

Quantum Chemical Studies of Ice-Bound Reactions of Carbonyl-Containing Species (Formaldehyde, Acetaldehyde, and Acetone) with Ammonia

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Carbonyl species have been observed in young stellar objects. Prior theoretical work showed that the reaction of formaldehyde with ammonia appears to possess only a very small reaction barrier when confined within in an ice matrix (D. E. Woon, *Icarus* 142, 550 1999). This and reactions of other carbonyl species with ammonia have great potential to be the pathways leading to the production of prebiotic molecules within icy grain mantles in dark interstellar clouds or on cold satellite surfaces. Computational studies on these reactions can provide insights into the reaction mechanisms and evaluate the possibility of certain reaction pathways. With such a goal, we explored the reactions between ammonia and formaldehyde, acetaldehyde, and acetone in the presence of ice water clusters. To examine the explicit impact of the water to the reaction barriers, we gradually increase the size of the cluster from $4\text{H}_2\text{O}$ to $12\text{H}_2\text{O}$. 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 calculations) were used to model reaction field solvation effects. We found that ammonia reacts with all three carbonyl species with no barrier to form 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. One of the intriguing features of the ammonia-acetaldehyde reaction is that it yields stereoisomers with slightly different reaction barriers and thus a preference for one over the other.

Support for this work was provided by the NASA Astrobiology: Exobiology and Evolutionary Biology Program (grant NNX07AN33G).