Photochemistry of Cycloheptatriene in solid *para*hydrogen

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Cyclic hydrocarbons with diene bonding in a ring structure are of interest in various fields of biological and material sciences due to their unique electron configuration and high chemical reactivity. Specifically, the photochemical reactions of those cyclic hydrocarbons are known to involve several processes, such as ring closure, ring opening, and the formation of small ring compounds. Cycloheptatriene (C_7H_8: CHT) is a seven-membered ring compound with three diene bonds in its ring structure, and it has a wide range of applications in chemical synthesis and biological research. The photochemistry of CHT, irradiated with a low pressure Hg arc lamp, has been studied in Ar and N_2 matrices, in which bicyclo[3.2.0]hepta-2,6-diene (BCHD) was detected as the sole photochemical product [1)]. In this study, we investigated the photochemistry of CHT in solid *para*hydrogen, irradiated with an ArF excimer laser (193 nm) and the fifth harmonic Nd: YAG laser (216 nm), aiming to confirm the photochemical stability, reactivity, and photochemical products.

The mixture of CHT and *para*hydrogen was condensed on the cold substrate at 4.2 K cooled down by a closed-cycle GM refrigerator. The CHT in solid *para*hydrogen was irradiated by an ArF pulsed laser (MPB CEX-100) or a Nd:YAG laser (Litron Lasers NanoS), and photochemical products were measured by FT-IR (Brucker, IFS 125HR). To confirm the spectral assignment of the reactants and products, DFT calculations (Gaussian03/16 DFT/UB3LYP/6-311(d,p)) were performed.

In the subtracted IR spectra of CHT in solid *para*hydrogen after ArF irradiation, we observed the peaks of BCHD as the initial photoproducts. Upon prolonged irradiation using ArF, cyclopentadiene (Cpd) and acetylene were also detected, accompanied by a decrease in BCHD. Therefore, we assumed that Cpd and acetylene are produced as decomposition products of BCHD. At lower concentrations, we observed that BCHD and Cpd are produced initially, and both molecules are decomposed, leading to the production of methane and ethylene after further ArF irradiation. The stability and reactivity of photochemical products of CHT in solid *para*hydrogen will be discussed. This work was partially supported by Research Institute for Science and Technology of Tokyo Denki University Grant Number Q23K-03/Japan.

[1)] Samuni, U.; Kahana, S.; Haas, Y. Matrix Photochemistry of Cycloheptatriene: Site Effects *J. Phys. Chem. A* **1998**, 102 4728