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H-Atom Yields from the Photolysis of Acetylene and from the Reaction of C₂H with H₂, C₂H₂, and C₂H₄[†]

Tamás Kovács, Mark A. Blitz, and Paul W. Seakins*

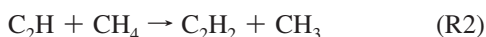
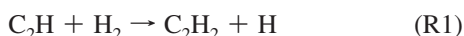
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The photolysis of acetylene at 193 nm has been investigated as a source of the ethynyl radical, C₂H, for product branching ratio studies, particularly the formation of H atom product as the photolysis, producing a 1:1 ratio of C₂H and H, provides an internal calibration. Previous literature had suggested that C₂H and H may only be a minor component of acetylene photolysis at 193 nm. Acetylene was photolyzed at low laser energy densities (<7 mJ cm⁻²), with H atoms being observed as a function of time by VUV laser induced fluorescence. When C₂H was reacted with C₂H₂, a reaction that is known to produce H atoms with unit yield, the ratio of photolytic H atom production to chemical production was 0.96 ± 0.03. The rate coefficient for the reaction of C₂H with C₂H₂ could accurately be retrieved from the time evolution of the H atom signal. The results suggest that acetylene photolysis at low laser energies is a good source of C₂H for product branching studies, and the technique has been applied to the reactions of C₂H with ethene and propene. For the reaction with ethene between 23 and 81 Torr, the yield of H is 0.94 ± 0.06, suggesting that an addition elimination mechanism dominates with the formation of vinylacetylene and H atoms. For the reaction of C₂H with propene, no H atom product was observed, putting a lower limit of <5% for H atom production. Possible explanations for the low H atom yield are discussed. The implications of these results in combustion and planetary atmospheres are briefly considered.

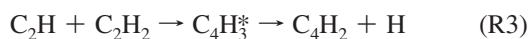
Introduction

The ethynyl radical, C₂H, plays an important role in the production of soot during combustion¹ and in the production of polyenes in the reducing atmospheres of the outer planets^{2,3} and in the interstellar medium.³ The radical can undergo two main types of reaction; a direct abstraction typified by the reaction with H₂ or saturated alkanes



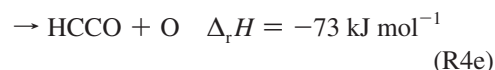
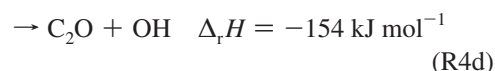
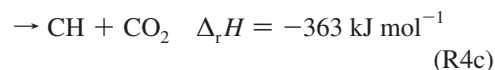
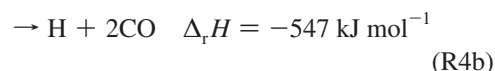
Alternatively, for reactions with unsaturated hydrocarbons or radical species such as O₂, the reaction proceeds via the formation of a complex that can either break up to yield products or be stabilized by collisions with a bath gas. The high heat of formation of the ethynyl radical ($\Delta_f H^\circ \text{C}_2\text{H} = 567 \pm 1 \text{ kJ mol}^{-1}$ ^{4,5}) means that in many cases a variety of product channels are thermodynamically accessible, including the production of electronically excited products.

The reaction of C₂H with acetylene is typical of the complex-forming mechanism; in this case, only one product is thermodynamically accessible from the dissociation of the complex

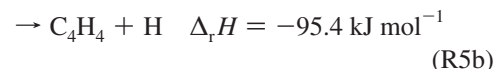
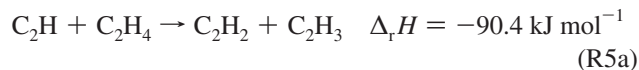


However, for the reaction of C₂H with O₂, an important reaction in combustion, a large number of product channels are accessible

with the different products having a potentially significant effect on subsequent chemistry



For the reaction of C₂H with ethene, there are two thermodynamically accessible channels



Reaction R5a could potentially take place via either a direct abstraction or an addition elimination mechanism.

The kinetics of C₂H have received considerable attention, particularly in the studies led by Leone and coworkers,^{6–8} Curl, Glass, and coworkers,^{9,10} and Peeters and coworkers.^{11,12} Sims

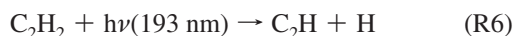
[†] Part of the special section “30th Free Radical Symposium”.

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and coworkers have made measurements at very low temperatures using a continuous-flow Laval system,¹³ and Leone and coworkers have more recently measured C₂H kinetics around 100 K using a pulsed Laval system.¹⁴ C₂H has predominantly been generated by the excimer laser photolysis of C₂H₂ or CF₃C₂H at 193 nm and monitored by IR absorption. Additional studies have been performed by Laufer and Fahr, who have authored a review on the reactions of C₂H and other unsaturated radicals.⁵

In contrast with the kinetics, much less is known about the products of C₂H radical reactions. Quantitative product studies of radical reactions are challenging experiments because many of the spectroscopic techniques used to monitor radical concentrations do not provide absolute concentrations. The calculation of radical concentrations from photolysis fluence measurements is subject to many uncertainties. An alternative approach is to use a calibration reaction, a reaction of the radical that produces the target product with a well-defined, ideally 100%, product yield. Issues around quantitative product determinations have recently been reviewed.¹⁵

For C₂H studies, reactions R1 and R3 provide a suitable calibration reaction for H atoms because H + C₂H₂ and H + C₄H₂, respectively, are the only possible products under our experimental conditions. C₄H₃ can be produced from reaction R1 at high pressures; however, previous calculations¹¹ have shown that stabilization should not occur under our conditions, a prediction verified in the current study. Uncertainties exist over the yield of C₂H from the 193 nm photolysis of acetylene, the most convenient source of C₂H. Early studies suggested that triplet acetylene or vinylidene (H₂CC) was the dominant product,¹⁶ secondary reactions of such species could distort the kinetics of H atom formation. The photolysis of acetylene is particularly appealing for H atom studies because C₂H and H are formed in identical amounts from the primary photodissociation



potentially providing an internal calibration¹⁷ of C₂H and H. However, alternative multiphoton dissociations that yield H atoms or secondary chemistry will negate this advantage.

More recently Lauter et al.¹⁸ have demonstrated that reaction R6 is the dominant channel for acetylene dissociation at 193 nm with a quantum yield of 0.94 ± 0.12 , suggesting that, in contrast with the earlier studies, acetylene photolysis should be a clean source of C₂H. The objective of this article is to confirm the suitability of acetylene photolysis as a source of C₂H for H-atom product studies and to see whether the potential advantages of an internal calibration can be realized. We subsequently apply this technique to determine the H-atom yield from the reaction of C₂H with ethene (R5a,R5b) and propene



Experimental Section

Reactions were carried out in a slow flow excimer laser flash photolysis apparatus with H-atom detection by VUV laser-induced fluorescence. The C₂H precursor, acetylene, reagent (if appropriate), and bath gas were metered using calibrated mass flow controllers and premixed before being flowed into the stainless steel reaction vessel. The reaction vessel was a stainless steel six-way cross with the photolysis, probe laser, and

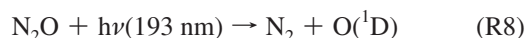
fluorescence detection axis mutually perpendicular to each other. The pressure within the cell was controlled by a needle valve located between the exit of the cell and the vacuum pump. The pressure in the cell was measured by a baratron-type pressure gauge, and all reactions were carried out at room temperature (295 ± 2 K).

C₂H radicals were generated by the photolysis of acetylene using a GAM EX5 excimer laser operating at 193 nm. H atoms were monitored by VUV laser-induced fluorescence at the Lyman- α transition at 121.56 nm. The technique has been used before in this laboratory to monitor H atom yields from CH,¹⁹ CN,^{20,21} and CH₂²² reactions. A 308 nm excimer laser (Lambda Physik LPX 100) pumped dye laser (Lambda Physik FL2002) was used for probing. Radiation (364.68 nm, $\sim 5\text{--}7$ mJ pulse⁻¹) was produced from a DMQ dye and was frequency tripled in krypton-argon mixture (Kr/Ar 1:2.5). Light (364.68 nm) was focused by a quartz lens (focal length = 15 cm) into a glass cell attached directly to the cell containing ~ 1000 Torr of Kr/Ar; the exact mixture varied depending on the laser energy. Lyman- α radiation was coupled to the cell perpendicularly to the photolysis beam through a MgF₂ window.

Fluorescence was detected perpendicularly to both laser beams by a solar blind photomultiplier tube (PMT, Perkin-Elmer CPM-18). The power of the VUV radiation was monitored by a second solar blind PMT (Thorn EMI Gencom, RFI/B-214 FV model) with exactly the same path length in the cell. Some of the probe light was reflected using quartz flat at 45° through a VUV interference filter and onto the second PMT. This resulting signal was used directly as the absorption signal and also to normalize the VUV LIF signal taking into account any temporal power fluctuations of the probe laser and attenuation by absorption.

By varying the time delay between the photolysis and probe beams, a time profile of the H atom concentration was recorded. The time between photolysis and probing was varied by a digital delay generator type DG 535 (Stanford Research Systems). The PMT outputs were converted by an AD converter and recorded and stored on a PC. In typical, the time profiles consisted of 200 points, where each time point was the average of 10–20 shots and the time interval between the points was 0.1 μ s. Photolysis laser powers were measured by a Gentec energy type power meter.

The power dependence of the acetylene photodissociation was investigated in detail. By varying the applied voltage to the excimer or by focusing or defocusing the photolysis laser beam (using either metal mesh filters or cylindrical lens), the light energy densities could be varied from 5×10^{15} to 3×10^{18} photon cm⁻². To investigate the yield of H atoms from both the photolysis of acetylene and the reaction of C₂H with calibrant and test molecules, the photolysis of N₂O at 193 nm in the presence of hydrogen was used as a well-characterized H-atom source. Photolysis of N₂O at 193 nm leads exclusively to the production of N₂ and excited oxygen atoms, O(¹D)



Sufficient hydrogen (typically 3.3×10^{17} molecule cm⁻³) is added to ensure that all oxygen atoms produced react rapidly with H₂ to generate an essentially instantaneous H atom signal. The H atom concentration can be calculated from the well-determined N₂O absorption cross section at 193 nm (8.95×10^{-20} cm² 23), unit quantum yield, and the measured laser photon density.

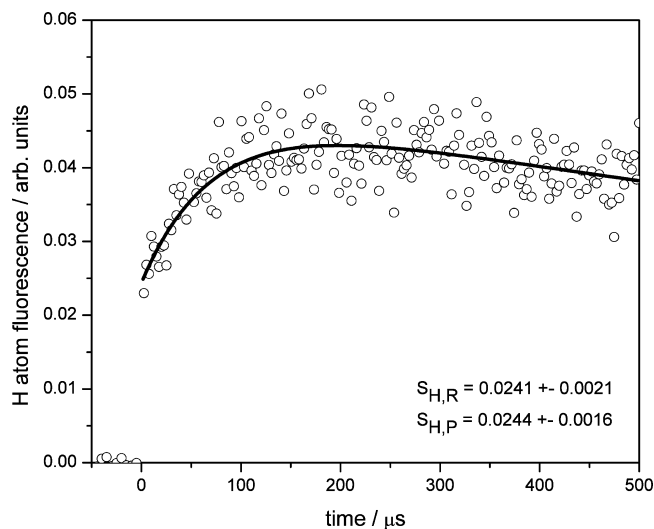


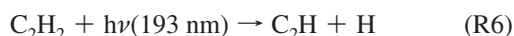
Figure 1. Typical experimental H atom profiles following the photolysis of acetylene (pressure 42 Torr Ar, $[C_2H_2] = 1.6 \times 10^{14}$ molecule cm^{-3} , laser fluence = 7 mJ cm^{-2}). The solid line is a fit to reaction R1.

Argon (BOC Pureshield) and helium (BOC VP grade, 99.9999%) were admitted directly from cylinders without purification, whereas acetylene (Aldrich, 99.9+%, HPLC grade), ethylene (Aldrich, 99.9+%, HPLC grade), and propylene (Aldrich, 99.9+%, HPLC grade) were stored diluted in helium in glass bulbs following freeze–pump–thaw purifications.

Results and Discussion

a. Reaction with Acetylene at Low Photolysis Powers.

Figure 1 shows an experimental profile of the H atom signal following the photolysis of an acetylene and argon mixture at low excimer fluences (7 mJ cm^{-2}). A prompt rise in H atom signal is seen to be consistent with the photolysis process



followed by a slower exponential rise in the signal associated with the reaction of C_2H with acetylene. Under these conditions, where $[C_2H_2] \gg [C_2H]$ ($[C_2H]_0 = 1.4 \times 10^{11}$ molecules cm^{-3} and $\sim 1/1000$ th $[C_2H_2]$), the production of H atoms should be controlled by pseudo-first-order kinetics. Traces such as Figure 1 were fit with eq E1, which accounts for both prompt photolytic production and the chemical production of H atoms and subsequent slow removal due to diffusion and reaction with acetylene.

$$I_{f,H} = \frac{S_{H,R}k'_3}{k_d - k'_3}(e^{-k'_3t} - e^{-k_d t}) + S_{H,P}e^{-k_d t} \quad (E1)$$

where $I_{f,H}$ is the observed H atom fluorescence, $S_{H,R}$ is the signal associated with H atoms produced in reaction R3, k'_3 is the pseudo-first-order rate coefficient for the removal of C_2H ($k'_3 = k_3[C_2H_2] + c$), k_d is the rate coefficient for H atom loss (mainly via diffusion), and $S_{H,P}$ is the signal associated with prompt H production from acetylene photolysis.

The ratio of $S_{H,R}/S_{H,P}$ was 0.96 ± 0.03 for 48 experiments carried out at low photolysis laser fluences (<7 mJ cm^{-2}) and with acetylene concentrations from $(1.5 \text{ to } 2.3) \times 10^{14}$ molecule cm^{-3} and total pressures (23–98 Torr). Under these conditions,

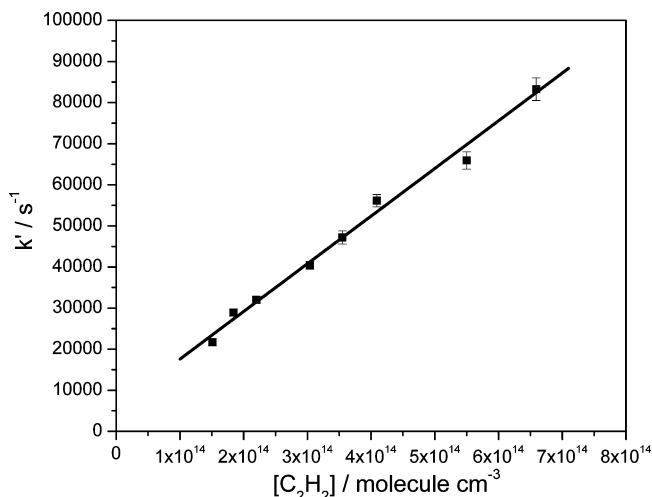


Figure 2. Bimolecular plot (k'_3 vs $[C_2H_2]$) for reaction R3 at 298 K and 23 Torr. The bimolecular rate coefficient obtained as the gradient is $(1.16 \pm 0.06) \times 10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$, where the errors are statistical only at the 1 sigma level.

TABLE 1: Summary of 298 K Rate Coefficients for the Reaction $C_2H + C_2H_2$

author	date	$10^{10} \times k_{298}/cm^3$ molecule $^{-1}$ s $^{-1}$	comments
this work	2009	1.2 ± 0.2	monitoring H atom production
Ceursters et al. ¹¹	2000	1.3 ± 0.1	monitoring chemiluminescence via reaction of $C_2H + O_2$
Farhat et al. ¹⁰	1993	1.6 ± 0.3	monitoring C_2H by IR absorption
Pederson et al. ⁶	1993	1.2	monitoring C_2H by IR absorption
Koshi et al. ²⁴	1992	1.5 ± 0.3	monitoring C_4H_2 by mass spectrometry or H atoms by VUV absorption
Shin and Michael ⁴³	1991	1.4	monitoring H atom production by VUV resonance absorption
Stephens et al. ⁹	1987	1.5	monitoring C_2H by IR absorption

the expected 1:1 relationship is observed on the basis of $C_2H + H$ being the sole products of acetylene photolysis at low powers and $C_4H_2 + H$ being the sole products of reaction R3 at these pressures (20–300 Torr argon).

Further evidence of the sole production of C_2H and H at low laser fluences comes from the good agreement obtained when we compare our observed H atom signal from acetylene photolysis with that from N_2O photolysis in the presence of H_2 , for which the cross section and yield of H (via $O^1D + H_2$) are known. The calculated quantum yield of H at 193 nm with a laser photon fluence of 8.2×10^{15} photons cm^{-2} is 1.02 ± 0.05 .

The rise in the concentration of H atoms from reaction R3 can clearly be seen, and by carrying out measurements over a range of acetylene concentrations, it is possible to extract the bimolecular rate coefficient for reaction R3. Figure 2 shows an example of a bimolecular plot (pseudo-first-order rate coefficient for H production vs $[C_2H_2]$), and the resultant bimolecular rate coefficient (the gradient of plot) is compared with literature values in Table 1.

Our determination, $(1.2 \pm 0.2) \times 10^{-10}$ cm^3 molecule $^{-1}$ s $^{-1}$, where the error includes both statistical uncertainties and

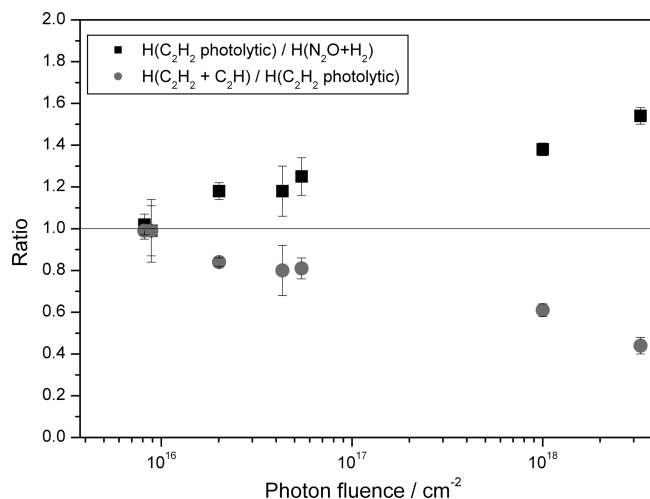


Figure 3. Variation of the ratio of prompt to reactive H with photon fluence.

estimates of systematic errors (flow controller and pressure calibrations), is in excellent agreement with literature values of $k_{3,298}$, which have been measured using a wide variety of techniques including monitoring both reagents and products. This excellent agreement suggests that there are no unexpected sources of H in our system. Koshi et al.²⁴ measured identical values for $k_{3,298}$ by monitoring H atom production by VUV absorption and C_4H_2 by mass spectrometry. They argued that this precluded significant involvement of vinylidene, which would produce $C_4H_2 + H_2$ on reaction with acetylene, distorting the kinetics of C_4H_2 versus H production. Interestingly Koshi et al. do show a figure for H-atom production; the figure shows equal concentrations of photolytic and reactive H, but Koshi et al. did not exploit this for product studies.

The invariance of the H atom yield with pressure (20–300 Torr argon) shows that stabilization of the C_4H_3 radical is not significant up to 300 Torr. This is to be expected from the potential energy surface (PES) of reaction R3. Ceusters et al.¹¹ have calculated the PES using B3LYP or CCSD(T) calculations at the 6-311++G(d,p) level. The formation of C_4H_3 (–239 kJ mol^{–1} relative to entrance channel) is barrierless, and the loose barrier for production of $H + C_4H_2$ is ~73 kJ mol^{–1} below the entrance channel. Alternatively, the initial $C_4H_3^*$ radical can isomerize via a 1,2 H-atom shift with a barrier of ~173 kJ mol^{–1} to produce the more stable $HC\equiv C-C\cdot=CH_2$ radical (–285 kJ mol^{–1}) with respect to entrance channel. The only calculated fate of this radical is also H atom elimination with a barrier of ~187 kJ mol^{–1}.

b. Acetylene Photolysis at High Laser Fluences. As the excimer laser pulse energy density is increased above 10 mJ cm^{–2}, the ratio of prompt to reactive H increases above unity. The prompt photolysis signal increases with laser pulse energy in a nonlinear fashion indicating that multiphoton processes are involved. The reactive H atom signal decreases in comparison with the prompt signal, and the relationships of the two signals are shown in Figure 3. The symmetry of the plot suggests that the source of the additional photolytic H comes at the expense of the reactive H, that is, that it is the photolysis of C_2H to give $C_2 + H$ that is the source of the photolytic H.

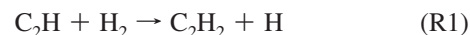
The coproduct of C_2H photolysis, C_2 , can be formed in either the ground singlet state $X^1\Sigma_g^+$, the first excited triplet state $a^3\Pi_u$, or possibly higher states.²⁵ Previous studies indicate that predominantly ground-state C_2 (6.6:1) is formed from 193 nm photolysis of acetylene.²⁶ However both forms of C_2 are reactive

with rate coefficients for $^1C_2 + C_2H_2$ of $(4.1 \pm 0.4)^{27}$ or $(3.5 \pm 1.0)^{28} \times 10^{-10}$ cm³ molecule^{–1} s^{–1} and for $^3C_2 + C_2H_2$ of $(1.1 \pm 0.1) \times 10^{-10}$ cm³ molecule^{–1} s^{–1}.^{27,28} The reaction proceeds via the formation of the diacetylene complex, and the expected products of diacetylene dissociation are $C_4H + H$.²⁹ However, these molecular beam studies²⁹ also show that the lifetime of the diacetylene, which is in a deep well with barriers to dissociation of 577 and 544 kJ mol^{–1} to reagents and products, respectively, is long compared with the rotational period, even at a collision energy of 29 kJ mol^{–1}. Under our room-temperature thermal conditions, the complex lifetime is expected to be much longer, and hence it is likely that the diacetylene complex is collisionally stabilized under our experimental conditions, explaining the reduction of reactive H-atom signal on the formation of C_2 .

Adding oxygen to the system provides a sensitive diagnostic for the presence of C_2 . In the presence of oxygen, a very strong VUV emission could be observed at photolysis laser powers where there was significant deviation from the 1:1 photolytic/reactive H atom ratio. Photolysis laser powers were reduced until the chemiluminescence disappeared. The origin of the chemiluminescence will be discussed in a future paper on the C_2H/O_2 system.

Lauter et al.¹⁸ found that C_2H photolysis becomes important only at fluences above 100 mJ cm^{–2}. They typically used 2–45 mJ cm^{–2} photolysis fluence, and single photon absorption was reported under these conditions. Our results suggest that there may be ~10% C_2H photolysis at the upper end of their linear photolysis region, which may have been within their error limits for detection. Low powers of 121.6 nm probe radiation (<25 μJ cm^{–2}) were enough to generate additional H atom signal, presumably from C_2H photolysis, followed by H detection in the same laser pulse.¹⁸ The low concentrations of C_2H and low probe energies negate this process under our experimental conditions, but some effects from the high intensities of the 364.8 nm light in combination with the VUV radiation were observed. These could be avoided by adjusting the lens focusing the light into the tripling cell such that the intensity in the reaction cell was reduced.

c. H Atom Yields from the Reaction of C_2H and H_2 . The reaction of C_2H with hydrogen



should show the same behavior as reaction R3, that is, a 1:1 relationship between the H produced from C_2H_2 photolysis and the H produced from reaction R1, and Figure 4a shows that this indeed is the case. Low concentrations of acetylene (typically $\sim 1 \times 10^{13}$ molecule cm^{–3}) and high concentrations of hydrogen are used to ensure that a majority of the C_2H reacts with hydrogen. In Figure 4a, the rise time now corresponds to the pseudo-first-order rate coefficient, k'_1 , for reaction of C_2H and H_2 , and Figure 4b shows the resultant bimolecular plot. The measured bimolecular rate coefficient is compared with previous literature values in Table 2.

As expected from a simple abstraction reaction, there was no dependence of the H-atom yield with total pressure (20–100 Torr Ar). The prompt and reactive H atom signal from the C_2H/H_2 system showed a very similar dependence with laser power as the earlier C_2H/C_2H_2 system. The increase in prompt H can again be explained by C_2H photolysis, and the lack of reactive H atom signal is due to the very slow rate of reaction of either state of C_2 with H_2 ($< 3 \times 10^{-16}$ cm³ molecule^{–1} s^{–130}).

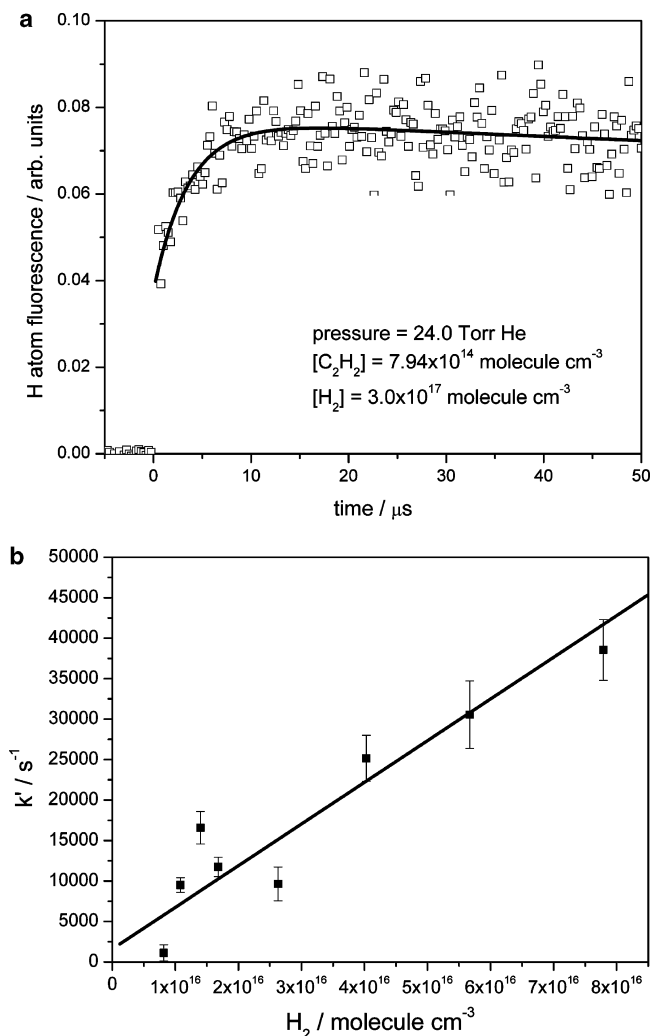


Figure 4. (a) H atom profile from reaction R1 (pressure 24 Torr He, $[\text{C}_2\text{H}_2] = 7.9 \times 10^{14} \text{ molecule cm}^{-3}$, $[\text{H}_2] = 3.0 \times 10^{17} \text{ molecules cm}^{-3}$). (b) Bimolecular plot for reaction R1 at 298 K and 24 Torr helium. The bimolecular rate coefficient is $(5.15 \pm 0.42) \times 10^{-13} \text{ molecule}^{-1} \text{ s}^{-1}$, where the errors are statistical at the 1 sigma level.

TABLE 2: Summary of 298 K Rate Coefficients for the Reaction $\text{C}_2\text{H} + \text{H}_2$

author	date	$10^{13} \times k_{298} / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	comments
this work	2009	5.2 ± 0.8	monitoring H atom production
Peeters et al. ¹²	2002	5.6 ± 0.6	C_2H monitored via chemiluminescence from $\text{C}_2\text{H} + \text{O}_2$
Opansky and Leone ⁸	1996	4.6 ± 0.7	C_2H monitored via IR absorption
Farhat et al. ¹⁰	1993	4.7	C_2H monitored via IR absorption
Koshi et al. ²⁴	1992	4.6	decrease in C_4H_2 product measured with increasing H_2
Stephens et al. ⁹	1987	4.8	C_2H monitored via IR absorption

d. H-Atom Yield from the Reaction of $\text{C}_2\text{H} + \text{C}_2\text{H}_4$ and C_3H_6 . The studies of the H atom yield from ethene and propene were slightly complicated by the production of H atoms from substrate photolysis. Background traces in the absence of acetylene were recorded to take into account this source of H. Figure 5 shows the H atom yield from the reaction of C_2H with

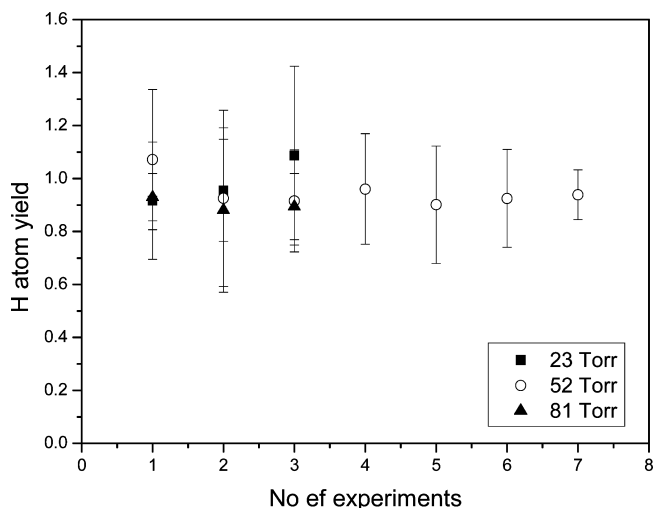


Figure 5. Variation of H atom yield from the reaction of C_2H and C_2H_4 as a function of argon bath gas pressure.

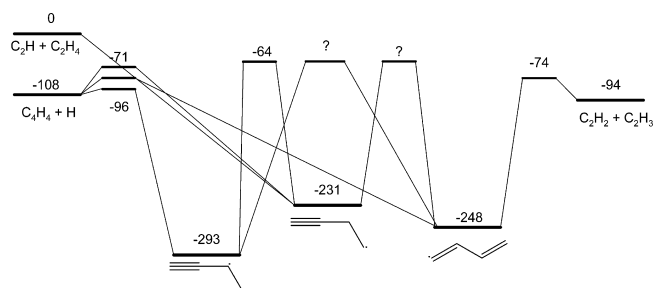


Figure 6. Schematic of the potential energy surface for $\text{C}_2\text{H} + \text{C}_2\text{H}_4$. All energies are in kilojoules per mole.

C_2H_4 (reactions R5a and R5b). The average H atom yield is 0.94 ± 0.06 (errors are 1σ) over a total pressure of 23–81 Torr. Figure 5 also shows that there is no systematic variation of yield with pressure; therefore, stabilization of the C_4H_5^* intermediate does not appear to be occurring at these pressures. The only other thermodynamically accessible products are $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3$, which could be formed either from a direct abstraction or following a rearrangement of the energized C_4H_5 intermediate; however, for the reasons outlined below, we would not expect reaction R5a to contribute significantly.

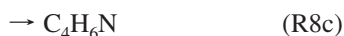
Opansky and Leone⁸ have correlated activation energies of C_2H abstraction reactions with bond dissociation energies. Direct abstraction by C_2H from C_2H_4 would be expected to have a positive activation energy; indeed, high-level calculations by Temelso et al.³¹ do calculate barrier heights of 4–8 kJ mol^{-1} for reaction R5a at various levels of theory. However, the overall reaction exhibits a negative temperature dependence^{8,13} and a similar room temperature rate coefficient as reaction R3; the overall kinetics appear to be more compatible with an addition elimination mechanism.

Following addition, two different 1,2-H-atom migrations could occur with the resultant isomers fragmenting to form either vinylacetylene + H (reaction R5b) or acetylene + vinyl (reaction R5a). The enthalpy of formation of the initial vinyl radical has been calculated as $\Delta_f H^0$ (0 K) 389 kJ mol^{-1} ,³² and the enthalpies of the other two C_4H_5 isomers have been calculated by both Hansen et al.³² and Wheeler et al.³³ Figure 6 shows a schematic of the possible PES adapted from the above references. Some barrier heights are unknown, but by comparison with analogous systems, we do expect these to be below the energy of the entrance channel.

Although the formation of vinyl and acetylene is likely to be possible via isomerizations with barriers below the entrance channel, the observation of near-unity H-atom yield suggests that these isomerizations, which would occur via relatively tight transition states, cannot compete with the looser transition states for H-atom elimination either from the initially formed adduct $\text{HC}\equiv\text{CCH}_2\text{CH}_2\cdot$ or from the more stable $\text{HC}\equiv\text{CCH}\cdot\text{CH}_3$ radical formed via a 1,2-H-atom migration (given the tight transition state for the 1,2 migration, the contribution from this channel is, however, likely to be limited). The isoelectronic reaction of CN with C_2H_4 also produces essentially unity H-atom yield.^{20,34}

No H-atom signal was observed from the reaction of C_2H + propene at 50 Torr total pressure. Uncertainties in the analysis put an upper limit of 5% on H-atom production. Various reasons can be postulated for the lack of H-atom production from reaction R7: (1) Under our experimental conditions, collisional stabilization of this system (which is larger than $\text{C}_2\text{H} + \text{C}_2\text{H}_4$) is essentially complete. (2) 1,2-H migration from the initial adduct, forming the more stable $(\text{CH}_3)\text{CH}_2\text{-C}\cdot\text{H-C}\equiv\text{CH}$ radical, is more rapid than H-atom elimination. Methyl radicals will be preferentially produced from the fragmentation of $(\text{CH}_3)\text{CH}_2\text{-C}\cdot\text{H-C}\equiv\text{CH}$. (3) Direct abstraction to form the resonantly stabilized allyl radical occurs.

Whereas it is not possible to be definitive with the current experimental measurements, some pointers to the products can be gained from comparison with the isoelectronic CN + propene reaction (R8a–R8d), which has recently been investigated experimentally and through theoretical calculations.^{21,35}



For this reaction (and the larger CN + *iso*-butene reaction), a pressure-dependent H-atom yield was observed²¹ over the range of 2–200 Torr (i.e., both reactions R8a and R8c were occurring), suggesting that whereas the initial complex formed between C_2H and propene might be collisionally stabilized, complete stabilization of the complex would not be expected under our experimental conditions.

Extrapolation of the H-atom yield from reaction R8a to zero pressure predicted an H-atom yield of ~50%.²¹ This experimental yield was consistent with preferential, but not exclusive, formation of the secondary radical following CN addition and competition between 1,2-H atom migration, with subsequent methyl elimination, and H atom dissociation from the secondary radical. Broadly similar results were obtained in the more recent study of Trevitt et al.³⁵ using photoionization mass spectrometry to observe cyanoethene (+ CH_3) or $\text{C}_4\text{H}_5\text{N}$ (+H) species. In the low-pressure study of Trevitt et al., H atom elimination was the minor channel ($25 \pm 15\%$), but error bars of the zero-pressure H-atom yields overlap. It is possible that the analogous C_2H system behaves differently with a more facile 1,2-H-atom migration. Given the similarities in behavior between the C_2H and CN + ethene systems, this seems unlikely, but either high-level calculations or experimental observation of the CH_3 yield are needed to confirm the role of isomerizations following addition.

The final possibility is that direct abstraction to yield C_3H_5 and C_2H_2 is dominating. Calculations for H atom abstraction

by C_2H from isobutane predict a negative activation energy for this abstraction system with a relatively weak C–H tertiary bond ($\text{DH}_{298} = 403 \text{ kJ mol}^{-1}$ ³⁶), and earlier measurements by Hoobler et al.³⁷ do indeed measure a slight negative temperature dependence for reaction R7 and a fast rate coefficient of $9.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature. The C–H bond leading to allyl is significantly weaker ($\text{DH}_{298} = 369 \text{ kJ mol}^{-1}$ ³⁸), and given the correlation between activation energies of abstraction reactions and bond dissociation energies observed by Opansky and Leone,⁸ one would expect H-atom abstraction by C_2H to form allyl and acetylene to be barrierless and possibly competitive with addition/elimination.

e. Implications. This work has demonstrated that the H-atom yield of C_2H reactions can be studied using the photolysis of acetylene at low laser energy densities at 193 nm as an internal calibration. This reaction can now be used as the basis for the study of H-atom yields from other C_2H reactions, and the H-atom yields from O_2 and NO will be the subject of a future paper.

Internal calibration systems have the major advantage that the H-atom signal does not need to be corrected for the different detection efficiency in the presence of either the calibrant or test reagents. This is particularly important if H_2 is used as the calibration reaction because H_2 can quench Lyman- α fluorescence.²⁰ However, internal calibrations do introduce a significant alternative source of error in that the signal directly following photolysis, at zero time, needs to be accurately determined. For normal calibration reactions, this is a straightforward process for exponential growth, which starts at zero signal at zero time. However, for internal calibrations, this approach is not possible, introducing additional random errors and limiting the concentration of substrate that can be introduced.

The reaction of C_2H with C_2H_4 (R5a and R5b) is of potential importance in both combustion chemistry and in the reducing atmospheres of the outer planets and their satellites. C_4H_5 species can be formed either by stabilization at high pressures of the C_4H_5^* intermediate formed in reactions R5a and R5b or from the addition of H atoms to vinylacetylene. The reactions of C_4H_5 isomers with acetylene have been implicated in the first steps of soot formation.^{39,40} In planetary atmospheres, the formation of vinylacetylene is one example of the growth of larger functionalized compounds. Such molecules are important in the synthesis of yet larger compounds and hazes, but also, because they photolyze at longer wavelengths than simple alkenes or alkynes,⁴¹ they can be a source of radicals lower in the atmosphere.

A recent model for haze formation in Titan's atmosphere⁴² includes only the $\text{C}_4\text{H}_4 + \text{H}$ channel from reactions R5a and R5b, and this work confirms that this will be the only important reaction under such conditions. The same model has H + unidentified coproducts for reaction of C_2H with C_3H_6 (reaction R7). In this case, the current studies suggest that this is incorrect and that for alkenes with allylic hydrogens, the efficiency of C_2H reactions in promoting molecular growth may need to be adjusted.

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