Kinetic studies Np(VI) ligand exchange using NMR

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The future of the nuclear industry depends on a fundamental understanding of environmental risks associated with nuclear accidents and waste storage, which relies on accurate models to predict migration of the radionuclides through engineered barriers, soil and groundwaters. Accurate data from experiments are needed to effectively build these actinide transport models. Accurate data with respect to neptunium is especially relevant due to its long half-life, and mobility in the environment.

Carbonate ligand exchange rates on the $[NpO_2(CO_3)_3]^{4-}$ ion were determined using a selective-excitation experiments that yield kinetic information about the rates of substitution directly. The chemical-shift difference between the bound carbonate peak and the bulk carbonate peak, however, is small (~12 kHz) such that we could not selectively excite a peak using a conventional 180° long pulse. Instead, we adapted an approach we previously employed to study $[UO_2(CO_3)_3]^{4-}$ species, which also has close chemical shifts[1].

These experiments extend work previously done by Stout *et al*. [2] by increasing the pH range of experiments from 8.1<pH<10.5. Over the pH range 9.3≤pH≤ 10.5, the rate of exchange and activation energy demonstrate no pH dependence, and we find an average rate, activation energy, enthalpy, and entropy of k^{298} = 40.6(± 4.3) s^{-1}, E_a=45.1(±3.8) kJ mol^{-1}; $\Delta H^{\ddagger}$ =42.6(±3.8) kJ mol^{-1}, $\Delta S^{\ddagger}$ = -72(±13) J mol^{-1} K^{-1} respectively. Below pH=9, we see evidence for a proton enhanced pathway, as the pH decreases, the rates incease. The lowest pH sample at pH=8.1 had a rate and enthalpy: k^{298} = 157(±6.2) s^{-1} and $\Delta H^{\ddagger}$ =25.7(±9 kJ mol^{-1}). The lower activation enthalpy is anticipated to reflect a contribution from the enthalpy of protonation[3].

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[1] Johnson *et al* (2011) *Chemphyschem* ***12***, 2903-2906 [2] Stout *et al* (1992) C.*Transuranium elements: a half century*. An American Chemical Society Publication: Washington D.C. [3] Panasci *et al* (submitted) *Inorg. Chem.*