

Infrared Laser Absorption Measurements of the Kinetics of Propargyl Radical Self-Reaction and the 193 nm Photolysis of Propyne

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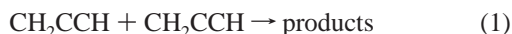
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Received: January 8, 2003; In Final Form: April 9, 2003

Infrared laser absorption spectroscopy is used to investigate recent discrepancies in measurements of the propargyl radical self-reaction rate coefficient and product formation in 193 nm photolysis of propyne. The cross section of the propargyl radical is measured relative to that of HCl using the Cl + propyne reaction, yielding a peak absorption cross section (assuming Doppler-limited line shapes) of $(1.9 \pm 0.4) \times 10^{-18} \text{ cm}^2$ for the P(12) line of the ν_1 fundamental at 296 K. The rate coefficient for the propargyl radical (CH_2CCH) self-reaction is determined by modeling the infrared absorption of the propargyl radical formed in the 193 nm photolysis of propargyl chloride (HCCCH_2Cl) and propargyl bromide (HCCCH_2Br), using a more precise literature determination of the pressure-broadened absorption cross section. The propargyl self-reaction rate coefficient so obtained, $(3.9 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is consistent with several recent measurements but disagrees significantly with the one previous infrared absorption determination. Both the propargyl radical and acetylene (HCCH) are observed in the 193 nm photolysis of propyne (CH_3CCH). The propargyl is formed promptly following the UV photolysis pulse, and the magnitude of the signal is unaffected by the addition of O_2 . The observed propargyl signal is consistent with direct CH_2CCH formation in the 193 nm photolysis of propyne and appears inconsistent with formation by secondary reactions of the 1-propynyl radical (CH_3CC). The observed CH_2CCH yield per 193 nm photon absorbed is 0.49 ± 0.10 .

Introduction

The self-reaction of the propargyl radical (H_2CCCH) is generally believed to be the most important cyclization step in flames of aliphatic fuels^{1,2}



Propargyl is the smallest unsaturated hydrocarbon radical to be resonance stabilized. Because of resonance stabilization, propargyl forms weak bonds with stable molecules such as molecular oxygen and is more resistant to pyrolysis than nonresonance stabilized hydrocarbon radicals. Consequently, propargyl is relatively unreactive in flames and may attain relatively high concentrations.³ High concentrations and relatively rapid self-reaction make propargyl self-reaction an important initiation step for building higher hydrocarbons in flames. Miller and Melius² calculate that the propargyl self-reaction forms aromatic ring products such as benzene or phenyl + H. These initial aromatic species can then go on to react to form the polyaromatic hydrocarbons (PAH) associated with soot.

The second-order rate constant (k_1) for the self-reaction of propargyl has been experimentally determined at room temperature by several different techniques.^{4–6} Morter et al.⁶ made the first measurement of the room-temperature second-order rate constant by using time-resolved infrared (IR) absorption on the ν_1 (P12) acetylenic C–H stretch of the propargyl radical at 3314.703 cm^{-1} . They obtained the IR cross section of the

propargyl radical by comparison of the absorption of the propargyl line to the absorption of Br ($F = 2 \leftarrow 3$, $^2\text{P}_{1/2} \leftarrow ^2\text{P}_{3/2}$) at 3685.225 cm^{-1} , where propargyl radical and Br atom were formed by 193 nm photolysis of propargyl bromide (HCCCH_2Br). By fitting observed propargyl signal decays from propargyl chloride photolysis to a second-order rate equation, they obtained a second-order rate constant of $(1.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The work of Morter et al. included extensive tests to rule out the effects of secondary chemistry; nevertheless, Atkinson and Hudgens⁵ contend that these tests are insufficient and that the propargyl signal obtained when using propargyl chloride as the propargyl precursor is significantly affected by secondary reactions. The $\text{C}_3\text{H}_3\text{Cl}_2$ radical, formed when the photolytically produced Cl recombines with propargyl chloride, is proposed to react rapidly with propargyl



Atkinson and Hudgens observed the time-resolved propargyl radical absorption at 332.5 nm following ultraviolet photolysis of several precursors. To obtain a consistent value for rate constants k_1 and k_2 , they modeled the propargyl signal obtained for three different precursors and deduced a second-order rate constant of $4.3 \pm 0.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for propargyl self-reaction. Fahr and Nayak⁴ measured the propargyl self-reaction rate relative to the methyl radical (CH_3) self-reaction rate by using gas chromatographic/mass spectrometric end product analysis. Fahr and Nayak maintained that the effects of secondary reactions involving $\text{C}_3\text{H}_3\text{Cl}_2$ were insignificant in their experiments when using propargyl chloride as the precursor, and they obtained a very similar self-reaction rate constant to Atkinson and Hudgens, $4.0 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$

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s^{-1} . The recent multiple-well time-dependent master equation calculations of Miller and Klippenstein⁷ were constrained to agree with the measurement of Fahr and Nayak at room temperature. Recent measurements of the propargyl self-reaction rate coefficient at higher temperature by Knyazev and co-workers⁸ and Hippler and co-workers⁹ also appear consistent with a room temperature value of the rate coefficient significantly lower than the infrared absorption measurements.

The possibility of production of the propargyl radical from the 193 nm photolysis of propyne (CH_3CCH) has also been of recent interest. The dissociation energy of the acetylenic C–H bond ($CH_3CC-H = 130 \text{ kcal mol}^{-1}$) of propyne is significantly greater than the methyl C–H bond ($H-CH_2CCH = 89 \text{ kcal mol}^{-1}$).¹⁰ There is some evidence that 193 nm photolysis results in the breaking of the stronger bond to form 1-propynyl radical (CH_3CC). Satyapal and Bersohn¹¹ reported observing D atoms but no H atoms from the 193 nm photolysis of CH_3CCD , indicating that 1-propynyl is the only C_3H_3 radical formed from the photolysis. Seki and Okabe¹² investigated the 193 nm photolysis of CD_3CCH by end product analysis with a Fourier transform IR spectrometer. They measured the formation of HCl and DCl from the reaction of Cl_2 with H or D produced from 193 nm photolysis of CD_3CCH . They obtained a yield of 0.7 for HCl and were unable to observe any DCl formation, again suggesting $CD_3CC + H$ as the major product of the photolysis. A small yield of acetylene (~ 0.11) was also detected.¹² Sun et al.¹³ used tunable vacuum UV to photoionize the 193 nm photoproducts of a molecular beam containing propyne or allene (H_2CCCH_2). The C_3H_3 photoproduct from allene had a photoionization threshold of $\sim 8.5 \text{ eV}$, whereas the major C_3H_3 photoproduct from propyne had a threshold of $\sim 10.25 \text{ eV}$. These photoionization energies agree well with those of the propargyl radical and 1-propynyl radical, respectively. Sun et al. also measured the $C_3H_3:C_3H_2$ ratio from 193 nm propyne photolysis to be 56:44 by using time-of-flight measurements with electron impact ionization detection. Ni et al.¹⁴ observed that the $C_3H_3:C_3H_2$ ratio was dependent on the 193 nm fluence and concluded that C_3H_2 is produced almost exclusively by multiphoton absorption, with a one-photon C_3H_2 yield of no more than 0.5% of the C_3H_3 yield. Ni et al. also observed an extremely small amount of methylene formation.

Opposing the picture of exclusive acetylenic bond fission is ample evidence that the UV photolysis of propyne results in the formation of at least some propargyl radical. Propargyl radical formation at UV wavelengths greater than 193 nm was observed by Ramsay and Thistlethwaite.¹⁵ This flash photolysis study observed the same diffuse absorption bands in the 290 to 345 nm region from photolysis of propargyl bromide, allene, propargyl chloride, and propyne. These UV bands have been assigned to the propargyl radical. Atkinson and Hudgens⁵ also observed formation of the propargyl radical from the photolysis of propyne at 193 nm by using time-resolved UV absorption at 332.5 nm. Galli et al.,¹⁶ using mass spectrometric end product analysis, reported that 1,5-hexadiyne and not 2,4-hexadiyne was the dominant C_6H_6 product from 206 nm photolysis of propyne. Chen et al.¹⁷ found that 243.1 nm photodissociation of vibrationally excited propyne- d_3 , isoenergetic to 193 nm photolysis of vibrationless propyne, produced both D and H atoms with a D:H ratio of 2:1. Qadiri et al.¹⁸ studied allene and propyne photolysis at 203.3, 209.0, and 213.3 nm by using Rydberg atom photofragment translational spectroscopy. They found the translational energy of the H produced from both precursors to be identical and that the translational energy distribution is

described well by a statistical model that assumes H_2CCCH as the partner at all wavelengths measured.

Qadiri et al.¹⁸ suggested that the apparently conflicting experimental evidence could be rationalized if propyne had a barrier to acetylenic H dissociation in the excited state. Thus, at 193 nm, the propyne would possess enough internal energy to form 1-propynyl directly, but at the lower photolysis energies ($\lambda > 193 \text{ nm}$) of their experiments,¹⁸ the barrier would prevent excited-state dissociation. Propargyl radical would then be formed by dissociation on the ground state. Atkinson and Hudgens⁵ postulate that the propargyl radical might not be formed directly from the 193 nm photolysis, but rather by a rapid secondary reaction



The rate constant of reaction 3 is not known, but the analogous reaction of the ethynyl radical (HCC) with propyne has a large room-temperature rate constant of $2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.¹⁹ However, it is not clear that this reaction would be exclusively an abstraction reaction, as CCH could add to the propyne as well. A fast abstraction reaction could reconcile the observation of propargyl with exclusive acetylenic bond fission in the 193 nm photolysis of propyne. If this reaction were the source of propargyl, then introduction of a competitor for the 1-propynyl radical (e.g., O_2) would reduce the observed propargyl signal.

This work investigates the discrepancies between the previous IR absorption experiments⁶ and other recent measurements of the propargyl self-reaction.^{4,5,8,9} The infrared absorption of the propargyl radical is observed at the same transition (P(12) at 3314.703 cm^{-1})²⁰ as the previous experiments. The IR cross-section previously measured by Morter et al.⁶ is confirmed by comparing absorption of propargyl radical and HCl from the reaction of Cl with propyne. However, the apparent second order rate constant derived by fitting presently observed propargyl signals to a second-order rate equation is less than half that reported in the previous IR determination. Modeling the propargyl signal from propargyl chloride and propargyl bromide photolysis by using the mechanisms of Atkinson and Hudgens⁵ and Fahr and Nayak⁴ yields a self-reaction rate coefficient of $k_1 = (3.9 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Prompt IR absorption from propargyl radical is observed from 193 nm photolysis of propyne. The signal onset and magnitude of the propargyl signal is not affected by the addition of molecular oxygen indicating that reaction 3 is not the source of the propargyl radical. Rather, the results are consistent with direct formation of propargyl in the 193 nm photolysis with a yield of $\Phi_{CH_2CCH} = 0.49 \pm 0.10$. Acetylene is also observed as a product of 193 nm propyne photolysis and appears to be formed vibrationally hot. The acetylene is not a product of secondary photolysis of the propargyl radical. The signal onset and magnitude of the acetylene signal is also not affected by the addition of molecular oxygen, implying that reactions of 1-propynyl are not the source of acetylene. The observed $[HCCH]/[CH_2CCH]$ ratio is ~ 0.2 .

Experimental Section

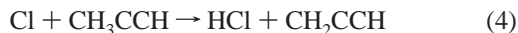
The pulsed photolysis/long path absorption method used in this experiment is similar to that employed in previous experiments.²¹ Propargyl radicals, HCl, and acetylene are observed by direct absorption of a tunable Li:RbCl color center laser. The probe is split into two beams: one impinges on a reference detector (I_0), and the other is directed through the cell and onto

a second detector (I). The absorption is monitored in time as the difference between balanced signal (I) and reference (I_0) detectors. In the self-reaction rate constant measurements, the IR probe beam and the UV photolysis beam are overlapped throughout the entire length of the 160 cm flow cell using dielectric mirrors that reflect 193 nm but are transparent to the IR wavelengths used. For the remaining experiments, the IR laser output is passed 20 times through the reaction zone using a spherical Herriott-type multipass cell.²² In this configuration, the 193 nm photolysis beam passes through the center of the Herriott mirrors and travels on axis through the quartz flow cell. The total effective length of the region where the IR probe beam and UV photolysis beam overlap is ~ 20 m.

Gases are delivered by calibrated mass flow controllers. The excimer laser dissociates approximately 10^{-3} of the photolyte each shot, and the entire cell volume is refreshed every 4–5 shots at the 1 Hz repetition rate of the experiments. Propargyl chloride (98%) and propargyl bromide (delivered as 80 wt % solution in toluene) are purified by vacuum distillation before use. The manufacturer-stated gas purities are propyne (lot analysis) 98.6%, He 99.9999%, and CO₂ 99.995%. Reactant concentrations in the measurements of the propargyl absorption cross section are [Cl₂] = 5.46×10^{14} cm⁻³, [CO₂] = 8.42×10^{16} cm⁻³, and [CH₃CCH] = 9.19×10^{15} cm⁻³ with He added to 6 Torr. The self-reaction rate coefficient measurements are typically carried out at 16 Torr total pressure (He) with [CO₂] = 3.96×10^{16} cm⁻³ and [HCCCH₂Cl] = 0.70×10^{15} cm⁻³ or [HCCCH₂Br] = 0.60×10^{15} cm⁻³. Most of the determinations of propargyl and acetylene yield in propyne photolysis are carried out at a total pressure of 16 Torr with [CO₂] = 3.96×10^{16} cm⁻³, [CH₃CCH] = 8.60×10^{15} cm⁻³, and the bulk He.

Results

IR Cross Section Measurement. To obtain the second-order rate constant for a self-reaction from an absorption signal, the absorption signal must be converted to absolute concentration. Thus, any error in the IR cross section creates a proportional error in the second-order rate constant determination. The propargyl radical is formed by the reaction of Cl atoms with propyne. Cl is generated by photolysis at 355 nm of Cl₂, and CH₂CCH is subsequently generated by the reaction of Cl with propyne. At room temperature, 70% of the Cl abstracts a hydrogen to produce the propargyl radical²¹



The formation of propargyl and HCl in reaction 4 are followed by their IR absorptions at 3314.703 cm⁻¹ (ν_1 P(12))²⁰ and 3045.058 cm⁻¹ (H³⁵Cl $\nu = 1 \leftarrow 0$ R(8))²³ respectively. The relative peak absorption of propargyl radical can then be compared to the peak absorption of the HCl. The HCl signal is biexponential, with some HCl being formed slowly through secondary reactions.²¹ The signals are fit to a biexponential rate equation to obtain the HCl absorption due to direct hydrogen abstraction only. Provided that the observed absorptions are small, the relative cross section for propargyl can be obtained as follows:

$$\sigma_{\text{C}_3\text{H}_3} = \frac{\text{absorption}_{\text{C}_3\text{H}_3} \cdot \sigma_{\text{HCl}}}{\text{absorption}_{\text{HCl}}} \quad (5)$$

The peak absorption of the Doppler-limited R(8) line of the H³⁵Cl fundamental is 0.2298 cm⁻¹ Torr⁻¹ for natural abundance

HCl at 295 K,²⁴ corresponding to an effective peak cross section of 7.02×10^{-18} cm².

To limit the effects of pressure broadening in the cross section experiment, the experiment is performed at a relatively low total pressure of 6 Torr. The peak absorption of the prompt propargyl signal is found to be $(2.1 \pm 0.3) \times 10^{-3}$, and the peak absorption of the prompt HCl signal is found to be $(7.9 \pm 1.0) \times 10^{-3}$ from the biexponential fits. The propargyl cross-section was determined to be $(1.9 \pm 0.4) \times 10^{-18}$ cm² by using the Pine et al.²⁴ Doppler-broadened HCl cross-section and eq 5. The cross section determined in this manner is only slightly larger than that determined by Morter et al.⁶ ($1.5 \pm 0.1) \times 10^{-18}$ cm². The measurements of Morter et al. used a direct photolytic method and explicitly accounted for pressure broadening effects by scanning over the Br reference transition and, hence, may be expected to be more accurate than the present simple comparison of amplitudes. The previous cross section determination and the present kinetics experiments are carried out at higher He pressure (15 Torr) with 1 Torr of CO₂ added and will have larger pressure broadening effects. The present apparatus is not suited to accurate measurement of line shapes. However, if the collisional broadening of the propargyl P(12) line were similar to the ~ 40 MHz broadening observed by Morter et al.⁶ for the Br (²P_{1/2}, F = 2 \leftarrow ²P_{3/2}, F = 3) transition, the present determination would correspond to a pressure-broadened peak cross section of $\sim 1.6 \times 10^{-18}$ cm² under the conditions of the kinetics experiments. The uncertainty limits of the present results encompass the previous determination, and there is no reason to suspect an error in the IR cross section for the nearly 3-fold difference in rate constant between the previous infrared absorption results and other experiments.

Self-Reaction Rate Coefficient. Because the present cross-section measurement is in agreement with the more precise determination by Morter et al.,⁶ their value for the pressure-broadened absorption cross section is used to obtain the self-reaction rate constant for propargyl radical, under the same conditions as the previous IR experiments. Propargyl radicals are produced by 193 nm photolysis of propargyl chloride and propargyl bromide. Figure 1 shows the decay traces of the propargyl radical formed from the two precursors. The propargyl radical signal from propargyl bromide photolysis decays slightly faster than that from photolysis of propargyl chloride. The propargyl signals are well-fit by a second-order rate equation that includes a baseline term

$$[\text{CH}_2\text{CCH}]_t = \text{baseline} + \frac{1}{\frac{1}{[\text{CH}_2\text{CCH}]_0} + 2k_1t} \quad (6)$$

The fits of the propargyl chloride data yield a $k_{1,\text{apparent}} = (5.8 \pm 1.0) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and a baseline shift of -6.0×10^{11} cm⁻³, or $(I - I_0) = -1.4 \times 10^{-4}$. The fits of the propargyl bromide data yield a $k_{1,\text{apparent}} = (7.3 \pm 0.7) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ and a baseline shift of 4.6×10^{11} cm⁻³ (1.1×10^{-4}). Figure 2 shows that the decay of propargyl from 193 nm photolysis of propargyl chloride is independent of UV power, as observed by Morter et al.⁶ The use of a simple second-order fit to derive k_1 has been contested by Atkinson and Hudgens⁵ because of the contributions of secondary and side reactions. Comparison of measurements of propargyl disappearance with end-product measurements,⁴ which should be less sensitive to side reactions, appears to support Atkinson and Hudgens's contention. The value for k_1 is derived from an analysis of the present data using the mechanism of Atkinson and Hudgens⁵ as described in the Discussion section below.

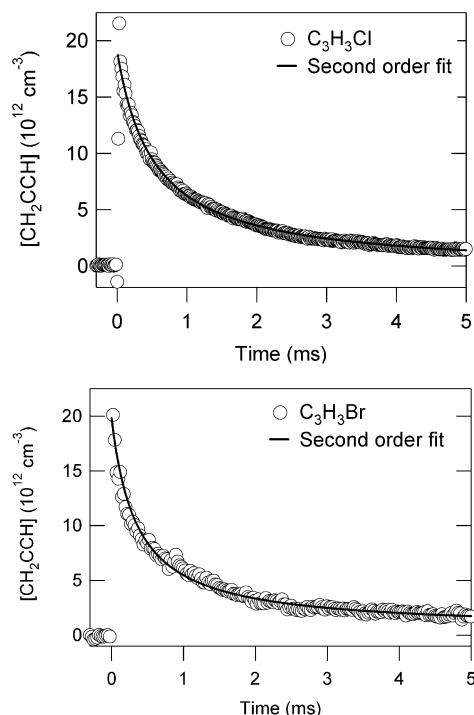


Figure 1. (Above) Propargyl absorption at 3314.703 cm^{-1} after 193 nm photolysis of propargyl chloride. (Below) Propargyl absorption after 193 nm photolysis of propargyl bromide. Only every 25th data point is displayed for clarity. The signals are fit to a second-order rate equation and yield apparent second-order rate constants of $k = (5.8 \pm 1.0) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ for the propargyl chloride and $k = (7.3 \pm 0.7) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ for the propargyl bromide precursor.

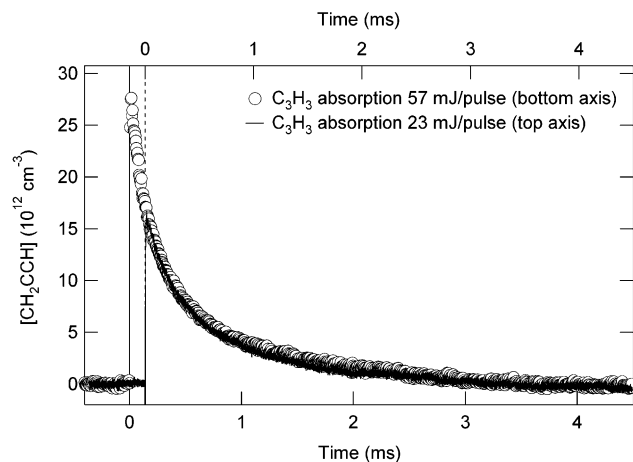


Figure 2. Propargyl absorption at 3314.703 cm^{-1} following HCCCH₂-Cl photolysis at two different 193 nm powers. The propargyl decay rate is not affected by the UV fluence.

The overall second-order rate constant for propargyl removal as determined by using eq 6 for propargyl chloride photolysis is slightly less than half the rate constant previously determined by Morter et al.⁶ using the same technique under similar conditions. The infrared absorption of propargyl has a slightly faster decay when using propargyl bromide as precursor than when using propargyl chloride, similar to the behavior previously observed by Morter et al. and opposite the effect observed by Atkinson and Hudgens⁵ using UV cavity ringdown at 332.5 nm to probe propargyl. The present configuration subjects the reaction mixture to 4–5 photolysis pulses. Atkinson and Hudgens proposed that secondary chemistry induced by product photolysis could markedly increase the observed propargyl decay rates. However, the present decay with propargyl chloride

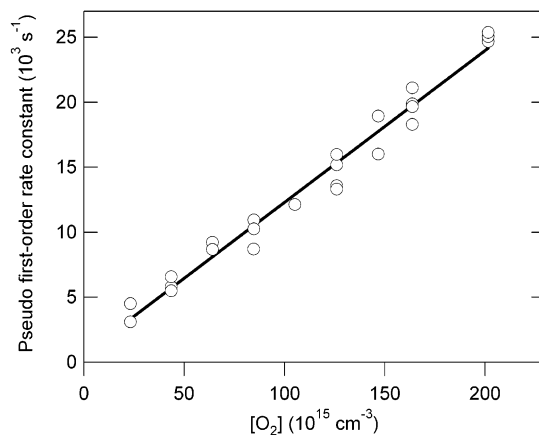
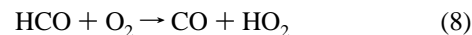
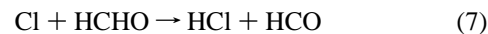


Figure 3. Pseudo-first-order rate constant of the propargyl signal decay vs the concentration of O₂. The slope to the linear fit yields a second-order rate constant for CH₂CCH + O₂ of $k_9 = (1.16 \pm 0.8) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

photolysis is slightly slower than those observed by Atkinson and Hudgens under single-shot photolysis conditions, suggesting that product photolysis may be an unimportant factor in the propargyl decay.

To investigate the possible effect of secondary reactions of the Cl atom produced in the propargyl chloride photolysis, Morter et al.⁶ added formaldehyde and O₂ to convert the Cl into the relatively inert HO₂ by the following reaction sequence:



They then fit the propargyl decay signals to a first plus second-order rate equation where the first-order component is the pseudo-first-order rate constant for the reaction of propargyl with oxygen:



and the second-order component is for reaction 1. They obtained a second order rate constant for the propargyl self-reaction similar to what they previously determined and derived a second-order rate constant for reaction 9 of $k_9 = 2.3 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 20 Torr He. Atkinson and Hudgens⁵ also measured the second-order rate constant of the reaction of propargyl with molecular oxygen. The Atkinson and Hudgens measurement of this second-order rate constant ($1.01 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$) at 2671 Pa (20 Torr) is approximately half the measurement of Morter et al.⁶ Figure 3 shows the pseudo-first-order rate constant ($k_9 [\text{O}_2]$) as a function of O₂ concentration at a constant total pressure of 16 Torr (He buffer). The pseudo-first-order rate constant is obtained by fitting the propargyl signal decay to a first-order rate equation. The slope of the linear fit in Figure 3 corresponds to a second-order rate constant of $(1.16 \pm 0.08) \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The current IR absorption measurements are in agreement with the UV absorption measurements for the room-temperature rate constant for the reaction of propargyl with O₂. It is unclear why previous IR absorption measurements for the rate constants of reaction 1 and 9 are both a factor of ~ 2 larger than the current determination using the same methodology. In discussions with Glass and Curl,²⁵ they recall that it was possible, though unlikely, that the transient digitizer time base could be wrong by a factor of 2 in their work. They say that, unlikely as this

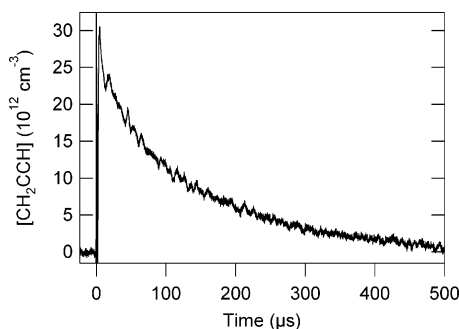


Figure 4. Propargyl signal at 3314.703 cm^{-1} from 193 nm photolysis of propyne with 16 Torr of total pressure.

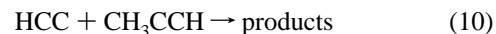
possibility seems, it would explain why both rate constants are about a factor of 2 too large.

Propyne Photolysis. The propargyl radical has previously been observed by UV absorption from 193 nm photolysis of propyne.⁵ Figure 4 shows the infrared absorption of the propargyl radical observed from 193 nm photolysis of propyne. The signal appears promptly after the UV photolysis flash. To measure the yield of propargyl radical for the 193 nm photolysis of propyne, the cell is set up for single pass absorption, under conditions similar to those of Morter et al.⁶ so that the $[\text{CH}_2\text{CCH}]$ formed could be determined accurately. The UV absorption is determined by measuring the photolysis power with and without propyne in the cell. The number of 193 nm photons absorbed can also be calculated by using the UV cross section of propyne ($3 \times 10^{-19}\text{ cm}^2$)²⁶ at 193 nm. Table 1 lists the measured and calculated UV absorption of propyne and the resulting peak $[\text{CH}_2\text{CCH}]$ obtained from the propargyl signal. The ratio of $[\text{CH}_2\text{CCH}]_{\text{peak}}/[\text{Photon}]_{\text{abs}}$ is measured to be $\Phi = 0.49 \pm 0.10$; if the literature UV cross section is used, then $\Phi = 0.55 \pm 0.10$.

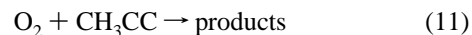
Propargyl is not the only product observed from the 193 nm photolysis of propyne. Figure 5 shows the IR signal of acetylene at 3313.9346 cm^{-1} ($\text{R}(13)$ ($\nu_2 + \nu_4 + \nu_5$)) from 193 nm photolysis of propyne at a total pressure of 16 Torr with and without $7.6 \times 10^{16}\text{ cm}^{-3}$ of CO_2 . The rise of the acetylene absorption is more rapid when CO_2 is added indicating that C_2H_2 is most likely being formed vibrationally and rotationally hot. Also seen in Figure 5 is the absorption at the acetylene transition when propargyl bromide is photolyzed at 193 nm. The propargyl bromide and propyne concentrations are set such that an equal amount of the propargyl radical is produced in both systems. Acetylene is not a major product in the 193 nm photolysis of propargyl bromide. Because the $[\text{CH}_2\text{CCH}]$ and UV power are equal for both traces, the observed acetylene cannot arise from subsequent UV photolysis of the propargyl radical. Using the literature Doppler-broadened IR cross section for the acetylene transition ($2.50 \times 10^{-17}\text{ cm}^2$)²⁷ and comparing it to the observed propargyl signals from the above experiments yields a $[\text{HCCH}]_{\text{peak}}/[\text{CH}_2\text{CCH}]_{\text{peak}} \sim 0.2$. Given the rapid appearance of acetylene, it is likely at least partially a primary photolysis product. The observed yield of acetylene is very similar to the yield reported by Seki and Okabe.¹²

In order for previous experimental evidence of 1-propynyl formation to be consistent with the UV and IR absorption experiments that observe propargyl radical formation from 193 nm photolysis, the 1-propynyl radical must rapidly convert to the propargyl radical. Direct isomerization is unlikely to occur as the 1-propynyl does not have sufficient internal energy ($\sim 18\text{ kcal mol}^{-1}$) to overcome the calculated isomerization barrier ($\sim 36.4\text{ kcal mol}^{-1}$)²⁸ to form the propargyl radical. Atkinson

and Hudgens⁵ instead proposed that reaction 3 may occur rapidly and convert between the two radicals. The rate constant for this reaction has not been measured, but the analogous reaction of the ethynyl radical (C_2H) has recently been determined¹⁹



The rate constant (k_{10}) at room temperature is indeed very large ($2 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$), and a similar rate constant for reaction 3 could conceivably account for the propargyl formation observed in the UV and IR absorption experiments. To check if the observed propargyl signal was coming from reaction 3, oxygen was added to compete with propargyl formation from reaction 3



The rate constant of 1-propynyl with molecular oxygen has not been measured, but the analogous reaction of ethynyl radical has a rate constant at 297 K of $(3.17 \pm 0.07) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.²⁹ Propyne ($[\text{CH}_3\text{CCH}] = 2.13 \times 10^{15}\text{ cm}^{-3}$) is photolyzed at 193 nm in the presence of O_2 ($[\text{O}_2] = 8.64 \times 10^{16}\text{ cm}^{-3}$) at a total pressure of 16 Torr (He buffer). Figure 6 shows the propargyl signal with and without the O_2 added to the reaction mixture. Whereas the signal decays faster with O_2 added, there is virtually no difference in the peak propargyl absorption.

Discussion

Propargyl Radical Self-Reaction. In their investigation of the propargyl radical self-reaction, Atkinson and Hudgens⁵ rejected simple second-order fits because of the probable influence of side reactions, and they instead modeled their UV absorption signals by using integrated rate equations. Table 2 lists the mechanisms used by Atkinson and Hudgens to model the propargyl UV absorption and by Fahr and Nayak⁴ to model end product formation from 193 nm photolysis of propargyl chloride. Because of the small C_3H_2 yield in the 193 nm photolysis of propargyl chloride, Atkinson and Hudgens ignored C_3H_2 reactions when modeling the propargyl signal from propargyl chloride photolysis. They did include these reactions when they modeled their propargyl signal from propargyl bromide photolysis because the 193 nm propargyl yield from propargyl bromide is only 0.5.³⁰ Table 3 lists the reactions used by Atkinson and Hudgens⁵ to model propargyl UV absorption when using propargyl bromide as the precursor. These different reaction models are used to model the propargyl IR signal for propargyl chloride and propargyl bromide photolysis. Figure 7 shows a comparison of the models to the present infrared absorption data. The Atkinson and Hudgens⁵ model decays too fast for both systems, and the Fahr and Nayak⁴ model decays slightly too fast. The Fahr and Nayak model is adapted to produce a best fit to the current data by adjusting the two rate constants (k_3 and k_1) for the $\text{C}_3\text{H}_3 + \text{C}_3\text{H}_3\text{Cl}_2$ and C_3H_3 self-reaction. The k_1 and k_3 listed in Table 2 are the average values obtained by fitting 5 separate CH_2CCH signals from the 193 nm photolysis of propargyl chloride. The average value of k_1 is then used as a fixed parameter to model the propargyl signals obtained using propargyl bromide as the precursor as a check. The results of the two modified models are shown in Figure 7 for comparison. The resulting CH_2CCH self-reaction rate constant (using the literature determination of the pressure-broadened absorption cross section), $(3.9 \pm 0.6) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, is in good agreement with the two previous experiments. If the present determination of the cross section

TABLE 1: Propargyl Yield Measurements from 193 nm Photolysis of Propyne

[C ₃ H ₄] (10 ¹⁵ cm ⁻³)	(ΔI/I ₀)	incident fluence (mJ cm ⁻²)	absorbed photon density (10 ¹³ cm ⁻³)	[C ₃ H ₃] (10 ¹³ cm ⁻³)	propargyl yield
8.6	0.40 (0.34) ^a	25.7	6.3 (5.3) ^a	3.3	0.52 (0.62) ^a
8.6	0.46 (0.34) ^a	24.3	6.8 (5.0) ^a	2.8	0.41 (0.56) ^a
8.6	0.38 (0.34) ^a	23.4	5.3 (4.8) ^a	2.5	0.46 (0.51) ^a
4.3	0.19 (0.19) ^a	21.4	2.5 (2.4) ^a	1.3	0.54 (0.55) ^a
4.3	0.18 (0.19) ^a	20.8	2.3 (2.4) ^a	1.2	0.51 (0.49) ^a

^a Values in parentheses are calculated using literature absorption cross section of propyne.²⁶

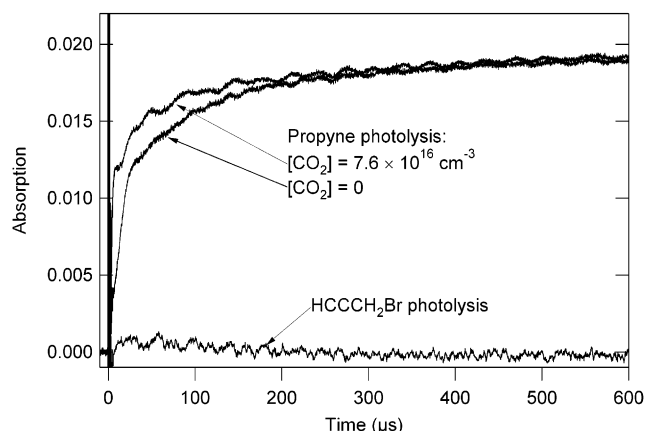


Figure 5. Acetylene signal at 3313.9346 cm⁻¹ from 193 nm photolysis of propyne at 16 Torr of total pressure. The middle trace is taken without CO₂ in cell and the uppermost is with [CO₂] = 7.6 × 10¹⁶ molecule cm⁻³. The lowest trace is the acetylene absorption following 193 nm photolysis of propargyl bromide at 16 Torr of total pressure. The propargyl bromide and propyne photolysis are performed under conditions such that the same absorption of propargyl is observed from both systems. The acetylene formation from 193 nm photolysis of propyne is not from secondary photolysis of propargyl.

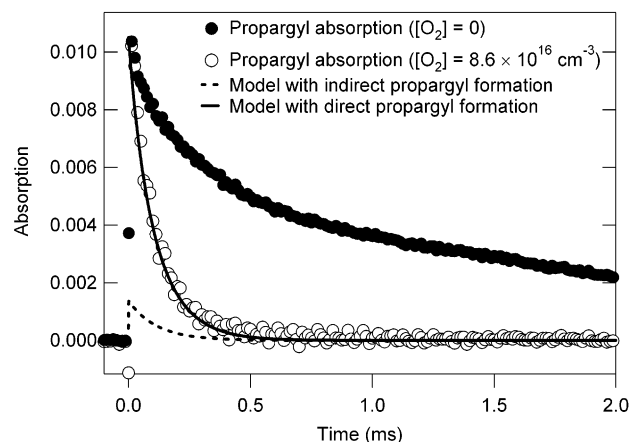


Figure 6. Solid circles display the propargyl absorption at 3314.703 cm⁻¹ from the 193 nm photolysis of propyne at 16 Torr of total pressure, and the open circles represent the observed propargyl absorption with added [O₂] = 8.64 × 10¹⁶ molecule cm⁻³. Only every 25th data point is displayed for clarity. The dashed line shows the predicted propargyl signal with O₂ added, if propargyl were formed from reaction of 1-propynyl with propyne with a rate constant of 2.0 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, assuming 1-propynyl reacts with O₂ with the same rate constant as ethynyl + O₂. The solid line shows the predicted propargyl signal with O₂ added if propargyl is formed directly from 193 nm photolysis of propyne.

were used, in conjunction with a ~40 MHz pressure broadening correction, the error estimate would increase by approximately a factor of 2, depending on the uncertainty assigned to the estimated pressure correction. The derived rate constant for C₃H₃ + C₃H₃Cl₂ is somewhat lower than the value used by Atkinson and Hudgens⁵ but is inside their uncertainty estimates.

TABLE 2: Kinetic Models Used to Interpret the Propargyl Reactions Following 193 nm Photolysis of Propargyl Chloride

reaction	rate constants (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)		
	Atkinson and Hudgens	Fahr and Nayak ^b	best fit
C ₃ H ₃ + C ₃ H ₃ → C ₆ H ₆	4.2 ± 0.9 ^a	4.0 ± 0.4	3.9 ± 0.6
C ₃ H ₃ + Cl → C ₃ H ₃ Cl	15 ^{a,c}	15 ^{a,c}	15 ^{a,c}
C ₃ H ₃ + C ₃ H ₃ Cl ₂ → products	7 ± 4 ^a	4 ^c	4 ± 0.4
C ₃ H ₃ Cl + Cl → C ₃ H ₃ Cl ₂	12 ± 2 ^d	12 ± 2 ^d	12 ± 2 ^d
C ₃ H ₃ Cl ₂ + Cl → products	15 ^{a,c}	15 ^{a,c}	15 ^{a,c}
C ₃ H ₃ Cl ₂ + C ₃ H ₃ Cl ₂ → products	3.4 ± 0.9 ^d	3.4 ± 0.9 ^d	3.4 ± 0.9 ^d
C ₃ H ₂ + C ₃ H ₂ → products		4 ^c	4 ^{b,c}
C ₃ H ₂ + C ₃ H ₃ → products		4 ^c	4 ^{b,c}

^a Reference 5. ^b Reference 4. ^c Estimated. ^d Reference 35.

TABLE 3: Rate Constants Used to Model Propargyl Reactions Following 193 nm Photolysis of Propargyl Bromide

reaction	rate constants (10 ⁻¹¹ cm ³ molecule ⁻¹ s ⁻¹)	
	Atkinson and Hudgens	present work
C ₃ H ₃ + C ₃ H ₃ → C ₆ H ₆	4.5 ± 2 ^a	3.9 ^b
C ₃ H ₃ + Br → C ₃ H ₃ Br	6.5 ± 5 ^a	6.5 ± 5 ^a
C ₃ H ₃ + C ₃ H ₃ Br ₂ → products	2.4 ± 2 ^a	2.4 ± 2 ^a
C ₃ H ₃ Br + Br → C ₃ H ₃ Br ₂	0.2 ^c	0.2 ^c
C ₃ H ₃ Br ₂ + Br → products	8 ^c	8 ^c
C ₃ H ₃ Br ₂ + C ₃ H ₃ Br ₂ → products	1.7 ± 1.1 ^c	1.7 ± 1.1 ^c
C ₃ H ₂ + C ₃ H ₂ → products	5 ^{a,d}	4 ^{d,e}
C ₃ H ₂ + C ₃ H ₂ Br → products	5 ^{a,d}	4 ^{d,e}
C ₃ H ₂ + C ₃ H ₃ → products	5 ^{a,d}	4 ^{d,e}

^a Reference 5. ^b Held fixed from HCCCH₂Cl experiments. ^c Reference 35. ^d Estimated. ^e Reference 4.

The inclusion of reactions of chlorinated species (primarily reaction 3) lowers the extracted rate constant k_1 relative to that obtained from a simple fit to a second-order decay. Because the experiments of Fahr and Nayak⁴ measure relative yields of hydrocarbon products, inclusion of the side reactions of C₃H₃-Cl₂ does not significantly change the interpretation of their results. Using the Fahr and Nayak mechanism, side reactions with C₃H₃Cl₂ do significantly reduce the overall product yields (contrary to the implication of their Table 2, which appears to have been calculated with too small an initial Cl atom concentration), but this change will be offset by a corresponding change in the derivation of the initial radical density. Their measurement of k_1 is therefore relatively insensitive to the contributions of chlorination chemistry. The fact that agreement of the time-resolved infrared absorption and end product analysis measurements of k_1 depends on inclusion of C₃H₃Cl₂ reactions supports Atkinson and Hudgens's interpretation of the importance of these reactions. The room-temperature value of k_1 derived from the present infrared absorption experiments ((3.9 ± 0.6) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹), from UV cavity ringdown measurements⁵ ((4.3 ± 0.6) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹), and

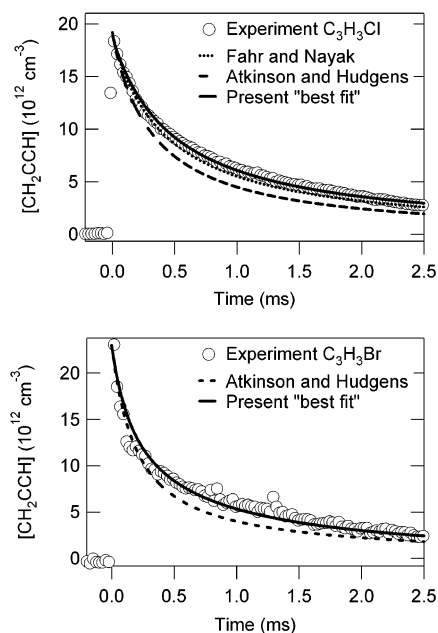


Figure 7. Propargyl absorption at 3314.703 cm^{-1} following 193 nm photolysis of propargyl chloride (above) and propargyl bromide (below). Only every 25th data point is displayed for clarity. The propargyl chloride signal is modeled using mechanisms of Atkinson and Hudgens⁵ (dashed line), Fahr and Nayak⁴ (dotted line), and a best fit (solid line) as described in the text. The propargyl bromide signal is fit to the model of Atkinson and Hudgens⁵ (dashed line), as well as a best fit (solid line) as described in the text.

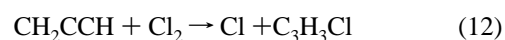
from relative end product yields,⁴ $(4.0 \pm 0.4) \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, are all in excellent agreement.

Propyne Photolysis. Consensus on propargyl production in the 193 nm photolysis of propyne may prove more elusive. A simple reaction model can be constructed by using reactions 1, 3, 9, 10, and 11 to predict the effect of adding O_2 to the propargyl signal if propargyl were being formed exclusively from reaction 3. Rate constants for 1-propynyl radical reactions with propyne and O_2 are taken to be the same as the corresponding reactions of C_2H . The results of the model are also shown in Figure 6. The predicted propargyl signal decreases by a factor of ~ 7 when the O_2 is added, contrary to the experimental observation. Even if the 1-propynyl + O_2 reaction were 10 times slower than the $\text{C}_2\text{H} + \text{O}_2$ reaction, the amplitude of the propargyl signal should be reduced by $\sim 40\%$. Acceptance of the postulate that 1-propynyl + propyne is responsible for propargyl formation would require both high reactivity of 1-propynyl with propyne and low reactivity with O_2 , a highly unlikely contingency. Also shown is a simple model of the propargyl signal that assumes the propargyl radical is formed directly from 193 nm propyne photolysis and then reacts with itself and with O_2 . The propargyl signal fits well to a simple simulation of direct formation followed by reaction with O_2 and, therefore, appears to imply that propargyl is formed directly in the 193 nm photolysis. The addition of $8.6 \times 10^{16}\text{ cm}^{-3}$ of O_2 does not affect the acetylene signal, indicating that the acetylene is not formed by secondary reactions of C_3H_3 . The energy of a 193 nm photon is sufficient to overcome the isomerization barrier to cyclopropene formation and subsequent dissociation to singlet $\text{CH}_2 + \text{acetylene}$.³¹ The observation of C_2H_2 is additional evidence for a significant role of ground-state dissociation in the 193 nm photolysis of propyne.

The amount of propargyl observed ($\Phi = 0.49 \pm 0.10$) from 193 nm photolysis of propyne is similar to the yield of C_3H_3 measured by Sun et al. ($\text{C}_3\text{H}_3:\text{C}_3\text{H}_2 = 56:44$).¹³ However, the

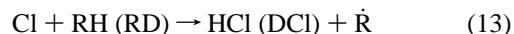
photoionization threshold in their experiments appears to identify the C_3H_3 signal as the 1-propynyl isomer and not propargyl. The sum of the propargyl and acetylene yields observed here is significantly less than 1, leaving the possibility of some 1-propynyl formation in the 193 nm photolysis of propyne. The infrared absorption of 1-propynyl has not been characterized, and it is not possible to observe it in the present experiments. If 1-propynyl were to react rapidly with propyne, it seems unlikely its formation would be directly observable under the current reaction conditions. However, in that case, the major product of reaction 3 cannot be the propargyl radical.

The observation of directly formed propargyl radicals appears to conflict with several previous experimental investigations. Seki and Okabe¹² set an upper limit of <0.05 propargyl chloride formation from 193 nm photolysis of mixtures of propyne and Cl_2 . However, this may not necessarily preclude propargyl radical formation, because the room-temperature rate of Cl_2 reaction with propargyl is small compared to the propargyl self-reaction rate



Extrapolating the rate coefficient of Timonen et al.³² to room-temperature yields $k_{12} = 3 \times 10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. A majority of the propargyl radicals formed under reaction conditions of Seki and Okabe may be removed by radical-radical reactions. Furthermore, because the reactions were run until $\sim 7\%$ of the reactants were depleted, absorption of 193 nm light by products could be significant. The propargyl chloride 193 nm cross section³³ is ~ 10 times greater than the propyne 193 nm cross section.

It is uncertain why Seki and Okabe would not see DCI formation from the photolysis of CD_3CCH in the presence of Cl_2 , regardless of the photolysis process. Some HCl (DCI) should be formed by reactions of Cl atoms



At the pressures of the Seki and Okabe experiments, the reaction of Cl with propyne favors HCl formation and not addition.²¹ Cl atoms could abstract D atoms from some of the large hydrocarbons being formed by propargyl self-reaction as well.

It is not clear why no H atom fluorescence was detected by Satyapal and Bersohn¹¹ from the 193 nm photolysis of $\text{CH}_3\text{-CCD}$. Based on the propargyl radical absorption observed in the current experiments, H atoms should have been produced. The high-resolution spectrum of the C–D stretch of CH_2CCD is known and assigned.³⁴ Although the current experiment cannot reach the C–D stretching region, detection of infrared absorption of CH_2CCD from 193 nm photolysis of CH_3CCD should be possible and would clarify the discrepancy between the current experiments and the Satyapal and Bersohn experiment.

Conclusions

There now appears to be a consensus among experimental methods that the room-temperature propargyl self-reaction rate is near $4 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Direct formation of propargyl ($\Phi = 0.49 \pm 0.10$) and acetylene ($\Phi \sim 0.1$) is observed in the 193 nm photolysis of propyne.

Acknowledgment. This work is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences, the U. S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia

Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94-AL85000.

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