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# Formation of Complex Organic molecules from Formaldehyde Chemistry in Cometary Ice Analogues

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There is convincing evidence that the formation of complex organic molecules occurred in a variety of astrophysical environments. Among them, precursors of biomolecules are of particular significance due to their exobiological implications. Hexamethylenetetramine (HMT, C6H12N4) and the polyoxymethylene (POM, -(CH2-O)n-) are of prime interest since they are supposed to be present in cometary environments. They are also ones of the main components of the organic residue formed from the warming of photolysed interstellar/cometary ice analogs. In this work, we study the warming of water-dominated cometary ice analogs containing formaldehyde (H2CO). Based on infrared and mass spectrometry measurements, and complemented by quantum chemical calculations, we report that NH2CH2OH, HOCH2OH, and POM are the only reaction products when the ice also contains NH3. The branching ratio between the three products strongly depends on the initial H2CO/NH3 concentration ratio. Moreover, the influence of the initial ice composition on the formation of POM oligomers (HO–(CH2O)n–H, n<5) as well as their thermal instability between 200 and 320 K are investigated. Finally, the implications of these results with respect to cometary nucleus chemistry and their impact on POM detection by the Rosetta mission are discussed. In addition, the mechanism for HMT formation in interstellar or cometary ice analogs containing H2CO, NH3, and HCOOH has been determined by combining laboratory experiments and DFT calculations. We show that HMT is thermally formed from H2CO and NH3 activated by HCOOH. Two intermediates has been unambiguously detected: NH2CH2OH and the trimer of CH2NH (1,3,5-triazinane, TMT). Unlike to what it was previously thought, HMT is not an indicator of ice photochemistry, but an indicator of thermal processing of ice. These results strengthen the hypothesis that HMT and its intermediates should be present in comets, where they may be detected with the COSAC or COSIMA instrument of the Rosetta mission.