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# A LABORATORY INVESTIGATION OF THE PRODUCTION AND PROPERTIES OF MOLECULAR AND RADICAL SPECIES PERTINENT TO PLANETARY ATMOSPHERES

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## ABSTRACT

Vinylidene($H_2C$=C) is shown to be the largest photodecomposition channel in the direct photolysis of both $C_2H_2$ and $C_2H_4$. The chemistry of $H_2C$=C as it relates to planetary atmospheres is discussed. The vinyl radical ($C_2H_3$), important in the acetylene chemistry cycle, has been directly observed spectroscopically and the kinetics of several key reactions of this species measured.

## INTRODUCTION

An understanding of the chemistry of planetary atmospheres is critically dependent upon knowledge of the kinetic parameters of a suite of elementary chemical reactions. In the outer planets and several of their satellites, where carbon-hydrogen chemistry is paramount, the important vacuum ultraviolet photochemically induced processes and reactions involve small hydrocarbon molecules and radicals. Photochemical processes of the major planetary hydrocarbon, $CH_4$, have been known quantitatively for several decades. The carbon containing free radicals formed in the $CH_4$ photolysis, $CH_2$ and $CH_3$ corresponding to $H_2$ and H formation respectively, lead, through self-reactions, to $C_2H_2$ and $C_2H_4$[1].

$$CH_2 + CH_2 = C_2H_2 + H_2 \text{ (or 2H)} \tag{1}$$

$$CH_2 + CH_3 = C_2H_4 + H \tag{2}$$

In this paper, we review the quantum yield of formation and identity of the free radicals produced in the vacuum ultraviolet photolysis of the two unsaturated hydrocarbons, $C_2H_2$ and $C_2H_4$, and kinetic processes of several previously non-investigated species.

## EXPERIMENTAL

The experimental apparatus used in the work to be described has been discussed in several papers from this laboratory[2], so will be described only briefly here. A photolysis flash of about 5us, full width at half-maximum intensity, has an output maximized in the vacuum ultraviolet region, the spectral region where the energy of the incident solar flux is sufficient to dissociate small hydrocarbon molecules and where the molecules of interest have their maximum optical absorption. Following the initial flash, a Garton-type analysis lamp of 1 us pulse width probed the photolysis mixture. The photolysis cells, constructed of either LiF or Suprasil, permitted photolysis to 105 nm or 155 nm, respectively. The output of the analysis flash, essentially continuous from 120 through 185nm, was focused through LiF optics onto the entrance slit of a 2 m Eagle vacuum spectrograph whose dispersion was 2.77A/mm. The temporal profile of all species was monitored directly through well-characterized absorptions.

## RESULTS

### Vinylidene Formation

Vinylidene ($H_2C=C$) was initially observed, in its electronically excited triplet state at 137 and 151 nm, following the photolysis of $C_2H_2$ in the vacuum ultraviolet[3]. The species has a long lifetime toward isomerization to acetylene and, therefore, may be of importance as an intermediate in planetary hydrocarbon systems if its quantum yield of formation from reasonable precursors is large. Acetylene is known to form both $C_2H$ and $C_2$ from photolysis in the vacuum ultraviolet with estimated primary quantum yields of 0.3 and 0.1 at 147 nm, respectively[4]. We find that $H_2C=C$ is formed with a quantum yield of 0.4 making it the single largest dissociative channel in the acetylene photodecomposition.

Previously, the formation of unmixed $H_2$ or $D_2$ from the low intensity photolysis of $C_2H_4$ and its deuterated isotopes provided evidence for production of vinylidene radicals, i.e.,

$$CH_2CD_2 = CH_2C + D_2 \text{ and } CD_2C + H_2 \qquad (3)$$

In our direct determination, we find a quantum yield equal to 0.75 +/- 0.2 for triplet vinylidene formation from ethylene. Though not directly observed, there is evidence that the remainder proceeds through vinyl ($C_2H_3$) radical formation. The work has been described in greater detail earlier[5].

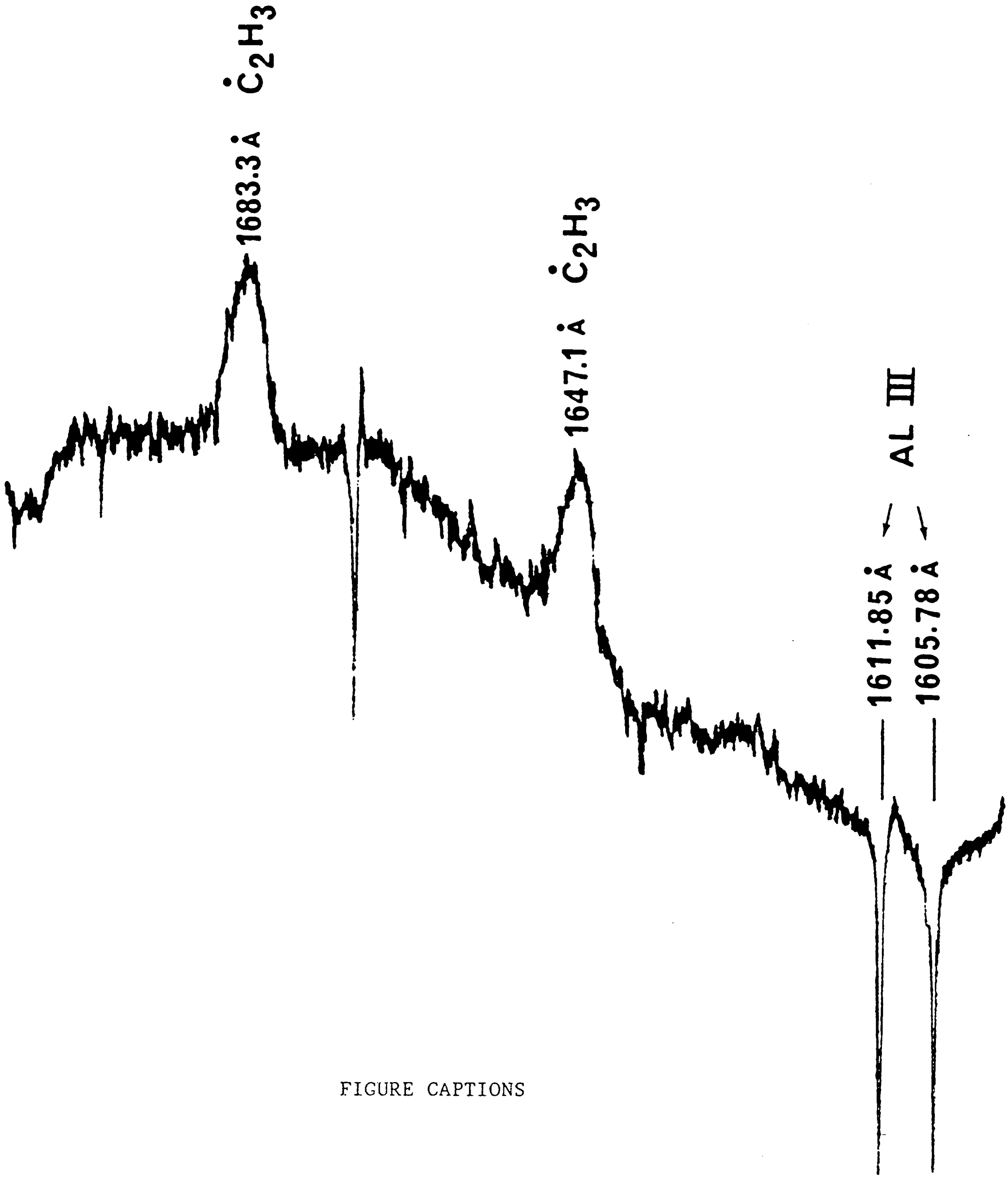
## Vinylidene Chemistry

The long-lived vinylidene moiety we observe is the electronically excited triplet that is calculated to be about 40-50 kcal/mol above the ground singlet state. The singlet, by comparison, has an ephemeral existence with a lifetime of the order of $10^{-12}$ seconds with respect to isomerization to acetylene. We have looked specifically for a chemical reaction, i.e., hydrogen abstraction, by triplet vinylidene with $H_2$, $CH_4$ and $C_2H_4$. Under conditions of our experiments, that is room temperature, we found no evidence for direct chemical reaction although the results with ethylene were less clear. Removal of the $H_2C{=}C$ in the absence of chemical reaction, presumably by quenching to the ground electronic state by added Ar, $H_2$, CO and $N_2$, occurred with reasonable rate constants. The slow rate observed for reaction agrees with predicted calculated values based upon a simple BEBO model[6].

## Vinyl Radical Absorption Spectrum

The vinyl ($C_2H_3$) radical has been implicated in the acetylene chemical cycle. Although several studies have utilized mass spectrometric detection for analysis, there has not been an observable, intense ultraviolet or visible spectral signature for this species, an omission that has probably limited kinetic studies of this species.

Using flash photolysis of selected precursors in conjunction with vacuum ultraviolet absorption spectroscopy we have observed two relatively intense transient absorption features that we attribute to the vinyl radical (Figure 1). The features at 164.71 and 168.33 nm are assigned on the basis of precursor, kinetic data, and the spacing between the bands. The optimum precursors were $Sn(C_2H_3)_4$ and $Hg(C_2H_3)_2$. The photolysis of either resulted in 1) the observed spectrum, 2) produced the expected dimerization product, 1,3-butadiene, that was observed by gas chromatographic analysis and 3) a spacing between the transitions of 1306 $cm^{-1}$ in agreement with both calculations and measurements of the vinyl ion spectrum. The spectrum was sufficiently intense, with extinction coefficients in excess of 1100 $atm^{-1}cm^{-1}$ that it could serve as a probe for kinetic studies. The work has been described in greater detail elsewhere[7].



## FIGURE CAPTIONS

Figure 1. Densitometer trace of the observed absorption bands of the $C_2H_3$ radical. The identified emission lines of Al III are from the source.

## Vinyl Radical Chemistry

The initial reaction of vinyl radicals studied using its optical absorption was its reaction with molecular $O_2$. This reaction had been examined earlier with alternate techniques[8] and confirmation of the kinetic parameters using the $C_2H_3$ vacuum ultraviolet absorption served, in part, to confirm the assignment of the carrier to the vinyl radical. A major loss mechanism in any system containing free radicals is the self-reaction of the two radicals; in this case to disproportionate forming $C_2H_2$ and $C_2H_4$ or to combine yielding 1,3-butadiene. The optical measurement of the radical concentration with time following its production by flash photolysis resulted in a rate constant of $1.0 \times 10^{-10} cm^3 molec^{-1} s^{-1}$. A ratio of 4.7 was found for the combination/disproportionation ratio as ascertained through gas chromatographic analysis of the products.

Future efforts in our studies of vinyl radical chemistry will be to examine other rapid radical-radical reactions that are conceptually of importance in planetary atmospheres; e.g., its reaction with $CH_3$ radicals. The reactions will also be investigated over a wide range of temperature to permit the direct use of the kinetic information in atmospheric models and to permit improved mechanistic understanding, on a molecular level, of this important class of reactions.

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