

A kinetic and thermodynamic investigation of phenols *para*-substituted with thiol (SR), sulfinyl (SOR), and sulfonyl (SO₂R) groups and *ortho*-substituted with thiol groups is reported. The effect of the sulfur substituents on the O-H bond dissociation enthalpy values, BDE(O-H), was measured by means of the EPR radical equilibration technique and the reactivity toward peroxy radicals, k_{inh} , of these phenolic antioxidants was determined by inhibited autoxidation studies. An inverse correlation between these two parameters was found. A *p*-SMe substituent decreased the BDE(O-H) value to a lesser extent than a *p*-OMe group (-3.6 vs -4.4 kcal/mol), whereas the effect of the same groups in an *ortho* position showed an opposite trend (-0.85 vs -0.2 kcal/mol). The latter result is explained in terms of the different strength of the intramolecular hydrogen bond between the OH proton and the sulfur or oxygen substituents in *ortho* derivatives. ESI-MS analysis of the products formed by reacting the sulfides with peroxy radicals from the azoinitiator AIBN revealed the formation of a complex mixture of products, which may play an important role in determining the overall antioxidant activity of the parent compounds.