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Quantum chemical study of methanol interaction with a pyrene-based acid

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The conversion of methanol (MeOH) to dimethyl ether (DME) is a large-scale industrial process, and developing advanced catalysts to reduce costs is important. Oxygen-containing carbons are promising metal-free catalysts for many reactions; therefore, this report presents quantum-chemical calculations (DFT, M062X/6-31G**/D3, ORCA 6.0.0) of the interaction between MeOH and pyrene-based acid (Pyr) in the gas phase at T = 0 K to elucidate the initial interaction mechanism for further investigation of the Methanol-to-DME conversion.

Geometry optimisation yielded two acid isomers (A and B), depending on the orientation of the –COOH group plane relative to the aromatic plane. The –COOH group was covalently bonded to the terminal hexagonal carbon atom (alpha carbon) of the Pyr molecule (instead of a hydrogen atom) in the so-called syn conformation (where the O=C–O–H dihedral angle (θ) is defined to be 0°). Isomer A has a more twisted –COOH group relative to the aromatic core (θ=19.96°) than isomer B (θ=0.82°), due to the asymmetry of the carbon skeleton. The total energy of the planar B-Pyr acid is lower by 5.95 kJ/mol than that of the twisted A-Pyr acid molecule.

Bader's Quantum Theory of Atoms in Molecules was used to identify the presence or absence of intramolecular hydrogen bonds (HB) in Pyr. The topological analysis of the electron density distribution confirmed the presence of two intramolecular HBs in the B-Pyr (between O atoms of the –COOH group and H atoms of the aromatic core), as evidenced by the presence of the corresponding bond critical points (BCPs) of type (3, –1). In contrast, only a single intramolecular HB was observed in the A-Pyr acid (between the O atom of the –OH group and the hydrogen atom of the aromatic core). Despite the C=O···H–C length being 2.361 Å (less than the sum of the van der Waals radii of the O and H atoms, which is 2.5 Å), there are no BCPs according to Bader's analysis. Two possible ways of MeOH interaction with the B-Pyr acid are considered: formation of a cyclic complex (CC) and attack of the –C=O of the Pyr by MeOH. The CC is stabilised by two intermolecular HBs, forming a six-membered ring (6MR) between the –COOH group atoms of the Pyr acid and the –OH group atoms of the MeOH molecule. The interaction energy is –66.48 kJ/mol. The CC have two tautomeric forms (causing asymmetry in the carbon skeleton), more twisted CCa and CCb, which can interconvert through an activation barrier of 42.40 kJ/mol. The transition state (TS) for the transition between CCa and CCb structural isomers is characterised by a flip-flop switching of a hydrogen atom between adjacent acceptor centres (two O atoms of the –COOH group and one O atom of the MeOH), forming a two-sided hydrogen trap. The configuration of CCb is thermodynamically more stable than CCa, since its formation energy is lower by 4.43 kJ/mol.

In the second pathway, the MeOH molecule attacks the C=O bond of the Pyr, forming a tetrahedral structure because the carbon atom orbitals in the –COOH group change hybridisation from sp2 to sp3. This atom is bound to four substituents: a Pyr-based group (–C16H9), two –OH groups and a single methoxy group (–OCH3). The analysis of the atomic vibrations for the cyclic four-membered TS structure confirmed the presence of a single imaginary frequency at i1620.70 cm–1. The activation barrier is +169.01 kJ/mol, and the adsorption energy is +23.88 kJ/mol.

Based on the obtained energetic parameters, it was established that the bonding of the MeOH molecule preferentially proceeds via the formation of 6MR CC structures, as this pathway is significantly more energetically favourable than direct attack on the C=O bond of the –COOH group.

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