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Formation and Characterization of the Uranium Methylidene Complexes $CH_2{=}UHX$ ($X = F$, Cl, and Br)

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The reactions between uranium atoms and CH_3X ($X = F$, Cl, and Br) molecules are investigated in a solid argon matrix. The major products formed on ultraviolet irradiation are the $CH_2{=}UHX$ methylidene complexes. DFT calculations predict these triplet ground-state structures to be stable and to have significant agostic interactions. Parallels between the uranium and analogous thorium methylidene complexes are discussed.

Introduction

High-oxidation-state transition metal alkylidenes ($M = CR_1R_2$) are of considerable interest for their catalytic activities,[1,2] and chemical vapor deposition applications.[3] Many early transition metal alkylidenes show agostic bonding interactions, and the study of these compounds aids in the understanding of this unique interaction between hydrogen and a transition metal center.[1,4−7] Although uranium−carbon multiple-bonded species and surface-stabilized alkylidenes involving actinides have been formed,[8,9] actinide alkylidenes have remained elusive despite the successful syntheses of similar transition metal species.[1,10] Recently, we have isolated thorium−carbon double-bonded methylidene complexes,[11,12] and we now employ matrix isolation methods in order to characterize similar uranium species.

Recently the Group 6 transition metal methylidenes formed by activation of methyl halides have been investigated.[13−16] These simple $CH_2{=}MHX$ species show less agostic interaction based on calculated CH_2 distortion than the Group 4 analogues.[17−20] As thorium methylidene complexes were found to be similar to those of the Group 4 transition metal complexes,[11,12] we anticipate that the reaction products formed between uranium and methyl halides will parallel the Group 6 methylidene complexes. In addition, α-H transfer also produced Group 6 $CH{\equiv}MH_2X$ methylidyne complexes,[13−16] and such a possibility also exists for uranium.

Methods

Our experimental setup has been described in detail elsewhere.[21,22] In brief, laser-ablated (pulsed Nd:YAG laser: 1064 nm, 10 Hz repetition rate, 10 ns pulse width) uranium atoms were reacted with 0.5% CH_3X ($X{=}F$, Cl, Br) or isotopic samples (^{13}C, D) diluted in argon and co-deposited onto a CsI window cooled to 8 K for the duration of 1 h. Infrared spectra were recorded for the reaction products on a Nicolet Magna 550 spectrometer with a HgCdTe type B detector cooled with liquid nitrogen at 0.5 cm^{-1} resolution. The matrix-isolated species were subjected to filtered and unfiltered irradiation from a medium-pressure mercury arc lamp (Philips, 175 W) and annealing to successively higher temperatures. Additional IR spectra were recorded after each procedure.

Density functional theory (DFT) calculations were carried out with the Gaussian 98 package.[23] The B3LYP hybrid functional was

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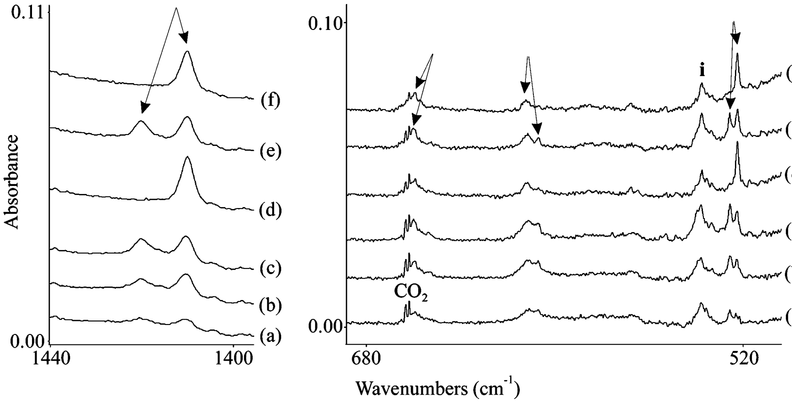

Figure 1. Infrared spectra in the 1440−1395 and 690−510 cm^{-1} regions taken after (a) laser-ablated uranium atoms are reacted with CH_3F diluted in argon and the resulting matrix sample is (b) irradiated with $\lambda > 290$ nm light, (c) irradiated with $\lambda > 220$ nm light, (d) annealed to 30 K, (e) irradiated with $\lambda > 220$ nm light, and (f) annealed to 35 K. Arrows indicate absorptions of the $CH_2{=}UHF$ product, and **i** marks absorption tentatively assigned to the $CH_3{-}UF$ insertion product.

used in all calculations.[24] All carbon, hydrogen, and halogen atoms were given a medium 6-311++G(2d,p) basis set,[25] and the electronic density of the uranium atom was represented by the SDD pseudopotential (32 valence electrons).[26] Geometries were fully optimized, and frequencies were computed analytically. All energy values reported include zero-point vibrational corrections. ΔE values (binding energy) were computed as the sum of the energies of the reactants minus the energy of the product.

Results and Discussion

The major products in the activation of methyl halides by uranium will be presented.

U + CH$_3$F. The reaction between uranium atoms and CH_3F yielded one major product with doublet absorptions at 1420.2 and **1410.4**, 660.2 and **659.4**, **611.6** and 607.5, and at 525.7 and **522.5** cm^{-1}. The four pairs of absorptions increased in intensity after irradiation using a Pyrex filter ($\lambda > 290$ nm) and full arc photolysis ($\lambda > 220$ nm). Upon annealing to 30 K, the absorptions listed in bold increased in intensity at the expense of the other band in the pair. A second full arc irradiation reversed the relative growth of the two bands, and annealing to 35 K again increased the bold absorptions (marked with arrows in Figure 1). This splitting of vibrational modes was also observed for the thorium atom and CH_3F reaction product, and we believe it is due to two different argon matrix trapping site configurations.[12] The sharp, weak 663.5, 661.9 cm^{-1} bands due to CO_2 impurity, for example, decrease on annealing presumably due to a change in matrix sites or aggregation. A minor product absorption at 537.7 cm^{-1} (labeled **i**) increased slightly on photolysis and sharpened and decreased slightly on annealing. In addition, weak bands were observed for intermediate species from CH_3F photodissociation, which have been identified previously.[27,28]

The two absorptions around 1415 cm^{-1} showed practically no carbon-13 shift and over 400 cm^{-1} deuterium shift (Table 1, H/D frequency ratio 1.399). In addition, these vibrational frequencies are in the region of U−H stretching modes,[29] which indicate that this product contains a U−H bond. The 659.4 cm^{-1} band shifted 19 cm^{-1} with carbon-13, and a pure C=U diatomic oscillator would shift 24.6 cm^{-1}, so this mostly C=U stretching mode also involves H(D) as the 52 cm^{-1} deuterium shift indicates. The doublet band centered around 610 cm^{-1} showed about a 5 cm^{-1} red shift upon carbon-13 substitution and about 125 cm^{-1} deuterium shift (Figure 2). This mode is roughly 20 cm^{-1} red-shifted from the CH_2 wagging mode of the $CH_2{=}ThHF$ complex,[12] and the small carbon and large hydrogen isotopic shifts are appropriate to assign the observed absorptions to this same mode of the uranium counterpart. The fourth mode was observed in the 525 cm^{-1} region. The small ^{13}C and D shifts indicate that this mode has practically no carbon and hydrogen character. Hence, it is assigned to a U−F stretching mode. A number of compounds have U−F stretching modes in this region.[30,31]

The four observed modes of the new product (U−H stretch, C=U stretch, CH_2 wag, and U−F stretch) identify the $CH_2{=}UHF$ complex with confidence. These are also the four modes that are predicted to be the most infrared active by our calculations (Table 1) for the triplet ground state methylidene complex, and the good agreement between

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Table 1. Observed and Calculated Fundamental Frequencies of $CH_2{=}UHF$[a]

	$CH_2{=}UHF$		$^{13}CH_2{=}UHF$		$CD_2{=}UDF$	
approximate mode	obsd	calcd (int)	obsd	calcd (int)	obsd	calcd (int)
CUF bend		113.3 (11)		112.1 (11)		107.6 (9)
CH_2 twist		241.2 (52)		241.1 (53)		177.8 (23)
HCUH distort.		380.6 (46)		380.5 (46)		270.9 (24)
CH_2 rock		426.5 (46)		426.0 (44)		305.4 (34)
CUH bend		525.9 (37)		522.6 (23)		412.9 (8)
U−F stretch	**522.5**, 525.7	541.2 (172)	**522.2**, 525.3	538.4 (190)	**522.1**, 525.2	532.9 (222)
C−U stretch	**659.4**, 660.2	618.1 (68)	**640.4**, 641.3	603.2 (51)	**607.0**, 608.6	562.9 (41)
CH_2 wag	607.5, **611.6**	631.9 (153)	602.2, **606.5**	624.9 (159)	482.8, **485.2**	495.5 (60)
CH_2 scis.		1373.6 (21)		1367.1 (21)		1034.3 (47)
U−H stretch	**1410.4**, 1420.2	1449.6 (505)	**1410.3**, 1420.1	1449.6 (505)	**1007.9**, 1015.2	1027.6 (227)
CH stretch		2751.8 (3)		2745.3 (4)		2004.6 (0)
CH stretch		3126.5 (3)		3116.4 (4)		2307.8 (0)

[a] Triplet ground-state B3LYP/6-311++G(2d,p)/SDD level of theory. All frequencies are in cm^{-1}, and computed infrared intensities are in km/mol.

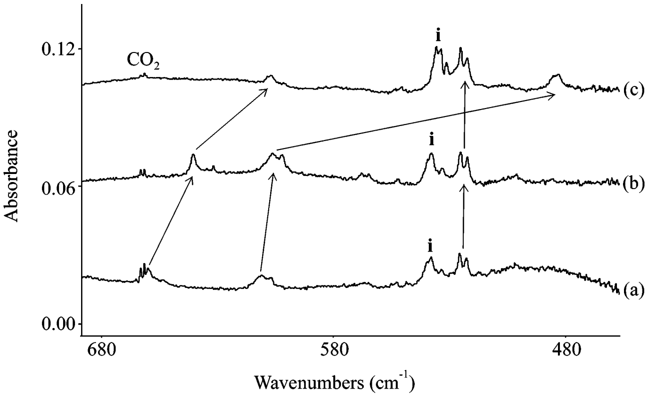

Figure 2. Infrared spectra taken in the 680−470 cm^{-1} region after laser-ablated uranium atoms are reacted with (a) CH_3F, (b) $^{13}CH_3F$, and (c) CD_3F diluted in argon. All spectra recorded after full arc irradiation. Lines indicate the isotopic shifts of the $CH_2{=}UHF$ product, and **i** marks the absorption tentatively assigned to the $CH_3{-}UF$ product.

theoretically calculated and experimentally observed frequencies supports our assignment. Note that the C−H stretching modes are far too weak to be observed in the IR spectrum. The U−H, CH_2, and U−F modes are predicted 2.7%, 3.2%, and 3.5% too high, which is typical for the B3LYP functional.[32] However, our calculation does predict greater mode-coupling and isotopic shifts for the U−F stretch than are observed. We should note though, that inspection of the displacement coordinates of this predicted vibration does show considerable mixing with other modes. In addition, the calculation predicts the C═U stretching mode about 6.4% below the observed value and to have only 14.9 cm^{-1} carbon-13 shift, which shows that the DFT approximation does not describe the methylidene C═U bond perfectly. The present C═U bond is longer (computed 2.078 Å) with a lower frequency than that in triplet CUO (computed 1.857 Å length, 852 cm^{-1} stretching frequency in solid argon).[33] In addition, we find a 8 kcal/mol higher energy quintet state $CH_2{-}UHF$ complex with a longer (2.386 Å) C−U single bond.

It is interesting to compare frequencies for $CH_2{=}ThHF$ (1380.5, 674.1, 634.0, and 518.6 cm^{-1})[12] and $CH_2{=}UHF$ (1410.4, 659.8, 611.6, and 522.5 cm^{-1}). Although the frequencies are close, the U−H and U−F stretching frequencies are slightly higher, but the C═U stretching frequency and the CH_2 wagging frequency are slightly lower for the uranium methylidene. Analogous relationships have been noted for UF_4 and ThF_4 and for UH_4 and ThH_4.[29,31,34]

The only other product band appeared at 537.7 cm^{-1} and showed 0.0 and 4.2 cm^{-1} isotopic (^{13}C and D, respectively) shifts, which suggests that this vibrational mode corresponds to a mostly U−F stretching coordinate. Also, this absorption does not track with the $CH_2{=}UHF$ product absorptions, and hence, it must be assigned to another reaction product. The most likely molecule is the $CH_3{-}UF$ insertion species, which is formed prior to the major $CH_2{=}UHF$ product. A calculation on this quintet molecule predicted a long C−U single bond (2.413 Å) and the U−F stretching mode to be the most intense IR active mode (over four times more intense than any other vibration) and at 536.6 cm^{-1} (with 0.2 and 2.0 cm^{-1} carbon-13 and deuterium shifts, respectively). Accordingly, we tentatively assign this single absorption to the $CH_3{-}UF$ primary insertion product trapped in the matrix, which is 21 kcal/mol lower in energy than $CH_2{=}UHF$. Its sharpening and slight decrease on annealing may be due to the removal of a less-stable matrix configuration.

Laser-ablated U atoms are also excited and react with CH_3F to form more $CH_3{-}UF$ than $CH_2{=}UHF$, as suggested by the relative intensities of the 537.7 and 522.5 cm^{-1} absorptions. However, on ultraviolet irradiation, the $CH_2{=}UHF$ absorptions increase much more than the $CH_3{-}UF$ band (Figure 1a−c). We propose that photoexcited uranium atom inserts to form $[CH_3{-}UF]^*$, which undergoes α-H transfer on the excited quintet potential energy surface to form quintet $[CH_2{-}UHF]^*$, and these intermediate states are relaxed by the matrix to either quintet $CH_3{-}UF$ or triplet $CH_2{=}UHF$. The latter appears to be the product favored by the matrix-trapping process, although it has higher energy. The same relationship was found for $CH_2{=}MoHF$, which was formed from $CH_3{-}MoF$, but the methylidene is only 5 kcal/mol higher in energy in the Mo case.[14]

$$\begin{tikzcd}
U^* + CH_3F \arrow[r] & {[CH_3{-}UF]^*} \arrow[r] \arrow[d] & {[CH_2{-}UHF]^*} \arrow[d] \arrow[l, phantom, "\text{matrix relax}" below, shift right=4ex] \\
 & CH_3{-}UF & CH_2{=}UHF
\end{tikzcd} \tag{1}$$

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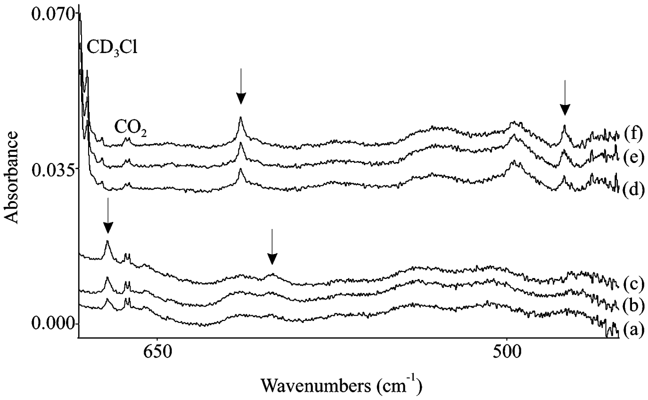

Figure 3. IR spectra in the 685−450 cm^{-1} region taken after (a) uranium atoms are reacted with with CH$_3$Cl in argon and the matrix is (b) irradiated with $\lambda > 290$ nm light and (c) irradiated with $\lambda > 220$ nm light and taken after (d) uranium is reacted with CD$_3$Cl in argon, and the matrix is (e) irradiated with $\lambda > 290$ nm light and (f) irradiated with $\lambda > 220$ nm light. Arrows indicate absorptions of the CH$_2$═UHCl product.

U + CH$_3$Cl. When uranium atoms were reacted with CH$_3$Cl, three product absorptions were observed at 1428.6, 671.4, and 600.5 cm^{-1}. All three absorptions appeared after sample deposition, increased in intensity after ultraviolet irradiation ($\lambda > 290$ nm and $\lambda > 220$ nm), sharpened without increase on annealing to 30 K, and remained unchanged after annealing to 35 K. Hence, all three of these absorptions are assigned to a common product. When experiments were performed with CD$_3$Cl, the lower two absorptions were observed at 614.3 and 475.5 cm^{-1} (Figure 3), and again these bands increased on UV irradiation, sharpened on the first annealing, and remained unchanged on the second annealing. The upper band was not observed, as it probably red-shifted to around 1020 cm^{-1} (similar to experiments with CH$_3$F), which is a region covered by a strong CD$_3$Cl precursor absorption. Finally, weak absorptions were observed for the CH$_2$Cl and CD$_2$Cl free radicals produced by precursor photolysis.[35,36]

Despite not observing the deuterated counterpart, the absorption at 1428.6 cm^{-1} is due to a U−H stretching mode. Notice that it is 8.4 (or 18.2) cm^{-1} blue-shifted from the equivalent mode in the CH$_2$═UHF complex. The absorption at 671.4 cm^{-1}, which shows a 57.1 cm^{-1} deuterium shift, corresponds to a mostly C═U stretch, and the large deuterium shift (125.0 cm^{-1}) of the absorption at 600.5 cm^{-1} indicates that this peak corresponds to a CH$_2$ wagging motion, following the analogous bands for CH$_2$═UHF. The reasonable agreement between these observed isotopic shifts and those predicted (Table 2) indicates these vibrations can all be assigned to the CH$_2$═UHCl molecule. We did not observe the U−Cl stretching mode, as our theoretical computations predicted it at 359.3 cm^{-1}, which is below the spectral limit of our instrument. Also notice that one observed vibration does not fit as well with our computed vibrational spectrum. The C═U stretching mode is predicted at 601.4 cm^{-1}, but is observed at 671.4 cm^{-1}, which indicates that our B3LYP calculations underestimate the C═U bond strength.

Table 2. Observed and Calculated Fundamental Frequencies of CH$_2$═UHCl[a]

	CH$_2$═UHCl		CD$_2$═UDCl	
approximate mode	obsd	calcd (int)	obsd	calcd (int)
CUCl bend		76.0 (8)		69.5 (7)
CH$_2$ twist		183.5 (12)		130.0 (6)
HCUH dist.		299.6 (32)		284.3 (23)
U−Cl stretch		359.3 (117)		315.7 (85)
CH$_2$ rock		410.8 (61)		250.6 (27)
CUH bend		534.3 (66)		410.4 (36)
C−U stretch	671.4	601.4 (80)	614.3	557.6 (53)
CH$_2$ wag	600.5	631.5 (123)	475.5	483.8 (98)
CH$_2$ scis.		1353.0 (27)		1027.1 (22)
U−H stretch	1428.6	1465.5 (488)	*b*	1039.2 (252)
CH stretch		2791.3 (4)		2032.7 (1)
CH stretch		3141.2 (1)		2319.9 (1)

[a] Triplet ground-state B3LYP/6-311++G(2d,p)/SDD level of theory. All frequencies are in cm^{-1}, and computed infrared intensities are in km/mol. [b] Region covered by CD$_3$Cl precursor absorption.

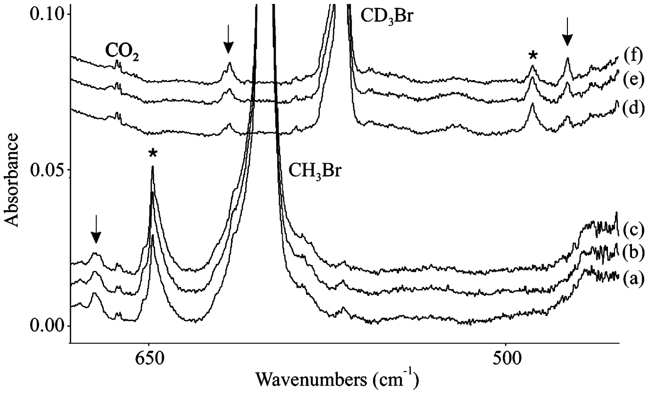

Figure 4. IR spectra in the 685−450 cm^{-1} region taken after (a) uranium atoms are reacted with with CH$_3$Br in argon and the matrix is (b) irradiated with $\lambda > 290$ nm light and (c) irradiated with $\lambda > 220$ nm light and taken after (d) uranium is reacted with CD$_3$Br in argon, and the matrix is (e) irradiated with $\lambda > 290$ nm light and (f) irradiated with $\lambda > 220$ nm light. Arrows indicate absorptions of the CH$_2$═UHBr product, and * marks common metal independent bands associated with the CH$_3$Br precursor (see text).

Our calculations also predict the CH$_3$−UCl insertion product to be 21 kcal/mol lower in energy and to exhibit a strong absorption (U−Cl mode) at 435 cm^{-1}, which is too low for us to measure in these experiments. An analogous mechanism is proposed for U and methyl chloride following eq 1, as excited U* is required for the reaction.

U + CH$_3$Br. Uranium atoms react with CH$_3$Br, and a single product is observed. A broad band at 1421.0 cm^{-1} tracks with a second product absorption at 672.6 cm^{-1}. When the experiment was performed with CD$_3$Br, two absorptions were observed at 616.1 and 474.0 cm^{-1} (Figure 4). These absorptions increased on ultraviolet irradiation and sharpened without net growth on annealing. All of these absorptions appeared in regions near the CH$_2$═UHF and CH$_2$═UHCl product absorptions, and this comparison suggests that they arise from the analogous CH$_2$═UHBr compound. In addition, the 648.5 and 488.8 cm^{-1} absorptions (denoted *) are common to other metal experiments with CH$_3$Br, and weak

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Table 3. Observed and Calculated Fundamental Frequencies of CH_2═UHBr[a]

	CH_2═UHBr		CD_2═UDBr	
approximate mode	obsd	calcd (int)	obsd	calcd (int)
CUBr bend		69.6 (6)		63.4 (5)
CH_2 twist		172.1 (18)		123.1 (10)
U−Br stretch		202.6 (32)		197.4 (14)
HCUH distort.		339.1 (86)		245.2 (55)
CH_2 rock		397.1 (52)		284.1 (33)
CUH bend		530.6 (56)		406.9 (27)
C−U stretch	672.6	599.0 (89)	616.1	561.0 (59)
CH_2 wag	*b*	632.4 (122)	474.0	479.1 (94)
CH_2 scis.		1347.2 (26)		1024.3 (23)
U−H stretch	1421	1452.9 (494)	*b*	1030.6 (254)
CH stretch		2795.7 (4)		2036.0 (1)
CH stretch		3142.5 (1)		2321.1 (1)

[a] Triplet ground-state B3LYP/6-311++G(2d,p)/SDD level of theory. All frequencies are in cm^{-1}, and computed infrared intensities are in km/mol. [b] Region covered by CH_3Br and CD_3Br precursor absorptions.

absorptions (not shown) are due to the CH_2Br and CD_2Br free radicals.[36,37]

The deuterium counterpart of the broad absorptions observed at 1421.0 cm^{-1} was not observed in our experiments. However, the 1400 cm^{-1} region of the spectrum is where we expect to observe U−H stretching frequencies.[29] If this is correct, such an absorption would show a deuterium shift to around 1000 cm^{-1}, which is covered by the CD_3Br precursor. The observed vibration at 672.6 cm^{-1} shows a 1.092 H/D ratio, which is only slightly larger than the predicted 1.068 H/D ratio for the C═U stretching mode of the CH_2═UHBr complex (Table 3). Again we note that, for this mode in particular, our theoretical computations predict a lower vibrational frequency than that observed. No other absorptions were observed in experiments with CH_3Br, but another absorption was observed at 474.0 cm^{-1} when uranium atoms were reacted with CD_3Br. The last strong absorption predicted by our computations on the CH_2═UHBr complex is the CH_2 wagging mode. The observed deuterium absorption fits this prediction well (the CD_2 wagging motion is predicted at 479.1 cm^{-1}), and the region where the CH_2 counterpart should be observed (near 600 cm^{-1}) is covered by a strong CH_3Br precursor absorption. Hence, we assign this deuterated counterpart absorption to a CD_2 wagging mode and all of these observed modes to the CH_2═UHBr complex.

Additional calculations find a stable CH_3−UBr complex that is 21 kcal/mol lower in energy than the methylidene and has its strongest absorption 428.4 cm^{-1} for the U−Br stretching mode. Such a band is too low for us to observe.

Finally, our B3LYP calculations converge triplet ground state structures for the methylidene complexes that are distinctly pyramidal around the uranium center (Figure 5). Notice the slight increase in the agostic H′−C−U angles and decrease in the C═U bond lengths with increasing halogen size. We also compute 7−8 kcal/mol higher energy quintet states (Figure 6) with longer C−U single bonds (2.386, 2.379, and 2.377 Å, respectively, for F, Cl, and Br) that we believe are intermediates in the photochemical reactions.

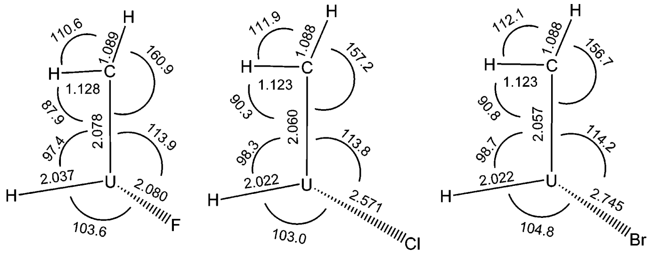

Figure 5. B3LYP/6-311++G(2d,p)/SDD optimized geometries of the CH_2═UHX (X = F, Cl, and Br) complexes. Bond lengths are in angstroms and angles are reported in degrees.

Theoretical Predictions of Periodic Trends. Our theoretical predictions for the three CH_2═UHX (X = F, Cl, Br) methylidenes allow us to consider the effects of different halogen substitution on these uranium compounds. In Table 4, we list the important methylidene complex characteristics from our optimized structures. It is first important to note that the agostic interaction as predicted from the C−H′ bond elongation and H′−C−U angle decreases in the order CH_2═UHF > CH_2═UHCl > CH_2═UHBr. This is opposite to that calculated for the thorium analogues.[12] However, the calculations predict a decrease in the mixed vibrational mode that most nearly approximates the C═U stretching coordinates but shorter C═U bonds with the heavier halogens, and this is accompanied by an observed increase in the mostly C═U stretching mode frequencies. This calculated trend is in opposition to the observed trend: we suspect that the DFT calculation in the absence of configuration interaction and spin−orbit coupling provides only an approximate description of the C═U bond and the coupling with nearby vibrational modes. Nevertheless, our DFT electronic structure calculations in the absence of spin-orbit coupling and configuration interaction for the triplet uranium methylidene complexes (the thorium analogues have singlet electronic states) suggest slightly more agostic distortion in the uranium than in the analogous thorium CH_2═MHX complexes.[12] The CH_2═MoHF and CH_2═ZrHF methylidenes exhibit the same relationsip.[14,20] The second important observation is that the Mulliken charge on the uranium metal center is most positive for the CH_2═UHF complex and decreases with the larger halogen atom complexes, which is the order found for the thorium complexes that have still higher Mulliken charges.[12] Electron density from the uranium atom appears to be donated to the halogen center. The last trend worth mentioning is that the binding energy is greatest (reaction is most favorable) for the CH_2═UHF complex, which is similar to the thorium analogues.[12]

Finally, we find that the singlet-state U(VI) CH≡UH_2F methylidyne complex, which has a short 1.913 Å C−U bond, is too high an energy species (49 kcal/mol higher than the triplet CH_2═UHF methylidene) to be formed here (Figure 6). We are unable to access photochemically the still higher-energy quintet or triplet intermediate states that could relax to the singlet methylidyne product. More electronegative substituents are needed to sustain the U(VI) oxidation state. In contrast, the analogous singlet CH≡MoH_2F and CH≡WH_2F methylidynes were favored products, but their energies are much closer (5 kcal/mol).[14,16] Apparently, the U 5f

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(37) Smith, D. W.; Andrews, L. *J. Chem. Phys.* **1971**, *55*, 5295.

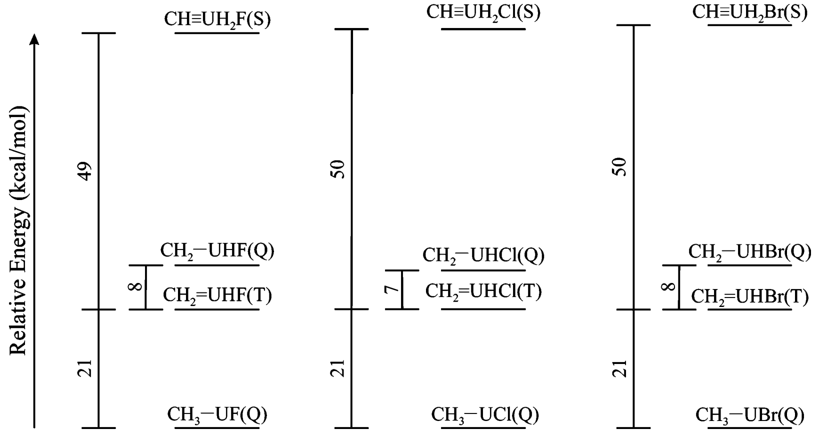

Figure 6. Relative energies of products formed in the reactions of U atoms and methyl halide molecules. Energies are computed at the B3LYP/6-311++G(2d,p)/SDD level of theory. S, T, and Q indicate singlet, triplet, and quintet electronic states, respectively.

Table 4. Geometrical Parameters and Physical Constants of Ground State $CH_2{=}UHX$ (X = F, Cl, and Br)[a]

parameter	$CH_2{=}UHF$	$CH_2{=}UHCl$	$CH_2{=}UHBr$
r(C−H)[c]	1.128, 1.089	1.123, 1.088	1.123, 1.088
r(C−U)	2.078	2.060	2.057
r(U−H)	2.037	2.022	2.022
r(U- - -H′)	2.328	2.352	2.356
r(U−X)	2.080	2.571	2.745
∠(HCH)	110.6	111.9	112.1
∠(CUX)	113.9	113.8	114.2
∠(CUH)	97.4	98.3	98. 7
∠(HUX)	103.6	103.0	104.8
∠(HCU)[c]	87.9, 160.9	90.3, 157.2	90.8, 156.7
Φ(HCUH)[c]	1.7, −163.5	17.7, −150.2	17.8, −151.2
Φ(HCUX)[c]	110.2, −55.0	125.8, −42.0	128.4, −40.6
sym.	C_1	C_1	C_1
q(C)[b]	−0.684	−0.649	−0.642
q(H)[b,c]	−0.305, 0.094, 0.098	−0.284, 0.093, 0.110	−0.282, 0.092, 0.111
q(U)[b]	1.336	1.154	1.131
q(X)[b]	−0.540	−0.423	−0.409
μ[d]	4.940	5.175	5.118
ΔE[e]	84	76	75

[a] Bond lengths and angles are in Å and degrees, respectively. All calculations were performed at the B3LYP/6-311++G(2d,p)/SDD level. [b] Mulliken atomic charge. [c] Numbers are in the order from the closest one to the metal atom to the furthest. [d] Molecular dipole moment in D. [e] Binding energy in kcal/mol.

orbitals are less effective in bonding with carbon 2p than the W 5d orbitals.

Conclusions

Reactions between uranium atoms and methyl halides have been investigated and the $CH_2{=}UHX$ (X = F, Cl, Br) complexes are the major reaction products. The reaction pathway on ultraviolet irradiation proceeds through the insertion $CH_3{-}UX$ complexes with α-H transfer on excited quintet potential energy surfaces to form the excited quintet $[CH_2{-}UHX]^*$ intermediates followed by matrix relaxation to the triplet methylidene complexes. Our DFT-optimized geometries show a considerable agostic interaction between the uranium center and one of the hydrogen atoms on carbon and slightly more agostic distortion of the CH_2 group in the uranium than in the thorium methylidene complexes. However, DFT calculations for triplet $CH_2{=}UHX$ complexes do not give as accurate vibrational mode descriptions as those for singlet $CH_2{=}ThHX$ species.[12] Although higher levels of theory will undoubtedly be required to describe the electronic structure of these triplet $CH_2{=}UHX$ methylidene complexes, DFT has provided a good prediction of the vibrational frequencies and support for the vibrational assignments for these first identified simple uranium methylidene hydride halide complexes.

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