Site-Specific Carbon–Carbon Bond Fission in Photoexcited Propyl Radicals Leads to Isomer-Selective Carbene and Radical Products

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ABSTRACT: Although there have been many studies of C–H bond fission in the UV photochemistry of alkyl radicals, very little is known about the possible occurrence of C–C bond fission. Here, we report that upon excitation at 248 nm, gaseous 1-propyl radicals primarily undergo C–C bond fission, producing methylene (CH2) and ethyl radicals (C2H5), rather than the more energetically favored methyl (CH3) and ethylene (C2H4). In contrast, the exclusive C–C bond fission products from 2-propyl radicals were ethylidene (CHCH3) plus methyl radicals (CH3). The isomer-selective formation of high-energy carbene + radical products involves excited-state site-specific C–C bond fission at the radical carbon, with quantum yields comparable to those for C–H bond fission. Our observations suggest that a general feature of alkyl radical photochemistry is predissociation of the initially formed Rydberg states by high-lying valence states, yielding high-energy carbene plus alkyl radical products.

Alkyl radicals are ubiquitous in chemistry, especially in combustion and atmospheric environments. The chemical kinetics, thermodynamics, and infrared spectroscopy of alkyl radicals on their ground potential energy surfaces are relatively well understood. On the other hand, there remains many unanswered questions about the photochemical dynamics of the electronically excited states of alkyl radicals accessed by near-UV excitation. Specifically, the role of nonadiabatic interactions between the optically bright states and lower lying surfaces, and the resulting degree of statistical vs nonstatistical dynamics in the ensuing dissociation reactions, are active areas of study.

The ultraviolet electronic absorption spectra of alkyl radicals have been assigned to excitation to 3s, 3p, and 3d Rydberg states of the neutral parents. Over the past decades, numerous experimental studies of C–H fission in alkyl radicals, ranging from the simplest, methyl (CH3), to larger species, have been carried out. Electronically excited alkyl radicals appear to decompose via at least two competing pathways, with considerable similarity for a range of radical sizes and complexity. Zhang and co-workers performed extensive studies of the C–H bond fission in alkyl radicals, including 1-propyl and 2-propyl, using H atom Rydberg tagging time-of-flight (HRTOF) spectroscopy. For both propyl radical isomers, H + propene products from β-hydrogen atom elimination were formed with bimodal translational energy distributions. The higher translational energy components, with an anisotropic angular distribution for 1-propyl and an isotropic angular distribution for 2-propyl, were attributed to direct excited-state decomposition. Lower translational energy components in both systems were ascribed to internal conversion to the ground-state surfaces, followed by C–H bond fission. The occurrence of hydrogen atom scrambling or α-hydrogen atom elimination, producing high-energy carbene products, was ruled out. Giegerich and Fischer have observed similar behavior using H atom photofragment imaging. More recently, Chicharro and co-workers studied C–H bond fission of several alkyl radicals following excitation to the higher energy 3d Rydberg states. A second C–H bond fission channel involving site-specific α-hydrogen atom elimination yielded high-energy carbene products.

To date, C–C bond fission has been observed only in the photodissociation of tert-butyl and cyclohexyl radicals. For tert-butyl radicals, C–C bond fission led to formation of dimethylcarbene plus methyl radicals; C–H bond fission produced isobutene + H. From the translational energy distributions in both channels, it was concluded that the reactions were direct rather than via internal conversion to the ground state. Our experiments were performed by using a rotatable source crossed molecular beams apparatus with fixed mass spectrometer detector employing single photon ionization using a high intensity 9.9 eV vacuum-ultraviolet (VUV) laser or conventional electron impact ionization. The radicals were produced by flash pyrolysis of a pulsed molecular beam containing 1- or 2-azopropane (2%) in helium. The NMR
spectra of the samples (see the Supporting Information) demonstrated that the azo compounds were >98% pure. The pyrolytic radical beam was collimated by two skimmers and crossed by the attenuated 248 nm output from an excimer laser (20 mJ/pulse, 20 ns, 30 Hz, 3 × 5 mm). The product time-of-flight (TOF) distributions were analyzed by a forward convolution method.21

The TOF spectra recorded at $m/e = 29$ for photodissociation of 1-propyl radicals (3s state) are shown in Figure 1, with the corresponding $P(E)$ also illustrated. We sought TOF spectra for the nascent methylene ($CH_2$) counterfragments using 9.9 eV photoionization. However, we were unable to see any signals at $m/e = 14$ using 9.9 eV photoionization. The adiabatic ionization energy of ground electronic state triplet methylene ($^3CH_2$) is 10.39 eV and for excited singlet methylene ($^1CH_2$) is 10.00 eV, with vertical values somewhat greater. In preliminary studies of the photodissociation of c-CH$_3$N$_2$, producing $^2$CH$_4$ + N$_2$, we observed very strong signals at $m/e = 14$, demonstrating that vibrationally excited singlet methylene can be readily detected at 9.9 eV. We therefore assign the methylene to ground triplet electronic state or to low vibrational levels of the singlet, which cannot be efficiently photoionized at 9.9 eV.

In Figure 2, the TOF spectra for the momentum-matched $m/e = 15$ and $m/e = 28$ products from 248 nm photolysis of 2-propyl radicals (3p state) are illustrated. The translational energy distribution is broad, peaking well away from zero with the most probable value $\sim 54$ kJ/mol. The $m/e = 15$ products are ascribed to nascent methyl radicals (CH$_3$), produced by C–C bond fission. The counterfragment signals at $m/e = 28$ are assigned to ethylidene (CH$_3$CH), which was characterized recently for the first time via photodissociation of methylketene and acrolein.21 Because of strong coupling between singlet and triplet CH$_3$CH states, isomerization to ethylene on the singlet surface after departure of the methyl counterfragment is expected.21 Although the ionization energy of internally cold ethylene is 10.5 eV,5 since ethylidene lies $\sim 300$ kJ/mol (3 eV) above ethylene, the high level of vibrational excitation facilitates ionization at 9.9 eV.21 A significant signal was also observed at $m/e = 26$, resulting from dissociative ionization to form C$_3$H$_5$+. The ratio of $m/e(s) = 28:26$ was found to be 2.0 ± 0.4 for the product from photodissociation of 2-propyl radicals at 248 nm. This is identical with the ratio observed for singlet ethylidene produced by 355.1 nm photodissociation of methylketene or 355 nm photodissociation of acrolein.21 For both propyl radical isomers, we were unable to observe any dependence of

Figure 1. Upper: TOF spectra for C$_2$H$_5$ ($m/e = 29$) from photodissociation of 1-propyl radicals. Black dots are experimental data, and solid green lines are calculated TOF spectra. Lower: optimized $P(E)$ distribution.

Figure 2. Upper: TOF spectra at indicated laboratory angles for photodissociation of 2-propyl radicals. Solid red lines are calculated TOF spectra for CH$_3$ + CH$_3$CH channel. Lower: optimized $P(E)$ distribution.
the signal levels on input laser polarization (see the Supporting Information), indicating that the angular distributions are isotropic, i.e., the anisotropy parameter ($\beta$) = 0 ± 0.2.\textsuperscript{22} While $\beta$ values near zero are often taken as evidence for excited-state lifetimes exceeding the picosecond time scales for parent rotation, alternative explanations are possible.\textsuperscript{22} Specifically, for 2-propyl radicals, UV excitation to the overlapping $3p_x$, $3p_y$, and $3p_z$ states should yield effective $\beta$ values significantly smaller than the limiting values, even for fast dissociation.\textsuperscript{14} Also, as discussed below, there is a significant level of vibrational excitation in the parent propyl radicals, effectively producing a distribution of parent initial vibronic symmetries, possibly also diminishing $\beta$.

By use of the currently accepted enthalpies of formation\textsuperscript{5} for the relevant species, at 248 nm (482 kJ/mol), the maximum theoretically calculated translational energies for the $CH_2 + C_2H_5$ products from photolysis of internally cold 1-propyl radicals, and for $CH_3 + CH_2CH$ from internally cold 2-propyl radicals, are both ~80 kJ/mol. On the ground-state potential energy surface (PES), C–H bond fission from either $C_3H_7$ isomer can proceed via small potential energy barriers. For 1-propyl radicals, C–C bond fission, producing $CH_3 + C_2H_4$ (ethylene), is more favorable than C–H bond fission, with the calculated C–C fission barrier lying ~21.3 kJ/mol lower than that for C–H fission.\textsuperscript{4} Our finding that the primary C–C bond fission channel for 1-propyl radical photodissociation is $C_2H_5 + CH_2$ rather than $C_2H_4 + CH_3$ clearly indicates that C–C bond fission primarily involves an excited-state mechanism rather than from internal conversion. For 2-propyl radicals, on the other hand, C–C bond fission on the ground-state surface correlates to ethylidene ($CHCH_3$) + $CH_3$, lying ~250 kJ/mol above the C–H bond fission products. Because of the high energy of this channel relative to C–H bond fission, C–C bond fission cannot be competitive with C–H bond fission for 2-propyl radicals on the ground PES. Thus, the significant yield of C–C bond fission products in 2-propyl radical photodissociation again points to the involvement of an excited-state mechanism.

We also recorded TOF spectra for propene ($C_3H_6; m/e = 42$) from the $\beta$-H atom elimination channels for each isomer.
(see the Supporting Information). We used bimodal P(E) distributions, similar to those reported by Zhang and co-workers,\textsuperscript{14} to satisfactorily simulate the TOF spectra for C–H bond fission for both 1- and 2-propyl radicals. In our study of the C–H bond fission channels, the “heavy” m/e = 42 propene products were detected. Because of conservation of linear momentum, the low-energy component of the P(E) for C–H bond fission reported by Zhang corresponds to production of C\(_2\)H\(_5\) that is constrained to scattering angles within 5° of the molecular beam. Because of the presence of free C\(_2\)H\(_5\) in the beam, we are not sensitive to C\(_3\)H\(_6\) + H products with \(E_{\text{trans}} < 90\) kJ/mol. As described in the Supporting Information, we determined the relative branching fractions for excited-state C–C bond fission and total C–H bond fission in 1-propyl radicals to be approximately 0.64 and 0.36, respectively. Thus, excited-state C–C bond fission is actually the dominant channel in the overall photodissociation dynamics of 1-propyl radicals. For 2-propyl radical photodissociation, the signal-to-noise ratio for the m/e = 15 products using 70 eV electron impact ionization was insufficient to allow for the determination of the C–C to C–H branching ratio. We plan to improve our apparatus in the near future to facilitate that determination.

A remarkable finding in this study is that the excited-state C–C bond fission channels for the two different propyl radical isomers yield different carbene + alkyl radical pairs. A correlation diagram for C–C bond fission in electronically excited propyl radicals is shown in Figure 4. This figure is similar to that for tert-butyl radicals, as discussed by Noller and co-workers.\textsuperscript{23} The 3\(s\) and 3\(p\) states are adiabatically bound and correlate to electronically excited states of the carbene + alkyl radical products. High-lying repulsive valence states of the propyl radical, correlating to the carbene + alkyl radical product asymptotes, facilitate nonadiabatic decay via C–C bond fission. For the 1- and 2-propyl radicals, the ground states of the carbene products, i.e., methylene and ethylidene, respectively, are both of triplet spin multiplicity.\textsuperscript{5,24}

In the case of 1-propyl radicals, we found possible evidence for an additional secondary C–C bond fission channel (see the Supporting Information). For radical beams produced by pyrolysis of 1-azopropane, the secondary C–C bond fission products appeared weakly at m/e = 15. Although a detailed analysis of this behavior requires further experimental study, several comments may be made at this time. For 1-propyl radicals, internal conversion to the ground state has been implicated from studies of the H atom product channels. Dissociation of hot ground-state 1-propyl radicals should actually favor C–C bond fission, producing CH\(_3\) + C\(_2\)H\(_4\) over a potential energy barrier that is lower than that for C–H bond fission.\textsuperscript{7} This may be the origin of the weak m/e = 15 signals that we observe.

An alternative possible source of m/e = 15 from photodissociation of beams produced by pyrolysis of 1-azopropane is from photodissociation of 2-propyl radicals. Because of a relatively high potential energy barrier\textsuperscript{8} on the ground state PES (see Figure 3; purple curve), isomerization of 1-propyl radicals to 2-propyl radicals in the high-temperature pyrolysis region is not expected to be competitive with C–H bond fission. However, C–H bond fission (1-C\(_3\)H\(_5\) \rightarrow C\(_2\)H\(_2\) + H) followed by bimolecular processes in the high-pressure region of the pyrolysis tube (e.g., C\(_3\)H\(_6\) + H \rightarrow 2-C\(_2\)H\(_4\)) might potentially lead to some degree of isomeric scrambling. Because the vertical ionization energies\textsuperscript{25} are 8.39 \textpm 0.01 eV for 1-propyl radicals and ~7.67 \textpm 0.02 eV for 2-propyl radicals, we plan to characterize the isomeric composition of our beams in upcoming experiments by photoionization spectroscopy by using a tunable VUV laser. We observed no evidence for the occurrence of any secondary C–C bond fission channels from 2-propyl radicals produced by pyrolysis of 2-azopropane.

Although the most probable translational energies seen in our study lie well below the thermodynamic maximum of 80 kJ/mol for vibrationally cold radicals, we observed high-energy tails in the P(E) distributions for both isomers approaching 180 kJ/mol, ~100 kJ/mol above the calculated maximum values. Although our m/e = 42 translational energy distributions resemble the high-energy components in the C–H bond fission distributions reported by Zhang,\textsuperscript{14} high-energy tails in the P(E) were also observed, again extending ~100 kJ/mol greater than calculated for cold radicals (see the Supporting Information). For weakly bound radicals such as propyl, significant excited vibrational populations approaching the dissociation limit may be present in thermal ensembles. Because vibrational cooling upon supersonic expansion is inefficient, it would not be surprising if vibrationally excited radicals are produced by pyrolysis. On the basis of our current results, we cannot entirely rule out the possibility that vibrational excitation leads to a higher probability for 248 nm absorption. We performed experiments in which the He carrier gas was replaced with a 1:9 N\(_2\) : He mixture in an effort to facilitate more efficient vibrational cooling upon supersonic expansion. Although we observed a small decrease in the high-energy component of the P(E), more work remains to be done to produce less vibrationally hot propyl radicals.

To summarize, the site-specific C–C bond fission channels from the 248 nm photodissociation of 1- and 2-propyl radicals lead primarily to isomer-selective carbene plus radical products. Our studies reveal that these channels occur at the radical carbon via a direct mechanism, involving predissociation by excited valence states, rather than from internal conversion. In light of the previous finding that dimethylcarbene + methyl was observed in tert-butyl radical photodissociation,\textsuperscript{16} excited-state C–C bond fission, producing high-energy carbenes plus alkyl radicals, appears to be a general feature of alkyl radical photochemistry.

### ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.1c03324.

Experimental methods and materials, data analysis; additional data and figures for the secondary C–C bond fission channel in 1-propyl radicals; additional data and figures for the C–H bond fission channels in 1- and 2-propyl radicals; incident laser polarization angles dependence study of the dominant C–C bond fission channels in 1- and 2-propyl radicals; and calculation of the branching fractions for excited C–C bond fission channel and total C–H bond fission channel in 1-propyl radicals (PDF)

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