

Quantum-chemical investigation of potential energy surface of piperylene in isoprene photochemical conversion

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Abstract

Piperylene is one of the large-tonnage by-products of petrochemical synthesis, which has not found wide practical application. Along with other factors, the formation of piperylene significantly reduces the efficiency of isoprene production by dehydrating the C₅ fraction. Therefore, finding ways of qualified use of piperylene is an important and actually task. We believe that piperylene to isoprene conversion can be one of the ways of such disposal. In this work theoretical methods considered the possibility of occurrence of direct photochemical isomerization of piperylene to isoprene, which consists of three sequentially occurring reactions: [2+2] photochemical cyclization of piperylene; isomerization 3-methylcyclobutene in methylcyclobutene and the disclosure of the latest in the isoprene in the reverse reaction [2+2] cyclization. For this purpose, using non-empirical approximation B3LYP/6-31G(d,p), we studied the surface of potential energy of the proposed piperylene-isoprene conversion scheme using quantum chemistry methods. The structures of pre-reaction complexes and transition States were determined and thermodynamic parameters of individual stages of the scheme were calculated.

According to the calculations, the direct conversion of piperylene to isoprene is found to be a weakly endothermic reaction. Analysis of the entropy factor shows that it is more profitable to carry out it at T < 150 °C, since in this case the free Gibbs energy does not exceed 9.6 kJ/mol ($\Delta G_r^{298} = 9$ kJ/mol). At temperatures above 150 °C, the entropy factor increases significantly, which is reflected in an increase in the free Gibbs energy ($\Delta G_r^{423} = 18.5$ kJ/mol). The best are the singlet reactions in this case activation energy does not exceed 200 kJ/mol.

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