

QUANTUM YIELD OF VINYLIDENE (3B_2) FROM THE VACUUM UV PHOTOLYSIS OF ACETYLENE AND ETHYLENE

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Summary

The primary processes in the photodecomposition in the vacuum UV of the unsaturated hydrocarbons acetylene and ethylene have been investigated. The formation of electronically excited triplet vinylidene ($H_2C=C$) radicals is shown to be a major process. The quantum yields of vinylidene production are equal to 0.4 and 0.75 from acetylene and ethylene respectively. Vinyl radical formation in the ethylene photolysis is discussed.

1. Introduction

The vacuum UV photochemistry of acetylene (C_2H_2) and ethylene (C_2H_4) have been extensively studied for the past several decades. However, with the advent of excimer lasers and the observation of new primary processes in their photolysis, there has been a recent renaissance in interest in these molecules. In particular, electronically excited vinylidene radicals ($H_2C=C$) have been directly observed by absorption spectroscopy following the vacuum UV photolysis of both C_2H_2 [1] and C_2H_4 [2].

$H_2C=C$ had earlier been surmised as an active intermediate in low intensity steady state vacuum UV decomposition studies of C_2H_4 but its direct observation is only recent [2] and then as the result of flash photolysis in the A ($^1B_{1u}$) and B ($^1B_{1u}$) states at wavelengths greater than 155 nm. Whether $H_2C=C$ is simply a radical of intellectual interest or one that plays a significant role in the photolysis of C_2H_4 has not been addressed previously.

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The photochemistry of C_2H_2 is somewhat enigmatic and complex. Its photolysis is the source of C_2H radicals, which have been implicated in diverse areas ranging from the chemistry of planetary atmospheres to combustion systems. The total quantum yield for dissociation of C_2H_2 is significantly less than unity [3] even though a variety of primary processes have been invoked.

Recent quantum yield determinations [3] at several wavelengths in the photochemically active vacuum UV region suggest two dissociative channels:



and



with the quantum yield of channel (1) equal to 0.1 independent of incident wavelength and that of channel (2) being 0.3 at 147 nm and 0.06 at 185 nm. It is suggested that the remaining process involves a non-dissociative excited state $C_2H_2^*$ which is sufficiently long lived that it may be deactivated either by an inert gas or, in a laboratory experiment, by the walls of the reaction vessel. The extended lifetime of the non-dissociative excited state of C_2H_2 has been well documented and, in fact, this state has been shown to be capable of undergoing reaction with labile hydrogen atoms [4]. It has been demonstrated that the excited acetylenic species produced by 147 nm photolysis of C_2H_2 has the unique structure of vinylidene [5].

The quantum yield from the production of $C_2H_2^*$ (corresponding to a vinylidene structure) remains to be determined in the region of 147 nm. A recent determination of the absorption coefficient of $H_2C=C$ [6] now permits us to determine directly the quantum yield for the production of this radical in the C_2H_2 photolysis as well as in any other photochemical substrate where $H_2C=C$ is a photoproduct. Comparison with previous results can then be made.

$H_2C=C$ in its lowest energy state is a singlet. The singlet state is truly ephemeral with respect to its isomerization to C_2H_2 , which is estimated to occur in less than 10^{-11} s [7]. The singlet ground state, therefore, will not be of chemical interest since it will isomerize very rapidly prior to possible reaction. $H_2C=C$ in its triplet excited state (3B_2) is long lived. Because of its extended lifetime the triplet $H_2C=C$ species may be of importance as an intermediate in the chemistry of hydrocarbon-containing systems. In this work we limit ourselves to the measurements of the quantum yields for triplet $H_2C=C$ from the photolysis of C_2H_2 and C_2H_4 .

2. Experimental techniques

The triplet species $H_2C=C$ was observed by absorption spectroscopy at 137 nm following the vacuum UV flash photolysis of either C_2H_4 or C_2H_2 . The C_2H_2 was conveniently monitored at 152 nm and diacetylene (C_4H_2)

at 145 nm. The laboratory apparatus and techniques used in these experiments have been discussed previously [2], so will be described only very briefly in this paper. Following the initial photolysis flash of about 7 μ s duration, a Garton-type analysis lamp of 2 μ s pulse width probed the photolysis mixture. In the C_2H_2 experiments the photolysis cell was constructed of LiF, which permitted the use of incident light at wavelengths down to 105 nm. The C_2H_4 experiments were carried out in a Suprasil cell whose transmission extended to 155 nm. The delay between the photolysis and analysis probe was conveniently varied through a photomultiplier-oscilloscope combination. The analysis flash, also essentially continuous in wavelength output throughout the vacuum UV from 120 - 185 nm, was focused through LiF optics onto the entrance slit of a 2 m Eagle mount vacuum spectrograph. The instrument dispersion was 2.77 $\text{\AA} \text{ mm}^{-1}$. Typical entrance slits of 20 μ m were adequate to produce sufficient plate darkening in a single flash. The data were analyzed by a densitometer procedure and reduced through the plate characteristic curve.

Samples to be photolyzed were prepared as dilute mixtures in helium. The concentration range of the precursor was limited by the experimental requirement of producing an adequate photofragment concentration while providing sufficient transmission through the cell to produce meaningful absorption data. Typical concentrations of C_2H_2 and C_2H_4 between 20 and 200 mTorr are optimum. Concentrations of the precursor, triplet $H_2C=C$, as well as C_4H_2 , the major product of C_2H_2 photolysis, could be monitored simultaneously by following the absorption in the vacuum UV.

3. Results and discussion

3.1. Acetylene

The time-dependent absorption, and hence concentration, of $H_2C=C$ triplet has a maximum at the shortest observation times following the excitation. This temporal behavior indicates that the process represents a primary photodissociation channel and does not involve intermediate formation of long-lived excited molecular states. The absolute concentration of $H_2C=C$ is obtained from the previously measured extinction coefficient of 694 $\text{atm}^{-1} \text{ cm}^{-1}$ (base e) and the Lambert-Beer law [6]. We can derive a value for the quantum yield of $H_2C=C$ formation: $\phi(H_2C=C) = 0.4$.

A major dissociative process in C_2H_2 photodecomposition at 147 nm is production of C_2H (ethynyl) radicals with a quantum yield of 0.3 [3]. In a laboratory experiment the sole fate of the C_2H radical is to produce C_4H_2 [8]. Therefore a measurement of the absolute C_4H_2 yield compared with that of $H_2C=C$ results in a "relative" determination of the quantum yield of $H_2C=C$ formation.

Our results show that the primary yield of $H_2C=C$ is 0.4. This compares with the C_4H_2 quantum yield of 0.3. The dissociative channels, *i.e.* production of C_2H and C_2 , have a total quantum yield of 0.4 with the remaining

process reported to be the formation of a metastable acetylene, $C_2H_2^*$. However, recent laser photodecomposition studies at 193 nm [9] suggest that the C_2 arises from secondary C_2H photolysis leading to an even lower primary decomposition quantum yield. The formation of $H_2C=C$ clearly represents the major single photochemical process in the C_2H_2 photolysis. The present experiments use broadband radiation and not monochromatic light. Nevertheless the maximum absorption of C_2H_2 in this spectral region is at 152 nm, the onset of the strong $\tilde{C}-\tilde{X}$ system, and the major portion of the flash photolysis probably occurs here. Since the 152 nm absorption is in the same band system as that at 147 nm, the excited electronic state will be the same and we are confident that the photochemistry should be similar at both wavelengths.

3.2. Ethylene

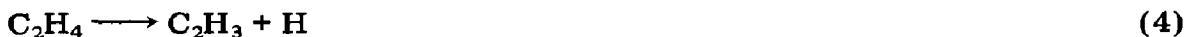
Excited triplet $H_2C=C$ is formed following the vacuum UV photolysis of C_2H_4 . Its concentration increases from a low value to a maximum at measurably long times following the initial excitation [2]. This indicates that $H_2C=C(^3B_2)$ formation does not represent a "primary" process. Based upon a recent study of the photodecomposition of vinyl chloride [10], we believe that the C_2H_4 decomposition, in part, proceeds through an excited metastable state of the precursor prior to its spin-allowed dissociation into triplet $H_2C=C$. The temporal profile of $H_2C=C$ is a function of pressure and appears to decrease with increasing inert gas pressure.

In the laboratory experiment, the $H_2C=C(^3B_2)$ concentration reaches a maximum at about 50 μs following the incident flash. In contrast to the C_2H_2 studies we do not have an absolute measure of the quantum yield of another reaction product. Therefore, we must compare the $H_2C=C$ concentration against that of the C_2H_2 product itself. The total quantum yield of C_2H_2 formation from C_2H_4 photolysis is estimated to be 1.0 [11].

Two equally important primary dissociative processes that lead to C_2H_2 have been recognized in the vacuum UV photolysis of C_2H_4 [12]. One process produces a C_2H_2 directly, presumably with a vinylidene structure, with the simultaneous formation of molecular H_2 through a 1,1-elimination



and the other proceeds through an excited vinyl radical (C_2H_3) that can be partially stabilized by collisions with high pressures of inert gas



The temporal profile of C_2H_2 production observed in the present work from the photolysis of the C_2H_4 is shown in Fig. 1. The broken sigmoid curve (curve B) is the calculated C_2H_2 production rate if it were entirely generated through a triplet $H_2C=C$ intermediate. The representation is clearly inadequate and the data indicate an additional, more rapid, C_2H_2 formation process. It is reasonable to ascribe that process to the unimolecular decomposition of the excited C_2H_3 radicals formed in the primary pho-

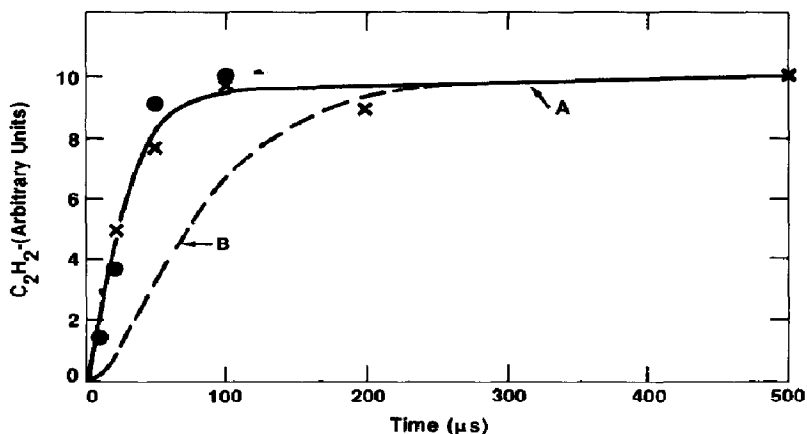


Fig. 1. Yield of C_2H_2 as a function of time following the photolysis of C_2H_4 (C_2H_4 , 20 mTorr; helium, 10 Torr): x, protonated, ●, deuterated; curve A, fit to the data; curve B, calculated (see text).

tolysis. Based upon thermochemical considerations, we would not expect C_2H_3 radical to dissociate into $H_2C=C$ but rather to C_2H_2 ($\Delta H_f\{H_2C=C(^3B_2)\} = 141 \text{ kcal mol}^{-1}$ based upon $\Delta H_f\{H_2C=C(^1A_1)\} = 100 \text{ kcal mol}^{-1}$ [13] and an $^1A_1-^3B_2$ splitting of 41 kcal mol^{-1} [14]; $\Delta H_f(C_2H_3) = 70.4 \text{ kcal mol}^{-1}$ [15]).

The results of the present work indicate that the final concentration of C_2H_2 is, within experimental error, equivalent to the concentration of $H_2C=C$ when it is at its maximum at $50 \mu s$ following the incident flash. This is inconsistent with the proposed postulate of equal probabilities for the dissociative primary channels assuming all the $H_2C=C(^3B_2)$ were to produce C_2H_2 . Since there is at least one other primary process that ultimately leads to C_2H_2 , namely reaction (4), it is clear that all the $H_2C=C$ cannot result in C_2H_2 product. We suggest that some triplet $H_2C=C$ may chemically react in this system.

A rapid rate constant for the interaction between $H_2C=C(^3B_2)$ and C_2H_4 has been reported [2]. We can estimate a rate constant for quenching to the ground state singlet of $3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, using the potential well depth correlation method [16]. With the concentrations of helium (10 Torr) and C_2H_4 (10 mTorr following the flash), we estimate that about 70% of the $H_2C=C$ leads to C_2H_2 . Further, at the low inert-gas pressures used in the present experiments, the $C_2H_3^*$ will not be stabilized by collision [12] and will dissociate rapidly, on the time scale of the experiments, to C_2H_2 . The data suggest that about 30% - 40% of the total C_2H_2 may arise by this path. The quantum yield for the channel leading to triplet $H_2C=C$ is probably more important than previously thought. Within the experimental error, we find $\phi(H_2C=C) = 0.75 \pm 0.2$.

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