Hydrogen Migration and Vinylidene Pathway for Formation of Methane in the 193 nm Photodissociation of Propene: $CH_3CH{=}CH_2$ and $CD_3CD{=}CD_2$

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Photodissociation channels and the final product yields from the 193 nm photolysis of propene-h_6 ($CH_2{=}CHCH_3$) and propene-d_6 ($CD_2{=}CDCD_3$) have been investigated, employing gas chromatography, mass spectroscopy, and flame ionization (GC/MS/FID) detection methods. The yields of methane as well as butadiene relative to ethane show considerable variations when propene-h_6 or propene-d_6 are photolyzed. This suggests significant variances in the relative importance of primary photolytic processes and/or secondary radical reactions, occurring subsequent to the photolysis. Theoretical calculations suggest the potential occurrence of an intramolecular dissociation through a mechanism involving vinylidene formation, accompanied by an ethylenic H-migration through the π-orbitals. This process affects the final yields of methane-h_4 versus methane-d_4 with respect to other products. The product yields from previous studies of the 193 nm photolysis of methyl vinyl ketone-h_6 and -d_6 ($CH_2{=}CHCOCH_3$, $CD_2{=}CDCOCD_3$), alternative precursors for generating methyl and vinyl radicals, are compared with the current results for propene.

Introduction

The utilization of deuterated isotopomers to ascertain and clarify the mechanisms of primary processes in molecular photodissociations has been known for close to a half-century.[1] Most frequently it has been applied to hydrocarbon processes where the source of molecular hydrogen product is of interest, i.e., whether the hydrogen is formed through a molecular detachment process or the result of atomic reactions. Consider the photolysis of ethane where the vacuum-ultraviolet-induced decomposition[2] produces hydrogen but photolysis of mixtures of -h_6 and -d_6 yield only H_2 and D_2 via molecular detachment:

$$CH_3CH_3 \rightarrow H_2 + C_2H_4 \tag{1}$$

$$CD_3CD_3 \rightarrow D_2 + C_2D_4 \tag{1a}$$

Site specificity information can also be determined from photolysis of CH_3CD_3:

$$CH_3CD_3 \rightarrow H_2 + D_2 + CHCD_3 + CH_3CD \tag{2}$$

The absence of HD product from (2) indicates a 1,1 rather than a 1,2 molecular detachment event.

Until recently, it has been generally assumed in isotopic studies that the occurrence of various photolytic C−C bond-breaking primary processes is independent of hydrogen-isotopic precursor. In studies involving product determinations, it is known that hydrogen isotopomers will affect the product ratio as isotope effects in H-abstraction reactions involved in secondary processes are well-known.[3] In addition, preferential C−H bond breaking in various deuterated ethylene isotopomers has been observed in vibrationally mediated photodissociation processes.[4]

Amongst unsaturated hydrocarbons, the photodissociation of ethylene has been the most studied extending over a large range of photon energies.[4] By comparison, propene photolysis has not been examined as frequently, but still, there have been a number of investigations over a large portion of its absorption spectrum including some at 185 nm,[5] close to the long-wavelength onset of propene's major absorption feature.[6] The photodissociation processes in propene are remarkably complex. Recent studies by Lee et al.[7] have focused upon the dynamics of the photodissociation at 157 nm where eleven primary photofragments from eight dissociation channels were observed.[7a] Several involve dissociation into three species (triple fragmentations). Previous results collectively indicate that the mechanism of the photodissociation of propene changes significantly over the range between 163 nm and 122 nm[8] so that the observed dominant processes, for example, at 157 nm may not be important at other incident energies.

In the present work, propene-h_6 and propene-d_6 have been photolyzed separately at the relatively low energy provided by 193 nm light. The final reaction products are analyzed to obtain information about the primary processes. The relative product yields for formation of methane-d_4 from the propene-d_6 are nearly a factor of 2 larger than the methane-h_4 yield from propene-h_6, suggesting differences in the various modes of the dissociation depending upon isotopic variability. The mechanisms for the formations of methane and other products are therefore examined theoretically in order to identify the reasons for significant changes of photolytic product distributions upon deuteration, and results of propene photolysis are compared with those of methyl vinyl ketone-h_6 and -d_6.

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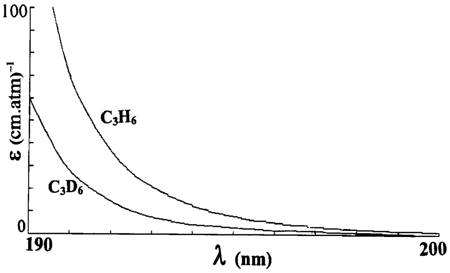

Figure 1. Absorption spectra of propene-h_6 and propene-d_6 at $T = 298$ K.

Experimental Section

Experiments were performed using 193 nm excimer laser photolysis and gas chromatography, mass spectroscopy, and flame ionization (GC/MS/FID) end product analysis methods, as described in detail previously.[9] Briefly, diluted mixtures of propene-h_6 or -d_6 in an excess of He, typically 133.3 Pa (1 Torr) or 266.6 Pa (2 Torr) of propene in 13.3 kPa (100 Torr) of He, were photolyzed at 193 nm. The laser energy as monitored at the source was typically about 150 mJ. A self-enclosed gas circulating pump was used to flow the gas mixture through the reaction cell so that the cell contents were replaced following each laser pulse (1 Hz). The active volume of the photolysis cell was 40 cm^3, which is about 0.05% of the total sample volume resulting in a significant dilution of the products. Thus, the photolysis of products were always kept at an insignificant level. The end product analysis was performed using an online Hewlett-Packard 6890-series gas chromatograph and 5970-series mass spectrometer. The photolyzed sample was admitted to an evacuated injection loop that was immersed in liquid N_2. The content of the reaction manifold was passed through the loop, and reaction products were collected while the He inert gas was pumped away. The concentrated sample was warmed to room temperature and directly injected onto two separate capillary columns by admitting the carrier gas into the collection loop. In a number of experiments the photolyzed sample was directly injected into the GC columns. Temperature programming of the oven was required to separate the products. The retention times and response of the gas chromatograph were calibrated by injection of standard samples with concentrations similar to those produced from the laser photolysis. The product yields were normalized relative to the parent concentration and the number of laser shots. Typically, 400 laser shots were adequate for producing sufficient products for GC/MS/FID analysis.

The apparatus used for the measurement of ultraviolet absorption spectra and cross-sections has been described previously.[10] Briefly it consists of a 1 m normal incidence vacuum monochromator with a grating blazed at 150 nm (600 lines/mm) and provided with a computer-controlled wavelength stepping motor drive, a computerized data acquisition system, analog to digital circuitry, and a gas-phase cell ($l = 17$ cm). Adherence to the Beer−Lambert absorption law was assured through variation of sample pressure. The gas-phase absorption cross-sections reported here between 190 and 200 nm are determined with a typical uncertainty of 2−4%.

Propene samples with highest available purity (99.9%) were used. Ultrahigh-purity He (99.9999%) was used for sample preparation and as the carrier gas for GC/MS/FID.

Results and Discussion

Absorption spectra of propene-h_6 and -d_6, shown in Figure 1, were measured between 190 and 200 nm with a typical uncertainty of 2−4%.[10] The spectra of both C_3H_6 and C_3D_6, in the wavelength range of these measurements are broad and structureless absorptions with C_3H_6 having larger cross-sections. At 193 nm, the absorption cross-section of C_3H_6 is approximately three times larger than that of C_3D_6.

The major reaction products of the 193 nm photolysis of propene (-h_6 and -d_6) as separated, identified, and quantified by GC/MS/FID methods were methane, acetylene, ethene, ethane, and 1,3-butadiene, plus an unidentified C_3 or C_4 product which has a retention time very close to that of butadiene. The product yields were determined from FID peak areas normalized to the parent concentration and the number of laser shots. The results are listed in Tables 1 and 2.

These results indicate that the product yields from photodissociation of C_3H_6 at 193 nm are generally larger than those from photolysis of C_3D_6. This is in agreement with a larger (≈3×) absorption cross-section of C_3H_6 at the photolysis wavelength of 193 nm as shown in Figure 1.

Accordingly, the average yield of the final photodissociation products relative to that of ethane derived from these experiments (given in parentheses) are as follows:

$$\begin{aligned} CH_2{=}CHCH_3 \rightarrow\ & CH_4\ (1.6 \pm 0.2),\\ & C_2H_2\ (3.6 \pm 0.3),\ C_2H_4\ (0.8 \pm 0.1),\ C_2H_6\ (1),\\ & CH_2{=}CHCH{=}CH_2\ (2.8 \pm 0.7),\ C_xH_y\ (0.8 \pm 0.3) \end{aligned}$$

$$\begin{aligned} CD_2{=}CDCD_3 \rightarrow\ & CD_4\ (3.1 \pm 0.3),\\ & C_2D_2\ (4.0 \pm 0.5),\ C_2D_4(1.2 \pm 0.1),\ C_2D_6\ (1),\\ & CD_2{=}CDCD{=}CD_2\ (1.8 \pm 0.2),\ C_xD_y\ (0.5 \pm 0.1) \end{aligned}$$

A major dissociation channel for propene, over the entire previously studied energy range from 157 to 185 nm, involves the formation of vinyl and methyl radicals:[5−7]

$$CH_3CH{=}CH_2 \rightarrow C_2H_3 + CH_3 \tag{3}$$

Another previously observed, but minor, photodissociation channel proceeds through a straightforward three-center elimination process involving the intramolecular migration of H-atom to form methane directly.[5a]

$$CH_3CH{=}CH_2 \rightarrow CH_4 + C_2H_2 \tag{4}$$

Following photolysis and dissociation at 193 nm (619.8 kJ/mol), the excess energy available for methane via reaction (4), ($\Delta H_{\mathrm{reacn}} = 131.4$ kJ/mol for acetylene co-product or 331.5 kJ/mol for vinylidene co-product)[11,12], is 488.4 or 288.3 kJ/mol depending on the isomeric form of C_2H_2. The acetylene or vinylidene would be left with a considerable portion of the excess energy after the relatively low-energy rupture. If acetylene is the co-product, it is unlikely that the methane would be left with enough internal energy to allow further dissociation into methyl radical and H-atom ($\Delta H_{\mathrm{reacn}} = 438.56$ kJ/mol). If the co-product was vinylidene secondary dissociation of the methane would not energetically be feasible.

The structure of the C_2H_2, i.e., whether it could be vinylidene, formed in reaction 4 was not previously discussed. However, earlier photolytic studies of propene at 185 nm[5a] as well as at shorter wavelengths[7a] report a triple fragmentation to methyl radical, H-atom, and acetylene (5), besides the single C−C bond dissociation.

$$CH_3CH{=}CH_2 \rightarrow C_2H_2 + CH_3 + H \tag{5}$$

TABLE 1: Product Yields from the 193 nm Photolysis of C_3H_6/He Mixtures, Normalized to the Parent Concentration and Number of Laser Shots

propene/He	CH_4	C_2H_2	C_2H_4	C_2H_6	C_xH_y	C_4H_6
1.5/100	0.050	0.139	0.025	0.042	0.024	0.075
1.5/100	0.064	0.125	0.024	0.036	0.010	0.059
1.5/100	0.053	0.102	0.019	0.029	0.026	0.072
2.0/100	0.044	0.109	0.021	0.027	0.018	0.066
2.0/100	0.033	0.071	0.016	0.020	0.024	0.058
2.0/100	0.036	0.076	0.017	0.022	0.027	0.079
5.0/100	0.048	0.115	0.025	0.039	0.028	0.129
5.0/100	0.048	0.117	0.025	0.030	0.029	0.116
5.0/100	0.069	0.167	0.035	0.042	0.016	0.114
5.0/100	0.048	0.097	0.024	0.029	0.027	0.099
average	0.049 ± 0.011	0.112 ± 0.028	0.023 ± 0.005	0.032 ± 0.008	0.023 ± 0.006	0.087 ± 0.026

TABLE 2: Yield of Products from 193 nm Photolysis of C_3D_6/He Mixtures, Normalized to the Parent Concentration and Number of Laser Shots

mixture	CD_4	C_2D_2	C_2D_4	C_2D_6	C_xD_y	C_4D_6
1.5/100	0.019	0.025	0.007	0.006	0.003	0.011
1.5/100	0.021	0.028	0.008	0.006	0.003	0.011
1.5/100	0.022	0.028	0.008	0.007	0.003	0.010
1.5/100	0.021	0.027	0.008	0.008	0.004	0.016
average	0.021 ± 0.001	0.027 ± 0.001	0.008 ± 0.001	0.007 ± 0.001	0.003 ± 0.0004	0.012 ± 0.003

Process 5 is energetically feasible ($\Delta H_{\text{reacn}} = 569.9$ kJ/mol)[11] at 185 nm. This additional process (5) is one of several major triple dissociations that are more efficient at higher photodissociation energies.

Abstraction of a primary H-atom by methyl radical from parent propene to form CH_4 (6) is exothermic by 63.2 kJ/mol [11] but is unlikely to be an important secondary process in the presence of highly reactive vinyl radical.

$$CH_3 + CH_3CH{=}CH_2 \rightarrow CH_4 + CH_2CHCH_2 \qquad (6)$$

The major secondary reactions of the radicals formed through (3), in the absence of reactive hydrogen donors, are expected to be the combination and cross-combinations of methyl or vinyl radicals resulting in ethane, propene, and 1,3-butadiene (reactions 7, 8a, and 9a) and disproportionation reactions (8b, 9b) resulting in methane, acetylene, and ethylene products.

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad (7)$$

$$CH_3 + C_2H_3 \rightarrow CH_3CH{=}CH_2 \qquad (8a)$$

$$\rightarrow CH_4 + C_2H_2 \qquad (8b)$$

$$C_2H_3 + C_2H_3 \rightarrow CH_2{=}CHCH{=}CH_2 \qquad (9a)$$

$$\rightarrow C_2H_4 + C_2H_2 \qquad (9b)$$

The major and most likely the sole source of ethane, noted above, is from the combination of methyl radicals (reaction 7): thus, ethane is used here as a reference product for comparative product yield determinations; the yield determination of 1,3-butadiene is uncertain because of the presence of the unidentified C_xH_y species in the gas chromatograph spectrum.

Acetylene and methane are likely formed both directly through the primary processes (reactions 4 and 5) and the secondary processes (reactions 6, 8b, and 9b). As shown later, the C_2H_2 formed in (4) may have a vinylidene structure. In general, radical−radical combination reactions are considerably faster than disproportionation channels.[9] A typical isotope effect of $k_H/k_D \sim 1.2$ is expected for the disproportionation channels, while the combination channels experience no isotope effect.

Methane is not commonly formed in a primary photodissociation process of hydrocarbons.[7a] The addition of O_2, a radical scavenger for methyl, in the photolysis of propene at 185 [5a] nm reduces the methane yield by a factor of 3, but not entirely. This is an indication of involvement of a non-free methyl radical formation process (4). The methane yields from the 193 nm photolysis of propene, relative to the yield of ethane, are

$$CD_4/C_2D_6 = 3.1 \pm 0.3 \qquad CH_4/C_2H_6 = 1.6 \pm 0.2$$

If the specific primary processes (3) in both deuterated and protonated isotopomers were similar in importance, then the product ratios would probably favor formation of the protonated methane species as there are significant isotope effects in subsequent hydrogen-abstraction reactions. As an example, an olefinic C−H bond is about 6.7 kJ/mol weaker than the similar C−D bond.[13]

Isotope effects of deuteration have been observed in the primary processes involved in photodissociation of olefins and saturated hydrocarbons.[14a,b] The preferential elimination of H-atoms vs D-atoms from hydrocarbon systems has been attributed to differences in the bond energies as well as to the structure of the activated complex. However, in the propene system at 157 nm, free-radical formation of methane requires a C−C and a C−H bond cleavage and the observed branching ratios of products suggest, at 157 nm, that about one-quarter of the products are formed after hydrogen transfer.[7b] The present results suggest that the intramolecular methane elimination process that requires an internal hydrogen transfer is of higher probability in the deuterated species than in the protonated precursor molecule, with respect to the ethane reference. Clearly, one bond that requires breaking in this mechanism is the ethylenic C−D bond. However, as noted, this bond is stronger than that of the protonated species and would appear to be less likely to occur.

Methane thus appears to be formed through two distinct mechanisms. Several independent pathways to a particular given photolysis or reaction product are not totally uncommon. A clear example is the photolysis of formaldehyde where product CO may be formed either rotationally cold or excited.[15] Interestingly, one of the proposed mechanisms in that system implies a movable H-atom that explores large regions of the reaction

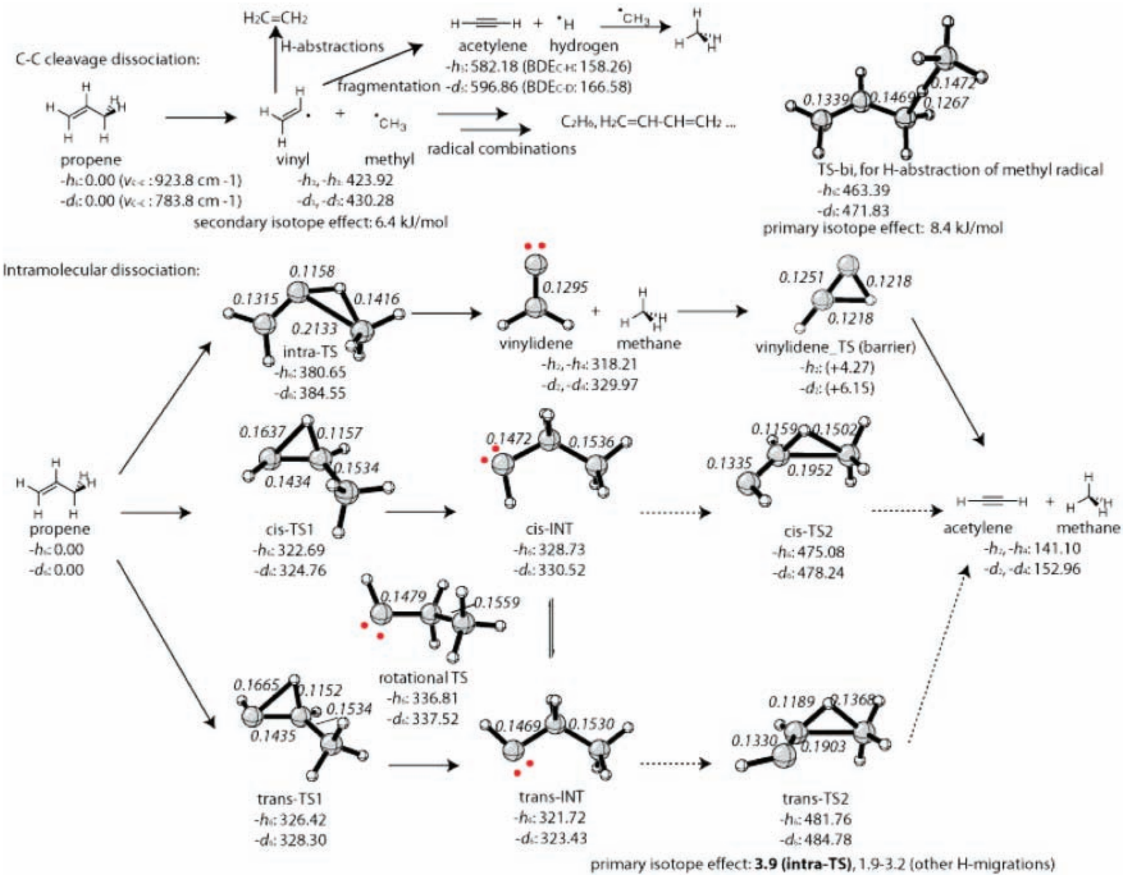

Figure 2. Computed isotope effects and reaction barriers in the two mechanisms, including the free-radical and unimolecular pathways. (CBS-QB3, energies in kilojoules per mole, distances in nanometers, identical energies for *si*- and *re*- faces in stereochemistry).

surface before bonding with the other H-atom, which may be somewhat analogous to the situation in propene photolysis. Yet more recently, examination of the rotational and translational energies of CO produced in the photolysis of acetaldehyde suggest that multiple mechanistic pathways may be operative. One pathway is proposed to be a "H-roaming" mechanism leading to the [$CH_3-HC(O)$]* channel that directly decays into the $CH_4 + CO$ product,[16] a process that again may be comparable to that in the photolysis of propene.

In the propene case, there is the C−C cleavage followed by barrierless radical−radical reactions to form ethane and butadiene as well as a [methyl + vinyl] cross-combination reaction to re-form propene. While most of the methane product is formed by the hydrogen-abstraction rather than through the unimolecular process, the latter formation mechanism may be similar to the formaldehyde and acetaldehyde situation. The overall energetic requirements for these various processes are not yet clear.

A robust computational technique, CBS-QB3, was used to calculate the C−C cleavage for the protonated and deuterated cases. The complete basis set (CBS-QB3) of Petersson and coworkers, using a combination of the DFT-level optimization with Moeller−Plesset correlation and coupled cluster single-point calculations, predict a high-quality energy value.[17−19] The method has been validated to have a mean error of ± 4 kJ/mol for the G2 test. In the present case for computing the isotope effects, the method is expected to result in higher accuracy since the calculation errors between parallel isotopic channels will be similar and cancel. The accuracy of the calculations may be surmised from the value obtained for the C−C bond in the protonated system equal to 423.9 kJ/mol, which is in excellent agreement with literature values (422.2[12] or 426.8 kJ/mol [11]). By comparison, the C−C bond in the propene-d_6 system is calculated to be 430.3 kJ/mol, leading to a secondary isotope effect of 6.4 kJ/mol that, interestingly, is similar to the primary isotope effect of the C−H and C−D bonds. Such substitution effects have been found to contribute a large fraction of the electronic energy required to break that particular bond and others as well.[20,21]

The same computational technique was utilized to examine the intramolecular dissociation of propene, both for protonated and deuterated structures. Similar to the H-roaming processes of formaldehyde and acetaldehyde, it was found that one of the hydrogen atoms from the -CH_2 end can "roam" along the C═C π-orbitals. The energetics associated with this process and the structures discussed are shown in Figure 2.

For the intramolecular dissociation, the intra-TS is a rate determining transition state by which the ethylenic hydrogen atoms on the middle carbon eliminate the methyl group. The normal mode of the imaginary frequency and IRC (intrinsic reaction coordinate) path confirm that the methyl group in the transition state complex is not an external free radical generated through the C−C cleavage (reaction 3). The resulting vinylidene product can isomerize into acetylene with a small reaction barrier of 4.3 (H-) or 6.2 (D-) kJ/mol. In addition, the intramolecular elimination is lower in energy than the C−C cleavage by 43.3 (-h_6) and 45.7 (-d_6) kJ/mol.

Interestingly, the transition structures (TS1's, *cis*-TS1, and *trans*-TS1) which connect to propene and to the secondary carbene-like intermediates (INTs) on the UB3LYP electronic energy surface appear to be metastable conformers at best: the *trans*-TS1 is separated from the carbene well (*trans*-INT) by a barrier of only 5 kJ/mol after the CBS-QB3 correction, the barrier for *cis*-TS1 disappears entirely, and both are lower than the C−C bond rotational barrier by 4−13 kJ/mol. The "para"-intermediate characteristic, that is, the chemical bond-breaking and -forming process is faster than internal C−C bond rotation, has also been observed in other biradical systems,[22] although here the flat potential area around TS1's and INT's is lower in energy by 146−163 kJ/mol than the energetically high-lying TS2 complexes. The complete potential energy surface suggests that one of the ethylenic H-atoms will "walk" from the vinyl end to the middle carbon in propene along the π-orbital. The reaction barrier for the H-migration is even lower than the energy required for the intramolecular methane elimination (intra-TS) of propene (380−385 kJ/mol), by 54−60 kJ/mol.

Methane formation via the above H-migration mechanism will compete with that via free methyl radical reactions. The H-abstraction for methyl radical needs a reactive hydrogen donor, such as either propene (reaction 6, Figure 2, TS-b$_i$, $\Delta H^\ddagger = 39-42$ kJ/mol) or vinyl radical (reaction 8b, $\Delta H^\ddagger = 9-11$ kJ/mol), and results in a considerable entropy loss in these reaction channels. Therefore, we predict that the intramolecular dissociation of propene (4) will be competitive with free-radical reactions.

The computed isotope effects of the intramolecular dissociation (3.9 kJ/mol) are substantially less than that of the energy-comparable C−C cleavage (6.4 kJ/ mol). This means that the overall isotope effects for the formation of methane and acetylene through the multiple channels can be smaller than those for ethane and butadiene. Thus, both of the two computed isotope effects are generally consistent with the photolytic experiments: if ethane-h_6/-$d_6 = c$, then butadiene-h_6/-$d_6 = 1.5c$, while methane-h_4/-$d_4 = 0.55c$ and acetylene-h_2/-$d_2 = 0.92c$. The remaining differences in isotope effect between ethane and butadiene, methane and acetylene, indicate that the propene dissociation is remarkably diverse.

As is usual, the smaller ratios of kinetic isotope effects correspond to the tighter (more compact) transition states. For example, in the transition state (intra-TS), the "flipping" hydrogen is in the middle of the two carbons with partially forming and breaking C−C bonds with lengths of 0.21 nm. This is to be compared with a C−C cleavage, where the bond dissociation is complete beyond a C−C distance of 0.3 nm.

Photolysis of ketones is an alternative approach for producing and studying hydrocarbon radicals. The 193 nm photodissociations of methyl vinyl ketone (MVK, reactions 10a−c), first reported from our laboratory, are considered a relatively clean source of both methyl and vinyl radicals with a quantum yield of nearly 1 and equal production yields of methyl and vinyl radicals.[23,24]

$$\mathrm{CH_3COC_2H_3} \rightarrow \mathrm{CH_3} + \mathrm{COC_2H_3} \rightarrow \mathrm{CH_3} + \mathrm{C_2H_3} + \mathrm{CO} \quad (10a)$$

$$\rightarrow \mathrm{CH_3CO} + \mathrm{C_2H_3} \rightarrow \mathrm{CH_3} + \mathrm{C_2H_3} + \mathrm{CO} \quad (10b)$$

$$\rightarrow \mathrm{CH_3} + \mathrm{C_2H_3} + \mathrm{CO} \quad (10c)$$

The yields of final products relative to the yields of ethane derived from our earlier studies are summarized below:[24]

$$\mathrm{CH_2{=}CHCOCH_3} \rightarrow \mathrm{CH_4}\ (0.40 \pm 0.03),\ \mathrm{C_2H_2}\ (1.36 \pm 0.22),\ \mathrm{C_2H_4}\ (0.49 \pm 0.04),\ \mathrm{C_2H_6}\ (1),\ \mathrm{C_3H_6}\ (1.34 \pm 0.10),\ \mathrm{CH_2{=}CHCH{=}CH_2}\ (0.52 \pm 0.10)$$

$$\mathrm{CD_2{=}CDCOCD_3} \rightarrow \mathrm{CD_4}\ (0.30 \pm 0.03),\ \mathrm{C_2D_2}\ (0.98 \pm 0.1),\ \mathrm{C_2D_4}\ (0.41 \pm 0.04),\ \mathrm{C_2D_6}\ (1),\ \mathrm{C_3D_6}\ (1.35 \pm 0.03),\ \mathrm{CD_2{=}CDCD{=}CD_2}\ (0.53 \pm 0.09)$$

Methane and acetylene yields relative to that of ethane are larger in the propene-h_6 and -d_6 photolysis than those observed in the photolysis of MVK.[24]

In the ketone system, the formation of methane is primarily through disproportionation of vinyl and methyl radicals (reaction 8b) that is highly exothermic with a small energy barrier (293 kJ/mol for the protonated system). Reaction 8b, as noted earlier, is not expected to be a major source of methane in the propene system, and any isotope effect would reduce it even further. The relative yields of C_2D_2 and C_2D_4 derived from either MVK or propene are quite comparable, leaving formation of CD_4 as the outlier. Processes 10a−c are endothermic by 355, 399, and 446 kJ/mol, respectively, while the propene dissociation via reaction 3 is endothermic by 423 kJ/mol.[11] Compared to the case of propene, photolysis of MVK at 193 nm (620 kJ/mol) results in higher concentrations of methyl and vinyl radicals because of the lower barrier.

The hydrogen-migration process of MVK does not affect the formation of methane, since the acetyl group traps the mobile hydrogen atom by forming acetaldehyde and acetylene. Therefore, both the theoretical analysis and the observed product distribution in the free-radical system of the precursor ketone photolysis provide support for an additional intramolecular mechanism for the formation of CD_4 in the photolysis of propene-d_6.

Conclusion

An experimentally observed discrepancy of the relative yield of methane from the photolysis of deuterated and protonated propene at 193 nm has been described. The results can be explained through a theoretical approach to understanding the energetics and structures of the dissociation intermediates. The overall system is described by an H- or D-atom that can "migrate" across the π-orbital system via an energetically competitive path describes the overall system. The lowest energy intramolecular dissociation is competitive with the C−C cleavage, and the primary isotope effect of the intramolecular reaction is about half of the secondary isotope effect of the C−C cleavage, which is contrary to the impression that deuteration only affects a C−C scission. It has been shown that the presence of a CO group, as in the case of methyl vinyl ketone, significantly inhibits the intramolecular formation of methane.

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