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VERY LOW TEMPERATURE FORMALDEHYDE REACTIONS AND THE BUILD-UP OF ORGANIC MOLECULES IN COMETS AND INTERSTELLAR ICES

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ABSTRACT

We have investigated thermally promoted reactions of formaldehyde (H_2CO) in very low temperature ices. No such reactions occurred in ices of pure formaldehyde. However, addition of trace amounts of ammonia (NH_3) were sufficient to catalyze reactions at temperatures as low as 40 K. Similar reactions could take place in interstellar ices and in Comets and produce considerable amounts of organic molecules.

INTRODUCTION

Formaldehyde (H_2CO) is present in comet ices at the few percent level relative to H_2O /1/. Also interstellar ices likely contain important amounts of formaldehyde /2,3/. We have studied if reactions involving the highly reactive H_2CO molecule can proceed at the low temperatures relevant to such environments. The set-up used in our experiments consists of a vacuum chamber containing a rotatable CsI substrate which can be cooled down to 10 K, on which gas-mixtures are condensed /3,4/. The condensed sample is monitored by a Fourier transform Infrared spectrometer. After condensation the sample was warmed-up at a rate of

2K/min. The warm-up was halted at regular intervals and IR spectra were taken to monitor the chemical evolution of the sample.

RESULTS

Figure 1 shows the thermal evolution of the condensed ice sample $H_2CO:NH_3=100:2$. The 10 K spectrum of the ice does not differ significantly from that of pure H_2CO. During warm-up, strong new features appear around 70 K and remain even after all H_2CO has sublimed. The infrared spectum of the newly formed component is characteristic for the H_2CO polymerization product polyoxymethylene (POM). Pure H_2CO ices, on the other hand, did not produce any new products during warm-up. Therefore, the presence of NH_3 in the ice seems necessary to decrease the reaction barrier and enable H_2CO reactions to take place at very low temperatures.

Figure 2 shows the appearance of POM as a function of temperature for binary mixtures with varying NH_3/H_2CO ratio's. It can be seen that the onset of the H_2CO reactions occurs at slightly higher temperatures for lower NH_3 abundances, i.e, around 40 K for $H_2CO/NH_3 = 4.3$ to around 70 K when $H_2CO/NH_3 = 0.02$. Also the disappearance of the H_2CO is displayed in figure 2 for the mixture $H_2CO/NH_3 = 0.6$ and for pure formaldehyde ice, showing that in the ammonia containing ice, the H_2CO disappears at considerably lower temperatures due to chemical reactions. In the pure ice, the formaldehyde is lost exclusively by sublimation.

In summary, it was found that thermally promoted formaldehyde reactions can take place at very low temperatures, i.e, 40 - 70 K, in the presence of, at least, trace amounts of NH_3. For ices containing only small amounts of ammonia, the reactions produce the formaldehyde polymer polyoxymethylene (POM). For a discussion of the formaldehyde chemistry in more complex ice mixtures we refer to Schutte et al. 1993 /4/.

ASTROPHYSICAL IMPLICATIONS

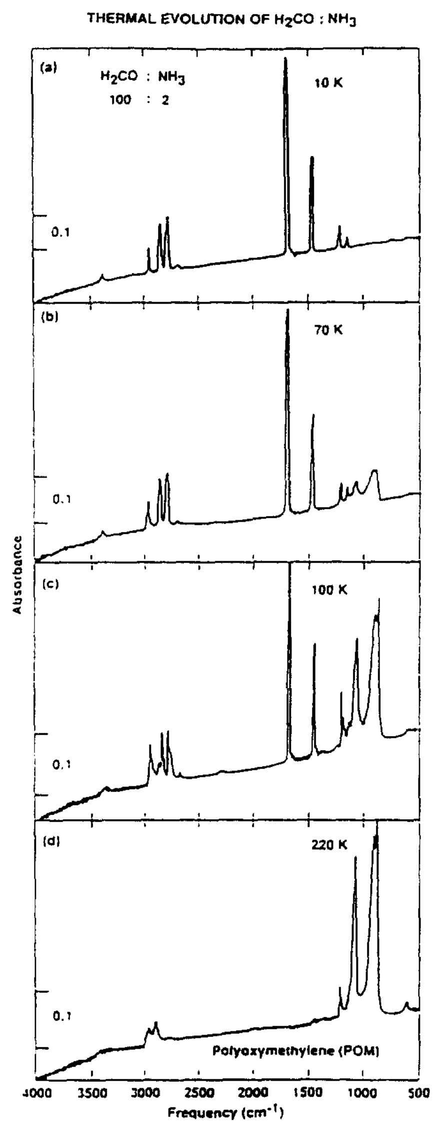

Figure 1. The spectral evolution of an H_2CO:NH_3 = 100:2 ice mixture during warm-up. (a) Directly after deposition at 10 K. This spectrum is essentially that of pure H_2CO as the NH_3 bands are very weak at this concentration; (b) After warm–up to 70 K (note the appearance of POM features); (c) After warm–up to 100 K; (d) After warm–up to 220 K (at this point the spectrum is characteristic of POM).

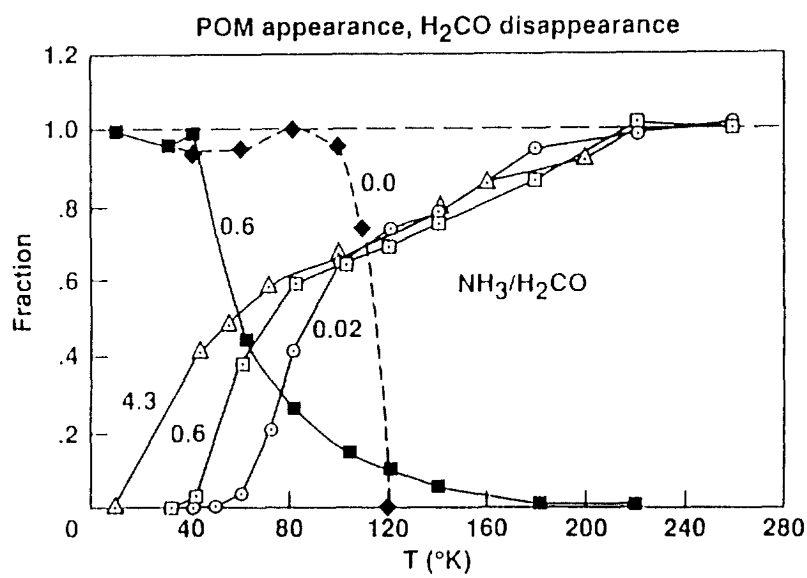

Figure 2. The growth of POM and the loss of H_2CO during warm–up for a number of ice mixtures of NH_3andH_2CO. The curves give the disappearance of H_2CO in the mixture $NH_3/H_2CO = 0.6$ (filled squares) and for pure H_2CO (filled diamonds), and the appearance of POM in the mixtures $NH_3/H_2CO = 0.02$ (open circels), 0.6 (open squares), and 4.3 (open triangles). The loss curves are normalized to 1 at the 10 K point and the growth curves are normalized to 1 at the 260 K point.

The results of our experiments indicate that thermally promoted formaldehyde reactions can take place at the ambient temperatures inside comet nuclei if some NH_3 is present /5,6/. Such reactions could be an important source of the organic molecules that have been found in the coma's of various comets. In interstellar ices formaldehyde reactions could take place when the temperature of the ice mantles is slightly raised above their nominal value inside dense clouds (about 10 K), for example, in the vicinity of protostars or in dense hot cores. Some of the reaction products may than sublimate and be observable in the gas phase /7/. An extensive discussion on the likely nature of the formaldehyde reaction products in cometary and interstellar ices and the amount of organics that may be produced will be given elsewhere /4,8/.

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