

THE FORMATION OF ACETIC ACID (CH₃COOH) IN INTERSTELLAR ICE ANALOGS

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ABSTRACT

Binary ice mixtures of methane (CH₄) and carbon dioxide (CO₂) ices were irradiated at 12 K with energetic electrons to mimic the energy transfer processes that occur in the track of the trajectories of MeV cosmic-ray particles. The formation of trans-acetic acid (CH₃COOH) was established through the appearance of new bands in the infrared spectrum at 1780, 1195, 1160, 1051, and 957 cm⁻¹; two dimeric forms of acetic acid were assigned via absorptions at 1757 and 1723 cm⁻¹. During warm-up of the ice sample, the mass spectrometer recorded peaks of *m/z* values of 60 and 45 associated with the C₂H₄O₂⁺ and COOH⁺ molecular ion and fragment, respectively. The kinetic fits of the column densities of the acetic acid molecule suggest that the initial step of the formation process appears to be the cleavage of a carbon-hydrogen bond from methane to generate the methyl radical plus atomic hydrogen. The hydrogen atom holds excess kinetic energy allowing it to overcome entrance barriers required to add to a carbon dioxide molecule, generating the carboxyl radical (HOCO). This radical can recombine with the methyl radical to form acetic acid molecule. Similar processes are expected to form acetic acid in the interstellar medium, thus providing alternatives to gas-phase processes for the generation of complex chemical species whose fractional abundances compared to molecular hydrogen of typically a few × 10⁻⁹ cannot be accounted for by solely gas-phase chemistry.

Subject headings: cosmic rays — ISM: molecules — methods: laboratory — molecular processes — planets and satellites: general

1. INTRODUCTION

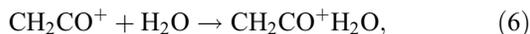
During the last few years, the search for astrobiologically important molecules such as acetic acid (CH₃COOH) and their structural isomers glycol aldehyde (HCOCH₂OH) and methyl formate (HCOOCH₃) in the interstellar medium received particular attention. The acetic acid molecule was first identified in the interstellar medium by Mehringer et al. (1997) toward the star-forming region Sgr B2 (N-LMH). Subsequently, it has also been identified in a variety of hot molecular cores (Remijan et al. 2002, 2003, 2004; Cazaux et al. 2003) and more recently toward the proto-planetary nebula CRL 618 (Remijan et al. 2005). Various gas-phase synthetic routes have been suggested to form this molecule. Huntress & Mitchell (1979) proposed a radiative association mechanism via reaction (1) followed by a dissociative recombination with an electron (eq. [2]),



Ehrenfreund & Charnley (2000) implied that protonated methanol can transfer an alkyl cation to formic acid (reaction [3]) followed by a dissociative recombination via reaction (4),



Furthermore, Blagojevic et al. (2003) recently suggested a multi-step reaction sequence via reactions (5)–(8),



However, there are several factors which indicate that gas-phase reactions alone cannot be responsible for the formation of acetic acid in these environments, suggesting that synthetic routes to acetic acid are also linked to interstellar ices. (1) Models based on gas-phase chemistry predict, for example for Sgr B2, fractional abundances of 2×10^{-11} and 3×10^{-12} compared to the observed value of $(0.8\text{--}6) \times 10^{-10}$ (Wlodarczak & Demaison 1988; Wootten et al. 1992; Remijan et al. 2002). (2) The rotational temperature of acetic acid is found to be over 100 K, consistent with sublimation from icy grains (Hasegawa et al. 1992; Remijan et al. 2002). (3) The velocity of acetic acid is found to be similar to that of other complex species thought to be formed within icy grains including propanenitrile, CH₃CH₂CN, the 2-cyanoethyl radical, CH₂CHCN, and methyl formate, HCOOCH₃ (Miao et al. 1995; Mehringer et al. 1997; Remijan et al. 2002). We would like to note that acetic acid is also thought to be present within comets, whereby an upper limit of 0.06% was recently proposed for comet C/1996 O1 (Hale-Bopp), as well as in the Murchison meteorite (Crovisier et al. 2004; Huang et al. 2005). Comets are thought to preserve the “pristine” interstellar material from which our solar system was formed and are often regarded as a source for prebiotic molecules to reach the Earth (Chyba & Sagan 1992; Ehrenfreund et al. 2004). If acetic acid was delivered to the Earth, it might be considered to be an important molecule on prebiotic Earth (Brack 1999; Huber & Wächtershäuser 1998). However, despite the importance of acetic acid in astrobiology, conclusive routes to form this molecule have not been resolved so far. In this paper, we present possible pathways for synthesizing acetic acid in interstellar ices containing carbon dioxide and methane. Logically, we would expect the formation of acetic acid within this ice mixture based on previous laboratory work conducted; (1) Bennett et al. (2005) irradiated ice mixtures of carbon monoxide (CO) and methane (CH₄), which were found to produce the methyl (CH₃) and formyl (HCO) radicals, which then recombined to produce

TABLE 1
INFRARED ABSORPTIONS OF THE METHANE AND CARBON DIOXIDE FROST
ALONG WITH THE ASSIGNMENTS OF THE OBSERVED BANDS

Band Position (cm^{-1})	Assignment	Characterization
4531.....	$\nu_2 + \nu_3$ CH ₄	Combination
4301, 4298.....	$\nu_3 + \nu_4$ CH ₄	Combination
4211, 4201.....	$\nu_1 + \nu_4$ CH ₄	Combination
3845.....	$3\nu_4$ CH ₄	Overtone
3701.....	$\nu_1 + \nu_3$ CO ₂	Combination
3595.....	$2\nu_2 + \nu_3$ CO ₂	Combination
3007, 3005.....	ν_3 CH ₄	Fundamental
2904.....	ν_1 CH ₄	Fundamental
2814.....	$\nu_2 + \nu_4$ CH ₄	Combination
2593.....	$2\nu_4$ CH ₄	Overtone
2335.....	ν_3 CO ₂	Fundamental
2276.....	ν_3 (¹³ CO ₂)	Isotope peak
1530.....	ν_2 CH ₄	Fundamental
1382.....	ν_1 CO ₂	Fundamental
1309, 1304, 1298, 1295, 1277.....	ν_4 CH ₄	Fundamental
667, 664, 659.....	ν_2 CO ₂	Fundamental
640.....	ν_2 (¹³ CO ₂)	Isotope peak

NOTE.—See references within Bennett et al. (2004; 2006) for more details.

acetaldehyde (CH₃CHO), and (2) Holtom et al. (2005) found the irradiation of ice mixtures containing carbon dioxide (CO₂) and methylamine (CH₃NH₂) were found to produce the carboxyl (HOCO) and aminomethyl (CH₂NH₂) radicals, which could recombine to form glycine (NH₂CH₂COOH).

2. EXPERIMENTAL

The experiments were carried out in a contamination-free ultra high vacuum stainless steel chamber (Bennett et al. 2004). This vessel is evacuated down to a base pressure of typically 5×10^{-11} torr using oil-free magnetically suspended turbomolecular pumps. A closed-cycle helium refrigerator cools a highly polished silver (111) monocrystal to 11.7 ± 0.3 K; the latter is held in the center of the chamber and is freely rotatable in the plane. A binary methane—carbon dioxide ice was prepared in a gas mixing chamber containing 385 mbar of methane (99.999%; Specialty Gas Group) and 127 mbar of carbon dioxide (99.999%; BOC Gases), which was then deposited through a glass capillary array held 5 mm from the silver target for 5 minutes at a background pressure in the main chamber of 10^{-7} torr. A Nicolet 510 DX Fourier transform infrared spectrometer is operated in an absorption-reflection-absorption mode (reflection angle $\alpha = 75^\circ$) and monitors the chemical changes during the irradiation of the solid sample. A quadrupole mass spectrometer (Balzer QMG 420) operating in residual-gas analyzer mode with the electron impact ionization energy at 90 eV allows us to detect any species in the gas phase during the experiment.

The column density of our sample (in molecules cm^{-2}) can be calculated via a modified Lambert-Beers relationship (Bennett et al. 2004). The column density of carbon dioxide was derived from the $\nu_1 + \nu_3$ combination band at 3701 cm^{-1} , the $2\nu_2 + \nu_3$ combination band at 3595 cm^{-1} , and the ν_3 band from the ¹³C isotope at 2277 cm^{-1} using absorption coefficients taken from Gerakines et al. (1995). The average derived column density was found to be $(2.96 \pm 1.94) \times 10^{17}$ molecules cm^{-2} . For methane, the column density was derived from the $\nu_3 + \nu_4$ combination band at 4299 cm^{-1} , the $\nu_1 + \nu_4$ combination band at 4201 cm^{-1} , and the $\nu_2 + \nu_4$ combination band at 2814 cm^{-1} , applying absorption coefficients taken from Gerakines et al. (2005). The

average derived column density was found to be $(7.40 \pm 1.80) \times 10^{16}$ molecules cm^{-2} . Therefore, the ratio of carbon dioxide to methane is approximately 4 : 1. Taking the densities of methane and carbon dioxide as 0.53 and 1.6 g cm^{-3} , respectively, the total thickness of the sample was found to be $172 \pm 51 \text{ nm}$ (Wyckoff 1965; Donnay & Ondik 1972). Table 1 shows the compilation of peaks identified from a typical infrared spectrum of the binary mixture of methane and carbon dioxide at 11.7 K .

The methane—carbon dioxide samples were irradiated isothermally at $11.7 \pm 0.3 \text{ K}$ with 5 keV electrons generated with an electron gun (Specs EQ 22/35) at beam currents of 100 nA for 1 hr by scanning the electron beam over an area of $3.0 \pm 0.4 \text{ cm}^2$. In theory this would mean during the irradiation the sample would be exposed to a total of 2.2×10^{15} electrons (7.5×10^{14} electrons cm^{-2}); however, not all of the electrons generated by our electron gun actually reach the target; the manufacturer states an extraction efficiency of 78.8% , meaning the actual number of electrons which hit the sample is reduced to 1.8×10^{15} electrons (5.9×10^{14} electrons cm^{-2}). After the irradiation is complete, the sample is then left isothermally for 1 hr , before being heated to 300 K at a rate of $0.5 \text{ K minute}^{-1}$.

3. RESULTS

3.1. Infrared Band Assignment

Table 2 summarizes the peak positions of the products identified after the condensed ice was subjected to irradiation from 5 keV electrons at $0.1 \mu\text{A}$ for 1 hr . Also listed are the products identified previously in the irradiation experiments of pure methane and carbon dioxide ices. Note that in regards to the characterizations of new species in this report we only focus on species pertinent to the formation of acetic acid within our ice matrix. The methyl radical, CH₃(X^2A_2''), was identified via its ν_2 (out-of-plane bending) absorption mode at 614 cm^{-1} (Fig. 1a), in good agreement with our previous identification of this radical in pure methane ices at 608 cm^{-1} (Bennett et al. 2006). In addition, we were also able to assign the peak at 3149 cm^{-1} as the ν_3 (CH stretching) mode of this species, previously found to absorb at 3150 cm^{-1} . The carboxyl radical, HOCO(X^2A'), was detected through its ν_2 (CO stretching) absorptions at 1847 and 1839 cm^{-1} (Fig. 1b); this is consistent with two different matrix sites of the trans isomer, which has previously been identified at 1846 cm^{-1} in an argon matrix (Jacox 1988), and at 1833 cm^{-1} in a carbon monoxide matrix (Milligan & Jacox 1971). The peak at 3632 cm^{-1} was found to correspond to the ν_1 (OH stretching) absorption identified at 3628 cm^{-1} within an argon matrix (Forney et al. 2003). The cis structure could not be positively identified.

The trans conformer of the acetic acid monomer was found via its ν_4 (CO stretch) at 1780 cm^{-1} , ν_8 (CHO rocking) at 1195 as well as 1160 cm^{-1} , ν_{15} (CH₃ rocking) at 1051 cm^{-1} , and the ν_9 (CH₃ rocking) mode at 957 cm^{-1} (Fig. 1c and 1d). These values compare nicely with previous matrix isolation studies of the trans conformer of monomeric acetic acid in argon. Absorptions appeared at 1779 , 1180 , 1151 , 1047 , and 986 cm^{-1} , respectively (Maçõas et al. 2004). Although the cis conformer of acetic acid could not be unambiguously assigned, several absorptions indicated the presence of two dimeric forms of acetic acid, which have been recently characterized by Sander & Ganterberg (2005). The structures of these dimers are shown in Figure 2 (Sander & Ganterberg 2005). The less stable structure A (C_s symmetry) was found to absorb at 1757 cm^{-1} , compared to the value of 1761 cm^{-1} in an argon matrix. The more stable isomer B (C_{2h} symmetry) absorbed at 1723 cm^{-1} in

TABLE 2
OBSERVED PEAK POSITIONS, ASSIGNMENTS, AND CHARACTERIZATIONS AFTER 1 hr
OF IRRADIATION VIA 5 keV ELECTRONS AT 0.1 μ A

Band Position (cm^{-1})	Literature Band Position (cm^{-1})	Assignment	Characterization
Bands Common to Irradiation of Pure Methane ^a			
614.....	608	ν_2 CH ₃	Out-of-plane
3149.....	3150	ν_3 CH ₃	CH stretching
2961.....	2961	ν_1 C ₂ H ₆	CH ₃ sym. str.
2883.....	2883	ν_5 C ₂ H ₆	CH ₃ sym. str.
1373.....	1373	ν_6 C ₂ H ₆	CH ₃ sym. def.
2975.....	2975	ν_{10} C ₂ H ₆	CH ₃ deg. str.
1464.....	1464	ν_{11} C ₂ H ₆	CH ₃ d- deform
821.....	822	ν_{12} C ₂ H ₆	CH ₃ rock
956.....	951	ν_7 C ₂ H ₄	CH ₂ wag
1438.....	1435	ν_{12} C ₂ H ₄	CH ₂ scissor
3093.....	3095	ν_9 C ₂ H ₄	CH ₂ asym. str.
3260.....	3267	ν_3 C ₂ H ₂	CH stretch
Bands Common to Irradiation of Pure Carbon Dioxide ^b			
2139.....	2139	ν_1 CO	CO stretch
Bands Unique to this Experiment			
3632.....	3628 ^c	ν_1 t-HOCO	OH stretch
1853.....	1861 ^d	ν_3 HCO	CO stretch
1847.....	1846 ^c	ν_2 t-HOCO	CO stretch
1839.....	1833 ^d	ν_2 t-HOCO	CO stretch
1780.....	1779 ^e	ν_4 t-CH ₃ COOH (M)	CO stretch
1757.....	1761 ^f	ν_4 t-CH ₃ COOH (A)	CO stretch
1723.....	1721 ^f	ν_4 t-CH ₃ COOH (B)	CO stretch
1717 br.....	1715, 1742 ^g	ν_2 H ₂ CO	CO stretch
	1731 ^h	ν_4 CH ₃ CHO	CO stretch
		R(R')C=O	CO stretch
1498.....	1494, 1498 ^g	H ₂ CO	CH ₂ scissoring
1350.....	1354 ^h	ν_7 CH ₃ CHO	CH ₃ deformation
1195.....	1180 ^e , 1184 ^h	ν_8 t-CH ₃ COOH	CHO rocking
1160.....	1151 ^e	ν_8 t-CH ₃ COOH	CHO rocking
1092.....	1091 ^d	ν_2 HCO	HCO bending
		R-O-R'	CO stretch
1076.....	1065 ^e , 1077 ^d	ν_4 t-HOCO	CO stretch
1051.....	1047 ^e	ν_{15} t-CH ₃ COOH	CH ₃ rocking
1041, 1021.....	1034 ⁱ	ν_{15} CH ₃ OH	CO stretch
957.....	986 ^e	ν_9 t-CH ₃ COOH	CH ₃ rocking

The band positions of the identified species are compared to our previous studies or those found in the literature. (M): monomer, (A): C_s dimer, (B): C_{2h} dimer.

^a Literature values taken from Bennett et al. (2006) and references within.

^b Literature values taken from Bennett et al. (2004) and references within.

^c Value from Forney et al. (2003).

^d Value from Milligan & Jacox (1971).

^e Value from Maçôas et al. (2004).

^f Value from Sander & Ganterberg (2005).

^g Value from Harvey & Ogilvie (1962).

^h Value from Hawkins & Andrews (1983).

ⁱ Value from Han & Kim (1996).

comparison with a value of 1721 cm^{-1} in the argon matrix (Fig. 1c; Sander & Ganterberg 2005)

3.2. Mass Spectrometry

The only signal observed via mass spectrometric analysis of the gas phase during irradiation of the sample was found at $m/z = 2$, i.e., molecular hydrogen, similar to the electron exposure of pure methane ices (Bennett et al. 2006). As the sample was warmed to 160 K, signals appeared at $m/z = 45$ and 60. This corresponds to the ions C₂H₄O₂⁺ and to the COOH⁺

molecular ion; the latter generated via dissociative ionization of acetic acid. At around 220 K, the signal could also be monitored at $m/z = 74$ as well as $m/e = 45$. These could indicate the presence of propionic acid (C₂H₅COOH) and its COOH⁺ fragment.

4. DISCUSSION

Having identified the acetic acid molecule in electron-irradiated methane-carbon dioxide ices, we would now like to kinetically fit the temporal evolution of the observed column densities of acetic acid and its precursor molecules during the irradiation of

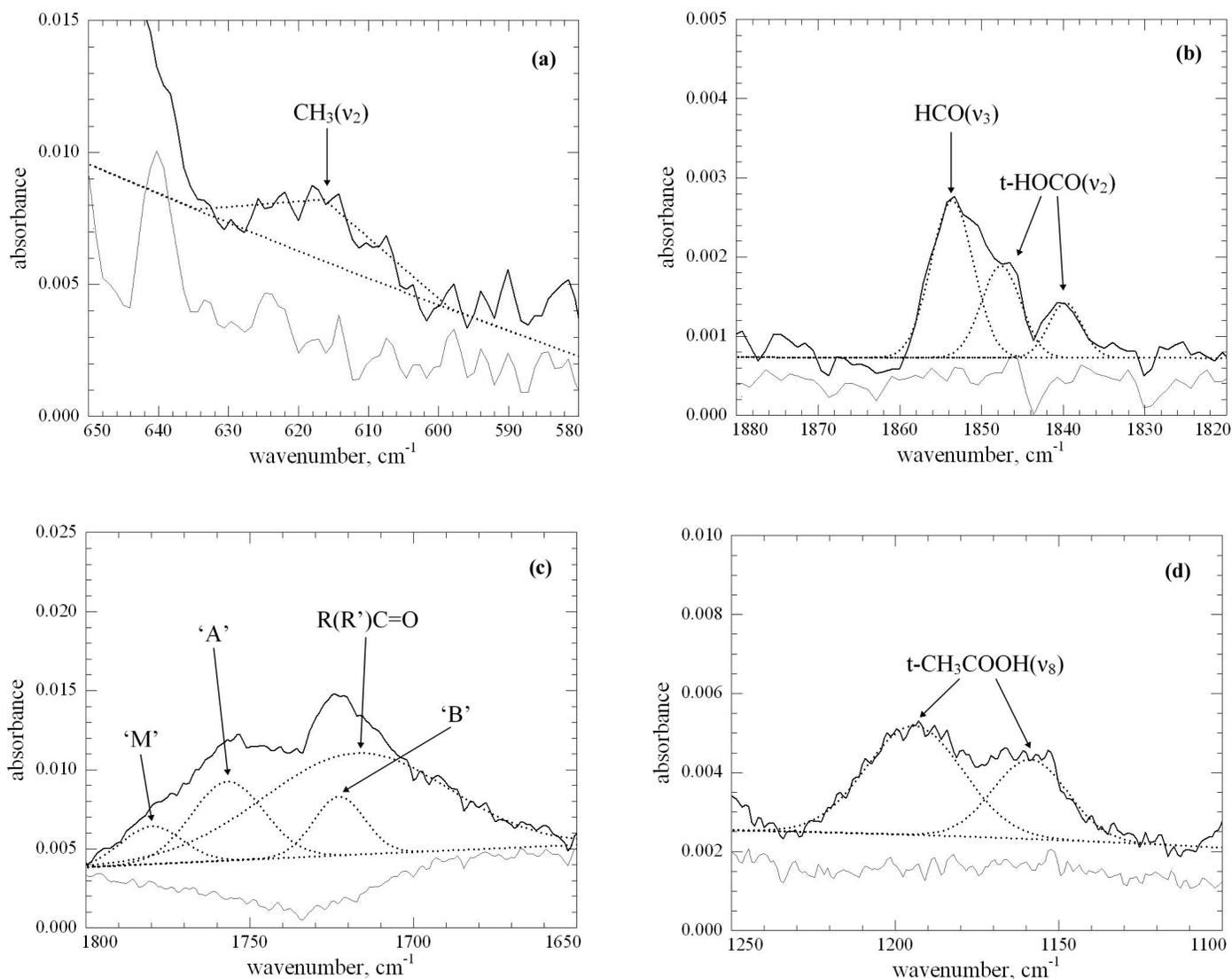
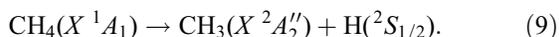


FIG. 1.—New infrared features relevant to the formation of acetic acid in the $\text{CO}_2 : \text{CH}_4$ frost after 1 hr of irradiation with 5 keV electrons at 100 nA (solid black line) as well as to how the infrared spectrum of the ice prior to irradiation (thin gray line). (a) ν_2 (out-of-plane bend) of the methyl radical at 614 cm^{-1} . (b) ν_2 (CO stretching) mode of the transcarboxyl radical at 1847 and 1839 cm^{-1} along with the ν_3 (CO stretching) mode of the formyl radical. (c) ν_4 (CO stretch) of trans acetic acid in monomeric, M, and dimeric forms A and B (shown in Fig. 2) along with a broad peak arising from $R(R')\text{C}=\text{O}$ stretches (where R and R' represent any other functional group). (d) Absorptions from the ν_8 (CHO rocking) mode of trans acetic acid. Gaussian fits on a linear baseline have been overlaid to aid the eye.

our sample. The proposed reaction scheme is summarized in Figure 3. Our results suggest that the initial step in the formation of acetic acid is the unimolecular decomposition of the methane molecule via cleavage of a carbon-hydrogen bond to generate a methyl radical and a hydrogen atom (reaction [9]),



This reaction is found to be endoergic by 439 kJ mol^{-1} (4.5 eV). Considering a unimolecular decomposition of methane and

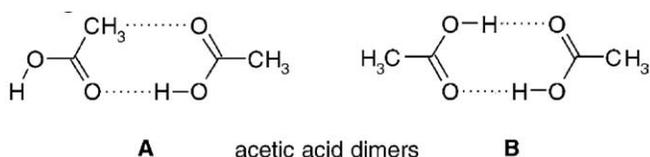


FIG. 2.—Chemical structures of the acetic acid dimers A (C_5) and B (C_{2h}) from Sander & Ganterberg (2005).

hence a first-order decay, the temporal profile of the methyl radical could be fit using a first-order rate law as follows,

$$[\text{CH}_3]_t = a(1 - e^{-k_1 t}). \quad (10)$$

The temporal evolution of the column density of the methyl radical was determined from the ν_2 (out-of-plane bending) absorption mode at 614 cm^{-1} using a calculated A value of $1.39 \times 10^{-17} \text{ cm molecule}^{-1}$ (Bennett et al. 2005). This yielded a rate constant of $k_1 = 2.85 \pm 0.67 \times 10^{-3} \text{ s}^{-1}$ and a value of

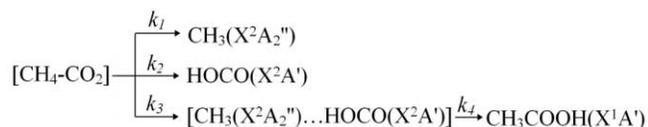
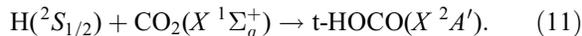
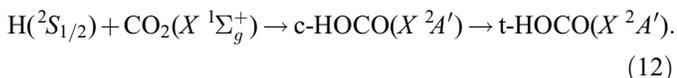


FIG. 3.—Reaction scheme used to fit the column densities of the methyl radical, carboxyl radical, and acetic acid observed during the irradiation.

$(4.34 \pm 0.17) \times 10^{14}$ molecules cm^{-2} for a (Fig. 4a). Note that this process also releases energetic hydrogen atoms. The hydrogen atoms hold an excess energy of a few electron volts (Bennett et al. 2006); these suprathermal hydrogen atoms can add to the carbon-oxygen double bond of the carbon dioxide molecule forming a trans-carboxyl radical,



Calculations at the MRCISD+Q/cc-pVTZ level of theory by Song et al. (2006) indicated that reaction (11) is exoergic by 21.7 kJ mol^{-1} (0.22 eV); however, it first must pass through the cis conformer as an intermediate in a process which is exoergic by 14.3 kJ mol^{-1} (0.15 eV). Both processes involve entrance barriers which must be overcome; the barrier to form the cis conformer was found to be $106.1 \text{ kJ mol}^{-1}$ (1.1 eV), and the barrier to the trans conformer was suggested to be 31.6 kJ mol^{-1} (0.33 eV). This indicates that the actual pathway follows a two-step sequence via reaction (12),



As we were unable in the present studies to isolate the cis conformer, our data suggest that either the cis conformer is too short-lived to be observed spectroscopically in our experiments or that a direct pathway to the trans conformer involving non-equilibrium chemistry is possible, despite the arguments that this transition state may be inaccessible (Song et al. 2006). The authors indicate that even if this pathway exists, a barrier of the same order (i.e., around 1.1 eV) would still need to be overcome, in order to form the carboxyl radical. This energy is supplied by the excess kinetic energy of the hydrogen atom produced from reaction (9). In the kinetic model we propose that the rate of formation of the carboxyl radical should be related to the suprathermal hydrogen atoms via a pseudo-first-order rate law involving an initial methane-carbon dioxide complex (Fig. 3),

$$[\text{t-HOCO}]_t = b(1 - e^{-k_2 t}). \quad (13)$$

For the carboxyl radical, we used the ν_2 (CO stretching) absorptions at 1847 and 1839 cm^{-1} to determine the temporal evolution of the column density, using an A value of $3.60 \times 10^{-17} \text{ cm molecule}^{-1}$ (Bennett et al. 2007; unpublished data). We use the approximation $e^x \approx 1 + x$ to derive equation (14). Our fitting procedure gives values of $bk_2 = 2.35 \pm 0.08 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$ (Fig. 4b),

$$[\text{t-HOCO}]_t \approx bk_2 t. \quad (14)$$

If both the methyl radical, $\text{CH}_3(X^2A'_2)$, and the carboxyl radical, $\text{HOCO}(X^2A')$, are generated inside the former matrix cage and also hold the correct geometry, then they can recombine without barrier to form acetic acid via reaction (15). If the recombination geometry is not reached or if the radicals are not generated in close proximity, then they remain isolated in the methane-carbon dioxide ice and do not recombine to form acetic acid,

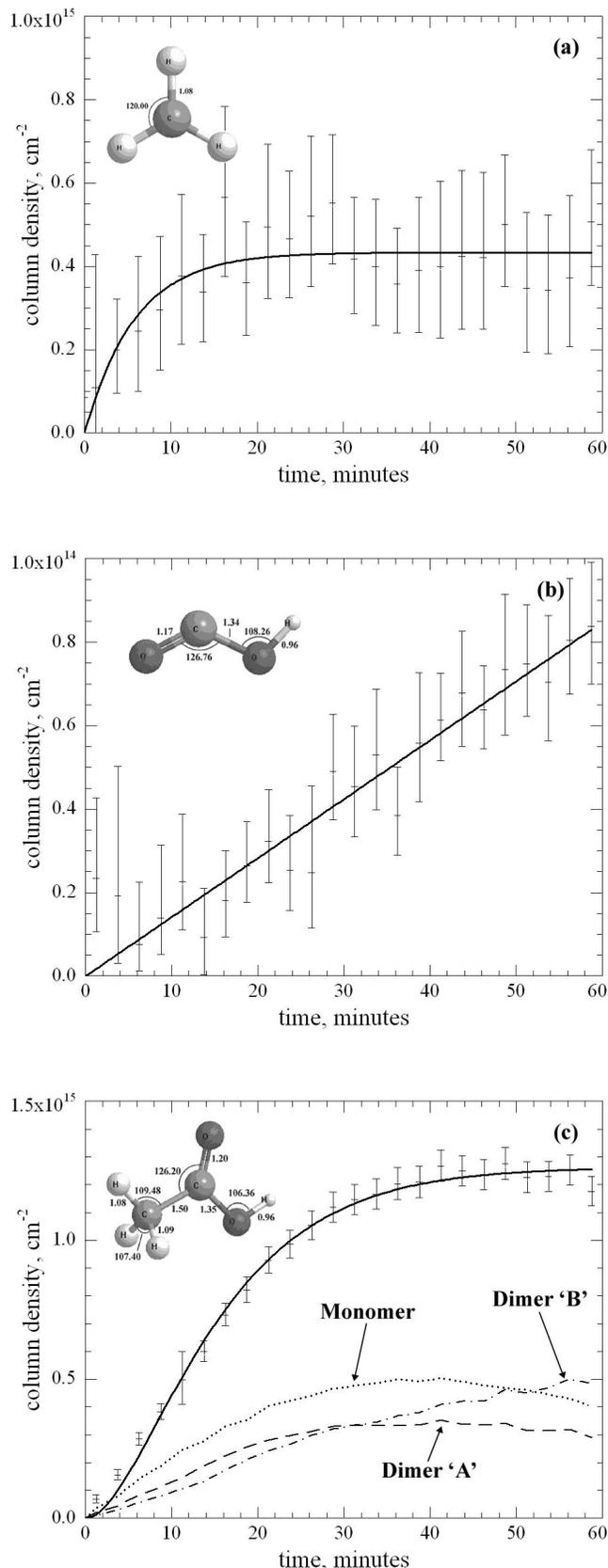
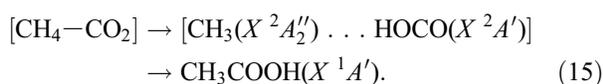


FIG. 4.—Temporal evolution of the column densities along with their kinetic fits shown for: (a) the methyl radical, traced by its ν_2 (out-of-plane bend) absorption at 614 cm^{-1} , fit by eq. (10), (b) the trans-carboxyl radical followed through its ν_2 (CO stretching) mode at 1847 and 1839 cm^{-1} , fit by eq. (14), and (c) trans-acetic acid, via the ν_4 (CO stretch), where the total column density (solid line) is the sum of the column densities of the monomer at 1780 cm^{-1} (dotted line), dimer A at 1757 cm^{-1} (dashed line), and dimer B at 1723 cm^{-1} (dot-dashed line) and is fit by eq. (16).

Note that the reaction between the two radical species is calculated to be exoergic by 365 kJ mol⁻¹ (3.78 eV), based on the potential energy surface calculated by Nguyen et al. (1995) at the QCISD(TC)/6-311++G(d,p) level of theory. To fit the data in our experiments, we suggest that the first step involves the pseudo-first-order generation of the methyl and carboxyl radicals in a matrix cage generated in the right orientation to recombine barrierlessly in a second reaction step to acetic acid. This process should follow a consecutive pathway via equation (16),

$$[t\text{-CH}_3\text{COOH}]_t = c \left(1 - \frac{k_4}{k_4 - k_3} e^{-k_3 t} + \frac{k_3}{k_4 - k_3} e^{-k_4 t} \right), \quad (16)$$

where the total column density for acetic acid was the summation of the column densities derived from the ν_4 (CO stretch) for the monomer at 1780 cm⁻¹, dimer A at 1757 cm⁻¹, and dimer B at 1723 cm⁻¹, assuming that their band strengths correspond to that calculated for the monomer of 5.19×10^{-17} cm molecule⁻¹. We found that fitting equation (16) to our data yielded values for the rate constants of k_3 [$(2.05 \pm 0.21) \times 10^{-3}$ s⁻¹] and k_4 [$(2.05 \pm 0.21) \times 10^{-3}$ s⁻¹] and a value of $c = (1.26 \pm 0.02) \times 10^{15}$ molecules cm⁻².

To rule out other possible formation mechanisms, we analyzed the potential energy surfaces for the photodissociation of acetic acid calculated at the QCISD(TC)/6-311G(d,p) level of theory by Nguyen et al. (1995) and at the MP2/cc-pVDZ level of theory by Fang et al. (2002). Here, we can likely rule out a direct pathway from the [CH₄-CO₂] complex on the singlet surface to form acetic acid, which requires overcoming a barrier of around 329 kJ mol⁻¹ (3.4 eV). Note that this pathway only produces trans-acetic acid via the intermediate cis isomer, which would be expected to be observed spectroscopically if this pathway was taken. Other pathways which can be excluded, based on the fact that the precursors were not observed in our experiment, involve the reactants (1) ketene (CH₂CO) and water (H₂O), (2) acetyl (CH₃CO) and the hydroxyl (OH) radicals, (3) atomic hydrogen and the carboxymethyl radical (CH₂COOH), and (4) atomic hydrogen and the acetyloxyl radical (CH₃COO).

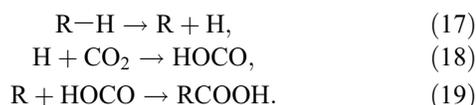
5. ASTROPHYSICAL IMPLICATIONS

We have demonstrated that the formation of acetic acid is possible in ice mixtures of carbon dioxide and methane, subject to irradiation by energetic electrons. It is thought that similar processes can occur within the icy grains of interstellar ices, which are known to be bombarded by irradiation from both UV photons and MeV ions, the latter of which is thought to transfer energy to the electronic systems of the molecules. Is our proposal that these processes can form acetic acid within interstellar ices reasonable? To answer this, we must consider the likelihood of finding neighboring methane and carbon monoxide molecules within such ices. In a recent study of 23 infrared sources carried out by Gibb et al. (2004) using the *Infrared Space Observatory (ISO)*, they were able to confirm the presence of methane in eight of these sources and present upper limits of methane abundance for a further eight sources (methane was also tentatively assigned as present in the spectrum from NGC 7538 IRS 1 and gas-phase methane was identified in Orion IRc 2). Typically, the abundance was low (1%–4%, relative to water), but in several sources it was found to be much higher (up to 17%). From the band profile and position, it was established that the methane residing within these ices is consistent with that of methane within a polar matrix. Carbon dioxide, on the other hand, is found to exist in both polar and

apolar ices, whereby it is expected that only the carbon dioxide residing in the polar ices can possibly be close enough to a methane molecule to react to produce acetic acid. Gibb et al. (2004) reported seven infrared sources which satisfy this requirement; AFGL 989 (CH₄ 1.9%, polar CO₂ 18.5%), GCS 31 (CH₄ <6.4%, polar CO₂ 23.4%), W33A (CH₄ 1.5%, polar CO₂ 11.2%), AFGL 2591 (CH₄ <2.7%, polar CO₂ 10%), S140 IRS 1 (CH₄ 0.92%, polar CO₂ 11%), NGC 7538 IRS 1 (CH₄ 1.5%, polar CO₂ 20%), and NGC 7538 IRS 9 (CH₄ 1.5%, polar CO₂ 15.4%). Note that each of these infrared sources was found to have high abundances of all of the complex organic species included within their search, namely, formaldehyde, H₂CO (5.81 μ m [1721 cm⁻¹]); formic acid, HCOOH (5.85 μ m, [1709 cm⁻¹], 7.25 μ m [1379 cm⁻¹]); the formate anion, HCOO⁻ (6.33 μ m [1580 cm⁻¹], 7.25 μ m [1379 cm⁻¹], 7.41 μ m [1350 cm⁻¹]); and acetaldehyde, CH₃CHO (5.83 μ m [1715 cm⁻¹], 7.41 μ m [1350 cm⁻¹]). Note that both formaldehyde and acetaldehyde were also identified as possible products from the irradiation of methane and carbon dioxide mixtures. Based on our laboratory results, if a search for acetic acid within interstellar ices were to be carried out, the most likely absorption features due to this molecule would include the ν_4 (CO stretch) at 1780 cm⁻¹ (5.62 μ m) and the ν_8 (CHO rocking) at 1195 cm⁻¹ (8.37 μ m). However, if acetic acid is produced within an astronomical ice, as we have already pointed out, this is likely to be in a polar environment, where the main matrix component is water, which will shift these absorption features.¹ However, based on the abundance of methane within these ices, it is likely that if acetic acid is formed within interstellar ices, its abundance will be much less than 1% (relative to water) and thus beyond the detection limits of current telescopes. Although we predict that acetic acid may be formed within interstellar ices, a realistic quantitative extrapolation as to how much could be formed in the interstellar medium based on our results is difficult at this stage until a more realistic model of the actual ice morphology can be produced as well as additional experiments carried out to test how the production rate of acetic acid is affected by the presence of additional matrix elements (most importantly, water). However, if acetic acid is produced within interstellar grains, it can then subsequently be released into the gas phase as the icy mantle begins to sublime as a young stellar object begins to form. This process is expected to enhance the abundance of acetic acid where the sublimation of interstellar ices is occurring, allowing an alternative to its production by solely gas-phase processes. Summarized, our laboratory experiments showed that solely acetic acid, but neither its methyl formate nor the glycolaldehyde isomer, can be formed in interstellar ices containing carbon dioxide and methane on interactions with energetic electrons. The formation pathways of the methyl formate and the glycolaldehyde isomers are currently under investigation. Our studies also indicate the likely probability for the production of propionic acid (C₂H₅COOH) by a similar reaction mechanism of ethane with carbon dioxide within these interstellar grains and would therefore be another candidate molecule to search for in the gas phase by microwave spectroscopy. A generalized reaction scheme for the production of carboxylic acids formed by radiolysis within interstellar grains in the interstellar medium could be (1) the radiolysis-induced cleavage of a sigma C–H bond of the hydrocarbon, followed by (2) the addition of the suprathreshold hydrogen atom to a neighboring carbon dioxide molecule, and finally,

¹ For an example spectrum of acetic acid in a water-dominated (10:1) matrix at 16 K, please refer to <http://www-691.gsfc.nasa.gov/cosmic.ice.lab/spectra.htm>.

(3) the recombination of both radicals in the matrix cage to produce a new carboxyl acid as depicted in reactions (17)–(19),



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