Carbon Suboxide in Astrophysical Ice Analogs

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As suggested by W. T. Huntress et al. (1991, Nature 352, 316–318), carbon suboxide (C₃O₂) is a potential extended source of both the CO and atomic carbon emission observed in cometary comae. However, laboratory experiments on the formation and stability of C₃O₂ in space environments have not been published. In this work, we study solid C₃O₂ in ices representative of cometary nuclei as well as interstellar icy grain mantles, specifically addressing the issues of C₃O₂ formation and stability under exposure to energetic processing in the forms of proton irradiation and UV photolysis. The formation rate of C₃O₂ is measured in laboratory ices of pure CO and CO₂ and mixtures of these molecules with H₂O at 18 K. Destruction rates in H₂O-dominated mixtures appropriate to a cometary nucleus or interstellar icy grain mantle are also measured. Differences in rates between photolysis and irradiation experiments are observed and quantified. Mid-infrared spectra of C₃O₂-containing mixtures are presented together with measurements of carbon suboxide’s infrared band strengths and vapor pressures from 110 to 125 K. Implications are discussed for the existence of C₃O₂ in ices representative of cometary nuclei as well as interstellar icy grain mantles, specifically addressing the issues of C₃O₂ formation and energetic processing in the gas phase of the interstellar medium or in cometary comae, because C₃O₂ is a linear, symmetric molecule with no dipole moment and hence no rotational transitions at submillimeter or radio wavelengths. It may be possible to detect cosmic C₃O₂ in the solid phase, however, since it forms a highly interactive crystalline matrix with a variety of absorption features throughout the mid-infrared region, e.g., Miller and Fately (1964).

In this paper, we study C₃O₂ under conditions that more appropriately reflect the environments and compositions of cometary and interstellar ices in order to understand its formation and stability in an astrophysical context. Experimental results are presented for solid C₃O₂ formation and energetic processing in laboratory analogs of astrophysical ices (both cometary and interstellar) at low temperature, T = 15–20 K. The laboratory system, sample preparation, and processing techniques are described in Section 2. Mid-IR spectra (5000–400 cm⁻¹; 2–25 µm) for C₃O₂ diluted in different ice matrices at 18 K are presented in Section 3, along with calculations of the strengths (“A values”) of the C₃O₂ IR absorption features and C₃O₂ vapor pressures from 110 to 125 K. The formation of C₃O₂ resulting from energetic processing of CO and CO₂ in pure form and in mixtures with H₂O by both proton irradiation and UV photolysis² is measured in Section 4, together with destruction rates in H₂O-dominated matrices. Implications for the existence of C₃O₂ in Venus were once attributed to C₃O₂ polymer by Kuiper (1957), but Plummer and Carson (1970) later presented spectroscopic evidence proving this to be incorrect. Suboxide polymers form when CO is processed (by electrolysis, irradiation, or photolysis) in the gas, liquid, or condensed phase (e.g., Lind 1928, Sugimoto et al. 1986, Briggs and Clay 1968, Haring et al. 1984). Studies of the electrical discharge of CO date back to Brodie (1873) who first showed that its decomposition products formed a reddish brown solid. If present on the surfaces of cometary nuclei, C₃O₂ polymers may contribute to their low geometric albedo, which is typically around 4% (as measured toward Comet Halley by, e.g., Sagdeev et al. (1986)).

Spectral features of monomeric C₃O₂ are unobservable in the gas phase of the interstellar medium or in cometary comae, because C₃O₂ is a linear, symmetric molecule with no dipole moment and hence no rotational transitions at submillimeter or radio wavelengths. It may be possible to detect cosmic C₃O₂ in the solid phase, however, since it forms a highly interactive crystalline matrix with a variety of absorption features throughout the mid-infrared region, e.g., Miller and Fately (1964).

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² Hereafter, to clearly distinguish one from the other, we refer to energetic processing by high-energy particles such as protons as “irradiation” and to processing by ultraviolet light as “photolysis.”
the ices found within interstellar clouds and in cometary nuclei and the possibilities for its detection in those environments are discussed in Section 5.

2. EXPERIMENTAL

Hudson and Moore (1995) have described the laboratory setup at NASA's Goddard Space Flight Center in detail. In summary, gases are prepared inside a vacuum manifold and vapor-condensed onto a cold (15–20 K) aluminum mirror suspended inside a stainless-steel high-vacuum chamber \( (P \approx 10^{-7} \text{ mm Hg}) \). Mixing ratios in the resultant ice are determined from the partial pressures inside the gas-filled manifold before condensation. Actual ratios in the resulting ice samples may vary slightly from these values because of effects of depositing through a narrow tube, (see, e.g., the discussion in Gerakines et al. (1995)), but any differences should not exceed a factor of 2. Since the differences in mixing ratios between the ice mixtures studied are large (100:1 or 10:1 matrix:suboxide ices are compared to those with ratios of about 1:1), the qualitative differences between the 100:1 or 10:1 ices and the 1:1 ices should not be significantly affected (such as those observed in the IR spectra; see Section 3). The quantitative measurements made do not depend critically upon the mixing ratio, but on the general nature of the ice (such as the rates of C₃O₂ formation in various pure ices and in an H₂O-dominated ice; see Section 3).

The temperature of the mirror may be controlled up to room temperature. IR spectra (with a spectral range of 5000 to 400 cm⁻¹ and resolutions from 1 to 4 cm⁻¹) are taken by diverting the beam of an FTIR spectrometer (Mattson Instruments) toward the ice-covered mirror, where it passes through the ice before and after reflection at the ice–mirror interface. Ices are processed by turning the mirror to face either a beam of 0.8-MeV protons generated by a Van de Graaff accelerator or UV photons from a microwave-discharged hydrogen flow lamp. Photons from the UV lamp, limited by the LiF window between the H₂ discharge and the vacuum system, fall in the wavelength range of 110–250 nm. The total UV photon flux at the ice sample was determined to be approximately \( 8.6 \times 10^{13} \text{ photons cm}^{-2} \text{ s}^{-1} \) by Gerakines et al. (2000), who describe this measurement in detail and outline the methods by which both irradiation and photolysis energy doses are calculated.

The C₃O₂ used in these experiments was generated by the method described by Miller and Fateley (1964). In summary, a mixture of CH₃COOH (malonic acid) and P₂O₅ (phosphorous pentoxide) in approximate 10:1 weight ratio was heated to 410–420 K for 1 h. The gases produced (H₂O, CO₂, C₃O₂, and CH₃COOH) were collected at 77 K using liquid N₂. We produced about 5 torr-liters of C₃O₂ (0.3 mmol) from approximately 5 g (50 mmol) of malonic acid using this method. Over the course of several days, the C₃O₂ stored in the glass bulb at about 15 torr was seen to decompose (through spectroscopy of the contents of the gas bulb) into CO₂ (approximately 1 torr of CO₂ per week of storage). This CO₂ gas was removed before each experiment using a liquid–solid bath of ethanol as described above.

Reagents used and their purities are as follows: H₂O (triply distilled, with a resistance greater than \( 10^7 \) ohm cm), CO (gas, Matheson, 99.99%), CO₂ (gas, Matheson, 99.995%), N₂ (gas, Air Products, 99.9995%), malonic acid, CH₃COOH (Aldrich, 99% purity), and phosphorous pentoxide, P₂O₅ (Aldrich, 98% purity).

3. RESULTS

Infrared Spectral Properties

The mid-IR spectrum (5000–400 cm⁻¹ or 2–25 μm) of pure C₃O₂ at 18 K is shown in Fig. 1 at a resolution of 4 cm⁻¹. Peak positions and vibrational mode assignments are listed in Table I. They are in close agreement with those of pure C₃O₂ at 100 K reported by Miller and Fateley (1964) and matrix-isolated C₃O₂ in Ar (Ames et al. 1963, Miller and Fateley 1964, Smith and Leroi 1966).

The strongest absorption in the IR spectrum of C₃O₂ (Fig. 1) is its \( \nu_3 \) anti-symmetric stretching vibration that falls near 2200 cm⁻¹ (4.5 μm). Using standard methods (of condensing a sample to a known thickness and assuming a mass density of 1 g cm⁻³), we used the area under this feature to calculate its integrated absorbance (a.k.a. “band strength” or “A value”) of \( A(C₃O₂, \nu_3) = (1.3 \pm 0.2) \times 10^{-16} \text{ cm molecule}^{-1} \). (Since we have assumed a mass density equal to that of water in our

![FIG. 1. Mid-IR spectrum (5000–400 cm⁻¹, 2–25 μm) of pure C₃O₂ at 18 K. Band assignments are taken from Miller and Fateley (1964) and Smith and Leroi (1966).](image-url)
calculations, the “true” magnitude of $A$ will scale inversely with the actual mass density of the C$_3$O$_2$ ice sample, which is unknown. The precision of our measurement is unaffected by the value of mass density.) This value of $A$ is about 15–20 times stronger than any of the other observed C$_3$O$_2$ mid-IR features (see Table I). It is comparable to that of the $\nu_3$ stretching vibration of H$_2$O at 3240 cm$^{-1}$ (3.1 $\mu$m), which has a band strength of about $1.6 \times 10^{-16}$ cm molecule$^{-1}$ (Hagen et al. 1983). The strength of the stretching vibration of CO near 2140 cm$^{-1}$ (4.67 $\mu$m) is 10 times lower than that of C$_3$O$_2$, at $1.1 \times 10^{-17}$ cm molecule$^{-1}$ (Jiang et al. 1975).

Pure C$_3$O$_2$ sublimes during warming in our system near 120 K. Evidence for a possible phase change (based upon changes in two of the overtone features) is seen between 50 and 75 K. McDougall and Kilpatrick (1965), who measured various thermodynamic properties of C$_3$O$_2$ over this temperature range, did not find evidence for a solid–solid phase transition, but the IR spectroscopic data (Fig. 2) do suggest a structural change in the C$_3$O$_2$ ice. Figure 2 contains spectra of the $\nu_1 + \nu_4$ (4000–3500 cm$^{-1}$), $\nu_3$ (2500–2000 cm$^{-1}$), and $\nu_4$ (1700–1450 cm$^{-1}$) C$_3$O$_2$ absorption features at 22, 50, 75, and 100 K. A gradual change is apparent in the $\nu_1 + \nu_4$ and $\nu_4$ features from 50 to 100 K, indicated by shifts in peak position, decreases in width, and increases in peak absorbance. The $\nu_3$ feature itself does not exhibit any significant changes over this temperature range, although the widths and peak absorbance values for its subpeaks near 2400 and 2100 cm$^{-1}$ do show change.

The C$_3$O$_2$ $\nu_3$ stretching feature’s position, width, and profile are all sensitive to the dilution of C$_3$O$_2$ in an ice matrix. Figure 3 contains the 2500–2000 cm$^{-1}$ (4–5 $\mu$m) spectra of pure C$_3$O$_2$ (from Fig. 1), and C$_3$O$_2$ diluted in matrices of N$_2$, CO$_2$, H$_2$O, and CO. Dilution factors are 100 : 1 (matrix : suboxide) except in the H$_2$O-dominated ice, where it is 10 : 1. The $\nu_3$ peak position (marked with asterisks in Fig. 3) varies by more than 50 cm$^{-1}$ as a result of the change in the ice matrix, from 2253 cm$^{-1}$ in an N$_2$ matrix to 2200 cm$^{-1}$ in the pure C$_3$O$_2$ sample (there is also a subpeak that falls at 2178 cm$^{-1}$ in the pure C$_3$O$_2$ sample). The width and profile of the feature also vary depending on the matrix. It is sharp and singly peaked in matrices of N$_2$, CO, and CO$_2$ (FWHM = 8–14 cm$^{-1}$). It takes on a broad Gaussian profile when diluted in an H$_2$O matrix (FWHM = 90 cm$^{-1}$), since the polar nature of the H$_2$O ice creates a high degree of molecular

<table>
<thead>
<tr>
<th>Position (cm$^{-1}$)</th>
<th>Assignmenta</th>
<th>Band strength, $A$ (10$^{-18}$ cm molecule$^{-1}$)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3744 m</td>
<td>$\nu_1 + \nu_4$</td>
<td>3.8 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>3043 m</td>
<td>$\nu_2 + \nu_3$</td>
<td>6 ± 1</td>
<td></td>
</tr>
<tr>
<td>2756 vw</td>
<td>$\nu_1 + \nu_4$</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>2666 vw</td>
<td>$\nu_3 + \nu_4$</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>2396 m</td>
<td>$\nu_2 + \nu_4$</td>
<td>8 ± 4</td>
<td></td>
</tr>
<tr>
<td>2200, 2177 vs</td>
<td>$\nu_3$</td>
<td>130 ± 20</td>
<td>CCO asym. str</td>
</tr>
<tr>
<td>2109 m</td>
<td>$\nu_3 - \nu_4$</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>1581 m</td>
<td>$\nu_4$</td>
<td>5 ± 3</td>
<td>CC asym. str</td>
</tr>
<tr>
<td>~540 w</td>
<td>$\nu_5$</td>
<td>1.4 ± 0.3</td>
<td>bend</td>
</tr>
</tbody>
</table>

*Assignments taken from Miller and Fateley (1964) and Smith and Leroi (1966).
interaction. In a pure C$_3$O$_2$ sample, the stretching feature is broad (FWHM = 67 cm$^{-1}$), double-peaked (peaks falling at 2200 and 2178 cm$^{-1}$), and asymmetric, with a long-wavelength wing that extends to about 2350 cm$^{-1}$ (4.26 μm). Within the 2200–2300 cm$^{-1}$ region, there is also a notable amount of substructure to the C$_3$O$_2$ feature, possibly because of C$_3$O$_2$ dimers, trimers, or higher $n$-mers. Table II summarizes the $v_3$ peak’s position and FWHM for pure C$_3$O$_2$ and C$_3$O$_2$ in several different ice matrices at 18 K.

### Vapor Pressure

The vapor pressure ($P_{\text{vap}}$) of C$_3$O$_2$ was measured at 110, 115, 120, and 125 K by observing the sublimation rate ($dN/dt$, in cm$^{-2}$ s$^{-1}$) at about 30 minutes of each temperature and using the relation

$$P_{\text{vap}} = (dN/dt) \times (2\pi m kT)^{1/2},$$

where $m$ is the molecular mass of C$_3$O$_2$ (68 amu). The term $dN/dt$ was determined at each temperature of interest by holding the sample at that temperature and measuring the linear change in $N$ versus time. The term $N$ was measured at various time steps by integrating the area underneath the C$_3$O$_2$ $v_3$ feature and dividing by its band strength (the measurement of which is described previously in this section). Calculated values of $P_{\text{vap}}$ are listed in Table III. At 110 K, pure C$_3$O$_2$ has a vapor pressure of 1.2 × 10$^{-8}$ mm Hg, but at 125 K, it has risen sharply to 5.8 × 10$^{-6}$ mm Hg (C$_3$O$_2$ vapor pressures for $T = 160$–248 K have been measured by McDougall and Kilpatrick (1965)). In comparison, the vapor pressure of H$_2$O ice, which depends on its crystalline state, can vary from $\sim$10$^{-7}$ to $\sim$10$^{-8}$ mm Hg at 125 K (Kouchi 1987).

### Suboxide Formation and Energetic Processing

As noted above, C$_3$O$_2$ and/or C$_3$O$_2$ polymers are known to form from pure CO energetically processed in its gas (Sugimoto et al. 1986), liquid (Briggs and Clay 1968), or solid phases (Haring 1984). Here, we measure the production rates of C$_3$O$_2$ from pure, solid CO at 18 K as processed by irradiation and by photolysis. This is the first direct comparison of pure CO irradiation and photolysis known to us. The IR spectrum of the pure CO sample at 18 K before and after processing is shown in Fig. 4, and each case. The spectrum of the CO + C$_3$O$_2$ 100:1 sample from Fig. 3 is presented for comparison; note that the broad feature near 2210 cm$^{-1}$ present in each of the pure CO spectra is not due to an impurity in the CO ice, but it is a weak absorption of CO itself exaggerated by the scale of the figure and is due to a combination of the CO lattice mode and fundamental stretching mode; see, e.g., Ewing and Pimentel (1961) or Pipes et al. (1978) for identifications of this feature. A forest of absorptions appears in the 2500–2000 cm$^{-1}$ (4–5 μm) range after irradiation processing. The major products formed in these experiments include CO$_2$ (peak near 2340 cm$^{-1}$), C$_3$O$_2$ (2242 cm$^{-1}$), and C$_2$O (1990 cm$^{-1}$; not shown in Fig. 4). Other, less abundant species such as C$_2$O$_3$ and C$_2$O are also likely sources of the other, unidentified peaks shown in Fig. 4 (irradiation case).

The abundances of the major products are plotted against the total applied energy dose in Fig. 5 for both irradiation and photolysis experiments. Formation yields have been measured from the slopes of the linear parts of the curves and are listed in Table IV, along with yields calculated from other ice experiments described below. Since the intrinsic band strength of C$_2$O is unknown, an estimate of its abundance was made assuming a value of $A = 1 \times 10^{-17}$ cm molecule$^{-1}$. Yields of CO$_2$ were

### Table II

Position and Width (FWHM) of the C$_3$O$_2$ $v_3$ Stretching Feature in Selected Mixtures at 18 K

<table>
<thead>
<tr>
<th>Ice mixture</th>
<th>Position (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure C$_3$O$_2$</td>
<td>2200, 2178</td>
<td>67</td>
</tr>
<tr>
<td>CO$_2$ + C$_3$O$_2$ (100:1)</td>
<td>2217</td>
<td>11</td>
</tr>
<tr>
<td>H$_2$O + C$_3$O$_2$ (10:1)</td>
<td>2233</td>
<td>90</td>
</tr>
<tr>
<td>CO + C$_3$O$_2$ (100:1)</td>
<td>2242</td>
<td>8</td>
</tr>
<tr>
<td>N$_2$ + C$_3$O$_2$ (100:1)</td>
<td>2253</td>
<td>14</td>
</tr>
</tbody>
</table>

### Table III

Vapor Pressure of C$_3$O$_2$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$P$ (10$^{-7}$ mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>115</td>
<td>0.90 ± 0.13</td>
</tr>
<tr>
<td>120</td>
<td>2.1 ± 0.1</td>
</tr>
<tr>
<td>125</td>
<td>58 ± 1</td>
</tr>
</tbody>
</table>

FIG. 4. Spectra of pure CO from 2500 to 2000 cm$^{-1}$ (4 to 5 μm) before and after processing at 18 K by proton irradiation (to a dose of 7.9 × 10$^{19}$ eV cm$^{-2}$) and UV photolysis (to a dose of 5.0 × 10$^{19}$ eV cm$^{-2}$). The spectrum of CO + C$_3$O$_2$ (100:1) at 18 K (bottom) is shown for comparison. The dotted line indicates the peak position of the C$_3$O$_2$ stretching feature in the CO + C$_3$O$_2$ (100:1) ice.
and Clay (1968) reported a value of $G_0$ for photolysis (differing by a factor of 17). This is the first time both measurements of the CO$_2$ and C$_3$O$_2$ yields are most likely destructed by irradiation at 77 K.

It is clear from Figs. 4 and 5 that C$_3$O$_2$ is much more effectively produced by irradiation than by photolysis. The measured C$_3$O$_2$ yields are 0.24 ± 0.04 for irradiation and 0.014 ± 0.001 for photolysis (differing by a factor of 17). This is the first time a significant difference has been reported in any direct comparison of these two processing techniques. The differences in both measurements of the CO$_2$ and C$_2$O yields are most likely linked to the strength of the CO bond, whose dissociation energy is 11.1 eV. While 0.8-MeV protons may easily break this bond directly, e.g.,

$$\text{CO} \rightarrow \text{C} + \text{O},$$

0.25 ± 0.04 molecules per 100 eV absorbed for irradiation and 0.9 ± 0.2 for photolysis, differing by a factor of about 3.6. Briggs and Clay (1968) reported a value of $G(\text{CO}_2) = 0.24 ± 0.01$ molecules per 100 eV for the gamma radiolysis of liquid CO at 77 K.

Note. Numbers in parentheses represent uncertainty in first digit (e.g., “0.25(4)” = “0.25 ± 0.04”). Negative values indicate yields of destruction.

6 to 10 eV photons cannot. Photolysis of CO proceeds through its indirect dissociation, a two-step process involving first the electronic excitation of one CO molecule (requires $E > 8.4$ eV) and its subsequent reaction with another to form CO$_2$ and a carbon atom,

$$\text{CO} \rightarrow \text{CO}^*, \quad (3)$$

$$\text{CO}^* + \text{CO} \rightarrow \text{C} + \text{CO}_2 \quad (4)$$

(Okabe 1978). Therefore, the formation of carbon chains and suboxides (C$_n$, C$_n$O, C$_n$O$_2$) is more effective in the irradiation case, whereas photolysis tends to form CO$_2$ before other carbon oxides.

C$_3$O$_2$ may also be a product to consider for CO$_2$ ice processing. In fact, C$_3$O$_2$ has been identified as a minor product in previous CO$_2$ processing studies with CO, CO$_2$, and O$_2$ in much higher abundances (e.g., Gerakines et al. 1996; Brucato et al. 1997). However, we find no indication of suboxide in the processed pure CO$_2$ ices studied here. Figure 6 contains IR spectra of the CO$_2$ ices in our processing experiments. Indeed, features due to CO (2139 cm$^{-1}$) and CO$_3$ (2046 cm$^{-1}$) appear strongly in our spectra (along with O$_3$ at 1045 cm$^{-1}$ and CO$_3$ at 1879 cm$^{-1}$; not shown in Fig. 6), but the C$_3$O$_2$ signal is not present. However, the feature of C$_2$O is found at 1991 cm$^{-1}$ (although weak). We place upper limits on the C$_3$O$_2$ yields of $G < 0.001$ molecules (100 eV)$^{-1}$ in both irradiation and photolysis cases (Table IV), based on the noise levels in our laboratory spectra. Yields of CO were measured at 1.1 ± 0.1 molecules (100 eV)$^{-1}$ for irradiation and 8.1 ± 0.3 for photolysis (see Table IV). The origin of this difference in formation yields may be that the CO produced from the parent CO$_2$ molecules is more easily destroyed by the irradiation (as indicated in the pure CO experiments described previously) and thus displays a lower net yield of formation.

\[ G(\text{CO}) \]
\[ G(\text{CO}_2) \]
\[ G(\text{C}_3\text{O}_2) \]

$\begin{array}{cccc}
\text{Initial ice} & p+ & UV & p+ & UV & p+ & UV \\
\hline
\text{CO} & \text{—} & \text{—} & 0.25(4) & 0.9(2) & 0.24(4) & 0.014(1) \\
\text{CO}_2 & 1.1(1) & 8.1(3) & \text{—} & \text{—} & <0.001 & <0.001 \\
\text{C}_3\text{O}_2 & 0.68(4) & 1.1(1) & 0.12(2) & 0.074(4) & -4.3(4) & -6.5(4) \\
\text{H}_2\text{O}+\text{C}_3\text{O}_2 & 0.063(8) & 0.045(5) & 0.019(4) & 0.13(1) & -0.13(1) & -0.47(9) \\
\end{array}$

$\begin{array}{l}
\text{Note.} \text{ Numbers in parentheses represent uncertainty in first digit (e.g., “0.25(4)” = “0.25 ± 0.04”). Negative values indicate yields of destruction.}
\end{array}$

\[ G(Y_{\text{CO}}) \]
\[ G(Y_{\text{CO}_2}) \]
\[ G(Y_{\text{C}_3\text{O}_2}) \]

\[ A = 1 \times 10^{17} \text{ cm molecule}^{-1} \]
We have also studied the processing of pure C$_3$O$_2$ samples at 18 K. Spectra are given in Fig. 7. The major products observed in both irradiation and photolysis experiments were CO (at 2138 cm$^{-1}$), CO$_2$ (at 2345 cm$^{-1}$), CO$_3$ (at 2056 cm$^{-1}$), and C$_2$O (at 1994 cm$^{-1}$). Other weaker features observed near 1948 and 1899 cm$^{-1}$ in the irradiation experiment are suggestive of longer carbon chains (e.g., Kurtz and Huffman 1990, Kranze et al. 1996). Yields measured in the irradiation experiment were $G$(CO) = 0.68 ± 0.04, $G$(CO$_2$) = 0.12 ± 0.02, and $G$($-C_3O_2$) = 4.3 ± 0.4. Yields in the photolysis experiment were $G$(CO) = 1.1 ± 0.1, $G$(CO$_2$) = 0.074 ± 0.004, and $G$($-C_3O_2$) = 6.5 ± 0.4. In each case, the suboxide destruction yield is much greater than the combined CO and CO$_2$ formation yields, suggesting the abundant formation of unidentified products such as C$_3$O$_2$ polymers.

CO and CO$_2$ are released during warming of the irradiated pure C$_3$O$_2$ sample. A residue remains at 290 K, and its spectrum is shown in Fig. 8. The spectrum of the room-temperature residue of irradiated CO, which was obtained with an FTIR microscope, is shown for comparison. The two spectra show some weak similarities, and the relative strengths of specific features vary from one to the other. The major peaks in the IR spectrum of the C$_3$O$_2$ residue (with possible functional group assignments based on their peak wavenumber) fall at 2156 (CO groups), 1781 (C==O bonds), 1617 (C ==C bonds), and 1388/1361 cm$^{-1}$ (O==C–O groups). Weak absorption features also appear in the 3600–2850 cm$^{-1}$ region, indicative of cyclic carbon structures; these features may imply the presence of C$_3$O$_2$ thermal polymer, as its structure is likely a polycyclic unsaturated lactone as described in Kybett et al. (1965) and the references therein. The residue of irradiated CO has a much weaker feature near 2160 cm$^{-1}$, and strong peaks at 1712, 1614, 1449, 1288, and 1031 cm$^{-1}$. Absorptions in the 3600–2850 cm$^{-1}$ region are much stronger in this case. The color of the CO residue is dark reddish brown, and further characterizations in the UV and visible wavelength regions are in progress.

Since the ice environments of comets and interstellar ices are typically thought to be H$_2$O-dominated, the formation and destruction of C$_3$O$_2$ should be considered in ice samples where CO, CO$_2$, and C$_3$O$_2$ have been diluted in H$_2$O. Work already present in the literature has shown that the major products of H$_2$O + CO processing are CO$_2$, HCO, H$_2$CO, and CH$_3$OH (photolysis: Sandford et al. 1988; irradiation: Hudson and Moore 1999). No detection of C$_3$O$_2$ has been noted. Previous studies...
of H$_2$O + CO$_2$ ices have shown that the major products of processing are CO, HCO, and H$_2$CO$_3$ (photolysis and irradiation: Gerakines et al. 2000), and, again, no detection of C$_3$O$_2$ was noted.

We have studied the processing of H$_2$O + C$_3$O$_2$ ice at low temperature. The H$_2$O + C$_3$O$_2$ (10 : 1) ice sample’s spectrum before and after processing is shown in Fig. 9. The two major products of both irradiation and photolysis were found to be CO and CO$_2$. Product column densities in the sample are shown in Fig. 10 as a function of absorbed energy dose. In the irradiation experiment, these species initially formed with yields of $G$(CO) = 0.063 ± 0.008 and $G$(CO$_2$) = 0.019 ± 0.004 (to a dose of 3 × 10$^{19}$ eV cm$^{-2}$, see Fig. 10). Yields dropped at higher doses. The C$_3$O$_2$ was destroyed by irradiation with a destruction yield of $G$($-$C$_3$O$_2$) = 0.13 ± 0.01 to a dose of 3 × 10$^{19}$ eV cm$^{-2}$.

In the photolysis experiment, where the total energy dose was 2.4 × 10$^{18}$ eV cm$^{-2}$, only linear production and destruction rates were apparent, and we measured yields of $G$(CO$_2$) = 0.13 ± 0.01, $G$(CO) = 0.045 ± 0.005, and $G$($-$C$_3$O$_2$) = 0.47 ± 0.09 (see Fig. 10).

4. DISCUSSION AND IMPLICATIONS

We have found that C$_3$O$_2$ has a mid-IR spectrum that is sensitive to the effects of dilution in a molecular matrix. The differences in the $v_3$ peak’s position between different ice matrices at low temperature are quite large. The extreme values of the peak position for the $v_3$ C$_3$O$_2$ features are 2253 cm$^{-1}$ in an N$_2$-dominated ice at 18 K and 2178 cm$^{-1}$ in a pure C$_3$O$_2$ ice at 18 K, with values for ices dominated by CO, CO$_2$, and H$_2$O falling in between. The width of the $v_3$ feature also varies greatly, from only 8 cm$^{-1}$ in a CO-dominated ice at 18 K to 90 cm$^{-1}$ in one that is H$_2$O-dominated as 18 K. Hence, the detection of this absorption feature in either the ISM or in planetary ices could lead to highly accurate determinations of the overall ice environment.

However, solid-phase C$_3$O$_2$ has not been positively identified in recent mid-infrared observations conducted by the Infrared Space Observatory (ISO). Figure 11 compares two ISO short-wavelength spectrometer (SWS) observations of high-mass protostars, W33A and NGC 7538 IRS9, to laboratory spectra of H$_2$O + C$_3$O$_2$ (10 : 1) and CO + C$_3$O$_2$ (100 : 1) at 18 K. Although small features do seem to exist in the spectral region near the expected position of the C$_3$O$_2$ $v_3$ stretching feature, these are likely well within the noise of the observed data. The observations of W33A

![Figure 9](image9.png)

**FIG. 9.** Spectra of H$_2$O + C$_3$O$_2$ (10 : 1) at 18 K from 2500 to 2000 cm$^{-1}$ (4 to 5 µm) before and after processing by proton irradiation (to a dose of 7.4 × 10$^{19}$ eV cm$^{-2}$) and UV photolysis (to a dose of 2.3 × 10$^{18}$ eV cm$^{-2}$).

![Figure 10](image10.png)

**FIG. 10.** Column density (10$^{17}$ cm$^{-2}$) versus energy dose (10$^{17}$ eV cm$^{-2}$) for the products of H$_2$O + C$_3$O$_2$ (10 : 1) ice processing at 18 K by both proton irradiation (open symbols) and UV photolysis (filled symbols). Squares represent CO$_2$, and circles CO.

![Figure 11](image11.png)

**FIG. 11.** ISO-SWS spectra of the protostars W33A (Gibb et al. 2000) and NGC 7538 IRS9 (Whittet et al. 1996) in the region of the C$_3$O$_2$ $v_3$ stretching feature. The dotted line indicates the position (2242 cm$^{-1}$) of the C$_3$O$_2$ $v_3$ stretching feature in the CO + C$_3$O$_2$ (100 : 1) ice sample.
(Gibb et al. 2000) were made at a spectral resolution of $\lambda/\Delta \lambda = 1500$, while those of NGC 7538 IRS9 (Whittet et al. 1996) have a lower resolution of $\lambda/\Delta \lambda = 500$. Upper limits on the C$_3$O$_2$ column density in these observations, based on the level of the noise between 2220 and 2250 cm$^{-1}$, are about $5 \times 10^{15}$ cm$^{-2}$ for W33A (0.05% of H$_2$O) and $1 \times 10^{15}$ cm$^{-2}$ for NGC 7538 IRS9: 0.01% H$_2$O; H$_2$O column densities in these lines of sight may be found in Gibb et al. (2000). Other molecules such as N$_2$O also have absorption features in the 2200–2300 cm$^{-1}$ region, and, if present, would lower this limit even further (N$_2$O has an absorption that falls at about 2235 cm$^{-1}$; see e.g., Elsila et al. 1997). This dearth of C$_3$O$_2$ comes despite the relatively high abundance of solid CO and CO$_2$ present in the sampled protostellar environments: the total amount of solid CO ranges from 2 to 15% of the H$_2$O ice column density (Gibb et al. 2000), and CO$_2$ from about 12 to 22% (Gerakines et al. 1999). Most other ice components are found at the 1% level relative to H$_2$O.

We have shown that C$_3$O$_2$ forms efficiently in pure CO ice samples when processed by irradiation with a yield of about 0.25 molecules per 100 eV absorbed. The yield of C$_3$O$_2$ by photolysis in similarly prepared CO ices is about 20 times smaller. However, it is not formed in significant abundances from pure CO$_2$ ice or from mixtures dominated by H$_2$O. Since interstellar ices toward massive protostars are largely composed of H$_2$O + CO$_2$ + CH$_3$OH in the ratio of approximately 100:20:10 (Gerakines et al. 1999; Dartois et al. 1999; Gibb et al. 2000), it may not be surprising to note that C$_3$O$_2$ is not found there.

This may not be the final verdict for interstellar solid C$_3$O$_2$, however, since an important observational bias exists in the ISO dataset because of the sensitivity limits of its instruments. The majority of sources observed were highly constrained to those bright in the mid infrared and, in the case of ice detections, almost entirely high-mass protostars. Detailed observations of a more varied set of sight lines, including those toward background field stars as well as lower mass embedded protostars, may yet yield a detection of interstellar C$_3$O$_2$, as, among other factors, the fraction of CO in the nonpolar (H$_2$O-poor) ice phase is higher in these colder environments (e.g., Chiar et al. 1995). Unfortunately, ISO observations toward the background field star Elias 16, which focused on detections of solid CO and CO$_2$ (Whittet et al. 1998), omitted the wavelength region containing the C$_3$O$_2$ v$_3$ stretch because of time constraints imposed by the low flux level of this source.

There are also no positive detections of C$_3$O$_2$ toward comets (see, e.g., Irvine et al. 2000). This may be due to the fact that gas-phase C$_3$O$_2$ easily dissociates in the environment of cometary comae, as described in detail in Huntress et al. (1991). There is, however, reason to believe that comets may provide an environment capable of producing C$_3$O$_2$. Comets contain large amounts of CO as a parent volatile in their nuclei, as evidenced by observations of the gases released in their comae (e.g., Irvine et al. 2000). This is not surprising, since comets are thought to have formed out of interstellar ices (either directly or indirectly) as the natal cloud condensed to form the young Sun. Highly volatile molecules such as CO may even be physically separated from H$_2$O in the nuclei of short-period comets by heating and recolliding during successive perihelion passages, resulting in a type of “cryogenic distillation.” The processing of such purer cometary CO ices by solar UV or galactic cosmic rays may lead to C$_3$O$_2$ in higher abundances than may be found in the interstellar medium. Based on our experiments, it is also likely that cometary C$_3$O$_2$ produced from energetic processing would remain intact in the nuclear ice or be converted by energetic processing to a dark polymeric residue. The large increase in the C$_3$O$_2$ vapor pressure from 110 to 125 K would imply that the release of C$_3$O$_2$ would increase greatly as the comet approached the Sun from a distance of about 7 to 5 AU. This increase in C$_3$O$_2$ would manifest itself as an increase in the amount of CO emission in the comet’s coma and the growth of an extended source of CO as the gas-phase C$_3$O$_2$ is dissociated. Of course, few comets are observed at such heliocentric distances because they are extremely faint, but emerging technologies, such as infrared interferometry or spaced-based telescopes, could make such observations possible.

**APPENDIX: A COMMENT ABOUT THE REPORTING OF PRODUCT YIELDS**

In this paper, we have presented initial formation and destruction yields for the products and reactants in our processing experiments. This is generally not the standard way of reporting radiolysis experiments, where a yield is reported after the application of a specified dose. For example, one might report that a certain number of molecules of product were created after a dose 100 eV, or that product’s yield, or “$G$ value.” If a higher dose is applied, it is possible that the value of $G$ reported (the number of products divided by total dose applied) will drop, as it represents the yield averaged over the course of the entire irradiation. This would most likely be due to the fact that the number of reactants is dropping while the number of products is rising, and the sample is approaching some sort of equilibrium chemistry (after which the reactant and product abundances remain constant). Such an example is shown in Fig. 5, where the average yield of C$_3$O$_2$ from CO is initially constant (as shown by the linear growth for doses less than about $2 \times 10^{19}$ eV cm$^{-2}$) and later drops as the energy dose is further increased.

We have not reported the equilibrium constants here or the average formation rates of products but rather the rates of formation given by the zeroth- or first-order chemical reaction kinetics that take place when the energy applied interacts with the reactant molecules. This happens to be the standard way in which UV photolysis results are reported; see, e.g., Gerakines et al. (1996). UV formation and destruction rates are generally given in terms of cross sections as opposed to yields, but the two parameters provide the same information about the reactions and may be directly compared by a reasonably simple transformation of units (see discussion in Gerakines et al. 2000).

Initial formation rates, as opposed to the equilibrium rates, are given priority here because it is rare in an astrophysical context, given the typically small number of interactions per molecule or per unit time, to find a system actually in chemical equilibrium. Moreover, the simple mixtures we are studying (we have included only one or two components) do not by any means represent the complex ices found in space, but are merely models for the behavior of certain astrophysical ice components. It is therefore more appropriate here to study the low-order reaction kinetics, as they may be more easily implemented in chemical models where many more components may be included.

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