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Structural and Kinetic Studies on Uranyl(V) Carbonate Complex Using ^{13}C NMR Spectroscopy

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We have measured ^{13}C NMR spectra of uranyl(V) carbonate complex in D_2O solution containing 1.003 M $Na_2{}^{13}CO_3$ at various temperatures. Two singlet signals corresponding to free and coordinated CO_3^{2-} were observed at 169.13 and 106.70 ppm, respectively. From the peak area ratio, the structure of the uranyl(V) carbonate complex was determined as $[U^VO_2(CO_3)_3]^{5-}$. Furthermore, kinetic analyses of the exchange reaction of free and coordinated CO_3^{2-} in $[U^VO_2(CO_3)_3]^{5-}$ were carried out using ^{13}C NMR line-broadening. As a result, the first-order rate constant at 298 K and the activation parameters for CO_3^{2-} exchange reaction in $[U^VO_2(CO_3)_3]^{5-}$ were evaluated as 1.13×10^3 s^{-1} and $\Delta H^\ddagger = 62.0 \pm 0.7$ kJ·mol^{-1}, $\Delta S^\ddagger = 22 \pm 3$ J·mol^{-1}·K^{-1}, respectively. We suggest that the exchange follows a dissociative mechanism as in the corresponding $[U^{VI}O_2(CO_3)_3]^{4-}$ complex.

Uranium(V) is unstable in solutions because of the disproportionation to uranium(IV) and uranyl(VI) species.[1] Therefore, the properties of U(V) species have not been clarified sufficiently. Recently, we performed electrochemical and spectroelectrochemical studies on some uranyl(VI) complexes to examine whether stable uranyl(V) complexes were formed.[2−4] As a result, we found that two uranyl(V) complexes, $[U^VO_2$(*N*,*N*′-disalicylidene-*o*-phenylenediaminato)-DMSO$]^-$ and $[U^VO_2$(dibenzoylmethanato)$_2$DMSO$]^-$ (DMSO = dimethyl sulfoxide), are stable in DMSO, and we also observed the electronic and IR spectra of the pure uranyl(V) complexes in nonaqueous solvents.

On the other hand, in aqueous solution, the only known stable uranyl(V) complex is a carbonate species formed in basic carbonate aqueous solution (pH > 11).[5−7] This complex is stable toward disproportionation to U(IV) and U(VI) carbonate complexes.[6] Cohen reported that the U(V) species in this system is colorless. We have confirmed this by observing the disappearance of the characteristic absorption band of uranyl(VI) carbonate complex ($[U^{VI}O_2(CO_3)_3]^{4-}$) at approximately 450 nm with the spectroelectrochemical technique using an optical transparent thin-layer electrode cell.[8] The composition of $[U^VO_2(CO_3)_3]^{5-}$ has been determined from potentiometric data.[6] Additionally, the composition and structure have been confirmed by using Raman,[9] EXAFS,[10] and quantum chemical methods.[11] However, little information is available concerning kinetics of uranyl(V) carbonate species, despite many data for uranyl(VI) complexes with carbonate[12,13] and other ligands.[14] Furthermore, there are no detailed studies on ligand exchange reactions even in other actinyl(V) with the exception of neptunyl(V) carbonates studied by Clark et al.[15] They reported that the ^{13}C NMR spectra of sample solutions containing the $[Np^VO_2(CO_3)_m]^{(2m-1)-}$ (m = 1 or 2) complex and $((C_4H_9)_4N)_2$-

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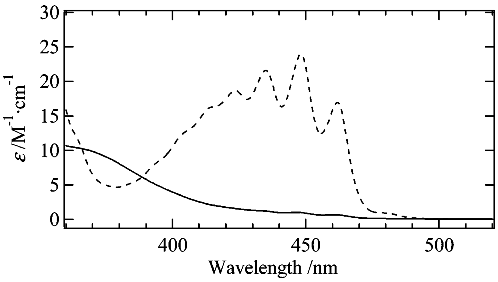

Figure 1. UV−visible absorption spectra of D_2O solution containing $[U^{VI}O_2(CO_3)_3]^{4-}$ (broken line) and the solution obtained after the reduction (solid line).

CO_3 show single broad signals due to CO_3^{2-} at 110.6 and 110 ppm, respectively, indicating rapid exchange between free and coordinated CO_3^{2-}, while the ^{13}C NMR spectrum of $[Np^VO_2(CO_3)_3]^{5-}$ in Na_2CO_3 solution shows a sharp signal for the free CO_3^{2-} at 165.8 ppm, implying slow chemical exchange on the NMR time scale. However, they have not carried out any kinetic analyses of these data.

In the present study, we have measured the ^{13}C NMR spectra for the uranyl(V) carbonate complex in basic carbonate aqueous solution and performed a kinetic analysis of the exchange between free and coordinated CO_3^{2-} in this complex.

As a starting material, $Na_4[U^{VI}O_2(CO_3)_3]$ was synthesized by the procedure reported previously.[16] The uranyl(V) carbonate (4.598×10^{-2} mol·dm^{-3} (M)) in D_2O (99.8 at. % D, ACROS) solution containing $Na_2{}^{13}CO_3$ (99 at. % ^{13}C, ISOTEC; 1.003 M) was prepared by electrochemical reduction of $[U^{VI}O_2(CO_3)_3]^{4-}$ on a Pt-plate working electrode at −0.950 V vs Ag/AgCl. The resulting solution was colorless as reported by Cohen[5] and Wester et al.[17] The UV−visible absorption spectra in Figure 1 show the disappearance of the characteristic absorption band of $[U^{VI}O_2(CO_3)_3]^{4-}$ with the reduction. This means that the $[U^{VI}O_2(CO_3)_3]^{4-}$ complex in the sample solution was completely reduced to the corresponding uranyl(V) carbonate complex. We could not observe any spectral changes for the sample solution in the tightly sealed quartz cell even during a period of several months. The pD (−log [D^+]) value of the sample solution was 11.96. The sample solution was deoxygenated by passing Ar gas through the solution for at least 3 h prior to all experiments and making all operations under Ar atmosphere. The ^{13}C NMR spectra were measured with JEOL JNM-LA300WB instrument (^{13}C, 75.45 MHz; reference, external TMS).

The ^{13}C NMR spectra of D_2O solutions containing the uranyl(V) carbonate (4.598×10^{-2} M) and Na_2CO_3 (1.003 M)[18] were measured at different temperatures. The resulting spectra in the range from 273 to 313 K are shown in Figure 2. At 273 K, two sharp singlet peaks were observed at 169.13 and 106.70 ppm. As reported previously,[12,13,19] the

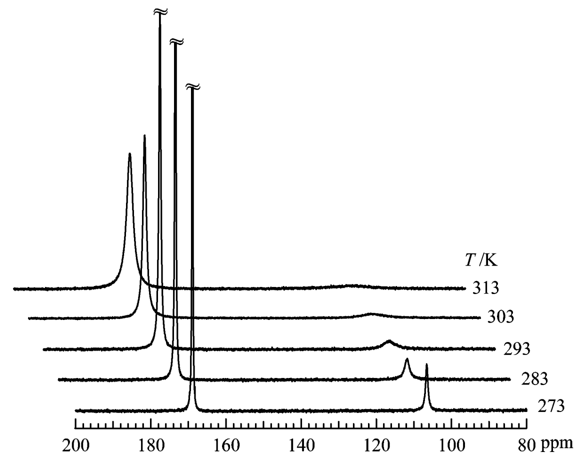

Figure 2. ^{13}C NMR spectra of D_2O solution containing $[U^VO_2(CO_3)_3]^{5-}$ (4.598×10^{-1} M) and Na_2CO_3 (1.003 M).

peak at 169.13 ppm is the result of fast exchange reaction between free CO_3^{2-} and DCO_3^-. Another singlet peak at 106.70 ppm can be assigned to the coordinated CO_3^{2-} in the uranyl(V) carbonate complex. Such a singlet peak indicates that the coordinated CO_3^{2-} exists in the same chemical environment. Furthermore, there is no peak at 168.22 ppm, which corresponds to the coordinated CO_3^{2-} in $[U^{VI}O_2(CO_3)_3]^{4-}$.[20] This means that the oxidation of uranyl(V) carbonate to $[U^{VI}O_2(CO_3)_3]^{4-}$ is negligible under the present experimental condition. From the areas of the peaks of the free and coordinated CO_3^{2-}, the number of CO_3^{2-} coordinated to the uranyl(V) complex was evaluated as 2.8 ± 0.1. This indicates that the uranyl(V) complex in this system is $[U^VO_2(CO_3)_3]^{5-}$.

As can be seen from Figure 2, the line-widths of the two signals corresponding to the free and coordinated CO_3^{2-} increase with increasing temperature, indicating an increase in the rate of the following ligand exchange reaction:

$$[U^VO_2(CO_3)_3]^{5-} + {}^*CO_3^{2-} \rightleftarrows [U^VO_2(CO_3)_2({}^*CO_3)]^{5-} + CO_3^{2-} \quad (1)$$

To analyze the rate of the CO_3^{2-} exchange by using the NMR line-broadening method, we measured the line-widths at half-height of the free CO_3^{2-} signal in the presence and absence of $[U^VO_2(CO_3)_3]^{5-}$ at different temperatures in the range from 273 to 333 K. Figure 3 shows a semilogarithmic plot of $(T_{2obs}^{-1} - T_{2n}^{-1})P_L/P_M$ against the reciprocal temperature. T_{2obs} and T_{2n} are the transverse relaxation times of free CO_3^{2-} in the presence and absence of $[U^VO_2(CO_3)_3]^{5-}$, respectively, and are related with the line-width ($\Delta\nu$) at half-height by $T_{2obs}^{-1} = \pi\Delta\nu_{obs}$ and $T_{2n}^{-1} = \pi\Delta\nu_n$. P_L and P_M are molar fractions of the free and coordinated CO_3^{2-}, respectively. Since the uranyl(V) ion has one unpaired electron in the 5f-orbital of uranium (i.e., $5f^1$ configuration), $[U^VO_2(CO_3)_3]^{5-}$ is paramagnetic. Hence, the temperature dependence of

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(20) If the sample solution is a mixture of uranyl(V) and (VI), the ^{13}C NMR signals due to the free CO_3^{2-} and the coordinated CO_3^{2-} in $[U^VO_2(CO_3)_3]^{5-}$ and $[U^{VI}O_2(CO_3)_3]^{4-}$ should be observed at 168.86, 106.52, and 168.22 ppm, respectively. The ^{13}C NMR spectrum of D_2O solution containing $[U^VO_2(CO_3)_3]^{5-}$, $[U^{VI}O_2(CO_3)_3]^{4-}$ and 1 M Na_2CO_3 at 273 K is shown in Figure S1 in the Supporting Information.

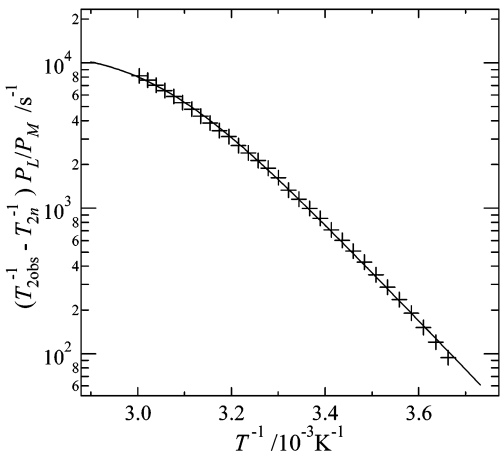

Figure 3. Plot of $(T_{2obs}^{-1} - T_{2n}^{-1})P_L/P_M$ vs. $1/T$ for the exchange of CO_3^{2-} in $[UO_2(CO_3)_3]^{5-}$. Experimental results are shown by +; full-drawn curve shows best fit of eq 2.

$(T_{2obs}^{-1} - T_{2n}^{-1})P_L/P_M$ for the present system can be described by eq 2:[21–23]

$$(T_{2obs}^{-1} - T_{2n}^{-1})P_L/P_M = \tau_M^{-1}[T_{2M}^{-2} + T_{2M}^{-1}\tau_M^{-1} + \Delta\omega_M^2]/[(T_{2M}^{-1} + \tau_M^{-1})^2 + \Delta\omega_M^2] \quad (2)$$

where T_{2M}, τ_M, and $\Delta\omega_M$ are the transverse relaxation time of coordinated CO_3^{2-}, the mean lifetime of the coordinated CO_3^{2-}, and the difference between chemical shifts of the free and coordinated CO_3^{2-}, respectively. The relationship between τ_M and the first-order exchange rate constant (k_{ex}) with temperature is

$$\tau_M^{-1} = k_{ex} = (k_BT/h)\exp[(-\Delta H^{\ddagger} + T\Delta S^{\ddagger})/RT] \quad (3)$$

and the temperature dependence of T_{2M} and $\Delta\omega_M$ is assumed to be given by eqs 4 and 5, respectively.[24,25]

$$T_{2M}^{-1} = C_M\exp(E_M/RT) \quad (4)$$

$$\Delta\omega_M = C_\omega/T \quad (5)$$

The kinetic parameters were determined by a nonlinear least-squares fit of $(T_{2obs}^{-1} - T_{2n}^{-1})P_L/P_M$ data to the equation obtained by substitution of eqs 3–5 into eq 2. In the fitting process, the values of C_M, E_M, and C_ω were roughly estimated and then constrained to 2.57×10^3 s^{-1}, 4.80 kJ·mol^{-1}, and 2.51×10^5 rad·s^{-1}·K^{-1}, respectively.[26] Subsequently, the activation parameters in reaction 1 were calculated as $\Delta H^{\ddagger} = 62.0 \pm 0.7$ kJ·mol^{-1} and $\Delta S^{\ddagger} = 22 \pm 3$ J·mol^{-1}·K^{-1} (SD = 0.03).[27] Using these values and eq 3, the k_{ex} value of reaction 1 at 298 K was evaluated as 1.13×10^3 s^{-1}. This is the first report of a rate constant for ligand exchange reaction in uranyl(V) complexes.

It should be noted that the exchange reaction between the free and coordinated CO_3^{2-} in $[U^VO_2(CO_3)_3]^{5-}$ is about 10^2 times faster and 10^5 times slower than those in $[U^{VI}O_2(CO_3)_3]^{4-}$ and $[Pu^{VI}O_2(CO_3)_3]^{4-}$, in which the exchange reactions follows a dissociative (D) mechanism.[12,15a] Their kinetic parameters ($\Delta H^{\ddagger}$/kJ·mol^{-1} and $\Delta S^{\ddagger}$ /J·mol^{-1}·K^{-1}) are 82 and 50 for U^{VI}, and 34 and 31 for Pu^{VI}, respectively. The positive $\Delta S^{\ddagger}$ value in the present study suggests that reaction 1 also occurs through the D mechanism. Moreover, the equatorial plane of $[U^VO_2(CO_3)_3]^{5-}$ is coordinatively saturated and has a structure similar to that of $[U^{VI}O_2(CO_3)_3]^{4-}$.[10,11] Hence, it seems reasonable to assume that reaction 1 proceeds through the D mechanism and that the difference in the dissociation rates in $[U^VO_2(CO_3)_3]^{5-}$ and $[U^{VI}O_2(CO_3)_3]^{4-}$ is related to the strength of bonding of CO_3^{2-}. This can be supported by the equilibrium constant (log K) for the following reaction:

$$[UO_2(CO_3)_2]^{n-4} + CO_3^{2-} = [UO_2(CO_3)_3]^{n-6} \quad (6)$$

where n is equal to 1 and 2 for uranyl(V) and uranyl(VI), respectively. The log K values in 1 M Na_2CO_3 are ~2 for n = 1 and 6.4 for n = 2.[7,15] Furthermore, the EXAFS study reported by Docrat et al.[10] shows that the bond distance between U and O of coordinated CO_3^{2-} in $[U^VO_2(CO_3)_3]^{5-}$ (2.50 ± 0.02 Å) is 0.07 Å longer than that in $[U^{VI}O_2(CO_3)_3]^{4-}$ (2.43 ± 0.02 Å). These data suggest that the dissociation of CO_3^{2-} from $[U^VO_2(CO_3)_3]^{5-}$ occurs more easily than from $[U^{VI}O_2(CO_3)_3]^{4-}$. In fact, the $\Delta H^{\ddagger}$ value of reaction 1 is much smaller than the corresponding reaction in $[U^{VI}O_2(CO_3)_3]^{4-}$, indicating a weaker bonding of the leaving CO_3^{2-} in $[U^VO_2(CO_3)_3]^{5-}$ than in $[U^{VI}O_2(CO_3)_3]^{4-}$. Our proposed D mechanism for reaction 1 is also consistent with the result of a quantum chemical study on the mechanism of water exchange reactions in $[U^VO_2(H_2O)_5]^+$ and $[U^{VI}O_2(H_2O)_5]^{2+}$ by Vallet et al.,[28] which suggested that the D mechanism is favored in the uranyl(V) aqua ions as a result of the weaker metal–ligand bond strength.

Supporting Information Available: ^{13}C NMR spectrum of D_2O solution containing uranyl(V) and (VI) carbonate complexes and 1 M Na_2CO_3 at 273 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) From Figure 2, it is reasonable to conclude that the transverse relaxation time of free CO_3^{2-} in the temperature range from 273 to 303 K is mainly controlled by τ_M^{-1}. Therefore, from the Eyring plot, we could estimate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as 61.8 kJ·mol^{-1} and 20 J·mol^{-1}·K^{-1}, respectively. These values are consistent with those obtained by fitting. The nonlinear least-squares fit to eq 2 gave a minimum error value, when the values of C_M and E_M were fixed to 2.57×10^3 s^{-1} and 4.80 kJ·mol^{-1}, respectively. The $\Delta\omega_M$ value was found to have no influence on the fit even in $\Delta\omega_M = 0$. This means that the line-widths in the range from 273 to 333 K in Figure 2 are independent of $\Delta\omega_M$. Furthermore, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated by changing C_M and E_M values in the ranges of $(2.35–2.70) \times 10^{-3}$ s^{-1} and 3.6–4.9 kJ·mol^{-1}, respectively. As a result, the variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were found to be ±0.7 and ±3, respectively.

(27) Normalized standard deviation = $[\Sigma\{(y_o - y_p)/y_o\}^2/(q - r)]^{1/2}$, where y_o and y_p are the observed and predicted values of $(T_{2obs}^{-1} - T_{2n}^{-1})$-$P_L/P_M$, q is the number of observed values, and r is the number of variable parameters used in the fit.

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