Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Activation of Carbon Dioxide by a Terminal Uranium-Nitrogen Bond in the Gas-Phase: A Demonstration of the Principle of Microscopic Reversibility

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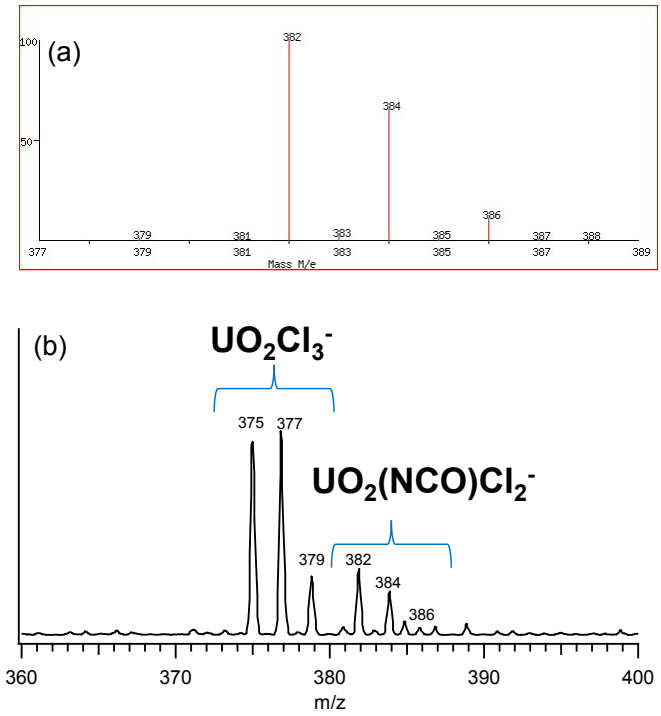

Figure S1. (a) Simulated mass spectrum of $UO_2(NCO)Cl_2^-$. (b) ESI mass spectrum showing $UO_2Cl_3^-$ and $UO_2(NCO)Cl_2^-$.

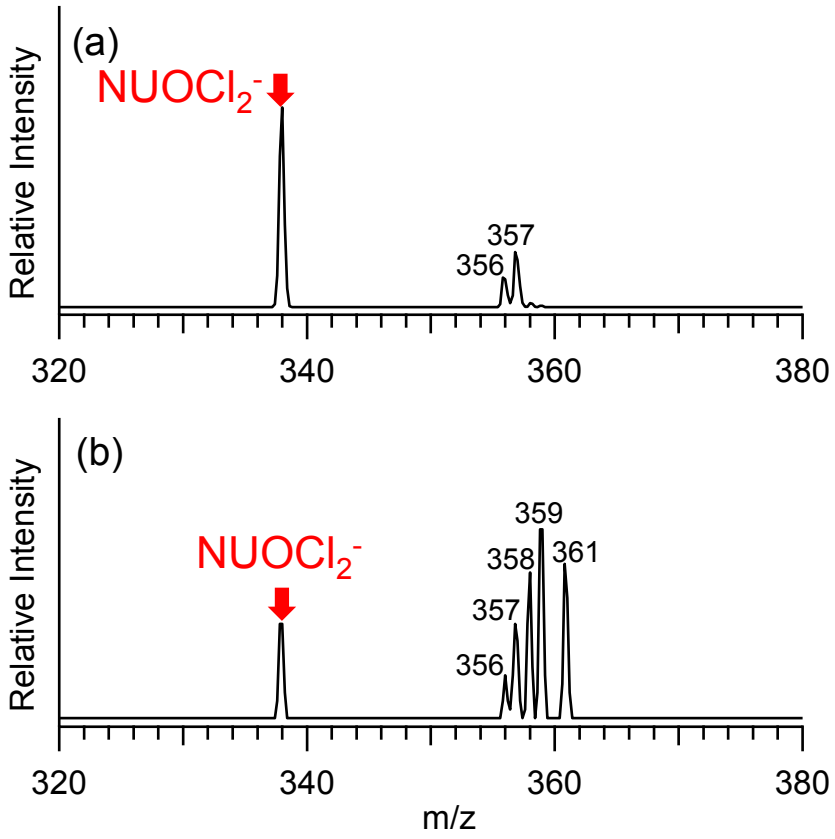

Figure S2. Mass spectra acquired after reaction of $NUOCl_2^-$. (a) for 100 ms with background $H_2{}^{16}O$; (b) for 200 ms with background $H_2{}^{16}O$ and added $H_2{}^{18}O$ at a ca. 1:3 ratio (based on the relative abundances of 356 m/z and 358 m/z, see below).

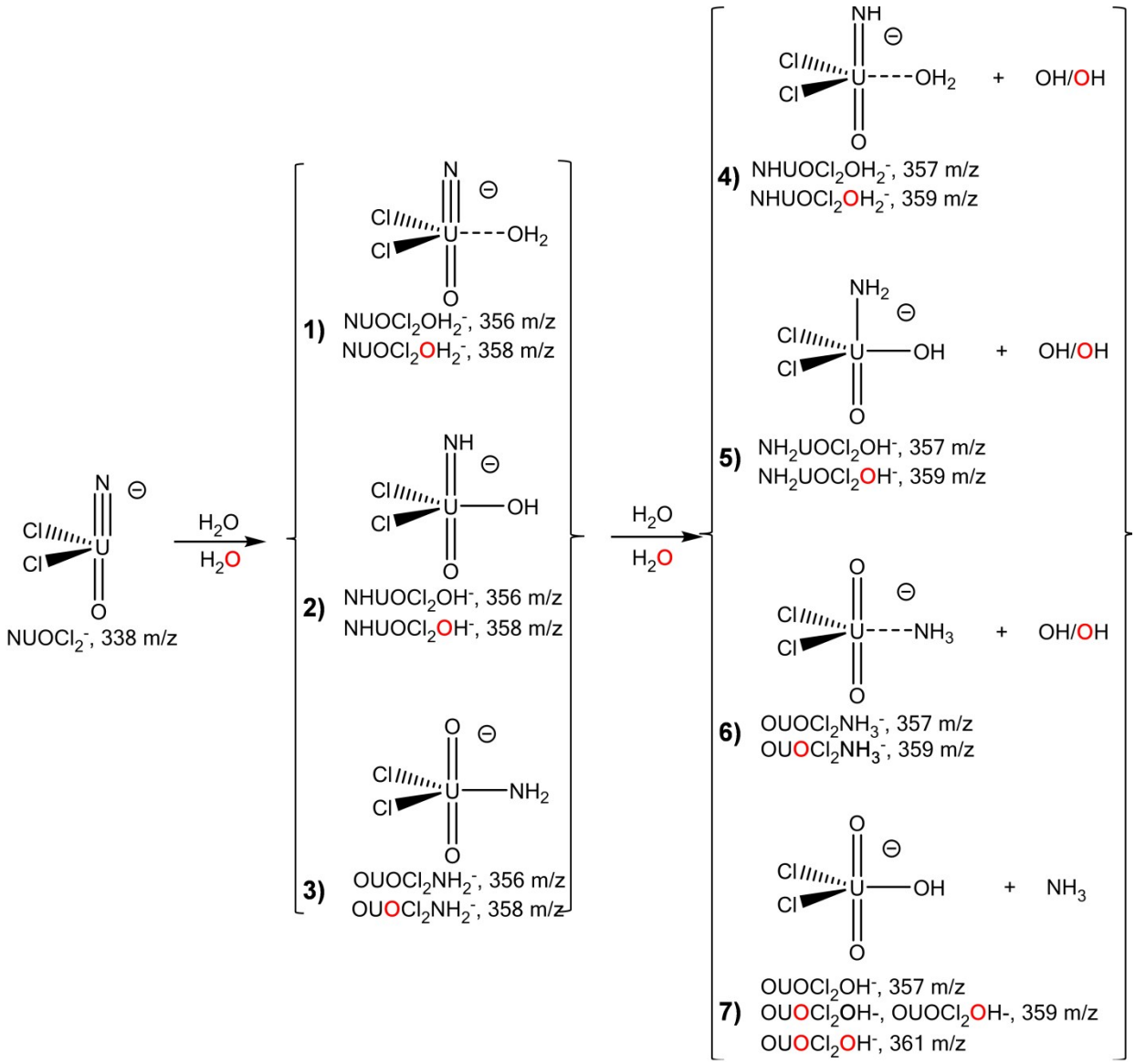

Figure S3. Possible sequential reactions of $NUOCl_2^-$ with a mixture of $H_2{}^{16}O$ and $H_2{}^{18}O$ (Fig. S2). Structures **1**, **2** and **3** are feasible for the first water addition; **3** is the most plausible. Reaction of the product of $H_2{}^{16}O$ addition to $NUOCl_2^-$ with a second $H_2{}^{16}O$ can result in either OH-elimination to form **4**, **5** and/or **6**, or NH_3-elimination to produce **7**, all at 357 m/z. Reaction of the two potential isotopomers from $H_2{}^{16}O$/ $H_2{}^{18}O$ addition to $NUOCl_2^-$ (356 and 358 m/z) yields a product at 361 m/z only for the NH_3-elinination pathway. The appearance of an intense peak at 361 m/z in Figure S2 (b) indicates that the dominant secondary product is **7**, most likely via hydrolysis of **3**.

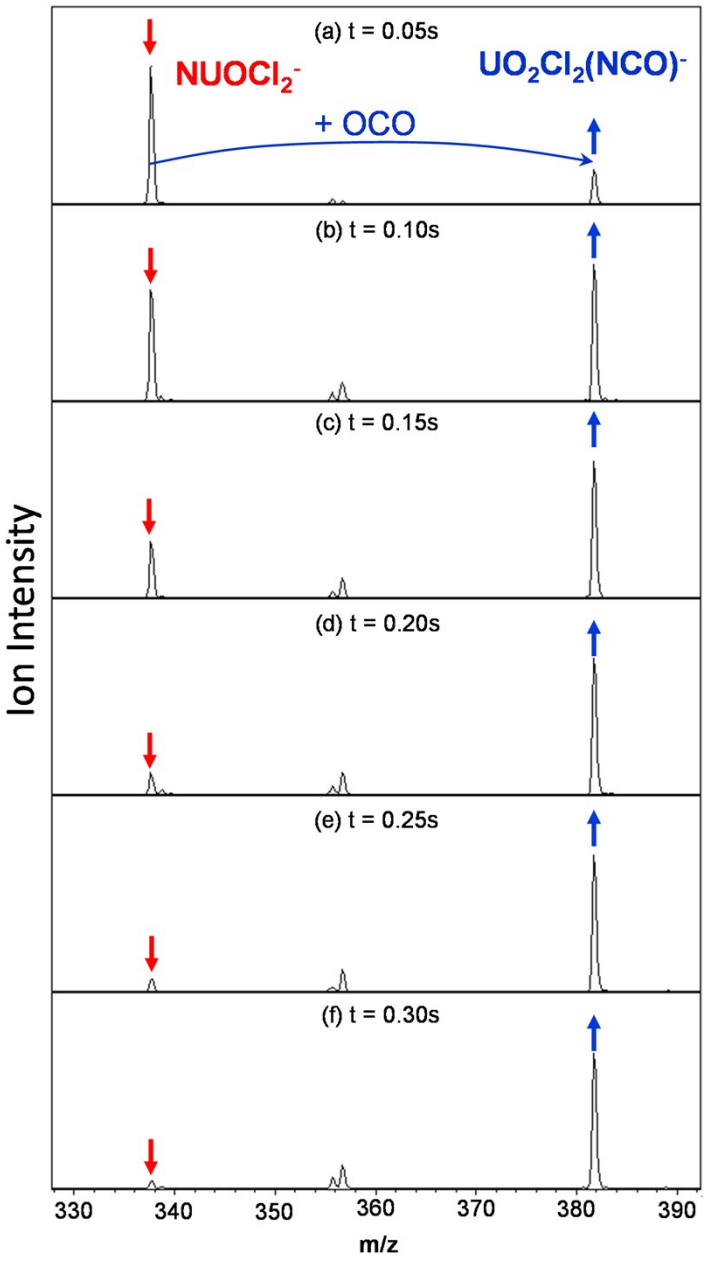

Figure S4. Mass spectra acquired after reacting isolated $NUOCl_2^-$ with a constant CO_2 and background water pressure for different times. These data were used to derive the kinetics plot shown in Figure 3. The increase for longer times in intensity of the 357 m/z peak relative to that at 356 m/z is consistent with sequential reaction with two water molecules, as described above. The total ion intensity for the six spectra varies by ca. 30%.