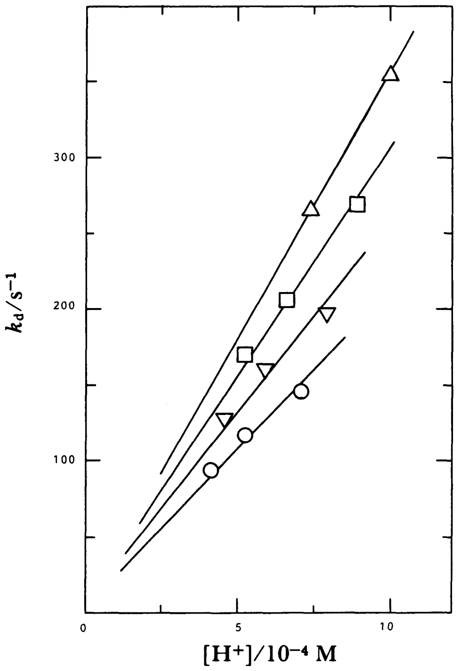

Fig. 3. Plots of k_d against [H$^+$] for the decomposition of $(UO_2)_2(OH)_2^{2+}$ complex: (○) 25 °C; (▽) 30 °C; (□) 35 °C; (△) 40 °C. The measurements were made by a JEOL GX-500.

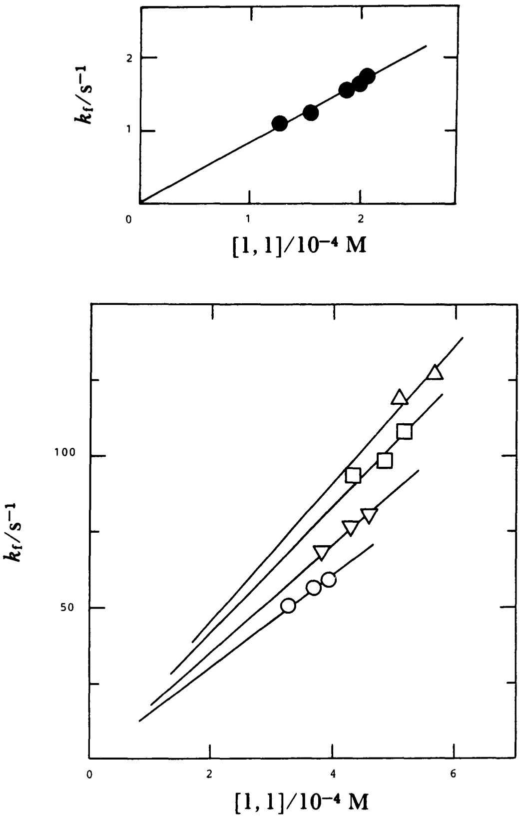

Fig. 4. a) A plot of k_f against [UO_2OH^+] at 5 °C. b) Plots of k_f against [UO_2OH^+] at various temperatures: (○) 25 °C; (▽) 30 °C; (□) 35 °C; (△) 40 °C. The NMR measurements were carried out by using a JEOL GX-400 (a) and a JEOL GX-500 (b).

neglected the effect of the existence of (3,5) species on τ, because the ^{17}O line-broadening of (3,5) species with increasing temperature is smaller than those of (1,0) and (2,2) species and [3,5] is much lower tha [1,1] and [2,2] in the sample solutions studied. The mean lifetimes of (1,0) and (2,2) species, $\tau_{1,0}$ and $\tau_{2,2}$, were evaluated from Eq. 4.

$$\tau = \tau_{1,0} P_{2,2} = \tau_{2,2} P_{1,0} \tag{4}$$

where the $P_{1,0}$ ($=1-P_{2,2}$) value is defined as [1,0]/([1,0]+2[2,2]). The values of P were calculated on the basis of thermodynamic parameters. The pseudo-first-order rate constants for formation and decomposition reactions, k_f and k_d, are expressed as

$$k_f = 1/\tau_{1,0} = -d[1,0]/[1,0]dt, \tag{5a}$$

$$k_d = 1/\tau_{2,2} = -d[2,2]/2[2,2]dt. \tag{5b}$$

The pseudo-first-order rate constants calculated are listed in Table 1. The rate constants for the formation of (2,2) species decrease with increasing [H$^+$], while the rate constants for the decomposition increase linearly with [H$^+$] (Fig. 4).

Eyring and co-workers[9] and Hurwitz and Atkinson[10] studied the kinetics of the formation reaction of (2,2) species by temperature- and pressure-jump relaxation methods and interpreted the relaxation times on the basis of the mechanism that the formation is initiated by the direct interaction of two uranyl ions, followed by fast subsequent abstraction of two hydrogen ions. This formation mechanism can be ruled out by the above results that the rate of the formation has an inverse relationship to [H$^+$]. However, it seems likely that the formation mechanism involves (1,1) species, because its concentration changes proportionally to 1/[H$^+$] as described by Eq. 1. As a result, the rate determining step in the formation of (2,2) species is postulated to be the bimolecular reaction (k_2, second-order rate constant) between (1,0) and (1,1) ions, followed by the fast abstraction of a hydrogen ion. Then k_f should be equal to k_2(1,1). This is demonstrated in Fig. 4-a. A plot of k_f determined at 5 °C by use of the GX-400 NMR spectrometer vs. [1,1] gives a straight line passing through the origin and the slope corresponds to the k_2 value. In Fig. 4-b, similar plots of k_f determined at various temperatures by the GX-500 NMR spectrometer vs. [1,1] are illustrated.

Table 1. Rate Constants for the Formation and Decomposition of $(UO_2)_2(OH)_2^{2+}$ Complex at 25 °C

Solution	i	ii	iii
−log[H$^+$]	3.15	3.28	3.38
k_f/s^{-1}	59.3	56.0	50.8
k_d/s^{-1}	93.8	117	146

A JEOL GX-500 NMR spectrometer was used for the NMR measurements.

Table 2. The Second-Order Rate Constants for the Formation and Decomposition of $(UO_2)_2(OH)_2^{2+}$ Complex

	25 °C	30 °C	35 °C	40 °C
$k_2/10^5\ M^{-1}\ s^{-1}$ [a)]	1.52±0.02	1.77±0.01	2.08±0.06	2.28±0.06
$k_{-2}K_a/10^5\ M^{-1}\ s^{-1}$ [b)]	2.10±0.09	2.54±0.13	3.04±0.08	3.46±0.11

a) $\Delta H^{\neq}=18.9\pm1.5$ kJ mol^{-1} and $\Delta S^{\neq}=-82.4\pm5.0$ J K^{-1} mol^{-1}.
b) $\Delta H^{\neq}=23.6\pm1.3$ kJ mol^{-1} and $\Delta S^{\neq}=-64.0\pm4.2$ J K^{-1} mol^{-1}.

A JEOL GX-500 NMR spectrometer was used for the NMR measurements. The GX-500 spectrometer gives better resolution for the signals of (1,0) and (2,2) than the GX-400 particularly at temperatures above 25 °C. The k_2 values are calculated from Fig. 4-b on the assumption that all the plots pass through the origin. The results are listed in Table 2 together with activation parameters for k_2 path. The k_2 value in the present study is about two times larger than the value ($6.4\times10^4\ M^{-1}\ s^{-1}$ in 0.5 M KNO_3 media at 25 °C) reported by Eyring et al.[11)] using the temperature-jump relaxation method. Wendt[15,16)] explained the formation reaction of dimer from $2MOH^{(z-1)+}$ (M^{z+}= Fe^{3+} and VO^{2+}) in terms of the Eigen-Wilkins mechanism[17] that the rate-determining step in the reaction is the loss of a water molecule from the inner hydration sphere of one $MOH^{(z-1)+}$ cation. The formation of (2,2) species from UO_2^{2+} and UO_2OH^+ may also be represented by

$$UO_2^{2+} + UO_2OH^+ \overset{K_E}{\rightleftharpoons} (UO_2^{2+}\cdots UO_2OH^+) \xrightarrow{k_{ex}}$$
$$[UO_2\text{-}OH\text{-}UO_2]^{3+} \xrightarrow[\text{fast}]{} (UO_2)_2(OH)_2^{2+} + H^+$$

where k_{ex} is the rate constant of water exchange in UO_2^{2+} ion, not in UO_2OH^+ ion because loss of a hydrogen ion from coordinated water is known to labilize metal ions for substitution reaction at another position,[18,19)] i.e. the rate for water exchange is expected to be faster in UO_2OH^+ than in UO_2^{2+}. The mechanism of water exchange in the uranyl ion was proposed to be dissociative interchange (I_d).[20)] The rate constant k_2 is given by

$$k_2 = K_E\,k_{ex} \tag{6}$$

The equilibrium constant, K_E, for the contact pair association between UO_2^{2+} and UO_2OH^+ ions can be estimated from the Eigen-Fuoss equation:[21)]

$$K_E = \frac{4\pi Na^3}{3000}\exp[-\{\frac{z_1z_2e^2}{aD} - \frac{z_1z_2e^2\kappa}{D(1+\kappa a)}\}/k_BT] \tag{7}$$

where

$$\kappa^2 = \frac{8\pi Ne^2\mu}{1000Dk_BT} \tag{8}$$

In these equations, N is Avogadro's number, a is the distance of closest approach between the two ions, e the electronic charge, D the dielectric constant, k_B the Boltzmann constant, T the absolute temperature, z_1 and z_2 the signed numbers of electronic charges on ions 1 and 2, and μ the ionic strength. In cases in which D=78.5, T=298 K, μ=0.5 M, and $a=6\times10^{-8}$ cm, Eq. 7 yields $K_E=0.20\ M^{-1}$. Rate constant k_{ex} is thus estimated to be $7.6\times10^5\ s^{-1}$ at 25 °C from Eq. 6. This estimated value is close to the rate constant for water exchange ($9.8\times10^5\ s^{-1}$ at 25 °C),[20)] which was determined in water–acetone mixture by the ^1H NMR line-broadening method on the assumption that the hydration number of the uranyl ion is four. This leads to the conclusion that the rate-determining step in the k_2 path is the loss of a water molecule in the equatorial plane of the uranyl ion.

The pseudo-first-order rate constants for the decomposition reaction of (2,2) species increase linearly with [H^+] in such low acid region as in this study. Frei and Wendt[12)] studied the decomposition reaction by $HClO_4$ ([H^+]<0.05 M) with the stopped-flow method and showed that the rate constant for the reaction approaches a limiting value at [H^+] in its high region. These results can be explained by the following two mechanisms: mechanism 1, the A–B–D–E pathway with B–D as the rate-determining step and mechanism 2, the A–B–D–E or A–C–D–E pathways with D–E as the rate-determining step. The basic distinction between the two mechanisms is that the rate-determining steps in mechanisms 1 and 2 are assumed to be the cleavage of the first and second

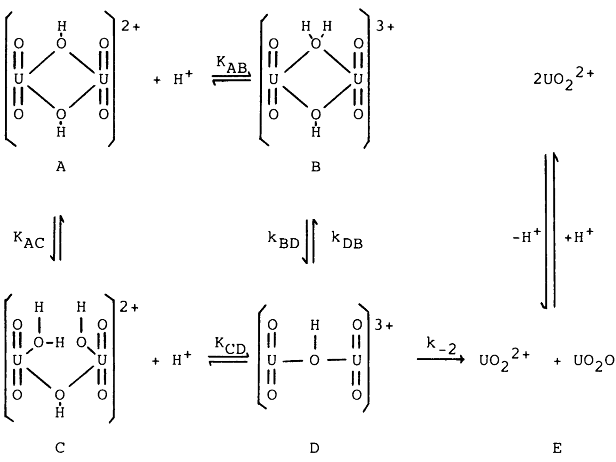

Table 3. The Second-Order Rate Constants for the Acid Decomposition Reaction of Di-μ-hydroxo Binuclear Complexes and Rate Constants for Water Exchange of the Composite Metal Ions at 25 °C

Binuclear complex	Rate const $M^{-1}\,s^{-1}$	Ref.	Metal ion	k_{ex} s^{-1}	Ref.
$[Cr(phen)_2OH]_2^{4+}$	2.3×10^{-6}	24	$Cr(NH_3)_5OH_2^{3+}$	5.5×10^{-5}	a)
$[Co(en)_2OH]_2^{4+}$	5×10^{-4}	28	$Co(en)_2(OH_2)_2^{3+}$	5.2×10^{-6}	b)
$[Co(NH_3)_4OH]_2^{4+}$	1.2×10^{-3}	c)	$Co(NH_3)_5OH_2^{3+}$	6.1×10^{-6}	19
$(VOH)_2^{4+}$	1.54	27	$V(OH_2)_6^{3+}$	5×10^{2}	d)
$(FeOH)_2^{4+}$	3.33	26	$Fe(OH_2)_6^{3+}$	1.6×10^{2}	18
$(VOOH)_2^{2+}$	2.6×10^{2}	16	$VO(OH_2)_5^{2+}$	5×10^{2}	e)
$(UO_2OH)_2^{2+}$	2.14×10^{5}	f)	$UO_2(OH_2)_5^{2+}$	7.6×10^{5}	f)

a) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958). b) S. Aygen, H. Hanssum, and R. van Eldik, *Inorg. Chem.*, **24**, 2853 (1985). c) A. B. Hoffmann and H. Taube, *Inorg. Chem.*, **7**, 903 (1968). d) A. D. Hugi, L. Helm, and A. E. Merbach, *Helv. Chim. Acta*, **68**, 508 (1985). e) K. Wüthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967). f) This work.

hydroxo bridges, respectively. Based on these mechanisms, k_d are given by

$$k_d = \frac{1}{2}\,\frac{K_{AB}[H^+]}{1+K_{AB}[H^+]}\,k_{BD} \tag{9a}$$

or

$$k_d = \frac{1}{2}\,\frac{K_a[H^+]}{1+K_a[H^+]}\,k_{-2} \tag{9b}$$

where K_a is defined as $[(UO_2)_2OH^{3+}]/[H^+][(UO_2)_2(OH)_2^{2+}]$. In the limiting case of $K_{AB}[H^+] \ll 1$ or $K_a[H^+] \ll 1$, k_d becomes $k_{BD}K_{AB}[H^+]/2$ or $k_{-2}K_a[H^+]/2$, either being the same form as the observed rate law. However, it appears unlikely that the rate for B–D step is slow to determine the whole, rate, because the dissociation of water in complex B will be labilized by the coordinated hydroxyl group and the rate is expected to be much faster than that of water exchange in the uranyl ion. Consequently we propose that the acid decomposition of (2,2) species proceeds through mechanism 2 rather than mechanism 1. According to mechanism 2 the slopes in Fig. 3 correspond to $k_{-2}K_a/2$, and the $k_{-2}K_a$ values at each temperature are listed in Table 2 along with activation parameters.

The existence of complex D, $(UO_2)_2OH^{3+}$, proposed in this study has been postulated in investigations of equilibrium reactions by several groups.[5,22,23] The approximate value of the equilibrium constant K_a can be obtained from the relationship $K_a = K_{21}/K_{22}$, where K_{21} is the equilibrium constant for the reaction $2UO_2^{2+}+H_2O=(UO_2)_2OH^{3+}+H^+$. With the use of the earlier data on K_{21} and K_{22},[5,22] K_a values at 25 °C are determined to be 63 and 28 M^{-1} in 3 and 0.1 M KNO_3 solutions, respectively. The limiting condition $K_a[H^+] \ll 1$ is therefore satisfied in the range of the acid concentrations in this study. The mechanism with the breakage of the second bridge as the rate-determining step, in which a single-bridged binuclear intermediate is formed, was also proposed in the decomposition reaction of di-μ-hydroxo-tetrakis(1,10-phenanthroline)-dichromium(III) ion.[24]

The rate law for the decomposition of $(UO_2)_2(OH)_2^{2+}$ ion is different from those of $(FeOH)_2^{4+}$,[16,25,26] $(VOOH)_2^{2+}$,[16] $(VOH)_2^{4+}$,[27] and $[Co(ethylenediamine)_2OH]_2^{4+}$,[28] which have both acid-independent and -dependent terms. The second-order rate constants for the acid-dependent path in the decomposition of related di-μ-hydroxo binuclear complexes are summarized in Table 3, which also contains the rate constants for water-exchange reaction in the composite metal ions. There appears to be some correlation between two rate constants, i.e. the more labile the substitution reactions, the faster the decomposition reactions.

The existence of $(UO_2)_2OH^{3+}$, which is one of the minor hydrolysis species of uranyl ions, has not been justified hitherto but is confirmed by this kinetic measurement.

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