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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 $C_2H_6:CH_4$ ratio in H_2O + hydrocarbon mixtures. © 1997 Academic Press

Three new cometary molecules, acetylene (C_2H_2), methane (CH_4), and ethane (C_2H_6), have been discovered recently in Comet Hyakutake, C/1996 B2. Acetylene was found by infrared measurements with an abundance relative to H_2O 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 CH_4, by Mumma *et al.* (1996). The C_2H_6 and CH_4 abundances, relative to H_2O, were $H_2O:C_2H_6:CH_4 = 100:0.4:0.7$, and it was suggested that this surprisingly high abundance of C_2H_6 might be due to H atom addition to acetylene (C_2H_2) 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 H_2O + 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 C_2H_6.

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 CH_4 hydrate produced gaseous C_2H_6 on warming (Stief *et al.* 1965). Moore *et al.* (1983) observed C_2H_6 formation in $H_2O:NH_3:CH_4$ mixtures, but with H_2O far from the dominant matrix material. A recent set of experiments by Gerakines *et al.* (1995) concerned low-temperature photolysis of pure CH_4, 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, N_2 was the matrix material, not H_2O. 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 H_2O-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 H_2O-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 $A(CH_4, 1300\ cm^{-1}) = 6.63 \times 10^{-18}$ cm molecule^{-1}, $A(C_2H_4, 1436\ cm^{-1}) = 2.93 \times 10^{-18}$ cm molecule^{-1}, and $A(C_2H_2, 1956\ cm^{-1}) = 3.19 \times 10^{-19}$ cm molecule^{-1}. For C_2H_6, $A(1464\ cm^{-1}) = 4.16 \times 10^{-18}$ cm molecule^{-1} and $A(2976\ cm^{-1}) = 1.05 \times 10^{-17}$ cm molecule^{-1} were used. All of these values were determined for H_2O-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 H_2O-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 $H_2O + CH_4$ mixtures after successive irradiations. The formation of C_2H_6 and the decrease of CH_4 are evident

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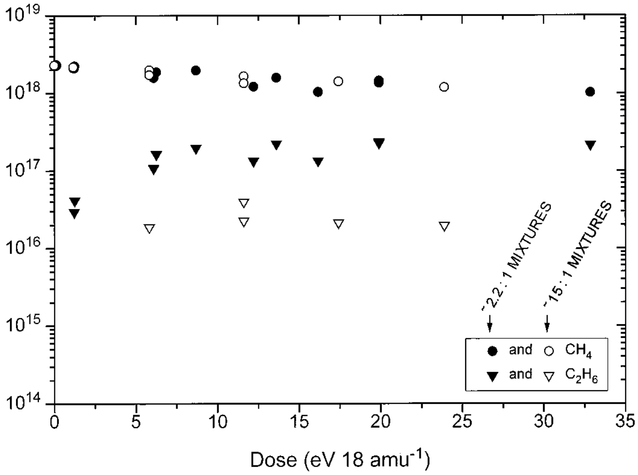

FIG. 1. Changes in CH_4 and C_2H_6 during proton irradiation of $H_2O + CH_4$ mixtures at 15 K. Solid (dark) symbols refer to mixtures initially with $H_2O:CH_4 \approx 2.2:1$ and open (hollow) symbols refer to mixtures initially with $H_2O:CH_4 \approx 15:1$.

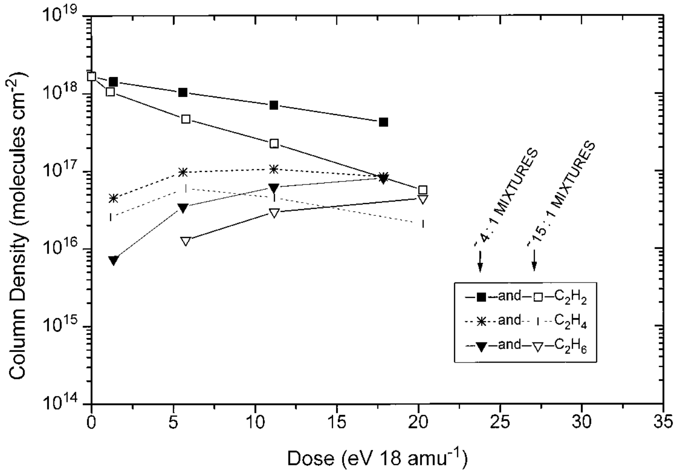

FIG. 2. Changes in C_2H_2 and C_2H_6 during proton irradiation of $H_2O + C_2H_2$ mixtures at 15 K. Solid (dark) symbols refer to a mixture initially with $H_2O:C_2H_2 \approx 4:1$ and open (hollow) symbols refer to a mixture initially with $H_2O:C_2H_2 \approx 15:1$.

from the figure. The final $C_2H_6:CH_4$ ratio was dependent on the initial CH_4 concentration, ranging from $C_2H_6:CH_4 \approx 0.3$, for a mixture initially having $H_2O:CH_4 = 2.2:1$, down to $C_2H_6:CH_4 \approx 0.03$ for a mixture initially having $H_2O:CH_4 = 15:1$. 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:

$$H_2O \rightarrow H + OH \text{ (by } p^+ \text{ radiolysis)}$$

$$OH + CH_4 \rightarrow H_2O + CH_3$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$

Other products identified, some tentatively, include propane (C_3H_8), methanol (CH_3OH), ethanol (C_2H_5OH), 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 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 $H_2O + C_2H_2$ 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:

$$H_2O \rightarrow H + OH \text{ (by } p^+ \text{ radiolysis)}$$

$$HC \equiv CH + H \rightarrow CH_2 = CH$$

$$CH_2 = CH + H \rightarrow CH_2 = CH_2$$

$$CH_2 = CH_2 + H \rightarrow CH_3 - CH_2$$

$$CH_3 - CH_2 + H \rightarrow CH_3 - CH_3$$

For a mixture initially with $H_2O:C_2H_2 = 15:1$, the final $C_2H_6:C_2H_2$ ratio was about 0.8. Methane also was produced by the irradiation of $H_2O + C_2H_2$ mixtures, and gave $C_2H_6:CH_4 = 0.8$, starting from a mixture with $H_2O:C_2H_2 = 15:1$. Starting with $H_2O:C_2H_2 = 4:1$ gave $C_2H_6:C_2H_2 = 0.2$ and $C_2H_6:CH_4 = 2$. Other new species identified were CH_3OH, C_2H_5OH, CO, CO_2, CH_3COH, and H_2CO, again some tentatively. A number of other potential products, such as butadiene ($CH_2 = CH - CH = CH_2$) and diacetylene ($HC \equiv C - C \equiv CH$), were sought but not found.

Figure 3 summarizes results on a three-component mixture which was initially $H_2O:CH_4:C_2H_2 = 10:0.6:1$. Here data are presented for four hydrocarbons, and the sequence $C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$ 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 $C_2H_6:C_2H_2$ is 1 and $C_2H_6:CH_4$ has reached 0.2.

The $C_2H_6:CH_4$ 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 $H_2O:X = 15:1$ mixtures ($X = CH_4$ or C_2H_2) and reasonably close to the value of 0.2 from our three-component mixture. The $C_2H_6:C_2H_2$

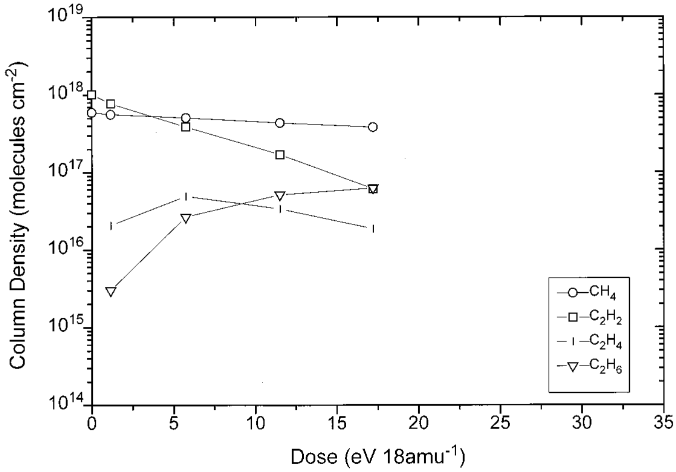

FIG. 3. Changes in CH_4, C_2H_2, C_2H_4, and C_2H_6 during proton irradiation of a $H_2O + CH_4 + C_2H_2$ mixture at 15 K. The initial proportions were $H_2O:CH_4:C_2H_2 = 10:0.6:1$.

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 CH_4 and C_2H_2 in forming C_2H_6 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 CH_4, C_2H_6, and C_2H_2 in comets, specifically reactions which can produce C_2H_6 at the expense of CH_4 and C_2H_2. These experiments, and additional ones performed with $H_2O + CH_4 + C_2H_2 + CO$ and $H_2O + C_2H_4$ mixtures, demonstrated that C_2H_6 is synthesized at ~15 K during the irradiation of solid-phase mixtures containing H_2O and simple hydrocarbons. These laboratory results support the suggestion (Mumma *et al.* 1996) that solid-phase chemistry can contribute to cometary C_2H_6. Our experiments offer no evidence that irradiation of solid $H_2O + CH_4$ mixtures produces C_2H_2.

Our experiments are not only helpful in interpreting past observations, they suggest new work for the future. For example, we have observed ethanol (C_2H_5OH) synthesis in many experiments, sometimes in reasonably high abundance. Specifically, irradiation of either an $H_2O:C_2H_2 = 15:1$ mixture or an $H_2O:CH_4:C_2H_2 = 10:0.6:1$ mixture produced comparable amounts of C_2H_5OH and methanol (CH_3OH). About 5×10^{16} molecules cm^{-1} of each alcohol was formed in each experiment. Since OH radicals are produced during the irradiation of H_2O, it is entirely reasonable to expect that the addition product of three H atoms and one OH radical to C_2H_2 might be observed, namely ethanol:

$$H_2O \rightarrow H + OH \text{ (by } p^+ \text{ radiolysis)}$$

$$HC \equiv CH + H \rightarrow CH_2 = CH$$

$$CH_2 = CH + H \rightarrow CH_2 = CH_2$$

$$CH_2 = CH_2 + H \rightarrow CH_3 - CH_2$$

$$CH_3 - CH_2 + OH \rightarrow CH_3 - CH_2OH.$$

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 C_2H_2, then the synthesis of ethanol appears likely. Based on our experiments, C_2H_5OH is a good candidate to include in searches for new cometary molecules.

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