

VINYLDENE (3B_2): AN ACTIVE INTERMEDIATE IN THE PHOTOLYSIS OF ETHYLENE

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Summary

Triplet vinylidene has been observed, by time-resolved absorption spectroscopy, as an intermediate in the vacuum UV flash photolysis of ethylene. The several primary photochemical processes are discussed. Rate constants for the interaction of both protonated and deuterated vinylidene species with C_2H_4 and C_2D_4 have been obtained. They are $1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively. The nature of the interaction between triplet vinylidene and ethylene is discussed.

1. Introduction

The chemistry of unsaturated carbene radicals is an area of expanding interest and has been the subject of several recent reviews [1]. Vinylidene ($H_2C=C$) is the simplest of this series, and as such continues to be of significant theoretical and experimental interest. In the present work, a study of the flash photolysis of ethylene, a transient absorption feature in the 137 nm region has been observed. This feature, which has previously been observed and ascribed to electronically excited triplet vinylidene [2], has now been observed in three systems: (1) the photolysis of acetylene, (2) the combination reaction of two triplet CH_2 radicals and (3) in the present work from the photolysis of ethylene. The vinylidene production from ethylene plus the spectral evidence previously noted further support the identification of the spectral carrier as the vinylidene radical, probably in the 3B_2 state. There is no evidence, in the ethylene system, of the formation of ground state vinylidene (1A_1).

Vinylidene radicals have previously been suggested as an intermediate in the vacuum UV photolysis of ethylene [3, 4]. In low intensity experiments, analysis of the hydrogen product from CH_2CD_2 at either 147 nm or

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123.6 nm [3] has demonstrated that the majority of the hydrogen is formed by elimination from the same carbon atom with the necessarily concomitant formation of vinylidene radicals, *e.g.*



While the interpretation of low intensity experiments suggests the presence of vinylidene as an intermediate, the technique does not permit delineation between the formation of either the ground singlet or the excited triplet state. Although the spectrum of ground state singlet vinylidene ($^1\text{A}_1$) is not known, its lifetime has been calculated to be about 10^{-11} s with respect to rearrangement to acetylene [5]. As a consequence of the extremely short lifetime, the temporal history of acetylene formation on a microsecond time scale would be invariant in the present experiment if vinylidene ($^1\text{A}_1$) were the sole precursor of acetylene. While there may be secondary sources of product acetylene in the photolysis of ethylene, the absence of acetylene at the shortest delay times, as reported here, necessarily implies the absence of singlet vinylidene. By way of contrast, the lowest excited state of vinylidene is a triplet ($^3\text{B}_2$) which is quite stable. Its stability is by virtue of the predicted large activation energy barrier (about 50 kcal mol $^{-1}$) to a 1,2 hydrogen migration on a triplet surface to produce acetylene.

In the present work, C_2H_4 or C_2D_4 has been photolyzed in the vacuum UV region from the onset of the ethylene absorption to about 155 nm, the transmission limit of the photolysis cell. The absorption corresponds to transitions from the ground state to both the $\tilde{\text{A}} \ ^1\text{B}_{1u}$ and $\tilde{\text{B}} \ ^1\text{B}_{1u}$ states (the V and 2R states). The presence of reactive intermediates and product acetylene was observed by time-resolved absorption spectroscopy in the vacuum UV region.

2. Experimental details

In the present work, C_2H_4 or C_2D_4 , neither of which had any discernible hydrocarbon impurities as determined by gas chromatography using flame ionization detection, was premixed with ultrahigh purity helium and expanded into a quartz reaction vessel. The transmission of the photolysis cell extended to 155 nm. The final composition in a typical experiment was 20 - 50 mTorr ethylene in 10 Torr helium. The flash photolysis-kinetic spectroscopy apparatus has been described previously in detail [2]. In brief, the photolysis cell was placed inside a chamber in which a photolysis flash through nitrogen could dissipate 2450 J in 7 μs . Actinometry, using gas chromatography and on the assumption that the acetylene production from ethylene has a quantum yield of unity, suggests that about 10^{16} photons per pulse are produced in each flash. The light output was monitored optically. Spectroscopic analysis was performed with a Garton-type analysis flash of 2 μs pulse width triggered at preset delay times with a photomultiplier-oscilloscope circuit. The vacuum UV output was focused through LiF optics

onto the slit of a 2 m Eagle mount spectrograph with a dispersion of 2.8 \AA mm^{-1} in first order. Spectra were recorded on vacuum-UV-sensitive plates. A single flash, through a $25 \text{ }\mu\text{m}$ slit, produced adequate plate darkening for densitometric analysis. The temporal history of triplet vinylidene was monitored at either 137.4 nm or 137.0 nm for the protonated and deuterated species respectively. The acetylene concentration was determined from its absorption ($\tilde{C}-\tilde{X}$) at 152.0 nm [6].

3. Results and discussion

The results indicate the absence of acetylene at the shortest delay times attainable with this system, *i.e.* $4 \text{ }\mu\text{s}$ after the flash. This indicates that little vinylidene (1A_1) is formed in the primary process since its rapid rearrangement would produce acetylene. The experimental result is in disagreement with the theoretical prediction of Evleth and Sevin [7] where it was suggested that formation of ground state singlet vinylidene is a favored reaction path for dissociation of twisted singlet ethylene.

Alternatively, the spin-forbidden process to form vinylidene (3B_2) in the primary process would result in a monotonic temporal decrease in its concentration as was observed in the photolysis of acetylene [8]. The actual vinylidene (3B_2) profile, for both protonated and deuterated species, is shown in Fig. 1. The temporal increase in the vinylidene concentration indicates it is formed in a secondary process, following the initial flash. The rise time was approximated by a $1/e$ time of $25 - 40 \text{ }\mu\text{s}$. Clearly, the choice of the rise time is not an exact fit, but, within the uncertainty of the data, it is an adequate representation and it serves to demonstrate that vibrationally relaxed triplet vinylidene also is not a primary product of the photolytic process. The vinylidene has a well-behaved decay in agreement with the previously measured [8] quenching rate by helium, $2.4 \times 10^{-14} \text{ cm}^3 \text{ mol}^{-1}$

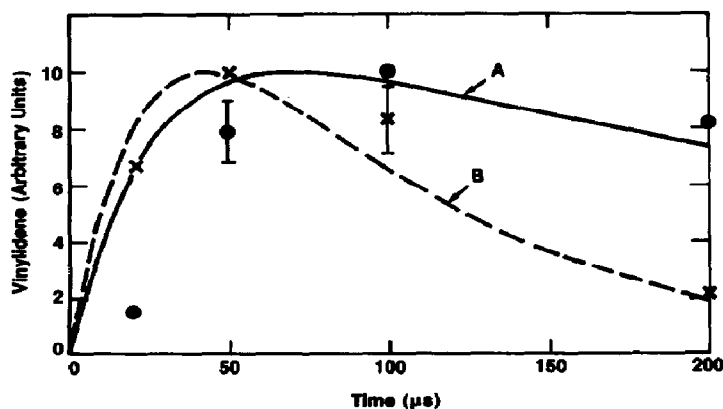


Fig. 1. Time profile for vinylidene (3B_2) (ethylene, 20 mTorr; helium, 10 Torr): curve A (●), deuterated species; curve B (×), protonated species. (See text for discussion of decay.)

ecule⁻¹ s⁻¹ for the deuterated species and 1.3×10^{-14} cm³ molecule⁻¹ s⁻¹ for the protonated species. The fits using these values are shown in Fig. 1. With the previously determined rate constant for vinylidene quenching by helium, a value for $k(\text{quenching} + \text{reaction}) = 1.4 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ was deduced for the interaction between ethylene and vinylidene (³B₂). Similarly, we have derived a rate constant of 1.4×10^{-12} cm³ molecule⁻¹ s⁻¹ for the C₂D₄ interaction with deuterated vinylidene.

The reduction of vinylidene (³B₂) with time includes contributions from both helium quenching and ethylene; its overall interaction with ethylene includes both quenching and possible reaction. Further evidence for the interpretation leading to the derived rate constants was obtained by photolysis of a fixed concentration of ethylene in the presence of varying quantities of helium diluent with measurement of the triplet vinylidene concentration at a fixed delay time of 10 μs. The data and fit using the previously derived rate constants $k(\text{C}_2\text{H}_4)$ and $k(\text{He})$ are shown in Fig. 2. The pressure dependence shown in Fig. 2 offers further corroboration that vibrationally relaxed triplet vinylidene, the carrier of the spectrum, is formed in a secondary process, probably involving a quenching reaction and/or production from another intermediate which has not been observed.

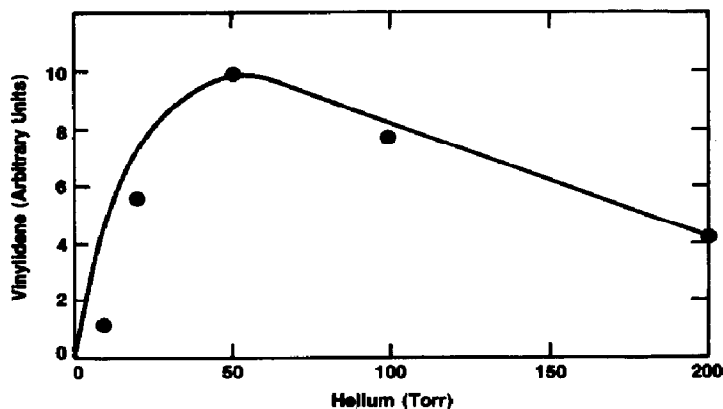


Fig. 2. Vinylidene (³B₂) concentration with added helium at a fixed 10 μs delay (substrate, ethylene at 20 mTorr).

It is worth noting that the rapid interaction of triplet vinylidene with ethylene, to the extent that it is a reaction, probably represents an addition process. A rate constant for the abstraction reaction has been calculated by the bond strength-bond length technique and is equal to about 3×10^{-16} cm³ molecule⁻¹ s⁻¹ at 300 K [9], at best a minor channel for the interaction. The absence of acetylene at the shortest delay time has been noted. However, the acetylene concentration does increase subsequently but at a much faster rate than is predicted from the decay of triplet vinylidene. This behavior indicates an additional source of acetylene in the photolytic system which we are unable to identify.

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