

## Cometary Implications of Recent Laboratory Experiments on the Photochemistry of the $C_2H$ and $C_3H_2$ Radicals

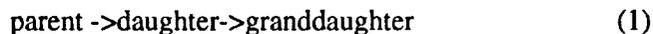
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### Abstract

Recent laboratory results on the photodissociation of the  $C_2H$  and  $C_3H_2$  radicals are described. These studies show that the  $C_2$  and  $C_3$  radicals are produced by the 193 nm photolysis of the  $C_2H$  and  $C_3H_2$  radicals, respectively. The quantum state distributions that were determined for the  $C_2$  radicals put certain constraints on the initial conditions for any models of the observed  $C_2$  cometary spectra. Experimental observations of  $C_2$  formed by the 212.8 nm photolysis of  $C_2H$  are used to calculate a range of photochemical lifetimes for the  $C_2H$  radical.

### Introduction

The formation of  $C_2$  and  $C_3$  in comets has been an intriguing problem in cometary astrophysics [Jackson, 1976]. Numerous laboratory studies suggest that these radicals cannot be produced as a daughter product by photolyzing a parent molecule. Rather, it has been postulated that they are formed as granddaughters via the following reaction scheme [Jackson, 1976]:



Cometary observations of the spatial profiles of  $C_2$  and  $C_3$  radicals have generally supported the idea that these are granddaughter species [Cochran, 1985 and O'Dell, 1988]. Alternate explanations are that these radicals result from ion-molecule reactions in the coma or some type of direct volatilization from grains and the cometary nuclei. These explanations are certainly more complicated than the photochemical formation of granddaughter species. It is important to test this proposed mechanism to determine what limitations must be placed on using it to explain cometary observations. In this paper, we will describe some recent laboratory experiments that do put restrictions on the use of this postulate to explain cometary observations.

### $C_2$

The laser-induced fluorescence (LIF), visible emission, time-resolved Fourier transform infrared emission spectroscopy, and photofragment time-of-flight techniques have all been used to establish that the mechanism for the primary and secondary photolysis of acetylene at 193 nm can be summarized by the following two reactions:



Fletcher and Leone have observed that the  $C_2H$  radical formed in reaction (2) is vibrationally excited with several quanta of energy in the bending mode [Fletcher and Leone, 1989]. Earlier it

had been argued that this must be the case, since the  $C_2H$  radical has enough internal energy such that a 193 nm photon can be used to excite it to the second excited state in the linear configuration, i.e., the  $B^2\Sigma^+$  state [Urdahl, et al., 1988]. Ab-initio theoretical calculations have shown the energies of this and the third excited state decrease when the  $C_2H$  radical bends away from the linear configuration of the ground state [Shih et al., 1979]. The energies of these excited states are still not accurately known, but recent experiments in our laboratory suggest that the  $B^2\Sigma^+$ , which becomes the  $3^2A'$  in the bent configuration, must be at about  $47,200 \pm 700 \text{ cm}^{-1}$  above the ground state. This number was derived from the observation of  $C_2(a^3\Pi_u)$  radicals with the LIF technique when  $C_2H_2$  was photolyzed at 212.8 nm. The error bars arise because the  $C_2H$  radical intermediate could have as many as 2 quanta of vibrational energy in the  $\nu_2$  bending mode. In comets, all of the  $C_2H$  radicals will be in the lowest vibrational and rotational levels of the ground electronic state. Thus one needs to add  $700 \text{ cm}^{-1}$  to the above figure to compensate for the vibrational energy that was present in the laboratory experiments. A correction also needs to be made for the fact that the energy of the  $C_2H$  excited state is higher when it is linear than when it is bent. The ab-initio theoretical calculations suggest that this correction could be as high as  $8100 \text{ cm}^{-1}$  [Shih et al., 1979]. The experimental observations and the theoretical calculations imply that photons with energies between  $47,200$  and  $55,300 \text{ cm}^{-1}$  will be able to dissociate cold  $C_2H$  radicals in comets.

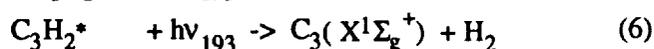
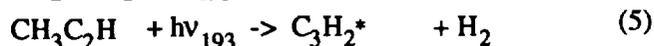
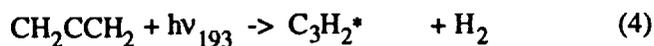
Maximum photochemical lifetimes can be calculated, with a few assumptions, using the above information and the data on the solar flux reported by Heubner and Carpenter, [1979]. First, it is assumed that the absorption cross section for solar radiation can be replaced by an averaged absorption cross section,  $\langle\sigma\rangle$ . This averaged absorption cross section is then combined with the solar radiation for a variety of different absorption bandwidths. The largest absorption bandwidth corresponds to a long wavelength absorption limit of 210.5 nm, while the smallest absorption bandwidth corresponds to an upper wavelength limit of 180.2 nm. Table 1 shows that the estimated photochemical lifetime can vary from 329 s to  $3.8 \times 10^5$  s depending on the absorption coefficient and bandwidth. The absorption bandwidth could be limited further if errors could be put on the ab-initio calculations, however the range of lifetimes are certainly within the range of lifetimes required by cometary observations [Fink et al., 1991].

The  $C_2$  products formed in reaction (3) have been observed to contain electronic, vibrational, and rotational energy. In comets, these radicals will also be excited since they will arise from the same excited electronic state of the  $C_2H$  radical. Once the  $C_2$  radicals are formed in comets, they will emit radiation in the singlet and the triplet manifolds and populate the various vibrational and rotational levels of the  $X^1\Sigma_g^+$  and the  $a^3\Pi_u$  states, respectively [Jackson, et al., 1991]. In the singlet manifold, the laboratory studies have shown that the  $A^1\Pi_u$ ,  $B^1\Delta_g$ , and the  $B^1\Sigma_g^+$  states are produced. Radiation from these excited singlet states could produce at least three different rotational and vibrational distributions in the  $X^1\Sigma_g^+$  state. Similarly, the laboratory

studies have also shown that  $C_2$  is formed in the  $a^3\Pi_u$  and  $b^3\Sigma_g^+$  states, so two distributions of vibrational and rotational levels could be present in the  $C_2$  ( $a^3\Pi_u$ ) in comets. Once the radicals reach their lowest electronic states in the singlet and triplet manifolds, they cannot relax further via infrared emission because the  $C_2$  radical has no permanent electric dipole moment. This argument suggests that the  $C_2$  radical in comets will be formed with two initial vibrational and rotational distributions in the  $a^3\Pi_u$  state, and at least three initial vibrational and rotational distributions in the  $X^1\Sigma_g^+$  state. Modeling of the Swan and the Phillips systems in comets should take into account these initial distributions [Gredel et al., 1989].

### $C_3$

Laboratory studies on allene ( $CH_2CCH_2$ ), and propyne ( $CH_3C_2H$ ), using the photofragment time-of-flight and laser-induced fluorescence techniques have shown that the  $C_3$  radical is produced by the following sequence of photochemical reactions at 193 nm:



LIF spectra taken during the photolysis of allene and propyne at 193 nm show that the rotational distributions of the  $C_3$  ( $X^1\Sigma_g^+$ ) radicals are identical, even though the spectrum obtained using propyne is considerably weaker than it is with allene [Gosine et al., 1991]. Theoretical calculations using RRKM theory suggest that the excited propyne molecules must first isomerize to excited allene before undergoing dissociation. For comets, the importance of this result is that it suggests that the  $C_3H_2$  radical, which is known to be one of the most abundant interstellar molecules, can be photolyzed to form  $C_3$ . It also suggests that the  $C_3H_2$  radical can be produced from a number of different parent molecules.

### Conclusions

Laboratory studies on photochemical sources for the daughter radicals that can dissociate to produce the  $C_2$  and  $C_3$  radicals have revealed certain constraints on their formation in comets. The acetylene studies suggest that an initial bimodal distribution of vibrational and rotational levels should be used in any modeling of the Swan system in comets. Limits have been placed on the energy of the upper electronic state of  $C_2H$  that may be involved in the production of  $C_2$  radicals in comets. A range of photochemical lifetimes have been calculated for the  $C_2H$  radical, and the results are consistent with cometary observations. Any molecule that can dissociate to produce the intermediate daughter radicals  $C_2H$  and  $C_3H_2$  will probably lead to the formation of the  $C_2$  and  $C_3$  cometary radicals.

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**Table 1****Calculated C<sub>2</sub>H Photochemical Lifetime at 1 AU**

Long Wavelength Absorption Edge (nm)	Averaged Absorption Cross Section $\langle\sigma\rangle(\text{cm}^2)$		
	$1 \times 10^{-16}$	$1 \times 10^{-17}$	$1 \times 10^{-18}$
	LIFETIME, $\tau$ , (s)		
210.5	329	3290	32900
200.0	844	8440	84400
190.5	1683	16830	168300
180.2	3786	37860	378600

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