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Photochemistry of acetylene at 1849 Å

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The photochemistry of acetylene at 1849 Å has been studied over the pressure range from 13 to 2660 N m^{-2} (0.1–20 Torr). The quantum yield of diacetylene formation has been measured as a function of C_2H_2 pressure and the partial pressures of He and N_2. The quantum yield of H_2 formation has also been obtained. It was concluded that the quantum yield for $C_2H_2 \xrightarrow{h\nu} C_2H + H$ is 0.06 and that for $C_2H_2 \xrightarrow{h\nu} C_2 + H_2$ is 0.1. The remaining process is the formation of a metastable acetylene which reacts either with C_2H_2 to form C_2H radicals or is deactivated by collisions with the walls or inert gases. The C_2H radicals react 0.240 ± 0.015 times as fast with C_2H_6 and 0.469 ± 0.041 times as fast with C_3H_8 as with C_2H_2. The role of acetylene photolysis in the Titan atmosphere is briefly discussed.

INTRODUCTION

Photochemistry of acetylene in the vacuum ultraviolet has been studied by many workers and is summarized in a previous publication.[1] At 1470 Å acetylene, formed in a Rydberg state, dissociates directly into $C_2H + H$ and $C_2 + H_2$ with quantum yields of 0.3 and 0.1, respectively. The remaining process is the formation of a metastable acetylene which reacts either with ground state acetylene to form C_2H radicals or is deactivated by collisions with the walls or inert gases.[1]

It is of interest to study the photochemistry of acetylene at 1849 Å where the $\tilde{B}\,{}^1B_u$ state is mainly formed.[2] Zelikoff and Aschenbrand[3] in 1956 studied the photolysis of acetylene at 1849 Å and found diacetylene, ethylene, hydrogen, vinyl acetylene, and benzene as products. More recently, Tsukada and Shida[4] have found diacetylene and benzene to be the major products at 1849 Å. These studies are, however, limited to acetylene pressures above 1 Torr and no reliable quantum yield measurements have been made, especially below 1 Torr.

Acetylene has recently been detected in the Jovian atmosphere[5] and in the Titan atmosphere[6] with mixing ratios of 10^{-7} and 2×10^{-6}, respectively. The photochemistry of acetylene in the 1500–2000 Å region at low pressure, particularly the quantum yield of C_2H production and the reactions of C_2H with H_2 and hydrocarbons, is important in understanding the photochemistry of Jovian and Titan atmospheres.[7] This work was initiated to obtain information on these issues.

EXPERIMENTAL

The 1849 Å light source was a sealed quartz tube containing a drop of Hg and 2 Torr of Ar excited by a microwave generator. The output of the lamp was measured by the production of H_2 in the photolysis of C_2H_4 and was about 10^{15} quanta s^{-1}. The lamp was attached to a 101 ± 1 cm^3 Pyrex reaction cell with an *O*-ring seal. The intensity of 1849 Å radiation was monitored by a solar blind photomultiplier with CsI cathode.

An absorption cell with two LiF windows was 154 ± 0.5 mm long and was made of stainless steel. The cell was attached behind the exit slit of a 1 m near normal incidence vacuum monochromator. The slit width of 50 μm was used corresponding to a nominal resolution of 0.8 Å. The amount of diacetylene produced was measured by absorption near 1650 Å as described before.[1] The minimum amount of diacetylene detectable by this technique was about 2 mTorr.

The exposure time ranged from 5 s to 4 min depending on the pressure of acetylene used, corresponding to 0.2% to 5% decomposition. The quantum yield of diacetylene was found to decrease with an increase of exposure time below 1 Torr of acetylene, indicating efficient photolysis of diacetylene at long exposure. Hence, care was taken to use minimum possible exposure time. The lamp intensity was frequently calibrated by measuring H_2 production from the photolysis of C_2H_4. Polymeric deposits on the window were occasionally removed by 10% HF solution. The pressure of acetylene and other gases was measured by a calibrated pressure transducer. The pressure of the noncondensable gas at liquid nitrogen temperature formed in the photolysis of acetylene, ethylene, and hydrogen bromide was measured and was taken as the yield of hydrogen.

The reaction mixtures of acetylene with other gases (N_2, He, C_2H_6, or C_3H_8) were prepared in a 5 dm^3 mixing bulb by first introducing the required pressure of C_2H_2 and adding to it successively higher pressures of the other gas. For each run approximately 5% of the mixture was removed from the bulb and the acetylene pressure was corrected accordingly.

The preparation of diacetylene was previously described.[1] Commercial research grade acetylene, ethylene, ethane, propane, and high purity N_2 and He were used without further purification. Bromine impurity in commerical hydrogen bromide was removed by vacuum distillation at about −125 °C. Commercial phosgene had a minimum stated purity of 99%.

The quantum yield at 1849 Å was obtained using ethylene as an actinometer. The quantum yield of hydrogen, the only noncondensable product of ethylene photolysis, was taken as 0.42.[8] This value was also confirmed in comparison with the H_2 quantum yield of unity in the 1849 Å photolysis of HBr.[9] Since absorption by acetylene is not complete in the pressure range used (13 to 2660 N m^{-2}) it is necessary to use actinometer pressures corresponding to the same optical densities as those of acetylene.

TABLE I. Absorption cross sections (σ) of C_2H_2, C_2H_4, HBr, and $COCl_2$ at 1849 and 2537 Å.

Gas	1849 Å σ (10^{-19} cm^2)	2537 Å σ (10^{-20} cm^2)
C_2H_2	6.30 ± 0.06 6.3 ± 0.7[a]	...
C_2H_4	3.05 ± 0.04 3.06[b]	...
HBr	19.0 ± 0.4 24[c]	0.35[d]
$COCl_2$	23.1 ± 0.8	7.33 ± 0.11

[a] From Ref. 10.

[b] From Ref. 8.

[c] From Ref. 11.

[d] From H. Okabe, J. Chem. Phys. **66**, 2058 (1977).

RESULTS

Absorption cross section

The absorption cross sections (σ) of C_2H_2, C_2H_4, HBr, and $COCl_2$ at 1849 and 2537 Å, obtained by using the Hg lamp as a light source, are given in Table I. σ is defined as $I_t = I_0 e^{-\sigma n l}$, where I_t and I_0 are, respectively, the transmitted and incident light intensities, n is the number of molecules per cm^3 at 23 °C and l is the path length in cm. These values were used to compute the quantum yield at 1849 Å. About twice as much ethylene as acetylene was used to obtain the same optical density. The absorption cross sections of acetylene and ethylene agree well with that, respectively, by Nakayama and Watanabe[10] and by Glasgow and Potzinger,[8] while HBr absorption is 20% lower than that measured by Huebert and Martin.[11] As shown in Table I, C_2H_2 and C_2H_4 have no measurable absorption at 2537 Å while $COCl_2$ has some absorption at 2537 Å. Hence, C_2H_4 is more suitable as an actinometer at 1849 Å. Absorption cross sections of acetylene in the 1800–1900 Å region are given in Table II and Fig. 1.

TABLE II. Some absorption cross sections (σ) of acetylene in the 1800–1900 Å region.

Wavelength Å	σ (10^{-19} cm^2)	Wavelength (Å)	σ (10^{-19} cm^2)
1801	11.0	1849	6.3
1812	3.8	1865	5.3
1824	8.3	1883	3.5
1836	5.7	1891	2.8
1848	7.3	1896	4.5

Photolysis of acetylene

The quantum yield of diacetylene formation $\phi_{C_4H_2}$ was obtained in the pressure range 13 to 2660 N m^{-2} (0.1 to 20 Torr) of acetylene and is shown in Fig. 2. The quantum yield starts at about 0.059 ± 0.005 (uncertainty, one standard deviation) and increases almost linearly with pressure below 1 Torr of acetylene [Fig. 2(A)], while above 1 Torr it increases to a maximum of 0.7 at 10 Torr and it decreases upon further increase of pressure [Fig. 2(B)].

The quantum yield of H_2 production in acetylene photolysis has also been measured in the 0.5 to 20 Torr region and is shown in Table III. The uncertainty of the quantum yield measurement was ± 10%.

Ethylene was also one of the products of acetylene photolysis at 1849 Å[3] as well as at 1470 Å.[1] The yield of ethylene, however, was not determined in this work.

Photolysis of acetylene in the presence of other gases

The addition of N_2 to acetylene reduced the formation of diacetylene in the 1849 Å photolysis of acetylene. The results are shown in Fig. 3(A). The $\phi_{C_4H_2}$ value reaches a constant value of about 0.05 by the addition of about 200 Torr of N_2 and no further decrease of $\phi_{C_4H_2}$ is observed up to a pressure of 500 Torr. The addition of He also quenches $\phi_{C_4H_2}$ to a value of about 0.05 above 150 Torr of He. This is shown in Fig. 3(B). The production of diacetylene in the photolysis of acetylene decreased with the addition of ethane which is shown in

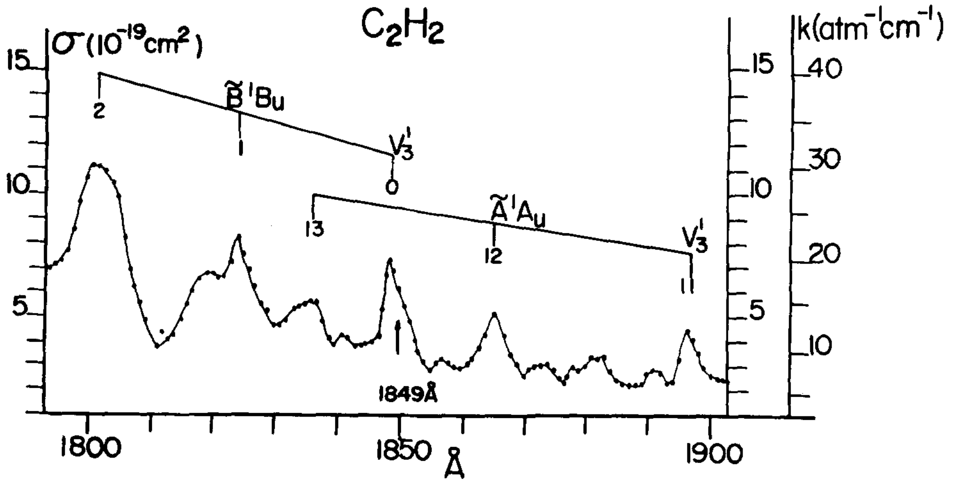

FIG. 1. Absorption cross sections (σ) of acetylene in the 1800–1900 Å region: resolution, 0.8 Å. Band assignments are made according to Ref. 2. The 1849 Å absorption corresponds to the transition to $\tilde{B}\,^1B_u\,(v_3' = 0)$ of C_2H_2; k is given in units of atmospheres (0 °C) and cm, base e.

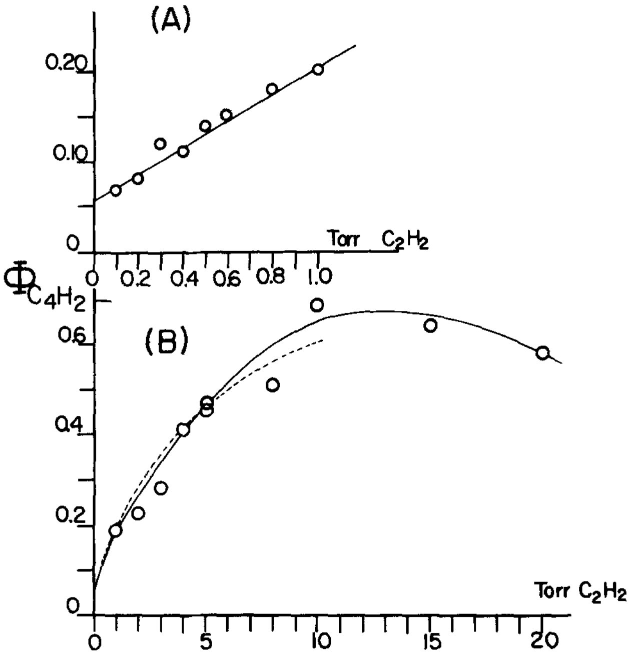

FIG. 2. Quantum yield of diacetylene in the photolysis of acetylene at 1849 Å; pressure range 13 to 2660 N m^{-2} (0.1 to 20 Torr); (A) $\phi_{C_4H_2}$ below 1 Torr of acetylene, (B) $\phi_{C_4H_2}$ in the 1 to 20 Torr range. A broken line in (B) is drawn according to Eq. (1). See the text.

Fig. 4(A). Figure 4(B) shows the decrease of $\phi_{C_4H_2}$ as propane is added. The extent of decrease is about twice as much in propane as in ethane.

DISCUSSION

Photolysis of acetylene

In accordance with the discussion given in a previous paper,[1] the overall photochemical process of acetylene at 1849 Å, as at 1470 Å, may be described as follows:

		Quantum Yield (1849 Å)
$C_2H_2 \xrightarrow{h\nu} C_2H_2^*$	(I)	
$C_2H_2 \rightarrow C_2H + H$	(II)	0.06
$C_2H_2^* \rightarrow C_2 + H_2$	(III)	0.1
$C_2H_2^* \rightarrow C_2H_2^{**}$	(IV)	0.84
$C_2H_2^{**} \xrightarrow{M} C_2H_2$	(V)	
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	(VI)	
$C_2H_2^{**} + C_2H_2 \rightarrow C_2H + C_2H_3$	(VII)	
$C_2H_2^{**} + 2C_2H_2 \rightarrow C_6H_6$	(VIII)	

where $C_2H_2^*$ signifies $\tilde{B}\,{}^1B_u$, $v' = 0$ (see Fig. 1) and $C_2H_2^{**}$ is a metastable (triplet) state with the same energy as $C_2H_2^*$, i.e., 6.71 eV corresponding to 1849 Å. The $C_2H_2^{**}$ molecule, if it does not react with C_2H_2, is deactivated by collisions with the walls, with inert gases M or by fluorescence [process (V)].

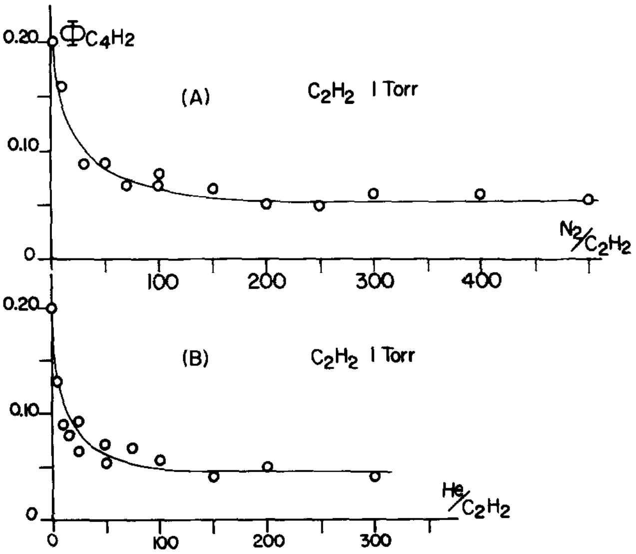

FIG. 3. (A) Effect of N_2 on the quantum yield of diacetylene formation; acetylene pressure, 1 Torr, λ = 1849 Å. (B) Effect of He on the quantum yield of diacetylene; acetylene pressure, 1 Torr λ = 1849 Å.

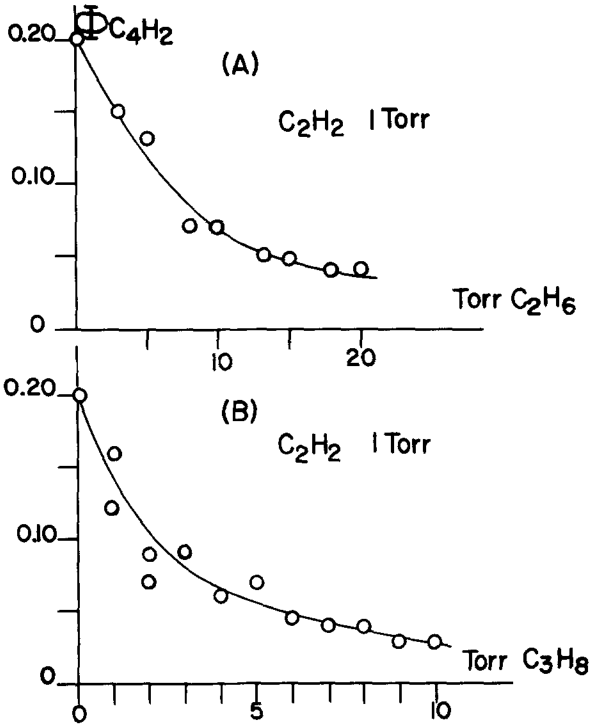

FIG. 4. (A) The quantum yield of diacetylene formation in the 1849 Å photolysis of acetylene as a function of the partial pressure of ethane; acetylene, 1 Torr. (B) The quantum yield of diacetylene formation as a function of the partial pressure of propane; acetylene, 1 Torr λ = 1849 Å.

TABLE III. Quantum yield of H_2 formation ϕ_{H_2} in acetylene photolysis at 1849 Å.

Pressure (Torr)	ϕ_{H_2}	Pressure (Torr)	ϕ_{H_2}
0.5	0.16	10	0.09
0.8	0.15	20	0.09
5.0	0.10		

The electronic state of $C_2H_2^{**}$ is uncertain. Four low lying triplet states, *cis* $^3A_2$ (4.50 eV), *trans* ^3A_u (4.13 eV), *trans* ^3B_u (3.78 eV), and *cis* $^3B_2$ (3.43 eV) have theoretically been predicted[12] below 6.71 eV. Then, the initially produced $C_2H_2^{**}$ molecule in process (IV) would have considerable vibrational energy. The quantum yield of process (II) may be obtained from $\phi_{C_4H_2}$ at the low pressure limit, i.e., 0.059 ± 0.005 [see Fig. 2(A)], since C_2H reacts exclusively with C_2H_2 to form diacetylene,[13] process (VI). This value is only 1/5 as large as the yield of 0.3 obtained at 1470 Å,[1] suggesting that dissociation is less important at 1849 Å than at 1470 Å. The quantum yield of H_2 production in acetylene photolysis is constant at 0.1 above 5 Torr (Table III), indicating process (III), the production of $C_2 + H_2$, is 0.1. The quantum yield increases to 0.16 below 1 Torr of acetylene. This excess H_2 of 0.06 may be formed by diffusion and wall combination of H atoms produced by processes (II) and (VI). It has been shown[14] that H atom diffusion becomes more important than H atom addition to C_2H_2 below 1 Torr of acetylene. It is most likely that C_2 in process (III) is formed in singlet $X\,^1\Sigma_g^+$ from the spin conservation rules. It is not known whether $C_2\,X\,^1\Sigma_g^+$ reacts with C_2H_2 to produce $2C_2H$.[15] If this is the case, $\phi_{C_4H_2}$ would be expected to be >0.2, much larger than 0.06 found experimentally. The increase of $\phi_{C_4H_2}$ with acetylene pressure (Fig. 2) indicates the occurrence of process (IV) followed by (VII) and (VI).

A weak fluorescence from acetylene has been observed by Hamai and Hirayama[16] at 2000 Å excitation but it decreased sharply with decreasing excitation wavelength and at 1849 Å no fluorescence was observed, indicating processes (II), (III), and (IV) are much more rapid than fluorescence.

The addition of N_2 or He reduces $\phi_{C_4H_2}$ to a limiting value of 0.05 as shown in Fig. 3. Since $C_2H_2 + C_2H_2 \rightarrow C_2H + C_2H_3$ is endothermic by 3.90 eV,[1] $C_2H_2^{**}$ must be deactivated below this energy by N_2 or He, so that the production of C_2H by process (VII) is no longer possible. On the other hand, process (II), the formation of C_2H from $C_2H_2^*$, must be rapid and the addition of N_2 or He should not affect this process. The limiting value of 0.05 corresponds to the quantum yield of process (II). The amount of N_2 or He required to reach this limiting value (100 to 150 Torr) is, as expected, much less than that at 1470 Å[1] (>400 Torr).

From processes (I)–(VII), we obtain

$$\phi_{C_4H_2} = \frac{k_{II}}{k_{II} + k_{III} + k_{IV}} + \frac{k_{IV}}{k_{II} + k_{III} + k_{IV}}\,\frac{k_{VII}(C_2H_2)}{k_V + k_{VII}(C_2H_2)}\,, \tag{1}$$

where k_{II}, etc., signifies the rate constant of the indicated process. From the foregoing discussion:

$$\frac{k_{II}}{k_{II} + k_{III} + k_{IV}} = \alpha = 0.06$$

and

$$\frac{k_{IV}}{k_{II} + k_{III} + k_{IV}} = \beta = 0.84\ .$$

Since $\phi_{C_4H_2}$ is linear with C_2H_2 pressure below 1 Torr [see Fig. 2(A)], $k_{VII}\,(C_2H_2)$ must be smaller than k_V in Eq. (1). In this case Eq. (1) becomes

$$\phi_{C_4H_2} = \alpha + \frac{\beta k_{VII}}{k_V}(C_2H_2)\ . \tag{2}$$

The slope in Fig. 2(A) gives 0.15 corresponding to $\beta k_{VII}/k_V$ in Eq. (2) from which $k_{VII}/k_V = 0.18$ is obtained where K_{VII} is in units of Torr^{-1} s^{-1} or $k_{VII} = 5.6 \times 10^{-18}\,k_V$ in units of cm^3 molecule^{-1} s^{-1}. The lifetime $1/k_V$ of $C_2H_2^{**}$ is estimated to be 1 ms[17] to 50 μs.[18] If $C_2H_2^{**}$ is *cis* $^3A_2$ (4.50 eV) with a radiative lifetime of 50 μs, $k_{VII} = 1.1 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} is obtained. At higher pressures of acetylene (>1 Torr), $\phi_{C_4H_2}$ is plotted against the pressure of C_2H_2 using Eq. (1). The plot is shown in Fig. 2(B) with a broken line. A reasonable agreement is seen with the experimental curve. At still higher pressures of acetylene (>10 Torr), $\phi_{C_4H_2}$ decreases, suggesting the occurrence of the additional process (VIII), the formation of benzene.

In the photolysis of acetylene at 1849 Å Tsukada and Shida[4] have found that the yield of benzene increases substantially above 10 Torr of acetylene while that of a diacetylene decreases in accordance with the present observation.

Photolysis of C_2H_2-C_2H_6, C_2H_2-C_3H_8 mixtures

The addition of RH(C_2H_6 or C_3H_8) to acetylene reduces $\phi_{C_4H_2}$ as shown in Fig. 4. The results can be explained by the competition between H atom abstraction by C_2H,[13,19]

$$C_2H + RH \rightarrow C_2H_2 + R \tag{IX}$$

and diacetylene formation

$$C_2H + C_2H_2 \rightarrow C_4H_2 + H\ . \tag{VI}$$

From (IX) and (VI), we obtain

$$\phi^0_{C_4H_2}/\phi_{C_4H_2} = 1 + \frac{k_{IX}(RH)}{k_{VI}(C_2H_2)}\ , \tag{3}$$

where $\phi^0_{C_4H_2}$ and $\phi_{C_4H_2}$ indicate the quantum yield of diacetylene without and with RH, respectively. Figure 5 shows the plot of $\phi^0_{C_4H_2}/\phi_{C_4H_2}$ against $(C_2H_6)/(C_2H_2)$ when C_2H_2 is at 1 Torr. The slope from the least squares analysis of the plot gives $k_{IX}/k_{VI} = 0.240 \pm 0.015$ where the error limit is one standard deviation of the mean. Likewise $\phi^0_{C_4H_2}/\phi_{C_4H_2}$ is plotted against the ratio $(C_3H_8)/(C_2H_2)$ as shown in Fig. 6, when C_2H_2 pressure is 1 Torr. The slope obtained by the least squares analysis is 0.469 ± 0.041. These results are given in Table IV, together with the data on the C_2H reactions with H_2 and CH_4. The rate constants are derived on the basis of 3×10^{-11} cm^3 molecule^{-1} s^{-1} for $C_2H + C_2H_2$.[20] The rate constant for C_2H_6, $k_{IX} = (0.72 \pm 0.05) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, obtained in this work is within the indicated error limit in excellent agreement with a value of $(0.65 \pm 0.04) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} obtained from the measurement of the rise time of C_2H_2.[19] The rate constant for $C_2H + C_3H_8 \rightarrow C_2H_2 + C_3H_7$ has apparently not been measured before. Rate constants obtained by three different methods in Table IV; (1) the rate of decrease in C_2H[13]; (2) the rate of increase in C_2H_2[20]; and (3) the decrease of the C_4H_2 yield in C_2H_2 photolysis by the addition of H_2,[1,20] CH_4[1] or C_2H_6, are in good agreement. On the other hand, rate constants for $C_2H + H_2$

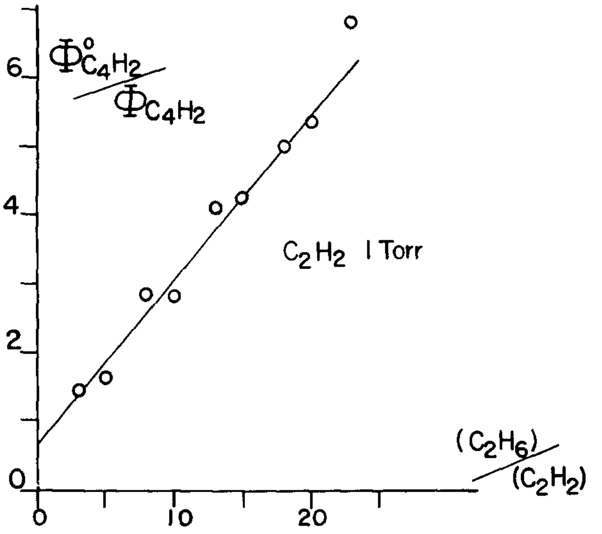

FIG. 5. The plot of the quantum yield of diacetylene formation in C_2H_2 photolysis to that in the photolysis of C_2H_2–C_2H_6 mixtures as a function of the ratio, C_2H_6/C_2H_2; acetylene, 1 Torr $\lambda = 1849$ Å. The slope gives the rate constant ratio of 0.240 ± 0.05 for $C_2H + C_2H_6$ to $C_2H + C_2H_2$ reactions.

and $C_2H + CH_4$ obtained from the decay of the $CH(A-X)$ chemiluminescence[21] generated in the C_2H–O_2–H_2 or C_2H–O_2–CH_4 mixtures are much larger than those based on the previously described three methods. The reason for this discrepancy is not clear.

It has been suggested[15] that $C_2\ X\ ^1\Sigma_g^+$ formed in process (III) may react rapidly with $RH(CH_4, C_2H_6)$ to produce C_2H,

$$C_2(X\ ^1\Sigma_g^+) + RH \rightarrow C_2H + R\ . \qquad (X)$$

If process (X) occurs in the photolysis of C_2H_2–RH mixtures, the additional C_2H produced would increase $\phi_{C_4H_2}$ in Eq. (3), resulting in smaller ratios for k_{IX}/k_{VI} than those obtained from the ratio of the rate of increase in $C_2H_2(k_{IX})$[19] to that in $C_4H_2(k_{VI})$.[20] The result that the two different techniques lead to nearly the same ratios suggests that the contribution from additional C_2H may be discounted.

TABLE IV. Reaction rates of C_2H with H_2 and hydrocarbons at room temperature.

Reaction	Ratio	Rate constant (10^{-11} cm^3 molecule^{-1} s^{-1})	
$C_2H + H_2 \rightarrow C_2H_2 + H$	0.0077 ± 0.0007^a 0.0049^b	0.023 ± 0.002^d 0.015^d	0.017^e 1.2 ± 0.3^f
$C_2H + CH_4 \rightarrow C_2H_2 + CH_3$	0.032 ± 0.002^a	0.10 ± 0.006^d	0.12 ± 0.02^g 0.48 ± 0.1^f
$C_2H + C_2H_6 \rightarrow C_2H_2 + C_2H_5$	0.240 ± 0.015^c	0.72 ± 0.05^d	0.65 ± 0.04^g
$C_2H + C_3H_8 \rightarrow C_2H_2 + C_3H_7$	0.469 ± 0.041^c	1.4 ± 0.1^d	...
$C_2H + C_2H_2 \rightarrow C_4H_2 + H$	1	3	3.1 ± 0.2^b 5^e

[a] From Ref. 1.
[b] From Ref. 20.
[c] In this work, the error limit is one standard deviation.
[d] Calculated from the ratios assuming 3×10^{-11} cm^3 molecule^{-1} s^{-1} for $C_2H + C_2H_2$.
[e] From Ref. 13.
[f] From Ref. 21.
[g] From Ref. 19.

TABLE V. Relative rates of reaction of C_2H with H_2 and hydrocarbons in the Titan atmosphere.

Molecule	Rate constant cm^3 molecule^{-1} s^{-1} at 170 K^a	Mixing ratio^b	Relative rate
CH_4	7×10^{-13}	3×10^{-2}	1
C_3H_8	1.4×10^{-11}	2×10^{-5}	1.3×10^{-2}
C_2H_6	7.2×10^{-12}	2×10^{-5}	0.7×10^{-2}
C_2H_2	3×10^{-11}	2×10^{-6}	3×10^{-3}
H_2	4.1×10^{-15}	$\sim 10^{-3}$	2×10^{-4}

[a] Calculated assuming activation energies of 2.9 and 0.5 kcal mol^{-1} for H_2 and CH_4, respectively, and no activation energy for other hydrocarbons, from R. L. Brown and A. H. Laufer, J. Phys. Chem. **85**, 3826 (1981).
[b] From Refs. 6 and 22.

The photochemistry of acetylene in the Titan atmosphere

The photochemical process of acetylene at 1849 Å may represent that of acetylene in the Titan atmosphere, where the solar radiation absorbed by acetylene is in the 1450–2370 Å region, radiation below 1450 Å being absorbed by methane, the predominant hydrocarbon in the Titan atmosphere.[6,22] The $\tilde{B}\ ^1B_u$ state of acetylene is mainly formed by absorption of light in the 1600–1850 Å region.[2] The metastable acetylene formed at 1849 Å with a quantum yield of 0.84 is quenched by abundant N_2 present in the Titan atmosphere.[22]

The rate constants of C_2H formed by the photolysis of C_2H_2 with H_2 and various hydrocarbons in the Titan atmosphere are given in Table V assuming 170 K.[22] The last column shows the rates relative to CH_4. The sensitized reaction of CH_4 decomposition by C_2H_2

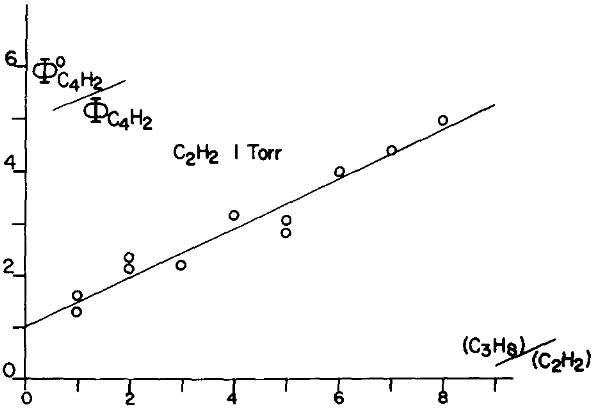

FIG. 6. The plot of the quantum yield of diacetylene formation in C_2H_2 photolysis to that in the photolysis of C_2H_2–C_3H_8 mixtures against the ratio C_3H_8/C_2H_2; acetylene, 1 Torr $\lambda = 1849$ Å. From the slope the rate constant ratio of 0.469 ± 0.041 is obtained for $C_2H + C_3H_8$ to $C_2H + C_2H_2$ reactions.

$$C_2H_2 \xrightarrow{h\nu} C_2H + H \ , \qquad \text{(II)}$$

$$C_2H + CH_4 \rightarrow C_2H_2 + CH_3 \ , \qquad \text{(XI)}$$

is the most important reaction route of C_2H. Strobel[7] estimates that the dissociation of CH_4 by C_2H is as important as the direct photolysis by sunlight. The sensitized decomposition of ethane and propane by acetylene is the main dissociation route of these hydrocarbons, since the direct photodissociation by sunlight is limited only in the 1450–1700 Å region.[23] The rate of reaction of C_2H with C_2H_2 to form C_4H_2 is only 0.003 of that with CH_4 and only small amounts of C_4H_2 (mixing ratio 10^{-7}–10^{-8}) are found in the Titan atmosphere.[6] Unlike the Jovian atmosphere where H_2 is 90%,[24] sensitized decomposition of H_2 by C_2H_2 is only 0.002 of that of CH_4; i.e., the conversion of methane to higher alkanes by the C_2H_2 catalyzed reaction is more likely to occur in the Titan atmosphere.

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