MATRIX ISOLATION FTIR AND AB INITIO STUDIES ON THE CONFORMATIONS OF DIMETHYL AND DIETHYL CARBONATE AND THEIR COMPLEXES WITH WATER

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Dimethyl carbonate (DMC) and diethyl carbonate (DEC) have been studied for their conformations using matrix isolation infrared spectroscopy and ab initio computations. In addition to the above studies, the complexes of the two compounds with water have also been studied. The experiments were corroborated with ab initio calculations at the $B3LYP/6-31++G**$ level. The organic carbonates were trapped in argon and nitrogen matrixes using an effusive source maintained at two different temperatures; i.e. room temperature and 170°C. In addition the matrix was also deposited using a supersonic jet source. These experiments were performed to alter the relative population of the various conformations, to aid us in the assignments of the vibrational features. The conformation of DMC corresponding to the global minimum of DMC was found to be a cis-cis conformer where the two methyl groups are found to be at cis position with respect to the carbonyl oxygen. The next higher energy conformer corresponded to a cis-trans structure with a near trans-near trans structure being the highest energy conformer. In our experimental matrix isolation spectra of DMC, we were able to assign features due to the cis-cis and cis-trans conformers. The features of the higher energy cis-trans conformer was confirmed with our experiments using the elevated temperature effusive source and the supersonic source. DEC displays a richer conformational landscape due to the presence of a longer carbon chain. The computational and experimental indicate that the ground state conformer for this compound is one in which carbon attached to oxygen adopts a cis configuration with respect to the carbonyl oxygen, while the terminal carbon adopts an anti conformation. A detailed study of the conformational picture of DEC will be presented. In addition to the above conformational studies, $1:1$ hydrogen bonded complexes of DMC and DEC with water were also observed in the matrix, which was corroborated by our computations. Studies of the water complexes of DMC and DEC will also be presented.