QUANTUM CHEMICAL CLUSTER STUDIES OF ICE-BOUND REACTIONS OF FORMALDEHYDE (H_2CO), ACETALDEHYDE (CH_3CHO), OR ACETONE (CH_3COCH_3) WITH AMMONIA (NH_3)

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While many of the reactions that can occur in icy grain mantles in cold interstellar clouds are either barrierless recombinations of open-shell radicals or are driven by energetic processing (photolysis, radiolysis, or shocks), there is a group of unusual reactions involving stable, closed-shell species that can also be efficient at very low temperatures. Previous experimental work[a] found that H_2CO and NH_3 can evidentally react at temperatures under 70 K if they are embedded within an ice matrix, a conclusion that was subsequently confirmed theoretically[b]. To assess the impact of including more water, cluster calculations were performed at the MP2/6-31+G** or B3LYP/6-31+G** level with up to $4H_2O$ and $12H_2O$, respectively. Electrostatic contributions from bulk ice were modelled with either PCM and IPCM reaction field solvation. In addition to revisiting $H_2CO + NH_3$, we also characterized the reactions of ammonia with acetaldehyde and acetone. The new work confirms that the reaction barriers are very small, but it also indicates that water induces a substantial interaction between NH_3 and the carbonyl species in the solvated pre-reaction complexes. In small clusters, the C-N distance decreases by about 1 Å, and partial charge-transfer complexes are formed. In large clusters, a proton transfers to yield cationic complexes. We will present an analysis of potentially observable vibrational features of these complexes.

[a]W. A. Schutte, L. J. Allamandola, and S. A. Sandford, *Science* 259, 1143 (1993); *Icarus* 104, 118 (1993).
[b]D. E. Woon, *Icarus* 142, 550 (1999).