

Dimethylcarbene versus Direct Propene Formation in Dimethylketene Photodissociation

Published as part of *The Journal of Physical Chemistry virtual special issue "125 Years of The Journal of Physical Chemistry"*.

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Cite This: <https://doi.org/10.1021/acs.jpca.1c03641>



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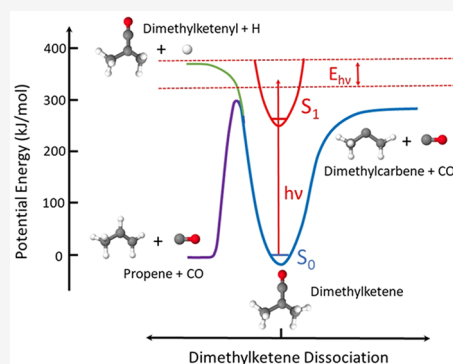


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ABSTRACT: Highly reactive carbenes are usually produced by photolysis of ketenes, diazoalkanes, or diazirines. Sequential kinetic pathways for deactivation of nascent carbenes usually involve bimolecular reactions in competition with isomerization producing stable products such as alkenes. However, the direct photolytic production of stable products, effectively bypassing formation of free carbenes, has been postulated for over 50 years but remains very poorly understood. Often termed “rearrangement in the excited state” (RIES), examples include 1,2-hydrogen migration within photoexcited carbene precursors yielding alkenes and the Wolff rearrangement in photogenerated carbonyl-substituted carbenes producing ketenes. In this study, the two competing CO elimination channels from photoexcited gaseous dimethylketene, producing dimethylcarbene and propene, were studied as a function of electronic excitation energy, under collision-free conditions, by using photofragment translational energy spectroscopy with vacuum ultraviolet photoionization of the products. A significant fraction of the dimethylcarbene \rightarrow propene isomerization exothermicity (~ 300 kJ/mol) was released as propene + CO translational energy, indicating that propene is formed prior to or concurrent with CO elimination. An increase in the propene yield with increasing excitation energy suggests that the effective potential energy barrier for this channel lies ~ 24 kJ/mol above the energetic threshold for dimethylcarbene formation via C=C bond fission. Possible mechanisms for direct propene elimination are discussed in light of the observed energy dependence for the competing pathways.



1. INTRODUCTION

With only six valence electrons at their reactive carbon centers, carbenes exhibit rich chemistry that is distinctly different for the singlet and triplet electronic states.^{1,2} Methylene (CH_2), the simplest carbene, has been the focus of extensive experimental and theoretical studies over many decades and is now well-characterized.^{3,4} In marked contrast, even the observations of free alkyl-substituted carbenes such as methylcarbene (CH_3CH)^{5–8} and dimethylcarbene (CH_3CCH_3)^{9–12} remain experimentally challenging. The paucity of experimentally derived insight pertaining to alkyl-substituted carbenes is attributable to their extremely short lifetimes due to rapid isomerization to alkenes by a 1,2-hydrogen shift.^{5–17} Theoretical studies predict a very small (~ 4 kJ/mol) potential energy barrier for isomerization of singlet methylcarbene to ethylene.⁷ However, for free dimethylcarbene, the analogous potential energy barrier is thought to be somewhat higher, with calculated values ranging from 10 to 31 kJ/mol.^{9,13,14,18}

Methylene possesses a triplet ground electronic state, having its two unpaired electrons residing in separate orbitals with parallel spins,^{3,4} with the spin-paired singlet state lying higher

in energy by ~ 38 kJ/mol.⁴ For methylcarbene, also known as ethylidene, the methyl substituent reduces the singlet–triplet energy gap to ~ 12.5 kJ/mol, with the triplet remaining the ground state.^{19,20} In dimethylcarbene, also known as methylethylidene, the second methyl group further stabilizes the singlet, now making it the ground state, with the excited triplet believed to lie ~ 10 kJ/mol higher in energy.^{20,21} Dimethylcarbene thus represents the simplest alkyl-substituted carbene with a highly reactive²² singlet ground electronic state configuration.

Diazoalkanes, or their more stable cyclic alkyldiazirine isomers, produce alkyl-substituted carbenes via N_2 elimination following electronic excitation.^{23–29} However, because of the high enthalpies of formation and relatively short-wavelength electronic absorption features of the parent molecules, the

Received: April 22, 2021

Revised: July 8, 2021

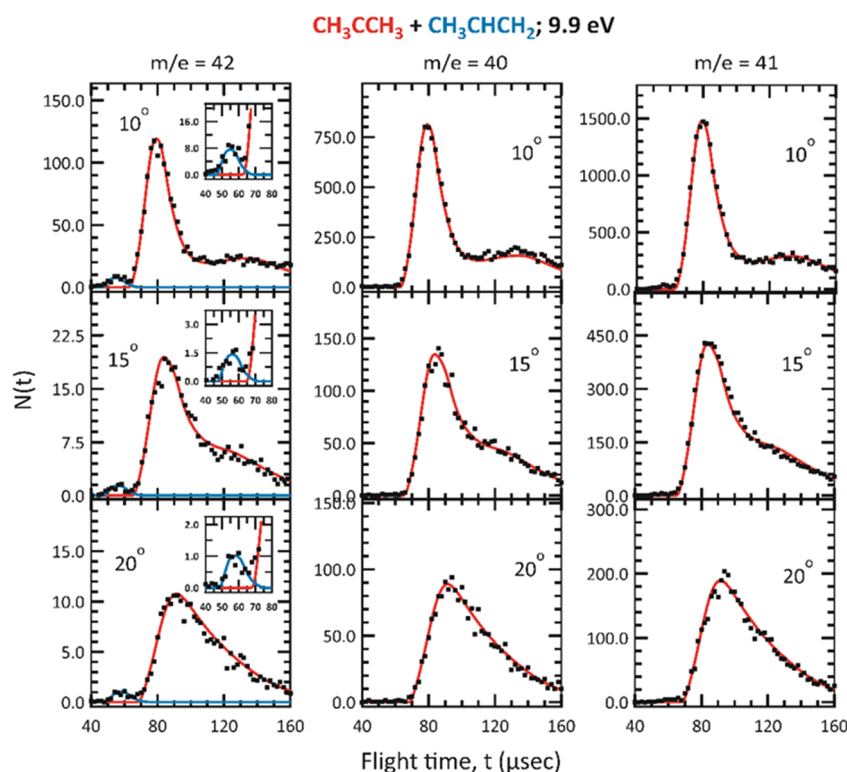


Figure 1. TOF spectra for products from 355.1 nm photodissociation of dimethylketene at indicated laboratory angles with 9.9 eV photoionization of neutral products: black dots are experimental data, red lines are calculated TOFs for the dimethylcarbene + CO channel, and blue lines are calculated TOFs for the direct propene + CO channel. The relevant $P(E)$ s are shown in Figure 2.

carbene products, if produced, are very highly internally excited and rapidly isomerize to alkenes, which typically lie ~ 300 kJ/mol (~ 3 eV) lower in energy than ground state carbenes.²⁰ The well-established, “conventional” kinetic mechanism after electronic excitation of stable precursors involves free carbene production followed by isomerization to alkenes.^{5–18} However, beginning with the earliest studies in the 1960s,^{24,25} “isomerization concurrent with N_2 loss” has been frequently hypothesized^{11,17,24–31} with the acronym “rearrangement in the excited state” (RIES), often used to denote photoinduced processes involving carbene precursors bypassing formation of free carbenes.³² The most extensively studied examples in which RIES is thought to occur include 1,2-hydrogen migration in alkyl-substituted carbene precursors forming alkenes^{9,11,17,26} and the photoinduced Wolff rearrangement in α -carbonyl-substituted carbene precursors.^{30,31} A number of theoretical studies^{33–36} as well as ultrafast time-resolved experiments^{26–28,37} have addressed the role of possible concerted and stepwise pathways for alkene production. Some of this work has led to the conclusion that alkyl-substituted diazirines are inefficient photolytic sources of alkyl-substituted carbenes due to predominant direct formation of alkenes via RIES.^{9,38} However, we note that several subsequent theoretical studies have not supported the RIES mechanism in these diazirine systems.^{23,29,33} Owing to the potential importance of dimethylcarbene in organic synthesis,³⁹ complex non-nitrogenous precursors for dimethylcarbene have been synthesized.³⁸ However, rather surprisingly, there have been no studies of the near-UV photochemistry of dimethylketene, a potentially important and convenient source of dimethylcarbene, following the early studies performed more than 50 years ago.^{40,41}

Recently, we reported that gas phase photolysis of the simplest alkyl-substituted ketene, methylketene, leads to production of stable triplet ethylidene, which was detected directly for the first time via photoionization mass spectrometry.⁸ The relatively low enthalpy of formation of methylketene (as compared to diazoethane and methyldiazirine), in part, helped facilitate production of stable ethylidene. By analogy, photolysis of dimethylketene is expected to produce dimethylcarbene, as is confirmed by the present work. In addition, we characterize the direct formation of propene via RIES as a function of excitation energy.

2. RESULTS AND ANALYSIS

We studied the photodissociation of gaseous dimethylketene using photofragment translational energy spectroscopy at four near-UV excitation wavelengths: 320.0, 340.0, 355.1, and 371.0 nm.^{8,42,43,45} A molecular beam containing dimethylketene, diluted to $\sim 1\%$ in helium, was crossed with a pulsed nanosecond near-UV laser in a vacuum chamber held at pressures below 1×10^{-6} Torr with the beam running.⁸ The neutral photodissociation products scattered out of the molecular beam and drifted with their nascent velocities 15.2 cm to a liquid nitrogen cooled detector ($P < 10^{-10}$ Torr) where they were photoionized at 9.9 or 8.8 eV by using a high-intensity pulsed vacuum-ultraviolet (VUV) laser.⁴³ The positive ions were mass selected by a quadrupole mass filter and detected as a function of their arrival times by scanning the delay of the VUV laser. The molecular beam source was rotatable relative to the fixed detector; in each experiment the product time-of-flight (TOF) spectra were measured for various product m/e values at several different angles between the beam and detector axes.⁸

2.1. Excitation at 355.1 nm. In Figure 1, the TOF spectra are shown for products detected at $m/e = 40$, 41, and 42, with the beam source set to the indicated angles relative to the detector axis, for photodissociation of dimethylketene at 355.1 nm. The corresponding product translational energy distributions, $P(E)$ s, derived from an iterative forward-convolution analysis of the TOF data (see the Supporting Information and ref 8 for details) are illustrated in Figure 2. At $m/e = 42$,

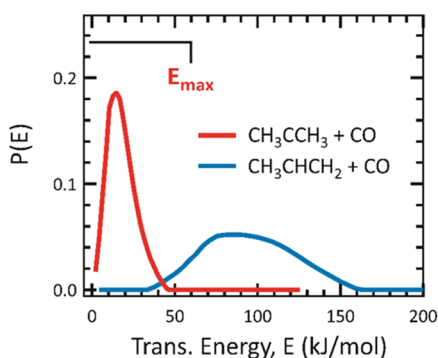


Figure 2. Translational energy distributions, $P(E)$ s, for the dimethylcarbene + CO channel in red and direct propene + CO channel in blue, from 355.1 nm photodissociation of dimethylketene. The maximum thermodynamically allowed translational energy for dimethylcarbene + carbon monoxide, calculated from theoretical enthalpies of formation, is indicated. The corresponding maximum thermodynamically allowed translational energy for the propene + CO channel is 342 kJ/mol.

corresponding to the parent ion of dimethylcarbene or propene (C_3H_6), two features are evident, exhibiting significantly different photoionization characteristics and translational energy distributions. At $m/e = 40$ and 41, only a single feature was observed, which was the same as the lower translational energy component of the $m/e = 42$ TOF, indicating that it resulted from secondary daughter ion fragments.

The experimental data at 355.1 nm can be interpreted with the aid of the schematic potential energy diagram shown in Figure 3. By analogy to ketene photodissociation, which has

been studied extensively both experimentally^{44,45} and theoretically,⁴⁶ the initially prepared, electronically excited (S_1) dimethylketene can undergo internal conversion to the ground singlet state, S_0 , which subsequently undergoes C=C bond fission to produce ground state singlet dimethylcarbene (denoted as CH_3CCH_3) plus CO with no potential energy barrier expected in excess of the bond dissociation energy.

The calculated maximum energetically allowed relative translational energy for the dimethylcarbene + CO channel is $E_{max} = 60$ kJ/mol at 355.1 nm excitation. As described in the Supporting Information, this maximum value was calculated by using the known photon energy and the 0 K enthalpies of formation of dimethylketene,^{47,48} dimethylcarbene,²⁰ and CO.²⁰ This calculated maximum corresponds to the limiting case in which all energy in excess of the C=C bond dissociation energy appears as $CH_3CCH_3 + CO$ relative translational energy.

The experimental $m/e = 41$ and 40 TOF spectra for the dimethylcarbene channel were simulated by using the same $P(E)$ distribution employed for $m/e = 42$ (Figure 2, red curve), demonstrating that the 9.9 eV photon induced fragmentation to $m/e = 41$ and 40 daughter ions through H and H_2 loss is not strongly dependent upon the internal energy of the neutral parent. The $m/e = 40$ and 41 daughter ion signal intensities were approximately a factor of 7 and 13, respectively, greater than the parent ions at $m/e = 42$. Significant fragmentation of dimethylcarbene (or highly vibrationally excited propene produced by isomerization of dimethylcarbene) upon 9.9 eV photoionization is expected on the basis of experimental and calculated thermodynamic quantities associated with the isomers of C_3H_6 , $C_3H_6^+$, and its daughter ions.^{20,49}

Isomerization of *free* dimethylcarbene to propene encounters a potential energy barrier calculated to lie between 10 and 31 kJ/mol.^{9,13,14,18} The degree to which free dimethylcarbene isomerizes to produce highly vibrationally excited propene during transit to the detector will depend upon its vibrational energy and the nature of the potential energy barrier for the 1,2-hydrogen shift. However, even for dimethylcarbene vibrational levels lying below the classical isomerization barrier, quantum mechanical tunneling is likely to be operative.⁵⁰ From the known isomerization exothermicity and relatively narrow

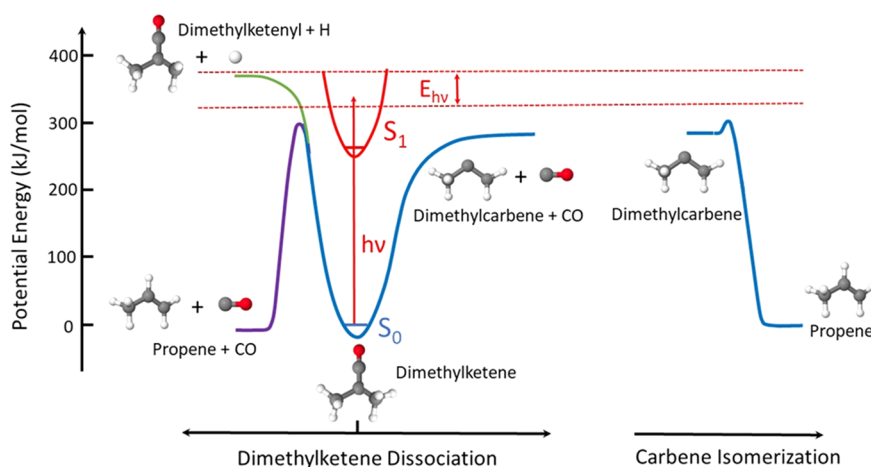


Figure 3. Potential energy diagram for dimethylketene dissociation producing dimethylcarbene + carbon monoxide. Propene can be subsequently formed through a sequential pathway involving carbene isomerization via 1,2-hydrogen migration. Alternatively, propene + carbon monoxide can be produced via a direct reaction mechanism effectively bypassing formation of free dimethylcarbene. The higher energy C–H bond fission channel producing dimethylketenyl radicals + H is also shown.

range of dimethylcarbene vibrational energies (inferred from the $P(E)$ shown in Figure 2), any propene molecules produced by isomerization from dimethylcarbene will have vibrational energies ranging from 296 to 340 kJ/mol. Because the calculated potential energy barrier heights for all possible unimolecular dissociation channels on the C_3H_6 PES,⁵¹ including H and H_2 elimination, exceed 340 kJ/mol, all nascent C_3H_6 (dimethylcarbene or propene) products observed in this experiment must be stable with respect to spontaneous unimolecular dissociation.

From the translational energy distribution shown in Figure 2, the most probable relative translational energy for the recoiling $CH_3CCH_3 + CO$ products is ~ 10 kJ/mol. From energy conservation, the remaining ~ 50 kJ/mol must be channeled into internal (electronic, vibrational, and rotational) energy of the $CH_3CCH_3 + CO$ products. Owing to the relatively high energy (26 kJ/mol) for CO ($v = 1$), the degree of CO vibrational excitation is expected to be small, similar to ketene photodissociation at 308 nm where only 2% of the CO correlated to singlet methylene is produced in $v = 1$.⁵² Because rotational excitation of the dimethylcarbene + CO products is also likely to be modest due to the near-zero exit impact parameter for C=C bond fission, the excess energy will be partitioned primarily into CH_3CCH_3 vibrational energy.

The high translational energy components of the $m/e = 42$ TOF spectra (Figures 1 and 2, blue lines) correspond to C_3H_6 products formed by CO elimination with relative translational energies significantly greater than the energetically calculated maximum (60 kJ/mol) for production of $CH_3CCH_3 + CO$. The maximum observed translational energy release for this channel was ~ 160 kJ/mol, with a most probable value of ~ 80 kJ/mol. The photoionization signals for this channel also differ significantly from those for dimethylcarbene. Most notably, this channel produces negligible daughter ions at $m/e = 41$ or 40, indicating that H and H_2 loss does not occur significantly upon 9.9 eV photoionization. As illustrated in Figure S2 of the Supporting Information, photoionization at 8.8 eV produces signals at $m/e = 42$ corresponding to only the dimethylcarbene channel, with no evidence for this higher translational energy component. From laser power dependence studies (see the Supporting Information), we confirmed experimentally that all signals result exclusively from single-photon absorption. Furthermore, from the dependence of this signal on the delay of the photodissociation laser relative to the pulsed valve, we verified that these contributions result from dissociation of dimethylketene parent monomers, not from van der Waals dimers or larger clusters.

Based on the considerations noted above, the high translational energy component at $m/e = 42$ must correspond to formation of lower energy C_3H_6 isomers (relative to dimethylcarbene). We assign this product channel to direct formation of propene + CO following electronic excitation of the parent dimethylketene molecule. This assignment is consistent with the known adiabatic ionization energy²⁰ of propene (9.72 eV) and is further supported by the 8.8 eV data, which shows that the direct propene channel is not detected by using 8.8 eV photoionization. While cyclopropane is also thermodynamically accessible from CH_3CCH_3 , it requires migration of two H atoms followed by ring closure, which is expected to be significantly less favorable.

The relatively high translational energy released for the propene + CO channel, reflecting the large exothermicity for isomerization to propene, requires that propene is formed

before or concurrent with CO elimination. Measurement of the product relative translational energy distributions thus provides definitive evidence for direct propene formation in the photodissociation of dimethylketene, effectively bypassing formation of free dimethylcarbene. In Figure 3, the direct propene channel is illustrated arising via a conventional "tight" transition state on the ground potential energy surface. The higher energy C–H bond fission channel producing dimethylketenyl + H, predicted by theoretical calculations, is also indicated.⁵³ Additional photochemical channels involving CH_3 elimination (nearly isoenergetic with H atom elimination)⁵³ and isomerization to methacrolein (energetically open)⁵³ are not included in Figure 3.

In the 355.1 nm photodissociation of dimethylketene, the ratio of measured TOF signals for the dimethylcarbene channel recorded at m/e values of 42:41:40 by using 9.9 eV photoionization was found to be approximately 1:13:7. In contrast, the direct propene channel yielded products exclusively detected at the parent mass, $m/e = 42$. Therefore, only $\sim 5\%$ of the neutral dimethylcarbene products yield parent ions at $m/e = 42$ upon photoionization at 9.9 eV, whereas this value is $\sim 100\%$ for propene.

If the relative photoionization cross sections at 9.9 eV were known, the absolute product yields for the two competing channels could be derived, under the reasonable assumption that no other photophysical processes (e.g., fluorescence) are operable in ketenes at excitation energies well above threshold for dissociation.⁴⁶ Unfortunately, the relative photoionization cross sections for the two $m/e = 42$ products at 9.9 eV are not presently known. At 9.9 eV, however, the photoionization cross section for propene (IE = 9.7 eV)²⁰ is expected to be smaller than for dimethylcarbene (IE = 7.7 eV).²⁰ Owing to the very large difference in ionization energies, the 9.9 eV photoionization cross sections could differ by a significant factor, perhaps as much as 10. Although we plan to carry out future experiments to determine absolute quantum yields for the competing pathways, for the present purposes, we define the "relative propene yield" as follows:

$$\text{relative propene yield} = \frac{\phi_{\text{pr}}}{\phi_{\text{pr}} + \phi_{\text{dmc}}} \quad (1)$$

where (i) ϕ_{pr} is the experimentally obtained branching fraction for propene + CO, derived from fitting the observed propene photoproducts in the $m/e = 42$ TOFs (detected by using 9.9 eV photoionization), uncorrected for the 9.9 eV propene photoionization cross section and the propene fragmentation pattern and, similarly, (ii) ϕ_{dmc} is the experimentally obtained branching fraction for dimethylcarbene + CO, derived from fitting the observed dimethylcarbene photoproducts in the $m/e = 42$ TOFs (detected by using 9.9 eV photoionization), uncorrected for the 9.9 eV dimethylcarbene photoionization cross section and dimethylcarbene fragmentation pattern. For this determination, the forward-convolution analysis program (see the Supporting Information) specifically accounts for the different inherent detection sensitivities for the two channels resulting from the different Jacobian factors associated with the CM \rightarrow LAB transformations.

The relative propene yield provides the simple means to quantify the propene yield relative to that for dimethylcarbene as a function of excitation energy. Based on our signal-to-noise ratios, for photodissociation of dimethylketene at 355.1 nm, corresponding to an excitation energy of 337 kJ/mol, the

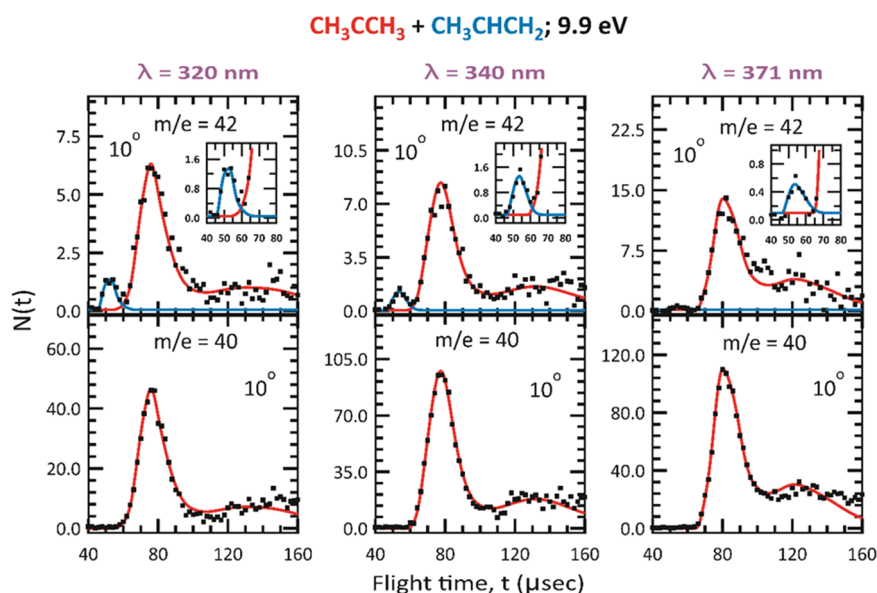


Figure 4. TOF spectra for $m/e = 42$ and 40 products from 320, 340, and 371 nm photodissociation of dimethylketene at 10° by using 9.9 eV photoionization of neutral products: black dots are experimental data, red lines are calculated TOFs for $\text{CH}_3\text{CCH}_3 + \text{CO}$ channel, and blue lines are calculated TOFs for propene + CO. The translational energy distributions are shown in Figure 5.

relative propene yield is 0.16 ± 0.03 and that for dimethylcarbene is 0.84 ± 0.03 .

2.2. Excitation at 320.0, 340.0, and 371.0 nm. To complement our study at 355.1 nm ($E_{hv} = 337$ kJ/mol), we performed a series of analogous photodissociation experiments at three additional wavelengths: 320.0, 340.0, and 371.0 nm. These wavelengths correspond to photon energies of 374, 352, and 322 kJ/mol, respectively. As described in the Supporting Information, using the enthalpies of formation for reactants and products, we calculated the 0 K dissociation energy producing dimethylcarbene + carbon monoxide to be ~ 276 kJ/mol. Because the internal energy of the jet-cooled parent dimethylketene molecules is negligible, the four wavelengths employed in this study together span a range of excitation energies lying between 46 and 98 kJ/mol above the calculated energetic threshold for production of singlet dimethylcarbene + carbon monoxide.

In Figure 4, the TOF spectra recorded at $m/e = 42$ and 40 at a laboratory angle of 10° for the three additional excitation wavelengths are plotted. We also recorded $m/e = 41$ data, which were very similar to those reported above for 355 nm. The associated product translational energy distributions, which vary with the initial excitation wavelengths, are shown in Figure 5. Additional experimental TOF data and calculated TOF spectra based on the $P(E)$ distributions recorded at other laboratory angles are provided in the Supporting Information. At 340.0 nm, the relative propene yield increased to 0.25 ± 0.03 , with this quantity increasing further to 0.32 ± 0.03 at 320 nm. For the experiments conducted at 371.0 nm, on the other hand, a significant decrease in the relative yield for the propene + CO channel was observed compared to that at 355.1 nm, with the relative propene yield falling to 0.10 ± 0.03 . The measured relative propene yield is plotted as a function of photon energy in Figure 6. Because the measured fragmentation patterns for the two product channels are approximately constant for different photoexcitation wavelengths, the relative propene yields at each excitation wavelength are proportional

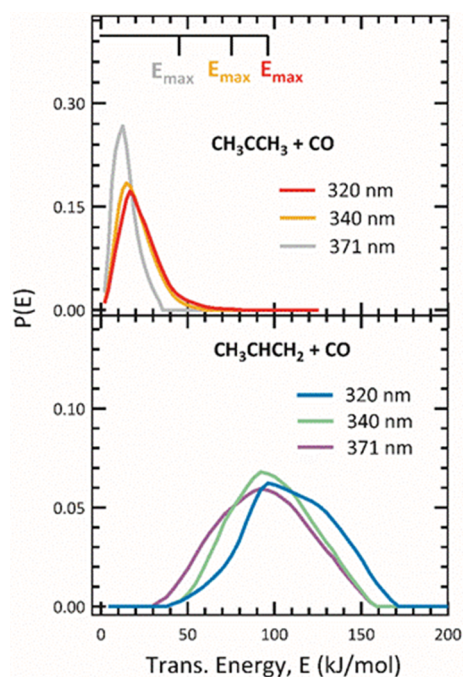


Figure 5. Top: translational energy distributions for the dimethylcarbene + CO channels at indicated excitation wavelengths. Calculated maximum thermodynamically allowed translational energies are indicated. Bottom: translational energy distributions for the direct propene + CO channels at indicated wavelengths.

to the absolute quantum yields to be determined in future work.

3. DISCUSSION

The electronic absorption spectrum of dimethylketene is continuous over the range of wavelengths studied (see Figure S1). By analogy to the well-known photochemistry of ketene, this absorption corresponds to excitation to the S_1 excited state of dimethylketene.⁴⁶ Because no additional optically bright

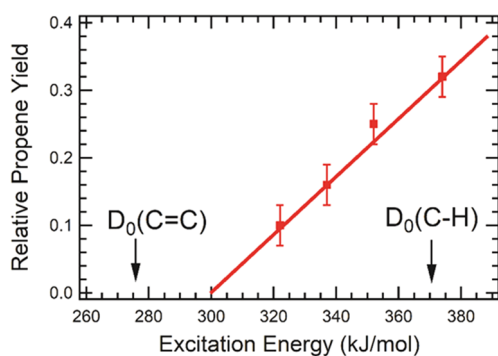


Figure 6. Plot of relative propene yields vs excitation energy for the four photodissociation wavelengths used in this study. The uncertainties in the measurements are indicated by the error bars. The extrapolation of the straight line to zero yield suggests an effective potential barrier for propene formation near 300 kJ/mol. The calculated energy threshold for C=C bond fission forming dimethylcarbene + CO is ~ 276 kJ/mol, and the C–H bond dissociation energy in dimethylketene forming dimethylketenyl + H is 371 kJ/mol.

excited states are expected in ketenes in this energy range, the strongly wavelength-dependent yield of the propene channel, increasing 3-fold upon increasing the total excitation energy from 322 to 374 kJ/mol, reflects a 3-fold increase in the propene yield following initial excitation to S_1 .

There have been no previous experimental or theoretical studies pertaining to direct alkene formation in the photodissociation of alkyl-substituted ketenes. Instead, most previous work has been on the photochemistry of diazoalkanes or alkyldiazirines,^{5–37} with the primary focus being the occurrence of H migration forming alkenes (RIES) or CO migration forming ketenes (Wolff rearrangement). As noted earlier, the term RIES (rearrangement in the excited state) has been applied to photoinduced reactions forming stable molecules, bypassing formation of free carbenes. The earliest evidence for RIES was that the photochemical product distributions in many cases differed from those produced via thermal decomposition.^{9,16} Additional evidence for RIES was based on the observation of stable alkene products at concentrations in excess of those expected from chemically trappable carbene intermediates.^{9–11,26,27} Correlations between the yields of products from RIES with bond energies in studies of a series of related molecules also provided support for a reaction mechanism bypassing the formation of free carbenes.^{11,26} More recently, in a number of time-resolved experiments, the observation of final products on subpicosecond time scales, which are much shorter than those for free carbene formation and decay, was taken as evidence for RIES in production of stable alkenes via concerted rearrangements.^{11,27–29} Studies of the Wolff reaction have similarly provided convincing evidence for concerted and stepwise processes.^{30,31,37}

A recurring question underlying the theoretical studies of the photochemistry of carbene precursors is whether dissociation occurs directly on an excited state (e.g., S_1), or via the ground state (S_0) following internal conversion.^{23,33–36} It has frequently been concluded that due to the presence of conical intersections, there exists efficient routes for rapid nonradiative transfer of population from initially prepared excited electronic states (S_1 or S_2) to the ground state, S_0 , of the parent molecules. For example, Bernardi and co-workers²³ found that

the calculated potential energy barriers for RIES on S_1 and S_0 were large for dimethyldiazirine, whereas internal conversion to was likely to be efficient due to the presence of conical intersections. They favored a stepwise mechanism, involving CO loss followed by rearrangement of free dimethylcarbene to propene, in direct contrast with conclusions from earlier experiments that RIES plays an important role in the decomposition of dimethyldiazirine.^{9,10}

We examined the dependence of the signal intensity from the two product channels as a function of incident laser polarization (see Figure S7). No polarization dependence was observed, indicating that the product angular distributions are spatially isotropic (with the anisotropy parameter, $\beta = 0.0 \pm 0.1$) relative to the electric vector of the incident laser beam.⁵⁴ Such behavior in the photodissociation of polyatomic molecules is often taken as evidence for dissociation lifetimes that are long relative to the picosecond time scales for parent rotation.⁵⁴ For ketene photodissociation, internal conversion to S_0 occurs prior to dissociation,⁴⁶ leading to dissociation time scales much longer than for dissociation on excited state surfaces.⁵⁵ For example, measured dissociation time scales ranged from 1.0 ns at excitation energies lying 6 kJ/mol above threshold to 19 ps at energies 67 kJ/mol above threshold.⁵⁶ Consequently, product angular distributions from ketene photodissociation are spatially isotropic.⁵² Analogous to the well-established behavior in ketene,⁴⁶ C=C bond fission producing singlet dimethylcarbene + CO is expected to occur on S_0 . Our finding that the direct propene angular distributions are spatially isotropic suggests that RIES also proceeds on S_0 for dimethylketene. However, the spatial anisotropy of the propene products might be reduced due to the occurrence of H atom migration prior to CO elimination. This could lead to product recoil at angles significantly different from those expected from the direction of the transition dipole moment, potentially reducing the product spatial anisotropy.⁵⁴ Thus, while we believe the propene channel also occurs on S_0 , reaction on S_1 cannot be entirely ruled out. Clearly, theoretical calculations on the ground and excited state PESs for dimethylketene dissociation, including potential energy barrier heights for direct and sequential propene formation via isomerization of dimethylcarbene, would provide important insight into the dissociation mechanism(s).

As noted above, the term RIES has been applied to a range of photochemical mechanisms in which formation of free carbenes is bypassed.^{11,12,16,17,27–29,32} In some of the experimental studies, RIES appears to compete with fluorescence¹¹ or with decay of transient excited species,^{27,29} thereby pointing to the involvement of electronically excited surfaces. However, recent quantum dynamics calculations on the closely related Wolff rearrangement in carbenes demonstrated that concerted and sequential reactions can involve both excited and ground state dynamics.^{34–36} In the parent carbene precursors, extended seams of conical intersections can efficiently funnel initial electronically excited populations to different regions of the ground state potential energy surface, thereby producing highly vibrationally excited molecules on S_0 that can decay via multiple reaction pathways.^{34–36,57} Because these ground state levels can be produced with highly nonstatistical vibrational populations, their reaction dynamics may differ significantly from those involving thermally excited ensembles.⁵⁷ Decay to the ground state via conical intersections can occur very rapidly,^{34–36} and product branching ratios need not be in accord with statistical

expectations.⁵⁷ Indeed, concerted unimolecular decomposition and isomerization on ground state PESs following internal conversion via conical intersections is a frequent occurrence in gas phase photochemistry.⁵⁸ From these considerations, we suggest that the term RIES remains appropriate even for rearrangement processes bypassing carbenes proceeding on S_0 , recognizing that the “excited state” may be highly reactive vibrationally excited levels of S_0 .

As illustrated in Figure 6, the relative yields for the propene + CO channel increased ~ 3 -fold, from 0.10 ± 0.03 at 322 kJ/mol to 0.32 ± 0.03 at 374 kJ/mol. As discussed in the Supporting Information, the 0 K thermodynamic threshold for C=C bond fission in dimethylketene producing dimethylcarbene + CO is ~ 276 kJ/mol, corresponding to an excitation wavelength of 433 nm. As illustrated in Figure S1, this wavelength threshold lies very close to the red edge (band origin) of the $S_0 \rightarrow S_1$ absorption spectrum. Because no potential energy barrier for dissociation on S_0 is expected above $D_0(\text{C}=\text{C})$, dissociation to form dimethylcarbene + CO is the dominant dissociation channel at $\lambda > 371$ nm.

The sharp increase in the relative yields for the propene channel appears at energies well above the calculated energetic threshold for simple C=C bond fission. From the energy dependence of the relative propene yield (Figure 6), the effective potential energy barrier for RIES in dimethylcarbene appears to lie near 300 kJ/mol, i.e., ~ 24 kJ/mol above $D_0(\text{C}=\text{C})$. Although some uncertainty exists in the 0 K C=C bond dissociation energy of 276 kJ/mol (calculated in the Supporting Information), our calculated $D_0(\text{C}=\text{C})$ is essentially identical with that reported recently in a theoretical study.⁵³ As shown in Figure 3, the 24 kJ/mol gap is close to the barrier for isomerization in free dimethylcarbene calculated in several previous theoretical studies.^{9,13,14,18}

The increase in direct propene formation at energies above the calculated $D_0(\text{C}=\text{C})$ might be interpreted in terms of a conventional “tight” transition state for concerted rearrangement (RIES) in dimethylketene. As discussed above, the isotropic polarization angular distributions and strong S_1/S_0 coupling in ketenes⁴⁶ points to the involvement of highly vibrationally excited levels of S_0 . The tight transition state for direct propene formation could correspond to a 1,2-H atom shift in dimethylketene with concurrent CO elimination via C=C bond fission. Although calculations on the $\text{C}_4\text{H}_6\text{O}$ PES have been carried out, the primary focus was on methacrolein, and only the simple bond fission channels involving dimethylketene were explored.⁵³ In ketene photodissociation, the transition states for the C=C bond fission on S_0 tighten with increasing excitation energy above threshold.⁵⁹ This dynamical bottleneck for the carbene channel, combined with possible nonstatistical dynamics due to S_1/S_0 conical intersections and/or quantum mechanical tunneling, may underlie the interesting energy dependence for the occurrence of RIES observed in this study.

Alternatively, the apparent onset of the direct propene channel at energies above $D_0(\text{C}=\text{C})$ might reflect the opening of a more complex unimolecular reaction mechanism. The potential energy barrier for isomerization of dimethylketene to methacrolein by a 1,3-H atom shift has been calculated to lie near 282 kJ/mol⁵³ and is therefore energetically accessible at the excitation wavelengths of this study. After isomerization to methacrolein, direct propene + CO formation can occur via a calculated potential energy barrier lying 344 kJ/mol above dimethylketene.⁵³ We also note that by analogy to the

photodissociation of formaldehyde (H_2CO) or acetaldehyde (CH_3CHO), H atom or CH_3 roaming mechanisms might potentially play a role in the direct propene + CO channel.^{60,61}

It is instructive to compare dimethylketene photodissociation to the dissociation dynamics of methylketene, which we recently reported produces stable triplet methylcarbene + carbon monoxide.⁸ For methylketene dissociation, the measured translational energy distributions for the competing ethylene + carbon monoxide products reflected the thermodynamics for the singlet ethylidene channel, with none of the exoergicity (~ 300 kJ/mol) of the 1,2-hydrogen shift appearing as relative product translational energy.⁸ This was clear evidence that the 1,2-hydrogen atom shift observed in methylketene was sequential, proceeding after departure of the CO molecule. The absence of RIES in methylketene photodissociation thus contrasts the behavior reported here for dimethylketene. This marked difference is likely to be a consequence of the different multiplicities of the potential energy surfaces for the reactions. For methylketene, dissociation to ground state triplet ethylidene + CO likely occurs on the low-lying triplet electronic surface of the parent molecule, on which H atom migration is expected to encounter a significant potential energy barrier. On the other hand, dissociation of dimethylketene to ground state singlet dimethylcarbene proceeds on the singlet ground state surface of the parent molecule, where a relatively low effective potential energy barrier facilitates direct propene formation via RIES.

4. CONCLUSIONS

Measurements of product translational energy distributions from the CO elimination channels in dimethylketene photodissociation facilitated a study of the competition between C=C bond fission producing dimethylcarbene and direct formation of propene via RIES. By carrying out studies over a range of excitation wavelengths in the gas phase, the role of initial excitation energy was probed under well-defined conditions, without the complicating factors of solvent. The relative yields for the propene channel from dimethylketene photodissociation increased sharply at excitation energies well above the threshold for the competing C=C bond fission channel producing carbenes. This indicates that the effective potential energy barrier for propene formation via RIES lies ~ 24 kJ/mol above $D_0(\text{C}=\text{C})$.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c03641>.

A detailed description of the experimental methods and analysis techniques; UV–vis absorption spectrum of gaseous dimethylketene; incident laser power dependence study for direct propene and dimethylcarbene photoproducts at 355.1 nm; TOF spectrum of dimethylcarbene product at 355.1 nm by using 8.8 eV photoionization; calculated fits for experimental TOF spectra at additional laboratory angles at 320.0, 340.0, and 371.0 nm; laser polarization dependence for direct propene and dimethylcarbene photoproducts at 355.1 nm; and calculations for determining the thermodynamically allowed maximum translational energy release (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-FG02-00ER15095.

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