

**DFT STUDY OF FREE GIBBS ENERGY ACTIVATION OF STAGES
OF CONVERSION OF PIPERYLENE TO ISOPRENE**

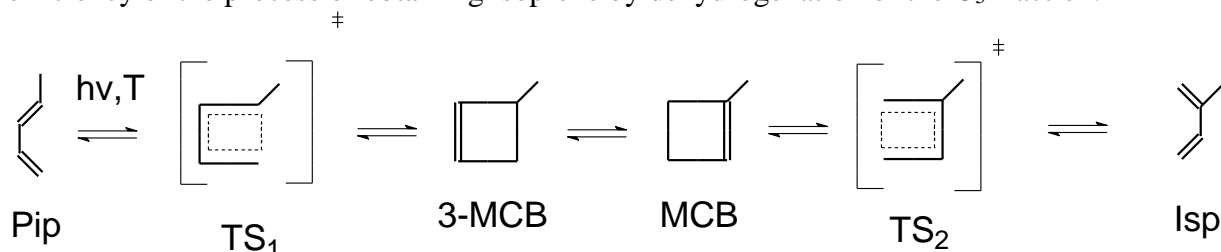
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The proposed scheme for the conversion of isoprene to piperylene can improve the efficiency of the process of obtaining isoprene by dehydrogenation of the C₅ fraction.



Using DFT methods, we calculated the Gibbs energies of activation of various stages of the scheme under consideration.

Table. Free Gibbs energies of activation ΔG_r^\ddagger (kJ/mol) of direct and inverse conversion stages

Stage	Transition State	ΔG_r^\ddagger (U)B3LYP/6-31G/d,p)		Exp.[1]
		singlet	triplet	
Pip → 3-MCB	TS ₁	194.7	439.5	-
3-MCB → Pip	TS ₁	127.4	372.1	127.5
Isp → MCB	TS ₂	186	408.8	-
MCB → Isp	TS ₂	139.9	362.7	146.7

When calculating, we took into account two variants of the spin states of the reagents: a triplet and a singlet. In the first case, the UHF approximation was used, in the second case - RHF. Calculations show that singlet reactions have lower values of activation energies, which are consistent with the literature data. The activation energies of the cyclization reactions are much larger than the activation energies of the cyclobutane ring opening reactions, in both cases, which is due to the known steric intensity of this cycle.

The activation energy of cyclization of piperylene in 3-methylcyclobutene is 8.7 kJ/mol greater activation energy of isoprene cyclization in methyl cyclobutene. In this case, the opening of the 3-methylcyclobutene ring to form piperylene is 12.5 kJ/mol higher than the analogous reaction for methylcyclobutene.

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