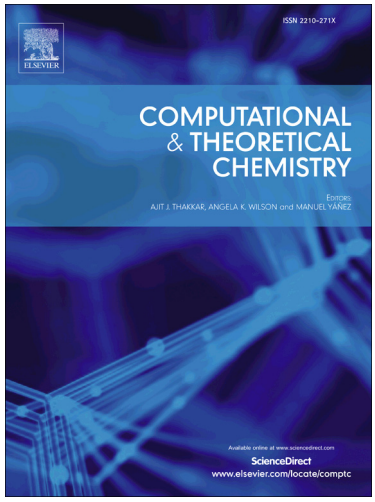

Functionalization of the sumanene by nitrous oxide: A mechanistic study

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Functionalization of the sumanene by nitrous oxide: A mechanistic study

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Abstract

The mechanistic study of the cycloaddition reaction of nitrous oxide onto sumanene nanostructure carried out systematically using quantum chemistry methods. The 1,3-dipolar cycloaddition reaction of nitrous oxide with different kinds of C–C bond of sumanene in thirteen pathways was investigated. Geometry of reactants, transition states, intermediates and products were optimized at B3LYP/6-311+G(d) level of theory. Vibrational frequencies and relative energies for all stationary points were determined. Thirty three transition states were identified for all pathways and confirmed by intrinsic reaction coordinate (IRC) calculations. The rate constants for all paths were calculated by using canonical transition state theory (CTST). Results showed that N_2O addition to flank position is more favorable than other positions of sumanene, energetically. The major products are sumanene with an epoxide group in flank, spoke and hub6 positions; also products with an enol or oxepin group in rim and hub5 positions, respectively. Also, for all five positions, in the first step, $C_{21}H_{12}N_2O$ with a pentagon heterocycle contain O–N–N will be formed. In subsequent steps, either N_2 extrusion or rearrangement can be done. Products related to outer positions of sumanene are more stable than corresponding products related to middle positions of sumanene (hub and spoke).

Keywords: Sumanene; Transition state; Density functional theory; Reaction mechanism; Functionalization; Carbon nanostructure.

1. Introduction

Bowl-shaped π-conjugated compounds, containing partial structures of fullerenes, such as sumanene ($C_{21}H_{12}$) and corannulene ($C_{20}H_{10}$) are important not only as model compounds of fullerenes but also for their own chemical and physical properties. They have been attracting great interests because of their promising potential for electrical materials [1, 2]. They are a group of key materials in the science of nonplanar π-conjugated carbon systems. Functionalization of the nanostructures for enhancement their properties such as solubility have been done, over the past few years. Functionalization of SWCNTs with polymers, carboxylic acid groups, with molecules through p-stacking, fullerene (C_{60}) and side-wall (covalent) functionalization have been reported in literatures, previously [3-8].