



Quantum chemistry and TST study of the mechanism and kinetics of the butadiene and isoprene reactions with mercapto radicals

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Abstract

The reactions of isoprene and butadiene with SH[•] radicals have been investigated by density functional theory and ab initio molecular orbital theories. We report the thermodynamics and kinetics of four different pathways, involving addition of SH[•] radicals to all double-bonded carbon atoms. Calculations have been performed on all stationary points using BHandHLYP functional, Moller–Plesset perturbation theory to second-order (MP2) and the composite CBS-QB3 method at the MP2 optimized geometries and frequencies. Pre-reactive complexes have been identified. The apparent activation energies are negative for SH[•] addition at the terminal carbon atoms and are slightly smaller than those for OH[•] addition at the same positions. The calculated overall rate coefficient for butadiene + SH[•] reaction at 298 K is in excellent agreement with the only available experimentally measured value. Activation energies and overall rate coefficients at different temperatures are predicted for the first time for butadiene + SH[•] and isoprene + SH[•] reactions. The reactions of butadiene and isoprene with SH[•] radicals were found to be about four times faster than with OH[•] radicals.

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