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# Pressure Dependence of Carbonate Exchange with [NpO$_2$(CO$_3$)$_3$]$^{4-}$ in Aqueous Solutions

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S *Supporting Information*

ABSTRACT: The rates of ligand exchange into the geochemically important [NpO$_2$(CO$_3$)$_3$]$^{4-}$ aqueous complex are measured as a function of pressure in order to complement existing data on the isostructural [UO$_2$(CO$_3$)$_3$]$^{4-}$ complex. Experiments are conducted at pH conditions where the rate of exchange is independent of the proton concentration. Unexpectedly, the experiments show a distinct difference in the pressure dependencies of rates of exchange for the uranyl and neptunyl complexes.
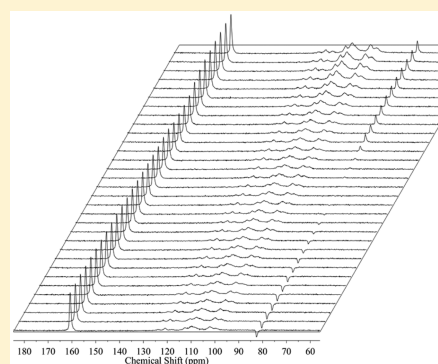
INTRODUCTION

Radionuclides are the primary hazard in nuclear waste both in the near and far future (>10^3 years).[1] The most persistent of the radioactive species are uranium and the transuranic elements, notably, isotopes of Np, Pu, Am, and Cm, and these must be isolated from the biosphere for tens of thousands of years. The concentrations of transuranic elements in waste vary depending upon the type of irradiated reactor fuel and, in some cases, on the nature of defense wastes and related waste forms. However, the primary source of anthropogenic radionuclides is from spent nuclear fuel (SNF) at both civilian and government power installations. Of the transuranic elements, ^{237}Np is of particular concern because it is a major contributor to the total radiation in SNF.[2] Along with the relatively high inventory in SNF, ^{237}Np has a long half-life ($t_{1/2} = 2 \times 10^6$ years), and it is mobile in oxygenated groundwaters due to its high solubility as an "-yl" oxocation and also as a tris-carbonato complex.[3]

In the United States there is no reprocessing of SNF, so the current plan for disposal is the long-term storage of these materials in a combination of pools at the reactor site itself, in tanks, and in a geological repository.[4] In cases of geologic storage, it is assumed that containers containing the radioactive waste will ultimately breach and leak into the environment.[5] Thus, it is the natural reactivity of the surrounding rocks, and the slow transit time of groundwater to the biosphere, that makes the repository safe. The ability of the rocks to impede the motion of radioactive solutes depends upon the mineralogy and the chemistry of the aqueous solutes.[6] The tris-carbonato complexes are particularly important due to the high

concentration of carbon dioxide in groundwaters and the weak reactivity of the large carbonato anions.

While geochemical studies of Np(VI) complexes are relatively rare, there is much work on the corresponding aqueous U(VI) species. These studies include the uptake of aqueous complexes by minerals, the kinetic behavior, and the susceptibility to microbial uptake, at least in oxic settings.[7−11] Experiments with the transuranic elements are inherently difficult, and predictions about their chemistry would be much simpler if experiments on the safer U(VI) counterparts provided a reliable guide.

The goal of this paper is to compare the kinetic behavior of two isostructural tris-carbonato complexes of Np(VI) and U(VI). We specifically examine the rates and pressure dependencies of the exchange of free and bound carbonate in the [NpO$_2$(CO$_3$)$_3$]$^{4-}$ complex, and compare the results to previous work on the [UO$_2$(CO$_3$)$_3$]$^{4-}$ complex. The working hypothesis is that the pressure dependence of the rate coefficients for the exchange of the bound carbonate will be virtually identical between the isostructural Np(VI) and U(VI) species under alkaline conditions. The Np(VI) experiments, however, are much more difficult because the complexes are paramagnetic, and the challenges of working with radioactivity are compounded by the extra hazards of working at high pressures.

Toth's group showed previously that the rate of exchange of the free aqueous carbonate with a bound carbonate in the

mononuclear $[UO_2(CO_3)_3]^{4-}$ ion has both a proton-mediated and a pH-independent pathway. Rates are independent of the free carbonate concentration, such that the total rate equation is described in eq 1:[12,13]

$$\text{rate} = (k_1 + k_2[H^+])[UO_2(CO_3)_3^{4-}] \qquad (1)$$

The square brackets here indicate molarity. For the $[UO_2(CO_3)_3]^{4-}$ ion, the rate of self-exchange decreases as a function of pressure such that positive activation volumes could be calculated from the experimental data at both neutral and basic pH.[14] Variable-temperature experiments similar to those of the Toth group were conducted on the $[NpO_2(CO_3)_3]^{4-}$ ion, and the neptunyl species was shown to have a rate law similar to that shown for the uranyl in eq 1, where no dependence on the concentration of free carbonate was exhibited.[15] This zeroth-order dependence on carbonate concentration was confirmed during the course of the study presented in this paper. However, the rate of self-exchange for the $[NpO_2(CO_3)_3]^{4-}$ complex as a function of pressure has not been reported in the literature.

Line-broadening techniques can yield kinetic information by sampling the T_2-relaxation pathway as a function of temperature and pressure. Exchange occurs when the nucleus changes environment from the free to the bound position, which contributes to the T_2 relaxation. Kinetic parameters can be extracted from the variation in line widths in well-suited cases. As one can see in Figure 1, however, increases in pressure cause
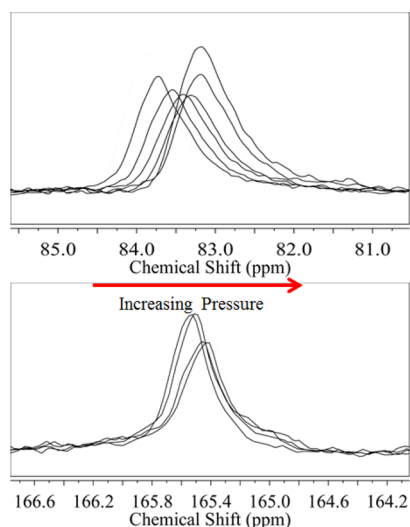

Figure 1. Pressure dependence of the ^{13}C chemical shift of the bound carbonate peak is small. Increases in pressure cause the peak to shift upfield, but only over a small range. Top: $[UO_2(CO_3)_3]^{4-}$. Bottom: $[NpO_2(CO_3)_3]^{4-}$.

only slight variations in the ^{13}C NMR peak width for either the diamagnetic $[UO_2(CO_3)_3]^{4-}$ ion (top) and the paramagnetic $[NpO_2(CO_3)_3]^{4-}$ ion (bottom).

As a complement to the line-broadening methods, Szabo et al.[16] employed a modified inversion–recovery method that probed the rate of exchange of water around the $[UO_2]^{2+}$ ion via the T_1-relaxation mechanism. This method has been adapted for use with these high-pressure experiments. The T_1 pathway is measured via a modified inversion–recovery sequence, such that the bound peak is selectively inverted

and the transference of magnetism is measured to the free carbonate peak.

The exchange is modeled using the McConnell formalism[17] of the Bloch equations,[18] which describe the kinetics of exchange of two nonequivalent sites:

$$\frac{dM_{z,\text{free}}(t)}{dt} = -\frac{[M_{z,\text{free}}(t) - M_{z,\text{free}}^{eq}]}{T_{1,\text{free}}} + k_{\text{bound}}M_{z,\text{bound}}(t)$$
$$- k_{\text{free}}M_{z,\text{free}}(t) \qquad (2)$$

$$\frac{dM_{z,\text{bound}}(t)}{dt} = -\frac{[M_{z,\text{bound}}(t) - M_{z,\text{bound}}^{eq}]}{T_{1,\text{bound}}}$$
$$+ k_{\text{free}}M_{z,\text{free}}(t) - k_{\text{bound}}M_{z,\text{bound}}(t) \qquad (3)$$

Here M_z is the magnetization in the z-direction with respect to time for the free or the bound ligand, T_1 is the longitudinal relaxation time for each species, and k is the rate constant for the exchange reaction between the two sites. Using these equations and a magnetization-transfer pulse sequence, a numerical solution can be found to yield the rates of exchange of carbonate that is bound to the metal center and free carbonate in solution.

■ EXPERIMENTAL SECTION

Caution! Neptunium-237 is an alpha (α) emitter that is potentially harmful. Extreme care must be taken when using this material, and it should be handled at a dedicated facility with the proper engineering controls. The experiments at pressure compound the hazard and must be conducted with care and secondary containment contingencies.

Solution Preparation. The neptunium starting material was acquired from available stocks at LLNL. The initial neptunium solution had a mixed valency and unknown salt concentration necessitating purification and oxidation state manipulation. After dehydration of the starting material, the neptunium was dissolved in 12 M HCl to reduce the neptunium to the Np(IV) oxidation state. This solution was then passed through an anion-exchange column containing DOWEX 1 × 8 resin as the solid phase. The Np(IV) adsorbed to the resin and was washed with 12 M HCl. The bound neptunium was eluted as Np(V) using 0.3 M HNO$_3$. The stock was then oxidized to Np(VI) using excess KBrO$_3$,[19] and the progress of the oxidation was monitored via UV–vis. The absence of the strong Np(V) peak at 981 nm and the presence of the Np(VI) peak at 1226 nm were considered strong evidence of complete oxidation to Np(VI). After the activity was determined using liquid-scintillation counting, an aliquot was removed to prepare the sample for NMR. The Np(VI) was initially precipitated from solution as the hydroxide solid, washed several times with 18 MΩ water with interspersed centrifugation, and redissolved into 500 μL of 18 MΩ water with ^{13}C-labeled Na$_2$CO$_3$ and 1.0 M NaNO$_3$ as the ionic medium. The pH was adjusted with dilute nitric acid and monitored with a combination electrode. Three solutions were made in this fashion, and the final concentrations of [Np(VI)] and [CO$_3$]$^{2-}_{\text{total}}$ were as follows: for the sample at pH = 9.45, 17.5 mM and 254.6 mM; for the sample at pH = 9.72, 26.6 mM and 330.9 mM; and for the sample at pH = 9.82, 15.8 mM and 217.2 mM, respectively.

Three samples from the pH 9.72 stock were also used in studies of serial dilution. These experiments employed a standard Bruker NMR probe, but were diluted from the stock 26.6 mM using a D$_2$O solution at 1.0 M NaNO$_3$ with varying levels of added carbonate. This dilution yielded ratios of [CO$_3$]$^{2-}_{\text{free}}$/[CO$_3$]$^{2-}_{\text{bound}}$ of 7.7, 9.3, and 12.3. [Np(VI)] varied between 14.2 and 16.1 mM in these solutions, while $\sum$[CO$_3$] varied between 418.2 and 567.6 mM. The pH in these solutions was constant at 9.7.

Samples were prepared at pH 9–10 to maintain a simple speciation where the $[NpO_2(CO_3)_3]^{4-}$ ion was the dominant aqueous neptunium

species. At higher and lower pH conditions, appreciable amounts of either partly hydrolyzed neptunium complexes or the trimeric neptunyl-carbonato complex can form, respectively.[20] These were avoided. No precipitation was observed in any of the NMR samples. The UV–vis indicated extensive complexation of $[NpO_2]^{2+}$ to form $[NpO_2(CO_3)_3]^{4-}$ ion. Finally, the ^{13}C NMR spectra indicated that trimeric neptunyl-carbonato species (found at 8 and −89 ppm) were absent at all conditions.

The samples were loaded into quartz NMR tubes (see the Supporting Information) and floated on fluorocarbon oil (poly-(chloro)trifluoroethylene) in order to maximize the number of spins in the NMR coil. A Teflon plug was inserted, and air was bled from the samples. The quartz tube was inserted into a phenolic secondary containment vessel in which the copper coil and sample were housed (see Supporting Information).

NMR Spectroscopy. NMR spectra used to confirm the zeroth-order dependence on carbonate were run on a 14.1 T magnet (150.8 MHz for ^{13}C) coupled to a Bruker Avance III console. The sample temperature was maintained at 25 (±0.1) °C using a prior calibration using 99.8% deuterated methanol as the standard.

Variable-pressure spectra were collected using a home-built NMR probe constructed of Berylco-25, Ti-Beta-C and Ti grade 5 alloys.[21,22] The probe was inserted into a 9.4 T magnet (100.6 MHz for ^{13}C) coupled to a Bruker Avance spectrometer. Pressure was applied via a syringe pump system using *n*-hexanes as a pressure-transfer fluid. Pressure was monitored and adjusted to maintain deviations to ≤1%. Temperature was constant at 25.1 ± 0.1 °C via a circulating water bath and monitored with an internal T-type thermocouple.

On both spectrometers, a selective-excitation inversion–recovery experiment was used to excite ^{13}C in the bound carbonate peak at 85 ppm. The data consisted of 32 variable-delay points spanning a range from 100 μs to 10 s. The acquisition time was 0.8 s, which allowed power to disperse in the circuit, and a final pulse delay was employed of 0.5 s for T_1 recovery. The total number of scans was 512; 32 000 points were collected, but only 8192 points were transformed for each FID. The spectral data from a typical experiment at elevated pressure are shown in the Supporting Information, along with the fitted T_1 values. The areas of each peak are plotted against variable-delay time and fit to eqs 2 and 3 using a nonlinear least-squares algorithm (MatLab) where the rate coefficients and T_1 parameters are allowed to float, though they are bound by realistic parameters. Values for these parameters are included in the Supporting Information. The fits to a set of intensity data for one experiment are shown in Figure 2.
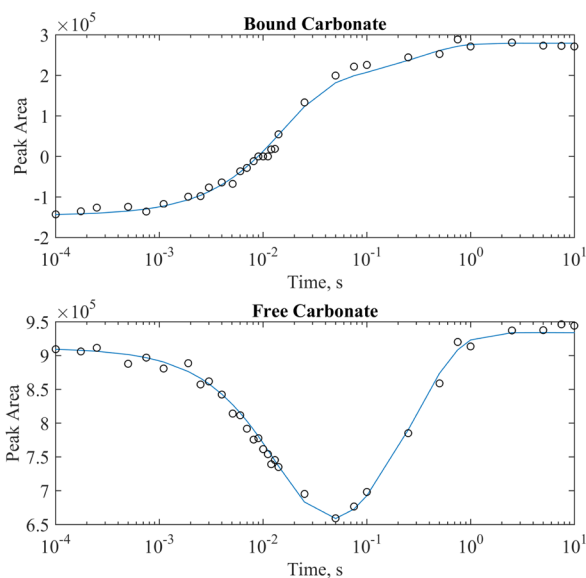

Figure 2. Typical fit of the experimental data (300 MPa, pH 9.45) to eqs 2 and 3, the Bloch–McConnell equations.

RESULTS

Measurements of the rate coefficients for the serially diluted solutions of the pH 9.72 stock show virtually no difference from those measured in the high-pressure probe at ambient conditions. These coefficients are compiled in Table 1. The

Table 1. Compiled Rate Coefficients for All Solutions, Measured at Ambient Pressure and 298 K[a]

pH	k_{bound} (s^{-1})	$[CO_3]^{2-}_{free}/[CO_3]^{2-}_{bound}$
9.45	32.8	3.9
9.72	31.9	3.2
9.82	33.7	3.6
9.72*	28.1	7.7
9.73*	27.5	9.3
9.77*	29.3	12.3

[a]Measurements were conducted on two separate spectrometers and two probes, with the data from the 14.1 T instrument marked with an asterisk (*).

slight variation in measurements between the two probes probably arises from slight differences in temperature calibration, not from random noise; the high-pressure probe has an internal thermocouple for *in situ* measurement. In spite of the slight difference, there is gratifying agreement between the two sets of measurements.

Experiments at pH 9.45 and pH 9.82 indicate that the rate coefficients for $[NpO_2(CO_3)_3]^{4-}$ are virtually independent of pressure, which is distinctly different than what was previously reported for the $[UO_2(CO_3)_3]^{4-}$ ion, where Johnson et al. reported a decrease in the self-exchange rate of carbonate by roughly 40% for the pH-independent pathway for exchange. In contrast, the ~9% increase in the self-exchange rate for $[NpO_2(CO_3)_3]^{4-}$ is not statistically distinct from zero (Figure 3) at the 95% confidence level. An additional experiment is shown Figure 4, with a higher density of data, showing a similar result. The new data are consistent with those of Panasci et al. at similar pH conditions and at ambient pressure.

One referee claims that the rate data for pH-independent exchange in the $[NpO_2(CO_3)_3]^{4-}$ ion are too scattered to extract activation volumes that can be compared to the uranyl data. We disagree.

There are two points to make. First, the scatter do not obscure the near-zero slope of the rate data, which have sufficient statistical strength to support the conclusion at the 95% confidence interval. The reason for the scatter in the Np(VI) data is that the T_1 relaxation rate is close to $\frac{1}{k_{bound}}$, as Np(VI) is paramagnetic in the $[NpO_2(CO_3)_3]^{4-}$ complex, and both values are on the order of 10^{-2} s.

Second, we believe that the largest source of uncertainty in comparing $[NpO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ lies in decisions about how to treat differences in the Brønsted acidities of the two complexes (see refs 23 and 24). Johnson et al. measured the pressure variation of pH and corrected their raw rate estimates for contributions from the proton-enhanced pathway for exchange. They used the ^{14}N NMR shifts of 1-methylimidazole as an internal pH indicator, just as we use the NMR shifts of ^{13}C-labeled KCN (see Supporting Information). The autoprotolysis of water has a reaction volume that varies from ca. −22 cm³ mol⁻¹ to ca. −14.6 cm³ mol⁻¹ over the pressure range 0.1−350 MPa, and this leads to small but appreciable changes in pH. In contrast to $[UO_2(CO_3)_3]^{4-}$,
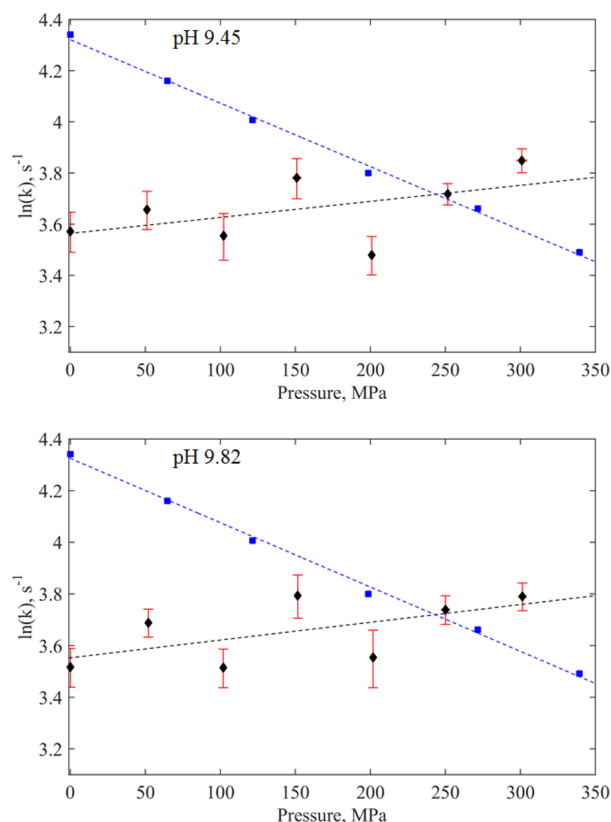
Figure 3. Natural logarithm of rate coefficient (k) versus pressure for the sample at pH 9.45 (top) and pH 9.82 (bottom). The error bars correspond to 95% confidence intervals. These are plotted in red for neptunyl, while the uranyl data are plotted in blue (from Johnson et al.). Both data are estimates for the pH-independent exchange pathway.
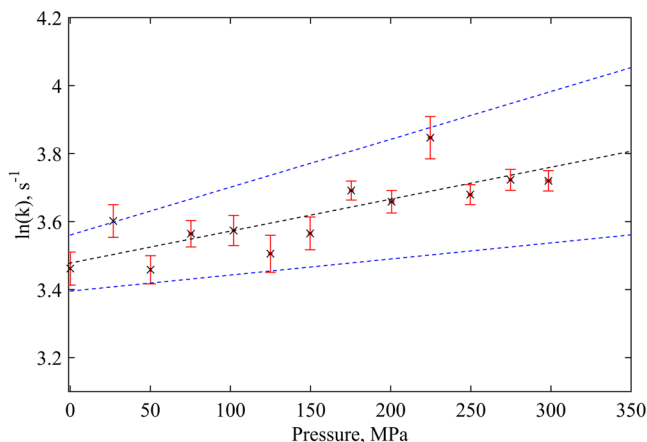

Figure 4. Natural logarithm of the rate coefficient (k) versus pressure for the pH 9.72 sample. The red bars correspond to the 95% confidence intervals of the fit of the data to the Bloch−McConnell equations while the blue bars correspond to the 95% confidence intervals with respect to the regression.

contributions by the pH-dependent pathway to measured rate coefficients are negligible for $[NpO_2(CO_3)_3]^{4-}$.

At the maximum pressure of this study (300 MPa), the calculated pH was 8.93, which remains well above the pH region where rates of carbonate exchange for $[NpO_2(CO_3)_3]^{4-}$ are affected by proton concentration (pH = 8.6). The pH where the proton-enhanced pathway becomes important may

vary with pressure. If so, it will shift to lower pH conditions, reflecting the changing acid/base properties of water with pressure. Using the parameters from Panasci et al. for the Np(VI)−carbonate system, the total contribution of the proton-mediated pathway to overall rates at pH 8.93 is estimated to be much less than one part in 10^6. Thus, rates for all $[NpO_2(CO_3)_3]^{4-}$ samples (pH 9.45, 9.72, and 9.82) can be attributed exclusively to the pH-independent pathway, which contrasts with the case of Johnson et al., for $[UO_2(CO_3)_3]^{4-}$ ions.

In summary, the rates of ligand exchange around the $[NpO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ ions are measurably different even if one claims that the pH where the proton-enhanced and unenhanced pathways become important also varies with pressure and pH, to parallel the changing acidity of water. This case would render unnecessary the corrections of Johnson et al., but then the differences in $\Delta V^\ddagger$ between the two species become a difference in reaction volumes for the acid−base reaction.

■ DISCUSSION

The slope of the fitted data relates to the activation volume ($\Delta V^\ddagger$) of the overall self-exchange reaction (see below):[25]

$$\left(\frac{\delta(\ln k)}{\delta P}\right)_T = -\frac{\Delta V^\ddagger}{RT} \tag{4}$$

Using eq 4, the average values of $\Delta V^\ddagger$ were calculated, along with the 95% confidence intervals due to the error in the slope (Table 1).

The Student's t test, when applied to the two experiments with $n = 7$, indicates that the $\Delta V^\ddagger$ values are not statistically distinct from zero at the 95% confidence level ($t = 2.36$, 2.37, $n = 7$). More importantly for our hypothesis, the $\Delta V^\ddagger$ values are distinctly different than those reported for the uranyl−carbonate system ($+6.6$ cm^3 mol^{-1}), also at the 95% confidence level. Using the higher density data ($n = 13$) set shown in Figure 4, we can distinguish ($t = 4.38$) an activation volume (-2.3 cm^3 mol^{-1}) distinct from 0 (Table 2), because the

Table 2. Values for the Calculated Activation Volumes and the Associated Error Due to the Regression[a]

pH	$\Delta V^\ddagger$, cm^3/mol	95% CI−, cm^3/mol	95% CI+, cm^3/mol
9.45	−1.55	−4.55	0.003
9.82	−1.70	−4.37	−0.001
9.72	*−2.33*	*−3.49*	*−1.17*

[a]The italicized data has a higher density of data ($n = 13$) versus the previous data set ($n = 7$).

increase in n decreases the standard error of the regression by $\sqrt{n}$. This value, of course, is also distinctly different from that for the uranyl−carbonate ion. The differences are also manifested in the other activation parameters. At high pH, the $\Delta S^\ddagger$ for the uranyl system is 50 J mol^{-1} K^{-1} while the $\Delta S^\ddagger$ for the neptunyl system has an accepted value of −70 J mol^{-1} K^{-1}.[13,26] There is some disagreement about the activation parameters of the uranyl system, as the Brucher et al. value of $\Delta S^\ddagger$ is opposite that measured by Stout et al.,[27] where $\Delta S^\ddagger = -40$ J mol^{-1} K^{-1}.

The reader is cautioned not to overinterpret these $\Delta V^\ddagger$ values and speculate about whether the elementary mechanism is associative or dissociative, as is commonly done for

homoleptic exchange reactions[28,29] because the exchange of carbonate is undoubtedly a multistep reaction with several elementary steps, and charge separation is a key step. However, from Panasci et al. (and confirmed here) the fact that the rate of exchange is zeroth-order with respect to free carbonate concentration suggests that the ring-opening step of the bidentate carbonate ligand controls the rate of the overall process. This supposition would also seem to indicate that an interchange-type process is occurring, as the opening of the ring would allow for a water molecule to enter into the equatorial plane and associate to the $[NpO_2]^{2+}$ center. A key point of any supposed reaction scheme is that, while the experimental activation volume is close to what is generally seen in the homoleptic interchange (I) mechanisms,[30] the change in charge due to the loss of the bound carbonate will cause a large change in activation volume that is not seen in simple solvent exchange. In general, $\Delta V^{\ddagger}$ is composed of two components, the intrinsic activation volume of the complex ($\Delta V^{\ddagger}_{int}$) and the electrostriction volume due to the charge on the complex ($\Delta V^{\ddagger}_{elect}$).[31] In water-exchange reactions, $\Delta V^{\ddagger}_{elect}$ is negligible, as the charge on a solvated complex does not change as the solvent is exchanged in the transition state; $\Delta V^{\ddagger}_{int}$ dominates the measurements.[32] In the case of the carbonate–ligand exchanging around the neptunyl center, the charge changes considerably: the total complex undergoes a change from −4 to −2 in charge in a key step, which, as $\Delta V^{\ddagger}_{elect}$ is proportional to the charge squared over the radius (Z^2/r), will change the $\Delta V^{\ddagger}_{elect}$ by an order of 4.[33] This electrostriction volume is also convoluted by the fact that the volume of the now-free carbonate is non-negligible (on the order of −4 to −10 cm^3/mol)[33] and is a charged species in solution that will cause more change to occur to $\Delta V^{\ddagger}_{elect}$.

Mechanistic interpretation of the measured $\Delta V^{\ddagger}$ value depends upon which step controls the overall rate. On the basis of the zeroth-order dependence on dissolved carbonate concentration, we speculate that rates are controlled by the first ring-opening step, or a subsequent carbonate-detachment step, as neither would be influenced by free aqueous carbonate ion. If the rate-controlling step were a ring-opening with a water nucleophile, then electrostriction would be minimal because there is no change to net charge. It is speculative, but the lone f-electron in Np(VI) could influence the net volume here. However, the most interesting result from this study is that the isostructural $[NpO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{4-}$ ions exhibit measurably distinct pressure dependencies for the reaction of the ring-opening of the carbonate ligand, where the same differences in charge and radius should occur. This difference seems to depend on the number of f-shell electrons, which is surprising. It has been shown computationally that free d-electrons do have the ability to alter the mechanism of exchange pathways in first-row transition metals.[34] It will be interesting to see if this trend is manifested further along the transuranic series via examination of carbonate exchange for the Pu(VI) and Am(VI) carbonato complexes with more valence f-electrons.[25]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02604.

Compiled fit data, pressure cell information, UV−vis spectra, and the determination of the pH dependence of the solutions on pressure (PDF)

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Notes

The authors declare no competing financial interest.

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