AB INITIO QUANTUM CALCULATIONS OF REACTIONS IN ASTROPHYSICAL ICES: ACETALDEHYDE AND ACETONE WITH AMMONIA

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Complex organic molecules, including amino acid precursors, have been observed in young stellar objects[a]. Both laboratory and theoretical studies have shown that ice chemistry can play an important role in low-temperature synthetic pathways, with water serving as a catalyst that can significantly enhance reaction rates by lowering barriers or eliminating them altogether. Reactions between carbonyl species and ammonia are particularly promising, as shown in previous studies of the formaldehyde-ammonia reaction[b]. In this study, we explore the reactions of ammonia with two larger carbonyl species, acetaldehyde and acetone, embedded in a water ice cluster. To examine the explicit impact of the water, we gradually increase the size of the cluster from $4H_2O$ to $12H_2O$. Cluster calculations were performed at the MP2/6-31+G** or B3LYP/6-31+G** level. In order to account for the electrostatic contribution from bulk ice, the Polarizable Continuum Model (PCM) and Isodensity Surface Polarized Continuum Model (IPCM) were used to model reaction field solvation effects. For both acetaldehyde and acetone, the reactant is a charge transfer complex (a partial charge-transfer complex in small clusters and full proton-transfer complex in larger clusters). Rearrangement to amino-hydroxylated products can occur by surmounting a small reaction barrier. Stereo-selectivity is observed in the case of acetaldehyde.

[a] P. Ehrenfreund and S. B. Charnley, Ann. Rev. Astron. Astrophys. 38, 427 (2000).

[b] W. A. Schutte, L. J. Allamandola, and S. A. Sandford, Science 259, 1143 (1993); Icarus 104, 118 (1993); D. E. Woon, Icarus 142, 550 (1999); S. P. Walch, C. W. Bauschicher, Jr., A. Ricca and E. L. O. Bakes, Chem. Phys. Lett, 333, 6 (2001).