Letter

Direct Observation of Ethylidene (CH$_3$CH), the Elusive High-Energy Isomer of Ethylene

Sagnik Datta and H. Floyd Davis*

Read Online

ACCESS | Metrics & More | Article Recommendations | SI Supporting Information

ABSTRACT: Despite experimental efforts spanning more than 80 years, there has been no direct observation of free ethylidene (CH$_3$CH), the simplest alkyl-substituted carbene. Here, we report that ethylidene is indefinitely stable in the absence of collisions if produced in the triplet ground state at energies below the threshold for intersystem crossing. Near-UV photolysis of gaseous methylketene, or propenal (followed by isomerization to methylketene), leads to CO loss producing triplet ethylidene, which is detected by photoionization mass spectrometry. Electronically excited singlet ethylidene is also produced, rapidly undergoing isomerization by a 1,2-hydrogen atom shift, producing highly vibrationally excited ethylene. The measured product translational energy distributions verify the theoretically calculated enthalpy of formation of triplet ethylidene and are consistent with a singlet−triplet energy gap of approximately 12.5 kJ/mol.
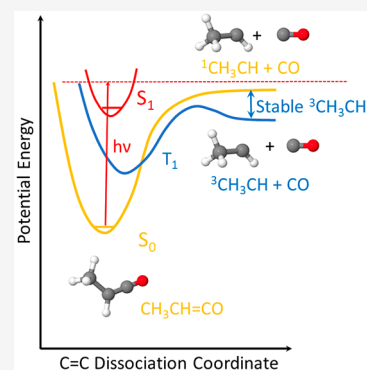
Chemists have long been fascinated by molecules exhibiting extreme reactivity and unconventional bonding. Among the most elusive organic molecules is ethylidene (CH$_3$CH), with a calculated enthalpy of formation about 300 kJ/mol (∼3 eV) above ethylene (CH$_2$=CH$_2$).[1] An early attempt at the production of ethylidene (also called methylcarbene), by Rice and Glasebrook in 1934, involved the thermal decomposition of diazoethane (CH$_3$CHN$_2$).[2] From their study, it was concluded that if formed, ethylidene is a transient species "of exceedingly short life", likely isomerizing rapidly to ethylene. Despite many experiments over the next eight decades, there remains no direct observation of ethylidene in the gas, liquid, or solid phases.[3−10]

As the simplest carbene capable of isomerization by a 1,2-hydrogen atom shift, ethylidene holds special importance as a prototypical short-lived species in organic chemistry.[3−11] It is thought to be produced from reactions of oxygen atoms with unsaturated hydrocarbons[12] and is initially formed by insertion of C(^{1}D) into CH$_4$.[13] Ethylidene has also been observed as a chemically bound species in surface chemistry experiments[14] and as a ligand in transition-metal complexes.[15]

The stability of ethylidene and the prospects for its observation have been topics of considerable interest.[3−10] Although early theoretical studies suggested an isomerization barrier of 0 kJ/mol,[1,16,17] i.e., that singlet ethylidene is a transition state for hydrogen scrambling in ethylene, some subsequent studies indicated that ethylidene represents a true local minimum on the singlet C$_2$H$_4$ potential energy surface.[5−10]

Several previous experiments have provided indirect evidence for ethylidene's existence. Seburg and McMahon photolyzed diazoethane in low temperature (8 K) inert gas matrices and suggested that a fraction of nascent ethylidene could be trapped through reaction with CO, prior to isomerization.[3] Similarly, in experiments involving the photolysis of deuterated 3-methyldiazirine in pentane solutions containing pyridine, Modarelli and Platz observed an ethylidene-d_4-pyridine ylide formed through a bimolecular addition reaction.[4]

Unlike most molecules, carbenes possess two nearby low-lying electronic states of different spin multiplicities, singlet and triplet, exhibiting distinct chemical and physical properties.[18−20] Although no experimental values exist for the enthalpies of formation for the singlet or triplet states of ethylidene, theoretical calculations predict that the singlet lies ∼12.5 kJ/mol above the triplet ground state.[1,21] In contrast to electronically excited singlet ethylidene (^{1}CH$_3$CH), the height of the potential energy barrier for 1,2-H atom migration in triplet ethylidene (^{3}CH$_3$CH) to produce "twisted triplet ethylene" has been calculated to be large (∼180 kJ/mol).[1,22] However, due to the close energetic proximity of the excited singlet state, it has been suggested that rapid intersystem crossing to the singlet surface could render observation of triplet ethylidene impossible.[17]
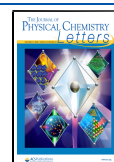
The near-UV photodissociation of ketene (CH$_2$CO) producing both singlet and triplet methylene (CH$_2$) plus carbon monoxide (CO) has been studied extensively, both theoretically[23] and experimentally.[20,24] By analogy, electronic excitation of methylketene might be expected to produce CH$_3$CH + CO. Early kinetics studies revealed that C$_2$H$_4$ + CO were among the primary stable products and that ethylidene is likely formed initially.[25] Although methylketene can be readily synthesized, it spontaneously dimerizes on a time scale of hours at −60 °C, rendering experiments requiring long data accumulation times quite difficult. This prompted our investigation of the photodissociation of propenal (CH$_2$═CHCHO, also known as acrolein), an isomer of methylketene, which has only been studied previously at higher excitation energies.[26−30]

We carried out parallel studies of the photodissociation of gaseous methylketene and propenal, using photofragment translational energy spectroscopy, at several UV excitation wavelengths. The theoretically calculated adiabatic ionization energy of ground state triplet ethylidene, yielding a parent ion at m/e = 28, is 8.51 eV.[21] This is much lower than the ionization energies of ethylene (10.5 eV) or carbon monoxide (14.0 eV), which also yield parent ion signals at m/e = 28.

A gaseous molecular beam, containing the parent molecule diluted (∼2%) in helium, was crossed by a pulsed UV laser in a rotatable source crossed molecular beams apparatus.[31−33] The neutral recoiling photofragments drift ∼15 cm out of the beam to a mass spectrometer detector (P < 1 × 10^{-10} Torr), where they are photoionized at either 8.8 or 9.9 eV using a high-intensity pulsed laser, mass selected, and counted. This provides a nearly background-free means for detection of ethylidene.

In Figure 1, the time-of-flight (TOF) spectra for photodissociation of methylketene at 355.1 nm, with the beam source angle set at 10° from the detector axis, are shown as solid dots. The superimposed solid lines are simulated TOF spectra, calculated using the indicated translational energy distributions $[P(E)]$ and known apparatus parameters (see Supporting Information). Applying the law of conservation of energy to the photodissociation of methylketene, the total energy of the excited parent molecule in excess of the dissociation energy must be channeled into internal energy (rotational, vibrational, and electronic) of the CH$_3$CH + CO products and into relative translational energy.[20]

As illustrated in Figure 2, electronically excited (S$_1$) methylketene can undergo intersystem crossing to the lowest triplet state (T$_1$), either directly or via S$_0$, which dissociates over a small potential energy barrier[27] to produce ^{3}CH$_3$CH + CO. The high translational energy component of the m/e = 28 TOF spectra (Figure 1, blue line) corresponds to stable ^{3}CH$_3$CH detected as the parent ion (CH$_3$CH$^+$) at m/e = 28 using 8.8 or 9.9 eV photoionization, or to a very minor extent as m/e = 26 (C$_2$H$_2^+$) daughter ions at 9.9 eV.

A second photodissociation channel was observed, yielding products detected at m/e = 28 or 26 with lower translational energies and distinctly different photoionization characteristics, simulated with orange lines in Figure 1. Products from the second channel are very weakly detectable at m/e = 28 using 8.8 eV photoionization, but they are observed at 9.9 eV at m/e = 28 and also yield very strong daughter ion signals at m/e = 26. By analogy to the well-studied production of singlet methylene from ketene photodissociation,[23,24] this second channel is attributed to formation of electronically excited
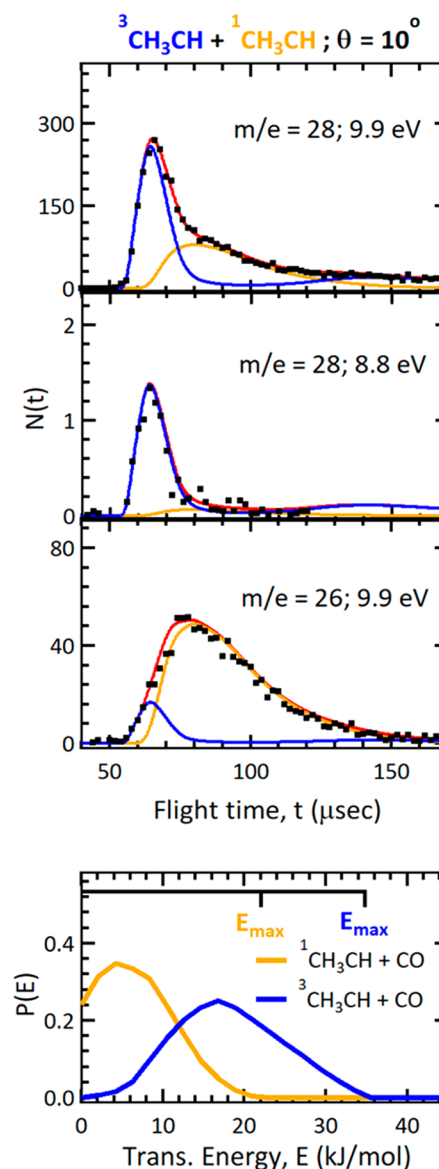

Figure 1. Upper: TOF spectra (10°) for indicated product masses from 355.1 nm photodissociation of methylketene. Solid black dots are experimental data; blue lines are calculated TOF spectra for ^{3}CH$_3$CH + CO, and orange lines are for ^{1}CH$_3$CH + CO channels. Red lines are the overall calculated TOF spectra. Lower: $P(E)$ distributions for the two corresponding product channels that are used to calculate the TOF spectra. E_{max} values are calculated maximum translational energies based on known photon energy and theoretically calculated enthalpies of formation of methylketene and products.

singlet ethylidene. The singlet and triplet ethylidene channels both contribute to all of the TOF spectra in Figure 1; only the relative contributions differ. The singlet ethylidene products undergo a 1,2-H atom shift to form highly vibrationally excited (∼3 eV) ethylene, which is the corresponding final product detected in the experiment. Although the ionization energy of vibrationally cold ethylene is 10.5 eV, due to the high level of vibrational excitation (∼3 eV) imparted to ethylene from the 1,2-H atom shift, photoionization proceeds readily at 9.9 eV, producing C$_2$H$_4^+$ parent ions detectable at m/e = 28 and a significant yield of C$_2$H$_2^+$ secondary daughter ions (m/e = 26)
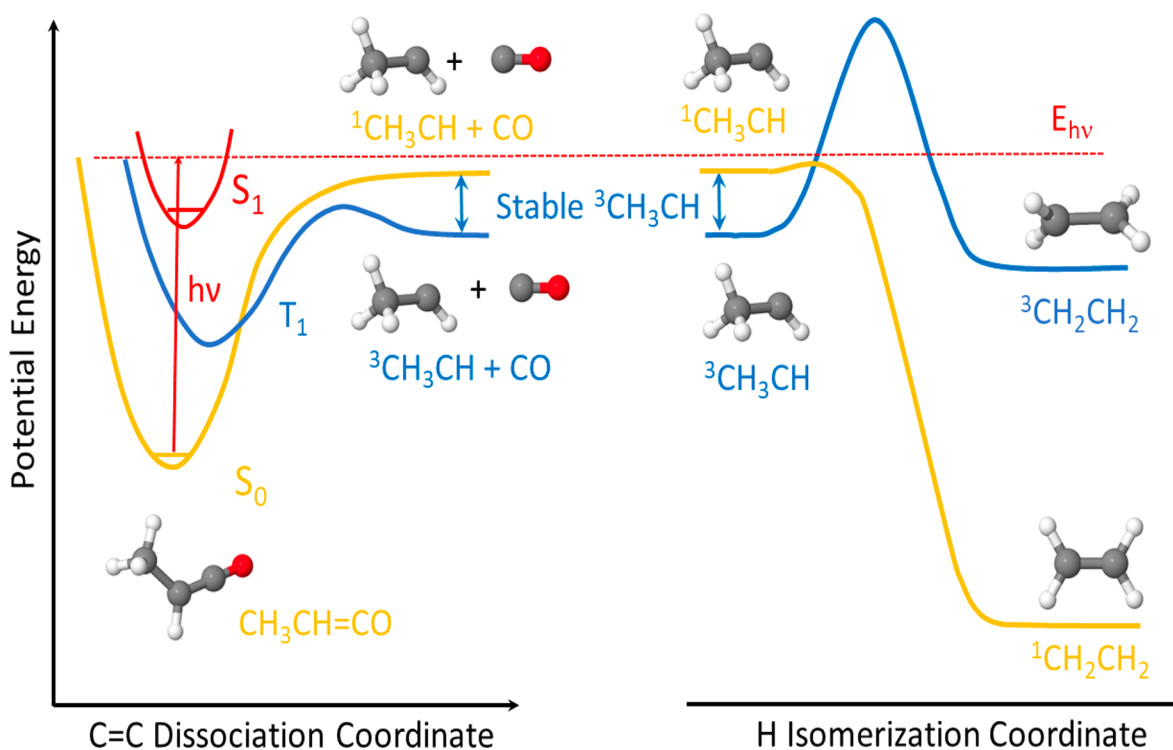
Figure 2. Schematic potential energy diagram for methylketene photodissociation producing ethylidene + carbon monoxide. Triplet ethylidene ($^3CH_3CH$) is stable to intersystem crossing and isomerization if produced with internal energies below the singlet electronically excited state ($^1CH_3CH$).

via H_2 elimination. Photoionization of vibrationally excited ethylene is relatively inefficient at 8.8 eV.

The maximum theoretical product translational energies (E_{max}) for $^3CH_3CH + CO$ (34.5 kJ/mol) and $^1CH_3CH + CO$ (22.0 kJ/mol) were calculated from the known photon energy and theoretically calculated enthalpies of formation of reactants and products.[21] For the calculations we used ΔH_f° = 361.35 ± 0.76 kJ/mol (0 K) for triplet ethylidene, ΔH_f° = 373.80 ± 0.87 kJ/mol (0 K) for singlet ethylidene, ΔH_f° = −55.3 ± 1.2 kJ/mol (0 K) for propenal, ΔH_f° = −54.7 ± 1.1 kJ/mol (0 K) for methylketene, and ΔH_f° = −113.803 ± 0.026 kJ/mol (0 K) for carbon monoxide.[21] Since the internal energies of the jet-cooled precursor molecules are negligible, these E_{max} values correspond to the limiting cases in which the rotational and vibrational energies of the triplet and singlet ethylidene plus carbon monoxide products are zero. During the analysis of the experimental data, we found that the maximum translational energy used in each $P(E)$ was in excellent agreement with the calculated values for E_{max}. As a test of the accuracy of the theoretically calculated enthalpies of formation of singlet and triplet ethylidene, for each system studied, we set the maximum energy in each $P(E)$ to be equal to the calculated E_{max}. As will be shown, our ability to accurately simulate TOF spectra for methylketene photodissociation at 355.1 nm and propenal photodissociation at 352.1 nm verifies the accuracy of the theoretically derived dissociation enthalpies producing triplet ethylidene plus carbon monoxide.[1,21]

Two plausible mechanisms have been discussed for the 1,2-H atom shift in photogenerated alkyl-substituted carbenes. The first is a sequential mechanism in which the H atom migrates after the molecular counterfragment, here CO, has departed.[7,34] An alternative mechanism, termed reaction in excited state (RIES), in this system would involve isomer-

ization of the carbene moiety within the parent methylketene prior to ejection of CO.[34] If RIES were to play a role, the very large exothermicity (∼300 kJ/mol) of the 1,2-H atom shift forming ethylene should lead to formation of a measurable fraction of products with translational energies exceeding those calculated for singlet ethylidene. Since the maximum product relative translational energies agree with theoretical values based on initial formation of singlet ethylidene, not ethylene, the process observed in this experiment must be sequential, with isomerization occurring after the CO has departed. We note that vibrationally cold ethylene, if formed, cannot be ionized at 9.9 eV.

In Figure 3, the TOF spectra and corresponding $P(E)$ distributions for the products from photodissociation of propenal at 352.1 nm, corresponding to excitation of a strong peak attributable to a spectroscopically assigned vibronic level lying 2541 cm^{-1} above the S_1 origin,[35] are illustrated. The most remarkable observation is that the TOF data are nearly identical to those from methylketene dissociation. The differences are very minor, reflecting the slightly differing photon energies and 0 K enthalpies of formation of propenal (−55.3 ± 1.2 kJ/mol) and methylketene (−54.7 ± 1.1 kJ/mol).[21] We conclude that following near-UV electronic excitation of propenal, isomerization to methylketene proceeds readily via a 1,3-hydrogen atom shift, followed by CO elimination producing ethylidene. Previous theoretical calculations revealed that the potential energy barrier for isomerization lies energetically well below barriers for all other competing propenal decomposition pathways.[27,28] For excitation at $\lambda > 340$ nm, isomerization to methylketene is expected to be the only energetically accessible nonradiative decay pathway.[28]
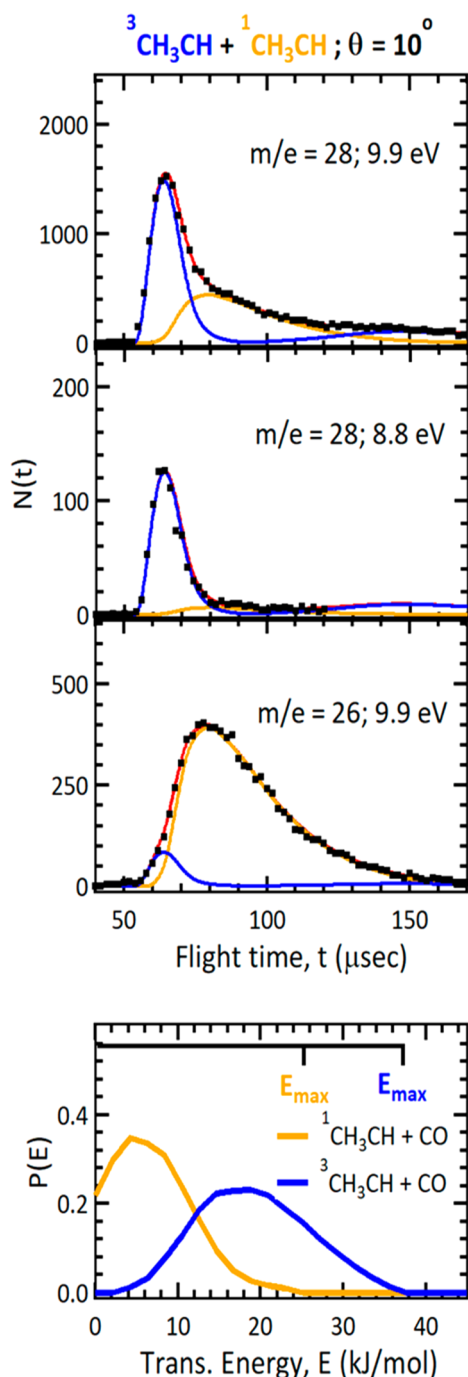
Figure 3. Same as Figure 1, but for ethylidene plus carbon monoxide product channels from 352.1 nm photodissociation of propenal.

Figure 4. Upper: Blue line shows the calculated TOF spectrum at 25° for 352.1 nm photodissociation of propenal using optimized $P(E)$, superimposed on experimental TOF (black dots). Lower: Optimized $P(E)$ shown as blue line. Pink and gray lines in upper and lower figures correspond to $P(E)$ distributions with $E_{max} \pm 4$ kJ/mol, respectively.

For the propenal data shown in Figure 3, the calculated values of E_{max} (here 36.8 and 24.3 kJ/mol for the triplet and singlet channels, respectively) were used as maximum energies in the $P(E)$ distributions, as before. Our sensitivity to the maximum product translational energy is greatest at large angles between the beam and detector axis. In Figure 4, the TOF spectrum for the triplet ethylidene products at 25° is shown. The solid blue line corresponds to the calculated TOF for $^3CH_3CH$ using the same $P(E)$ as used in Figure 3, with $E_{max} = 36.8$ kJ/mol.

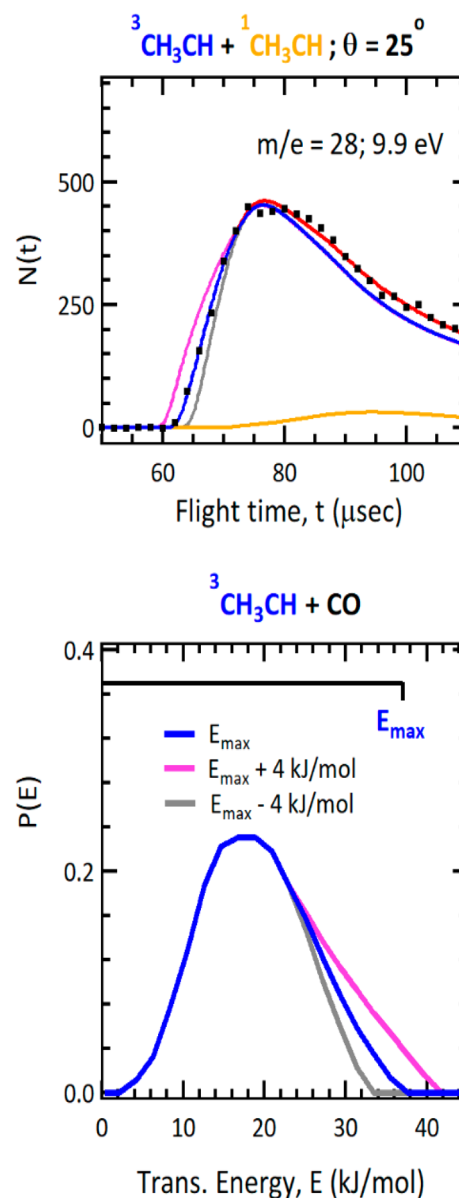Theoretical calculations are often considered to be of chemical accuracy if they lie within ~1 kcal/mol (4 kJ/mol) of

the true value. To assess the sensitivity of our TOF data to E_{max}, we calculated TOF spectra using $P(E)$ distributions for the triplet ethylidene channel with maximum energies of 40.8 and 32.8 kJ/mol, i.e., for $E_{max} \pm 4$ kJ/mol, shown as pink and gray solid lines in Figure 4, respectively. Considerably poorer agreements are observed for the earliest arrival times (60−75 μs), indicating that the calculated reaction enthalpy producing $^3CH_3CH$ + CO lies within 4 kJ/mol of the true value. Our ability to model the singlet ethylidene TOF data for photodissociation of methylketene at 355.1 nm and propenal at 352.1 nm is consistent with the calculated singlet−triplet gap of 12.5 kcal/mol. Because of overlap in the TOF spectra, deconvolution of the singlet and triplet channels in our analysis is not unique, so additional experiments are necessary before

we can comment further on the accuracy of the calculated singlet−triplet energy gap.

For excitation of methylketene or propenal at wavelengths longer than 340 nm, the only energetically accessible two-body photodissociation channels involve CO elimination producing ethylidene or ethylene.[27−29] Due to a relatively high potential energy barrier, the three-body channel producing HC≡CH, CO, and H_2 is inaccessible.[28] The excited state lifetime of propenal, determined from absorption line width measurements, is ∼2 ps.[35] Since the absorption spectrum of methylketene is unstructured, an even shorter excited state lifetime is anticipated. Therefore, fluorescence or phosphorescence, which occurs on time scales of nanoseconds or longer, must be negligible (<1%). Thus, CO elimination producing triplet and singlet ethylidene are the primary channels in the photodissociation of methylketene and propenal at $\lambda > 340$ nm.

An interesting question concerns the propensity for vibrationally excited triplet ethylidene to undergo intersystem crossing to the reactive singlet surface. Theoretical calculations have revealed the existence of a low energy seam connecting singlet and triplet ethylidene, lying only ∼4 kJ/mol above the singlet (∼16.5 kJ above the triplet).[36] Coincidentally, this intersystem crossing seam lies very close to the calculated potential energy barrier for the 1,2-H atom shift in singlet ethylidene.[9] Assuming a barrier height of 16.5 kJ/mol for intersystem crossing/isomerization, any $^3CH_3CH$ from propenal photodissociation at 352.1 nm (36.8 kJ/mol above threshold) with relative translational energies greater than 20.3 kJ/mol is expected to be stable. The sharp decrease in contributions to the $P(E)$ for the triplet ethylidene channel at translational energies below ∼20 kJ/mol, with a concomitant rise for singlet ethylidene, might be taken as evidence of intersystem crossing of triplet ethylidene, followed by 1,2-H atom migration. Thus, in addition to direct formation of singlet ethylidene by dissociation of methylketene on S_0, a secondary indirect source of singlet ethylidene can result from intersystem crossing of nascent vibrationally excited triplet ethylidene after the CO has departed. On the basis of our experimental results, we are not able to assess the relative importance of the two different sources of singlet ethylidene. Also, since the relative photoionization cross sections for triplet ethylidene and highly vibrationally excited ethylene are not currently known, absolute branching ratios for these channels cannot be derived from the present data.

Clearly, the key to the laboratory observation of ethylidene is production of triplet ground state molecules at levels of internal excitation lying below the energy of the excited singlet, so that intersystem crossing is energetically closed. Since the calculated potential energy barrier for the 1,2-H atom shift is ∼180 kJ/mol on the triplet PES,[1] triplet ethylidene produced in this manner is indefinitely stable in the absence of collisions.

The occurrence of intersystem crossing in the photochemistry of the carbonyl-containing precursor molecules is of critical importance in the production of stable triplet ethylidene. In addition, the presence of a potential energy barrier (see Figure 2) for dissociation of triplet methylketene[27] apparently leads to efficient partitioning of excess energy into product translational energy, thereby favoring production of vibrationally cold triplet ethylidene. In contrast, intersystem crossing does not play an important role in the photochemistry of nitrogen-containing precursors such as diazoethane and methyldiazirine.[3,7] In retrospect, it is perhaps not surprising that the previous attempts at production of stable ethylidene employing these precursors were unsuccessful.

■ AUTHOR INFORMATION

Corresponding Author

H. Floyd Davis − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, United States;* ⓸ orcid.org/0000-0003-3022-2088; Email: hfd1@cornell.edu

Author

Sagnik Datta − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14853-1301, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpclett.0c03282

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Nguyen, M. T.; Matus, M. H.; Lester, W. A.; Dixon, D. A. Heats of formation of triplet ethylene, ethylidene, and acetylene. *J. Phys. Chem. A* **2008**, *112*, 2082−2087.

(2) Rice, F. O.; Glasebrook, A. L. The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals, VII. The Ethylidene Radical. *J. Am. Chem. Soc.* **1934**, *56*, 741−743.

(3) Seburg, R. A.; McMahon, R. J. Photochemistry of Matrix-Isolated Diazoethane and Methyldiazirine: Ethylidene Trapping? *J. Am. Chem. Soc.* **1992**, *114*, 7183−7189.

(4) Modarelli, D. A.; Platz, M. S. Experimental Evidence for Ethylidene-d4. *J. Am. Chem. Soc.* **1993**, *115*, 470−475.

(5) Schaefer, H. F. The 1, 2-H Shift: A Common Vehicle for the Disappearance of Evanescent Molecular Species. *Acc. Chem. Res.* **1979**, *12*, 288−296.

(6) Evanseck, J. D.; Houk, K. N. Theoretical Predictions of Activation Energies for 1, 2-Hydrogen Shifts in Singlet Carbenes. *J. Phys. Chem.* **1990**, *94*, 5518−5523.

(7) Miller, D. M.; Schreiner, P. R.; Schaefer, H. F., III Singlet Methylcarbene: An Elusive Intermediate of the Thermal Decomposition of Diazoethane and Methyldiazirene. *J. Am. Chem. Soc.* **1995**, *117*, 4137−4143.

(8) Gallo, M. M.; Schaefer, H. F., III Methylcarbene: The Singlet-Triplet Energy Separation. *J. Phys. Chem.* **1992**, *96*, 1515−1517.

(9) Ma, B.; Schaefer, H. F., III Singlet Methylcarbene: Equilibrium Geometry or Transition State? *J. Am. Chem. Soc.* **1994**, *116*, 3539−3542.

(10) Hill, B. T.; Zhu, Z.; Boeder, A.; Hadad, C. M.; Platz, M. S. Bystander Effects on Carbene Rearrangements: A Computational Study. *J. Phys. Chem. A* **2002**, *106*, 4970−4979.

(11) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. The Electronic Structure of Methylenes. *J. Am. Chem. Soc.* **1968**, *90*, 1485−1499.

(12) Cavallotti, C.; Leonori, F.; Balucani, N.; Nevrly, V.; Bergeat, A.; Falcinelli, S.; Vanuzzo, G.; Casavecchia, P. Relevance of the Channel Leading to Formaldehyde + Triplet Ethylidene in the O(^{3}P) + Propene Reaction under Combusion Conditions. *J. Phys. Chem. Lett.* **2014**, *5*, 4213−4218.

(13) Leonori, F.; Skouteris, D.; Petrucci, R.; Casavecchia, P.; Rosi, M.; Balucani, N. Combined crossed beam and theoretical studies of the C(^{1}D) + CH$_4$ reaction. *J. Chem. Phys.* **2013**, *138*, 024311.

(14) Janssens, T. V. W.; Zaera, F. Chemistry of Ethylidene Moieties on Platinum Surfaces: 1, 1-Diiodoethane on Pt (111). *J. Phys. Chem.* **1996**, *100*, 14118−14129.

(15) Sharp, P. R.; Schrock, R. R. Multiple Metal-Carbon Bonds XIV - Preparation of Alkylidenetantalum Complexes by Alkylidene transfer from phosphoranes. The first ethylidene complex and how it decomposes. *J. Organomet. Chem.* **1979**, *171*, 43−51.

(16) Raghavachari, K.; Frisch, M. J.; Pople, J. A.; von R. Schleyer, P. The ground-state singlet potential surface for C$_2$H$_4$. *Chem. Phys. Lett.* **1982**, *85*, 145−149.

(17) Ha, T. K.; Nguyen, M. T.; Vanquickenborne, L. G. Ab Initio CI Study on the Singlet-Triplet Separation of Ethylidene, CH$_3$CH. *Chem. Phys. Lett.* **1982**, *92*, 459−461.

(18) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. Stable Carbenes. *Chem. Rev.* **2000**, *100*, 39−91.

(19) Stuyver, T.; Chen, B.; Zeng, T.; Geerlings, P.; DeProft, F.; Hoffmann, R. Do Diradicals Behave Like Radicals? *Chem. Rev.* **2019**, *119*, 11291−11351.

(20) Hayden, C. C.; Neumark, D. M.; Shobatake, K.; Sparks, R. K.; Lee, Y. T. Methylene singlet-triplet energy splitting by molecular beam photodissociation of ketene. *J. Chem. Phys.* **1982**, *76*, 3607−3613.

(21) Ruscic, B.; Bross, D. H. Active Thermochemical Tables (ATcT) values based on ver. 1.122g of the Thermochemical Network, 2019; available at https://atct.anl.gov/.

(22) Harding, L. B. Ab Initio Studies of 1, 2-H Migration in Open Shell Hydrocarbons. *J. Am. Chem. Soc.* **1981**, *103*, 7469−7475.

(23) Xiao, H.; Maeda, S.; Morokuma, K. CASPT2 Study of Photodissociation Pathways of Ketene. *J. Phys. Chem. A* **2013**, *117*, 7001−7008.

(24) Kim, S. K.; Choi, Y. S.; Pibel, C. D.; Zheng, Q. K.; Moore, C. B. Determination of the singlet/triplet branching ratio in the photo-dissociation of ketene. *J. Chem. Phys.* **1991**, *94*, 1954−1960.

(25) (a) Kistiakowsky, G. B.; Mahan, B. H. The Photolysis of Methyl Ketene. *J. Am. Chem. Soc.* **1957**, *79*, 2412. (b) Chong, D. P.; Kistiakowsky, G. B. The Photolysis of Methylketene. II. *J. Phys. Chem.* **1964**, *68*, 1793−1797.

(26) Fujimoto, G. T.; Umstead, M. E.; Lin, M. C. CO product energy distribution in the photodissociation of methylketene and acrolein at 193 nm. *J. Chem. Phys.* **1985**, *82*, 3042−3044.

(27) Fang, W.H. A CASSCF Study on Photodissociation of Acrolein in the Gas Phase. *J. Am. Chem. Soc.* **1999**, *121*, 8376−8384.

(28) Chin, C. H.; Lee, S. H. Theoretical study of isomerization and decomposition of propenal. *J. Chem. Phys.* **2011**, *134*, 044309.

(29) Chaudhuri, C.; Lee, S. H. A complete look at the multi-channel dissociation of propenal photoexcited at 193 nm: branching ratios and distribution of kinetic energy. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7312−7321.

(30) Dey, A.; Fernando, R.; Suits, A. G. State-resolved imaging of CO from propenal photodissociation: Signatures of concerted three-body dissociation. *J. Chem. Phys.* **2014**, *140*, 154301.

(31) Albert, D. R.; Davis, H. F. Studies of bimolecular reaction dynamics using pulsed high-intensity vacuum-ultraviolet lasers for photoionization detection. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14566−14580.

(32) Albert, D. R.; Proctor, D. L.; Floyd Davis, H. High-intensity coherent vacuum ultraviolet source using unfocussed commercial dye lasers. *Rev. Sci. Instrum.* **2013**, *84*, 063104.

(33) Yang, X.; Lin, J.; Lee, Y. T.; Blank, D. A.; Suits, A. G.; Wodtke, A. M. Universal crossed molecular beams apparatus with synchrotron photoionization mass spectrometric product detection. *Rev. Sci. Instrum.* **1997**, *68*, 3317−3325.

(34) Bonneau, R.; Liu, M. T. H.; Kim, K. C.; Goodman, J. L. Rearrangement of Alkylchlorocarbenes: 1,2-H Shift in Free Carbene, Carbene-Olefin Complex, and Excited States of Carbene Precursors. *J. Am. Chem. Soc.* **1996**, *118*, 3829−3837.

(35) Paulisse, K. W.; Friday, T. O.; Graske, M. L.; Polik, W. F. Vibronic spectroscopy and lifetime of S$_1$ acrolein. *J. Chem. Phys.* **2000**, *113*, 184−191.

(36) Kim, G. S.; Nguyen, T. L.; Mebel, A. M.; Lin, S. H.; Nguyen, M. T. Ab initio/RRKM Study of the Potential Energy Surface of Triplet Ethylene and Product Branching Ratios of the C(^{3}P) + CH$_4$ Reaction. *J. Phys. Chem. A* **2003**, *107*, 1788−1796.