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Transition State for the Gas-Phase Reaction of Uranium Hexafluoride with Water

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ABSTRACT. Density Functional Theory and small-core, relativistic pseudopotentials were used to look for symmetric and asymmetric transitions states of the gas-phase hydrolysis reaction of uranium hexafluoride, UF_6, with water. At the B3LYP/6-31G(d,p)/SDD level, an asymmetric transition state leading to the formation of a uranium hydroxyl fluoride, $U(OH)F_5$, and hydrogen fluoride was found with an energy barrier of +77.3 kJ/mol and an enthalpy of reaction of +63.0 kJ/mol (both including zero-point energy corrections). Addition of diffuse functions to all atoms except uranium led to only minor changes in the structure and relative energies of the reacting complex and transition state. However, a significant change in the product complex structure was found, significantly reducing the enthalpy of reaction to +31.9 kJ/mol. Similar structures and values were found for PBE0 and MP2 calculations with this larger basis set, supporting the B3LYP results. No symmetric transition state leading to the direct formation of uranium oxide tetrafluoride, UOF_4, was found, indicating that the reaction under ambient conditions likely includes several more steps than the mechanisms commonly mentioned. The transition state presented here appears to be the first published transition state for the important gas-phase reaction of UF_6 with water.

KEYWORDS. Uranium hexafluoride, transition state, hydrolysis, water, Density Functional Theory, DFT, Relativistic effective core potential, pseudopotential, actinides.

Introduction

The molecule uranium hexafluoride (UF_6) is synonymous with the nuclear industry. It is the basis for both the gaseous diffusion and gas centrifuge enrichment processes for nuclear fuel rods and weapon cores. The United States Department of Energy currently maintains approximately 57,000 cylinders containing a total of almost 700,000 metric tons of depleted UF_6. Of special concern is the reaction of UF_6 with water due to the corrosion caused by the hydrogen fluoride (HF) produced, which can significantly degrade the tanks commonly used for storage. Additionally, UF_6 is highly toxic, and the thermochemistry of its hydrolysis reaction plays an important role in its environmental dispersion by affecting the atmospheric transport of accidentally released UF_6.

Given the importance of the hydrolysis reaction of UF_6, the limited number of published studies focusing on the details of this reaction is rather surprising. Kessie reported overall reaction kinetics for uranium and plutonium hexafluoride in packed bed reactors.[1] Klimov, Kravetz, and Besmelnitzin published a brief note on the reaction suggesting that the rate limiting step in the hydrolysis of UF_6 to uranyl difluoride, UO_2F_2, was the first step of the following two-stage mechanism the proposed.[2]

$$UF_6 + H_2O \rightarrow UOF_4 + 2HF \quad (1)$$

$$UOF_4 + H_2O \rightarrow UO_2F_2 + 2HF \quad (2)$$

Sherrow and Hunt have studied the UF_6 + H_2O system with FTIR and have found indications that the reaction occurred spontaneously at temperatures above 30 K when UF_6 and H_2O were co-deposited in thin films without a rare gas matrix.[3] However, when the reactants were co-deposited in an argon matrix, the reaction required UV illumination to proceed. Additionally, at low water concentrations, the gas-phase reaction was not spontaneous and was surmised to be a surface reaction requiring a catalytic surface.

Although not specifically looking at the kinetics of the hydrolysis reaction, researchers have investigated the product composition of the reaction as a function of water concentration, i.e., humidity.[4] In that work, researchers found only UO_2F_2 product for UF_6:H_2O molar ratios of less than about five (5) and a new uranium oxofluoride compound, $U_3O_5F_8$, for UF_6:H_2O molar ratios greater than approximately fifty-five (55). No experiments were performed at ratios in between these two values and no reaction mechanisms were proposed. Additionally, several groups have studied the particle morphology[5-10] and reactor design for the production of particles from aerosols of UF_6.[11]

Some researchers have studied various uranium oxide, fluoride, and oxofluoride systems using computational chemistry and modern electronic structure methods. Privalov et al. studied the reaction enthalpies for the hydrolysis reactions of UO_3, UO_2F_2, and UF_6 and the gas-phase geometries and heat capacities of the corresponding reactants and products.[12] While failing to look for transition states of any of the reactions, they did determine a transition state (a planar D_{2h} structure) and barrier for the inversion of the fluorine atoms in UO_2F_2. Additionally, they found that their calculated enthalpies for reactions that produced HF were consistently more endothermic than the "experimental" values, which were "derived from a combination of experiments and theory."[12] The large, but consistent and correctable, overestimations were hypothesized to be due to poor treatment of the HF molecule by the methods and basis sets used.

Shamov, Schreckenbach, and Vo investigated "all the possible uranium (IV, V, VI) oxides, fluorides, and oxofluorides" with several different electronic structure methods and basis sets,[13] but focused on bond dissociation energies (BDEs) and reaction enthalpies. Other researchers have studied the geometry[14,15] and BDEs[16] of various halogenated uranium compounds finding that the optimized geometries of the molecules and the accuracy was sometimes dependent on the electronic structure method or basis set used. Others have focused on minimum energy structures or the number of hydrating water molecules in solvation complexes of uranyl ion (UO_2^{2+}),[17] halogenated uranyl compounds,[18-20] and uranyl hydroxides.[20,21]

Methods

When studying uranium, relativistic effects on the inner core electrons must be included. While spin-orbit coupling corrections may affect the energetics of open-shell configurations and transition states in actinide systems, the effects are generally negligible for uranium(VI) compounds and are otherwise limited to a few kcal/mol. This is within experimental error and is less significant than other sources of error in most computational methods applied to actinide systems.[13] As such it is reasonable to initially approach such systems of interest with scalar relativistic approaches, neglecting spin-orbit coupling. Previously mentioned researchers have used all-electron scalar relativistic approaches, the two-component third order Douglas-Kroll-Hess (DK3) Hamiltonian,[22,23] the zeroth-order regular approximation (ZORA),[24] and relativistic effective core potentials (RECPs) to account for these corrections. An added benefit of using RECPs is that the core potential implicitly accounts for a number of electrons, reducing the computational cost by reducing the number of electrons explicitly modeled. However, care must be applied when choosing how many electrons to include in the core. Batista et al. showed for uranium that a “large-core,” 78-electron RECP that included the 5s, 5p, and 5d electrons in the core failed to give accurate results in contrast to a “small-core,” 60-electon RECP that treated the 5s, 5p, and 5d shells as valence electrons.[25]

The electronic structure calculations presented here were performed using Density Functional Theory (DFT) and the Gaussian03 (G03)[26] implementation of the B3LYP hybrid functional, which includes a portion of the exact, Hartree-Fock exchange. The combination of DFT with small-core RECPs has been shown to yield good results for actinide systems at reasonable computational cost.[13,25] Additionally, hybrid functionals have been shown to be more accurate for uranium systems than DFT functionals based on the Generalized Gradient Approximation (GGA) for reaction enthalpies, molecular geometries, BDEs, and vibrational frequencies, except for U=O frequencies. As a check on our results, we have also used the PBE0 (commonly referred to as PBE1PBE in G03) DFT functional and second order Møller-Plesset perturbation theory (MP2) to study the stationary points and energetics of the hydrolysis reaction.

For uranium, the Stuttgart energy-adjusted, small-core RECP (SDD)[27] included with G03 was combined with the associated SDD basis set, also included in G03. (Note that the most diffuse primitive for each shell, each with an exponent of 0.005, was removed in order to obtain proper convergence of the electronic density.) For the light atoms, fluorine, oxygen, and hydrogen, a double-ζ, all-electron basis set with polarization functions on each light atom, i.e., the 6-31G(d,p) basis set, was used initially. The resulting configurations for the reactants, products, and transition state calculated using the 6-31G(d,p) basis set on the light atoms were used as initial configurations for corresponding minima and transition state optimizations where the light atom basis set was supplemented with diffuse functions, i.e., the 6-31++G(d,p) basis set. An ultrafine grid was used for the numerical integrations in the DFT calculations.

Sherrow's and Hunt's analysis of the FTIR spectra of UF_6 deposited with water in an argon matrix indicated that a 1:1 complex was formed with the UF_6 interacting with water through the oxygen.[3] As such, attempts to find transition states for the gas-phase hydrolysis reaction were started by performing a relaxed potential energy surface (PES) scan of the system while changing the U-O distance and searching for a maximum in the energy. For the relaxed PES scans where a maximum energy configuration was located, quadratic synchronous transit[28] calculations (denoted as QST3 in G03) were run using the maximum energy configurations as initial guesses. The final configurations from the QST3 scans were then used as initial configurations for fully-unconstrained transition state optimizations with analytical Hessians calculated at each step.

The U-O bond distance was chosen as the control variable for the relaxed PES scans to avoid biasing the results towards reactions involving only a single hydrogen atom. The scans were started at a U-O separation distance of 2.85 Å for four different symmetric configurations of C_S symmetry and one slightly asymmetric configuration as described in Figure 1. For the symmetric configurations, the plane of symmetry (roughly a horizontal plane perpendicular to the page in Figure 1) always contained the uranium and oxygen atoms. The difference between the initial configurations was whether the symmetry plane also included two fluorine atoms and two or no hydrogen atoms (Figure 1a and 1b, respectively), or four fluorine atoms and two or no hydrogen atoms (Figure 1c and 1d, respectively). The asymmetric configuration, Figure 1e, is only a slight distortion of the symmetric structure in Figure 1b, but is sufficient to break the symmetry within the calculations. All five configurations had the oxygen pointing towards and the hydrogen atoms pointing away from the uranium atom in agreement with the aforementioned results of Sherrow and Hunt.[3]

Results and Discussion

A maximum in the energy as a function of U-O separation distance was found for the asymmetric case as well as for three of the four symmetric cases. For structure 1d with four fluorine atoms and no hydrogen atoms in the plane of symmetry, the energy increased monotonically as the U-O separation distance was decreased. For the transition state optimizations using the three remaining symmetric cases, 1a, 1b, and 1c, no transition states were found, only higher-order saddle points with more than one imaginary vibrational frequency. For the asymmetric system, a stationary point with a single imaginary frequency was found at a U-O separation distance of 2.275 Å. Analysis of the vibrational modes confirmed that the mode with the imaginary frequency ($i455.3$ cm^{-1}) corresponded to a transfer of a hydrogen from the water oxygen to a fluorine and concomitant decrease in the U-O bond length and increase in the U-F bond length. An Internal Reaction Coordinate (IRC) scan from the transition state indicated that the transition state connected two local minima, one corresponding to the hydrogen as HF and one with the hydrogen as H_2O. A diagram of the reaction path is given in Figure 2.

In addition to analyzing the vibrational modes of the transition state, we also studied the modes of the optimized $UF_6 \ldots H_2O$ pre-reactive complex in order to compare with the experimental FTIR data.[3] The scaling factor from the NIST Computational Chemistry Comparison and Benchmark Database (CCCBDB) for B3LYP/6-31G(d,p)[29] was applied and the agreement between the scaled frequencies and the experimental results in Table 1 is quite good. (Note that the correction factor for B3LYP/6-31G(d,p), 0.961, is the same as the factor for B3LYP/SDD).

Neglecting zero-point energy (ZPE) corrections, our calculated energy barrier for the reaction is 86.7 kJ/mol. The inclusion of ZPE corrections lowers this barrier to 77.3 kJ/mol. The reaction is endothermic with a calculated enthalpy of reaction of +63.0 kJ/mol. Addition of diffuse functions to the light atoms did not significantly alter the structure of the reactant complex or transition state, only marginally increasing the energy barrier to 87.7 kJ/mol (78.2 kJ/mol with ZPE corrections). However, the inclusion of diffuse functions did significantly affect the interaction between the product HF and the hydroxyl group on the uranium. The result is the formation of a nearly linear F-H…O hydrogen-bonded structure and a lowering of the enthalpy of reaction to +31.9 kJ/mol (+26.0 kJ/mol with ZPE corrections). The hydrogen bond angle of 167.9° in the 6-31++G(d,p) F-H…O structure is more physically intuitive than the "bent" structure from the 6-31G(d,p) calculations and likely indicates that the 6-31G(d,p) basis set does not sufficiently capture the physics of this system, consistent with previous results.[12,13] Pertinent structural parameters and Mulliken atomic charges for the reactant, product, and transition state configurations for both basis sets are listed in Table 2.

An optimization in the 6-31G(d,p) basis set, but initiated from the configuration of the product minimum for the 6-31++G(d,p) basis set, failed to locate a corresponding local minimum and collapsed to the original minimum energy product structure calculated for the 6-31G(d,p) basis set. A similar calculation in the 6-31++G(d,p) basis set failed to find a local minimum corresponding to the 6-31G(d,p) minimum energy product structure as well. Optimizations using an even larger basis set (without analytical Hessians) resulted in negligible changes in the stationary point configurations, energy barrier, and reaction energy – this larger basis set was Dunning's augmented, correlation-consistent, triple-ζ basis set[30,31] for the light atoms and a quadruple-ζ, Stuttgart basis set[32] for uranium. Consequently, the combination of the 6-31++G(d,p) and SDD basis sets was assumed to be sufficiently accurate for the calculations reported here. Additional confirmation of the results is seen in Table 3 where calculations with the PBE0 DFT functional and with MP2 result in nearly identical configurations and similar energies, barriers, and enthalpies.

In agreement with reported, experimental enthalpies of reaction for gas phase hydrolysis reactions of UF_6,[12,13,33,34] but in contrast to experimental work reporting spontaneous reaction of

UF_6 with water to form UO_2F_2,[1,4,11,35-39] the calculated barrier is substantial and the gas-phase reaction is predicted to be endothermic at the current level of theory. This discrepancy may have several explanations. While the experimental enthalpy of reaction for the complete, gas-phase hydrolysis of UF_6 (Reactions 1 and 2 combined) is also endothermic,[12,13,33,34] phase change and solvation contributions make the physical reaction exothermic.[39,40] Such contributions are likely also important for the first step proposed here. Additionally, Privalov et al. estimated an error of approximately 21 kJ/mol per molecule of HF produced for reaction enthalpy calculations similar to those presented here.[12]

Given the presence of the asymmetric transition state and the lack of a symmetric transition state, the hydrolysis of UF_6 to UO_2F_2 likely involves a series of single fluorine atom removals in a scheme similar to Reactions 3-6.

$$UF_6 + H_2O \rightarrow U(OH)F_5 + HF \tag{3}$$

$$U(OH)F_5 + H_2O \rightarrow U(OH)_2F_4 + HF \tag{4}$$

$$U(OH)_2F_4 \rightarrow U(OH)OF_3 + HF \tag{5}$$

$$U(OH)OF_3 \rightarrow UO_2F_2 + HF \tag{6}$$

Secondary hydrolysis reactions, such as Reaction 4, may occur before, after, or concurrently with HF elimination reactions. The proposed initial hydrolysis reaction product, $U(OH)F_5$, and the possibility that the reaction proceeds by adding additional hydroxyl groups to the uranium may explain the difficulty researchers have had in producing UOF_4 by hydrolysis of UF_6.[4,38]

Conclusions

The combination of Density Functional Theory with small-core, relativistic pseudopotentials has been used to look for symmetric and asymmetric transitions states in the gas-phase hydrolysis reaction of uranium hexafluoride with water. The inability to find a symmetric transition state leading to the direct production of UOF_4 and HF indicates that the reaction chemistry likely includes several more steps than the mechanisms commonly used or described by previous researchers.[1,2]

The first step in the reaction pathway proposed here is the formation of a uranium hydroxyl fluoride, $U(OH)F_5$, and hydrogen fluoride with a calculated energy barrier of +77.3 kJ/mol and an enthalpy of reaction of +63.0 kJ/mol (both including zero-point energy corrections) at the B3LYP/6-31G(d,p)/SDD level. Addition of diffuse functions to the light atoms results in a negligible change in the pre-reactive complex structure, transition state, and the calculated barrier but alters the product complex, lowering the calculated enthalpy of reaction to +31.9 kJ/mol. The calculated transition state for this reaction appears to be the first published transition state for the gas-phase reaction of UF_6 with water. Additional research on similar systems and the inclusion of solvent effects using both explicit water or hydrogen fluoride molecules and implicit solvation models is ongoing and may provide further information on the proposed reaction mechanism and why researchers have been unable to produce UOF_4 by hydrolysis of UF_6 under ambient or near ambient conditions.[35-37]

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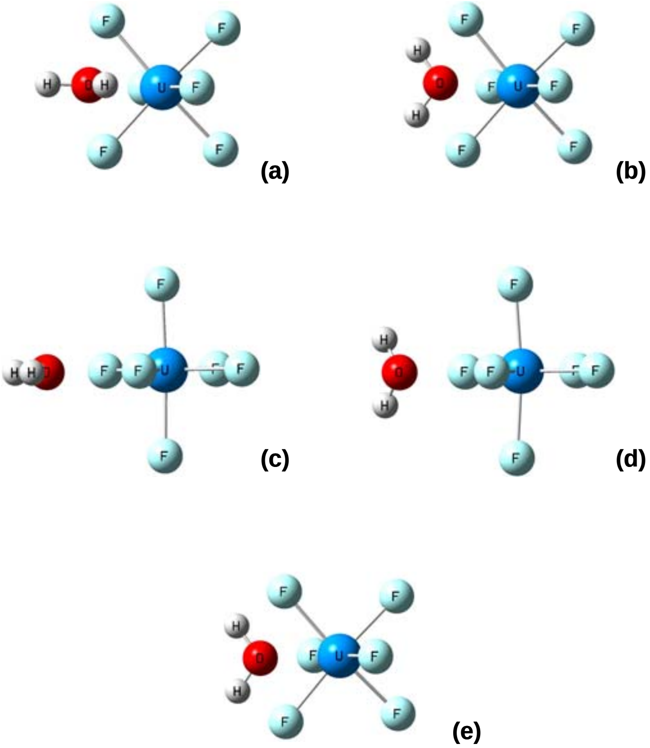

Figure 1. Uranium hexafluoride and water initial configurations.

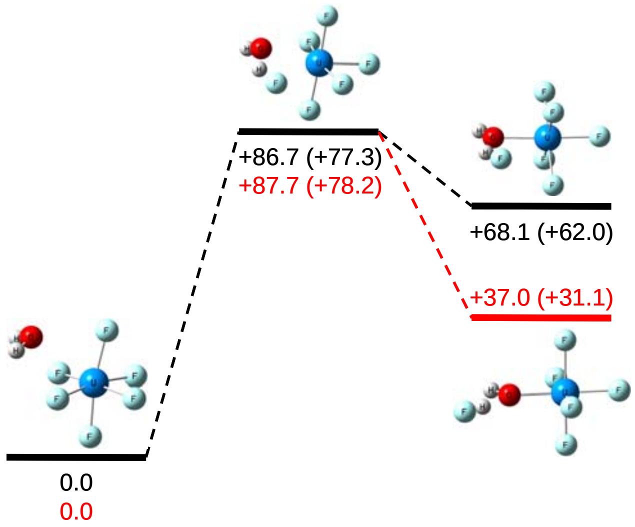

Figure 2. Calculated uranium hexafluoride hydrolysis reaction pathway energies (kJ/mol). B3LYP/6-31G(d,p)/SDD results in black, B3LYP/6-31++G(d,p)/SDD results in red, and results with zero-point energy corrections in parentheses.

Table 1: Vibrational frequencies for the pre-reactive uranium hexafluoride…water complex.

Experimental (cm^{-1})[a]	**Calculated (cm^{-1})[b]**	**Description**
587.8, 608.8	580 (604), 609 (634)	U-F Asymmetric Stretch
1585.6, 1588.5	1568 (1632)	H-O-H Bend
3623.4, 3624.7	3641 (3789)	O-H Symmetric Stretch
3717.9	3751 (3903)	O-H Asymmetric Stretch

[a] Ref. 3.

[b] B3LYP/6-31G(d,p)/SDD scaled and (unscaled) values.

Table 2: Pertinent structural parameters (bond lengths in Å and angles in degrees) and Mulliken atomic charges on relevant atomic centers for the calculated stationary points.

(a) B3LYP/SDD/6-31G(d,p)

	Reactant	**Transition State**	**Product**
$\mathbf{r}_{U\text{-}O}$	2.79	2.27	2.09
$\mathbf{r}_{U\text{-}F}$	2.03	2.43	3.08
$\mathbf{r}_{O\text{-}H}$	0.97	1.26	1.79
$\mathbf{r}_{F\text{-}H}$	2.28	1.09	0.94
$\angle_{O\ldots H\text{-}F}$	98.0	140.5	133.0
$\mathbf{q}_U$	+2.20	+2.15	+2.21
$\mathbf{q}_O$	-0.57	-0.68	-0.70
$\mathbf{q}_F$	-0.40	-0.39	-0.35
$\mathbf{q}_H$	+0.34	+0.45	+0.39

(b) B3LYP/SDD/6-31++G(d,p)

	Reactant	**Transition State**	**Product**
$\mathbf{r}_{U\text{-}O}$	2.85	2.28	2.07
$\mathbf{r}_{U\text{-}F}$	2.04	2.45	4.45
$\mathbf{r}_{O\text{-}H}$	0.97	1.23	1.82
$\mathbf{r}_{F\text{-}H}$	2.45	1.11	0.94
$\angle_{O\ldots H\text{-}F}$	89.3	139.5	167.9
$\mathbf{q}_U$	+2.63	+2.54	+2.73
$\mathbf{q}_O$	-0.76	-0.84	-0.88
$\mathbf{q}_F$	-0.46	-0.47	-0.44
$\mathbf{q}_H$	+0.39	+0.51	+0.44

Table 3: Calculated energy barriers ($\Delta E^{\ddagger}$), reaction energies (ΔE_r), and enthalpies ($\Delta H^{\ddagger}$ and ΔH_r) (in kJ/mol) for the initial reaction step of uranium hexafluoride and water using the SDD and 6-31++G(d,p) combined basis sets. Values include [neglect] zero-point energy corrections.

	B3LYP	PBE0	MP2
$\Delta E^{\ddagger}$ (0 K)	78.2 [87.7]	76.1 [85.5]	81.6 [92.1]
$\Delta H^{\ddagger}$ (298 K)	74.2	72.4	78.2
ΔE_r (0 K)	30.9 [36.8]	32.3 [38.8]	36.4 [44.7]
ΔH_r (298 K)	31.9	33.7	38.7

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SYNOPSIS TOC.