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Tunneling hydrogenation and deuteration of solid benzene without large kinetic isotope effects

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The hydrogenation/deuteration of interstellar aromatic hydrocarbons is of particular interest, because the presence of saturated cyclic hydrocarbons has been suggested in the interstellar medium, and interstellar deuterated aromatic and aliphatic hydrocarbons could account for deuterium enrichment observed in carbonaceous meteorites and interplanetary dust particles. Aromatic hydrocarbon is one of the main components of interstellar dust. In cold molecular clouds, H and D atoms can barrierlessly adsorb on the dust surface, and the gaseous atomic D/H ratio can be strongly enhanced to be 10^{-2} - 10^{-1} by gas phase chemistry. Therefore, efficient hydrogenation/deuteration reactions of aromatic hydrocarbons are expected. However, thermally activated reactions rarely occur over the activation energy barriers at low temperatures (10-50 K), and thus quantum tunneling becomes important.

The present study investigates the surface hydrogenation/deuteration reactions of amorphous solid benzene (C_6H_6) at low temperatures of 10-50 K. We exposed amorphous C_6H_6 solid samples to cold (120 K) H or D atoms. In situ infrared spectroscopy revealed that cyclohexane (C_6H_{12}) or deuterated cyclohexane ($C_6H_6D_6$) are efficiently formed by H or D atom addition to solid C_6H_6, respectively. Given the activation barriers and low temperatures, the hydrogenation/deuteration reactions proceeded via tunnelling.

Remarkably, the ratio of the hydrogenation/deuteration rates (H/D) was found to be 1-1.5 at 15-25 K, whereas the intrinsic H/D kinetic isotope effect (KIE) associated with tunneling was theoretically estimated to be over 100. Our result suggests that the intrinsic tunneling KIE can be considerably masked by surface processes that are insensitive to the isotope of the reactant atoms (e.g., adsorption and diffusion). The present study implicates that interstellar aromatic hydrocarbons can be hydrogenated or deuterated by the tunneling of H or D atoms at low temperatures. The tunneling KIE would not strongly inhibit the deuteration, and it might represent a major deuteration mechanism for interstellar aromatic hydrocarbons.

REFERENCES

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