

NOTE

Hydrocarbon Radiation Chemistry in Ices of Cometary Relevance

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Recent discoveries of acetylene, methane, and ethane in Comet Hyakutake, C/1996 B2, have led us to investigate these and other hydrocarbons in irradiated ices of cometary relevance. Laboratory experiments showed that chemical reactions, particularly those involving H atoms, influence the C₂H₆:CH₄ ratio in H₂O + hydrocarbon mixtures. © 1997 Academic Press

Three new cometary molecules, acetylene (C₂H₂), methane (CH₄), and ethane (C₂H₆), have been discovered recently in Comet Hyakutake, C/1996 B2. Acetylene was found by infrared measurements with an abundance relative to H₂O of 100:0.3–0.9 (Brooke *et al.* 1996; see also Tokunaga *et al.* 1996). Ethane also was found by infrared spectroscopy, along with CH₄, by Mumma *et al.* (1996). The C₂H₆ and CH₄ abundances, relative to H₂O, were H₂O:C₂H₆:CH₄ = 100:0.4:0.7, and it was suggested that this surprisingly high abundance of C₂H₆ might be due to H atom addition to acetylene (C₂H₂) on an icy grain mantle, or to solid-phase photolytic or radiation processing (Mumma *et al.* 1996). In this note, we report laboratory experiments relevant to these suggestions. We find that proton irradiation of H₂O + hydrocarbon solid mixtures results in the formation of new molecular products. Our work shows that H atom addition, among other processes, may indeed play a role in understanding cometary hydrocarbon abundances, particularly that of C₂H₆.

Relatively little experimental work on hydrocarbons in ices of cometary relevance has been published. An early study found that 77 K vacuum–UV photolysis of a CH₄ hydrate produced gaseous C₂H₆ on warming (Stief *et al.* 1965). Moore *et al.* (1983) observed C₂H₆ formation in H₂O:NH₃:CH₄ mixtures, but with H₂O far from the dominant matrix material. A recent set of experiments by Gerakines *et al.* (1995) concerned low-temperature photolysis of pure CH₄, and other materials, but not more complex hydrocarbons. Bohn *et al.* (1994) photolyzed hydrocarbons at low temperatures, but since their experiments were aimed toward understanding Triton and Pluto, N₂ was the matrix material, not H₂O. Still other experiments have concentrated on the production of room-temperature residues from hydrocarbons (Khare *et al.* 1989 and Strazzulla *et al.* 1984) or sputtering effects (Pirronello 1991 and Johnson *et al.* 1984). The work we report here differs from all these previous studies by its

emphasis on the chemistry of hydrocarbons in a H₂O-dominated mixture at ~15 K.

Details concerning our laboratory techniques are already in print (Moore *et al.* 1996, Hudson and Moore 1995, and references therein). Briefly, we condensed H₂O-rich gas-phase mixtures onto a cold finger at ~15 K in a vacuum chamber ($P \sim 10^{-8}$ Torr), after which an infrared (IR) spectrum of the solid mixture was recorded. Next, the icy sample was irradiated with a 0.8 MeV proton (p^+) beam from a Van de Graaff accelerator. IR spectra were recorded before and after each irradiation, as well as after various thermal annealings. Molecular abundances were determined by established procedures in which a laser interference system was used to measure ice thickness in a sample of known composition. Thicknesses and the intensities of specific IR bands were combined to calculate integrated absorbance values A in units of “cm molecule⁻¹” for molecules of interest. The paper of Hudgins *et al.* (1993), for example, gives additional experimental and theoretical details. In our radiation experiments, IR intensities (from integrated bands) in cm⁻¹, were divided by the appropriate A value to give column densities in molecules cm⁻². The A values used in this work were $A(\text{CH}_4, 1300 \text{ cm}^{-1}) = 6.63 \times 10^{-18}$ cm molecule⁻¹, $A(\text{C}_2\text{H}_4, 1436 \text{ cm}^{-1}) = 2.93 \times 10^{-18}$ cm molecule⁻¹, and $A(\text{C}_2\text{H}_2, 1956 \text{ cm}^{-1}) = 3.19 \times 10^{-19}$ cm molecule⁻¹. For C₂H₆, $A(1464 \text{ cm}^{-1}) = 4.16 \times 10^{-18}$ cm molecule⁻¹ and $A(2976 \text{ cm}^{-1}) = 1.05 \times 10^{-17}$ cm molecule⁻¹ were used. All of these values were determined for H₂O-dominated mixtures, and a density of 1 g cm⁻³ was assumed throughout.

It is important to appreciate that the incident protons from our Van de Graaff accelerator are the initiators of the chemical changes observed, but that they do not appear in the final products. The 0.8 MeV protons possess sufficient energy to pass through our icy samples (thicknesses of a few micrometers) and into an underlying substrate where they are counted. In passing through the ice, they initiate a series of ionizations and excitations whose net effect, for an H₂O-dominated mixture, is the production of H atoms and hydroxyl (OH) radicals (Spinks and Woods, 1990). It is these H and OH which are responsible for the bulk of the chemistry. Thus, an irradiation can be interpreted either as a simulation of cosmic ray bombardment of an ice or, alternatively, as a convenient way to produce H atoms for the study of their reactions. Note also that our radiation doses are expressed in units of eV absorbed per 18 amu molecule.

Figure 1 summarizes changes to H₂O + CH₄ mixtures after successive irradiations. The formation of C₂H₆ and the decrease of CH₄ are evident

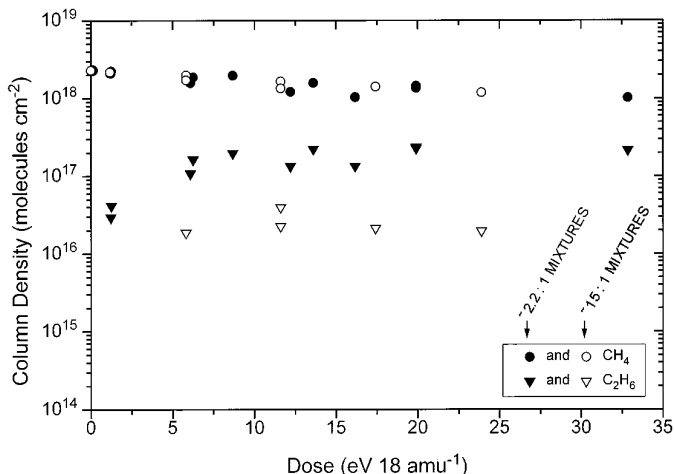
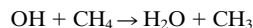
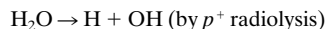


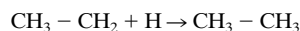
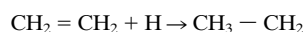
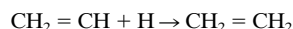
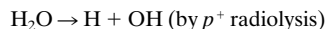
FIG. 1. Changes in CH_4 and C_2H_6 during proton irradiation of $\text{H}_2\text{O} + \text{CH}_4$ mixtures at 15 K. Solid (dark) symbols refer to mixtures initially with $\text{H}_2\text{O}:\text{CH}_4 \approx 2.2:1$ and open (hollow) symbols refer to mixtures initially with $\text{H}_2\text{O}:\text{CH}_4 \approx 15:1$.

from the figure. The final $\text{C}_2\text{H}_6:\text{CH}_4$ ratio was dependent on the initial CH_4 concentration, ranging from $\text{C}_2\text{H}_6:\text{CH}_4 \approx 0.3$, for a mixture initially having $\text{H}_2\text{O}:\text{CH}_4 = 2.2:1$, down to $\text{C}_2\text{H}_6:\text{CH}_4 \approx 0.03$ for a mixture initially having $\text{H}_2\text{O}:\text{CH}_4 = 15:1$. In all cases, the mechanism for C_2H_6 formation probably begins with H atom abstraction from CH_4 , followed by methyl (CH_3) radical dimerization to give C_2H_6 . For example:



Other products identified, some tentatively, include propane (C_3H_8), methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$), CO, CO_2 , acetaldehyde (CH_3COH), and formaldehyde (H_2CO). These will be examined in detail in a future paper. Neither C_2H_2 nor C_2H_4 was detected as a product in these experiments. For comparison purposes we note that our highest radiation dose, $30 \text{ eV molecule}^{-1}$, is far below that predicted for icy grains prior to accretion as cometesimals (Strazzulla and Johnson 1991, Baratta *et al.* 1994).

Figure 2 summarizes changes for the irradiation of $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ mixtures. A decrease in C_2H_2 is shown, along with a rise and fall for C_2H_4 , and a slow rise for C_2H_6 . The interpretation is that H atoms, produced from H_2O by the p^+ beam, react with C_2H_2 in a stepwise manner to form first C_2H_4 and then C_2H_6 :



For a mixture initially with $\text{H}_2\text{O}:\text{C}_2\text{H}_2 = 15:1$, the final $\text{C}_2\text{H}_6:\text{C}_2\text{H}_2$ ratio was about 0.8. Methane was also produced by the irradiation of $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ mixtures, and gave $\text{C}_2\text{H}_6:\text{CH}_4 = 0.8$, starting from a mixture with $\text{H}_2\text{O}:\text{C}_2\text{H}_2 = 15:1$. Starting with $\text{H}_2\text{O}:\text{C}_2\text{H}_2 = 4:1$ gave $\text{C}_2\text{H}_6:\text{C}_2\text{H}_2 =$

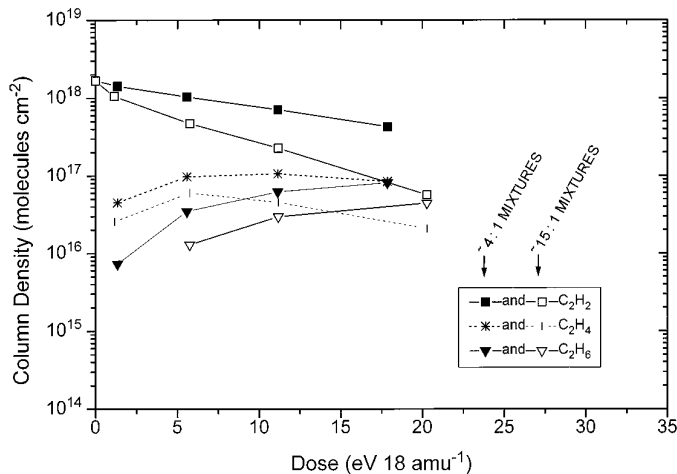


FIG. 2. Changes in C_2H_2 and C_2H_6 during proton irradiation of $\text{H}_2\text{O} + \text{C}_2\text{H}_2$ mixtures at 15 K. Solid (dark) symbols refer to a mixture initially with $\text{H}_2\text{O}:\text{C}_2\text{H}_2 \approx 4:1$ and open (hollow) symbols refer to a mixture initially with $\text{H}_2\text{O}:\text{C}_2\text{H}_2 \approx 15:1$.

0.2 and $\text{C}_2\text{H}_6:\text{CH}_4 = 2$. Other new species identified were CH_3OH , $\text{C}_2\text{H}_5\text{OH}$, CO, CO_2 , CH_3COH , and H_2CO , again some tentatively. A number of other potential products, such as butadiene ($\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$) and diacetylene ($\text{HC} \equiv \text{C} - \text{C} \equiv \text{CH}$), were sought but not found.

Figure 3 summarizes results on a three-component mixture which was initially $\text{H}_2\text{O}:\text{CH}_4:\text{C}_2\text{H}_2 = 10:0.6:1$. Here data are presented for four hydrocarbons, and the sequence $\text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$ is evident. It is also obvious that CH_4 decreases more slowly than C_2H_2 , an observation that might have been expected from the previous two figures. By the highest dose, the ratio $\text{C}_2\text{H}_6:\text{C}_2\text{H}_2$ is 1 and $\text{C}_2\text{H}_6:\text{CH}_4$ has reached 0.2.

The $\text{C}_2\text{H}_6:\text{CH}_4$ ratio found in Comet Hyakutake is about 0.6 (Mumma *et al.* 1996), between the values of 0.03 and 0.8 given above for our binary $\text{H}_2\text{O}:\text{X} = 15:1$ mixtures ($\text{X} = \text{CH}_4$ or C_2H_2) and reasonably close to the value of 0.2 from our three-component mixture. The $\text{C}_2\text{H}_6:\text{C}_2\text{H}_2$

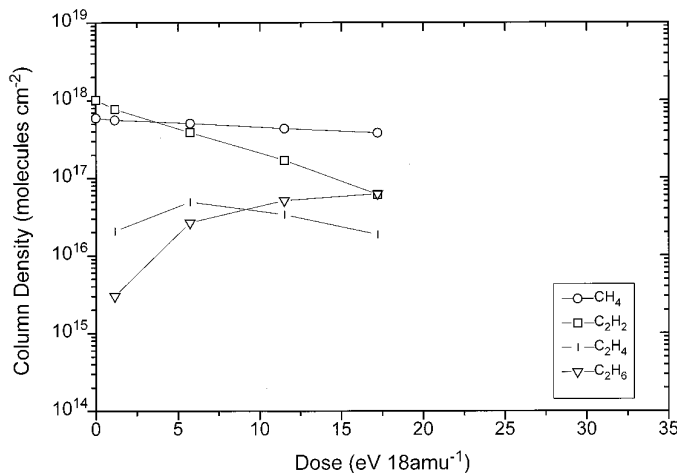
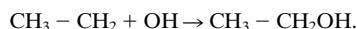
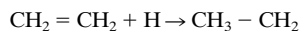
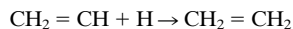
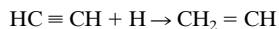
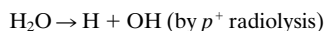


FIG. 3. Changes in CH_4 , C_2H_2 , C_2H_4 , and C_2H_6 during proton irradiation of a $\text{H}_2\text{O} + \text{CH}_4 + \text{C}_2\text{H}_2$ mixture at 15 K. The initial proportions were $\text{H}_2\text{O}:\text{CH}_4:\text{C}_2\text{H}_2 = 10:0.6:1$.

ratio in Comet Hyakutake is 0.5–1.3, which brackets the values of 0.8 and 1.0 in our experiments. The roles of CH₄ and C₂H₂ in forming C₂H₆ are under investigation and it seems likely that a laboratory mixture that closely matches the Hyakutake observations may be developed.

To summarize, we have presented experimental evidence for radiation-chemical reactions which could alter the abundances of CH₄, C₂H₆, and C₂H₂ in comets, specifically reactions which can produce C₂H₆ at the expense of CH₄ and C₂H₂. These experiments, and additional ones performed with H₂O + CH₄ + C₂H₂ + CO and H₂O + C₂H₄ mixtures, demonstrated that C₂H₆ is synthesized at ~15 K during the irradiation of solid-phase mixtures containing H₂O and simple hydrocarbons. These laboratory results support the suggestion (Mumma *et al.* 1996) that solid-phase chemistry can contribute to cometary C₂H₆. Our experiments offer no evidence that irradiation of solid H₂O + CH₄ mixtures produces C₂H₂.

Our experiments are not only helpful in interpreting past observations, they suggest new work for the future. For example, we have observed ethanol (C₂H₅OH) synthesis in many experiments, sometimes in reasonably high abundance. Specifically, irradiation of either an H₂O:C₂H₂ = 15:1 mixture or an H₂O:CH₄:C₂H₂ = 10:0.6:1 mixture produced comparable amounts of C₂H₅OH and methanol (CH₃OH). About 5 × 10¹⁶ molecules cm⁻¹ of each alcohol was formed in each experiment. Since OH radicals are produced during the irradiation of H₂O, it is entirely reasonable to expect that the addition product of three H atoms and one OH radical to C₂H₂ might be observed, namely ethanol:



Although ethanol and methanol are known interstellar molecules, only methanol has been detected in comets (Mumma *et al.* 1993). If, in a cometary or interstellar ice, OH exists in the presence of C₂H₂, then the synthesis of ethanol appears likely. Based on our experiments, C₂H₅OH is a good candidate to include in searches for new cometary molecules.

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