Formaldehyde and Organic Molecule Production in Astrophysical Ices at Cryogenic Temperatures

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Thermally promoted formaldehyde (H_2CO) reactions in cryogenic ices have been studied to test their importance as a source of organic molecules in comets and interstellar ices. Ices containing H_2CO, H_2O, CH_3OH, CO, and NH_3 were investigated by using infrared spectroscopy. Small traces of NH_3 ($NH_3/H_2CO \geq 0.005$) are sufficient to convert significant fractions (≥40%) of the H_2CO into more complex organics. However, H_2CO reactions do not proceed without NH_3. Spectral evidence for reaction onset appeared between 40 and 80 kelvin, depending on the ice. Five distinct products were formed. These principally consist of polyoxymethylene and related derivatives. Polyoxymethylene itself was not made in significant amounts in cometary analogs. These products differ from those produced by ultraviolet and particle irradiation. The nature and relative amounts of the products depend on the initial composition, making these materials excellent tracers of a comet's history. About 3% of the organics in p-Halley's coma could have been produced by thermal H_2CO reactions.

Formaldehyde (H_2CO) is present in cometary ices at the few percent level relative to H_2O, the dominant species (*1–3*). It is also expected to be important in interstellar ices (*4–6*). Formaldehyde is reactive. For example, it readily polymerizes to polyoxymethylene (POM) in the gas phase at room temperature (*7*). Previous experiments suggest that formaldehyde reactions may also occur at the very low temperatures in cometary nuclei and dense molecular clouds (*5, 8*). We have extensively tested these processes in the laboratory and found that, in astrophysically relevant ice mixtures containing H_2O, CH_3OH, H_2CO, NH_3, and CO, thermally promoted formaldehyde reactions take place at temperatures below those previously thought possible. This type of reaction may be an important source for some of the organic molecules in dense interstellar clouds and in comets.

The apparatus used in these experiments, an evacuated sample chamber containing a rotatable, 10 K, CsI substrate, coupled to a Fourier transform infrared (IR) spectrometer, is described in detail elsewhere (*6*). The formaldehyde was deposited onto the CsI substrate simultaneously with the other premixed sample gases but through a separate tube in order to prevent chemical reactions prior to the deposition. An IR spectrum of the 10 K ice was then taken. The ice sample was subsequently warmed up at a rate of 2 K per minute. The ice's chemical evolution was monitored by measuring the IR spectrum of the sample at various temperatures up to room temperature. This procedure was used to study a wide variety of H_2CO-containing ices including many binary mixtures as well as more complex, multicomponent analogs of astrophysical ices. The ice component concentrations given throughout this report represent relative number abundances (mole fractions). A detailed description of these experiments on H_2CO-containing ices will be reported elsewhere (*9*). Here we focus on the important astrophysical consequences of this new set of reactions.

The spectral evolution upon warmup of the astrophysical ice analog $H_2O:CH_3OH:H_2CO:CO:NH_3 = 100:50:4:1:1$ is shown in Fig. 1. This mixture is representative of interstellar-precometary ices as shown by the generally detailed agreement between the spectrum shown in Fig. 1A and the IR spectra of ices in dense clouds (*6, 11*). Upon warmup to 190 K, the original ice components sublime away and leave behind an organic residue (Fig. 1B). The IR spectrum of the residue has absorption features due to O–H, C–H, and C–O groups. During further warmup to 280 K, these absorption features disappear at different rates, indicating the presence of several molecular components. Warmup of similar ice mixtures without formaldehyde did not leave any detectable residue after ice sublimation, indicating that the compounds in these residues formed from chemical reactions involving H_2CO.

We have extensively investigated the role of the specific molecules of astrophysical significance: H_2O, CH_3OH, CO, and NH_3 in a large number of mixtures containing formaldehyde (*9*). In all cases, trace amounts of NH_3 ($NH_3/H_2CO \geq 0.005$) in the ice sample were required to obtain detectable quantities of residue. The fraction of formaldehyde initially present that was converted to organic products varied from ~40% for $NH_3/H_2CO = 0.005$ to near 100% for $NH_3/H_2CO \geq 2$ in $NH_3:H_2CO:H_2O$ mixtures with $H_2O/H_2CO \leq 50$. The IR spectra of the five products we isolated in the residues resulting from the warmup of various mixtures are shown in Fig. 2. The different products could be distinguished from one another by their varying volatility and varying abundance with initial ice composition. The positions and identifications of the IR features of each of the five products are listed in Table 1. The first product (Fig. 2A) was identified as polyoxymethylene (POM) by its characteristic IR spectrum. Products X, Y, and M (Fig. 2, B to D) must be small species (one to four C atoms) because they evaporated below 280 K. From the initial ice composition which favored a particular product, it was deduced that X is exclusively a reaction product of H_2CO with NH_3, M of H_2CO with CH_3OH, whereas Y seems to be formed by reactions of H_2CO with both H_2O and CH_3OH. Product Z is likely a polymer similar to POM, perhaps with some of the H atoms replaced by -OH groups. Possible identifications are shown in Table 2. The nature of the H_2CO chem-

Table 1. Infrared band positions (wavenumbers) and assignments of the species produced by H_2CO reactions in ices containing H_2O, CH_3OH, H_2CO, CO, and NH_3. See spectra in Fig. 2.

Vibration	POM*	X	Y	M	Z
O–H stretch		3060	3300	3300	3280
C–H stretch	2974	2950	2961	2954	2970
	2914	2880	2892	2895	2914
	2787		2780	2777	
NH_2 deformation		1608			
CH_2/CH_3 deformation	1465	1464	1360	1445	
	1430	1385		1410	
	1380				
C–O/C–N stretch	932	1006	1050	1058	1038
	902		960	982	993
Unidentified	1282		1178	1154	1280
	1233				1236
	1098				1122
	627				732

*Assignments for the POM features are approximate only. See (*10*) for exact assignments.

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istry depends strongly on the NH_3 concentration. For the mixture shown in Fig. 1A, when the NH_3/H_2CO ratio was very small (~0.02 or less), reactions of H_2CO with CH_3OH and H_2O predominated, producing M, Y, and some POM. When the NH_3/H_2CO ratio was between about 0.2 and 0.3, reactions between CH_3OH and H_2CO declined, reducing the production of M. Finally, at higher NH_3/H_2CO ratios, reactions of H_2CO with NH_3 and H_2O were important, whereas reactions with CH_3OH were not. In this case, the products were X, Y, and some POM. Product X, which appears to contain hydroxy and amino groups (Table 2), may be an amino acid precursor, requiring oxygen substitution of the two hydrogen atoms on the OH-containing carbon atom.

For the binary mixtures of H_2CO containing some NH_3, the IR spectra are simple, and spectral evidence for a new product is clear at 40 K. In the H_2O-rich ices, the IR spectra are rich, and unequivocal spectral structure due to products from H_2CO reactions is first evident at 80 K. It is not clear whether 80 K is the actual onset temperature in these more complex ices or the temperature at which enough new product formed to produce clear spectral structure.

The results of these experiments have important implications for both cometary science and interstellar chemistry. These experiments demonstrate that thermal H_2CO reactions in realistic astronomical ices can produce substantial amounts of complex organic material at very low temperatures. The organics produced are different from those produced by ultraviolet irradiation (*5*, *9*, *12*). Thus, analyzing cometary samples for the compounds produced by thermal H_2CO reactions and by energetic processing has the potential to provide deep insight into the processes that played important roles in a comet's history. Quantifying the amounts present would indicate the relative importance of these very different processes in a comet's history. These thermal reactions may also provide some explanation of why H_2CO has not yet been definitely detected in interstellar ice spectra, in spite of the ease with which it is

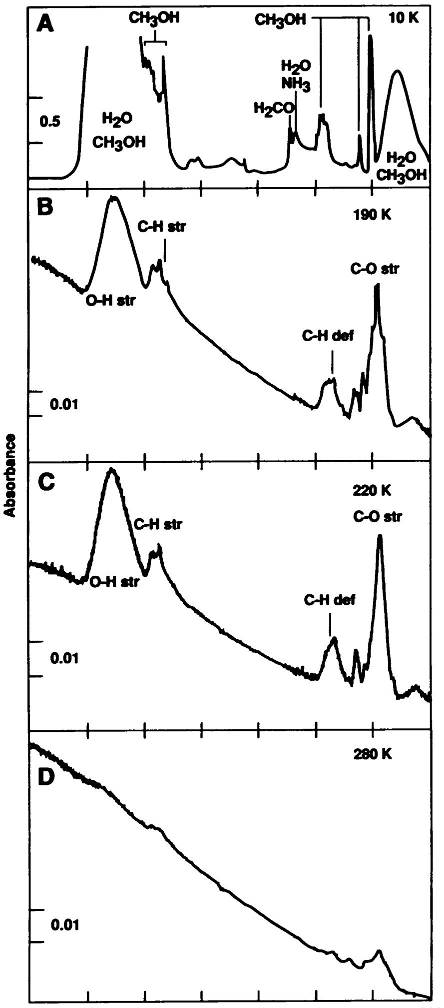

Fig. 1. Spectral evolution of an H_2O:CH_3OH:H_2CO:CO:NH_3 = 100:50:4:1:1 astrophysical ice analog upon warmup: (**A**) directly after deposition at 10 K; (**B**) after warmup to 190 K; (**C**) after warmup to 220 K; and (**D**) after warmup to 280 K. Abbreviations: str, stretch; and def, deformation.

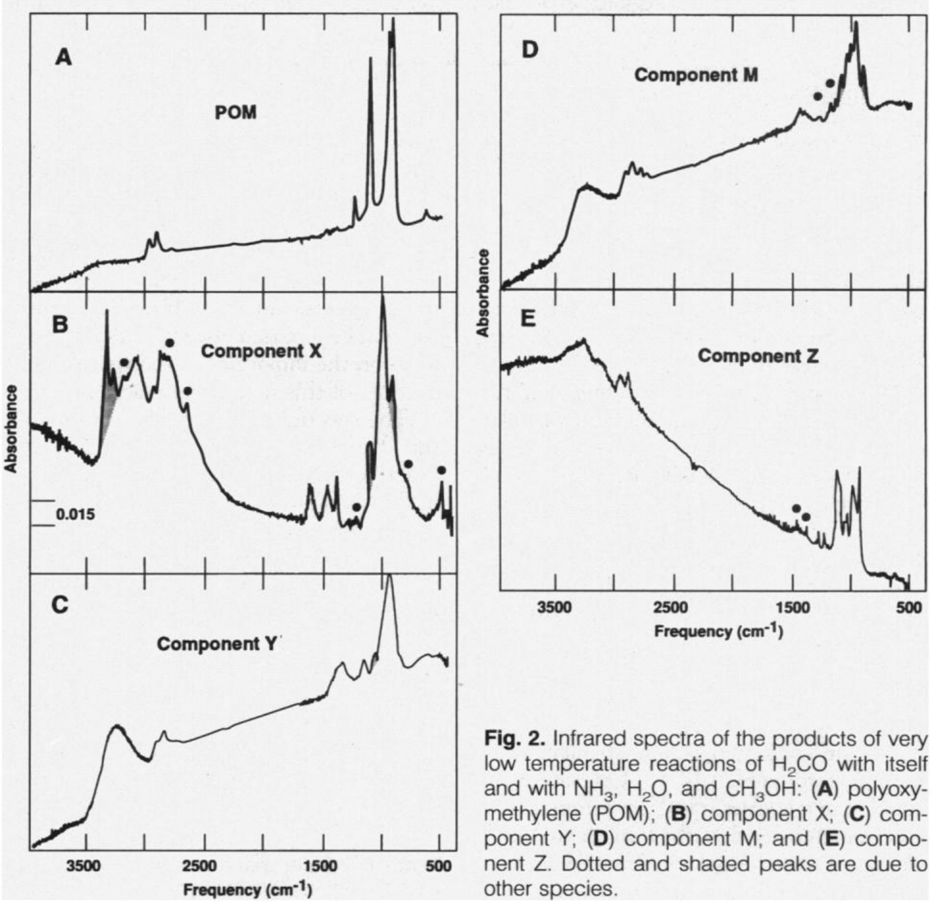

Fig. 2. Infrared spectra of the products of very low temperature reactions of H_2CO with itself and with NH_3, H_2O, and CH_3OH: (**A**) polyoxymethylene (POM); (**B**) component X; (**C**) component Y; (**D**) component M; and (**E**) component Z. Dotted and shaded peaks are due to other species.

Frequency (cm-1)
other species.

Table 2. Conditions and chemical formulae consistent with the infrared spectra of the products of thermal formaldehyde reactions in ice mixtures of H_2CO, CH_3OH, H_2CO, CO, and NH_3. Components:POM, polyoxymethylene; X, amine, hydroxy-substituted polyoxymethylenes; Y, POM-glycol family (such as methylene glycol and dioxymethylene glycol); M, γ- and δ-POM family; and Z, ? unidentified species.

Component	Conditions	Example formulae	
POM	H_2CO polymerizes with an NH_3 catalyst	$[-CH_2-O-]_n$	
X	H_2CO reacts with NH_3	$HO-CH_2-NH_2$	$HO-CH_2-O-CH_2-NH_2$
Y	H_2CO reacts with H_2O or with CH_3OH	$HO-CH_2-OH$	$HO-CH_2-O-CH_2-OH$
M	H_2CO reacts with CH_3OH	$H_3C-CH(OH)-O-CH_3$ $H_3C-O-CH_2-O-CH(OH)-O-CH_3$	
Z	Intermediary to POM and Y(?)	POM with OH groups replacing some H(?)	

produced in irradiation experiments and the high grain abundances (for example, 50% with respect to H_2O) predicted by interstellar chemistry models. Given interstellar cloud lifetimes, slight warming should suffice to convert the H_2CO to POM derivatives. These may be detectable as substructure near 1000 cm^{-1} (10 μm) on the interstellar silicate feature at the precise peak positions listed in Table 1. Furthermore, the compounds produced could participate in other reactions, providing a new set of complex organics not previously considered. In dense, hot cores where ice grains would evaporate, some of the products might be observable in the gas phase (*13*).

There are already applications for these results to comet science. We can use the H_2CO and NH_3 abundances determined for Comet Halley from ground-based and in situ measurements by Giotto and Vega to estimate that $\sim$3% of the organic in Comet Halley are produced by thermal H_2CO reactions in the nucleus. These molecules would be very oxygen-rich ($C/O \approx 1$) and would have alcohol-, ether-, and amine-type properties. The nature of the products and their relative abundances strongly depend on the initial ice composition and would therefore be a sensitive tracer of the chemical conditions inside the nucleus. Furthermore, these materials could contribute to the IR emission already detected from comets. Several of their CH stretching bands peak at positions spanned by the "3.4-μm" cometary emission feature (*14*).

Chemical analysis of the products of low-temperature H_2CO reactions are necessary to better characterize the molecules that are expected under astrophysical conditions. Such studies are essential to understand the origin of the organic molecules observed in the interstellar medium and in comets as well as the processes and the chemical conditions in the ices where they were formed.

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Specific Heat and Thermal Conductivity of Solid Fullerenes

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Evidence is presented that the lattice vibrations of compacted C_{60}/C_{70} fullerite microcrystals consist predominantly of localized modes. Vibrational motions of the rigid molecules ("buckyballs") have been identified as well as their internal vibrations. Debye waves play only a relatively minor role, except below $\sim$4 kelvin. By comparison with other crystalline materials, for these materials the Einstein model of the specific heat and thermal conductivity of solids, which is based on the assumption of atoms (in this case, buckyballs) vibrating with random phases, is in much better agreement with the measurements than the Debye model, which is based on collective excitations.

The first model for lattice vibrations of solids was proposed in 1907 by Einstein, who applied the quantum concept to the mechanical motion of individual atoms in a crystal lattice that he assumed to be vibrating with random phases (*1*). He subsequently found that this model was inadequate, its most drastic shortcoming being that it led to a thermal conductivity that disagreed with the observation on crystals both in magnitude and in temperature dependence (*2*). This disagreement was removed by Debye (*3*) and by Born and von Karman (*4*), who demonstrated that in crystalline solids the atoms vibrate collectively as elastic waves. This picture has been tested extensively and is now generally accepted. Exceptions have been noted, however. In amorphous solids and certain disordered crystals, for example, the thermal conductivity above $\sim$50 K can be well described with Einstein's picture (*5, 6*) (although the cause for the random phase of vibration of the neighboring atoms, the crucial assumption in Einstein's picture, is not yet understood). Also, in some crystalline polymeric solids, the specific heat has been shown to be well described over a wide temperature range with a set of Einstein modes consisting of vibrational motions of certain molecular units (*7*). However, in crystal lattices of simple atomic constituents, the model of collective wave motion has always been found to be correct.

We report here on a polycrystalline disordered solid of a rather simple composition in which the lattice vibrations are predominantly localized. Above $\sim$4 K, both its specific heat and its thermal conductivity can be quantitatively described with Einstein's model, thus showing clearly the limitations of the commonly used picture that is based on plane waves.

The starting material was microcrystalline ($\sim$1 μm) commercial (*8*) fullerite powder containing $\sim$85% C_{60} and $\sim$15% C_{70} molecules (buckyballs), which had been extracted with toluene. Without any further treatment, the powder was compressed in a pellet press at 3000 atm, which resulted in pellets of a strength comparable to that of soft pencil graphite. This procedure enabled us to prepare samples of sufficient size to perform the measurements. Their mass density $\rho = 1.54$ g cm^{-3} ($\pm 10\%$) was close to the theoretical density ($\rho_{\text{theor}} = 1.676$ g cm^{-3}) of the face-centered-cubic (fcc) lattice. From Debye-Scherrer x-ray diffraction measurements, an fcc lattice constant of $a = 14.1 \pm 0.1$ Å was determined, near the accepted value for pure C_{60} ($a_{60} = 14.186$ Å) (*9*). X-ray line shapes of the powder as received and of the compact solid were virtually identical. We also investigated the thermal properties of compacts made of C_{60} starting material and obtained similar results (*10*). Thus, the presence of C_{70} appears to be irrelevant as far as the observations reported here and their interpretation are concerned. To avoid any ambiguity, however, we refer to the samples studied here as C_{60}/C_{70} compacts. Small changes of the low-temperature specific heat were also observed when the starting material or the

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