Unique properties of *para*-hydrogen matrix isolation: bevel-gear type rotation and hydrogen tunneling reactions

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Solid *para*-hydrogen (p-H_2) has emerged as a novel host for matrix-isolation studies. Due to its unique properties, this quantum solid has revealed several applications unachievable with noble-gas matrix-isolation techniques, such as the presence of single-axis internal rotation, production of free radicals upon photolysis *in situ*, and hydrogen tunneling reactions.[1,2]

Whether the structure of C_6H_6X (X = halogen) is an open or a bridged form has been debated. We previously made use of the diminished cage effect of p-H_2 to generate Cl atoms from *in situ* photolysis of Cl_2 to react with C_6H_6 to produce C_6H_6Cl.[3] The observed IR spectra clearly indicated that C_6H_6Cl has a η_1 structure with σ-bonding. Unlike the C_6H_6Cl σ-complex, the observed infrared spectrum from Br + C_6H_6 indicates that C_6H_6Br is an open-form π-complex. Furthermore, lines of the two CH out-of-plane bending modes associated with mainly even- and odd-numbered carbons, predicted near 672 and 719 cm^{-1}, merged into a broad line at 697.3 cm^{-1}, indicating that these modes become nearly equivalent as Br migrates from one carbon atom to another. Quantum-chemical calculations support that the benzene ring performs a bevel-gear-type rotation with respect to Br. Furthermore, observation of only *trans-ortho*- and *trans-para*-$C_6H_6Br_2$ suggests that this gear-type motion allows the additional Br atom to attack C_6H_6Br only from the opposite side of the Br atom in C_6H_6Br.

H-atom tunneling reactions play important roles in astrochemistry, but an understanding of these reactions is still in its infancy. We have investigated reactions of H atoms with astronomically relevant species such as methanol, formamide, methyl formate, acetamide, acetic acid, glycine, methyl amine, and N-methyl formamide $HC(O)NHCH_3$ in solid p-H_2. Among them, H-abstraction and H-addition reactions of formamide or methyl amine form a dual cycle that chemically link $HC(O)NH_2$ and HNCO or CH_3NH_3 and CH_2NH, respectively. In reaction H + *trans*-NMF, surprisingly, isomer *cis*-NMF, which has higher energy, increased continuously in darkness, demonstrating a previously overlooked and seemingly unlikely isomerization process. These results indicate that, unlike the dual cycle of H-abstraction and H-addition channels chemically linking formamide and HNCO, H addition to CH_3NCO produced only *cis*-•C(O)NH(CH_3) radical that led to the formation of *cis*-NMF via further H addition.

References:

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