

ditions, a sharp ^{13}C resonance was observed at δ 200.1, which is incompatible with that reported for $[\text{Re}(\text{CO})_3\text{OH}]_4$.¹⁸

Scheme 1 shows the sequences of events we believe explain the observed products. The initial step involves hydride attack at the rhenium center to give $[(\eta^3\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3\text{H}^-]$ (2). A fast follow-up reaction of 2 with the second equivalent of hydride affords $[(\eta^1\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3\text{H}_2^-]$ (3), which releases indenide and the putative species $[\text{Re}(\text{CO})_3\text{H}_2^-]$. Support for the indenyl $\eta^3 \rightarrow \eta^1$ transformation stems directly from the work of Casey.^{3,4} Since no intermediates were observed, we conclude that the addition of hydride to 1 represents the rate-determining step. Proof for this was obtained by using the larger hydride reagent LS-Selectride,¹⁹ which led to the formation of indenide and $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^-$ slowly over the course of several days. Moreover, this first step has also been reported to be rate determining in the reaction of 1 with PMe_3 and PBu_3 .^{3,4} It is of interest to compare the ease of indenide loss in our reaction with that for $(\eta^1\text{-C}_9\text{H}_7)\text{Re}(\text{NO})(\text{Me})(\text{PMe}_3)_3$, which gives an ionic $\eta^0\text{-C}_9\text{H}_7$ group at elevated temperature,⁴⁰ and the thermolysis reactions of 1 with EtOH/pyridine and acetone/ H_2O , which afford indenene⁵ and 1-indenyl-2-propanol,^{3b} respectively. Presumably the increased charge density at the rhenium center in 3 is responsible for this facile indenide displacement.

The assemblage of the tetrarhenium cluster $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^-$ from $[\text{Re}(\text{CO})_3\text{H}_2^-]$ is less straightforward but can be considered by recognizing the fact that $[\text{Re}(\text{CO})_3\text{H}_2^-]$ is formally a $d^6\text{-ML}_5$ species that is isolobal with carbene.²⁰ Dimerization is predicted to give the 32-electron complex $[(\text{CO})_3\text{Re}(\mu_2\text{-H})_4\text{Re}(\text{CO})_3]^{2-}$.²¹ If this dimer is considered as a M_2L_9 facial bioctahedral complex (i.e., $[(\text{CO})_3\text{Re}(\mu_2\text{-H})_3\text{Re}(\text{CO})_3]^{3-}$ and $[\text{H}^+]$), it is predicted to be unstable in the absence of a Jahn–Teller distortion.²² Loss of hydride would allow for the formation of the known 30-electron complex $[(\text{CO})_3\text{Re}(\mu_2\text{-H})_3\text{Re}(\text{CO})_3]^{13,22,23}$ and furnish the observed hexaethylborohydride anion.²⁴ While experimentally untested, dimerization of $[(\text{CO})_3\text{Re}(\mu_2\text{-H})_3\text{Re}(\text{CO})_3]^-$ under our reaction conditions would then yield the electron-precise cluster $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^-$.

Experimental Section

Materials and Methods. $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$ was prepared according to the literature.⁹ The hydride reagents Super-Hydride and LS-Selectride were purchased from Aldrich as 1.0 M THF solutions and used as received. All reactions were conducted under argon with Schlenk techniques.²⁵ THF was distilled from sodium/benzophenone ketyl and stored under argon in Schlenk vessels. THF- d_8 was bulb-to-bulb distilled from CaH_2 on the vacuum line and immediately used. The C and H analysis was performed by Atlantic Microlab, Atlanta, GA.

The infrared spectra were recorded as previously described.²⁶ ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Varian 300-VXR spectrometer. ^{11}B NMR spectra were recorded at

96 MHz and are referenced relative to external $\text{BF}_3\cdot\text{Et}_2\text{O}$, taken to have $\delta = 0$.

Reaction of $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$ with $[\text{Et}_3\text{BH}][\text{Li}]$. To 50.0 mg (0.13 mmol) of $(\eta^5\text{-C}_9\text{H}_7)\text{Re}(\text{CO})_3$ in a 50-mL Schlenk tube was added 10 mL of THF, followed by 0.26 mL (0.26 mmol) of a 1.0 M $[\text{Et}_3\text{BH}][\text{Li}]$ solution. The reaction was stirred for 5 min and then monitored by IR spectroscopy, which revealed the complete conversion to $[\text{H}_6\text{Re}_4(\text{CO})_{12}]^-$. Excess tetraphenylphosphonium chloride, $[\text{Ph}_4\text{P}][\text{Cl}]$, was next added and the solution was stirred overnight. After filtration, the THF solution was layered with degassed heptane, which afforded yellow crystals of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Ph}_4\text{P}]_2$. Yield: 36.2 mg (63.2%) of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Ph}_4\text{P}]_2$. IR (THF) of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Li}]_2$: $\nu(\text{C})$ 1992 (s), 1906 (vs) cm^{-1} . IR (THF) of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Ph}_4\text{P}]_2$: 1991 (s), 1900 (s, broad) cm^{-1} . UV-vis (THF) of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Ph}_4\text{P}]_2$: ~ 295 (sh), 330 (sh) nm; ^1H NMR (THF- d_8) of $[\text{H}_6\text{Re}_4(\text{CO})_{12}][\text{Ph}_4\text{P}]_2$: δ 7.26 (dd), 6.48 (t), 6.29 (dd), 5.87 (d), -5.50 ($\mu_2\text{-H}$, hexaethylborohydride anion), -17.40 ($\mu_2\text{-H}$, Re-H). $^{13}\text{C}\{^1\text{H}\}$ (^{13}C enriched 1 in THF): δ 200.1. Anal. Calcd for $\text{C}_{60}\text{H}_{46}\text{P}_2\text{O}_{12}\text{Re}_4$: C, 40.80; H, 2.61. Found: C, 41.49, H, 3.78. Note: despite repeated recrystallizations, an acceptable microanalysis could not be obtained due to the presence of $[\text{C}_9\text{H}_7]^-$, as determined by ^1H NMR analysis.

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Carbonate Exchange for the Complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ in Aqueous Solution As Studied by ^{13}C NMR Spectroscopy¹

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Uranyl carbonate complexes are the most stable inorganic species of uranium(VI) and have exceptional importance in the extraction process in uranium mining² and in the migration of UO_2^{2+} in ground water.³ The equilibria in the $\text{UO}_2^{2+}\text{-CO}_3^{2-}$ system have been studied in detail, and the complexes $\text{UO}_2(\text{CO}_3)_n^{2-2n}$, where $n = 1\text{--}3$, and the complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ have been found to dominate in aqueous solution.^{4,5} A structural study has been performed,⁶ but only preliminary results have been published on the ligand-exchange kinetics of $\text{UO}_2(\text{CO}_3)_3^{4-}$.^{7–9} In this note, we report a ^{13}C NMR study on the dynamics of the $\text{UO}_2(\text{CO}_3)_3^{4-}\text{-CO}_3^{2-}$ system in aqueous solution.

Experimental Section

Solutions. Known volumes of $\text{UO}_2(\text{ClO}_4)_2$ stock solution and a weighed quantity of ^{13}C -enriched (99%) Na_2CO_3 and/or NaHCO_3 (Stohler Isotope Chemicals) were mixed to prepare NMR samples. The ionic medium was 1 M NaClO_4 . The total concentration of uranyl, c_{UO_2} , varied between 0.005 and 0.027 M, and the total carbonate concentration, c_{CO_3} , was always higher than $3c_{\text{UO}_2}$. pH was regulated by careful addition of concentrated NaOH or HClO_4 in order to avoid dilution and to prevent changes in c_{CO_3} . The ratio $c_{\text{CO}_3}/c_{\text{UO}_2}$ was also checked by measuring the integrals of the NMR signals of the free (CO_3^{2-} and/or HCO_3^-) and the coordinated carbonate (cf. Figure 1). The hydrogen ion concentration was measured with a glass electrode calibrated by Irving's method.¹⁰

NMR Measurements. The ^{13}C NMR spectra were measured by using Bruker MSL200 and AM400 spectrometers. Typical NMR parameters (Bruker MSL200): spectral window = 1000 Hz, pulse width = 10 μs (90° pulse), pulse repetition time = 4 s. These parameters were controlled to give quantitative spectra. The chemical shifts are referred to

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- (18) Cf. the ^{13}C resonance (δ 196.7) for $[\text{Re}(\text{CO})_3\text{OH}]_4$ recorded in THF- d_8 . See ref 17.
- (19) Aldrich's tradename for lithium triisobutylborohydride, $[(\text{CH}_3)_2\text{CHC}(\text{H})(\text{CH}_3)_2\text{BH}][\text{Li}]$.
- (20) (a) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.
- (21) For simplicity's sake, we have shown this dimer to exist as the tetra-bridged-hydride dimer, but note that other hydride arrangements would also satisfy the EAN rule.
- (22) For extended Hückel studies on M_2L_9 complexes, see: (a) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219. (b) Dedieu, A.; Albright, T. A.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141. (c) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.
- (23) For related 30-electron complexes formed by dimerizations, see: (a) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27. (b) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722.
- (24) For reviews dealing with the hydride donation properties of organometallic complexes, see: (a) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1. (b) Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1.
- (25) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
- (26) Nunn, C. M.; Cowley, A. H.; Lee, S. W.; Richmond, M. G. *Inorg. Chem.* **1990**, *29*, 2105.

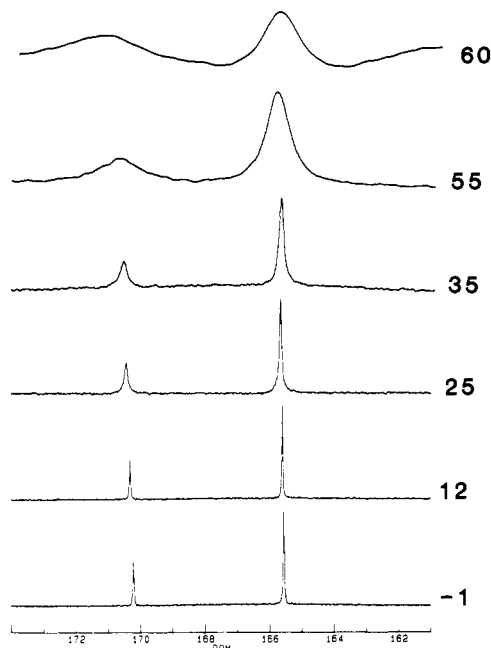


Figure 1. 50.3-MHz ^{13}C NMR spectra for solutions containing $\text{UO}_2\text{-(CO}_3)_3^{4-}$ ($\delta = 170.53$ ppm at 25°C) and free carbonate (averaged signal for HCO_3^- and CO_3^{2-}) at different temperatures (numbers to the right: T , $^\circ\text{C}$). $c_{\text{UO}_2} = 0.020$ M, $c_{\text{CO}_3} = 0.190$ M, and $\text{pH} = 9.03$.

external TMS. The experimental line widths, $\Delta\nu_{\text{obs}}$, were obtained by curve-fitting assuming Lorentzian line shapes for well-separated signals and by complete line shape analysis for overlapping signals. The temperature was controlled by an external (nonspinning) Pt resistance thermometer in the sample position. The samples contained 10% (v/v) D_2O as internal field/frequency lock.

Results and Discussion

At $\text{pH} > 7$, two exchange processes occur. The first one, $\text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^-$, is very fast on the actual NMR time scale.¹¹ Thus, it does not affect the exchange broadening in the $\text{UO}_2\text{-(CO}_3)_3^{4-}$ system. We have determined the value of $K_a = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-]$ using a combination of ^{13}C NMR spectroscopy and potentiometry and the equation $\text{p}K_a = \text{pH} + \log [(\delta_{\text{CO}_3} - \delta_{\text{obs}})/\delta_{\text{obs}} - \delta_{\text{HCO}_3}]$,¹² where δ_{obs} is the observed chemical shift of the time-averaged signal at a given pH and $\delta_{\text{CO}_3} = 171.05$ ppm and $\delta_{\text{HCO}_3} = 163.29$ ppm are the (experimentally determined) individual chemical shifts of CO_3^{2-} and HCO_3^- , respectively. The latter shifts are about 1 ppm higher than those given by Strom et al.⁷ This difference can be caused by the different ionic medium and by the different proportion of D_2O .

$\text{p}K_a$ values of $9.55 (\pm 0.05)$ and $9.90 (\pm 0.03)$ (throughout the paper, the values in parentheses represent $\pm\sigma$) have been determined at 25°C and in the ionic media of 1 M NaClO_4 (10% v/v D_2O) and 3 M NaClO_4 (no D_2O), respectively. At $I = 1$ M the agreement with the literature is excellent,¹³ but at $I = 3$ M our

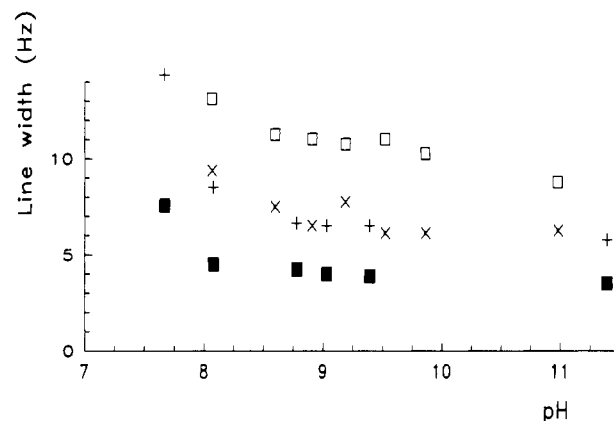


Figure 2. ^{13}C NMR line widths for complexed-carbonate (X, +) and free-carbonate (square, filled square) signals versus pH . $c_{\text{UO}_2} = 0.020$ M; $c_{\text{CO}_3} = 0.113$ and 0.190 M, respectively.

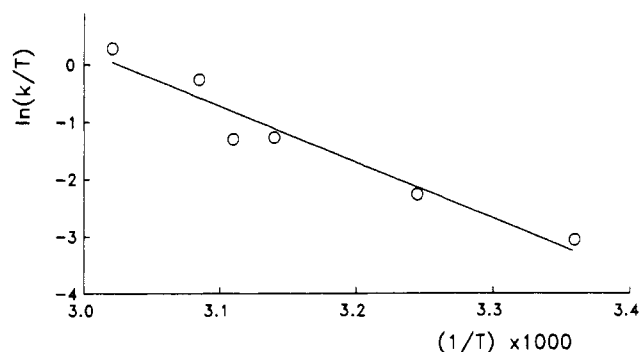
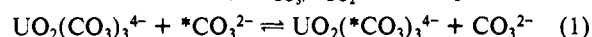


Figure 3. Arrhenius plot for reaction 3. $\text{pH} = 9\text{--}11$, $c_{\text{UO}_2} = 0.020$ M, and $c_{\text{CO}_3} = 0.113$ M.

value is higher compared to $\text{p}K_a = 9.63$.¹⁴ Frydman et al.¹⁴ used a different experimental method (potentiometry) for their determination. The effect of ionic strength, which can be predicted by using of Davies' equation,¹⁵ makes our value more probable. The advantages of a combined pH -potentiometric-NMR method as compared to potentiometry alone, especially for volatile substances, are discussed in a recent paper.¹⁶

The second process, i.e. the exchange between the complexed and the free carbonate, is (at $c_{\text{CO}_3}/c_{\text{UO}_2} > 3$ and $\text{pH} > 7$)



In Figure 1, some typical ^{13}C NMR spectra for this system are shown. Below room temperature, the exchange reaction is slow on the actual time scale (cf. Figure 1). The chemical shift for the species $\text{UO}_2(\text{CO}_3)_3^{4-}$ is 170.53 ppm at 25°C , which can be compared to 167.6 ,⁶ 167.7 ,⁹ and 168.9 ppm.⁷ The two former values are probably altered by the fast exchange with the free carbonate; the latter differs from our value by 1.6 ppm, which can perhaps be explained by the presence in our solutions of 1 M Na^+ , which can form ion pairs with the negatively charged $\text{UO}_2(\text{CO}_3)_3^{4-}$ species.

At higher temperature, a substantial line broadening is observed. Hence, the pseudo-first-order rate constant can be calculated from the spectra for both signals as $k_{\text{obs}} = 1/(\text{lifetime}) = \pi(\Delta\nu - \Delta\nu^0)$, where $\Delta\nu$ is the exchange-broadened and $\Delta\nu^0$ is the nonexchange line width. Since at the chosen conditions all uranyl is present as the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex,^{4,5} the following species can represent possible reactants: $\text{UO}_2(\text{CO}_3)_3^{4-}$, CO_3^{2-} ; HCO_3^- ; H^+ ; OH^- or H_2O .

- (1) Presented at the XXth International Conference on Solution Chemistry, Jerusalem, Israel, Aug 1989; see Abstracts, p 41.
- (2) Merritt, R. C. *The Extractive Metallurgy of Uranium*; U.S. Atomic Energy Commission: Washington, DC, 1971; pp 83-108.
- (3) Grenthe, I.; Lemire, R. J.; Muller, A. B.; Nguyen-Trung, C.; Wanner, H. *Chemical Thermodynamics of Uranium*; OECD-NEA: Paris, 1991.
- (4) Grenthe, I.; Ferri, D.; Salvatore, F.; Riccio, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2439.
- (5) Bidoglio, G.; Cavalli, P.; Grenthe, I.; Omenetto, N.; Qi, P.; Tanet, G. *Talanta*, in press.
- (6) Åberg, M.; Ferri, D.; Glaser, J.; Grenthe, I. *Inorg. Chem.* **1983**, *22*, 3981.
- (7) Strom, E. T.; Woessner, D. E.; Smith, W. B. *J. Am. Chem. Soc.* **1981**, *103*, 1255.
- (8) Stout, B. E. M.S. Thesis, Florida State University, Tallahassee, FL, 1985.
- (9) Maya, L.; Begun, G. M. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2827.
- (10) Irving, H. M.; Miles, M. G.; Pettit, L. P. *Anal. Chim. Acta* **1967**, *38*, 475.
- (11) Patterson, A.; Ettinger, R. *Z. Elektrochem.* **1960**, *64*, 98.
- (12) Blixt, J.; Györi, B.; Glaser, J. *J. Am. Chem. Soc.* **1989**, *111*, 7784.

- (13) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1976; Vol. 4, p 37.
- (14) Frydman, M.; Nilsson, G.; Rengemo, T.; Sillén, L. G. *Acta Chem. Scand.* **1958**, *12*, 878.
- (15) Butler, J. M. *Carbon Dioxide Equilibria and Their Applications*; Addison-Wesley Publishing Co., Inc.: Reading, MA, 1982.
- (16) Banyai, I.; Blixt, J.; Glaser, J.; Toth, I. Submitted for publication.

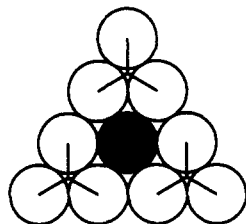
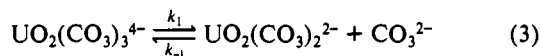


Figure 4. Structure of the complex $\text{UO}_2(\text{CO}_3)_3^{4-}$: filled circle, UO_2 moiety; open circles, carbonate oxygens.

In order to evaluate the rate law for the exchange reaction, the dependence of the line width of the coordinated carbonate signal on the pH was measured (Figure 2). The experimental findings show clearly that for $\text{pH} > 8.7$ line widths are independent of the pH. The line widths of the coordinated carbonate signal are also independent of the free-ligand concentration at constant $[\text{UO}_2(\text{CO}_3)_3^{4-}]$ and of the total uranyl concentration at constant $c_{\text{CO}_3}^{\text{free}}$. Therefore, the rate equation is

$$\text{rate} = -d[\text{UO}_2(\text{CO}_3)_3^{4-}]/dt = k_1[\text{UO}_2(\text{CO}_3)_3^{4-}] \quad (2)$$

with $k_1 = 13 (\pm 3) \text{ s}^{-1}$, calculated from the line width of $\text{UO}_2(\text{CO}_3)_3^{4-}$ signal. ($\Delta\nu_0^0$, the nonexchange line width of the $\text{UO}_2(\text{CO}_3)_3^{4-}$ signal, was measured to be $1.0 (\pm 0.3) \text{ Hz}$ at -1°C and assumed not to be much different at 25°C . This assumption was based on the fact that the nonexchange line width of the free-carbonate signal, $\Delta\nu_{\text{free}}^0$, which could be measured directly in solutions not containing uranium, was not significantly changed within this temperature range.) Thus, the mechanistic consideration is quite straightforward: the mechanism is dissociative according to the following reaction



The Arrhenius plot (Figure 3) gives $\Delta H^\ddagger = 82 (\pm 11) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = 50 (\pm 30) \text{ J mol}^{-1} \text{ K}^{-1}$. The positive value of the activation entropy is in agreement with our proposal that the dissociation of the carbonate ligand from the $\text{UO}_2(\text{CO}_3)_3^{4-}$ complex is the rate-determining step (eq 3). This proposal seems reasonable, since the complex is coordinatively saturated (three carbonate ligands are bidentately bound to the UO_2^{2+} ion in the equatorial plane with uranyl oxygens perpendicular to the plane¹⁷) (cf. Figure 4). There is no water in the inner coordination sphere of $\text{UO}_2(\text{CO}_3)_3^{4-}$ in the solid state.¹⁷ Neither does there seem to be any water coordinated to uranyl in the structurally related complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ in aqueous solution.⁶ Hence, it seems less probable that the complex $\text{UO}_2(\text{CO}_3)_3^{4-}$ is aquated in solution. Thus, a second-order reaction is less probable. Obviously, water molecules can take part in the exchange reaction (3). However, water exchange for $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ is relatively fast, $k = 7.6 \times 10^5 \text{ s}^{-1}$.¹⁸ In addition, coordination of negative ions to the metal ion weakens and labilizes the metal-water bond(s).^{18,19} Concluding, even if coordination of water to a uranyl complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$ or $\text{UO}_2(\text{CO}_3)_2^{2-}$, occurs, an association or a dissociation of water will not be the rate-determining step for reaction 3.

Tomiyasu and Fukutomi²⁰ reviewed some ligand-exchange reactions involving uranium. For these reactions, mostly D or I_d mechanisms were proposed for monodentate ligands, but no conclusion was reached for more complicated systems of bidentate or mixed-ligand complexes.

(In order to further confirm the dissociative character of the ligand-exchange reaction, one could follow a ligand substitution reaction:



- (17) (a) Coda, A.; Della Giusta, A.; Tazzoli, V. *Acta Crystallogr.* **1981**, *B37*, 1496. (b) Mereiter, K. *Ibid.* **1988**, *C44*, 1175.
 (18) Jung, W.-S.; Harada, M.; Tomiyasu, H.; Fukutomi, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3895.
 (19) Haim, A.; Wilmarth, W. K. *Inorg. Chem.* **1962**, *1*, 582.
 (20) Tomiyasu, H.; Fukutomi, H. *Bull. Res. Lab. Nucl. React. (Tokyo Inst. Technol.)* **1982**, *7*, 57.

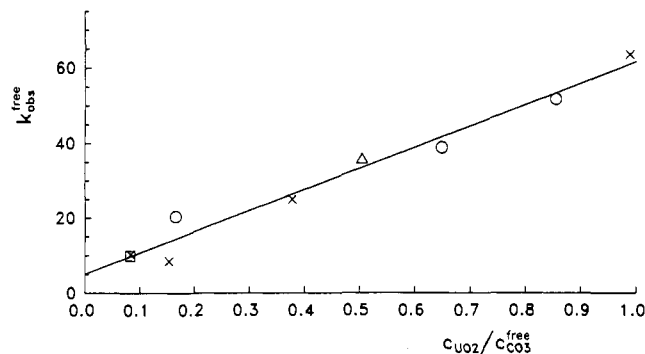


Figure 5. $k_{\text{obs}}^{\text{free}}$ versus $c_{\text{UO}_2}/c_{\text{CO}_3}^{\text{free}}$. $\text{pH} = 9.0 \pm 0.1$; $c_{\text{UO}_2} = 0.0045$ (\square), 0.010 (\circ), 0.020 (\times) and 0.027 M (Δ) (± 0.001 M).

in which the rate-determining step could be the dissociation of the carbonate ion. Unfortunately, according to our knowledge there is no mono- or bidentate ligand L for which the forward reaction mentioned above is thermodynamically favorable.)

Since the rates of the formation and of the dissociation of $\text{UO}_2(\text{CO}_3)_3^{4-}$ have to be equal, one can calculate the value of k_{-1} for the back-reaction (cf. eq 3) using the stability constant $K_3 = [\text{UO}_2(\text{CO}_3)_3^{4-}]/([\text{UO}_2(\text{CO}_3)_2^{2-}][\text{CO}_3^{2-}]) = 2.24 \times 10^6 \text{ M}^{-1}$.⁵ Thus, $k_{-1} = k_1 K_3 = 2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

From the line width of the free-carbonate signal a value of k_{-1}' ($k_{-1} = k_{-1}'/3$; cf. eq 3) can also be calculated:

$$\text{rate} = -dc_{\text{CO}_3}^{\text{free}}/dt = k_{\text{CO}_3}^{\text{free}} = k_{-1}'[\text{UO}_2(\text{CO}_3)_2^{2-}][\text{CO}_3^{2-}] \quad (4)$$

where $c_{\text{CO}_3}^{\text{free}} = c_{\text{CO}_3} - 3c_{\text{UO}_2}$. Substituting $[\text{UO}_2(\text{CO}_3)_2^{2-}] = [\text{UO}_2(\text{CO}_3)_3^{4-}]/\{K_3[\text{CO}_3^{2-}]\}$ and $c_{\text{UO}_2} = [\text{UO}_2(\text{CO}_3)_3^{4-}]$ into eq 4 and rearranging give

$$k_{\text{obs}}^{\text{free}} = (k_{-1}'/K_3)(c_{\text{UO}_2}/c_{\text{CO}_3}^{\text{free}}) \quad (5)$$

Figure 5 shows that the plot of $k_{\text{obs}}^{\text{free}}$ versus $(c_{\text{UO}_2}/c_{\text{CO}_3}^{\text{free}})$ gives a straight line with a slope of $k_{-1}'/K_3 = 57 (\pm 4) \text{ s}^{-1}$. Thus, this slope yields $k_{-1}' = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. In order to compare this value to the value calculated above from the coordinated carbonate signal, one has to divide k_{-1}' by the stoichiometric factor equal to 3. The result is $4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is in reasonable agreement with the value of $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ calculated from $k_{-1} = k_1 K_3$ (see above). This means that the simple two-site-exchange model is applicable to this system. The intercept of Figure 5 is $\pi(\Delta\nu_0^0) = 5 (\pm 2) \text{ Hz}$. Hence, the nonexchange line width of the free-carbonate signal, $\Delta\nu_0^0$, is equal to $1.6 (\pm 0.6) \text{ Hz}$, which is not significantly different from the measured value, $\Delta\nu_{\text{free}}^0 = 0.5 (\pm 0.2) \text{ Hz}$. The latter was obtained for solution not containing uranyl at 25°C and was independent of pH in the range $7.5 < \text{pH} < 11.5$.

At pH values lower than 8.6 the exchange rate is considerably higher and a different exchange mechanism seems to dominate.⁷

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A Planar Binuclear Tetrabenzoporphyrin and Its Dicopper Derivative

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Several porphyrin dimers with relatively rigid structures have received increasing attention mainly to elucidate intramolecular interactions. Two porphyrins have been connected, for example, through two positions of either benzene,¹ naphthalene,^{2a} anthra-