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Formaldehyde chemistry in cometary ices: implication for the Rosetta mission

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Abstract

Laboratory simulations on interstellar or cometary ice analogues are crucial to understand the formation of complex organic molecules that are detected in these environments. The aim of this work is to consolidate the knowledge of ice chemical evolution during the star formation process by investigating the influence of thermal reactions as a source of the chemical evolution in space. In this study, we are focused on the thermal reactivity of a H_2O-dominated cometary ice analogues that contain H_2CO and NH_3 by means of Fourier transform infrared spectroscopy (FTIR), mass spectrometry and B3LYP calculations

1. Introduction

The solar system may have formed during the contraction of an interstellar cloud resulting in a new-star and a proto-planetary disk formation. The comets would be then the result of dust and gas accretion in the disk. The presence of highly volatile molecules in the cometary nuclei and the similarity of their composition with interstellar matter strongly suggest that these bodies are the most pristine remainders of the primitive solar nebula composition. Hence, the studies of comets are crucial to understand the history of our solar system [1]. In addition, knowing the internal composition of the nucleus would also provide insights on the nature of the available organic compounds that could have been delivered on the early Earth.

In this work, we study the warming of cometary water-dominated ices containing NH_3 and H_2CO. Based on infra-red and mass spectrometry measurements and complemented by quantum chemical calculations, we report that NH_2CH2OH, $HOCH_2OH$, and POM are the actual reaction products[2-4]. Moreover, the influence of the initial ice composition on the formation of POM oligomers ($HO-(CH2O)_n-H$, n<5) alongside their thermal instability between 200-320 K is investigated. The implications of theses results for cometary nucleus chemistry and their impact on POM detection by the Rosetta mission are finally discussed.

2. Results

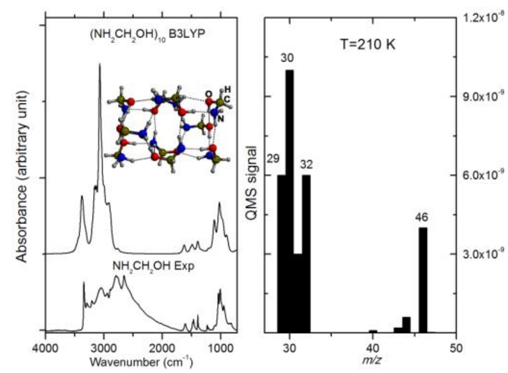

Figure 1: **Left panel**: FTIR spectrum of aminomethanol (NH_2CH_2OH) formed from the warming of a H_2O:NH_3:H_2CO (10:5:0.3) ice mixture. This experimental spectrum is compared with B3LYP/6-31+G(d,p) simulated one for the $(NH_2CH_2OH)_{10}$ system, the optimized structure of which is also shown. **Right Panel**: mass spectrum recorded at 210 K of NH_2CH_2OH.

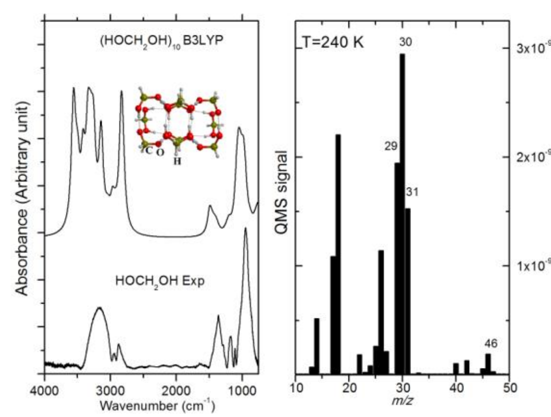

Figure 2 : **Left panel**: FTIR spectrum of methyleneglycol ($HOCH_2OH$) formed from the warming of a H_2O:NH_3:H_2CO (10:0.1:0.4) ice mixture. This experimental spectrum is compared with B3LYP/6-31+G(d,p) simulated one for the $(HOCH_2OH)_{10}$ system, the

optimized structure of which is also shown. **Right Panel**: mass spectrum recorded at 210 K of ($HOCH_2OH$).

In the case of H_2O:NH3:H_2CO ice mixtures where the NH_3/H_2CO concentration ratio is higher than one, the product formed is aminomethanol (NH_2CH_2OH), indicating exclusive reaction between the H_2CO and NH_3 components (Fig 1) [2,3]. In the case of $H_2O:NH_3:H_2CO$ ice mixtures where NH_3/H_2CO concentration ratio is lower than one, the product formed is methyleneglycol ($HOCH_2OH$), indicating exclusive reaction between the H_2CO and H_2O components (Fig 2) [4]. Pure POM, X-(CH_2O)n-H is obtained from a water-dominated ice in which NH_3 is present in trace amounts, probably due to a H_2CO self-polymerization activated by NH_3. Figure 3 shows the POM formation after the warming of an ice mixture of $H_2O:NH_3:H_2CO$ with a 10:0.02:1 [1, 5].

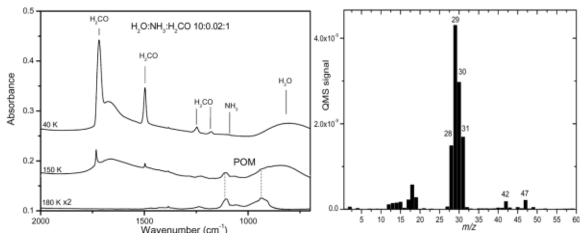

Figure 3 : **Right panel**: FTIR spectra of a $H_2O:NH_3:H_2CO$ ice mixture in a 10:0.02:1 concentration ratio at 40 K, 150 K, and 180 K. Temperature ramp: 4K/min. **Left panel** : mass spectrum of POM recorded during its sublimation at 240 K.

POM formed during the warming consists of short chain polymers (i.e, oligomer of formaldehyde HO-(CH2-O)n-H, n<5) which are volatile for temperature higher than 200 K. This suggests that gas phase detection by the ROSINA instrument on-board Rosetta mission would be the most appropriate instrument to detect POM. Moreover, the reported mass spectra of NH_2CH_2OH, $HOCH_2OH$, and POM might help in the interpretation of data that will be recorded by this instrument [5].

3. Summary and Conclusions

The low-temperature thermal reaction of NH3 and H2CO in water-dominated ices leads to the formation of polyoxymethylene (POM) $HO(CH_2O)_nH$, aminomethanol (NH_2CH_2OH), and methyleneglycol ($HOCH_2OH$). Since H_2O, NH_3, and H_2CO are known constituents of interstellar or pre-cometary ices their formation is likely in warm environment such as hot cores or in cometary environments. We also investigate the influence of the initial ice composition on the thermal stability of POM. We show that in water-dominated ice analogues only short chain polymers of POM (*i.e* HO-(CH_2-O)$_n$-H, n<5) are efficiently formed, suggesting that gas phase detection by the ROSINA instrument on-board Rosetta mission would indeed be the most appropriate instrument to detect POM. Moreover, the reported mass spectra of NH_2CH_2OH, $HOCH_2OH$, and POM might help in the interpretation of data recorded by this instrument.

Acknowledgements

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