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Kinetic Behavior of Carbonate Ligands with Different Coordination Modes: Equilibrium Dynamics for Uranyl(2+) Carbonato Complexes in Aqueous Solution. A ^{13}C and ^{17}O NMR Study

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The dynamics of the carbonate and the uranyl exchange in aqueous solutions of uranyl(VI) carbonate has been studied in the pH-range $6 < pH < 9$ and in the temperature range -5 °C $< t < +85$ °C using ^{13}C and ^{17}O NMR line broadening, selective magnetization transfer and 2-dimensional exchange spectroscopy (2D-EXSY). This extensive experimental approach was necessary in order to cover the vastly varying time scales for the different exchange processes. Two uranyl complexes dominate the investigated chemical system: the **MONO**nuclear $UO_2(CO_3)_3^{4-}$ and the **TRIN**uclear $(UO_2)_3(CO_3)_6^{6-}$ complex. In the MONO complex, all the three ligands are bidentately coordinated to uranium. The TRIN complex comprises two different types of carbonate ligands: three **TERM**inal carbonates with bidentate coordination to the uranium atoms and three **CENT**ral carbonates with a rare μ_3-coordination to two uranium atoms. In addition, **FREE** carbonate can be present in the studied solutions as CO_3^{2-}/HCO_3^- or CO_2(aq), and participate in exchange reactions. The proton exchange for CO_3^{2-}/HCO_3^- is known to be very fast, but it is very slow for HCO_3^-/CO_2(aq). Thus, the exchange between four carbonate sites had to be considered: MONO, CENT and TERM, and FREE. Carbonate exchange for the MONO complex has been been found to proceed according to two parallel pathways. The first is a dissociative ("water-assisted") process, $UO_2(CO_3)_3^{4-}$ $(k_1) \rightharpoonup$ $UO_2(CO_3)_2^{2-} + CO_3^{2-}$, with a first-order rate equation: $rate = k_1$[MONO], where $k_1 = 11(3)$ s^{-1} at 298 K, which dominates at high pH-values. This pathway was proposed in our previous paper and is confirmed here for a much wider uranyl concentration range. The second is a proton-catalyzed reaction with the following rate law: $rate = k_2$·[MONO]·[H$^+$], where $k_2 = 2.32(0.03) \times 10^9$ M^{-1} s^{-1}, $\Delta H^\ddagger = 52(1)$ kJ mol^{-1}, and $\Delta S^\ddagger = 110$ J mol^{-1} K^{-1}, which dominates the carbonate exchange for pH < 8.6 and shows no dependence on the free carbonate concentration. This reaction is almost 2 times faster in D_2O than in H_2O. It is proposed that this is a dissociative process with fast protonation of the non-coordinated carbonate oxygen in MONO, followed by a water-assisted dissociation of the carbonate ligand. The rate of carbonate exchange for the TRIN complex is independent of the free carbonate concentration and is much larger for the TERMinal ligands, $k_{obs} = 42(3)$ s^{-1} at pH = 6.1, than for the CENTral ligands, $k_{obs} = 1.4(0.3)$ s^{-1} at the same pH. Whereas the former reaction (i.e. TERM $\leftrightarrow$ FREE) represents a similar type of exchange as that for the MONO complex, the CENT reaction proceeds through a decomposition of the entire TRIN complex (i.e. TRIN $\leftrightarrow$ MONO). This has been proved by the simultaneous line broadening of the ^{17}O signal of the TRIN uranyl group and the ^{13}C signal of CENT carbonate at increasing temperature, in combination with ^{17}O NMR magnetization-transfer experiments and the observation that after 5 s ^{17}O-enriched uranyl oxygens of the TRIN complex were already equilibrated with the nonenriched uranyl oxygens of MONO. The mechanism of carbonate and uranyl exchange processes is discussed in the framework of the structure of the interacting species. The ^{17}O and ^{13}C NMR spin−lattice relaxation times, T_1, of the different species have been determined.

Introduction

Both components of the title system deserve considerable attention. Extensive physicochemical investigations of uranyl compounds, including detailed studies of uranyl carbonate complexes, have provided suitable background for the nuclear energy industry.[1] The importance of these compounds in the extraction processes in uranium mining[2] and their role in migration of UO_2^{2+} in ground water is well established. The carbonate ligand, present almost everywhere in our natural environment, is one of the most important reactive anions. Kinetic studies of metal/organic ligand/carbonate systems can serve as a model for several biochemical processes of carbonate. Studies of the carbonic anhydrase enzyme and its models,[3,4] and other processes like the "synergistic anion effect" of HCO_3^- in transferrin[5] also call for further work in order to establish the relation between the structural and kinetic behavior of metal carbonates.[6]

In the aqueous U(VI)−CO_3^{2-}−H$^+$ system two very stable binary species dominate in a wide pH range, according to

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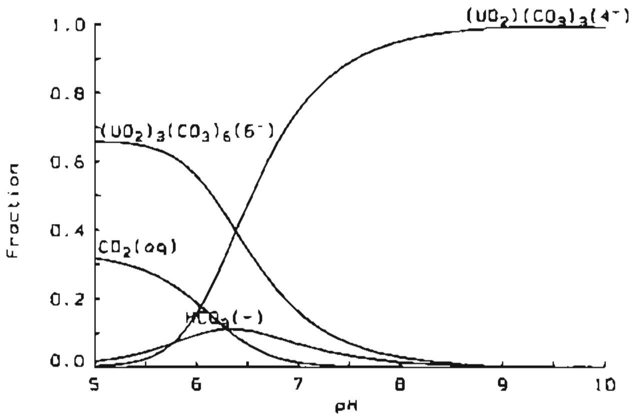

Figure 1. Fraction of carbonate present in the various species as a function of pH for the total concentrations: T_U = 100 mM, T_{CO_3} = 300 mM. The equilibrium constants were taken from ref 1 (and are given in Table S1 of the Supplementary Material).

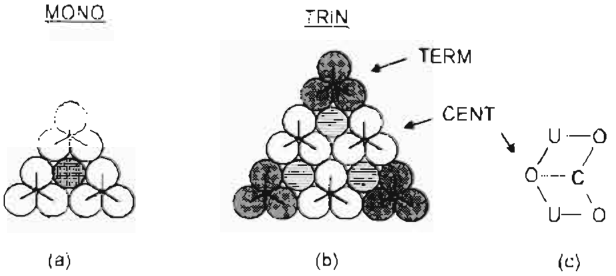

Figure 2. Proposed structures of the dominating uranyl carbonato complexes in aqueous solution: (a) MONOnuclear complex, $UO_2(CO_3)_3^{4-}$; (b) TRINuclear complex, $(UO_2)_3(CO_3)_6^{6-}$; (c) CENTral carbonate ligand in the TRIN complex showing an unusual coordination mode.

thorough equilibrium studies: a trimer, $(UO_2)_3(CO_3)_6^{6-}$ (TRIN) and a monomer, $UO_2(CO_3)_3^{4-}$ (MONO), (see Figure 1). The two complexes are structurally related to each other (see Figure 2) and to the solid UO_2CO_3.[7] The carbonates are bidentate in MONO in the solid and probably also in solution. If this is the case, the UO_2^{2+} ion does not coordinate water into the inner coordination sphere even in solution: the uranium atoms are eight-coordinated by six carbonate oxygens in a plane and two -yl oxygens perpendicular to the plane. The structure of TRIN is known from a solution X-ray diffraction study.[8] In the TRIN complex, three bidentate carbonates occupy terminal positions (TERM), and the remaining three ligands in central positions (CENT) belong to a rare type of μ_3-bridging carbonates[9,10] (see Figure 2c). The coordination sphere of the UO_2^{2+} ions is complete both in the TRIN and in the MONO complex.

We have recently studied the ligand exchange reaction between MONO and free carbonate ions in aqueous solution at pH > 8.7.[11] This reaction has a dissociative rate-determining step and is relatively slow, $k = 13\ s^{-1}$; it proceeds through the dissociation of one carbonate ion from the complex. In the present paper we present a study of the dynamic processes taking place in the equilibrium system containing MONO, TRIN and non-coordinated carbonate (FREE) in the pH range 6–9. We have used two experimental tools, ^{13}C and ^{17}O NMR, each giving specific (and often complementary) information on the studied exchange reactions. The time scales for the different reaction paths were covered using line broadening, selective magnetization-transfer (MT) and 2D-EXSY techniques in solutions with varying composition in the temperature range −5 °C to +85 °C. Mechanism of carbon and oxygen exchange processes will be discussed in relation to the structure of the interacting species.

Experimental Section

Solutions. The uranium(VI) perchlorate stock solution was prepared and analysed by the method described elsewhere.[12]

^{17}O NMR measurements were performed in ^{17}O-enriched samples using $H_2{}^{17}O$ (17.55 atom% ^{17}O, ISO-YEDA Co, Rehovot, Israel) in two ways:

(1) Enrichment of the -yl oxygens of uranyl(2+) was accomplished by UV-irradiation of the $UO_2(ClO_4)_2$ stock solution to which a small amount of $H_2{}^{17}O$ was added, with a mercury lamp.[13] No ^{17}O-enrichment of the uranyl oxygens was observed without UV irradiation. (2) Enrichment of the carbonate sites was achieved by keeping an approximately 1 M solution of $NaHCO_3$ in ^{17}O-enriched water overnight at elevated temperature. The resulting solution was then used to prepare the uranyl carbonate complexes. The equilibration between ^{17}O-enriched water and fully deprotonated or uranyl-coordinated carbonates was found to be much slower; ^{17}O-enrichment was not observed even after a few days at room temperature.

Preparation of the NMR Samples. The trinuclear uranyl carbonate (TRIN) samples were prepared *in situ* in 10 mm outer diameter NMR tubes which were closed with serum caps to prevent CO_2 from escaping. Four equivalents of $NaH^{13}CO_3$, (Larodan Fine Chemicals AB, 99% ^{13}C), $NaClO_4$ (Merck) and H_2O was weighed into the NMR tube, which was then filled with CO_2 gas (natural isotope distribution). Then, 1 equiv of the $UO_2(ClO_4)_2$ stock solution was carefully added drop by drop into the tube. The mixture was intensively stirred in an ultrasonic bath. The almost quantitative formation of the complex, $(UO_2)_3(CO_3)_6^{6-}$, resulted in release of 2 equiv of proton from $H^{13}CO_3^-$, and a formation of 2 equiv of $^{13}CO_2$ from the excess of $H^{13}CO_3^-$. The pressure in the NMR tube was then decreased to the atmospheric one by releasing some part of the gas. The formation of $UO_2(CO_3)_3^{4-}$ from $(UO_2)_3(CO_3)_6^{6-}$ and vice versa was achieved by addition of acid or base into the NMR tube and was followed by ^{13}C and/or ^{17}O NMR. $HClO_4$ or Na_2CO_3 and/or NaOH solution was injected into the NMR tube by a syringe piercing the serum cap. The pressure in the NMR tube was equilibrated to atmospheric pressure after each injection.

The constancy of the ionic medium in the samples was ensured by keeping the sodium ion concentration constant; $[Na^+]$ = 1.0 M. Recording of quantitative ^{17}O and ^{13}C NMR spectra required relatively high concentration of the highly charged TRIN complex; thus, a rigorously constant ionic strength could not be kept. The distribution of species was calculated using the equilibrium constants from ref 1 (see Table S1, in *Supplementary Material*) and controlled by measuring peak integrals in ^{13}C and ^{17}O NMR spectra. At the actual experimental conditions (including variable temperature) the calculated and experimental species concentrations were not significantly different.

NMR Measurements. Most of the NMR spectra were recorded on a Bruker AM400 spectrometer using 10 mm (outer diameter) spinning sample tubes, (in a few cases, a Bruker MSL200 spectrometer was used). The probe temperature was regulated using a Bruker Eurotherm variable temperature control unit. The temperature was measured by a calibrated Pt-100 resistance thermometer. Spectra were recorded in unlocked mode. The NMR parameters were chosen to obtain quantitative integrated intensities for the measured signals, and were typically:

^{13}C NMR, at 100.6 MHz: pulse width = 10 μs, (≈40° pulse), number of scans = 32, pulse repetition time 4 s, spectral window = 5000 Hz, digital resolution = 0.4 Hz/point. The chemical shifts are given in ppm toward higher frequency with respect to external water-

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soluble TMS at 25 °C. ^{17}O NMR, at 54.2 MHz: pulse width = 10 μs ($\approx 40°$ pulse), number of scans: 4–20000, spectral window = 80000 Hz, pulse repetition time = 0.1 s. The chemical shifts are given in ppm toward higher frequency with respect to external tap water at 25 °C.

Selective inversion transfer experiments were performed using a DANTE pulse train.[14] The DANTE pulses were typically 1 μs long and the selectivity was regulated by the delay time between the pulses.

For ^{13}C NMR 2D-EXSY experiments, a standard phase-sensitive NOESY pulse sequence (TPPI)[15] provided with the spectrometer was used. NMR parameters were chosen in order to obtain approximately quantitative spectra. ^{13}C NMR, at 100.6 MHz: pulse width = 90° (23 μs), number of scans = 16, pulse repetition time 10 s, spectral window = 1300 Hz, digital resolution = 1.3 Hz/point.

Some additional experimental details are given in the caption for Figure 10.

Data Treatment

Equilibrium Calculations. The equilibrium distribution of the samples was calculated using the PSEQUAD computer program[16] and represented graphically by the SED program[17,18] using selected equilibrium data.[1,19] A pH-electrode could not be used to measure pH in an NMR tube without losing carbon dioxide. Therefore, the total proton concentration (required for the calculations), which was set equal to the concentration of $[HCO_3^-]$ at pH $\approx$ 6, was experimentally checked using ^{13}C NMR integrals of the well-resolved signals of the FREE carbonate and the TRIN complex (NMR spectra recorded overnight at −5 °C). A good estimate of the total concentrations in the sample could also be obtained from the weights of solid $NaHCO_3$, the $UO_2(ClO_4)_2$ stock solution, and the “lost” CO_2 during the preparation of the TRIN complex. Equilibrium concentration of H^+ in some samples was determined directly in the NMR tubes from the ^{13}C NMR chemical shift of the HCN/CN^- buffer according to the well-defined formula[20,21]

$$\mathrm{pH} = 9.01 + \log[(\delta_{\mathrm{obs}} - 114.97)/(167.4 - \delta_{\mathrm{obs}})]$$

Dynamic Calculations. In the slow exchange regime on the actual chemical shift time scale, where the exchanging sites appear in the NMR spectrum as separate, exchange-broadened signals,[22] the exchange data were obtained from the line shape of the separated NMR peaks. Line broadening (in Hz) due to the chemical exchange was calculated as $\Delta\nu_{1/2} = (\Delta\nu_{1/2}^{\mathrm{obs}} - \Delta\nu_{1/2}^{0})$, where $\Delta\nu_{1/2}^{\mathrm{obs}}$ is the observed line width, and $\Delta\nu_{1/2}^{0}$ is the nonexchange line width of the signal, respectively. $\Delta\nu_{1/2}^{0}$ was measured in independent experiments for species existing individually, or in equilibrium (in very slow exchange) with other species at low temperature. For all exchanging sites in ^{13}C NMR, $\Delta\nu_{1/2}^{0} \approx 1$ Hz was obtained. (The determination of the corresponding value for the ^{17}O NMR signal of the uranyl oxygen will be discussed below.) Line widths were measured by fitting a Lorenzian curve to the experimental signal by using the standard Bruker software. In some cases deconvolution of overlapping peaks was done using WINNMR program (Bruker-Franzén, Bremen) which yielded both the integrals and the line widths.

Rate constants were calculated by using the formula $k_{\mathrm{obs}} = \pi\Delta\nu_{1/2}$.[22] Rate equations were deduced from the variation of k_{obs} with equilibrium concentrations of different species. In cases, when the chemical exchange was too slow to cause any measurable line broadening, magnetization-transfer experiments were performed and evaluated according to eq 1, where the

$$d(\mathbf{M} - \mathbf{M}(\infty))/dt = \mathbf{R}\,(\mathbf{M} - \mathbf{M}(\infty)) \qquad (1)$$

vector of the z-magnetization is $\mathbf{M}$ at time t and $\mathbf{M}(\infty)$ at time $t = \infty$. The number of elements of the vectors is equal to the number of separated peaks. The off-diagonal elements of matrix $\mathbf{R}$ are the rate constants k_{ij}, (where $i \neq j$) and the diagonal elements are the sum of k_{ji} and $1/(T_1)_i$ (where $j \neq i$ and $(T_1)_i$ is the spin–lattice relaxation time for site i (see Supplementary Material for details). Equation 1 was solved in two ways. When only two exchanging sites were present, an analytical solution was obtained[23] and the Gauss–Newton–Marquardt algorithm was used for fitting to the experimental curves. In each series of experiments, one peak was inverted by a 180° pulse and then both peaks were observed using a delayed 90° pulse. In the consequent calculations, both series of experiments were treated in parallel. For quantitative analysis the integrals of the deconvoluted peaks were used. The pulse imperfections were corrected by treating the initial and equilibrium magnetizations as adjustable parameters in the least-squares refinements.

When more than two exchanging sites were present, the solution of eq 1 was written in the following form:

$$\mathbf{M}(t) = \mathbf{M}(\infty) + \exp(\mathbf{R}t)[\mathbf{M}(0) - \mathbf{M}(\infty)] \qquad (2)$$

($\mathbf{M} = \mathbf{M}(0)$ for $t = 0$). The rate parameters were obtained from eq 2 by using the Gauss–Newton–Marquardt algorithm applied after diagonalization of $\mathbf{R}$ (see Supplementary Material). Throughout this paper the uncertainty in the determined parameters, 1σ, is given in parentheses after the refined value.

Results and Discussion

1. Assignment of the NMR Signals. A straightforward way to assign NMR signals in a well-described equilibrium system in the “slow exchange regime” on the actual NMR time scale is to change the distribution of the species by varying the solution composition. In our case the concentration of two components in the system could be followed: UO_2^{2+} by ^{17}O NMR and CO_3^{2-} by both ^{17}O and ^{13}C NMR. For practical reasons, namely because of the possible selective enrichment and the very large ^{17}O NMR chemical shift difference between the -yl oxygen and the carbonate oxygen regions, two types of ^{17}O-enriched samples were made (see Experimental Section):

a. Solutions ^{17}O-enriched on the UO_2^{2+} sites and ^{13}C-enriched on the carbonate sites were prepared from ^{17}O-enriched $UO_2(ClO_4)_2$ stock solution (only -yl sites enriched) by addition of ^{13}C-enriched $NaHCO_3$. Both ^{17}O NMR (-yl oxygen region) and ^{13}C NMR spectra were recorded (see Figure 3).

b. In order to record the carbonate region of the ^{17}O NMR spectra (Figure 4), ^{17}O-enriched HCO_3^- was used for preparation of the solutions of the studied complexes, $(UO_2)_3(CO_3)_6^{6-}$ and $UO_2(CO_3)_3^{4-}$. The experimental results (Figures 3 and 4) led to the following assignments.

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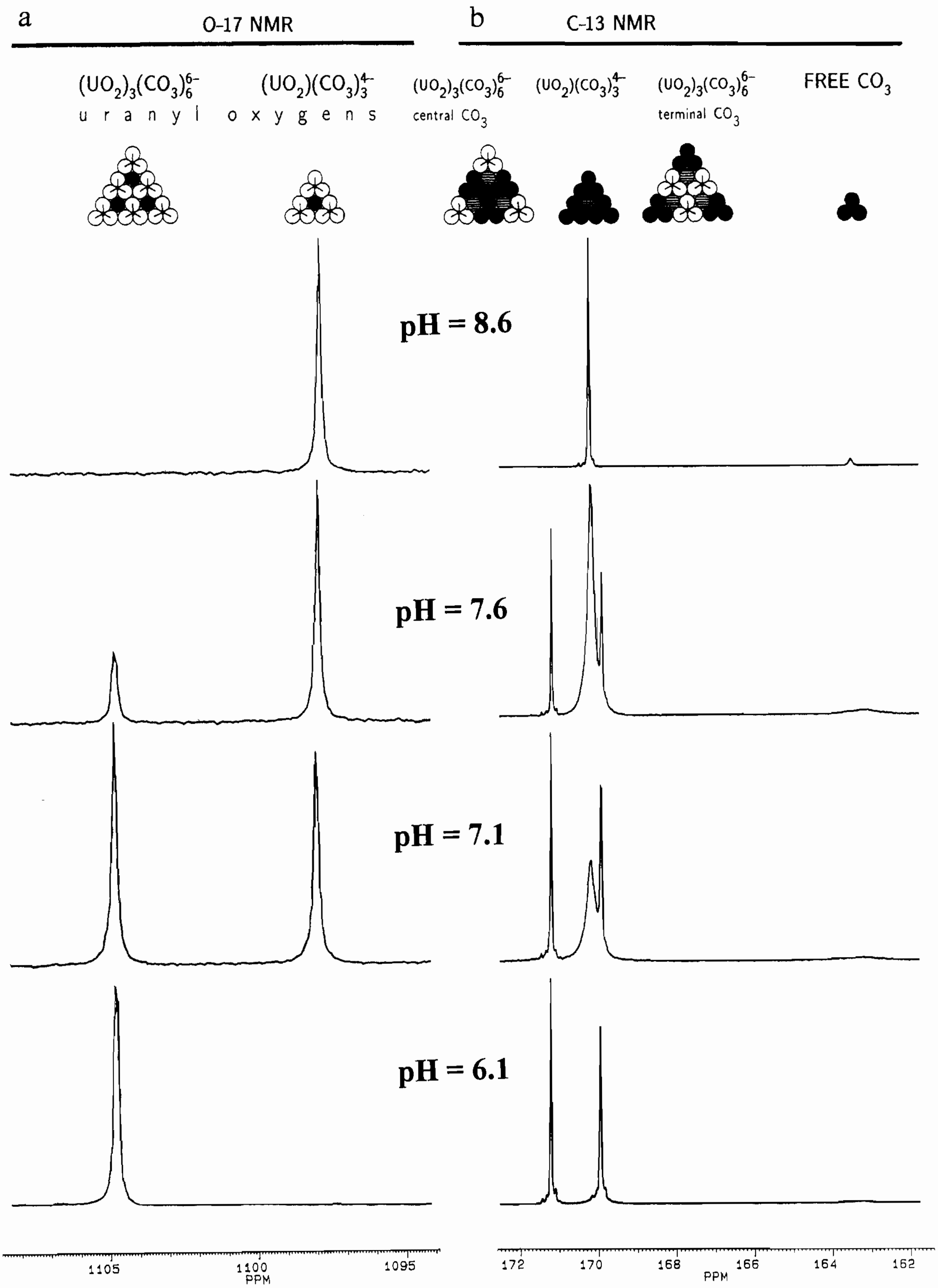

Figure 3. (a) ^{17}O NMR and (b) ^{13}C NMR spectra of solutions with a varying carbonate/uranyl ratio. The resulting pH value is shown for each solution. T_U = 100 mM; T_{CO_3} = 210 mM (pH = 6.1), 250 mM (pH = 7.1), 280 mM (pH = 7.7), and 305 mM (pH = 8.6). T = 273 K.

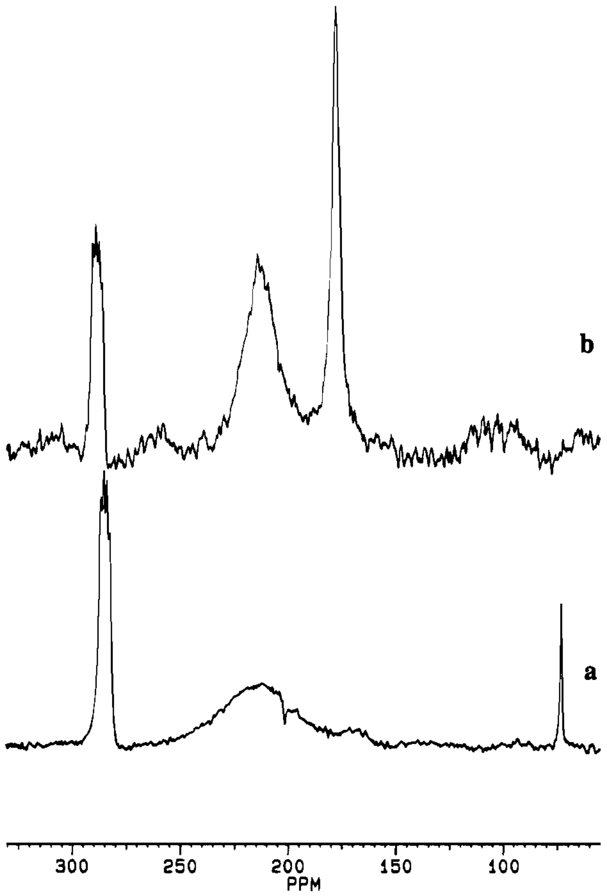

Figure 4. Carbonate region of the ^{17}O NMR spectra of (a) TRIN, (b) MONO, and FREE. $T = 298$ K. The peak in Figure 4a at about 73 ppm corresponds to $CO_2(aq)$, and that at ≈290 ppm is due to ClO_4^-. Key: (a) $T_U = 100$ mM, $T_{CO_3} = 210$ mM, pH = 6.1; (b) $T_U = 100$ mM, $T_{CO_3} = 400$ mM, pH = 9.2.

(i) ^{17}O NMR. In the series of spectra shown in Figure 3a, the dominating species in the starting solution (pH = 6.1) was the TRINuclear complex, $(UO_2)_3(CO_3)_6^{6-}$ (≈95% of the total UO_2^{2+}). The ^{17}O NMR spectrum of this complex shows a sharp signal (half width, $\Delta\nu_{1/2}^{obs} \approx 6$ Hz) at 1104.8 ppm. As expected, it is close to the chemical shift of the signal of the free UO_2^{2+} (1118.2 ppm, 50 mM $UO_2(ClO_4)_2$ in 1 M $NaClO_4$, 25 °C), and hence can be assigned to the uranyl site in TRIN. A broad signal at ca. 215 ppm (Figure 4a, $\Delta\nu_{1/2}^{obs} \approx 2000$ Hz) belongs to the coordinated CO_3^{2-} ligands. The signals of the two different types of carbonate of TRIN (four different oxygen sites, see Figure 2b) could not be resolved, neither at room temperature nor at elevated temperatures. The broadening is probably caused by the quadrupolar relaxation and/or exchange processes. The line shapes of ^{17}O NMR spectra for the carbonate ligand were not used to evaluate the dynamics. The narrow signal at 73 ppm is due to dissolved CO_2. The splitted signal at about 289 ppm originates from the (not enriched) ClO_4^-; a large solvent water peak (not shown) appears at about −1.5 ppm in 1 M $NaClO_4$.

Upon addition of Na_2CO_3 into the sample a new narrow signal ($\Delta\nu_{1/2}^{obs} \approx 6$ Hz) at 1098.1 ppm appears in the ^{17}O spectrum, and it is assigned to the uranyl oxygens of the MONOnuclear complex, $UO_2(CO_3)_3^{4-}$ (Figure 3a, pH = 7.1). If more carbonate is added, the intensity of the MONO signal increases; at the same time, the intensity of the signal of TRIN gradually decreases (Figure 3a, pH = 7.7 and 8.6). It is important to note that no other signal has been detected in this region of the ^{17}O NMR spectra.

The separated ^{17}O NMR signals of the coordinated carbonate of MONO and the FREE ligand can be seen at about 215 ppm $\Delta\nu_{1/2}^{obs} \approx 1000$ Hz) and at 178 ppm, ($\Delta\nu_{1/2}^{obs} \approx 200$ Hz) respectively (Figure 4b). The FREE signal is actually the time-averaged signal of HCO_3^- ($\delta = 172$ ppm) and CO_3^{2-} ($\delta = 189$ ppm), which could be measured in separate samples. The latter value can be compared to the chemical shift of CO_3^{2-} measured previously, 192 ppm.[24]

This assignment of the signals for the $(UO_2)_3(CO_3)_6^{6-}$ complex supersedes the assignment in our earlier paper.[25] We have not been able to reproduce the previous spectrum, but it was probably a result of sample decomposition resulting in a mixture of hydroxo−carbonato uranyl complexes.

(ii) ^{13}C NMR. The ^{13}C NMR spectrum of the TRIN complex shows two signals with equal intensity, at 171.42 and 170.10 ppm (at 25 °C), assigned to the "central" (CENT) and the "terminal" (TERM) carbonates, respectively (Figure 3b, pH = 6.1). This assignment is tentative, based on the structural similarity between the carbonates in the MONO complex and the terminal carbonates of the TRIN complex[8,26a] but is also supported by the relative kinetic inertness of the "central" site compared to the "terminal" carbonate (see below). The signal of the MONO complex appears at 170.27 ppm (25 °C, 1 M Na^+).[11] The two signals (170.10 and 170.27 ppm) can be resolved only at lower temperature. The change in the intensities when Na_2CO_3 is added to the TRIN complex (Figure 3b) is analogous to that for the ^{17}O signals of the UO_2^{2+} in these complexes. The exchange-broadened signal at 163.0 ppm corresponds to the free HCO_3^-. There is also a sharp peak due to dissolved CO_2 at 127.4 ppm (not shown in the figure).

2. Dynamic Studies. (i) MONO Complex and FREE. Previously, we have studied the pH dependence of the ^{13}C NMR line broadening in the $UO_2(CO_3)_3^{4-}-H^+-CO_3^{2-}$ system at 25 °C and pH > 8.6.[11] Now, the region 6 < pH < 9 was explored. In this pH region there is no buffer effect related to the $H^+-CO_3^{2-}$ system, and attempts to measure or calculate the pH gave uncertain results. In order to provide a buffer, some $Na^{13}CN$ was added to a solution (total concentrations: $T_U = 83$ mM, $T_{CO_3} = 400$ mM, $T_{CN} = 25$ mM) in a septum-sealed NMR tube and the pH was adjusted by addition of small amounts of 6 M $HClO_4$. The dilution was negligible. The advantage of this unusual buffer is that the chemical shift of the exchange-averaged ^{13}C NMR signal of the $HCN-CN^-$ system is changing with pH. Thus, it was possible to control the pH (see Experimental Section) in the NMR tube without opening it and loosing carbon dioxide. No chemical interaction was observed between the cyanide buffer and the studied chemical system (see below).

The experimental results are shown in Figure 5 (and in Figure S2 in Supplementary Material). The simultaneous broadening of the peaks can be attributed to a two-site chemical exchange process. The effect of the H^+-CN^- buffer on the MONO−HCO_3^- exchange system was checked experimentally at the total cyanide concentration $T_{CN} = 70$ mM, with similar concentration of MONO and HCO_3^- as in the sample where $T_{CN} = 25$ mM. The line broadening ($\Delta\nu_{1/2}$) of the MONO signal versus [H^+] is shown in Figure 5a; there is a linear relationship. Both series of experiments (see line a) gave the same results within the

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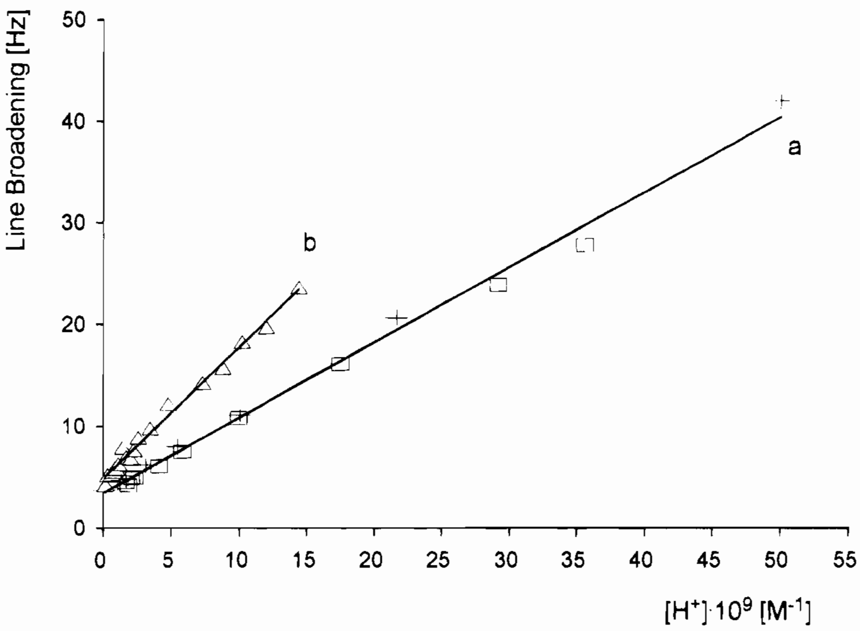

Figure 5. Line broadening due to chemical exchange of the ^{13}C NMR signal of MONO as a function of pH or pD. T = 298 K. Key: (a) (□) T_U = 83 mM, T_{CO_3} = 400 mM, T_{CN} = 25 mM in H_2O; (+) T_U = 100 mM, T_{CO_3} = 400 mM, T_{CN} = 70 mM in H_2O; (b) (△) T_U = 100 mM, T_{CO_3} = 400 mM, T_{CN} = 70 mM, in D_2O (98%).

experimental uncertainty. Thus, no significant kinetic effect of the HCN/CN$^-$ buffer had to be considered at our experimental conditions and, hence, the rate equation is

$$\frac{-d[\mathrm{MONO}]}{dt}\left(\frac{1}{[\mathrm{MONO}]}\right) = k_{obs}(\mathrm{MONO} \leftrightarrow \mathrm{FREE}) = k_1 + k_2[\mathrm{H}^+] \quad (3)$$

Least-squares fitting of the straight line led to the following rate constants: k_1 = 10.6(2.5) s^{-1} and k_2 = 2.32(0.03) × 10^9 M^{-1} s^{-1} (as expected, the analysis of the line broadening of the FREE signal is in agreement with these results, since for a two-site system $p_1k_1 = p_2k_2$, where p_1 and p_2 are the relative populations of the sites, and k_1 and k_2 are the rate constants for the exchange reaction from site 1 and from site 2, respectively). The first-order rate constant is in good agreement with the one measured earlier at pH > 8.6, k_1 = 13(3) s^{-1}.[11] This experimental finding supports our former suggestion of an exclusively dissociative reaction at higher pH values, because the present study extended the total concentration range of uranyl up to 200 mM (in the earlier paper 5−27 mM) and still no bimolecular route was found. This is in contrast to a previous study[26b] which was based on ^{13}C NMR line broadening measurements for only one total concentration and one carbonate/uranyl ratio.

A similar series of experiments was carried out on a sample prepared in 98 % D_2O in order to study the possible solvent kinetic isotope effect (see Figure 5b). In heavy water the protonation constant of DCN, (K = [DCN]/[D$^+$][CN$^-$]), has a value of pK_D = 9.37.[27] The evaluated rate constants in D_2O are k_1 = 15(2) s^{-1} and k_2 = 4.1(0.1) × 10^9 M^{-1} s^{-1}. The value of about 0.57 for the ratio k_2^H/k_2^D is related to the deuterium isotope effect (for further discussion, see Mechanistic Considerations), whereas there is no significant isotope effect for k_1.

In order to estimate the activation parameters of the bimolecular reaction (k_2 route) the temperature dependence of the line broadening for both the MONO and FREE signals was measured. The data for the solution with the composition T_U = 110 mM, T_{CO_3} = 730 mM, [UO$_2$(CO$_3$)$_3$$^{4-}$] = 0.98$T_U$, and [HCO$_3$$^-$] ≈ 400 mM at pH ≈ 7.1 (pH is somewhat uncertain because of the low buffer capacity in this pH region) were used to calculate the rate constant, k_2, using the equation $k_{obs} = \pi\Delta\nu$, and eq 3: $k_2 = (k_{obs} - k_1)/[\mathrm{H}^+]$. Now, using the known activation parameters of the k_1-route ($\Delta H^\ddagger$ = 82 kJ mol^{-1} and $\Delta S^\ddagger$ = 50 J mol^{-1} K^{-1} [11]) an Eyring plot was calculated. Least-squares optimization gives $\Delta H^\ddagger$ = 52(1) kJ mol^{-1} and $\Delta S^\ddagger$ = 110(3) J mol^{-1} K^{-1} (see Table 1). The relatively broad temperature region and good accuracy of the line width measurements for this solution permitted the evaluation of the activation parameters, but the low standard deviations can be considered only as the errors of the linear regression analysis (as discussed by Honan et al.).[28a]

Table 1. Determined Kinetic Parameters in the $UO_2^{2+}-CO_3^{2-}$ System[a] at T = 298 K (One Standard Deviation is given in Parentheses)

exchange rate consts		activation params	
in H_2O	in D_2O	$\Delta H^\ddagger$/ (kJ mol^{-1})	$\Delta S^\ddagger$/ (J mol^{-1}K^{-1})
	path I (MONO ⟷ FREE)		
k_1 = 11(3) s^{-1}	15(2)	82.0[b]	50[b]
	path II (MONO ⟷ FREE)		
k_2 = 2.32(0.03) × 10^9 M^{-1} s^{-1}	4.1(0.1) × 10^9	52(1)	110(3)
	path III (TERM ⟷ FREE)		
k_{obs} = 42(3) s^{-1}	≈40	48(2)	−55(6)
	path IV (CENT ⟷ TERM)		
k_{obs} = 1.4(0.3) s^{-1}	not determined	58(2)	−48(7)

[a] The rate constants are given for a whole complex (i.e. not for one ligand only). [b] Reference 11.

(ii) TRINuclear Complex and FREE. The high stability of the TRIN complex makes it possible to prepare a solution containing almost only this species (see Figure 3, pH = 6.1). The ^{13}C NMR signal integrals of the CENTral and the TERMinal carbonate signals are equal, but the latter one is

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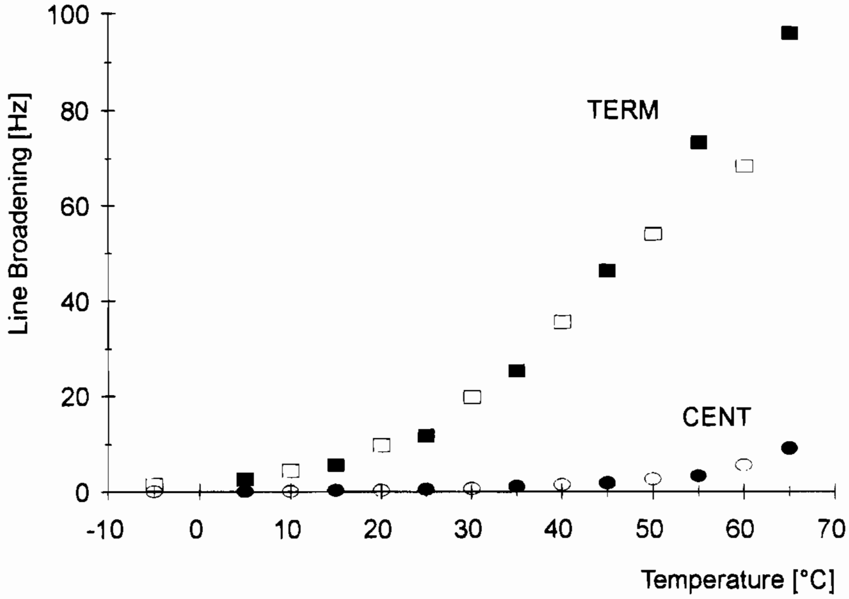

Figure 6. Line broadening of the ^{13}C NMR signals of the $(UO_2)_3(CO_3)_6^{6-}$ *vs* temperature. Experimental results from two series of measurements are summarized: (filled symbols) $T_U = 237$ mM, $T_{CO_3} = 499$ mM, $T_H = [HCO_3^-] = 12$ mM, $[(UO_2)_3(CO_3)_6^{6-}] = 229$ mM (96.5%), the rest of the uranyl forms minor species $UO_2(CO_3)_3^{4-}$ (2.25%), $UO_2(CO_3)_2^{2-}$ (0.97%), and $UO_2(CO_3)$ (0.24%) at pH = 6.1; (unfilled symbols) $T_U = 100$ mM, $T_{CO_3} = 210$ mM, $T_H = [HCO_3^-] = 10$ mM, $[(UO_2)_3(CO_3)_6^{6-}] = 95$ mM (95%), $UO_2(CO_3)_3^{4-}$ (2.4%), $UO_2(CO_3)_2^{2-}$ (1.7%), $UO_2(CO_3)$ (0.7%) at pH = 6.2.

somewhat broadened even at 0 °C. The line width of the ^{13}C NMR signals of the $(UO_2)_3(CO_3)_6^{6-}$ increases with increasing temperature. Experimental results from two series of measurements are summarized in Figure 6. The broadening is attributed to a chemical exchange: it cannot be an intramolecular two-site exchange between the CENT and TERM carbonates, since their population is equal but their ^{13}C NMR signals are not equally broadened. Rather, it is a multisite exchange system involving three major sites: the two sites of the TRIN complex and HCO_3^-. These are the only detectable signals even at the lowest measurable temperature, see Figure 3, pH = 6.1. Other minor species (*e.g.* about 2% MONO) remain hidden, either because of fast relaxation and/or fast chemical exchange. In the latter situation, the minor species are probably averaged with the signal of the MONO complex, rather than with the small signal of the free carbonate, which appears exactly at 163.0 ppm, i.e. at the chemical shift of HCO_3^-. A coincidence of the chemical shifts for these minor complexes and the TERM signal cannot be ruled out. Concluding, the line broadening can be described by a three-site model:

$$\text{CENT} \leftrightarrow \text{TERM} \leftrightarrow \text{FREE} \qquad (4)$$

The population of the free carbonate site is quite low, $p_{FREE} = 0.028$, so that the broadened signal escapes observation at higher temperatures. Therefore, only the line broadening of the major signals was used in the calculations. The pseudo-first-order rate constants at 25 °C were found to be: $k_{obs}(\text{CENT} \leftrightarrow \text{TERM}) = 1.4\ s^{-1}$ (as extrapolated from high temperature ^{13}C NMR line broadening data), $k_{obs}(\text{TERM} \leftrightarrow \text{FREE}) = 42(3)\ s^{-1}$ at pH ≈ 6.1, the "self pH" of the TRIN. Unfortunately, we could not study the pH-dependence of the $k_{obs}(\text{TERM} \leftrightarrow \text{FREE})$ (1) at lower pH, because of the formation of UO_2CO_3 and the precipitation of $UO_2CO_3(s)$ upon addition of acid to the sample, and (2) at higher pH, in the pH-range 6.5−7.5 (with very low buffer capacity), because of the formation of MONO when carbonate is added and because of the formation of mixed hydroxo/carbonato complexes when OH^- is added. (Determination of the rate law for the TRIN complex would demand a large amount of additional experimental work and is outside the scope of this paper.) On the other hand, it is important to note that $k_{obs}(\text{MONO} \leftrightarrow \text{FREE})$ at pH = 6.1 can be calculated to $1.8 \times 10^3\ s^{-1}$, which is almost 2 orders of magnitude faster than the carbonate exchange of the TRIN complex. This fact can be illustrated by the ^{13}C NMR spectrum of a solution containing both MONO and TRIN (see Figure 3b, at pH = 7.1 and 7.6) where the MONO signal is substantially broadened due to exchange with FREE, whereas the signals of TRIN are much less broadened.

In order to check the solvent isotope effect for the TRIN, a sample with the same composition as that in Figure 3, i.e. $T_U = 100$ mM and $T_{CO_3} = 210$ mM, but prepared in 98% D_2O, was measured at 25 °C; no significant solvent isotope effect was observed for $k_{obs}(\text{TERM} \leftrightarrow \text{FREE})$, similarly to the k_1-route of the MONO complex.

At lower temperatures, the exchange related to CENT was too slow to be followed by line broadening, see Figure 6. However, it could be studied by ^{13}C NMR magnetization-transfer technique, because the longitudinal relaxation times (T_1) of the different carbonate sites are large enough in comparison with the lifetimes of these sites. T_1-values were measured in separate samples by the inversion recovery method and are as follows: CO_3^{2-}, 35 s; HCO_3^-, 16 s at room temperature. A typical magnetization-transfer experiment is shown in Figure 7a.

The evaluation of the time constants was done using a two-site model, taking into account only the mutual exchange between the CENT and TERM signals. The measured and calculated values of magnetization are shown in Figure 7b. Values of signal integrals for both sites at time $t = 0$ and $t = \infty$ (**M**(0) and **M**(∞), respectively), k_{obs} and T_1 were fitted, giving $k_{obs} = 1.4(0.3)\ s^{-1}$ and $T_1 = 4(2)$ s (25 °C). (During the evaluation of the magnetization-trasfer experiments we have observed that the standard deviation in the obtained rate constants is relatively low. On the contrary, the relaxation times are not well-determined: the possible reason for this behavior is the imperfection of the DANTE pulse train and thus the necessity for a simultaneous refinement of **M**(0) and **M**(∞). This increases the number of refined parameters and the standard

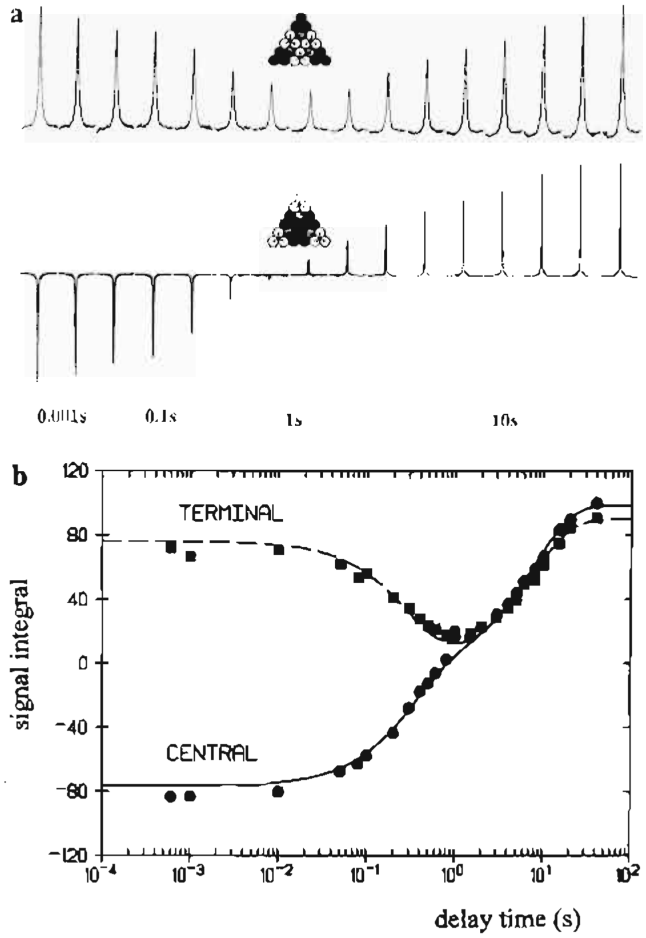

Figure 7. ^{13}C NMR, selective magnetization-transfer between the CENT (lower trace) and the TERM carbonate sites in the TRIN complex (T_U = 100 mM, T_{CO_3} = 210 mM, pH = 6.1, temperature = 298 K). Key (a) peak intensity as a function of the delay time; (b) evaluation of the time constants was done using a two-site model, taking into account only the mutual exchange between the CENT and TERM sites. The measured (■, ●) and calculated values of magnetization are shown (arbitrary units).

deviations in all the refined parameters, but most significantly in the relaxation times.) The temperature dependence of the obtained rate constant is summarized in Figure S3, Supplementary Material. The evaluation of the two series of experiments, i.e. (1) inverting CENT and (2) inverting the TERM signal resulted in the same numerical values of the time constant (within the experimental uncertainty). There is a virtual discrepancy between this two-site model and the three-site model required to describe the line shape observed at higher temperature in the same system. In fact, the effect of HCO_3^- on the result of the magnetization transfer experiment is negligible for three reasons: (1) the chemical exchange between the TERM and HCO_3^- is fast enough (compared to the exchange between CENT and TERM) so that the sites TERM and FREE are in spin equilibrium at any time of the magnetization transfer experiment; (2) the population of HCO_3^- is small (p_{FREE} = 0.028), and thus, only a small portion of the negative magnetization can be transferred to that site and undergo T_1 relaxation there; (3) the relaxation of ^{13}C in HCO_3^- is substantially slower than that for the complexed carbonates, and hence, the "leaking magnetization" is negligible. These circumstances allow the simplification of the exchange system to a "pseudo-two-site" model (see Supplementary Material).

The pseudo-first-order rate constant at 25 °C, k_{obs}(CENT $\rightleftharpoons$ TERM) =1.4(0.3) s^{-1}, is in good agreement with the value determined from the line broadening experiments (see above). The advantage of the magnetization-transfer experiment compared to the line broadening technique is that the former allowed a separation of the effect of the two reactions for the TERM site, namely the slow reaction between TERM and CENT from a faster one between TERM and HCO_3^-. (Note, that there is no significant line broadening of the CENT signal below room temperature. Eyring plots of the measured rate constants are shown in Figure S3, Supplementary Material.) The least-squares optimization gave $\Delta H^{\ddagger}$ = 58(2) kJ mol^{-1} and $\Delta S^{\ddagger}$ = −48(7) J mol^{-1} K^{-1} for the CENT $\rightleftharpoons$ TERM exchange and $\Delta H^{\ddagger}$ = 48(2) kJ mol^{-1} and $\Delta S^{\ddagger}$ = −55(6) J mol^{-1} K^{-1} for the TERM $\rightleftharpoons$ FREE exchange. Both sets of activation parameters are probably related to composite reactions; consequently, they can be used to calculate the pseudo-first-order rate constant values at different temperatures, but not for assignment of the reaction mechanism.

(iii) Solutions of MONO, TRIN, and FREE. At higher pH values and at higher carbonate/uranyl ratios, TRIN and MONO complexes coexist. In order to follow the distribution of $U^{17}O_2$-enrichment between the uranyl−carbonate complexes as a function of time, a cold solution of MONO (natural abundance ^{17}O) was injected into a cold (0 °C) solution of TRIN (^{17}O-enriched on the UO_2-site) inside the NMR magnet. The first ^{17}O NMR spectrum could be recorded about 5 s after the mixing, and at this time the $U^{17}O_2$-enrichment was already equilibrated between the two complexes (T_U = 100 mM, T_{CO_3} = 250 mM, pH ≈ 7 after mixing). It is well-known that the (uncatalyzed) oxygen exchange between the UO_2^{2+} unit and the bulk water is very slow ($k = 4.8 \times 10^{-8}$ s^{-1}).[28b] Thus, the upper limit for the lifetime of the uranyl group in the uranyl carbonate complexes at 0 °C is about 1.5 s, i.e. $k_{obs} > 0.7$ s^{-1}.

On the other hand, an ^{17}O NMR magnetization-transfer experiment proved that no exchange occurs on the T_1 time scale between the UO_2 sites of the MONO and TRIN at 25 °C in the same sample, in which 50% of the total uranyl is in TRIN and 50% in the MONO complex. Taking into account that the relaxation times (T_1 values for both TRIN and MONO are ca. 65 ms at room temperature), the lifetime of -yl oxygens can be estimated to $\tau > 3T_1 \approx 0.2$ s, i.e. $k_{obs} < 5$ s^{-1}. Certainly, the process is too slow, 0.7 $s^{-1} < k_{obs} < 5$ s^{-1}, to be quantitatively studied using the line broadening technique, since it corresponds to an exchange broadening of only 0.2 Hz < $\Delta\nu$ < 1.6 Hz in addition to the natural ^{17}O NMR line width of 6 Hz for both TRIN and MONO (determined in separate samples, see Figure 3a); the situation is similar for ^{13}C NMR at and below the room temperature.

The line-broadening technique becomes much more useful at higher temperature. Relatively narrow ^{17}O NMR signal of the uranyl oxygens of the UO_2^{2+}(aq) ion was observed by Jung et al.[13] and its line width is practically constant over 40 °C. We have measured the temperature dependence of the ^{17}O NMR line width for the uranyl oxygens of the MONO complex in the presence of some excess carbonate. We obtained 6, 3.6, and 2.8 Hz at 25, 40, and in the range 55−85 °C, respectively: a behavior similar to the free uranyl ion. These values were assumed to be equal to the nonexchange line width for the MONO complex as well as for the TRIN complex. (For the latter it is not possible to avoid the formation of minor species, and thus more sites for the -yl oxygen atoms.) The structural similarity between the two complexes was assumed to justify this approximation.

As expected, an increase of the exchange rate at higher temperature resulted in broadening of both the ^{17}O and ^{13}C NMR signals. The experimental results are shown in Figure 8 (for a solution with the total concentrations T_U = 100 mM, T_{CO_3} =

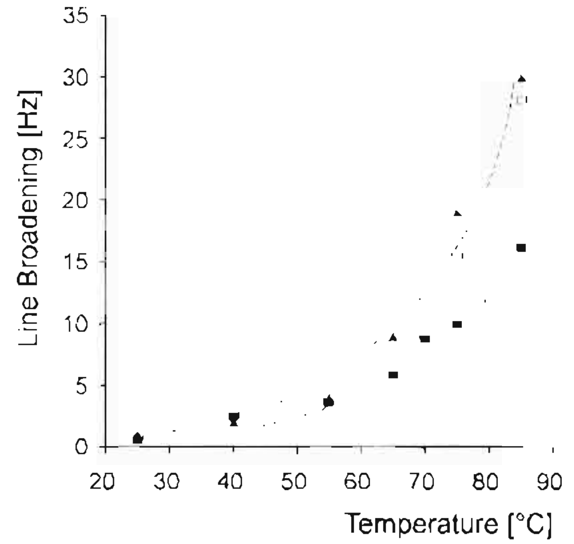

Figure 8. Temperature dependence of ^{17}O NMR line broadening for the uranyl oxygens in TRIN (▲) and in MONO (■); and of the ^{13}C NMR line broadening for the CENT (□) site. T_U = 100 mM, T_{CO_3} = 265 mM, pH ≈7.7, where TRIN = 37% and MONO = 63% of the uranyl concentration.

265 mM; pH ≈7.7, where TRIN = 37% and MONO = 63% of the total uranyl concentration). The observed broadening is smaller for the ^{17}O NMR signal of the more populated MONO complex compared to the less populated TRIN complex suggesting a mutual two-site exchange. An important finding is that the exchange broadening in Hz of the ^{13}C NMR signal for the CENT site of the TRIN complex is equal (within the experimental error) to the ^{17}O NMR line broadening of the TRIN complex. (In other words, $p_{\mathrm{TRIN}}\Delta\nu_{1/2,\mathrm{CENT}}(^{13}\mathrm{C}\ \mathrm{NMR}) \approx p_{\mathrm{TRIN}}\Delta\nu_{1/2,\mathrm{TRIN}}(^{17}\mathrm{O}\ \mathrm{NMR}) \approx p_{\mathrm{MONO}}\Delta\nu_{1/2,\mathrm{MONO}}(^{17}\mathrm{O}\ \mathrm{NMR})$, where p_{TRIN} and p_{MONO} are the relative populations of the two sites.) This is most significant at highest studied temperatures where the signals are substantially exchange-broadened. This finding represents a direct experimental evidence that the two phenomena originate from the same reaction, and because the ^{17}O-sites are in different complexes, the reaction has to be assigned to an intermolecular exchange process. This process was followed previously (see above) by a ^{13}C NMR magnetization-transfer between the CENT and TERM sites, but that experiment did not allow us to decide whether the reaction was intra- or intermolecular. One can note that the two other exchange sites in ^{13}C NMR, TERM and MONO, are also affected by this slow reaction, but their broadening is dominated by the much faster exchange with the free HCO_3^-. The rate constants and the activation parameters measured for the different reactions are summarized in Table 1.

In order to obtain an overview over the entire chemical system and to confirm the determined exchange pathways, a solution containing all the four main sites, MONO, TRIN (TERM and CENT), and FREE, present in comparable concentrations, was prepared (T_U = 50 mM, T_{CO_3} = 170 mM, pH ≈ 6.6). Two ^{13}C NMR experiments were performed on this solution at −5 °C: selective magnetization transfer and 2D EXSY (2-Dimensional EXchange SpectroscopY).

Selective magnetization-transfer experiment can be performed in several ways, but the inversion of the HCO_3^- peak offered some advantages: it appears far (about 7 ppm) from the nearest signal (TERM), so there is no problem with pulse selectivity, and it relaxes slowly (T_1 = 16 *s* at room temperature). The distribution of the magnetization *vs* delay time (t) is shown in Figure 9. For t < 20 ms, the dominating process is the exchange between HCO_3^- and the MONO complex, there is practically no "leaking magnetization" in this region. At $t \approx 50$ ms also the TERMinal site gets involved in the exchange. The minimum intensity of TERM appears at about t = 1 *s*. The intensity of the CENT signal starts to decrease slightly at $t \approx 2$ *s*. At $t \approx 30$ *s*, there is no remaining effect of the selective inversion.

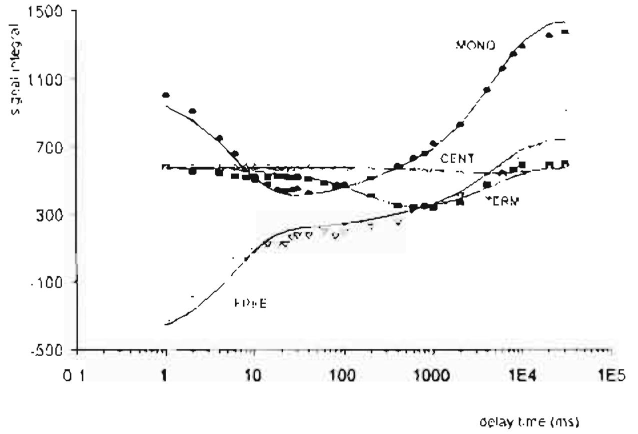

Figure 9. ^{13}C NMR selective magnetization-transfer results for a solution containing four major carbonate sites: TERM, CENT, MONO, and FREE, at 268 K (T_U = 50 mM, T_{CO_3} = 170 mM, pH ≈ 6.6). The integrals are given in arbitrary units. For the ^{13}C NMR spectrum, see Figure 10.

A quantitative evaluation of the four-site magnetization-transfer system at −5 °C (see curves in Figure 9) gave the following parameters: k_{obs}(FREE ↔ MONO) = 109(12) s^{-1}, k_{obs}(FREE ↔ TERM) = 2.6(0.4) s^{-1}, k_{obs}(TERM ↔ CENT) = 0.08(0.07) s^{-1}, $1/T_1$ (TERM)= 1.2(0.1) s^{-1}, and $1/T_1$(CENT) = 0.2(0.3) s^{-1}. Calculated values of the signal integrals (in arbitrary units, after deconvolution of the overlapping peaks), M(0) at t = *0* and M(∞) at t = ∞ are, respectively, −464(34) and 746(22) for FREE, and 1044(36) and 1436(37) for MONO. For both TERM and CENT, M(0) = M(∞) = 577(5). No other exchange reactions were considered, and the relaxation rates for FREE and MONO were negligible compared to those for TERM and MONO and were set to zero. Of the totally eighteen parameters (four T_1, four M(0), four M(∞), and six k_{obs}), ten parameters were least-squares refined. The calculated pseudo-first-order rate constants span over more than 3 orders of magnitude: the two larger ones are due to the dominating exchange reactions, between FREE and MONO and FREE and TERM; the small one is due to the TERM ↔ CENT exchange, and is close to the limit of the method. The fitted relaxation rate for CENT is uncertain because the T_1 relaxation is dominated by the TERM site, and the contribution of CENT is very little (see above).

A single ^{13}C NMR 2D EXSY spectrum of the same solution as above provides an overview over several exchange reactions (see Figure 10). This spectrum represents a "photograph" of all changes of the carbon positions in the solution between the time t = 0 and the chosen mixing time, in this case τ_m = 1 s. The spectrum has not been evaluated quantitatively since, according to our experience,[29] the accuracy of the 2D EXSY method is usually lower than that of magnetization-transfer and, thus, no new information was expected. However, the qualitative picture agrees well with the results described above. Thus, the crosspeaks in box 1 correspond to the chemical exchange between FREE and MONO (peak to the left) and between FREE and TERM (peak to the right). It is difficult to compare the cross-peak volumes in the figure (which are proportional to the exchange rates between the corresponding sites) because of the

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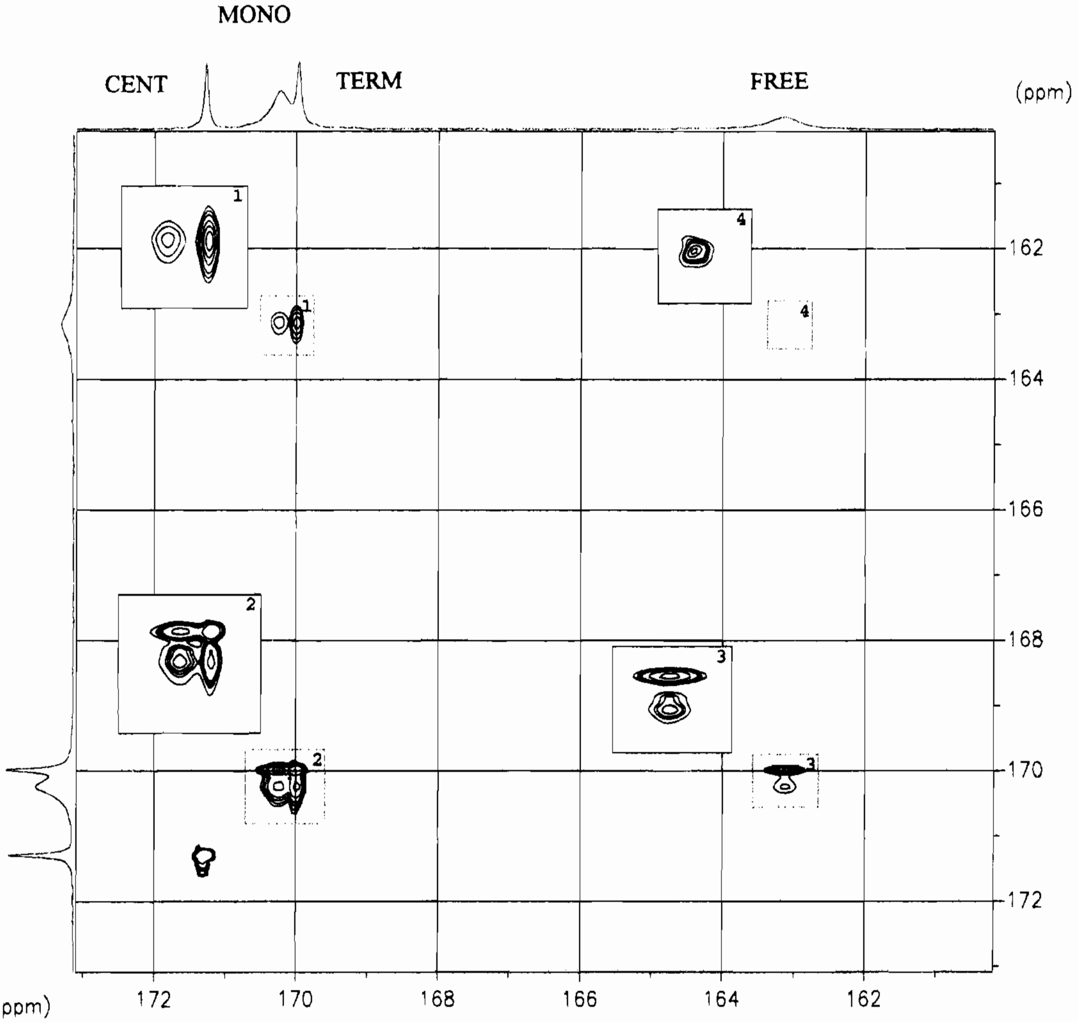

Figure 10. 100 MHz ^{13}C NMR 2D EXSY spectrum (TPPI) for the same solution as in Figure 9. $T = 268$ K. Mixing time $\tau_{mix} = 1$ s. Conditions: 256 incremented experiments, each consisting of 16 scans and collected in 2 K data points; pulse repetition time = 10 s. Fourier transformation was performed in 2K × 2K points. Weighting function in *f2* is Gaussian and in *f1* is a shifted sine–bell function. The chemical shifts are given toward higher frequency from TMS.

Table 2. Comparison of the Results Obtained from a Single Four-Site Magnetization-Transfer Experiment ($T = -5$ °C, pH ≈ 6.6) and Those from Table 1 (Recalculated to -5 °C)

rate const	four-site inversion transfer	calcd from data in Table 1
k_2(FREE ⟷ MONO)/M^{-1} s^{-1}	$4.3(0.5) \times 10^8$	2.3×10^8
k_{obs}(FREE ⟷ TERM)/s^{-1}	2.6(0.4)	3.6
k_{obs}(TERM ⟷ CENT)/s^{-1}	0.08(0.07)	0.08

peak overlap and because of the different line widths. Also, overlapping cross-peaks can be seen for the TERM and MONO signals, see box 2. It does not mean that there is a *direct* exchange reaction between TERM and MONO, only that after 1 s carbonate has been exchanged between these two sites. Not surprisingly, no cross-peaks were detected for the CENT signal at this mixing time, because of the inertness of this carbonate site.

The cross peaks in Figure 10 can be compared to a cross-section at $t = 1$ s in Figure 9. The results of both four-site magnetization-transfer and 2D-EXSY experiments are in good agreement with the time constants (values of k_{obs} and T_1) measured for selected parts of the exchange system (see Table 2).

Mechanistic Considerations

The proposed scheme for the dynamics in the equilibrium system including $(UO_2)_3(CO_3)_6^{6-}$, $UO_2(CO_3)_3^{4-}$, and free carbonate is summarized in Figure 11. Before discussing the different reactions, we will refer shortly to previous exchange studies of UO_2^{2+}-ligand systems.[30] It seems to be established that the ligand exchange reactions in organic solvents are much faster for monodentate ligands[28a] than for the less studied bidentate ligands.[26a] Dissociative mechanism is suggested for complexes with saturated coordination sphere of the UO_2^{2+} center.[31,32] For complexes with less-crowded inner sphere, bimolecular reactions were found and explained by an associative mechanism.[28a]

In the present system, three carbonates of MONO act as bidentate ligands.[7] The exchange between the coordinated carbonate and the free ligand is quite slow at higher pH values[11,33] compared to a similar exchange for monodentate O-donor ligands. This "water-catalyzed" route[4] is shown as **I** in Figure 11. The activation parameters of this reaction follow the linear free energy relationship found for ring-opening reaction of many different bidentate carbonate complexes.[4] We have not found any second-order reaction with free carbonate.

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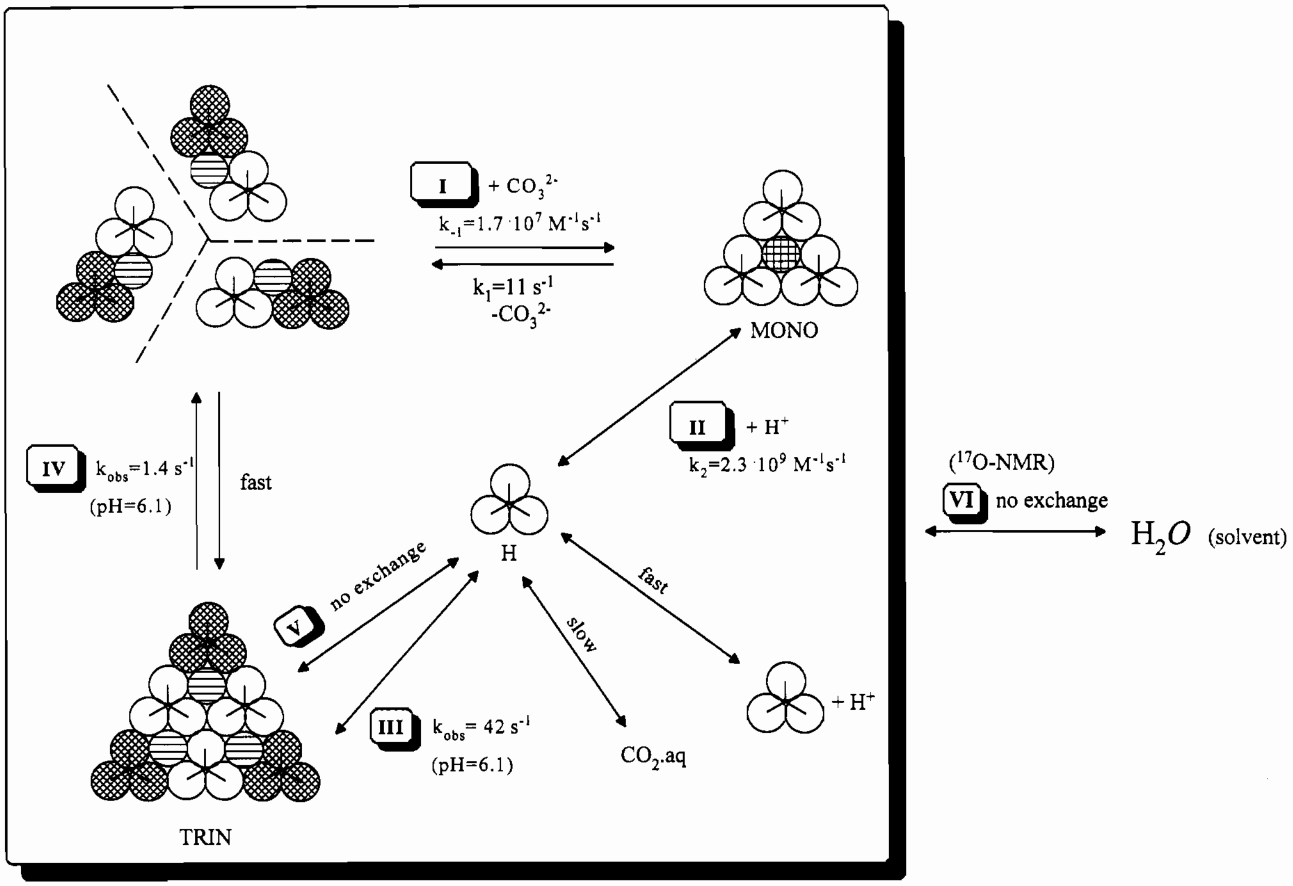

Figure 11. Summary of the dynamic processes in aqueous solutions of uranyl(2+) and carbonate. Rate constants for the different exchange processes are given. Note that no evidence is presented that the thermodynamically stable complex $UO_2(CO_3)_2^{2-}$ (see ref 1) acts as an intermediate in reaction **III**.

This supports our former suggestion of an exclusively dissociative reaction at higher pH values, because the present study extended the total concentration range of uranyl up to 200 mM (while earlier it was 5−27 mM). The value of k_{-1} in Figure 11 was calculated as $k_{-1} = k_1K_3$, where K_3 is the stepwise formation constant of MONO.[1]

There is a proton-catalyzed exchange reaction between MONO and FREE, see route **II.** The rate constant of this reaction is close to the value of diffusion-controlled bimolecular reactions, if this is a real bimolecular path. The reaction is faster in D_2O than in H_2O, $k_2^H/k_2^D = 0.57$ (see Table 1). A possible explanation is that this reaction is not bimolecular but rather goes through a protonation preequilibrium as follows:

$$[UO_2(^*CO_3)_3]^{4-} + H^+ \overset{K_p}{\longleftrightarrow} [UO_2(^*CO_3)_3H]^{3-} \qquad (5)$$

$$[UO_2(^*CO_3)_3H]^{3-} \xrightarrow{k'_2} [UO_2(CO_3)_2]^{2-} + H^*CO_3^- \qquad (6)$$

$$[UO_2(CO_3)_2]^{2-} + HCO_3^- \xrightarrow{k'_{-2}} [UO_2(CO_3)_3H]^{3-} \qquad (7)$$

From eqs 5−7, it follows that the determined rate constant k_2^H is equal to K_pk_2' if $K_p[H^+] \ll 1$. Activation parameters of this kind of acid-catalyzed reactions do not result in good isokinetic plot, indicating the composite character of these parameters.[4] The larger reaction rate in D_2O than in H_2O can be explained by the importance of the preequilibrium, in which the weaker acid (MONO)-D^+ is formed in higher concentration compared to the (MONO)-H^+.[34] (It can be noted, that an opposite solvent isotope effect for metal−carbonate complexes has also been reported.[35]) The proton catalysis might also be affected by the "nonparticipating ligands" in mixed ligand metal−carbonate complexes and will be discussed in connection with pathway **III.**

In the literature, two different mechanisms have been proposed for the proton-catalyzed carbonate dissociation from the coordination sphere of a metal ion. Both are in agreement with the occurrence of the fast pre-equilibrium shown in eq 5. The difference between them is the identification of the reaction step summarized in eq 6. Mønsted et al.[3] suggested that in the reaction step (6) a proton transfer inside the protonated complex, from the noncoordinated oxygen to the coordinated oxygen of the carbonate ligand, is the rate-determining step. Buckingham and Clark describe a H_2O penetration to the coordination sphere of the metal ion as the second step and a decarboxylation as the third.[36] From our data, it is not easy to decide which of these mechanisms is active. Possibly, the large deuterium effect observed here supports the latter mechanism, since if the proton transfer would be the "bottleneck" of this reaction, it would be slowed down by replacing a proton by a deuteron (assuming that the intramolecular motion of a deuteron is slower than that of a proton, i.e. similarly as in the bulk). In any case, the rate of the MONO ⟺ FREE reaction is not dependent on the free carbonate concentration, which is in agreement with a dissociative reaction mechanism. Also the large and positive value of the activation entropy (see Table 1) points toward this conclusion.

The two different sites of TRIN, CENT and TERM, behave quite differently compared to each other but also compared to

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(34) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper & Row: New York, 1987; pp 433.

(35) Sastri, V. S.; Harris, G. M. *J. Am. Chem. Soc.* **1970**, *92*, 2943.

(36) Buckingham, D. A.; Clark, C. R. *Inorg. Chem.* **1993**, *32*, 5405.

the structurally related MONO complex. We could not explore pathway **III** in detail (see above); thus, it is difficult to decide whether this reaction is proton-catalyzed or not. The absence of a significant solvent isotope effect (see Table 1) may indicate a similar reaction mechanism for both reactions, MONO $\Leftrightarrow$ FREE (route **I**) and TERM $\Leftrightarrow$ FREE (route **III**), i.e. "water-catalyzed" dissociation of the carbonate. A larger exchange rate is observed for the TERM carbonate located in the more structured TRIN, as compared to MONO (42 s^{-1} *vs* 11 s^{-1}). However, we have to make an allowance for the fact that the pH/pD values of the solutions used to study the solvent isotope effect are not known exactly. Moreover, as a consequence of the different protonation/deuteration constant of the ligand (e.g. $pK_{HCO_3} = 10.3$ and $pK_{DCO_3} \approx 11$[4]), the equilibrium distribution can be changed slightly and hence, a small pH-shift could cancel out the possibly present isotope effect. On the other hand, if we suppose proton catalysis to be in action for route **III** (in analogy to route **II**), it is clear from k_{obs} that the proton-catalyzed exchange TERM $\Leftrightarrow$ FREE is much slower than MONO $\Leftrightarrow$ FREE (k_{obs}(TERM,FREE) = 42 s^{-1}; k_{obs}(MONO $\Leftrightarrow$ FREE) at pH = 6.1 can be calculated to 1.8×10^3 s^{-1}). These experimental findings are interesting because the building blocks of the two complexes are exactly the same and the neighbor ligands to the TERM sites are also carbonates.

The carbonates at the CENT sites are of the rare and expectedly very inert μ_3-type (see Figure 2c), previously found only in one case, namely in the crystal structure of μ-carbonato-bis(2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper(II) perchlorate.[10] As expected, no direct exchange occurs between the μ-type CENT and FREE (pathway **V**).

The average charge per UO_2 unit in $(UO_2)_3(CO_3)_6^{6-}$ is -2 compared to -4 in $UO_2(CO_3)_3^{4-}$; the difference might result in a lower ability of TRIN to be protonated during the catalytic preequilibrium. The unique coordination mode of CENT could also contribute as a "nonparticipating ligand" effect. No second-order reaction was found between TRIN and FREE in a broad range of the total concentration (up to $T_U = 200$ mM) as could be expected for the complex having a tightly occupied inner coordination sphere for all three U(VI) centers.

The only reaction of CENT is pathway **IV**. Its rate constant, $k_{obs} = 1.4$ s^{-1}, is the smallest one measured in this system, and it was difficult to decide whether it was due to an intramolecular or an intermolecular exchange. Solely on the basis of ^{13}C NMR magnetization-transfer measurements, this rate constant could be attributed to an intramolecular exchange between TERM and CENT, but this reaction wouldn't explain the exchange of the UO_2^{2+} units between TRIN and MONO (as found by ^{17}O NMR experiments, see above). ^{17}O NMR line broadening measurements at higher temperature clearly prove, that this slow reaction occurs through a decomposition of the trinuclear complex. We have no information about the fragments formed during the decomposition of TRIN: they could be, for example, three thermodynamically stable species $UO_2(CO_3)_2^{2-}$, or a MONO complex and $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)$. The rupture could also be a proton-assisted reaction. The protonation of the μ_3-type CENTral ligand is less probable compared to the bidentate TERMinal.[3] In the rare case when a proton transfer to CENT would occur, the TRINuclear complex could decompose according to:

$$[(CENT)_3(UO_2)_3(TERM)_3H]^{5-} \Leftrightarrow [H(CENT)_3(UO_2)_3(TERM)_3]^{5-} \quad (8)$$

$$[H(CENT)_3(UO_2)_3(TERM)_3]^{5-} \Leftrightarrow 3[UO_2(CO_3)_2]^{2-} + H^+ \quad (9)$$

The recombination of the fragments to TRIN and the formation of MONO from the fragments are fast reactions and are in agreement with both the carbonate exchange between CENT and TERM, and the UO_2^{2+} exchange between TRIN and MONO.

Route **VI** is shown only to note the absence of any measurable oxygen exchange between the species of the studied system and the bulk water. It is in agreement with the literature,[4] as is also the "slow exchange regime" for the $HCO_3^-{-}CO_2(aq)$ system and the "fast exchange regime" for the proton exchange between HCO_3^- and CO_3^{2-} on both the ^{17}O and the ^{13}C NMR time scales.

We note a similarity in the values of activation enthalpy for the reactions II, III and IV; it could be due to the dissociation of one protonated carbonate ligand in MONO or TRIN. However, we do not want to speculate further on the origin of this similarity because of the composite nature of these values. The activation entropies for both pathways of the MONO $\Leftrightarrow$ FREE exchange (k_1 and k_2) are positive which would be in agreement with a dissociative mechanism for these reactions; the opposite would be valid for the TRIN complex. However, the $\Delta S^{\ddagger}$ values are uncertain, and this uncertainty is due not only to the extrapolation to $1/T = 0$ (the obtained standard deviations are small but they represent only the formal uncertainty of the least-squares procedure). What is more important, the composite nature of the described processes decreases the predictive value of all activation parameters (see, for example, ref 37 for $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ and ref 38 for $\Delta V^{\ddagger}$). Therefore, the rate law and other chemical and structural information constitute normally a more clear-cut tool for proposing a reaction mechanism.

In conclusion, we have observed a clear correlation between the dynamic behavior and the coordination mode of the carbonate ligand in the three different sites of the studied uranyl complexes. The use of multinuclear NMR and the combination of the different time scales of the applied NMR techniques represent an obvious advantage in the evaluation of this fairly complicated system.

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Registry Numbers (supplied by author): $(UO_2)_3(CO_3)_6^{6-}$, 17872-00-3; $(UO_2)_3(CO_3)_6^{6-}$, 75311-41-0.

Supplementary Material Available: Equilibrium constants for the studied species (Table S1), a uranium distribution diagram (Figure S1), ^{13}C NMR spectra of solutions of MONO as a function of pH (Figure S2), Eyring plot for TRIN obtained from ^{13}C NMR results (Figure S3), and text giving the general solution of the multisite exchange problem and mathematical treatment of magnetization-transfer experiments for ligand exchange between TRIN (two sites) and FREE (6 pages). Ordering information is given on any current masthead page.

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