

Quantum-Chemical Modeling of S- and Se-Containing Derivatives of Sterically-Hindered Phenols and their Interaction with Peroxides

G.Yu. Kolchina*, E.M. Movsumzade**, A.Yu. Bakhtina**, E.R. Babayev***

*Sterlitamak branch of the Bashkir State University, Sterlitamak, Russia,

**Ufa State Petroleum Technological University, Ufa, Russia,

***Institute of Chemistry of Additives after Academician A.M. Guliyev, Baku, Azerbaijan

Abstract

Sterically-hindered phenols have well proven themselves as antioxidant additives. The essence of their antioxidant activity lies in the fact that they interrupt the oxidation chain easily giving up the hydrogen atom of the hydroxyl group of the radical and thereby deactivating them.

We have established that S- and Se-containing derivatives of sterically-hindered phenols apparently exhibiting the effect of auto-synergism have more effective antioxidant anticorrosive and antimicrobial properties. This explains the great interest in them as additives to lubricating oils.

To compare the antioxidant activity of the studied compounds we studied the kinetics of the stage of inhibition of the oxidation process by sterically-hindered phenols by the example of the reaction with the HOO-radical. Experimental theoretical studies have shown that the hindered phenols (and the phenoxy radicals obtained from them) can be considered effective inhibitors of the oxidation of organic substances since they fully satisfy the requirements that are imposed on strong antioxidants. Such phenols readily react with the ROO-radicals, interrupting the oxidation chain.

During the analysis of the energy profiles of the reactions, activation energies were obtained for the studied S- and Se-containing derivatives of sterically-hindered phenols. The relatively small values of activation energies can be explained from the standpoint of the theory of triplet perturbations. The activation energy of the radical detachment reaction depends on the energy of the non-bonding orbitals of the intermediate state, which is also relatively small in view of the small binding energy of O-O (88 kJ/mol, for comparison, the C-C bond energy is 382 kJ/mol).

The greatest activation energy in this type of reaction is 4,4'-dithiobis(2,6-di- α -methylbenzylphenol), and the smallest - 2,2'-dithiobis(4-methyl-6- α -methylbenzylphenol). The lowest activity of 4,4'-dithiobis(2,6-di- α -methylbenzylphenol) can be explained by steric hindrance of convergence of the active radicals and the hindered phenol. The highest activity of 2,2'-dithiobis(4-methyl-6- α -methylbenzylphenol) is probably due to the fact that this hindered phenol has electron-donor groups at the m- and p-positions that promote the inhibition reaction and while it has less steric hindrance.