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

Misaela Francisco-Márquez\textsuperscript{a}, J. Raul Alvarez-Idaboy\textsuperscript{b,*}, Annia Galano\textsuperscript{a}, Annik Vivier-Bunge\textsuperscript{a}

\textsuperscript{a}Departamento de Química, Universidad Autónoma Metropolitana, Iztapalapa, México D.F. 09340, Mexico
\textsuperscript{b}Facultad de Química, Departamento de Física y Química Teórica, Universidad Nacional Autónoma de México, México D.F. 04510, Mexico

Received 18 June 2007; accepted 14 January 2008
Available online 19 January 2008

Abstract

The reactions of isoprene and butadiene with SH\textsuperscript{+} 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\textsuperscript{+} 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\textsuperscript{+} addition at the terminal carbon atoms and are slightly smaller than those for OH\textsuperscript{+} addition at the same positions. The calculated overall rate coefficient for butadiene + SH\textsuperscript{+} 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\textsuperscript{+} and isoprene + SH\textsuperscript{+} reactions. The reactions of butadiene and isoprene with SH\textsuperscript{+} radicals were found to be about four times faster than with OH\textsuperscript{+} radicals.

© 2006 Elsevier B.V. All rights reserved.

Keywords: SH radical; Atmospheric oxidation; Gas phase addition; Negative activation energy