UV-Absorption Spectra of the Radical Transients Generated from the 193-nm Photolysis of Allene, Propyne, and 2-Butyne

Askar Fahr*[†,‡] **and Allan H. Laufer**[†,§]

Department of Chemistry, American University, Washington D.C. 20016-8014, and Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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The 193-nm photochemistry of allene ($H_2C{=}C{=}CH_2$), propyne ($H_3C{-}C{\equiv}CH$), and 2-butyne ($H_3C{-}C{\equiv}C{-}CH_3$) has been examined, and the UV spectral region between 220 and 350 nm has been surveyed for UV-absorption detection of transient species generated from the photolysis of these molecules. Time-resolved UV-absorption spectroscopy was used for detection of transient absorption. Gas chromatographic/mass spectroscopic (GC/MS) analysis of the photolyzed samples were employed for identification of the final photodissociation products. An emphasis of the study has been on the examination of possibilities of formation of different C_3H_3 isomeric radicals, that is, propargyl (H_2CCCH) or propynyl (H_3CCC), from the 193-nm photolysis of these molecules. Survey of the UV spectral region, following the 193-nm photolysis of dilute mixtures of allene/He resulted in detection of a strong absorption band around 230 nm and a weaker band in the 320-nm region with a relative intensity of about 8:1. The time-resolved absorption traces after the photolysis event show an instantaneous rise, followed by a simple decay. The spectral features, observed in this work, following 193-nm photolysis of allene are in good agreement with the previously reported spectrum of H_2-CCCH radical in the 240- and 320-nm regions and are believed to originate primarily from propargyl radicals. In comparison, the spectra obtained from the 193-nm photolysis of dilute mixtures of $HCCCH_3$/He and CH_3-$CCCH_3$/He were nearly identical, consisting of two relatively broad bands centered at about 240- and 320-nm regions with a relative intensity of about 2:1, respectively. In addition, the time-resolved absorption traces after photolysis of propyne and 2-butyne samples, both in the 240 and 320 nm regions, indicated an instant rise followed by an additional slower absorption rise. The distinct differences between the results of allene with those of propyne and 2-butyne suggest the observed absorption features following 193-nm photolysis of these molecules are likely to be composite with contributions from a number of transient species other than propargyl radicals. Propyne and 2-butyne are structurally similar. The methyl (CH_3) and propynyl ($CH_3C{\equiv}C$) radicals are likely to be among the photodissociation products of 2-butyne, and similarly, propynyl is likely to be a photodissociation product of propyne. GC/MS product analysis of photolyzed 2-butyne/He mixtures indicates the formation of C_2H_6 (formed from the combination of CH_3 radicals), and a number of C_6H_6 and C_4H_6 isomers formed from self- and cross reactions of C_3H_3 and CH_3 radicals, including 1,5-hexadiyne and 2,4-hexadyine, that are potential products of combination reactions of propargyl as well as propynyl radicals.

Introduction

Developments and advances in the study of the spectroscopy and kinetics of small hydrocarbon radicals continue unabated with intellectual interest progressing toward larger and more complex species. The formation of the particular radical in a form that is amenable to further study is often through photolysis of a precursor that, predictably if possible, will form the radical of interest. Therefore, it is with the C_3 unsaturated species where the propargyl radical has been formed through the photolysis of both propargyl halides[1] as well as certain hydrocarbon precursors.[2] Within the hydrocarbon framework, photolysis of either allene ($CH_2{=}C{=}CH_2$) or propyne ($CH_3C{\equiv}CH$) have been reported to generate various C_3H_3 and C_3H_2 radical isomers.[3,4,5] A number of these experiments[4,5] have examined the intermediate photolytic product(s) through the use of a molecular beam with mass spectrometric analysis. Jackson et al.[6] have reported two primary channels deduced from time-of-flight measurements of the fragments produced from the 193-nm photolysis of allene. The two channels, $H + C_3H_3$ and $H_2 + C_3H_2$, have quantum yields of 0.89 and 0.11, respectively. Also they found that, once H_2CCC is formed in the primary photodissociation of allene, its most probable internal energy is ~43 kcal/mol (180 kJ/mol). Similarly, any HCCCH formed from propyne through the molecular detachment of H_2 can also have high internal energy. Mebel et al.[3] have investigated the potential energy surfaces of various primary and secondary products of the photodissociation of allene and propyne including isomers of C_3H_4, C_3H_3, C_3H_2, and C_3H and their isomerization and dissociation channels in the ground and excited states. Earlier results obtained from the photolysis of propyne[7,8] in static systems at reasonable pressures find the propynyl radical to be a major dissociation product. However, the system is quite complex because other primary processes have been observed including formation of CH_2 with

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* To whom correspondence should be addressed. E-mail: fahr@american.edu.

[†] Guest scientist at National Institute of Standards and Technology.

[‡] American University.

[§] National Institute of Standards and Technology.

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a quantum yield reported to be 0.11.[8] Recent experimental results seem to contradict the earlier conclusions reached in the photolysis of allene and propyne. Ashfold et al.[9] in a recent beam experiment suggest the photodissociation at 193 nm occurs on the ground-state potential surface following an internal conversion process and that the radical produced, following isomerization and vibrational redistribution, is the propargyl species. In another molecular-beam experiment involving multiple photons incident on CD_3CCH but at energies that are quite comparable to those achieved at 193 nm, the opening of another channel to form propynyl was observed.[10] With all of these possible processes and the complexity associated with the mechanism, the ultraviolet absorption characteristics of the resultant transient species have not been examined, but because the precursors are of current interest, the nature of the optical properties of the transients formed during the photolysis are, similarly, of interest and may provide further evidence for the nature of the primary processes. Although the photodissociation dynamics of allene and propyne have been investigated in a number of laboratories there is no reported experimental study on the photodissociation of 2-butyne ($CH_3C{\equiv}CCH_3$), a structurally similar species.

Experimental Procedures

Excimer laser photolysis, coupled with time-resolved absorption spectroscopy and gas chromatography/mass spectroscopy (GC/MS) methods have been employed for this study. Spectral measurements are performed between the range of 225−350 nm. Briefly, the 193-nm output of an ArF excimer laser is expanded to fill the photolysis cell side-on through a Suprasil flat window. A self-enclosed gas-circulating pump is used to flow the gas mixture through the reaction cell so that its contents are replaced several times each second, which is faster than the 1-Hz pulse rate of the excimer photolysis laser and allows for the replacement of the photolyzed sample. A total system volume of more than 2000 times that of the active photolysis volume was used. Because of the significant product dilution, the photolysis of products is kept at a negligible level.

For the transient absorption measurements, the monitoring light from a high-pressure xenon lamp is passed through a multipass reaction cell, deflected by a prism, and then focused onto the slit of a monochromator. The signal from the photomultiplier is read by a digitizer and then by a computer and is averaged into memory. The 0.3-m monochromator used in these experiments is equipped with a 2400 grooves/mm grating blazed at 300 nm. The time-resolved absorption signals, with a time resolution of 0.5 μs, were obtained at selected wavelengths with a minimum interval of 0.2 nm or larger. The ArF excimer laser pulse duration was typically 50 ns with maximum pulse energy of about 150 mJ.

A number of product analysis experiments were performed, using an on-line gas chromatograph, which is interfaced with a mass spectrometer and flame ionization detectors (FIDs). The retention times and the response factors of the spectrometer and FIDs were calibrated using known samples of expected reaction products.

Dilute mixtures of the radical precursor in He, typically 5×10^{15} molecules cm^{-3} of the precursor molecule in about 20 kPa (150 Torr) He, were used. The radical precursors with highest available purity (~99%) were used after successive freeze−pump−thaw cycles.

Results and Discussion

Allene. Time-resolved absorption traces were averaged and recorded, after the 193-nm photolysis of dilute mixtures of allene in He (0.5 Torr [65 Pa]/200 Torr [27 kPa] He). Figure 1 displays examples of the time-resolved absorption traces collected at 240 and 330 nm following photolysis of allene/He samples. The absorption traces of the transient products show an instantaneous rise, after the photolysis pulse, followed by a simple decay. No secondary temporal increases in absorption were observed.

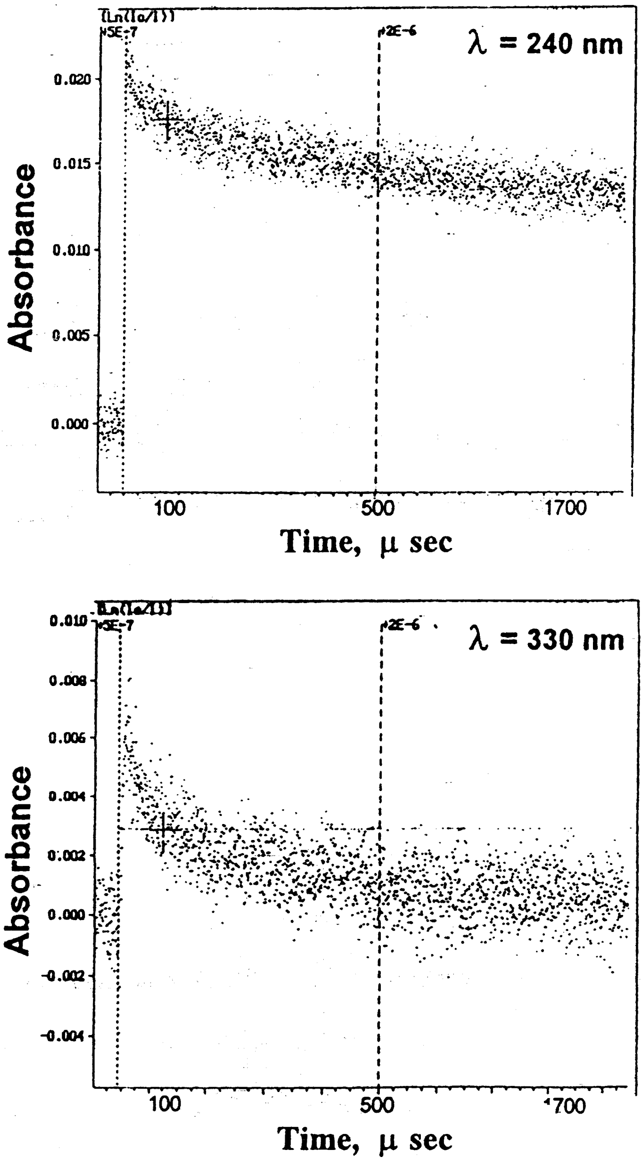

Figure 1. Time-resolved absorption trace from 193-nm photolysis of allene probed at 240 and 330 nm.

Spectral measurements in the present work were performed at selected wavelengths between the range of about 220−360 nm and under identical experimental conditions (laser energy, sample concentration, and pressure). The maximum initial absorbance (A_{max}) and the absorbance at long delay times (A_{tail}) were determined from the time-resolved absorption traces, and the derived wavelength-dependent absorption spectrum is shown in Figure 2. The formation of propargyl radicals from the 193-nm photolysis of allene has been well-documented[4−6] (reaction 1).

$$H_2CCCH_2 \rightarrow H_2CCCH + H \qquad (1)$$

The strong feature observed at 240 nm overlaps with the reported spectrum of both the propargyl[1a,b] (H_2CCCH) as well as with that of the propadienylidene ($H_2C{=}C{=}C{:}$) radical.[11] A

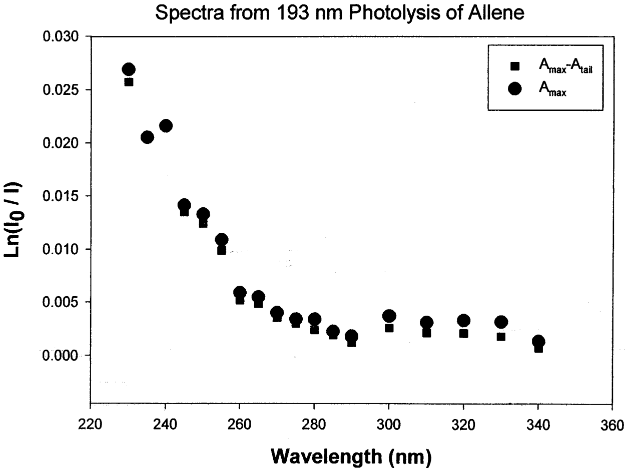

Figure 2. Absorption spectra of transient species generated from 193-nm photolysis of allene.

weaker band in the 300−340-nm region is also observed. The relative intensity of the two absorption bands is about 8:1.

The GC/MS final product analyses of the photolyzed samples identified a number of C_2 to C_6 hydrocarbon products, including 1,5-hexadiyne, which is the product of the propargyl combination reaction. In addition, a significant quantity of propyne (15−20% of the initial allene) was detected, which indicates that a substantial allene → propyne isomerization occurs.

Propyne. Time-resolved absorption traces were averaged and recorded, after the 193-nm photolysis of dilute mixtures of propyne in He (0.5 Torr [65 Pa]/200 Torr [27 kPa] He). Examples of time-resolved absorption signals collected at 240 and 330 nm are depicted in Figure 3.

Time-resolved absorption traces, both in the 240 and 330 nm regions, indicated an instant rise after the photolysis event (A_{rise}). However, the traces in the 240-nm region show an additional slower absorption rise followed by a decay to a nonzero baseline (A_{tail}). In comparison, time-resolved absorption traces in the 330-nm region showed a less pronounced second increase but a faster decay to a near-zero baseline (A_{tail}). A significant variation of $A_{\mathrm{rise}}/A_{\mathrm{tail}}$ at different wavelengths was observed. Absorbance values, A_{rise} and ($A_{\mathrm{rise}} - A_{\mathrm{tail}}$), versus the wavelength are plotted in Figure 4. The derived absorption spectrum exhibits two relatively strong absorption features: one in the 240-nm region and a weaker one in the 320-nm region with a relative intensity of about 2:1.

A number of previous studies have shown that the photolysis of propyne at 193 nm primarily produces the propynyl (CH_3-CC) radicals.[5] Photolysis of specific deuterated samples of propyne (CH_3CCD) has shown that breakage of the stronger acetylenic C−D bond to form D atoms [7,8] is a dominant primary process (reaction 2a).

$$CH_3{-}C{\equiv}CD \rightarrow CH_3C{\equiv}C + D \tag{2a}$$

However, other primary processes certainly can also occur. A molecular-beam experiment indicated that the dominant C_3H_2 fragment is the propadienylidene (H_2CCC) radical[5] with the concomitant formation of molecular H_2 (reaction 2b).

$$CH_3{-}C{\equiv}CH \rightarrow HC{=}C{=}CH + H_2 \tag{2b}$$

Further, about 10% of the primary processes form CH_2 and C_2H_2[7,9] (reaction 2c).

$$CH_3{-}C{\equiv}CH \rightarrow CH_2 + C_2H_2 \tag{2c}$$

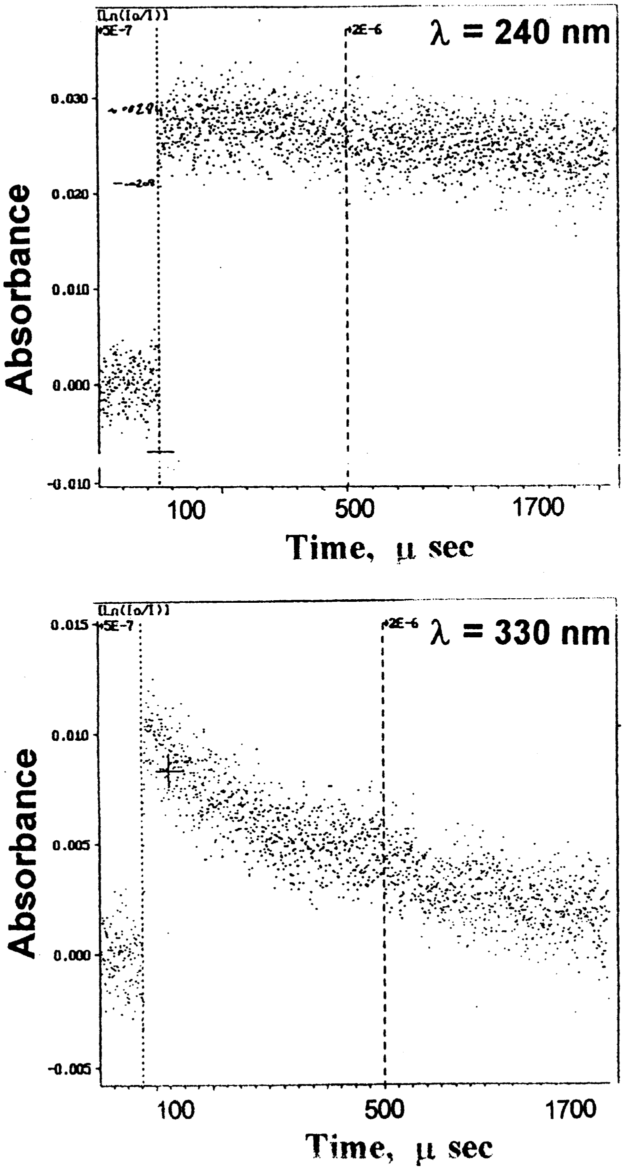

Figure 3. Time-resolved absorption trace from 193-nm photolysis of propyne probed at 240 and 330 nm.

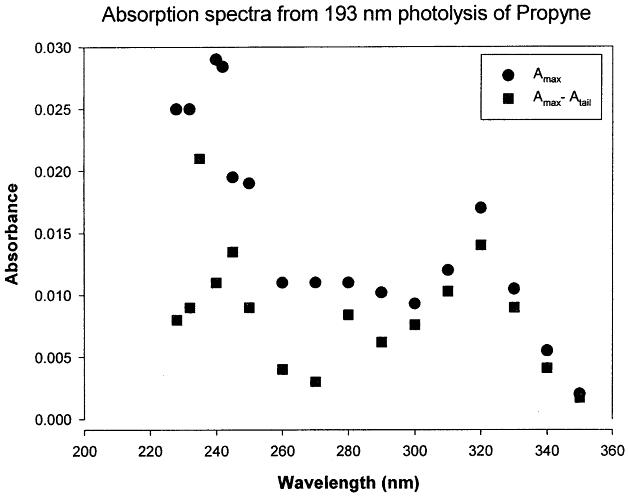

Figure 4. Absorption spectra of transient species generated from 193-nm photolysis of propyne.

As a result of the plethora of processes, it may be anticipated that the observed time-resolved absorption will be complex and be an agglomeration of individual spectra.

A number of recent results[9,10,12] suggest that the major primary dissociation product arising from photolysis of propyne at 193 nm is the propargyl radical, a result that is contrary to earlier interpretations of experiments suggesting that the major decomposition fragment was the propynyl radical.[4,5,7,8] In the present work, the initial strong absorption observed at 240 nm is similar to that observed from allene photolysis and may be attributed to the initial formation of the propargyl radical, but in comparison with spectra observed following photolysis of allene, the origin of the more intense absorption band in the 320-nm region, observed from photolysis of propyne, is not clear. Further, the genesis of the observed slow, secondary rise of transient absorption at 240 nm, following photolysis of propyne, is similarly not immediately obvious. However, it is likely that the absorption features observed following photolysis of propyne are composite absorptions with contributions from more than one transient species.

Of the two possible primary processes from the photolysis of propyne (2d and 2e)

$$CH_3{-}C{\equiv}CH \rightarrow CH_2C{\equiv}CH + H \tag{2d}$$

$$CH_3{-}C{\equiv}CH \rightarrow CH_3C{\equiv}C + H \tag{2e}$$

the initial formation of propargyl radical (2d) is thermodynamically favored. Formation of propargyl from propyne is endothermic by about 89 kcal/mol (373 kJ/mol), while that for formation of the propynyl radical (2e) is endothermic by 128.7 kcal/mol (538.5 kJ/mol).[5] While the propynyl radical, in principle, can isomerize to the lower energy propargyl species there is insufficient energy at 193 nm to allow the radical isomerization to proceed because there is a barrier of about 34 kcal/mol (142 kJ/mol)[13] to its occurrence.

An alternate mechanism involves internal conversion of the electronically excited propyne to its vibrationally excited ground state followed by dissociation to propargylene (HCCCH) plus H_2 or its isomerization to allene.[3] Recent experiments that examined the total kinetic energy release of H or D atoms from the photolysis of allene and propyne confirm that the probable mechanism involves the internal conversion, noted above, followed by the isomerization of the vibrationally excited ground state, which is faster than their unimolecular dissociation.[9] Very recent results on the photodissociation of vibrationally excited propyne-d_3 indicates that more than a single process is involved; propargyl radicals are formed through a dissociation that occurs from the ground state following an internal conversion process and intramolecular vibrational energy redistribution.[10] However, these workers also noted that the acetylenic C−H bond can break, forming the propynyl radical, in a process that occurs directly from particular vibrational levels of the upper excited electronic state. The ground-state dissociation may also proceed through a molecular H_2 elimination yielding H_2CCC. However, more importantly, the HCCCH radical may have adequate internal energy to isomerize to H_2CCC.[3]

Interestingly, the electronic absorption spectrum that has been assigned to the $C^1A_1{-}X^1A_1$ transition of the propadienylidene ($H_2C{=}C{=}C$) radical has an onset at 259 nm and a maximum quite close to 240 nm[11] and, as noted earlier, is found as a product of the photolysis of propyne and allene. At 193 nm, the dissociation of the propynyl photofragment to the propadienylidene species is endothermic by about 70 kcal/mol (≈293 kJ/mol). If the observed spectrum is due to the $H_2C{=}C{=}C$ radical, then its formation may be a slightly delayed photodissociation through the intercession of an excited state. The strong feature at 240 nm observed in this work and in that of others[1b] was not detected in the earlier cavity ring-down studies of Atkinson and Hudgens.[14] Recent results on the 193-nm photolysis of propyne cast into question the nature of the primary process.[12] Using infrared laser absorption spectroscopy, both propargyl and acetylene, consistent with a primary process, are observed. The observed quantum yield of primary propargyl was reported as $\Phi = 0.49 \pm 0.10$. Acetylene is also observed as a primary fragment with a quantum yield of 0.11. As noted,[12] the sum of the quantum yields is less than 1, indicating that other processes must, in fact, occur. Whether some propynyl radicals are formed and contribute to the observed spectra or other species such as a cyclic C_3H_3 radical intermediate are the source of the absorption at 320 nm is not clear. In addition, the various reported experimental studies have been performed over a rather wide pressure range. Considering that access to particular vibrationally excited modes in the 193-nm excitation region of the parent propyne molecule has been reported to open additional channel(s) to propynyl formation, a composite absorption spectrum might be expected.[10] To assist in identification of the origin(s) of the UV-absorption features observed from the 193-nm photolysis of propyne, the following study of the 193-nm photolysis of 2-butyne was performed.

2-Butyne. Although propyne ($CH_3C{\equiv}CH$) and 2-butyne ($CH_3C{\equiv}CCH_3$) are structurally similar, it might be intuitively expected that the dissociation of 2-butyne will proceed via reaction 3. However, as noted earlier, primary formation of propargyl is favored thermodynamically and it is predicted that propargyl ($H_2CC{\equiv}CH$) radicals will be formed upon photolysis of 2-butyne as the major primary photodissociation process (3).[15] At the relatively high energies associated with 193-nm photolysis, it is possible the propynyl ($CH_3C{\equiv}C$) and methyl (CH_3) radicals may be formed directly, as in the propyne case

$$CH_3C{\equiv}CCH_3 \rightarrow CH_3C{\equiv}C + CH_3 \tag{3}$$

Reaction 3 is predicted to represent about 24% of the primary photodissociation processes.[15]

Under similar conditions to those of the previous experiments, dilute (0.25% photolysate, 200 Torr [27 kPa] He) and flowing mixtures of 2-butyne were photolyzed by 193-nm excimer laser radiation and time-resolved absorption traces were averaged and recorded at various wavelengths.

Time-resolved absorption traces, shown in Figure 5, at 330 nm indicated an instant rise after the photolysis event (A_{max}) followed by decay to a non-zero baseline. At 240 nm, the instant rise is followed by an additional slower increase, which then decays to a nonzero baseline.

As in the case of the results from propyne photolysis, a significant variation of $A_{max}/A_{tail,}$ particularly at shorter wavelengths, was observed. Absorbance values, A_{max} and $A_{max} - A_{tail}$ versus wavelength are plotted in Figure 6.

The absorption spectra of the transient product(s) in the region of 220−360 nm, determined from the 193-nm photolysis of 2-butyne, are similar to the results of propyne photolysis and exhibit two relatively strong absorption bands, one in the 240-nm region and a weaker one in the 320-nm region with a relative intensity of about 2:1. The GC/MS analysis of the photolyzed samples identified ethane as well as a number of C_4H_6 and C_6H_6 isomeric products, which are confirmatory of the photolytic formation of methyl radicals and thus, by difference, propynyl (CH_3CC) radicals. CH_3 formation has been predicted to represent about 24% of the primary processes.[15]

The similarities in the absorption spectra and the temporal dependencies derived from both propyne and 2-butyne suggest that the transient absorptions at 240 and 330-nm regions,

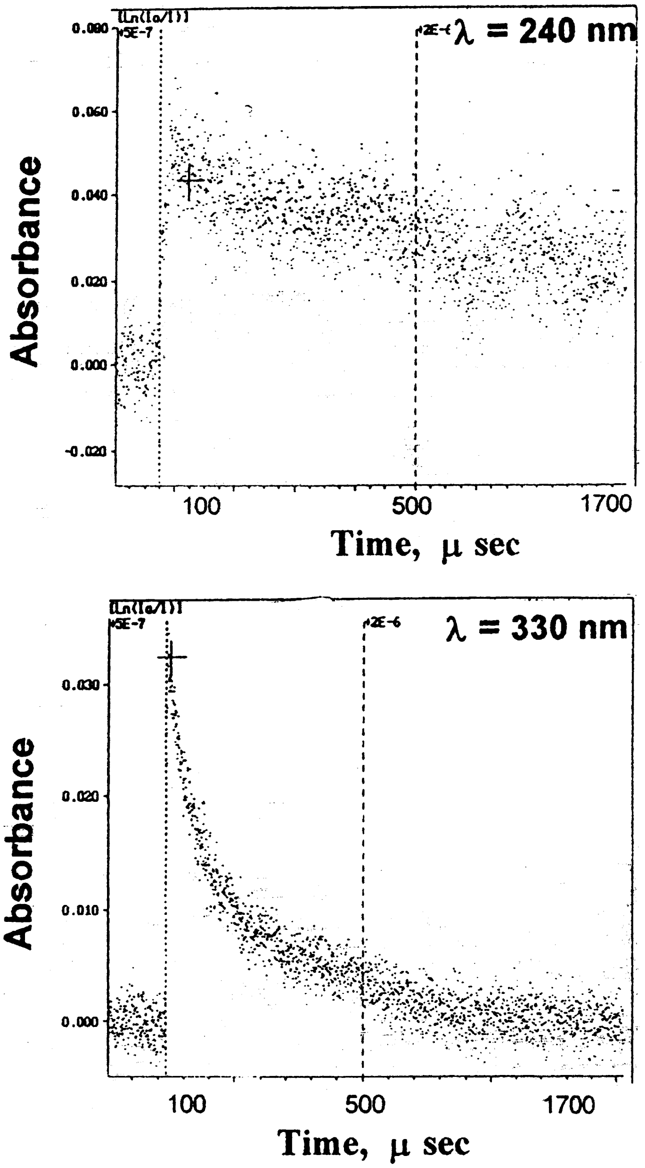

Figure 5. Time-resolved absorption trace from 193-nm photolysis of 2-butyne probed at 240 and 330 nm.

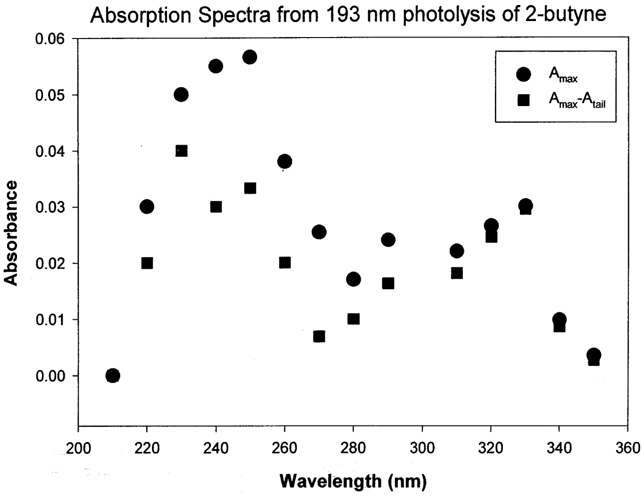

Figure 6. Absorption spectra of transient species generated from 193-nm photolysis of 2-butyne.

following photolysis of these molecules, have contributions, in part, from radicals other than propargyl, possibly propynyl radicals. To assess the absorption characteristics formed through possible secondary processes, time-delayed absorbances following the photolysis of both propyne and 2-butyne were determined and are illustrated in Figure 7.

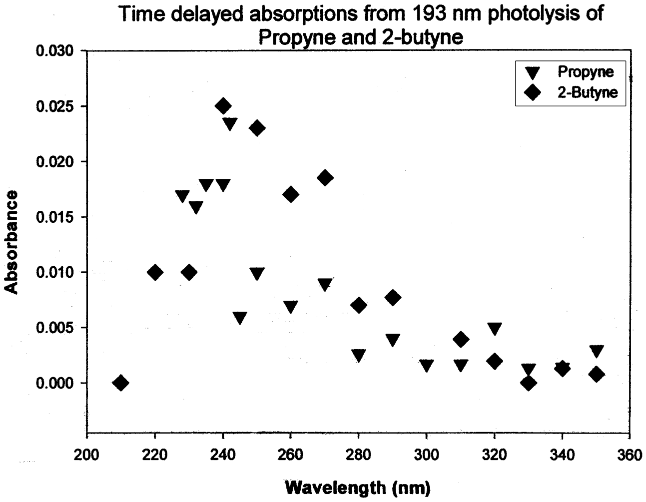

Figure 7. Time-delayed absorption spectra of transient species generated from 193-nm photolysis of propyne and 2-butyne.

The results qualitatively illustrate the presence of strong "delayed" absorption bands in the 240-nm region from both photolysates and represent contributions from the various isomeric forms of C_3H_3 radicals including propargyl. In these systems, secondary dissociation of the primary radical, for example, propargyl to propadienylidene, is unlikely because the loss of an H atom is endothermic by more than 100 kcal/mol (418 kJ/mol)[1,16] and the extra energy available following the initial dissociation of the propyne at 193 nm is about 61 kcal/mol (255 kJ/mol). The latter would be just sufficient, however, to allow for the dissociation of propynyl radicals to propadienylidene.[17]

The comparison of spectral results for allene with those of propyne and 2-butyne show distinct and important differences. In our view, the observed differences can only be explained by the presence of and contribution(s) from transient species other than propargyl radicals. Otherwise, the transient absorption traces and the spectra derived from the three systems should be identical if the absorbing species are only propargyl radicals.

Conclusions

The 193-nm photolysis of allene, propyne, and 2-butyne produce transient species that have a strong absorption band around 240 nm and a weaker band in the 330-nm region. Although the systems investigated are relatively small, the primary processes involved in the photodissociation of these molecules are, nevertheless, quite complicated. The fact that possible multiple photodissociation channels and isomerization of the primary radicals formed may occur is shown by the time-dependent absorption spectra of the products and may be taken as evidence of the complexity of the systems. The distinct differences between the time-resolved absorption traces and wavelength-dependent spectra derived following 193-nm photolysis of allene with those of propyne and 2-butyne suggest that the observed absorption features following photolysis of propyne and 2-butyne are likely to be composite with contributions from propargyl radicals and other transient species, including propynyl radicals.

Considering the structural similarities of various C_3H_3 isomers, particularly propargyl and propynyl, it is not surprising for these species to have similar UV-absorption characteristics. The absence of a firm spectral assignment indicates the necessity of further experimentation with improved temporal and spectral resolution. The fine differences in absorption characteristics of these species can be identified by TOF studies and high-resolution UV/IR spectroscopic methods (not currently available in this laboratory). These results suggest that spectral observations provide valuable information that is adjunct to molecular beam experiments and provide data not obtainable by other techniques.

In addition, it is needless to say that theoretical predictions of the energetics and absorption characteristics of various C_3H_3 species would be very valuable and helpful.

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