

The role of intramolecular hydrogen bonding (HB) on the bond dissociation enthalpy (BDE) of the phenolic O-H and on the kinetics of H-atom transfer to peroxy radicals (k_{inh}) of several 2-alkoxyphenols was experimentally quantified by the EPR equilibration technique and by inhibited autoxidation studies. These compounds can be regarded as useful models for studying the H-atom abstraction from 2-OR phenols, such as many lignans, reduced coenzyme Q and curcumin. The effects of the various substituents on the BDE(O-H) of 2-methoxy, 2-methoxy-4-methyl, 2,4-dimethoxyphenols versus phenol were measured in benzene solution as -1.8; -3.7; -5.4 kcalmol⁻¹, respectively. In the case of polymethoxyphenols, significant deviations from the BDE(O-H) values predicted by the additive effects of the substituents were found. The logarithms of the k_{inh} constants in cumene were inversely related to the BDE(O-H) values, obeying a linear Evans–Polanyi plot with the same slope of other substituted phenols and a y-axis intercept slightly smaller than that of 2,6-dimethyl phenols. In the cases of phenols having the 2-OR substituent included in a five-membered condensed ring (i.e, compounds **9–11**), both conformational isomers in which the OH group points toward or away from the oxygen in position 2 were detected by FTIR spectroscopy and the intramolecular HB strength was thus estimated. The contribution to the BDE(O-H) of the ortho-OR substituent in **9**, corrected for intramolecular HB formation, was calculated as -5.6 kcalmol⁻¹. The similar behaviour of cyclic and non-cyclic ortho-alkoxy derivatives clearly showed that the preferred conformation of the OMe group in ortho-methoxyphenoxy radicals is that in which the methyl group points away from the phenoxy oxygen, in contrast to the geometries predicted by DFT calculations.