

Photo-induced hydrogen exchange reaction between methanol and glyoxal: formation of hydroxyketene.

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Streszczenie

We study the structure and photochemistry of the glyoxal-methanol system (G-MeOH) by means of FTIR matrix isolation spectroscopy and ab initio calculations. The FTIR spectra show that the non-hydrogen-bonded complex, G-MeOH-1, is present in an inert environment of solid argon. MP2/aug-cc-pVDZ calculations indicate that G-MeOH-1 is the most stable complex among the five optimized structures. The interaction energy partitioned according to the symmetry-adapted perturbation theory (SAPT) scheme demonstrates that the dispersion energy gives a larger contribution to the stabilization of a non-hydrogen-bonded G-MeOH-1 complex than compared to the hydrogen-bonded ones. The irradiation of G-MeOH-1 with the filtered output of a mercury lamp ($\lambda > 370$ nm) leads to its photo-conversion into the hydroxyketene-methanol complex HK-MeOH-1. The identity of HK-MeOH-1 is confirmed by both FTIR spectroscopy and MP2/aug-cc-pVDZ calculations. An experiment with deuterated methanol (CH_3OD) evidences that hydroxyketene is formed in a photo-induced hydrogen exchange reaction between glyoxal and methanol. The pathway for the photo-conversion of G-MeOH-1 to HK-MeOH-1 is studied by a coupled-cluster method [CR-CC(2,3)]. The calculations confirm our experimental findings that the reaction proceeds via hydrogen atom exchange between the OH group of methanol and CH group of glyoxal.

Adres publiczny

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