SUPPORTING INFORMATION

Gas-phase synthesis of $[O=U-X]^+$ (X= Cl, Br and I) from a UO_2^{2+} precursor using ion-molecule reactions and an $[O=U\equiv CH]^+$ intermediate

Justin Terhorst[1], Samuel Lenze[1], Luke Metzler[1‡], Allison N. Fry[1†], Amina Ihabi[1], Theodore Corcovilos[2] and Michael J. Van Stipdonk[1]

[1]Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh PA 15282 USA
[2]Department of Physics, Duquesne University, Pittsburgh PA 15282 USA

Figure S1. Product ion spectra generated by isolation (MS^6 stage) of $[OUI]^+$ (*m*/*z* 381) for reaction with H_2O: (a) 10 ms reaction time, (b) 100 ms reaction time and (c) 10 s reaction time. In the figure, precursor ion is indicated with bold font and reaction products identified with italicized font.

Figure S2. Comparison of product ion spectra generated by isolation (MS^6 stage) of $[OUI]^+$ (*m*/*z* 381) for reaction with (a) H_2O and (b) CH_3OH. A 100 ms reaction time was used to generate each spectrum. In the figure, precursor ion is indicated with bold font and reaction products identified with italicized font.

Figure S3. Reaction energy diagram for the reaction of $[OUCH]^+$ with CH_3I via pathway 1, as outlined in the text. Data in blue represents structures (minima and transition states) in the singlet spin state. Species in the triplet spin state are indicated in red. Data generated by the B3LYP/SDD/6-311+G(d,p) level of theory.

Figure S4. Reaction energy diagram for the reaction of $[OUCH]^+$ with CH_3I via pathway 2, as outlined in the text. Data in blue represents structures (minima and transition states) in the singlet spin state. Species in the triplet spin state are indicated in red. Data generated by the PBE0/SDD/6-311+G(d,p) level of theory.

Figure S5. Reaction energy diagram for the reaction of $[OUCH]^+$ with CH_3I via pathway 2, as outlined in the text. Data in blue represents structures (minima and transition states) in the singlet spin state. Species in the triplet spin state are indicated in red. Data generated by the B3LYP/SDD/6-311+G(d,p) level of theory.

Figure S6. Product ion spectra generated by isolation (MS^5 stage) of $[OUCH]^+$ (*m*/*z* 267) for reaction with dichloromethane (CH_2Cl_2): (a) 1 ms reaction time, (b) 10 ms reaction time and (c) 100 ms reaction time. In the figure, precursor ion is indicated with bold font and reaction products identified with italicized font.

Figure S7. Product ion spectra generated by isolation (MS^5 stage) of $[OUCH]^+$ (*m*/*z* 267) for reaction with allyl bromide ($CH_2CH=CH_2Br$): (a) 1 ms reaction time, (b) 10 ms reaction time and (c) 100 ms reaction time. In the figure, precursor ion is indicated with bold font and reaction products identified with italicized font.

Figure S8. Product ion spectra generated by isolation (MS^5 stage) of $[OUCH]^+$ (*m*/*z* 267) for reaction with allyl bromide ($CH_2CH=CH_2I$): (a) 1 ms reaction time, (b) 10 ms reaction time and (c) 100 ms reaction time. In the figure, precursor ion is indicated with bold font and reaction products identified with italicized font.

Coordinated for relevant minima and transition state structures are available from the corresponding author upon request. vanstipdonkm@duq.edu

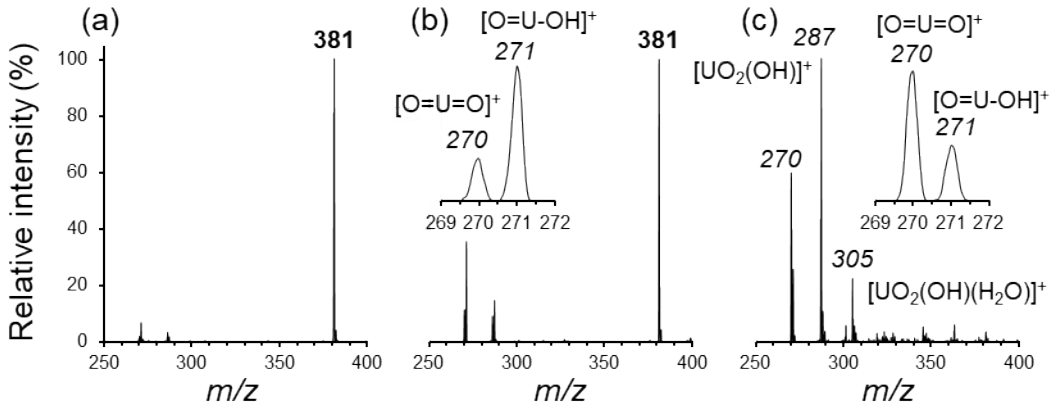

Figure S1.

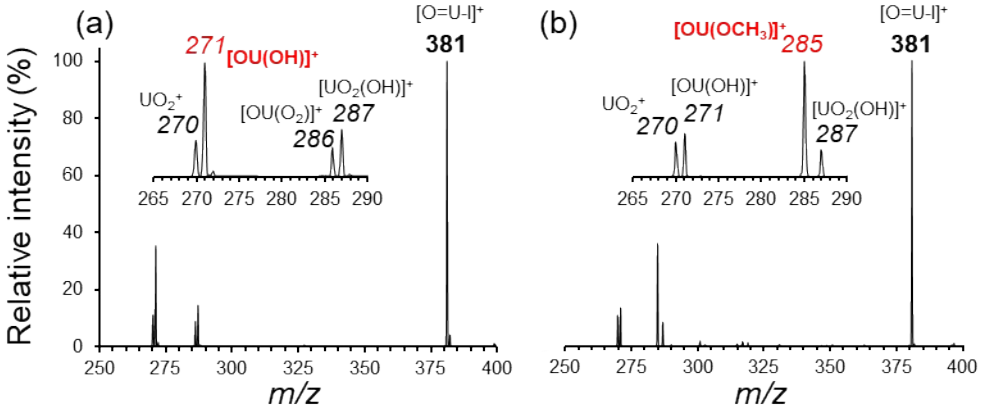

Figure S2

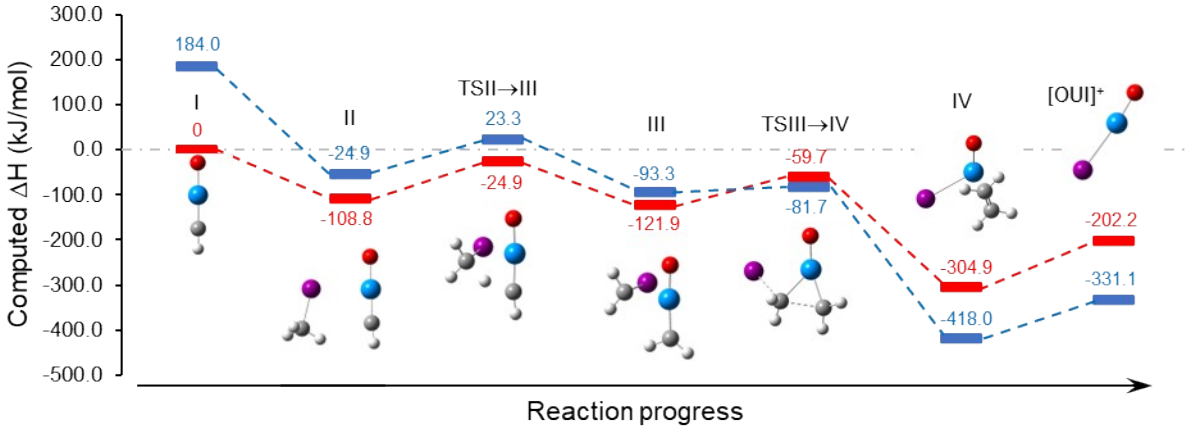
300.0
200.0
100.0
0.0
-100.0
-200.0
-300.0
-400.0
-500.0
Computed ΔH (kJ/mol)
184.0
I
0
II
-24.9
-108.8
TSII→III
23.3
-24.9
III
-93.3
-121.9
TSIII→IV
-59.7
-81.7
IV
-304.9
-418.0
[OUI]+
-202.2
-331.1
Reaction progress

Figure S3.

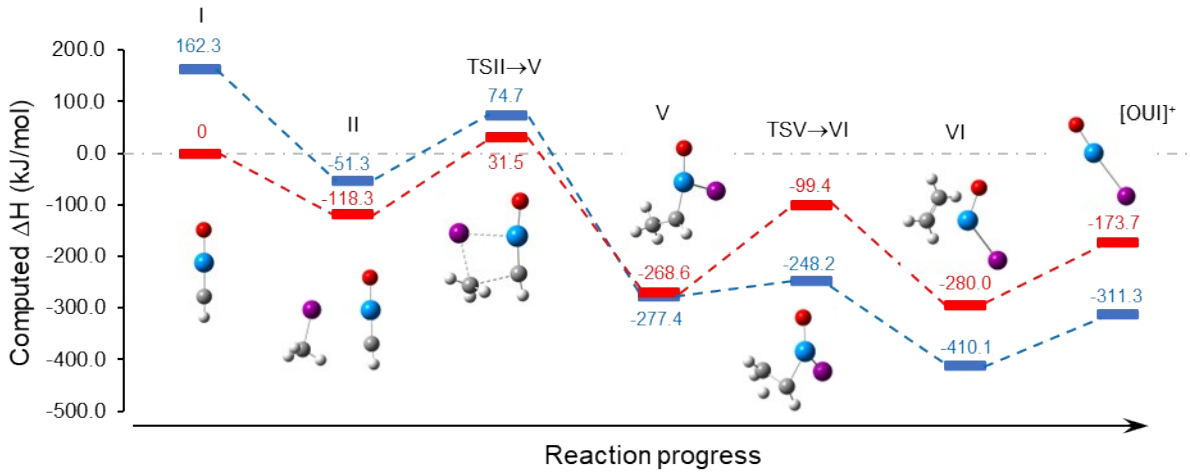
I
162.3
200.0
100.0
0.0
-100.0
-200.0
-300.0
-400.0
-500.0
Computed ΔH (kJ/mol)
0
II
-51.3
-118.3
TSII→V
74.7
31.5
V
-268.6
-277.4
TSV→VI
-99.4
-248.2
VI
-280.0
-410.1
[OUI]+
-173.7
-311.3
Reaction progress

Figure S4.

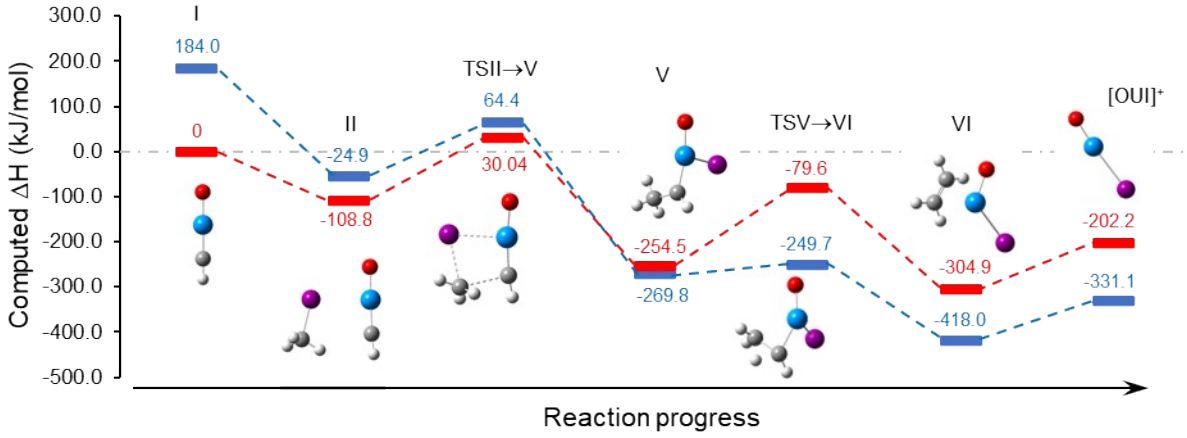

Figure S5.

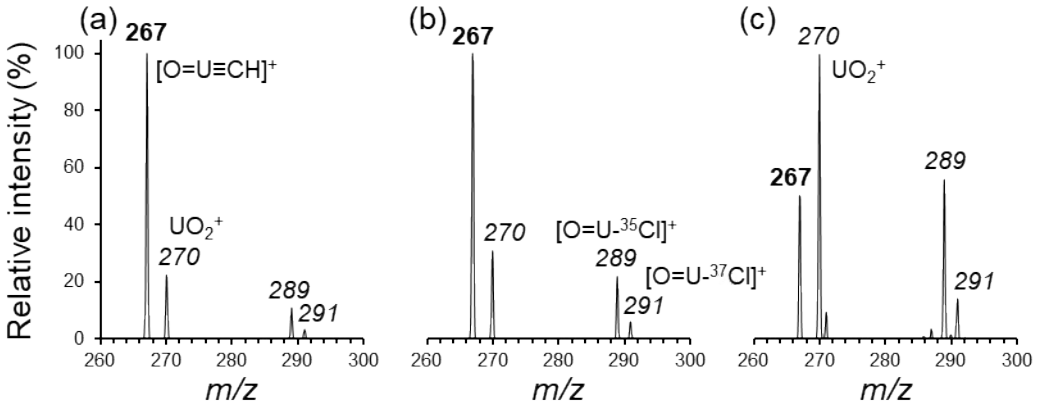

Figure S6.

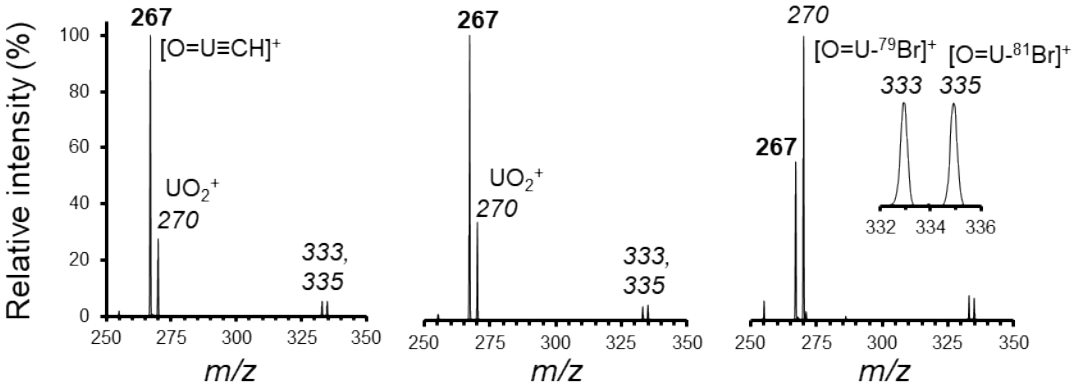

Figure S7.

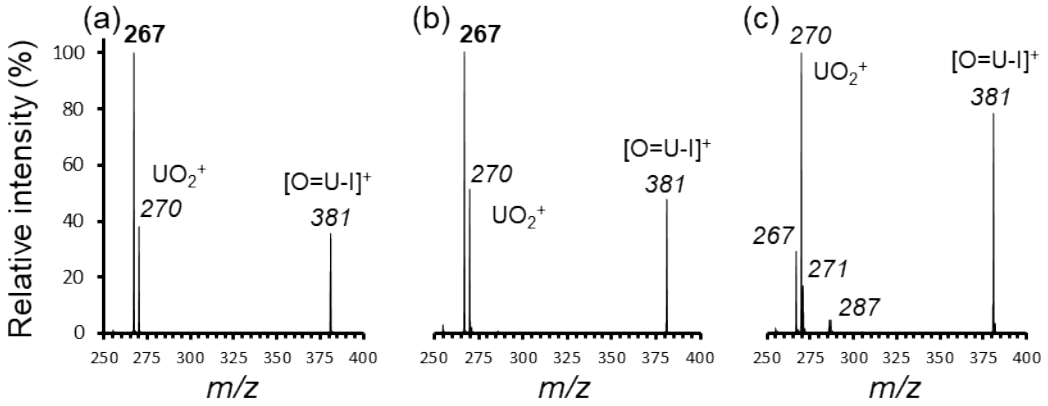

Figure S8.