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Theoretical characterization of the thermodynamics of the photoisomerizations of ethylene and propylene

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Abstract

A number of structures which may play a role in the thermal and triplet photochemistry of ethylene and propylene are calculated using ab initio methods. The energies and other properties obtained from these ab initio calculations are employed to calculate the heats of formation of the structures using the bond additivity correction (BAC) method of Carl Melius. Generally, the heats of formation appear to be accurate to within several kilocalories per mole, even for the triplet states and transition states encountered in this study. A final analysis reaches the conclusion that the triplet-sensitized photochemistries of ethylene and propylene occur through the hot ground states of these materials rather than through their respective triplet states.

Keywords: Ethylene; Photoisomerization; Propylene; Theoretical characterization; Thermodynamics

1. Introduction

The photochemistries of ethylene, propylene and the higher olefins have been extensively reviewed [1], and will not be repeated fully here. The excited singlet (193 nm) photochemistry of ethylene is the best understood of all the olefins. Recent beam experiments [2] have examined the kinetic energies of ejected molecular hydrogen and have proposed the branching ratios between three-centred and four-centred eliminations. Other recent studies [3] have shown that vinyl radical + H products are obtained from hot ground state ethylene (${}^1C_2H_4^\ddagger$). The generation of acetylene + H_2 occurs even in condensed phase ethylene singlet photochemistry (for a review, see Refs. [1,4]). The same reaction (Eqs. (1a) and (1b)) occurs in both excited singlet and triplet photochemistry and in the pyrolysis of ethylene. A difference between the mechanisms of excited singlet and triplet photochemistry is evident because the mercury-sensitized photolysis reaction (Eq. (1b)) is quenched by collision. Therefore two different mechanisms can be proposed, one occurring directly from the excited singlet state (Eq. (1a)) and one occurring via intersystem crossing from triplet ethylene to hot ground state ethylene (Eq. (1b)). The "directness" of Eq. (1a) is implied by the very high kinetic energy of the ejected H_2 molecules, which is itself a measure of the astatistical distribution of the available energy of the reaction.

$$ {}^1C_2H_4^* \rightarrow {}^1HCCH + H_2 \qquad (1a) $$

$$ Hg^* + {}^1C_2H_4 \rightarrow {}^3C_2H_4^\ddagger \leftrightarrow {}^1C_2H_4^\ddagger \rightarrow {}^1HCCH + H_2 \qquad (1b) $$

Deuterium scrambling occurs in the condensed phase in the photochemistry of the singlet state, while the vinyl + H route is nearly eliminated. All these observations confirm that, in the excited singlet photochemistry of ethylene, Eq. (1a) and hydrogen scrambling occur directly from the excited state. This is qualitatively explained by a theoretical treatment [4] of the singlet hypersurfaces of ethylene, showing two conical intersections, in which the excited singlet state of ethylene can go directly either to singlet vinylidene + H_2 or to singlet ethylidene (CH_3CH:). Both of these carbene species have essentially no barriers to isomerization to HCCH or ethylene respectively [5,6]. The latter is the route for deuterium scrambling. The mechanism for deuterium scrambling by direct photolysis (Eq. (2a)) is different from that for mercury sensitization or sensitization by other triplet sensitizers (${}^3S^*$) (Eq. (2b)) [7]. In Eq. (2a), the 1,2-H shift occurs along a surface initially in the electronically excited singlet state, which becomes ground state after

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passing through the conical intersection region. However, in Eq. (2b), the isomerization to $^1\mathrm{CHD_2CH:}^\dagger$ occurs in the ground state by another trajectory.

$$^1\mathrm{D_2CCH_2^*} \rightarrow {}^1\mathrm{CHD_2CH:}^\dagger \leftrightarrow {}^1\mathrm{CHD{=}CHD}^\dagger \tag{2a}$$

$$^3\mathrm{S^*} + {}^1\mathrm{D_2CCH_2} \rightarrow {}^3\mathrm{D_2CCH_2^\dagger} \leftrightarrow {}^1\mathrm{D_2CCH_2^\dagger} \leftrightarrow {}^1\mathrm{CHD_2CH:}^\dagger \tag{2b}$$

In the region of these conical intersections, the excited state can also relax adiabatically to the ground state surface producing a hot ground state species. The vinyl + H channel (Eq. (3a)) has been predicted theoretically [4] to occur only from a hot ground state species and not directly from the excited state. In this model, $^1\mathrm{D_2CCH_2^\dagger}$ can also be generated as an energized species with enough energy to convert to $^1\mathrm{CHD_2CH:}^\dagger$ prior to being thermalized by bimolecular collisions.

With regard to the generation of the $\mathrm{H_2C{=}CH + H}$ diradical pair via the triplet state, this can occur in two ways (Eqs. (3b) and (3c)).

$$^1\mathrm{C_2H_4^*} \rightarrow {}^1\mathrm{C_2H_4^\dagger} \rightarrow \mathrm{H_2C{=}CH + H} \tag{3a}$$

$$^3\mathrm{C_2H_4^*} \rightarrow {}^1\mathrm{C_2H_4^\dagger} \rightarrow \mathrm{H_2C{=}CH + H} \tag{3b}$$

$$^3\mathrm{C_2H_4^\dagger} \rightarrow \mathrm{H_2C{=}CH + H} \tag{3c}$$

Molecular beam experimental work also yields evidence that a four-centred 1,2-elimination of H_2 from ethylene to give acetylene occurs directly. In the ground state surface, the transition state yielding this pathway is of second order [5] with an energy 125.5 kcal mol^{-1} above ethylene. In addition, this particular pathway has not yet been examined theoretically to see whether the excited state surface approaches the ground state in the manner predicted by Woodward–Hoffman rules. Indeed, this may be a complication in the calculations reported [5] and needs reinvestigation.

The singlet photochemistries of the higher olefins are more complicated and suggestive of occurrence, for the most part, through hot ground state intermediates [1]. It is unlikely that any theoretical studies will be reported in the near future on the excited singlet hypersurfaces of higher olefins, because of their orbital size and the methodological difficulties in treating electronically excited singlet state species (especially with geometry optimization) having the same symmetry as lower energy species. However, the treatment of the lowest triplet state hypersurfaces can be computed using geometry optimizations at the unrestricted Hartree–Fock (UHF) level, but further corrected at the correlative level using Moller–Plesset theory [5]. As will be shown here, major portions of the ground state singlet surface can also be calculated using currently available standard methodologies.

Another advantage of studying theoretically the triplet photochemistries of the olefins is that the initial energies encountered are lower (112.7 kcal mol^{-1} using Hg) than those species generated by direct photolysis (approximately 150 kcal mol^{-1}). The lower energy photolysis reduces the number of structures and processes which need to be considered. For instance, in the case of the Hg-sensitized photochemistry (112.7 kcal mol^{-1}) of ethylene, only the generation of acetylene + H_2 is observed plus intramolecular deuterium scrambling and cis–trans isomerization. Triplet sensitizers with even lower energies can be used, in which case only isomerization and scrambling are observed [7,8], a procedure which can aid in the estimation of the threshold energies of some of the processes which occur and have not been reported in pyrolysis chemistry (made complicated by secondary reactions).

The complication in the analysis of the triplet photochemistry of olefins involves the determination of how the final reaction channels are achieved: either from triplet intermediates or from hot singlet ground state species generated from intersystem crossing. As argued previously [4] and outlined below, the triplet-sensitized photochemistry of ethylene, yielding HCCH + H_2 and deuterium scrambling, involves hot ground state singlet processes. We argue for a similar mechanism in propylene. We do not discuss cis–trans isomerization, since it is an event which occurs thermally in the case of deuterated ethylenes and propylenes in the singlet state. Since the minima of triplet ethylene and propylene are both twisted, isomerization is direct and occurs during the relaxation of these species from their Franck–Condon geometries.

2. Technical aspects

The computational investigation of the triplet species is easier than that of electronically excited singlet states for several reasons. First of all, only one low-lying triplet species is likely to exist in the small olefins and this species should be valence π–π^* in character [9]. This allows a calibrated ab initio method to be employed: the bond additivity correction (BAC) method of Melius and coworkers [10]. The BAC method yields heats of formation generally accurate to within several kilocalories per mole. The BAC method also judges the accuracy of its own estimate of each value obtained. This can be contrasted with semiempirical methods which have an average error of 6–9 kcal mol^{-1} and give no warning of the dubious nature of a particular value. Both BAC and semiempirical methods are calibrated to known experimental values, although BAC is more precise.

The GAUSSIAN 94 program was employed [11] for the quantum mechanical part of the calculations. The geometries were optimized at the 6-31G* SCF closed shell or UHF open shell level and tested for the necessary number of positive force constants for minima (all) and transition states (one negative). Using work stations, most of the structures reported here were easily computed. (Structural details are not published here. However, e-mail access to the GAUSSIAN archive files is provided by contacting either ev@liliput.lct.jussieu.fr or gdemare@ulb.ac.be.) The BAC program uses as input the frequency GAUSSIAN archive file calculated at the 6-31G* level, and the MP4 archive file calculated at the 6-31G**//6-31G* levels. All singlet structures were tested for restricted Hartree–Fock (RHF) stability using the Stable = opt key word in GAUSSIAN 94. If the solution was unstable, a UHF singlet broken symmetry calculation was performed and included as a third BAC archive file. The BAC program does a spin correction of the BAC enthalpy. This correction may be important in some of the UHF calculations of the doublet and triplet species. However, it also occurs in the UHF singlets. SCF instabilities are encountered in species such as singlet ethylidene and vinylidene. These spin corrections can be as much as 6–7 kcal mol^{-1} in certain cases. The species which are SCF unstable are noted in the tables. Both programs were used on IBM/6000 work stations.

3. Results and discussion

3.1. Ethylene

Table 1 shows the BAC heats of formation for 16 species. The order shown below ethylene itself represents ascending energy. If triplet Hg was placed in this table, its energy of 112–113 kcal mol^{-1} would place it in relative energy at 124 kcal mol^{-1}, roughly around that of vinyl + H. Any species having a higher energy than this could not be generated in the Hg-sensitized photochemistry of ethylene, except by bimolecular triplet–triplet annihilation yielding excited singlet ethylene.

Since the BAC method was calibrated using a certain number of known structures, the fact that H, H_2, ethylene and acetylene are accurately estimated within the ± 1.0 kcal mol^{-1} precision estimated by the program is not surprising. Since, to our knowledge, the BAC method has not been used previously to estimate triplet species for which the singlet ground states are much more stable, the computed heat of formation of the twisted ethylene triplet of 79 ± 1.0 kcal mol^{-1} may be a first attempt at this kind of evaluation. A rough "experimental" guess of this value is difficult, but we can assign a value of 78 kcal mol^{-1} by assuming that the twisted triplet and twisted ground state singlet of ethylene (the latter is a transition state for thermal cis–trans isomerization) have about the same energy.

Another verification of the validity of the BAC method is the estimate of 71 kcal mol^{-1} for the heat of formation of the vinyl radical, which is within 1 kcal mol^{-1} of the experimental values and computes the bond energy in ethylene at 110 kcal mol^{-1} (as proposed in the literature [16–18]). However, there is another recent estimate at 116.7 ± 1.2 kcal mol^{-1} [18]. This value would revise the experimental heat of formation of the vinyl radical to 77.1 kcal mol^{-1}, which is outside the error range of the BAC value of 71 ± 3.5 kcal mol^{-1}. The vinyl radical is highly spin contaminated, and variations in the intermediate Moller–Plesset energy produce this uncertainty (±3.5 kcal mol^{-1}) in the estimate of the precision of BAC. Similar uncertainties are present in the BAC heats of formation of the ethylidene singlet, as well as several other structures shown in Table 1. However, examination of Table 1 gives the impression that the heats of for-

Table 1
BAC heats of formation (kcal mol^{-1}) for the ethylene series

Structure	$\Delta H_{f,300}$	Estimated error[a]	Experimental or estimated
H	52.1	0	52.1[b]
H_2	0.0	1.0	0
${}^1H_2C{=}CH_2$ (ground state singlet)	12.3	1.0	12.5[b]
${}^1HCCH$	54.2	1.0	54.2[b]
${}^3C_2H_4$ (π,π^* triplet)	79.2	1.9	78[c]
${}^3CH_3CH$	84.1[a]	1.7	
${}^1CH_3CH$	88.0	3.5	95 or lower, see text
${}^1H_2C{=}C$	100.0[a]	1.5	
TS, ${}^1C_2H_4 \rightarrow {}^1H_2C{=}C + H_2$	112.5	2.5	[d]
${}^2H_2C{=}CH$	71.0	3.5	72[e], 70[f]
(${}^2H_2C{=}CH + H$)	(123.1)	3.5	(122.5[g], 129.2[h])
${}^1CH_3CH \rightarrow {}^1HCCH + H_2$	126.8	3.4	
TS, ${}^3C_2H_4 \rightarrow {}^3CH_3CH$	130.7	1.8	
TS, ${}^3C_2H_4 \rightarrow {}^2H_2C{=}CH + H$	130.9	1.6	
${}^3H_2C{=}C$	146.0	3.7	
${}^3HCCH$	145.5	1.4	

[a] Corrected for UHF singlet instability.
[b] Ref. [12].
[c] Ref. [13]. The cis–trans isomerization barrier is assumed to produce a singlet diradical which is degenerate with the triplet.
[d] The BAC archives give a value of 110.4 kcal mol^{-1} (see also Ref. [14] for the same value).
[e] Ref. [15]. BAC archives give the same value as reported here. This is also the case for ethylene, acetylene, H_2 and H.
[f] Ref. [16].
[g] Ref. [17].
[h] Ref. [18].

mation estimated are good to within several kilocalories per mole. Normally this precision would be good enough, except for the fact that the C–H bond energy in ethylene is in the region of the energy of the species generated by energy transfer from excited Hg (112.7 kcal mol^{-1}). Since the vinyl + H channel is not seen in this photochemistry, its non-appearance may be taken as a measure of the lower limit of the ethylene C–H bond energy. However, we show that Eqs. (3a)–(3c) have different thresholds; a barrier occurs in the triplet surface giving vinyl + H.

The first item of note is that the triplet states of both acetylene and vinylidene are computed to be much too high for generation in mercury-sensitized photochemistry. In addition, the formation of vinyl + H is barely at the energy of the energized triplet or hot ground state ethylene generated by energy transfer from Hg. Several other processes seem more definitely excluded. First, the direct generation of acetylene + H_2 from singlet ethylidene rather than ethylene has a much higher activation energy (transition state (TS), $\Delta H_{f,300} = 126$ kcal mol^{-1} vs. 112.5 kcal mol^{-1}). The lower channel to obtain these products is that passing through the vinylidene intermediate at 112.5 kcal mol^{-1}, a full 10 kcal mol^{-1} below the energy of the species generated by energy transfer from excited mercury. However, to achieve both of these channels, triplet ethylene would have to undergo intersystem crossing to singlet ethylene. The threshold for the vinylidene + H_2 channel is, in energy terms, just above whatever species is generated by benzene triplet sensitization ($^3S^* = 84$ kcal mol^{-1}) of ethylene. Therefore the vinylidene + H_2 channel is not available below 100 kcal mol^{-1} above the ground state of ethylene and, indeed, is not observed experimentally. However, the calculations show that the generation of singlet and triplet ethylidene is energetically possible by energy transfer from triplet benzene ($^3S^* \equiv$ benzene triplet, Eq. (2b)). These species are computed to lie at 76 and 72 kcal mol^{-1} above ground state ethylene respectively. Therefore the experimentally observed scrambling of deuterium using benzene triplet as a sensitizer is theoretically possible.

The possibility that deuterium scrambling occurs via triplet ethylidene has been raised previously [4], but the position of the transition state was not characterized energetically with any precision in previous computations [19–22]. The relaxed triplet state of ethylene has a heat of formation of 79 kcal mol^{-1} (Table 1). The transition state computed here has a heat of formation of 130.7 ± 1.8 kcal mol^{-1} which constitutes a barrier of 52 kcal mol^{-1} and, in any case, places this isomerization, in energy terms, above that available by Hg or benzene sensitization. Any deuterium scrambling in the triplet-sensitized photochemistry almost certainly comes from singlet ethylidene via $^1C_2H_4^{\ddagger}$. Earlier work on triplet ethylidene [19,20] gave barrier estimates for triplet ethylidene isomerization to ethylene triplet varying from 24 to 83 kcal mol^{-1}, while Harding's [21] SOGVB/6-31G**/3-21G value of 53 kcal mol^{-1} is close to that estimated here.

The very high barrier for the $^3C_2H_4 \rightarrow {}^3CH_3CH$ transformation can be attributed to the two unpaired electrons on the carbene site occupying different orbitals. This 1,2-H shift is topologically identical with the 1,2-H shift in the ethyl radical: the moving H atom migrates towards an orbital space already having one electron. On the other hand, in both ethylidene singlet and vinylidene, the H atom moves towards unoccupied electron space, conceptually equivalent to the 1,2-H shift in the ethyl cation in which the "transition state" is actually more stable than the open form of the species [5]. The ethyl radical and ethylidene triplet isomerisations can be classed as radical transfers (three-electron orbital space), while the ethylidene singlet and vinylidene isomerizations are hydride transfer in character (two-electron space). The BAC barrier computed for the 1,2-H shift (TS, $\Delta H_{f,300} = 71.1$ kcal mol^{-1}) in the ethyl radical ($\Delta H_{f,300} = 28.8$ kcal mol^{-1}) is 42.3 kcal mol^{-1}. However, deuterium scrambling in the thermal heating of CD_3CH_2 would be small since the lower energy channel gives $D_2C{=}CH_2 + D$ ($\Delta H_{f,300} = 67.3$ kcal mol^{-1} for the transition state). This latter channel is also looser and therefore entropically favoured.

In the case of ethylene, there is no barrier for the incoming channel, H + vinyl → $^1C_2H_4$ [23]. This is generally true for radical–radical recombinations yielding singlet structures. However, this is not generally true along the triplet diradical surfaces, since the two interacting radicals (R and R′) possess electrons having the same spin. The $R\uparrow \, \uparrow R'$ interaction is repulsive along the initial portions of the incoming channel $R\uparrow + \uparrow R'$. Indeed, for the interaction $H\uparrow + \uparrow HC{=}CH_2$, which will eventually create a C–H bond in triplet ethylene, there must be a barrier, and the transition state must twist around the double bond to obtain the final structure of triplet ethylene (Fig. 1(a)). This is why the transition state for $^3C_2H_4 \rightarrow {}^2H_2C{=}CH + H$, at 130.9 kcal mol^{-1}, is higher than the biradical limit of $^2H_2C{=}CH + H$ (123.1 kcal mol^{-1}). This distorted transition state for triplet-to-radical pair transformations will also be encountered in the case of propylene.

It should be finally pointed out that the energies of the singlet species dealt with here are approximately in agreement with the directly computed MP4/6-31G** values [5].

3.2. Propylene

3.2.1. Pyrolysis

Table 2 shows approximately 20 species and transition states discussed here. As in the case of Table 1, any heats of formation found in the literature are in good agreement with the BAC values. The estimated BAC error (±4.2 kcal mol^{-1}) for the allyl radical is much larger than evident by comparison with the experimental values (±1 kcal mol^{-1}). However, in either case, this presents no problem in the following analysis.

A complete theoretical treatment of the propylene hypersurface, even with regard to its thermal chemistry, is not possible using the SCF/UHF methodologies employed here. In particular, the cyclopropane → propylene isomerization

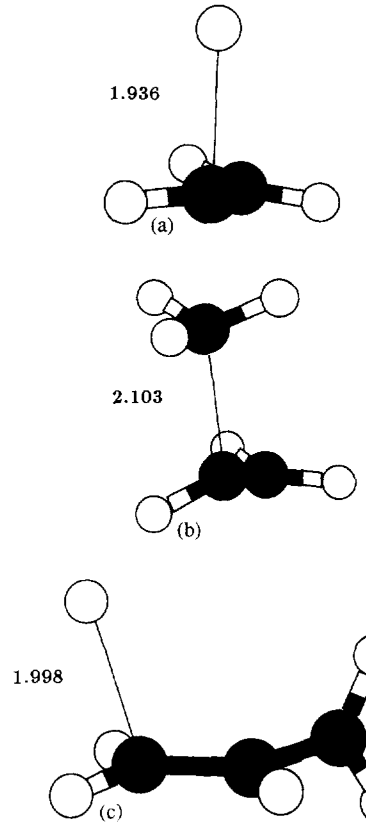

Fig. 1. (a) Transition state for triplet ethylene giving vinyl radical + H atom. (b) Transition state for triplet propylene giving methyl radical + vinyl radical. (c) Transition state for triplet propylene giving allyl radical + H.

should only be treatable at the MCSCF level. However, the BAC procedure is not calibrated at the MCSCF multireference MP level. In spite of this significant problem, we address ourselves to some aspects of the proposed pyrolysis mechanism as recently analysed in a shock tube study [24].

The shock tube study proposes four principal unimolecular initiating reactions

$$ {}^1C_3H_6 \rightarrow CH_3 + CH{=}CH_2 \qquad (4)$$

$$ {}^1C_3H_6 \rightarrow H + \text{allyl} \qquad (5)$$

$$ {}^1C_3H_6 \rightarrow CH_4 + HCCH \qquad (6)$$

$$ {}^1C_3H_6 \rightarrow H_2 + C_3H_4 \qquad (7)$$

Eqs. (4) and (5) have been proposed in previous pyrolysis studies [25]. Eq. (4) (11%) and Eq. (5) (89%) constitute the major components of the mercury-sensitized decomposition of propylene [1,26], together with a minor amount of cyclopropane. The generation of a minor amount (4%) of CH_4 occurs in direct photolysis, depending on the excitation energy [1]. From Table 2, we can compute the threshold activation enthalpies (300 K) of Eqs. (4)–(7) at 100.6, 85.6, 120.2 and 100.3 kcal mol^{-1} respectively. Eqs. (4) and (5) should lack a recombination barrier [23,27]. This will also be the case for the singlet surface recombinations of propen-1-yl and propen-2-yl with H, which have higher threshold enthalpies (111.6 and 107.8 kcal mol^{-1} respectively) than the allyl + H or CH_3 + vinyl fragmentations. The shock tube study attributes threshold enthalpies (0 K) of 99.8 and 85.3 kcal mol^{-1} to Eqs. (4) and (5) with high pressure activation energies of 88 and 80 kcal mol^{-1} respectively. The high pressure activation energies of Eqs. (6) and (7) are assigned at 73.8 and 80 kcal mol^{-1} respectively. Similarly, the activation energy for ethylene → $H_2 + C_2H_2$ is assigned a value of 77 kcal mol^{-1}, which is significantly lower than the enthalpy barrier of 100 kcal mol^{-1} discussed here. The shock tube kinetic modelling is essentially a fitting process and the values of these activation energies cannot be fully compared with the work discussed here. Nevertheless, it is evident that Eq. (6), as calculated here, has a much higher activation energy than that attributed in the pyrolysis model. There may be other channels for the generation of CH_4 + HCCH, in particular a 1,2-elimination process from propylene and not the propylidene singlet. Even so, it must be said that the lack of appearance of this channel photochemically, except in much higher energy photolyses, tends to support the hypothesis that the CH_4 + HCCH channel threshold is at much higher energies than proposed in the shock tube study.

3.2.2. Photochemistry

Eqs. (4) and (5) are open, loose channels, whereas Eqs. (6) and (7) have tight, well-defined transition states. Our calculations indicate that Eqs. (4), (5) and (7) can occur in the mercury-sensitized photochemistry of propylene if ${}^3C_3H_6^\ddagger \rightarrow {}^1C_3H_6^\ddagger$ intersystem crossing occurs. As for direct access to Eqs. (4) and (5) from ${}^3C_3H_6^\ddagger$ along a triplet surface to the respective triplet biradical pairs, the transition states for these processes (Figs. 1(b) and 1(c)) have barriers, as in the case of ${}^3C_2H_4^\ddagger \rightarrow H + C_2H_3$. The triplet surfaces for allyl + H and CH_3 + vinyl have barrier enthalpies of 107.3 and 114.8 kcal mol^{-1} respectively above ground state propylene. The latter value marginally excludes the occurrence of cleavage to CH_3 + vinyl in the mercury-sensitised triplet photochemistry of propylene. Therefore the ${}^3C_3H_6$ species exists in a deep valley compared with these two triplet exit channels. These exit channels have tight transition states and energies in the same region as the ${}^3C_3H_6^\ddagger$ species generated by energy transfer from excited Hg. Qualitatively, we expect that the ${}^3C_3H_6^\ddagger$ species will have a reasonably long lifetime (tunnelling effects excluded) and plenty of time to undergo intersystem crossing to ${}^1C_3H_6^\ddagger$.

Therefore the critical problem in deciding whether the product-forming stages in the triplet photochemistry of propylene occur from ${}^3C_3H_6^\ddagger$ or ${}^1C_3H_6^\ddagger$ revolves around the experimental confirmation of the isomerization channels. If the product-forming reacting species is ${}^1C_3H_6^\ddagger$, the threshold enthalpy for the formation of allyl + H is calculated from the BAC heats of formation in Table 2 at 85.6 kcal mol^{-1}. The methyl + vinyl radical channel is 100.6 kcal mol^{-1} (observed experimentally), but the isoenergetic channel, decomposition to $CH_3CH{=}C{:} + H_2$ (100.6 kcal mol^{-1}) is not reported. Both the singlet 1,2-H isomerization through 1-propylidene (77.6 kcal mol^{-1}, but no minimum on the surface as in the case of ethylidene) and the singlet 1,3-H isomerization to regenerate propylene (83.5 kcal mol^{-1}) are sufficiently close energetically to the allyl + H singlet channel (85.6 kcal mol^{-1}) to be competitive in the dynamics of ${}^1C_3H_6^{\ddagger}$ generated either by Hg or lower energy sensitizers. In the case of benzene, only the isomerization channels are available.

One experimental study on the sensitization (benzene, Hg, Cd) of *cis*- and *trans*-propylene-1,3,3,3-d_4 [28] shows no deuterium scrambling. However, another study [29] on *cis*-propylene-1-d_1 shows both propylene-2-d_1 and propylene-3-d_1 formation, in the ratio of one to five, independent of the propylene pressure. In the latter study, the formation of propylene-2-d_1 could not be successfully rationalized, but the formation of propylene-3-d_1 was attributed to the recombination of H + allyl-1-d_1, yielding $CH_2{=}CH{-}CH_2D$. An alternative possibility proposed here is the intervention of 1,2- and 1,3-isomerizations in the intramolecular dynamics of ${}^1C_3H_6^{\ddagger}$. The problem with this hypothesis is the lower energy of the 1-propylidene singlet structure, which can be dynamically sampled in the dynamics of ${}^1C_3H_6^{\ddagger}$ (although no minimum on the hypersurface). However, this should favour 1,2- over 1,3-scrambling, the latter having a tighter transition state and being higher in energy. The investigation of the effect of sensitizer energies on these possible channels may clarify the situation. One of the missing elements in the analysis of the behaviour of ${}^1C_3H_6^{\ddagger}$ is the lack of sufficient computational knowledge of the cyclopropane–singlet trimethylene diradical surface and the 1,2-H transition state energetics taking these species to propylene. The experimental activation energy for the isomerization of cyclopropane to propylene is about 78 kcal mol^{-1} above ground state propylene (see Table 2, [13]). A 1,2-H shift must take place and qualitatively is in this same energy region.

The final question concerns the possibility of 1,2-H and 1,3-H scrambling when ${}^3C_3H_6^{\ddagger}$ is the product-forming species. Firstly, as in the case of triplet ethylene–ethylidene, the transition state for ${}^3C_3H_6^{\ddagger} \rightarrow {}^3CH_3CH_2CH$ has a barrier of 49.6 kcal mol^{-1}, which places it above the energy of the ${}^3C_3H_6^{\ddagger}$ species obtained from mercury sensitization. Thus 1,2-deuterium scrambling is ruled out by this pathway. Another 1,2-H transfer can give ${}^3C_3H_6 \rightarrow {}^3CH_2CH_2CH_2$, yielding a triplet biradical with an activation enthalpy of 107.9 kcal mol^{-1} above propylene. This energy is barely accessible by mercury sensitization. This radical can then undergo intersystem crossing to the singlet diradical ${}^1CH_2CH_2CH_2$, which can undergo ring closure to give cyclopropane. Cyclopropane is seen in the triplet photochemistry of propylene as a minor product [26]. Its formation can also be rationalized from ${}^1C_3H_6^{\ddagger}$ as discussed above. Triplet 1,3-H transfer taking triplet propylene back to triplet propylene has an activation enthalpy of 112.0 kcal mol^{-1} above the propylene ground state, which is essentially the energy of the species generated by mercury sensitization and appears even less probable than 1,2-H transfer in the triplet state. The triplet fragmentation barrier to

Table 2
BAC heats of formation (kcal mol^{-1}) for the propylene series

Structure	$\Delta H_{f,300}$	Estimated error[a]	Experimental or estimated
${}^2CH_3$	34.9	1.2	34.8, 35.1[b]
Propylene, ${}^1C_3H_6$	5.3	1.2	4.9[c]
Cyclopropane	10.2	1.5	12.7[c]
Propylene, ${}^3C_3H_6$	72.5	2.0	
${}^3CH_2CH_2CH_2$ (diradical)	74.7	2.0	≈ 78[d]
${}^3CH_3CH_2CH$ (1-propylidene)	78.8	1.7	
TS, ${}^1C_3H_6 \rightarrow {}^1CH_3CH_2CH$	80.4	1.1	
${}^1CH_3CH_2CH$	82.9[a]	3.4	
Allyl, ${}^2C_3H_5$	38.8	4.2	39.1[b]
(Allyl + H)	(90.9)		(91.2)[b]
TS, 1,3-H transfer, ${}^1C_3H_6 \leftrightarrow {}^1C_3H_6$	88.8[a]	4.7	
TS, ${}^1C_3H_6 \rightarrow {}^1CH_3CH{=}C{:} + H_2$	105.9	2.1	
(${}^2CH_3 + {}^2CH_2CH$)	(105.9)		(105.5)[b]
(TS, ${}^3C_3H_6 \rightarrow {}^2C_3H_5$(allyl) + H)	112.6	2.9	
${}^2CH_3C{=}CH_2$, propen-2-yl	61.0	3.5	
(${}^2CH_3C{=}CH_2 + H$)	(113.1)		
TS, 1,2-H transfer, ${}^3C_3H_6 \rightarrow {}^3CH_2CH_2CH_2$	113.2	1.6	
${}^2CH_3CH{=}CH$, *cis*-propen-1-yl	64.7	3.5	
(${}^2CH_3CH{=}CH + H$)	(116.9)		
TS, 1,3-H transfer, ${}^3C_3H_6 \leftrightarrow {}^3C_3H_6$	117.3	1.6	
TS, ${}^3C_3H_6 \rightarrow {}^2CH_3 + {}^2CH_2CH$	120.1	2.5	
TS, ${}^3C_3H_6 \rightarrow {}^3CH_3CH_2CH$	122.1	1.6	
${}^1CH_3CH_2CH \rightarrow CH_4 + {}^1HCCH$	125.5[a]	5.1	

[a] Corrected for UHF singlet instability.
[b] Ref. [17].
[c] Ref. [12].
[d] Ref. [13]. If we assume that the ring opening of cyclopropane goes through a species close in structure to a singlet diradical and that the singlet and triplet are nearly degenerate. The recommended E_a value is 65.5 kcal mol^{-1}, above the ground state of cyclopropane.

allyl + H lies at a lower energy, i.e. 107.3 kcal mol^{-1} above the propylene ground state.

The major difference between ethylene and propylene is that the latter has an H loss channel about 25 kcal mol^{-1} lower in energy. In addition, in propylene, this H loss channel is in near energetic competition with the isomerization channels. Dynamically, we expect scrambling to occur more easily in the case of ${}^1C_2H_4^\dagger$ than ${}^1C_3H_6^\dagger$.

4. Conclusions

The study presented here tends to support the hypothesis that the mercury-sensitized photochemistry of both ethylene and propylene is dominated by hot ground state species. Because of the high barriers encountered for both bond breaking along the triplet surfaces and isomerization, the triplet states are likely to undergo intersystem crossing to give rise to ${}^3C_2H_4^\dagger \rightarrow {}^1C_2H_4^\dagger$ and ${}^3C_3H_6^\dagger \rightarrow {}^1C_3H_6^\dagger$. All the other processes occur from these vibrationally excited ground state species.

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