Reactions of Actinide Metal Atoms with Ethane: Computation and Observation of New Th and U Ethylidene Dihydride, Metallacyclopropane Dihydride, and Vinyl Metal Trihydride Complexes

Han-Gook Cho,[†] Jonathan T. Lyon,[‡,§] and Lester Andrews*,[‡]

Department of Chemistry, University of Incheon, 177 Dohwa-dong, Nam-ku, Incheon, 402-749, South Korea, and Department of Chemistry, University of Virginia, P.O. Box 400319, Charlottesville, Virginia 22904-4319

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A combined computational and experimental investigation provides evidence that excited thorium and uranium atoms activate ethane to form the vinyl metal trihydride, metallacyclopropane dihydride, and ethylidene metal dihydride for thorium and the latter complex and the inserted ethyl metal hydride for uranium. These products are trapped in solid argon and identified through deuterium isotopic substitution and vibrational frequencies calculated by densitiy functional theory. Comparisons are made with group 4 and methane reaction products. Numerous calculations using several methods show that these simple ethylidene complexes are more distorted by the agostic interaction than the corresponding methylidene species. This enhanced agostic interaction probably arises from methyl hydrogen to α-H repulsions, which leads to a substantial decrease in the α-H to Th agostic interaction distance, and contributes to our understanding of agostic distortion in organometallic complexes.

Introduction

Reactions of gas phase transition metal atoms with hydrocarbons provide models for condensed phase systems that are important to understanding homogeneous catalysis.[1] Although gas phase investigations found ground-state Zr to be unreactive with ethane, laser-ablated excited Zr atoms react with ethane in complementary matrix isolation studies.[2] As in methane experiments, the initial step is C−H insertion, but the most stable product in the ethane system is the zirconium dihydride metallocycle whereas the agostic methylidene dihydride complex is the most stable product in the methane system.[3,4] Also of interest is the trihydride product C_2H_3-ZrH_3, which is almost as stable, but the methane analogue HC-ZrH_3 is too high energy to be trapped. However, fluorine substitution alters the relative energies and allows the FC-ZrF_3 product to be prepared.[5,6] Hence, the relative energies of possible products affects their yield in energy-driven metal atom reactions and serves as a guide in the search for new product molecules.

Complexes containing a carbon−transition metal double bond are important for understanding metal coordination and for developing catalyst systems to be used in alkane activation.[7,8] A number of early transition metal alkylidenes are agostic, and these species provide a means to characterize the agostic interaction of hydrogen to a transition-metal center. Agostic bonding in these compounds involves α-H-to-metal interaction and stabilization of the *C*═M double bond, and the simplest methylidene model systems made by methane activation can contribute to understand this bonding interaction through detailed quantum chemical calculations.[9–12]

A new generation of simple methylidene complexes has been investigated through reactions of excited early transition metal atoms with methane during condensation in excess argon.[3,4,13–15] These reactions have been extended to actinide metals, and thorium performs under such conditions very much like zirconium.[16] Uranium also forms the methylidene dihydride complex, which exhibits more agostic distortion than the thorium counterpart.[12,16,17] The reaction involves the basic C−H insertion step followed by one α-H transfer to the metal center to give the methylidene, but the transfer of a second α-H to the metal center to form the trihydride is highly endothermic for group 4 metal atoms. On the other hand, the heavier group 6 metal atoms readily produce methylidyne trihydride complexes.[18,19]

Next we investigate reactions of the early actinide metals Th and U with ethane and compute the stabilities of the several products as a guide for their identification in the solid matrix sample from calculated frequencies. As outlined previously,[17] uranium chemistry is important because we need to obtain energy from nuclear sources and to keep our environment free of waste materials containing radioactive elements. Furthermore, the chemistry of Th compared to group 4 and to U is interesting in its own right.

Experimental and Theoretical Methods

The experimental apparatus has been described previously.[20,21] Thorium and uranium atoms, produced by laser-ablation of metal targets (Oak Ridge National Laboratory) with a Nd:YAG laser (5 to 20 mJ/pulse), were codeposited with a dilute mixture (1−3%) of reagent gas (C_2H_6, Matheson; C_2D_6, MSD Isotopes) in argon onto a CsI window cooled to 8 K. The reaction products were frozen in the argon matrix, and their infrared spectrum recorded on a Nicolet 550 spectrometer. Matrix samples were irradiated for 20 min periods by a medium pressure mercury street lamp with the globe removed (λ > 220 nm) with or without optical glass filters and were subsequently annealed to various temperatures. Additional infrared spectra were recorded following each procedure.

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* Author to whom correspondence should be addressed. E-mail: lsa@virginia.edu.

[†] University of Incheon.

[‡] University of Virginia.

[§] Present address: Fritz-Haber Institut der Max-Planck Gesselschaft, Faradayweg 4-6, 14195 Berlin, Germany.

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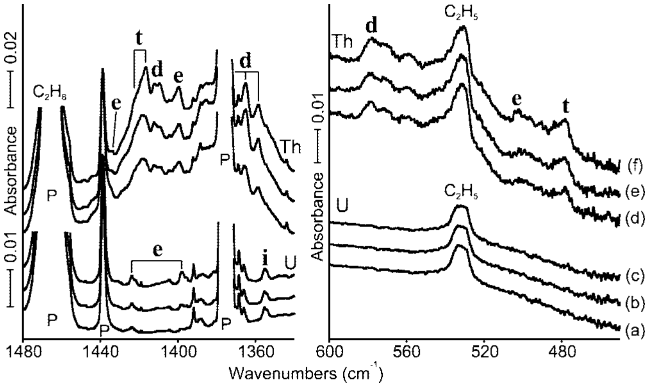

Figure 1. Infrared spectra in the 1480−1340 and 600−450 cm^{-1} regions for Th and U atom and ethane reaction products in solid argon at 8 K. (a) Laser-ablated U codeposited with 1% ethane in argon for 60 min, (b) after visible (>420 nm irradiation), and after (c) UV irradiation (240−380 nm). (d) Laser-ablated Th codeposited with 2% ethane in argon for 60 min, (e) after >290 nm irradiation, and (f) after >220 nm irradiation. P denotes ethane precursor absorptions.

Theoretical calculations on possible reaction products were performed using the Gaussian 03 program system.[22] In all instances, the B3LYP hybrid density functional was employed.[23] Carbon and hydrogen atoms were given the large 6−311++G(3df,3pd) Gaussian basis and uranium the small (60 electron) core SDD pseudopotential, and the medium 6−311++G(2d,p) basis was utilized for C and H atoms in calculations with thorium.[24,25] Such DFT calculations predict vibrational frequencies with reasonable accuracy for actinide metal compounds.[16,17]

Results and Discussion

New product absorptions in laser-ablated thorium and uranium atom experiments with ethane will be compared with frequencies calculated for the most stable products in these reactions. In all experiments methane, ethylene, and ethyl radical absorptions from the vuv laser plume photolysis of ethane were observed.[2,26] We seek new product bands that are unique to a particular metal atom in chemical reactions with ethane.

Infrared Spectra. Experiments were performed with Th and with U using different ethane concentrations and laser ablation energies to ensure that the primary products we observe involve one metal atom and one ethane molecule. Increasing the ethane concentration broadened product absorptions without changing their relative intensities, which suggests that these are first-order reactions in ethane, as found for group 4 reactions.[2] Infrared spectra are compared in Figure 1 for both metals so that unique metal dependence can be shown. New absorptions were observed at 1416.5, 1409.5, 1399.7, 1365.0, and 1358.5 cm^{-1} for thorium, which are listed in Table 1 along with several weaker absorptions. The bands labeled **e** (for ethylidene) increased slightly on sequential >290nm and >220 nm irradiations while the t (for trihydride) bands almost doubled on each irradiation and the d (for dihydride) bands increased more on >290 nm than >220 nm exposure. Subsequent annealing to 30 K and >220 nm irradiation had little additional effect on the spectrum. This photolysis behavior and band correlation was reproduced in a separate experiment. In contrast two different new weaker absorptions, labeled **e** at 1424.0 and 1398.4 cm^{-1} observed with uranium, increased slightly in concert with both visible and UV irradiations, but another band labeled **i** at 1355.6 cm^{-1} was not altered. Annealing to 28 K had little effect on these bands, which are listed in Table 2. Again, these weak absorptions and their behavior were reproduced.

TABLE 1: Absorptions (cm^{-1}) Observed in Reaction of Thorium Atoms with Ethane

Th + C_2H_6	Th + C_2D_6	identification
1434.1	1026.0	e, $CH_3(H)C{=}ThH_2$
1422 sh	1016 sh	t, $CH_2{=}CH{-}ThH_3$
1416.5	1012.9	t, $CH_2{=}CH{-}ThH_3$
1412.0		d, $(CH_2)_2{-}ThH_2$
1409.5	1006.2	d, $(CH_2)_2{-}ThH_2$
1399.7	998.0	e, $CH_3(H)C{=}ThH_2$
covered	986.4	d, $(CH_2)_2{-}ThH_2$
1365.0	976.7	d, $(CH_2)_2{-}ThH_2$
1358.5	972.6	d, $(CH_2)_2{-}ThH_2$
576		d, site $(CH_2)_2{-}ThH_2$
504		e, $CH_3(H)C{=}ThH_2$
479		t, $CH_2{=}CH{-}ThH_3$

TABLE 2: Absorptions (cm^{-1}) Observed in Reaction of Uranium Atoms with Ethane

U + C_2H_6	U + C_2D_6	identification
1424.0	1016.7	e, $CH_3(H)C{=}UH_2$
1398.4	999.0	e, $CH_3(H)C{=}UH_2$
1355.6	973.0	i, $CH_3CH_2{-}UH$

Spectra for both metals reacting with C_2D_6 are shown in Figure 2. The thorium spectra display a similar contour as found for the C_2H_6 counterparts, and new bands appeared at 1012.9, 1006.2, 998.0, 976.7, and 972.6 cm^{-1}; however, an additional **d** component was observed at 986.4 cm^{-1}, whose counterpart was masked by the C_2H_6 band at 1374 cm^{-1} in Figure 1. Again, the **t** bands increased more on irradiation than the **e** and **d** bands. The two **e** bands for uranium were observed at 1016.7 and 999.0 cm^{-1}, and the **i** band appeared at 973.0 cm^{-1}.

Identification of Thorium Products. We expect thorium reaction products to be similar to those for group 4, but the calculated energy profile (Figure 3) reveals a major difference: the insertion product is much higher energy for thorium, but the ethylidene dihydride, metallacyclopropane dihydride, and vinyl metal trihydride complexes are low enough in energy to be viable products. The product absorbance in Zr experiments,[2] for example, is about four times larger than for Th. This is in

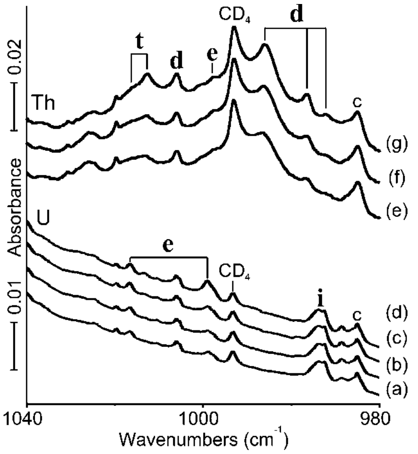

Figure 2. Infrared spectra in the 1030−970 cm^{-1} region for Th and U atom and ethane-d_6 reaction products in solid argon at 8 K. (a) Laser-ablated U codeposited with 1% ethane-d_6 in argon for 60 min, (b) after visible (>420 nm irradiation), after (c) UV irradiation (240−380 nm), and (d) after UV irradiation (>220 nm). (e) Laser-ablated Th codeposited with 2% ethane-d_6 in argon for 60 min, (f) after >290 nm irradiation, (g) after >220 nm irradiation. CD_4 is produced in the deposition process, and c denotes a common band in all ethane experiments.

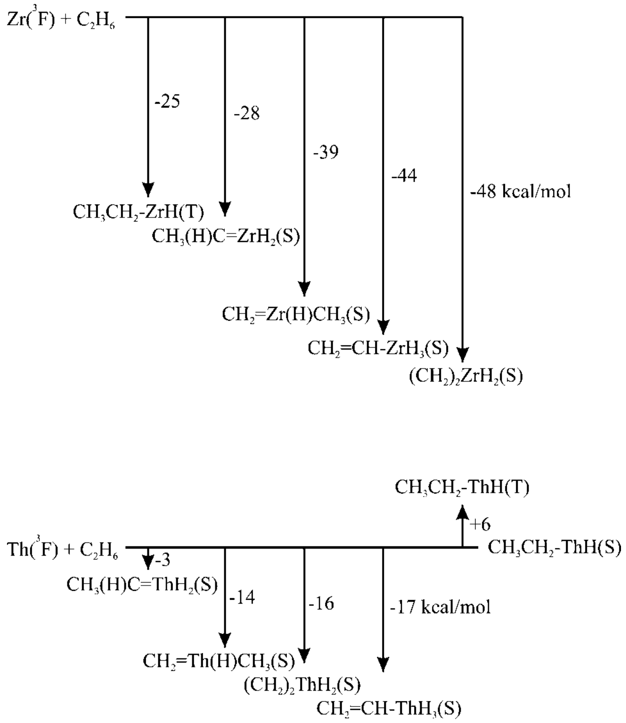

Figure 3. Energy profile diagram for Zr and Th reaction products with ethane calculated with the B3LYP density functional, Pople style basis sets, and SDD pseudopotential. S and T indicate singlet and triplet electronic states. The $CH_2{=}M(H)CH_3$ complexes, which follow C−C bond insertion, were not observed here.

part due to the fact that Th is more refractory, harder to ablate, and a lower concentration of Th atoms is present. This argues strongly that the product spectrum is dominated by single metal species. In addition, 2−5% methane concentrations are often used in matrix isolation experiments without significant reactions with a second precursor molecule, since methane and ethane are relatively unreactive toward these metal atoms, particularly in comparison with halogen substituted methanes.[15–17] This is another reason why product absorbances are weak in these experiments.

After C−H insertion by excited Th atoms, this energized inserted (**i**) species undergoes α-H-transfers to give the ethylidene dihydride (**e**) and the trihydride (**t**) or *β*-H transfer to form the metallacyclopropane dihydride (**d**).

$$Th^{*} + C_2H_6 \rightarrow CH_3CH_2{-}ThH(i) \rightarrow CH_3(H)C{=}ThH_2(e) \rightarrow CH_2{=}CH{-}ThH_3(t) \quad (1a)$$

$$Th^{*} + C_2H_6 \rightarrow CH_3CH_2{-}ThH(i) \rightarrow (CH_2)_2{-}ThH_2(d) \quad (1b)$$

The singlet insertion product is isoergic with the reagents and has its strongest absorption according to calculation at 1474 cm^{-1}, and such an absorption, if present, is totally masked by the strong ethane precursor band. The strongest absorptions are Th−H stretching vibrations, and Table 3 lists these modes for three low energy products. Thorium hydride molecules have previously been observed in this spectral region.[27,28] Our experience with $CH_2{=}ThH_2$ is that these harmonic calculations (unscaled) predict argon matrix frequencies within a few wavenumbers.[16] The highest, strongest frequencies are predicted for the trihydride, and the principal band at 1416.5 cm^{-1} (deuterium counterpart 1012.9 cm^{-1}, H/D ratio = 1.398) is assigned to the strong antisymmetric Th−H stretching mode. An associated shoulder absorption at 1422 cm^{-1} is assigned likewise, but the highest weaker band calculated at 1482 cm^{-1} is covered by precursor. An important lower frequency ThH_3 deformation mode calculated at 505 cm^{-1} is observed at 479 cm^{-1}, which helps to sort out the Th−H absorbing species.

The metallacyclopropane dihydride is a major product with group 4 metals, and the next set of bands, which are believed to be split by the matrix at 1412.0, 1409.5, 1365.0, 1358.5 cm^{-1}, are assigned to the two Th−H stretching modes. An additional matrix split component is observed only for the deuterium species at 986.4 cm^{-1} as the hydrogen counterpart is covered by ethane precursor absorption. Such splitting of vibrational bands by the matrix host is often observed and is more common with larger atoms, such as Th, for example.[15] This dihydride molecule also has a strong ThH_2 bending mode computed at 576 cm^{-1} and observed at this position. Although the ethylidene dihydride is not as low in energy as the above products, the three calculated Th−H stretching and ThH_2 bending frequencies in Table 3 correlate with the three **e** bands at 1434.1, 1399.7, and 504 cm^{-1} and support this assignment.

Identification of Uranium Products. The analogous reaction with uranium produced weaker product absorptions, and since the infrared intensities of Th−H and U−H are comparable (Tables 3 and 4), we conclude that Th is more reactive than U with ethane, a conclusion also reached for methane.[16,17]

$$U^{*} + C_2H_6 \rightarrow CH_3CH_2{-}UH(i) \rightarrow CH_3(H)C{=}UH_2(e) \quad (2)$$

As found for methane, the C−H insertion species in the quintet ground-state is the lowest energy product, and it has one strong infrared band calculated at 1353 cm^{-1}. The weak 1355.6 cm^{-1} product absorption with deuterium counterpart at 973.0 cm^{-1} (H/D ratio 1.393) is appropriate for $CH_3CH_2{-}UH$, which has the lowest frequency U−H stretching mode of the products considered here. The analogous $CH_3{-}UH$ species was observed at 1368 cm^{-1}.[17] Two weak bands at 1424.0 and 1398.4 cm^{-1} increase together on irradiation, and these U−H stretching modes[29,30] (H/D ratios 1.401, 1.400) are best assigned to the ethylidene dihydride complex based on correlation with the calculated U−H stretching frequencies at 1443 and 1406 cm^{-1} (Table 4). The ethylidene complex is 13 kcal/mol higher energy than the insertion product, but as in the methane case, this product is also observed in the reaction with excited uranium atoms.[17] Another possible product, namely the uranium metallacyclopropane dihydride is only 10 kcal/mol higher in energy than the insertion product, and its triplet state has a very strong U−H stretching mode calculated at 1355 cm^{-1}. We believe that the 1355.6 cm^{-1} band is more likely to be due to the lowest energy species, the insertion product, but we cannot rule out the cyclic dihydride. As for methane, the trihydride is a higher energy (+14 kcal/mol) species,[17] and in marked contrast with thorium, the vinyl uranium trihydride is not a player here.

We note that methyl substitution into uranium methylidene dihydride red shifts the calculated and observed U−H stretching frequencies by 30−40 cm^{-1} whereas methyl substitution in the thorium system has little effect (1−2 cm^{-1}) on the calculated and observed Th−H stretching frequencies. So the increased agostic interaction in the U species comes at a small price for the U−H bond stretching frequencies.

Structures. The product structures calculated using the B3LYP density functional are compared in Figures 4 and 5. The higher energy triplet $CH_3CH_2{-}ThH$ insertion product is shown above the lower energy singlet state, which has the same energy as the reagents. We notice immediately that the ethylidene complex parameters that are common with the meth-

TABLE 3: Strongest and Structurally Descriptive Vibrational Modes (cm^{-1}) Calculated for the Lowest Energy Thorium Atom and Ethane Reaction Products[a]

e, $CH_3(H)C{=}ThH_2$	d, $(CH_2)_2{-}ThH_2$	t, $CH_2{=}CH{-}ThH_3$
1435 (340), Th−H str	1418 (377), Th−H str	1482 (295), Th−H str
1398 (111), CH_3 def	1374 (967), Th−H str	1429 (71), CH_2 bend
1395 (609), Th−H str	980 (27), CH_2 wag	1422 (780), Th−H str
1118 (47), anti C−C−Th str	576 (150), ThH_2 bend	1412 (820) Th−H str
513 (156), ThH_2 bend	467 (72), anti C_2−Th str	963 (28), CH_2 wag
486 (86), H−C−Th−H dihed	410 (23), sym C_2−Th str	551 (92), anti ThH_2 bend
		545 (65), anti ThH_2 bend
		505 (344), sym ThH_3 def

[a] Calculated using B3LYP/6−311++G(2d,p)/SDD, frequencies in cm^{-1}, intensities in parentheses (km/mol).

TABLE 4: Strongest (U−H) Stretching Vibrational Modes (cm^{-1}) Calculated for the Lowest Energy Uranium Atom and Ethane Reaction Products[a]

e, $CH_3(H)C{=}UH_2$	d, $(CH_2)_2{-}UH_2$	t, $CH_2{=}CH{-}UH_3$
1443 (467) U−H str	1424 (76) CH_2 bend	1530 (806), U−H str
1406 (575) U−H str	1403 (340) U−H str	1526 (331), U−H str
	1355 (1175) U−H str	1451 (956), U−H str
		1426 (20) CH_2 bend

[a] Calculated using B3LYP/6−311++G(3pd,3df)/SDD, frequencies in cm^{-1}, intensities in parentheses (km/mol).

ylidene complex are in agreement including the *C*=Th double bond and the Th−H bond lengths and the bond angles around the Th metal center. These two related structures are compared in Figure 6 for identical B3LYP calculations using the large Gaussian basis and the small core pseudopotential.[16] However, the remaining α-H is 0.013 Å longer and distorted 8.2° more for the ethylidene dihydride than for the methyidene dihydride complex. Similar calculations using the BPW91 pure density functional find more agostic distortion, as reported previously,[32] [the α-H length 1.130 Å and agostic angle 89.9° for the methylidene and the α-H length 1.142 Å and agostic angle 83.9° for the ethylidene], which predicts the α-H 0.012 Å longer and distorted 6.0° more for the ethylidene dihydride complex. This increase in computed agostic distortion when hydrogen is replaced by a methyl group is comparable to the increase found with U (7.4°), Ti (7.9°), Zr (9.4°), and Hf (10.6°) using B3LYP density functional results for both complexes.[2,15] Calculations with other theoretical methods have also been done to confirm this trend. Identical MP2 wave function based calculations[22] using 6−311++G(2d,p)/ SDD basis sets find the agostic angle to be 5.5° smaller and the C−H bond 0.013 Å longer in the Zr ethylidene, and the Hf complex agostic parameter differences are exactly the same. Repeated computation using the CCSD approach gave the α-H 0.013 Å longer and distorted 6.7° more for the ethylidene zirconium dihydride. This enhanced agostic interaction probably arises from methyl hydrogen to α-H repulsions, which leads to a substantial decrease in the α-H to Th agostic interaction distance from 2.485 Å to 2.354 Å in the Figure 6 structures. Similar computations for complexes with additional methyl groups on the *β* carbon have no effect on the agostic distortion.[31] Furthermore, the agostic distortion for the uranium ethylidene is about 3° more than for the thorium analogue, a difference comparable to that calculated for the corresponding methylidene complexes.[17]

Again the U−H dihydride bonds are about 0.06 Å shorter than the Th−H bonds as found for the methylidene complexes,[17] but the singlet insertion product is lower energy than the triplet state, and the singlet structure has a shorter Th−H bond than the quintet state uranium insertion product. In contrast the higher energy triplet thorium insertion product has a longer (2.070 Å) Th−H bond length.

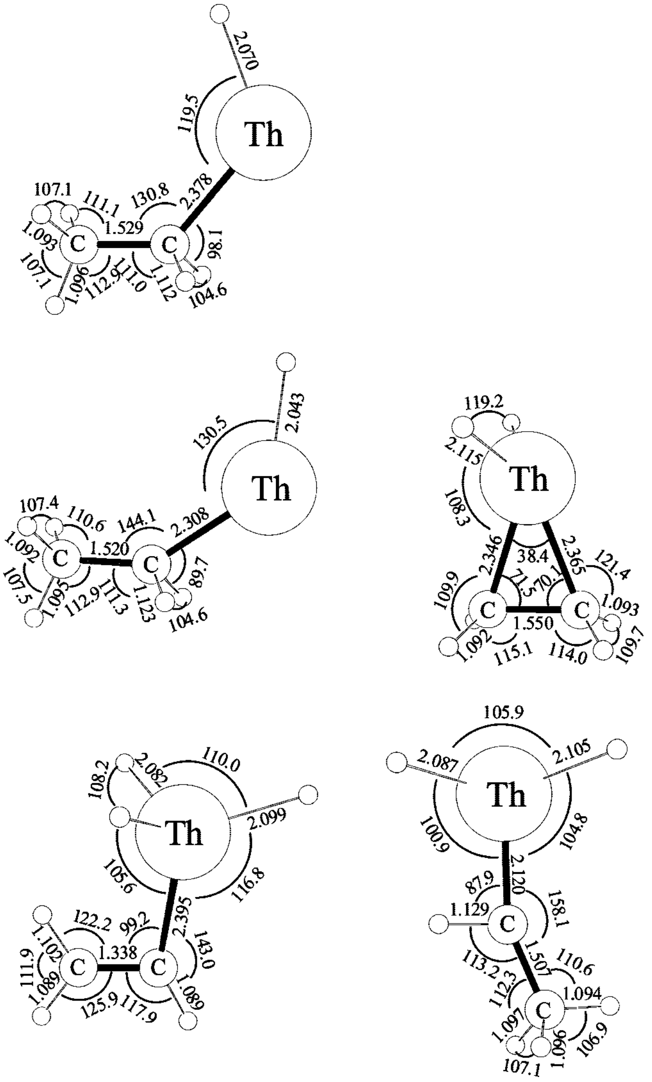

Figure 4. Structures computed for molecules involved in the Th reaction with ethane. The top insertion product is the lowest triplet state, and all others are singlet ground states. B3LYP/6−311++G(2d,p)/SDD. Bond distances in angstoms and angles in degrees.

Contrasting Th and U Reactions. A simple comparison of the energies in Figure 3 and the structures in Figures 4 and 5 provides a rationale for the observed product distribution. Reaction (1) proceeds on the triplet potential energy surface (PES) through UV excitation, and reaction (2) goes through the quintet PES also with UV excitation. So both reactions begin with considerable excess energy. It is straightforward to visualize how the triplet excited $CH_3CH_2{-}ThH$ species undergoes both α-H and *β*-H transfers to form the succession of lower energy products. This was the case with all group 4 metals although

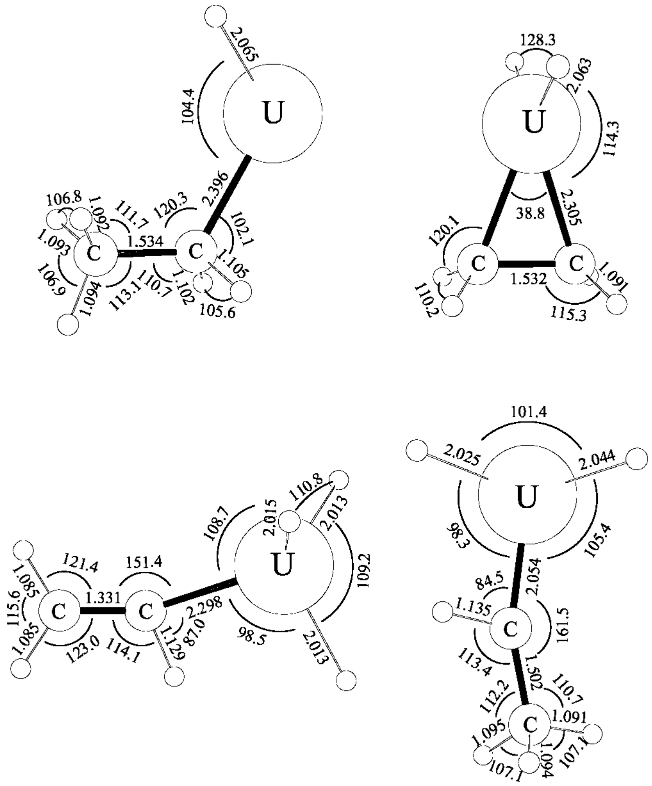

Figure 5. Structures computed for molecules involved in the U reaction with ethane. The insertion product is quintet ground-state, and the others are triplet states. B3LYP/6−311++G(3dp,3df)/SDD. Bond distances in angstroms and angles in degrees. The uranium cyclopropane has the C_{2v} triplet state structure, which is 10 kcal/mol higher energy than the insertion product. The triplet ethylidene is 13 kcal/mol higher and the triplet trihydride is 14 kcal/mol higher than the insertion product.

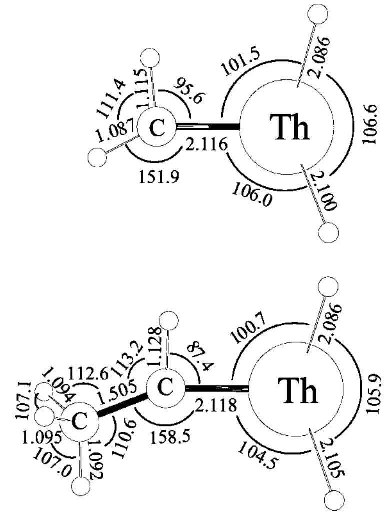

Figure 6. Comparison of calculated structures for methylidene and ethylidene dihydride molecules in Th reactions with methane and ethane. Both are singlet ground states. B3LYP/6−311++G(3dp,3df)/SDD. Bond distances in angstroms and angles in degrees.

the ethylidene gave way to the lower energy trihydride complex.[2] However, the excited quintet CH_3CH_2−UH species undergoes only the shorter distance α-H-transfer and not the longer distance β-H transfer, as the resulting cyclic dihydride is a higher energy product. Thus, even though β-H-transfer in the Th reactions involves a longer distance, the process is exothermic, whereas β-H-transfer in the U reaction would go a shorter distance, but the product formed would be higher energy, and accordingly the uranium cyclic species is not observed in these reactions. Finally, it is important to note that the experimental product absorbances show that U is less reactive than Th with ethane, an observation also made for methane.[16,17]

Conclusions

Thorium and uranium atoms, excited in the ablation process or by ultraviolet irradiation, activate ethane to form vinyl thorium trihydride, thorium metallacyclopropane dihydride, and thorium ethylidene metal dihydride and the latter for uranium based on evidence from a combined theoretical and experimental investigation. The quintet insertion ethyl uranium hydride is calculated to be the lowest energy product, and it is also detected here through its U−H stretching mode based on comparison with calculated frequencies. Under similar experimental conditions, Th is more reactive with ethane than U, as also found for methane.[15–17] In contrast to group 4, the inserted ethyl thorium hydride is calculated to be higher in energy with a singlet ground state, which is not observed for Th, whereas the ethylidene complex is observed for Th and not for group 4, according to comparison with computed frequencies. It is interesting to note that calculated structures show increased agostic distortion for the ethylidene complexes relative to their methylidene counterparts, which probably arises from methyl hydrogen to α-H repulsions. This leads to a substantial decrease in the α-H to Th agostic interaction distance and contributes to our understanding of the important agostic interaction in transition and actinide metal complexes.

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