Hydrogen atom addition reactions to solid benzene by quantum tunnelling and its strong structure dependence

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Aromatic and aliphatic hydrocarbons are abundant in the interstellar medium, and they carry a number of infrared features. Benzene (C_6H_6), the simplest aromatic hydrocarbon, has been detected in circumstellar environments such as post-asymptotic giant branch objects. Recent experimental studies reported that aromatic hydrocarbons such as C_6H_6 and naphthalene ($C_{10}H_8$) are efficiently produced in cold interstellar clouds via gas-phase reactions [1]. One might expect that the formation of saturated hydrocarbon can be easily achieved in these regions considering the overabundance of hydrogen in the interstellar medium. However, an activation barrier of about 20 kJ mol^{-1} generally exists for hydrogenation of aromatic hydrocarbon in order to break the aromaticity. At typical interstellar grain temperatures, i.e., at T~10–50 K, C_6H_6 weakly adsorbs on the surface of interstellar dust grain through van der Waals forces, which should only acts as an inert surface. Therefore, Hydrogen (H) atoms cannot add to the C_6H_6 by overcoming the activation barrier.

The present study shows that H atoms can efficiently add to C_6H_6 molecules on the surface of amorphous C_6H_6 at 10–50 K by quantum tunneling to form the cyclic saturated hydrocarbon, cyclohexane (C_6H_{12}).

$$C_6H_6 + H \rightarrow C_6H_7, \quad E_a = 15.5 \text{ kJ mol}^{-1}, \quad (1)$$
$$C_6H_7 + H \rightarrow C_6H_8, \quad (2)$$
$$C_6H_8 + H \rightarrow C_6H_9, \quad E_a = 6.3 \text{ kJ mol}^{-1}, \quad (3)$$
$$C_6H_9 + H \rightarrow C_6H_{10}, \quad (4)$$
$$C_6H_{10} + H \rightarrow C_6H_{11}, \quad E_a = 10.5 \text{ kJ mol}^{-1}, \quad (5)$$
$$C_6H_{11} + H \rightarrow C_6H_{12}, \quad (6)$$

Here, E_a represents the activation barrier in the gas phase. The radical–radical recombination reactions (2), (4), and (6) should be barrier-less. We also report that the surface structure strongly determined the hydrogenation efficiency; hydrogenation was completely suppressed on a crystalline C_6H_6 surface.

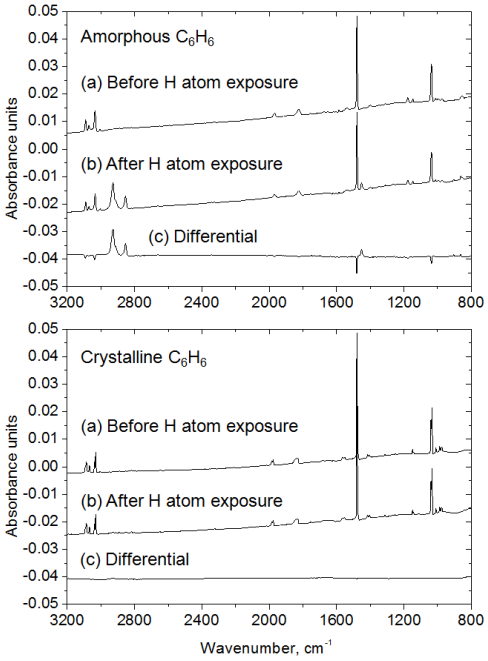

Fig.1 Infrared absorption spectra over the range of 3200–800 cm^{-1} for (upper panel) amorphous solid C_6H_6 and (lower panel) the crystalline C_6H_6 of 6×10^{15} molecules cm^{-2} at 20 K: (a) before and (b) after cold H atom exposure for 180 min. (c) differential spectra upon H atom exposure on the two surfaces ((b) − (a)).

References

[1] Jones et al., 2010, PNAS 108, 452.