

Supplemental Information

Experimental Setup Details

Uranium hexafluoride (UF_6) was used from stock material on hand at Oak Ridge National Laboratory. Distilled deionized (18.2 M Ω) water was placed in a polychlorotrifluoroethylene container and connected to a stainless-steel gas handling manifold. The water was frozen with liquid nitrogen and the system was evacuated to remove air from the polychlorotrifluoroethylene container. The water was allowed to thaw, and the head space was opened to vacuum briefly several times to ensure that higher freezing temperature gases (e.g. CO_2) were removed as well. The UF_6 and H_2O were always isolated from each other within the gas handling manifold to prevent hydrolysis and formation of uranium solids. A 5-meter path length, stainless-steel gas cell with zinc selenide windows from Pike Technologies, Inc. coupled to an ABB MB3000 FTIR spectrometer was employed for all spectroscopy measurements. Prior to each reaction condition, the gas cell was evacuated, purged with ultra-high purity (UHP) nitrogen, evacuated, and backfilled with fluorine gas. The fluorine was left in the system until the pressure and consecutive IR spectra recorded were constant (typically several hours). The system was then evacuated, purged with UHP nitrogen, and evacuated to an absolute pressure less than 0.01 Torr in preparation for a measurement. This process was performed between before each individual measurement.

Experimental Measurement Details

Water vapor was introduced into the wet portion of the manifold until the desired pressure was reached as monitored using a capacitance manometer. A valve was then closed, isolating a 3.1 cc volume of this vapor directly above the gas cell. UF_6 vapor was introduced into the gas cell from the manifold by way of a controlled leak valve while continuously taking IR measurements. Pressure of the UF_6 was monitored directly by employing the Beer-Lambert law with a laboratory developed constant for the 625 cm^{-1} band of UF_6 in the absorbance spectrum. When the pressure reached the desired value, the leak valve was closed. At this point IR spectra were collected in a kinetic mode, recording the absorbance at the 625 cm^{-1} band. After 25 measurements (2.73 seconds/measurement), a valve operation allowed the water vapor to expand into the gas cell (560.8 cc volume). Measurements continued for approximately 3 minutes. The system was then opened to vacuum for several minutes to remove all gases and excess water. All conditions were performed at least three times and the reported results are the average of those measurements.

Calculations to compensate for reaction with materials of construction

A gradual decrease in signal intensity was observed in the UF_6 IR spectra recorded at the low-pressure conditions used and is assumed to be reaction of the gas with materials of construction. The reaction was slowed after passivating and drying surfaces by the introduction of fluorine gas between reaction conditions, however, the effect was seen in all measurements. Since the hydrolysis reaction is significantly faster than the reaction with materials of construction (~7.5 times faster for the slowest reaction), a linear extrapolation (described below) was performed to resolve the two different rates within the measurement. All initial rate measurements were corrected to compensate for this effect.

To correct for reaction with materials of construction, the first 25 measurements were taken prior to the introduction of water into the system. A linear least-squares regression fit was applied to

the first 25 measurements. All absorbance values were then adjusted by subtracting the time multiplied by the slope of the pre-water linear regression from the absorbance value. By setting the moment of water introduction as time zero, the rate of reaction with materials of construction is accounted for without adjusting the concentration at time zero. The corrected data has a slope of zero for the first 25 measurements and the initial rate is calculated by applying a linear least-squares regression fit to the first five data points after introduction of water. An example of data before and after drift correction is shown in Figure S1. Then the first five corrected data points after time zero (introduction of water) were used to determine the initial rate of hydrolysis.

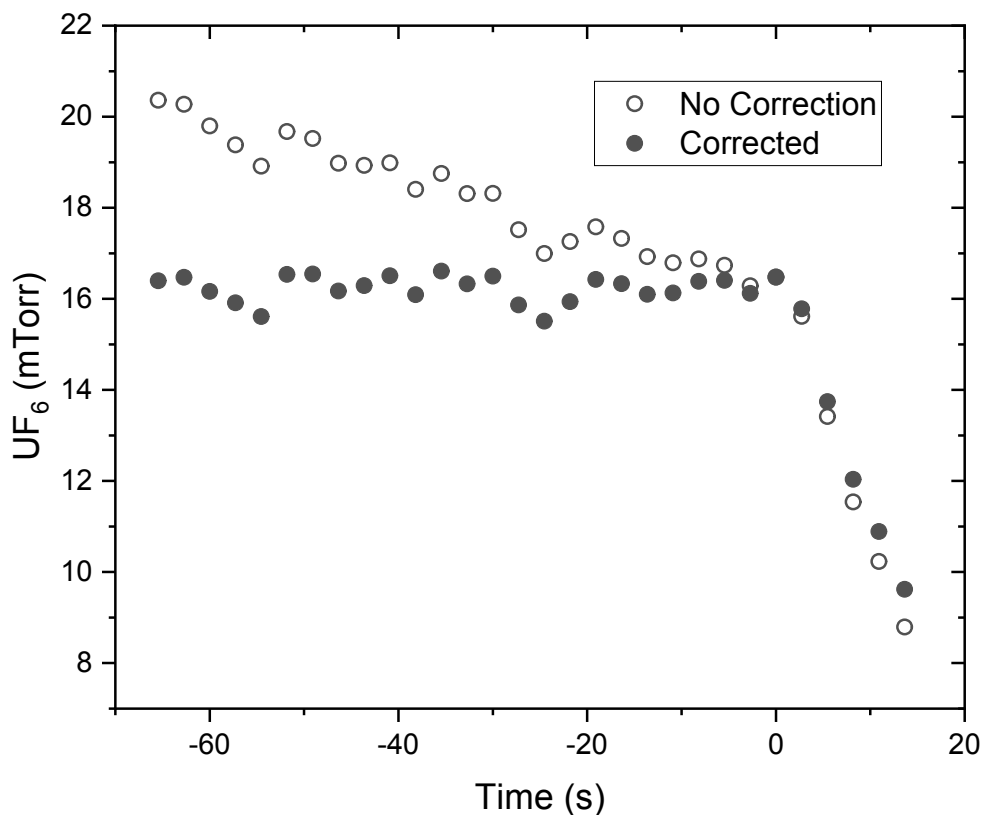


Figure S1: Example of experimental data before (open circles) and after (filled circles) correction. Water was introduced to the gas cell at time zero. Initial rate is calculated using a linear least-squares regression fit of the first five data points after time zero.

The uncorrected and corrected hydrolysis reaction rates as well as the reaction rate with materials of construction ($t < 0$ rate) are given in Table S1 for comparison. Only the corrected data was used for further kinetic analysis within the paper.

Table S1: Measured initial rates of reaction (uncorrected), corrected rates (hydrolysis reaction rate), and $t < 0$ rates (reaction with materials of construction) for various UF_6 and H_2O concentrations.

H_2O (mTorr)	UF_6 (mTorr)	Measured Rate (mTorr/s)	Corrected Rate (mTorr/s)	$t < 0$ Rate (mTorr/s)
60 ± 2	8.2 ± 0.5	0.438 ± 0.006	0.387 ± 0.008	0.051 ± 0.007
60 ± 2	16.2 ± 1.0	0.617 ± 0.073	0.556 ± 0.071	0.061 ± 0.007
60 ± 2	30.2 ± 1.9	0.755 ± 0.302	0.709 ± 0.321	0.046 ± 0.019
80 ± 3	9.1 ± 0.6	0.747 ± 0.098	0.702 ± 0.100	0.046 ± 0.013
80 ± 3	18.6 ± 1.5	1.057 ± 0.063	1.018 ± 0.066	0.038 ± 0.007
80 ± 3	28.3 ± 1.6	1.358 ± 0.126	1.312 ± 0.112	0.046 ± 0.015