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Mechanism of isomerization radical adducts of addition of thiophenol radical to quinone imine

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Abstract

On the example of adducts appearing at thiophenol radical addition to the cyclohexadiene moiety of the quinone imine, the methods of quantum chemistry are consider the possible mechanisms of isomerization of mentoned intermediates to corresponding phenoxyl and aromatic aminyl radicals. It is shown that the value of activation energy of intramolecular transfer of atom H of C-H bond from the point of connection of radical $PhS^{\cdot}$ so large, that can equal or even exceed C-H bond dissociation energy. Thus the intramolecular rearrangement of radical adducts appears to be improbable. The alternative bimolecular mechanism of atoms H transfer is considered with participation the additional molecule of thiol, that executes the role of reaction catalyst because of formation of the six-member transition state and the high exothermicity of reaction. The obtained data show that such mechanism can provide the rapid transfer of atom H.