Dissociation Energies of O−H Bonds of Phenols and Hydroperoxides

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1. Introduction

The bond dissociation energy is very important characteristic of molecule that usually refers to standard thermodynamic state in gas phase (298 K, pressure 1 atm). When these thermodynamic quantities are known they become an invaluable tool for calculation of activation energies and rate constants of homolytic reactions.

Phenols are widely used as antioxidants for stabilization of organic compounds and materials. Many organic compounds are oxidized by oxygen due to contact with air. Phenols are used for stabilization of variety organic products such as polyolefins, polystyrene, and rubbers (Hamid, 2000; Scott, 1980; Pospisil & Klemchuk, 1990; Scott, 1993), monomers (Mogilevich & Pliss, 1990), hydrocarbon fuels (Denisov & Kovalev, 1990), lubricants (Kuliev, 1972), edible fats and oils (Emanuel & Lyaskovskaya, 1961), cosmetics, drugs *etc*.

Autooxidation of substrate RH proceeds as free radical chain process with participation of free radicals R$^\bullet$ and RO$_2^\bullet$ and formation of hydroperoxide ROOH (Emanuel et al., 1967; Mill & Hendry, 1980; Denisov & Khudyakov, 1987; Denisov & Afanas'ev, 2005). The kinetic scheme of chain oxidation of a hydrocarbon is presented below.
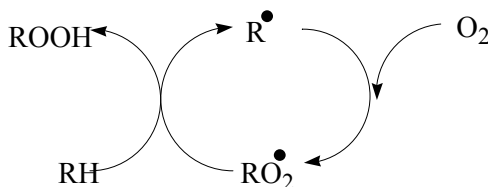
Phenols (ArOH) act as chain breaking inhibitors of this process. They stop developing of chain oxidation by reacting with peroxy radicals (Emanuel et al., 1967; Mill & Hendry, 1980; Denisov & Khudyakov, 1987; Roginsky, 1988; Denisov & Azatyan, 2000; Denisov & Afanas'ev, 2005; Lucarini & Pedulli, 2010).

$$RO_2^\bullet + ArOH \rightarrow ROOH + ArO^\bullet$$

$$RO_2^\bullet + ArO^\bullet \rightarrow \text{Molecular products}$$
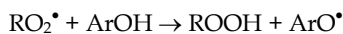
The first reaction is the limiting step of chain termination. The rate and activation energy of this reaction depends on the dissociation energy of O−H bond of reacting phenol and

formed hydroperoxide. So, these characteristics of phenols and hydroperoxides are the key values in thermodynamics of antioxidative action of phenols.

Natural phenols play very important role in preventing free radical oxidation in living bodies. Vitamin E (tocopherols) is present in cellular membranes and edible oils and functions as efficient inhibitor of lipid peroxidation in biomembranes (Burton & Ingold, 1986; Denisov & Afanas'ev, 2005). Polyfunctional phenols (flavonoids, flavones *etc.*) play important role in the biology of plants (regulation of gene expression, gene silencing, organization of metabolic pathways) (Grotewold, 2006). The bond dissociation energies for such biologically important phenols were estimated recently (Denisov & Denisova, 2009).

2. Experimental methods of estimation of dissociation energy of O−H bonds of phenols

2.1 Calorimetric method

The most of phenoxyl radicals are unstable and rapid disappear by reactions of recombination and disproportionation (Denisov & Khudyakov, 1987; Roginsky, 1988; Denisov & Afanas'ev, 2005). However, there are a few stable phenoxyl radicals and one of them is 2,4,6-tri-*tert*-butylphenoxyl. In contrast to most free radicals, solutions of the 2,4,6-tri-*tert*-butylphenoxyl radical may be prepared and these solutions are stable in the absence of oxygen and other reactive compounds. This unique property was used by L. Mahoney *et al.* for to perform the direct calorimetric determination of the heat of its reaction in systems were the heats of formation of the other reactants and products are known. The following reaction was chosen for such study (Mahoney et al., 1969).
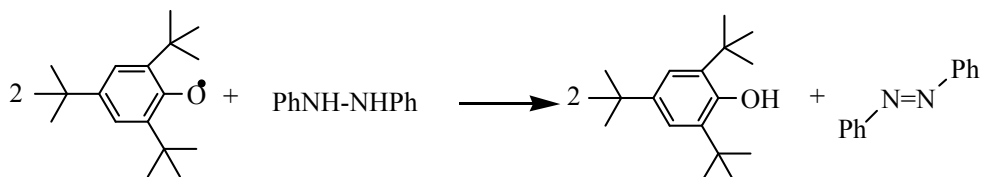
In the result of this reaction all molecules of hydrazobenzene are transformed into *trans*-azobenzene when phenoxyl is taken into excess.

The calorimeter with base line compensator and sample injection assembly was used for this study. Plots of the calories absorbed *vs.* moles of compound dissolved were linear with essentially zero intercepts. The values of the partial molar enthalpies of solution at infinite dilution for phenol and for azobenzene were not altered by the presence of the 2,4,6-tri-*tert*-butylphenoxyl radical in the solvent. For the determination of the heats of reaction of the 2,4,6-tri-*tert*-butylphenoxyl with hydrazobenzene a concentrated solution of the radical (0.2 − 0.5 M) was used. The enthalpy of reaction was measured in three solvents: CCl_4, C_6H_6 and PhCl. The enthalpies of solid reactants solution were estimated and were found to be equal (in benzene): 13.2 kJ/mol for ArOH, 11.8 kJ/mol for analogue of ArO$^\bullet$, 19.7 kJ/mol for PhNHNHPh, and 21.1 kJ/mol for *trans*-PhN=NPh. They were taken into account at calculation of enthalpy of reaction (ΔH). From the last the difference of enthalpies was calculated:

$$\Delta H_f^0(ArO^\bullet) - \Delta H_f^0(ArOH) = 121.9 \pm 0.4 \ \ kJ/mol \ (298 \ K, 1 \ atm., benzene) \tag{1}$$

As well as this difference is equal to $D_{O-H} + \Delta H_f^0(H^\bullet)$ and $\Delta H_f^0(H^\bullet)$ = 218 kJ/mol (Lide, 2004) the D_{O-H} = 339.9 kJ/mol. The following values of reactant and product were used at this calculation: ΔH_f^0(PhNHNHPh) = 221.3 kJ/mol and ΔH_f^0(trans-PhN=NPh) = 320.0 kJ/mol. Recently the following correction was proposed with using the new value of ΔH_f^0 (trans-PhN=NPh) = 310.4 kJ/mol according that D_{O-H} = 335.1 kJ/mol (Mulder et al., 2005).

2.2 Chemical Equilibrium (CE)

The value of D_{O-H} of 2,4,6-tri-*tert*-butylphenol appeared to be very claiming in the method of chemical equilibrium due to stability of formed phenoxyl radical. Chemical equilibrium

$$Ar_1O^\bullet + Ar_iOH \rightleftharpoons Ar_1OH + Ar_iO^\bullet$$

where $Ar_1O^\bullet$ and $Ar_iO^\bullet$ are reactive free phenoxyl radicals, cannot be achieved in solution owing to very fast recombination or disproportionation of these species. Such an equilibrium can be attained only when both radicals are stable and do not enter the recombination reaction. In this case the equilibrium concentrations of both radicals can be determined by electron paramagnetic resonance spectroscopy or spectrophotometrically (Mahoney & DaRooge, 1975; Belyakov at al., 1975, Lucarini at al., 1994). The equilibrium constant (K) is calculated from the ratio of the equilibrium concentrations of the molecules and radicals:

$$K = \frac{[Ar_1OH]_\infty [Ar_iO^\bullet]_\infty}{[Ar_iOH]_\infty [Ar_1O^\bullet]_\infty} \tag{2}$$

The equilibrium enthalpy (ΔH) is calculated from the temperature dependence of equilibrium constant K. On the other hand, the equilibrium enthalpy of this reaction is equal to the difference between the dissociation energies (D_{O-H}) of the bonds involved in the reaction

$$\Delta H = D_{O-H}(Ar_iOH) - D_{O-H}(Ar_1OH) \tag{3}$$

provided that solvation of reactants makes an insignificant contribution to the equilibrium. This can be attained by carrying out experiments in no polar solvents. As the reference phenoxyl radical $Ar_1O^\bullet$ were used 2,4,6-tri-*tert*-butylphenoxyl ((Mahoney & DaRooge, 1975; Lucarini at al., 1994), galvinoxyl (Belyakov at al., 1975), and ionol (Lucarini et al., 2002). Calculations of the equilibrium constant K from the reactant concentration ratio were followed by calculations of the Gibbs free energy of equilibrium:

$$\Delta G = -RT\ln K \tag{4}$$

The equilibrium enthalpy was determined using the temperature dependence of the equilibrium constant. Experience showed that in such reactions one has $\Delta H \cong \Delta G$ within the limits of error in measurements. The dissociation energies of the O−H bonds in phenols thus measured are listed in Table 1.

It was found that this approach can also be used in studies of the systems characterized by recombination of phenoxyl radicals formed. Here, the reaction conditions are chosen in such a fashion that the equilibrium between reactants is attained rapidly and the phenols are consumed slowly, so it is possible to monitor each reactant and calculate the equilibrium constant. This allowed the range of phenols with known O−H bond dissociation energies to be extended.

Having determined the equilibrium constant, it is possible to estimate the O−H bond strength difference between two phenols. To calculate the absolute value of D_{O-H}, one must know the D_{O-H} value for one phenol. For 2,4,6-tri-*tert*-butylphenol, D_{O-H} = 339.9 kJ/mol (see **2.1**), which is in good agreement with the D_{O-H} value for unsubstituted phenol (D_{O-H} = 369.0 kJ/mol, see (Denisov & Denisova, 2000). For galvinol, D_{O-H} = 329.1 kJ/mol. The error in estimating D_{O-H} values is only 1.1 kJ/mol (Lucarini at al., 1994). When equilibrium between $Ar_1O^{\bullet}$ and Ar_1OH was studied in the solvent (S) that forms hydrogen bond with phenol, the difference in hydrogen bond enthalpies was taken into account. The point of difference is that sterically no hindered phenols form hydrogen bond $Ar_1OH…S$ and 2,4,6-tri-*tert*-butylphenol (Ar_1OH) practically does not. Therefore the enthalpy of hydrogen bond $Ar_1OH…S$ should be abstracted from enthalpy of equilibrium. For example, hydrogen bond enthalpy $\Delta H(C_6H_5OH…C_6H_6)$ = −4 kJ/mol (Mulder et al., 2005).

In order to evaluate the dissociation energies of O−H bonds in various phenols, Mahoney and DaRooge (Mahoney & DaRooge, 1975) measured the equilibrium constant $K = k_1/k_{-1}$ for the reactions

$$RO_2^{\bullet} + Ar_iOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROOH + Ar_iO^{\bullet}$$
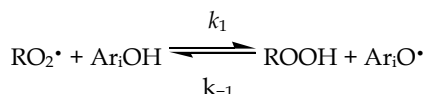
To this end, 9,10-dihydroanthracene (RH) was oxidized with oxygen in the presence of corresponding hydroperoxide (ROOH) and phenol (Ar_iOH) at 333 K with azoisobutyronitryl as initiator. The experimental conditions were chosen in such a manner that the equilibrium was established in the system and the chain termination step was limited by the recombination of $Ar_iO^{\bullet}$ and $ROO^{\bullet}$ radicals. In this case the rate (v), of the chain oxidation process is satisfactorily described by the following equation:

$$v = k_p[RH]\sqrt{\frac{k_{-1}[ROOH]v_i}{2k_t k_1[Ar_iOH]}} \, , \tag{5}$$

where k_p and k_t are the rate constants for the reactions of $RO_2^{\bullet}$ with RH and $RO_2^{\bullet}$ with $ArO^{\bullet}$, respectively, and v_i is the initiation rate. The dependence of the chain oxidation rate v on the ROOH and ArOH concentrations was used to determine the $k_p/(2k_tK)^{1/2}$ ratio and then the equilibrium constant $K = k_1/k_{-1}$ was calculated using known values of ratio $k_p(2k_t)^{-1/2}$. The $\Delta D = D(ArO−H) – D(ROO−H)$ values were determined assuming that $\Delta H = \Delta G = −RT\ln K$. The values of $D(ArO−H)$ calculated relative to the O−H bond dissociation energy of *sec*-ROOH (365.5 kJ/mol) are listed in Table 1. The values of D_{O-H} measured for the same phenol in different papers are in good agreement. For example, for 4-methylphenol (*para*-cresol) D_{O-H} = 360.7 ± 1.0 kJ/mol, for 4-*tert*-butylphenol D_{O-H} = 359.1 ± 1.6 kJ/mol, for 4-methoxyphenol D_{O-H} = 348.2 ± 1.1 kJ/mol.

| Substituents of Phenol, Phenol	Ar$_1$OH or ROOH	ΔD, kJ/mol	D, kJ/mol	Ref
3-Me	ROOH	−2.5	363.0	Howard & Ingold, 1965
4-Me	ROOH	−3.7	361.8	Howard & Ingold, 1965
4-Me	ROOH	−6.1	359.4	Mahoney & DaRooge, 1975
4-Me	2,4,6-tri-*tert*-butylphenol	20.9	360.8	Lucarini & Pedulli, 2010
4-CMe$_3$	ROOH	−4.6	360.9	Howard & Ingold, 1965
4-CMe$_3$	ROOH	−6.0	359.5	Mahoney & DaRooge, 1975
4-CMe$_3$	2,4,6-tri-*tert*-butylphenol	17.1	357.0	Lucarini & Pedulli, 2010
4-Ph	ROOH	−12,5	353.0	Mahoney & DaRooge, 1975
2-OMe	2,4,6-tri-*tert*-butylphenol	19.2	359.1	Lucarini & Pedulli, 2010
3-OMe	ROOH	0.7	364.8	Howard & Ingold, 1965
4-OMe	ROOH	−16.5	349.0	Howard & Ingold, 1965
4-OMe	ROOH	−16.6	348.9	Mahoney & DaRooge, 1975
4-OMe	2,4,6-tri-*tert*-butylphenol	6.7	346.6	Lucarini & Pedulli, 2010
3-COOEt	ROOH	7.8	373.3	Mahoney & DaRooge, 1975
4-NH$_2$	2,4,6-tri-*tert*-butylphenol	−12.1	327.8	Lucarini & Pedulli, 2010
4-Cl	ROOH	1.9	367.4	Howard & Ingold, 1965
2-Me, 6-Me	ROOH	−15.3	359.2	Howard & Ingold, 1965
2-Me, 6-Me	2,4,6-tri-*tert*-butylphenol	13.8	353.7	Lucarini & Pedulli, 2010
3-Me, 5-Me	2,4,6-tri-*tert*-butylphenol	22.6	362.5	Lucarini & Pedulli, 2010
2-Me, 6-CMe$_3$	ROOH	−20.1	345.4	Howard & Ingold, 1965
2-CMe$_3$, 6-CMe$_3$	ROOH	−11.1	354.4	Howard & Ingold, 1965
2-CMe$_3$, 6-CMe$_3$	ROOH	−12.2	353.3	Mahoney & DaRooge, 1975
2-CMe$_3$, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	6.7	346.6	Lucarini & Pedulli, 2010
3-CMe$_3$, 5-CMe$_3$	ROOH	−4.5	361.0	Mahoney & DaRooge, 1975
3-CMe$_3$, 5-CMe$_3$	2,4,6-tri-*tert*-butylphenol	22.6	362.5	Lucarini & Pedulli, 2010
2-OMe, 4-Me	2,4,6-tri-*tert*-butylphenol	11.3	351.2	Lucarini & Pedulli, 2010

2-OMe, 4-OMe	2,4,6-tri-*tret*-butylphenol	4.2	344.1	Lucarini & Pedulli, 2010
3-OMe, 5-OMe	2,4,6-tri-*tret*-butylphenol	23.0	362.9	Lucarini & Pedulli, 2010
2-OMe, 6-OMe	2,4,6-tri-*tert*-butylphenol	8.4	348.3	Lucarini & Pedulli, 2010
2-Me, 4-Me, 6-Me	2,4,6-tri-*tert*-butylphenol	6.3	346.2	Lucarini & Pedulli, 2010
2-Me, 4-CN, 6-Me	ROOH	2.5	368.0	Howard & Ingold, 1965
2-CMe$_3$, 4-Me, 6-CMe$_3$	Galvinol	14.6	343.7	Belyakov at al., 1975
2-CMe$_3$, 4-Me, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	0.3	340.2	Jackson & Hosseini, 1992
2-CMe$_3$, 4-Me, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−0.8	339.1	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-CMe$_3$, 6-CMe$_3$	Galvinol	11.5	340.6	Belyakov at al., 1975
2-CMe$_3$, 4-CH$_2$Ph, 6-CMe$_3$	Galvinol	6.9	336.0	Belyakov at al., 1975
2-CMe$_3$, 4-Ph, 6-CMe$_3$	Galvinol	9.7	338.8	Belyakov at al., 1975
2-CMe$_3$, 4-Ph, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	0.0	339.9	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-CH=CHPh, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−9.6	330.3	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-OMe, 6-CMe$_3$	Galvinol	−2.7	325.7	Belyakov at al., 1975
2-CMe$_3$, 4-OMe, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−13.5	326.4	Jackson & Hosseini, 1992
2-CMe$_3$, 4-OMe, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−12.1	327.8	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-OCMe$_3$, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−5.9	334.0	Howard & Ingold, 1965
2-CMe$_3$, 4-OCMe$_3$, 6-CMe$_3$	Galvinol	2.0	331.1	Belyakov at al., 1975
2-CMe$_3$, 4-CHO, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	15.2	355.1	Jackson & Hosseini, 1992
2-CMe$_3$, 4-CHO, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	12.5	352.4	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-C(O)Me, 6-CMe$_3$	Galvinol	24.1	353.2	Belyakov at al., 1975
2-CMe$_3$, 4-CH=NOH, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−4.8	335.1	Jackson & Hosseini, 1992
2-OH, 4-CMe$_3$, 6-CMe$_3$,	Ionol	−7.1	331.5	Lucarini et al., 2002
2- CEtMe$_2$, 4-OH, CEtMe$_2$,	Ionol	−0.8	337.8	Lucarini et al., 2002
2-CMe$_3$, 4-CH$_2$NMe$_2$, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	0.7	340.6	Jackson & Hosseini, 1992
2-CMe$_3$, 4-NO$_2$, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	15.5	355.4	Jackson & Hosseini, 1992
2-CMe$_3$, 4-NO$_2$, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	15,5	355.4	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-Cl, 6-CMe$_3$	Galvinol	16.3	345.4	Belyakov at al., 1975

2-CMe$_3$, 4-Cl, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	5.0	344.9	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-COOMe, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	12.1	352.0	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-COOH, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	13.0	352.9	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-CN, 6-CMe$_3$	ROOH	−7.7	357.8	Howard & Ingold, 1965
2-CMe$_3$, 4-CN, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	12.5	352.4	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-SMe, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	−7.5	332.4	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-S(O)Me, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	6.3	346.2	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-SO$_2$Me, 6-CMe$_3$	2,4,6-tri-*tert*-butylphenol	6.7	346.6	Lucarini & Pedulli, 2010
2-CMe$_3$, 4-CMe$_3$, 6-SMe	2,4,6-tri-*tert*-butylphenol	8.8	348.7	Lucarini & Pedulli, 2010
2-OMe, 4-OMe, 6-OMe	2,4,6-tri-*tert*-butylphenol	−5.0	334.9	Lucarini & Pedulli, 2010
2-Me, 3-Me, 4-OMe, 6-Me	2,4,6-tri-*tert*-butylphenol	−8.4	331.5	Lucarini & Pedulli, 2010
2-Me, 3-Me, 4-OMe, 5-Me, 6-Me	2,4,6-tri-*tert*-butylphenol	2.9	342.8	Lucarini & Pedulli, 2010
2-Naphthol	ROOH	−6.4	359.1	Mahoney & DaRooge, 1975
Galvinol	2,4,6-tri-*tert*-butylphenol	−11.5	328.4	Howard & Ingold, 1965
Indol	2,4,6-tri-*tert*-butylphenol	−14.8	325.1	Howard & Ingold, 1965

Table 1. The values of D_{O-H} of substituted phenols estimated by **CE** method (D_{O-H} = 339.9 kJ/mol for 2,4,6-tri-*tert*- butylphenol D_{O-H} = 329.1 kJ/mol for galvinol, and D_{O-H} = 365.5 kJ/mol for *sec*-ROOH (Denisov & Denisova, 2000))

2.3 Low pressure pyrolysis of substituted anisoles (VLPP)

The direct approach to estimation of dissociation energy of O-H bond of phenol via reaction

$$C_6H_5OH \rightarrow C_6H_5O^\bullet + H^\bullet$$
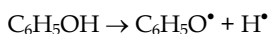
cannot be successful due to the presence of a competing tautomerization of phenol to the cyclohexa-2,4-dienon (Zhu & Borzzelli, 2003.). An indirect way to assess the phenolic O−H bond dissociation energy is by studying the temperature dependence of the rate constant for O−C bond dissociation in phenyl ethers, such as anisoles (Suryan et al., 1989a; Suryan et al., 1989b) and benzylphenyl ether (Pratt at al., 2001). In these studies, dissociation rates of substituted anisoles were determined in the gas phase by a method of very-low-pressure pyrolysis (**VLPP**). This method provides a straightforward means for determining decomposition rates in the absence of bimolecular reactions. Anisoles are especially suited

for study by this method, since their low O−Me bond strengths (ca. 268 kJ/mol) cause them to homolyze under relatively mild (for **VLPP**) conditions (800-1200 K). The decomposition of substituted anisoles was found to proceed exclusively by simple homolysis (Suryan et al., 1989a).

General operating principles of the **VLPP** technique have been described by Golden et al (Golden et al., 1973). Anisole decomposition were performed at T = 800 ÷ 1200 K and pressure p = 10^{-2} ÷ 10^{-4} Torr monitored periodically and percentage dissociation was reproducible to ±1% (Suryan et al., 1989b). An electron impact quadruple mass spectrometer, tuned to 70-eV ionization energy, was used to monitor reactant decomposition. Unimolecular reaction rate constants, k_{uni}, under **VLPP** conditions were calculated from the equation (Suryan et al., 1989a).

$$k_{uni}/k_e = x/(1-x) = (I_0 - I)/I. \qquad (6)$$

where, k_e, the escape rate constant is $3.965(T/M)^{1/2}$ s^{-1} for the 3-mm aperture reactor, M is the molecular weight, T is the temperature (K), and x represents the fraction of reactant decomposed. The latter value was derived from mass spectrometer signal intensity of the parent molecular ion before reaction (I_0) and after reaction (I) at an ionization energy of 70 eV (Suryan et al., 1989a).

| Y	2-Y		3-Y		4-Y		Ref
	ΔD, kJ/mol	D_{O-H}, kJ/mol	ΔD, kJ/mol	D_{O-H}, kJ/mol	ΔD, kJ/mol	D_{O-H}, kJ/mol	
Me	−10.9	358.1	−2.1	366.9	−7.9	361.1	Suryan et al., 1989b
CH=CH$_2$	−10.5	358.5					Suryan et al., 1989b
OMe	−17.6	351.4	−4.6	264.4	−16.3	352,7	Suryan et al., 1989a
OMe	−17.1	351.9			−13.0	356.0	Pratt at al., 2001
C(O)Me	−6.0	333.9	0.8	369.8	2.5	371.5	Suryan et al., 1989b
OH	−29.9	310.0	1.2	370.2	−10.5	358.5	Suryan et al., 1989a
OH	−30.1	338.9			−11.3	357.7	Pratt at al., 2001
NH$_2$	−30.9	309.8	−1.7	367.3	−12.5	356.5	Suryan et al., 1989b
CN	−0.9	339.0	−0.4	368.6	1.2	370.2	Suryan et al., 1989b
NO$_2$	−5.6	334.3	−2.1	366.9	4.6	373.6	Suryan et al., 1989b
F	−8.0	361.0	3.8	372.8	−4.6	264.4	Suryan et al., 1989b
Cl	−9.2	359.8	0.8	369.8	−4.6	264.4	Suryan et al., 1989a
Br	−7.1	361.9					Suryan et al., 1989a
CF$_3$					9.2	378.2	Pratt at al., 2001

Table 2. Dissociation energies of O−H bonds (in kJ/mol) in substituted phenols estimated by **VLPP** technique, $D_{O-H}(C_6H_5OH)$ = 369.0 kJ/mol

For a meaningful comparison of rate constants for the different reactions, they were converted to their high-pressure (collision-frequency independent) values. This was done with RRKM theory (Robinson & Holbrook, 1972). The pre-exponential A factor of $10^{15.5}$ s^{-1} was assumed for all reactions. Activation energies were used for to calculate D_{O-C} at standard conditions using the equation (Mulder et al., 2005):

$$D_{O-C} = E_{uni} + RT_m - \Delta C_P(T_m - 298), \qquad (7)$$

where T_m is the average temperature of experiment, ΔC_P is the average change in heat capacity between T_m and $T = 298$ K. The errors in rate constants, measured at 50% decomposition, were approximately 10%.

As well as the enthalpy of exchange reaction

$$PhOH + YC_6H_4OMe \rightleftharpoons YC_6H_4OH + PhOMe$$
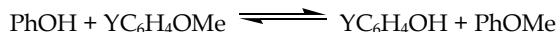
was proved to be very small (Suryan et al., 1989a) one can use the differences in dissociation energy of C−O bonds of substituted anisoles for evaluation of dissociation energy of O−H bonds of phenols. The results of calculation of dissociation energy for O−H bonds in substituted phenols taking into account $D_{O-H}(C_6H_5OH) = 369.0$ kJ/mol (Denisov & Denisova, 2000) are presented in Table 2.

2.4 Estimation of bond dissociation energy from kinetic measurements

In the framework of the intersecting parabolas model (**MIP**) the transition state of a radical reaction, for example

$$RO_2^{\bullet} + ArOH \rightarrow ROOH + ArO^{\bullet}$$
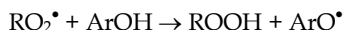
is treated as a result of intersection of two potential energy curves (Denisov, 1997; Denisov, 1999; Denisov & Denisova, 2000; Denisov & Afanas'ev, 2005; Denisov et al., 2003). One of them characterises the potential energy of the stretching vibration of the attacked ArO−H bond as a function of the vibration amplitude while the other characterises the potential energy of the vibration of the ROO−H bond being formed. The stretching vibrations of the bonds are considered harmonic. A free radical abstraction reaction is characterised by the following parameters:

1. classical enthalpy ΔH_e. which includes the zero-point vibrational energy difference between the bond being cleaved and the bond being formed;
2. classical potential activation barrier E_e which includes the zero-point vibrational energy of the bond being cleaved;
3. parameter r_e equal to the total elongation of the bond being cleaved and the bond being formed in the transition state;
4. coefficient b ($2b^2$ is the force constant of the bond being cleaved);
5. parameter α (α^2 is the force constant ratio of the reacting bonds);
6. pre-exponential factor A_0 per equally reactive cleaved bond (in the molecule) involved in the reaction. The rate constant is expressed via Arrhenius equation: $k = n_{OH}A_0\exp(-E/RT)$ where n_{OH} is a number of OH groups with equireactivity. All these values are connected via equation:

$$br_e = \alpha\sqrt{E_e + \Delta H_e} + \sqrt{E_e} \ . \tag{8}$$

The **MIP** method allows the variety of radical reactions to be divided into classes using experimental data. Each class is characterised by the same set of parameters mentioned above. An individual reaction belonging to a certain class is characterised by the classical enthalpy H_e and classical activation energy E_e that for the written above reaction is expressed by the equation (at $\Delta H_e(1 - \alpha^2) << (br_e)^2$):

$$\sqrt{E_e} = 0.496\, br_e + 0.507\, (br_e)^{-1}\Delta H_e, \tag{9}$$

were parameter br_e = 13.16 $(kJ/mol)^{1/2}$ for reaction $RO_2^\bullet$ + phenol and br_e = 14.30 $(kJ/mol)^{1/2}$ for reaction $RO_2^\bullet$ + sterically hindered phenol (Denisov & Denisova, 2000). A method for estimating the bond strengths from the kinetic data developed in the framework of the **MIP** model, involves a number of versions (Denisov, 1995a; Denisov, 1995b; Denisov, 1997; Denisov, 1999; Denisov & Tumanov, 2005).

1. With the measured rate constants k_i or the k_i/k_1 ratios for a reaction class of the type $RO_2^\bullet$ + ArOH it is possib1e to estimate the difference in bond strengths between the Ar_iOH and Ar_1OH compounds. The rate constant ratio k_i/k_1 allows to calculate the activation energies difference:

$$\Delta E_i = E_i - E_1 = RT\ln(n_i k_1/n_1 k_i) \tag{10}$$

where n_1 and n_i are respectively the numbers of equally reactive bonds in the Ar_1OH and Ar_iOH molecules attacked by the $RO_2^\bullet$ radical. From Eqn. (8) it follows that the relation between the ΔE_i value and the enthalpy difference $\Delta(\Delta H_i)$ between these reactions has the form:

$$\Delta(\Delta H_i) = 1.945\, br_e\left(\sqrt{E_{e1}+\Delta E_i} - \sqrt{E_{e1}}\right) + 0.0274\,\Delta E_i \tag{11}$$

On the other hand, the enthalpy difference $\Delta(\Delta H_i)$ = $D_i - D_1$ and the strength of the Ar_iO-H bond can be calculated using the equation:

$$D_i = D_1 + 1.945\, br_e\left(\sqrt{E_{e1}+\Delta E_i} - \sqrt{E_{e1}}\right) + 0.0274\,\Delta E_i \tag{12}$$

Thus, calculations of the D_i values require knowledge of the D_1, E_{e1}, k_1/k_i ratio, and the parameters characterising a given reaction class (parameter br_e and coefficient α). Experience showed that the error in ΔD measurements is $1.5 \div 2.5$ kJ/mol.

2. Using different radicals (e.g. $R_iOO^\bullet$) in a series of radical reactions $R_iOO^\bullet$ + RH belonging to the same class allows the approach to be employed for evaluating the R_iOO-H bond strengths. In this case Eqn. (12) takes the form:

$$D_i = D_1 + 2\alpha^{-2}br_e\left(\sqrt{E_{e1}} - \sqrt{E_{e1}+\Delta E_i}\right) + (\alpha^{-2}-1)\Delta E_i \tag{13}$$

where E_{e1} refers to reaction $R_1O_2^\bullet$ + RH, coefficients α and b_{re} see in Handbook (Denisov & Denisova, 2000). This version of the technique was used in estimating the D_{O-H} values in hydroperoxides (see **4.1**).

3. The D_i value for a free radical abstraction reaction can also be evaluated from the absolute value of the rate constant k_i. (Denisov & Tumanov, 2005).

   Limitation imposed on the method is associated with the enthalpy of reaction (Denisov, 1997; Denisov & Denisova, 2000). The case in point is that Eqn (8) is valid for reactions belonging to the same reaction class and characterised by enthalpies lying in the interval $\Delta H_{emin} < \Delta H_e < \Delta H_{emax}$. The activation energy for a highly exothermic reaction ($\Delta H_e < \Delta H_{emin}$) is nearly zero (more correctly, $E = 0.5RT$) and independent of ΔH. Therefore the enthalpies ΔH_e of these reactions cannot be estimated from the E_e values. The ΔH_{emin} va1ue depends on the br_e and α parameters and on the zero-point

vibrational energy of the bond being cleaved. The activation energies of highly endothermic reactions ($H_e > \Delta H_{emax}$) is approximately equal to ΔH:

$$E = \Delta H + 0.5\, RT. \qquad (14)$$

The bond dissociation energies estimated from experimental data on reactions of peroxyl radicals with phenols in hydrocarbon solutions are given in Table 3.

Substituents of Phenol, Phenol	Phenol, YC$_6$H$_4$OH		2,6-Di-*tert*-butylphenol	
	ΔD_{O-H}, kJ/mo1	D_{O-H}, kJ/mo1	ΔD_{O-H}, kJ/mo1	D_{O-H}, kJ/mo1
H	0.0	369	7.7	347.6
2-Me	−9.1	359.9		
3-Me	−2.3	366.7		
4-Me	−6.8	362.2	0.0	339.9
2-CMe$_3$	−15.2	353.8		
4-CMe$_3$	−8.9	360.1	0.0	339.9
4-Ph			−1.3	338.6
4-CH$_2$Ph			0.7	340.6
4-CMe$_2$Ph			1.1	341.0
4-CHPh$_2$			3.3	343.2
4-OMe			−8.3	331.6
4-OCMe$_3$	−21.2	347.8	−7.9	332.0
2-OH	−29.4	339.6		
3-OH	0.1	369.1		
4-OH	−17.0	352.0		
4-COOH	2.7	371.7	9.8	349.7
4-C(O)H			8.8	348.7
4-C(O)Me			6.5	346.4
4-COOCMe$_3$			8.8	348.7
4-CH$_2$COOH			−2.3	337.6
4-CH$_2$COOMe			3.8	343.7
4-(CH$_2$)$_2$COOC$_{18}$H$_{37}$			0.6	340.5
4-CH$_2$NH$_2$			−4.2	335.7
4-NHAc			−12.3	327.6
4-NO			7.0	346.9
4-NO$_2$	3.8	372.8	19.0	358.9
4-CN			13.4	353.3
4-Cl			5.5	345.4
4-SPh			7.4	347.3
2-Me, 3-Me	−13.5	355.5		
2-Me, 4-Me	−8.5	360.5		

2-Me, 6-Me	−14.4	354.6		
3-Me, 4-Me	−14.4	354.6		
3-Me, 5-Me	−4.3	364.7		
2-Me, 4-CMe$_3$	−9.1	359.9		
2-CMe$_3$, 4-CMe$_3$	−9.5	359.5		
3-CMe$_3$, 5-CMe$_3$	−6.6	362.4		
2-CMe$_3$, 4-OMe	−25.6	343.4		
2-OH, 4-CMe$_3$	−26.6	342.4		
2-Me, 4-OH	−19.2	349.8		
2-Me, 4-Me, 6-Me	−21.5	347.5		
2-Me, 4-Me, 5-Me	−12.2	356.8		
2-CMe$_3$, 4-Me, 6-Me	−13.2	355.8		
2-CMe$_3$, 4-CMe$_3$, 6-CMe$_3$	−13.1	355.9		
2-Me, 4-CH$_2$NH$_2$, 5-Me	−20.9	348.1		
2-Me, 4-Cl, 5-Me	−17.6	351.4		
2-S(CH$_2$)$_2$CN, 4-Me, 6-CHMePh	−21.5	347.5		
2-Me, 4-CH$_2$NH$_2$, 6-CMe$_3$	−18.4	350.6		
2-Me, 3-Me, 4-Me, 6-Me	−21.4	347.6		
2-Me, 3-Me, 5-Me, 6-Me	−17.8	351.2		
2-Me, 3-Me, 4-Me, 5-Me, 6-Me	−28.5	340.5		
2-OH, 3-CMe$_3$, 5-CMe$_3$	−28.7	340.3		
2-OH, 3-CMe$_3$, 6-CMe$_3$	−29.5	339.5		
3-Me, 4-CH$_2$COOH, 5-Me	−19.0	350.0		
2-Me, 4-CH$_2$CN, 6-Me	−15.0	354.0		
2-Me, 3-Me, 4-OH, 5-Me	−24.3	344.7		
2-OMe, 3-OMe, 4-OH, 6-Me	−25.2	343.8		
1-Naphthol	−25.6	343.4		
2-Naphthol	−15.2	353.8		
1-Hydroxyfluorene	−30.7	338.3		
1-Hydroxyphenanthrene	−14.3	354.7		
2-Hydroxyphenanthrene	−2.0	367.0		
3-Hydroxyphenanthrene	−6.5	362.5		
4-Hydroxyphenanthrene	−12.8	356.2		
3,8-Pyrendiol	−53.1	315.9		
3,10-Pyrendiol	−51.3	317.7		

Table 3. The values of D_{O-H} for phenols estimated by **MIP** (Denisov, 1995a; Denisov & Denisova, 2000)

2.5 Photoacoustic calorimetry (PAC)

Photoacoustic calorimetry is a thermodynamic method of estimation of bond dissociation energies in solution. The physical principle of **PAC** is the following (Rothberg et al., 1983; Simon & Peters, 1983; Grabowski et al., 1984). Very rapid heat release from a photoinitiated process in liquid generates a pressure wave. This wave propagates through the solution at the speed of sound. Detection and quantification of this pressure wave is the bases of the technique.

The values of dissociation energies of O−H bonds in phenols were estimated by (Wayner et al., 1995; Wayner et al., 1996; Laarhoven et al., 1999). Di-*tert*-butyl peroxide was used as photoinitiator. Pulses from a nitrogen laser (λ = 337.1 nm; pulse width 10 ns; power, 10 mJ per pulse; repetition rate, 5 Hz) were used to photolyse di-*tert*-butyl peroxide in solution.

$$Me_3COOCMe_3 + h\nu \rightarrow 2\ Me_3CO^\bullet$$
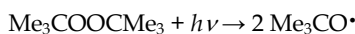
The formed *tert*-butoxy radicals react very rapidly with phenol with evolution of heat.

$$Me_3CO^\bullet + ArOH \rightarrow Me_3COH + ArO^\bullet$$
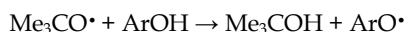
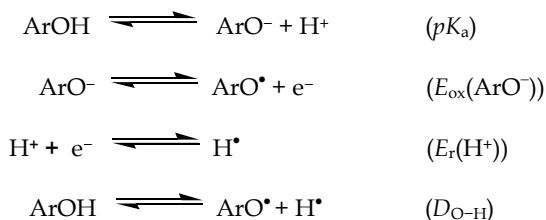| Substituents of Phenol	ΔD, kJ/mol	D, kJ/mol
4-H	0.0	369.0
4-CMe$_3$	−7.9	361.1
4-OMe	−24.3	344.7
4-CF$_3$	13.4	382.4
4-CN	23.4	392.4
4-Cl	1.7	370.7
2-Me, 4-Me, 6-Me-	−23.0	346.0
2-CMe$_3$, 4-Me, 6-CMe$_3$	−32.2	336.8
2-CMe$_3$, 4-CMe$_3$	−21.8	347.2
2-Me, 4-OMe, 6-Me-	−42.3	326.7

Table 4. Dissociation energies of O−H bonds of phenols measured by **PAC**, benzene, T = 298 K, (Wayner et al., 1996; Laarhoven et al., 1999)

An iris ensured that only a very small part of the light passed as a fine beam through the centre of the cell, and a low powered lens was used to correct for the slight divergence of the beam. The heat evolved as a result of the photoinitiated reactions caused a shock wave in the solution, which was transmitted at the speed of sound to the cell wall. Here, the primary wave and its many reflections were detected in a time-resolved mode by a piezoelectric transducer. The transducer signals were amplified and were recorded on a storage oscilloscope. A quartz plate was used to reflect part of the laser beam to a reference device, so that corrections could be made for variations in the laser power. On prolonged irradiation some drift in this device occurred, presumably because small convection currents were set up in the solution. However, the problem was easily

overcome by slowly flowing the solution through the cell with a peristaltic pump. Signals from the reference transducer were amplified and were stored in a second channel of the oscilloscope. The time profiles of the photoacoustic waves were quite reproducible so long as the geometry of the apparatus remained unchanged. The measurements from a line of laser shots were averaged to give the amplitudes of the photoacoustic waves due to sample and reference. In the photoacoustic experiment, an important condition was that the heat evolved in a given reaction was released in a time that was short with respect to the response of the transducer. This was tested by different ways. The samples used in the photoacoustic experiments were always carefully deoxygenated by nitrogen or argon purging and were flowed through the cuvette so as to avoid problems associated with sample depletion and product formation. Samples that were oxygen-sensitive were always prepared in an inert atmosphere since oxidation generally gave rise to colored impurities which affected the optical properties of the solutions. The results of D_{O-H} estimation of a line substituted phenols are listed in Table 4. The results on D_{O-H} estimation in C_6H_5OH see in paragraph 3.

2.6 Acidity − oxidation potential method (AOP)

The theoretical basis for acidity − oxidation − potential method (**AOP**) (Bordwell & Bausch, 1986; Bordwell et al., 1991) lies in thermochemical cycle:

$$ArOH \rightleftharpoons ArO^- + H^+ \qquad\qquad (pK_a)$$

$$ArO^- \rightleftharpoons ArO^\bullet + e^- \qquad\qquad (E_{ox}(ArO^-))$$

$$H^+ + e^- \rightleftharpoons H^\bullet \qquad\qquad (E_r(H^+))$$

$$ArOH \rightleftharpoons ArO^\bullet + H^\bullet \qquad\qquad (D_{O-H})$$

Equilibrium acidity measurements and oxidation potentials, both measured in Me_2SO solution and can be combined to obtain relative homolytic dissociation energy of O−H bond of phenol. Since E_{red} for the proton is constant, differences in the sum of the oxidation potentials of the anions and the acidity constants for their conjugate acids (pK) can be taken as measures of relative bond dissociation energy:

$$\Delta D_{O-H}(kJ/mol) = 5.73\Delta pK_{ArOH} + 96.48\Delta E_{ox}(ArO^-) \qquad\qquad (15)$$

This approach is limited in practice by the irreversibility of the oxidation potentials for most anions. Nevertheless, there was observed that when families of anions wherein basicities have been changed by remote substitution are used, good correlations between E_{ox} and pK_{ArOH}, or between E_{ox} and log k for electron-transfer reactions, are often obtained. In these instances, the extent of irreversibility of E_{ox} throughout the family appears to be similar enough to permit estimates of relative bond dissociation energies by this method.

Lind et al. measured the constant of equilibrium in aqueous solution:

$$ArO^- + ClO_2^\bullet \rightleftharpoons ArO^\bullet + ClO_2^-$$
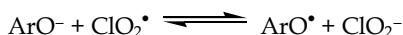
using pulse radiolysis technique (Lind et al., 1990). The values of ΔD_{O-H} estimated by two methods are listed in Table 5.

Substituents of Phenol, Phenol	ΔD_{O-H}, kJ/mol, (Bordwell & Cheng, 1991)	ΔD_{O-H}, kJ/mol, (Arnett et al., 1990)	ΔD_{O-H}, kJ/mol, (Lind et al., 1990)
H	0.0	0.0	0.0
2-Me	−6.9		
3-Me	−1.9		
4-Me	−4.8	−18.7	−0.9
3-Me, 5-Me	−3.1		
2-Me, 6-Me	−18.2		
4-CMe$_3$	−4.8	−7.3	
2-CMe$_3$, 6-CMe$_3$	−32.4		
2-CMe$_3$, 4-CMe$_3$, 6-CMe$_3$	−32.0		
4-Ph	−9.4		
2-OMe	−16.1		
3-OMe	1.5		
4-OMe	−22.0	−22.2	−23.4
4-O$^-$	−70.5		−66.1
4-OH	−34.9		−33.5
3-NH$_2$	−7.7		
3-NMe$_2$	−8.2		
4-NH$_2$	−52.5		−53.1
4-NMe$_2$	−40.0		−58.6
4-F		−1.9	−3.3
2-Cl	0.6		
3-Cl	8.2		
4-Cl	1.9	7.5	−2.5
3-Cl, 5-Cl	16.9		
3-Cl, 4-Cl , 5-Cl	13.6		
4-Br	3.6		−0.4
4-I			−1.2
3-CF$_3$	16.5		
4-CF$_3$	22.8		
3-SO$_2$Me	10.2		
4-SO$_2$Me	21.5		
3-C(O)Me	8.2		
4-C(O)Me	12.3		2.1
4-C(O)Ph	11.1		
4-OC(O)Me		−11.5	
4-CO$_2^-$			7.1
3-CN	16.9		
4-CN	18.2	6.1	19.7
3-NO$_2$	18.6		
4-NO$_2$	20.3	9.1	25.1
1-Naphthol	−24.5		
2-Naphthol	−7.7		

Table 5. The values of ΔD_{O-H} of substituted phenols measured by electrochemical techniques

3. Dissociation energies of O−H bonds of phenols

3.1 Dissociation energy of O−H bond of C6H5OH

As was shown earlier, the O−H bond of simplest phenol C_6H_5OH plays a key role among a line of different substituted phenols. The absolute value of $D_{O-H}(ArOH)$ can be calculated via difference of bond dissociation energies: $\Delta D_{O-H} = D_{O-H}(ArOH) - D_{O-H}(C_6H_5OH)$ and the last can be estimated by a line of methods. The values of $D_{O-H}(C_6H_5OH)$ were measured during last 20 years and are collected in Table 6.

Year	$D_{O-H}(C_6H_5OH)$, kJ/mol	Method	Ref.
1989	374.5	**VLPP** (gas)	Suryan et al., 1989a
1990	369.5	Shock tube (gas)	Walker & Tsang, 1990
1991	375.9	**AOP** (Me₂SO)	Bordwell & Cheng, 1991
1995	365.3	**PAC** (C_6H_6)	Wayner et al., 1995
1996	369.4	**CE** (C_6H_6)	Lucarini et al.,1996
1998	376.6	Negative ion cycle (gas)	DeTuri & Ervin, 1998
2000	369.0	Recommended	Denisov & Denisova, 2000
2003	368.2	Recommended	Luo, 2003
2004	359.0	Negative ion cycle (gas)	Angel & Ervin, 2005
2005	362.3	Recommended	Mulder et al., 2005

Table 6. The values of $D_{O-H}(C_6H_5OH)$ estimated by different techniques

It is seen from Table 6 that experimental values of $D_{O-H}(C_6H_5OH)$ vary from 359 to 377 kJ/mol, the mean value of $D_{O-H}(C_6H_5OH)$ = 369.0 ± 5.7 kJ/mol. This value coincides with that recommended in Handbook (Denisov & Denisova, 2000) and the last is in good agreement with D_{O-H} of hydroperoxides (see paragraph 4).

In recent years, quantum chemical methods, particularly density functional theory, are often used for the assessment of the dissociation energy of O−H bond in phenols. Let us know that the results of calculation as a rule, differ substantially from the experimental values. As we see experimental $D_{O-H}(C_6H_5OH)$ = 369 ± 6 kJ/mol and calculated values are sufficiently lower (see Table 7).

Method	D_{O-H}, kJ/mol	Method	D_{O-H}, kJ/mol
6-31G	332.8	6-31+G(d,p)	344.2
6-31G(d)	327.7	6-311+G(d,p)	347.5
6-31G(d,p)	346.2	6-311+G(2d,p)	348.0
6-31G(d,p)	341.7	6-311+G(2d,2p)	350.7
6-31G(d,p')	361.3	6-311+G(3d,p)	350.1
6-31+G(d)	328.9	G-3	369.0

Table 7. Values of $D_{O-H}(C_6H_5OH)$ calculated by density functional theory (Wright et al., 1997; Luzhkov, 2005; Mulder et al., 2005)

3.2 Dissociation energies of O−H bond of substituted phenols

As was shown earlier, the influence of substituent of aromatic ring on D_{O-H} is very important. As well as each technique has its specific peculiarities that may influence on the measured value ΔD_{O-H} it would be useful to compare them. This comparison is performed in Table 8.

Substituents of Phenol, Phenol	CE	VLPP	MIP	AOP	PAC	D, kJ/mol
	ΔD, kJ/mol	ΔD, kJ/mol	ΔD, kJ/mol	ΔD, kJ/mol	ΔD, kJ/mol	
2-Me		−10.9	−9.1	−6.9		360.0 ± 1.6
3-Me	−6.0	−2.1	−2.3	−1.9		365.9 ± 1.7
4-Me	−8.3 ± 1.0	−7.9	−6.8	−4.8		361.6 ± 1.3
4-CMe$_3$	−10.0 ± 1.6		−8.9	−4.8	−7.9	361.1 ± 0.5
4-Ph	−16.0			−9.4		356.3 ± 3.3
3-OH		1.2	0.1			368.4 ± 0.7
4-OH		−10.9 ± 0.4	−17.0	−34.9 (?)		355.1 ± 3.0
2-OMe	−9.9	−17.6		−16.1		354.5 ± 3.3
3-OMe	−4.2	−4.6		1.5 (?)		364.6 ± 0.2
4-OMe	−20.8 ± 1.1	−14.6 ± 1.7		−22.0	−24.3	346.6 ± 1.4
3-NH$_2$		−1.7		−7.7		364.3 ± 3.0
4-NH$_2$	−41.2	−12.5 (?)		−52.5		322.2 ± 5.6
3-CN		−9.4		16.9 (?)		359.6
4-CN		1.2		18.2	23.4	389.8 ± 2.6
3-NO$_2$		−2.1		18.6 (?)		366.9
4-NO$_2$		4.6	3.8	20.3		373.2
4-F		−4.6		−2.6		365.4
2-Cl		−9.2		0.6 (?)		359.8
3-Cl		0.8		8.2 (?)		369.8
4-Cl	−1.6	−4.6		1.9	1.7	368.4 ± 2.7
4-CF$_3$		9.2		22.8 (?)		378.2
2-Me, 6-Me	−12.5 ± 2.7			−18.2		353.7 ± 2.8
3-Me, 5-Me	−6.5			−3.1		364.2 ± 1.7
3-CMe$_3$, 5-CMe$_3$	−8.0		−6.6			361.7 ± 0.7
2-CMe$_3$, 6-CMe$_3$	−19.0 ± 3.4		−22.6	−32.4 (?)		349.1 ± 1.6
2-CMe$_3$, 4-Me, 6-CMe$_3$	−27.0 ± 1.5		−13.1(?)	−32.0	−32.2	338.6 ± 2.4
1-Naphthol			−25.6	−24.5		344.0 ± 0.6
2-Naphthol	−9.9		−15.2	−7.7		358.1 ± 3.1
Indol	−43.9		−41.8			326.2 ± 1.0

Table 8. Comparison of ΔD (kJ/mol) = $D(\text{Ar}_i\text{OH})$ − $D(\text{C}_6\text{H}_5\text{OH})$ for substituted phenols estimated by various methods, $D(\text{C}_6\text{H}_5\text{OH})$ = 369.0 kJ/mol (see Tables 1−5); data marked by (?) were not included in the calculation of mean values of ΔD

We observe a good agreement between ΔD measured by different methods for phenols with alkyl, alkoxyl, and amino substituents. However, for phenols with polar electronegative substituents such as Cl, CF$_3$, CN, and NO$_2$ method **AOP** gives much higher absolute values of ΔD in comparison with another methods. The possible explanation of these discrepancies lies in strong additional solvation of polar groups in such strong polar solvent as dimethylsulfoxide used in **AOP** method.

3.3 Dissociation energies of O−H bonds of natural phenols

Bioantioxidants play very important role in biological processes and are under intensive investigation during last a few decades. Among them only for tocopherols and ubiquinols were measured their O−H bonds dissociation energies (Denisov & Denisova, 2000; Luo, 2003). These important characteristics for many natural phenolic compounds (flavonoids et al.) were estimated only recently (Denisov & Denisova, 2008). The list of these data is given in Table 9.

Phenol	Site of O−H bond	D_{O-H}, kJ/mol	Method	Ref.
α-Tocopherol	6	328.9	**CE**	Jackson & Hosseini, 1992
α-Tocopherol	6	330.1	**CE**	Lucarini et al., 1996
α-Tocopherol	6	330.0	**MIP**	Denisov, 1995
α-Tocopherol	6	327.3	**CE**	Lucarini et al., 1994
α-Tocopherol	6	323.4 ± 8.0	**PAC**	Wayner et al., 1996
α-Tocopherol	6	338.5	**AOP**	Bordwell & Liu, 1996
β-Tocopherol	6	335.2	**MIP**	Denisov & Denisova, 2009
β-Tocopherol	6	335.6	**MIP**	Denisov, 1995
β-Tocopherol	6	335.3 ± 2.0	**MIP**	Denisova & Denisov, 2008
γ- Tocopherol	6	334.8	**MIP**	Denisov & Denisova, 2009
γ-Tocopherol	6	335.1	**MIP**	Denisov 1995
γ-Tocopherol	6	334.9 ± 2.0	**MIP**	Denisova & Denisov, 2008
δ- Tocopherol	6	341.4	**MIP**	Denisov & Denisova, 2009
δ- Tocopherol	6	342.8	**MIP**	Denisov, 1995
δ- Tocopherol	6	335.6	**PAC**	Wayner et al., 1996
δ- Tocopherol	6	341.5 ± 2.0	**MIP**	Denisova & Denisov, 2008

Ubiquinol-0	1,4	343.8	**MIP**	Denisov, 1995
Ubiquinol-0	1,4	346.0	**MIP**	Denisova & Denisov, 2008
Ubiquinol-2	1,4	344.3	**MIP**	Denisov, 1995
Ubiquinol-2	1,4	345.7	**MIP**	Denisova & Denisov, 2008
Ubiquinol-6	1,4	344.3	**MIP**	Denisov, 1995
Ubiquinol-6	1,4	345.7	**MIP**	Denisova & Denisov, 2008
Ubiquinol-9	1,4	344.8	**MIP**	Denisova & Denisov, 2008
Ubiquinol-10	1,4	345.6	**MIP**	Denisova & Denisov, 2008
5-Hydroxy-2,4,6,7-tetramethyl-2,3-dihydrobenzo[b]furan	5	326.7	**MIP**	Denisov & Denisova, 2009
5-Hydroxy-2,2,4,6,7-pentamethyl-2,3-dihydrobenzo[b]furan	5	326.4	**MIP**	Denisov & Denisova, 2009
5-Hydroxy-2,2,4,6,7-pentamethyl-2,3-dihydrobenzo[b]furan	5	323.4	**CE**	Jackson & Hosseini, 1992
5-Hydroxy-2-carboxy-2,4,6,7-tetra-methyl-2,3-dihydrobenzo[b]furan	6	334.0	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-5,7,8-trimethylchromane	6	330.9	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-hydroxymethyl-2,5,7,8-tetramethylchromane	6	330.9	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-methoxy-2,5,7,8-tetramethylchromane	6	334.4	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-carboxy-2,5,7,8-tetramethylchromane	6	336.5	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-methylcarboxy-2,5,7,8-tetramethylchromane	6	333.3	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-carboxymethyl-2,5,7,8-tetramethylchromane	6	333.0	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2-methylcarboxymethyl-2,5,7,8-tetramethylchromane	6	330.9	**MIP**	Denisov & Denisova, 2009
6-Hydroxy-2,2,5,7,8-pentamethylchromane	6	328.9	**MIP**	Denisov & Denisova, 2009

6-Hydroxy-2,2,5,7,8-pentamethylchromane	6	328.4	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,2,8-trimethyl-5,7-diethylchromane	6	331.9	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,2-dimethyl-5,7-diethylchromane	6	333.6	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,2,8-trimethyl-5,7-diisopropylchromane	6	337.0	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,2-dimethyl-5,7-diisopropylchromane	6	335.7	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5-methyl-7-*tert*-butylchromane	6	332.5	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5-isopropyl-7-*tert*-butylchromane	6	340.7	**MIP**	Denisova & Denisov, 2008
6-Hydroxytocol	6	340.1	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5,7-diethyltocol	6	333.9	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5,7-diethyl-8-methyltocol	6	331.9	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5,7-diisopropyltocol	6	335.7	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5,7-diisopropyl-8-methyltocol	6	336.3	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5-methyl-7-*tert*-butyltocol	6	333.2	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5-isopropyl-7-*tert*-butyltocol	6	339.3	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-5,7,8-trimethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	332.5	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,5,7,8-tetramethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	333.9	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,2,5,7,8-pentamethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	333.4	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2-phytyl-2,5,7,8-tetramethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	333.3	**MIP**	Denisov, 1995
6-Hydroxy-2-phytyl-2,5,7,8-tetramethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	334.7	**MIP**	Denisova & Denisov, 2008

6-Hydroxy-2-methylcarboxy-2,5,7,8-tetramethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	337.8	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,5-dimethyl-2-phytyl-7,8-benzochromane	6	321.4	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-2,5-dimethyl-2-phytyl-7,8-benzochromene	6	322.1	**MIP**	Denisova & Denisov, 2008
6-Hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydro-2*H*-1-benzothiopyran	6	329.8	**MIP**	Denisova & Denisov, 2008
5,7,8-Trimethylselenotocol	6	335.7	**MIP**	Denisova & Denisov, 2008
5-Hydroxy-2,4-dimethyl-2,3-dihydro-benzo[b]selenophene	5	334.5	**MIP**	Denisova & Denisov, 2008
5-Hydroxy-2-methyl-2,3-dihydro-benzo[b]selenophene	5	342.3	**MIP**	Denisova & Denisov, 2008
Kaempferol	7,4′	348.9	**MIP**	Denisova & Denisov, 2008
Morin	7,4′	363.6	**MIP**	Denisova & Denisov, 2008
Ubichromenol	1,4	350.2	**MIP**	Denisova & Denisov, 2008
Quercetin	4′	343.0	**MIP**	Denisova & Denisov, 2008
(−)-Epicatechin	4′	346.2 ± 1.8	**MIP**	Denisova & Denisov, 2008
(−)-Epicatechin	4′	339.7	**CE**	Lucarini et al., 2002
6,7-Dihydroxyflavone	6	332.3	**MIP**	Denisova & Denisov, 2008
7,8-Dihydroxyflavone	8	333.0	**MIP**	Denisova & Denisov, 2008
Chrysin	7	357.1	**MIP**	Denisova & Denisov, 2008
Galangin	7	363.1	**MIP**	Denisova & Denisov, 2008
Dihydroquercetin	4′	343.6	**MIP**	Denisova & Denisov, 2008

Catechin	4′	348.1 ± 1.3	**MIP**	Denisova & Denisov, 2008
Hesperitin	3′	353.8	**MIP**	Denisova & Denisov, 2008
Fisetin	4′	348.0 ± 1.7	**MIP**	Denisova & Denisov, 2008
Gallic acid	4	347.4	**MIP**	Denisova & Denisov, 2008
Propyl gallate	4	334.6	**MIP**	Denisova & Denisov, 2008
Propyl gallate	4	339.7	**CE**	Lucarini et al., 2002
Myricetin	4′	340.9	**MIP**	Denisova & Denisov, 2008
(−)-Epigallocatechin	4′	344.6	**MIP**	Denisova & Denisov, 2008
Rutin	4′	343.2 ± 0.6	**MIP**	Denisova & Denisov, 2008
Hesperidin	3′	345.8	**MIP**	Denisova & Denisov, 2008
Luteolin	4′	342.7	**MIP**	Denisova & Denisov, 2008
Nordihydroguaiaretic acid	4,4′	351.3	**MIP**	Denisova & Denisov, 2008
Caffeic acid	4	339.8	**MIP**	Denisova & Denisov, 2008
(−)-Epigallocatechin gallate	4′,4″	338.7 ± 0.3	**MIP**	Denisova & Denisov, 2008
β-Glucogallin	4	335.0	**MIP**	Denisova & Denisov, 2008
(−)-Epicatechin gallate	4′,4″	339.6 ± 1.3	**MIP**	Denisova & Denisov, 2008
Tannic acid	4	341.6	**MIP**	Denisova & Denisov, 2008
Pentagalloylglucose	4	338.1	**MIP**	Denisova & Denisov, 2008

Table 9. The values of D_{O-H} of natural phenols (D_{O-H}(α-tocopherol) = 330.0 kJ/mol), the second column contains the sites of O−H groups with equireactivity

As seen from the data in Table 9, all ubiquinols possess virtually the same dissociation energy of the O−H bond, which is independent of the length of a 2-substituent. An average value of D_{O-H} is 345.2 ± 0.8 kJ/mol (8 measurements). It should be borne in mind that both OH groups in ubiquinols are involved in hydrogen bonding with the *ortho*-methoxy groups. Phenolic groups form very strong intramolecular hydrogen bonds. For instance, in a phenolic crown ether (for the structure, see Ref. (Pozdeeva et al., 1989) the enthalpy of formation of such a bond is 21 kJ/mol, whereas the concentration of free OH groups is only 0.1% at 323 K. According to a theoretical calculation performed by density functional theory (Heer et al., 2000) the difference $\Delta\Delta G^{\neq}$ (298 K) for two transition states for the abstraction of an H atom by the methoxyl radical from a hydrogen-bonded OH group of ubiquinol-0 and from a free OH group is 7.5 kJ/mol. Assuming that $\Delta E(RO_2^{\bullet} + \text{ubiquinol}) = \Delta\Delta G^{\neq}(MeO^{\bullet} + \text{ubiquinol})$ and using Eqn. (12), we obtain the value of D_{O-H} = 329.0 kJ/mol for a free OH group of ubiquinols, *i. e.,* almost the same as that for α-tocopherol.

In tocopherols, the value D_{O-H} depends on the number and arrangement of methyl groups in the aromatic ring (see Table 9). At the same time, replacement of methyl groups by ethyl, isopropyl, and *tert*-butyl ones in positions 5 and 7 affects slightly the D_{O-H} values of tocols:

Compound	R^1	R^2	D_{O-H}, kJ/mol
6-Hydroxytocol	H	H	340.1
6-Hydroxy-5,7-diethyltocol	Et	Et	333.9
6-Hydroxy-5,7-diisopropyltocol	Me$_2$CH	Me$_2$CH	335.7
6-Hydroxy-5-isopropyl-7-*tert*-butyltocol	Me$_2$CH	Me$_3$C	339.3

Substitution of phytyl (Pht) for the methyl substituent in position 2 exerts virtually no effect on the value of D_{O-H} of 6-hydroxychromanes: D_{O-H}(2-Me, 2-Me) − D_{O-H}(2-Me, 2-Pht) = 0.4 ± 0.7 kJ/mol (7 pairs of compounds from Table 9 were compared). In 6-hydroxy-5,7,8-trimethylchromanes, the nature of substituents in position 2 virtually has no impact on the dissociation energy of the O−H bond: for seven phenols, the average value is 332.8 ± 2.0 kJ/mol. However, the nature of 5,7,8-substituents in 6-hydroxy-2,2-dimethyl-chromane appreciably influences the value of D_{O-H} altering it in the range 328 to 341 kJ/mol. Substitution of a naphthalene ring for the benzene ring on going from γ-tocopherol (3) to 6-hydroxy-2,5-dimethyl-2-phytyl-7,8-benzochromane reduces D_{O-H} by 13 kJ/mol (see Table 9). Substitution of S and Se for O atoms in α-tocopherol results in a small decrease in dissociation energy: D_{O-H} are 330.0, 334.0 and 335.7 kJ/mol for α-tocopherol, S-, and Se-analogs, respectively. The presence or the absence of methyl groups in position 2 in 6-hydroxy- 5,7,8-trimethyl-3,4-dihydrobenzothiopyrans does not affect the dissociation energy of the O−H bond: D_{O-H} (in kJ/mol) = 332.5 (2-H, 2-H), 333.9 (2-H, 2-Me), 333.4 (2-Me, 2-Me) (see Table 9).

The molecules of chrysin and galangin contain two phenolic groups. One of them, *viz.,* the OH group in position 5 is linked to the adjacent carbonyl group by a hydrogen bond, hence it is the 7-OH group that is the most reactive. As a result, for chrysin and galangin the number of equireactive O−H bonds (n_{O-H} is 1), and D_{O-H} differ little: 357.1 (chrysin) and 363.1 (galangin) kJ/mol, respectively. For morin, D_{O-H} of the OH groups in positions 7 and 4' are apparently roughly the same and equal to 363.6 kJ/mol (n_{O-H} = 2).

In catechol (1,2-dihydroxybenzene), one hydroxyl group weakens the adjacent O−H bond (thus, in pyrogallol D_{O-H} = 339.9 kJ/mol, while in phenol D_{O-H} = 369.0 kJ/mol). A hydrogen bond increases effective strength of O−H bond roughly by 10 kJ/mol (for comparison, in

quercetin D_{O-H} = 343.0 kJ/mol and in hesperitin D_{O-H} = 353.8 kJ/mol); in the latter compound, the peroxyl radical attacks the OH group linked to a methoxy group by a hydrogen bond. Thus, in catechol only one OH group reacts with $RO_2^{\bullet}$, the second is inactive due to the formation of a strong hydrogen bond.

An average value of D_{O-H} in flavanones and flavones is 344.7 ± 2.6 kJ/mol. In 1,2,3-trihydroxybenzenes only one O−H bond actively reacts with $RO_2^{\bullet}$, whereas the other two are involved in hydrogen bonding. For such phenols a fairly wide range of D_{O-H} values is observed: 347.4 (gallic acid), 337.2 ± 2.5 (propyl gallate), 340.9 (myricetin), 344.6 ((−)-epigallocatechin), 343.2 (rutin), 345.8 (hesperidin) and 338.7 kJ/mol ((−)-epigallocatechin gallate).

Thus, dissociation energies of the O−H bond in natural antioxidants ranges from 330 (for α-tocopherol) to 364 kJ/mol (for morin). These compounds compose a group with very close values of of D_{O-H}; it includes tocopherols, ubiquinols, flavones, flavanones and gallates. The diversity of their structures seems to be associated with the peculiarities of the media where they manifest their antioxidant activity.

3.4 Influence of structure on D_{O-H} of phenols

The most important factor affecting the strength of the O−H bond is the stabilization of a phenoxyl radical due to the overlap of the unpaired electron orbital of the oxygen atom with the π-electrons of the benzene ring. The stabilization energy can be judged by a comparison of the dissociation energy of the O−H bond in phenol (PhOH) (D_{O-H} = 369 kJ/mol) and in an aliphatic alcohol ROH (D_{O-H} = 432 kJ/mol) (Luo 2003). The difference is 63 kJ/mol therefore reactions of peroxyl radicals (D_{O-H} = 365.5 kJ/mol) with most of phenols, which are essential for the inhibition of oxidation, are exothermic.

The second factor that influences the dissociation energy of the O−H bonds of substituted phenols is the inductive effect of alkyl, in particular, methyl, groups. Below the data are given that illustrate the role of the inductive effect of methyl groups on the dissociation energy of the O−H bond in phenols: $\Delta D = D(MeC_6H_4OH) - D(C_6H_5OH)$ kJ/mol (see Tables 2-4, 8).

Substituent	ΔD, kJ/mol	Substituent	ΔD, kJ/mol	Substituent	ΔD, kJ/mol
2-Me	−9.0	2-Me, 3-Me	−13.5	3-Me, 4-Me	−14.4
3-Me	−3.1	2-Me, 4-Me	−8.5	3-Me, 5-Me	−4.8
4-Me	−7.4	2-Me, 6-Me	−15.3	2-Me, 4-Me, 6-Me	−13.2

We observe stronger effect on the D_{O-H} for *ortho*- and *para*-methyl groups than that of *meta*-methyl group. There is no additivity in action of two or more methyl groups on D_{O-H} of substituted phenol. Analogous effect is also observed in tocopherols: the more methyl substituents are present in the benzene ring of a tocopherol the weaker is its O−H bond.

Phenol	n_{Me}	D_{O-H}, kJ/mol
α-Tocopherol	3	330.0
β-Tocopherol	2	335.5
γ-Tocopherol	2	335.5
δ-Tocopherol	1	361.5

The third factor is the enhancement of the stabilization of a phenoxyl radical due to interaction of the p-electrons of the N or O atom of amino- and alkoxy- substituent or a hydroxyl group with the π-electrons of the benzene ring (mesomeric effect). The magnitude of this effect is clearly seen from the following comparison:

Substituent of Phenol	ΔD, kJ/mol	Substituent of Phenol	ΔD, kJ/mol	Substituent of Phenol	ΔD, kJ/mol
3-OH	−0.6	3-MeO	−4.4	3-NH$_2$	−4.7
4-OH	−13.9	4-MeO	−19.1	4-NH$_2$	−46.8
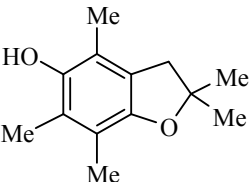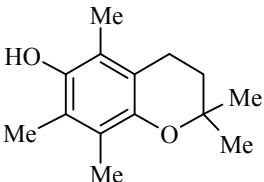
All these substituents reveal a weak effect on D_{O-H} in *meta*-position and very strong in *para*-position.

The fourth factor is influence of electronegative substituents that attract the π-electron density of benzene ring and often increase the dissociation energy of O−H bond. Down are given examples of such influence.

Substituent of Phenol	ΔD, kJ/mol	Substituent of Phenol	ΔD, kJ/mol	Substituent of Phenol	ΔD, kJ/mol
3-CN	−9.4	3-NO$_2$	−2.1	4-COOH	2.7
4-CN	1.2	4-NO$_2$	4.2	4-CF$_3$	9.2

It is seen that influence of substituent depends on position: in *meta*-position these substituents decrease D_{O-H} and in *para*-position increase D_{O-H}. Quite another effect have haloid substituents (F, Cl, Br): in *meta*-position they increase D_{O-H} of phenols and in *ortho*- and *para*-position diminish it (see Table 2).

The fifth factor is the stereoelectronic one, which has been discussed in detail by Burton et al. (Burton et al., 1985). The point is that for bicyclical phenols, such as hydroxychromanes and hydroxybenzofurans, an important parameter is the angle θ between the C−O bond of the annulated oxygen-containing ring and the plane of the benzene ring. The smaller this angle the larger the overlap of the p-electron orbitals of the O atom of the pyran or furan ring with the π-electcons of the benzene ring and the higher the stabilization energy of the phenoxyl radical. This is exemplified by the data given below:

Angle θ, deg	6	17
D_{O-H}, kJ/mol	326.4	328.9

The sixth factor is the intramolecular hydrogen bonding. The value of input of the intramolecular hydrogen bond into D_{O-H} of *ortho*-methoxyphenol can be evaluated from comparison of ΔD_{O-H} estimated by **CE** and **VLPP** methods. In the **CE** method, the equilibrium
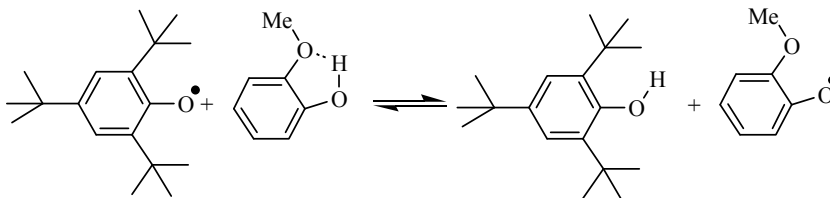
proceeds with *ortho*-methoxyphenol with intramolecular hydrogen bond and the value of ΔD_{O-H} = −9.9 kJ/mol (see Table 8) included the input of hydrogen bond into energy of *ortho*-methoxyphenoxyl radical stabilization. In the **VLPP** method ΔD_{O-H} = −17.6 kJ/mol (see Table 8) was calculated from comparison of activation energies of decomposition of anisole and *ortho*-methoxyanisole and evidently does not include the energy of the hydrogen bond. So, we can evaluate the difference in O−H bond dissociation energies in *ortho*-methoxyphenol with and without hydrogen bond as $\Delta D_{O-H\ldots O}$ = −9.9 − (−17.6) = 7.7 kJ/mol. A very close value ($\Delta D_{O-H\ldots O}$ = 7.5 kJ/mol) gives a quantum chemical calculation of the Gibbs energy of the transition state for the reaction of the methoxyl radical with *ortho*-methoxyphenol in two distinct states, viz., with a free OH group and with that bound by a hydrogen bond (Heer et al., 2000).

The influence of remote hydrogen bond on D_{O-H} value of phenol was found recently by Foti et al. (Foti et al., 2010). The comparison of reactivity of 3 substituted phenols in their reactions with peroxyl ($k(RO_2^{\bullet})$) and diphenylpycrylhydrazil (DPPH$^{\bullet}$) radicals demonstrated the diversity as the result of formation of remote intermolecular hydrogen bond.

Phenol			
$k(RO_2^{\bullet})$, l/mol s (303 K)	4.7×10^5	7.2×10^5	2.5×10^5
$k(DPPH^{\bullet})$, l/mol s (303 K)	1.8×10^3	4.4×10^3	2.0×10^2
ΔD_{O-H}, kJ/mol	0.0	−2.5	1.6

One sees that remote hydrogen bonds have appreciable effect on the phenolic bond dissociation energy. Intermolecular *para*-OH…*meta*-OMe hydrogen bond weaken, while *meta*-OH…*para*-OMe hydrogen bond strengthen O−H bond dissociation energy compared with similarly substituted 3,4-dimethoxyphenol.

4. Thermochemistry of hydroperoxides

4.1 Dissociation energies of O−H bonds of hydroperoxides

The O−H bond dissociation energy in *tert*-butyl hydroperoxide was measured by Holmes et al. using masspectrometry technique and appearance energy measurements (Holmes et al., 1991) and was found be equal to 258.6 kJ/mol. All tertiary alkylperoxy radicals has the same

activity in reactions of hydrogen atom abstraction (Howard, 1972) and hence all tertiary alkylhydroperoxides have the same D_{O-H}. Secondary alkylperoxy radicals are more active than tertiary as hydrogen atom acceptors due to the last have lower D_{O-H} (Mill & Hendry, 1980; Denisov & Afanas'ev, 2005). The difference in activation energies of reactions:

$$R'O_2{}^\bullet + RH \rightarrow R'OOH + R^\bullet$$
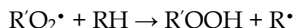
between sec-$R'O_2{}^\bullet$ and $tert$-$R'O_2{}^\bullet$ was found be equal to 3.1 ± 1.6 kJ/mol (Denisov & Denisova, 1993). The calculated via **MIP** method (Eqn. 13) value of $\Delta D_{O-H} = D_{O-H}(sec\text{-}R'O_2{}^\bullet) - D_{O-H}(tert\text{-}R'O_2{}^\bullet)$ is equal to 6.9 kJ/mol and hence $D_{O-H}(sec\text{-}ROOH) = D_{O-H}(tert\text{-}ROOH) + 6.9 = 365.5$ kJ/mol. All primary and secondary alkylhydroperoxide have practically the same D_{O-H} (Howard, 1972). In accordance with these data is equilibrium constant between secondary and tertiary hydroperoxides and peroxy radicals (Howard et al., 1968).
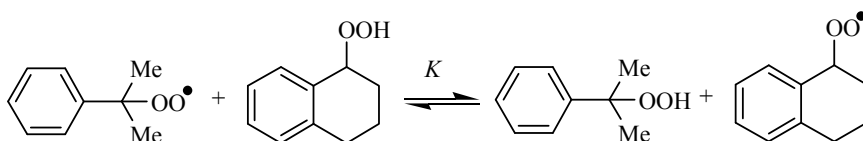
This equilibrium was found be moved to the left and equilibrium constant $K = 0.24$ (303 K). As well as enthalpy of equilibrium $\Delta H \cong \Delta G = -RT\ln K$, so $\Delta H = \Delta D_{O-H} = 3.6$ kJ/mol. Mahoney and DaRooge studied the equilibrium between sec-peroxyl radical and 2,4,6-tri-$tert$-butylphenol (Mahoney & DaRooge, 1975).
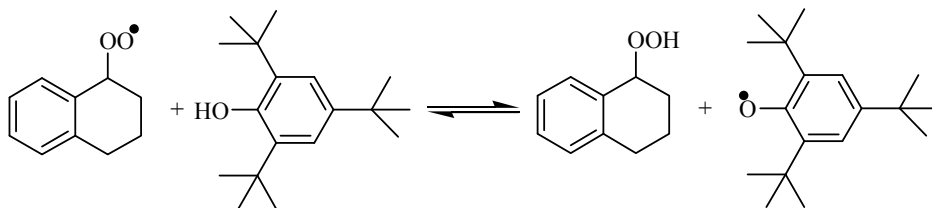
The value of $D_{O-H}(ROOH)$ calculated from enthalpy of this equilibrium was found to cover the interval $362 \div 369$ kJ/mol. All data mentioned above are in agreement with the recommended value $D_{O-H}(sec\text{-}ROOH) = 365.5$ kJ/mol (Denisov & Denisova, 2000, Denisov et al., 2003). For the O−H bond dissociation energy of hydrogen peroxide is recommended the value $D_{O-H}(HOOH) = 369.0$ kJ/mol (Luo, 2003, Lide, 2004).

Functional groups (Y = OH, >C(O) *etc.*) in hydroperoxides influence on their O−H bond dissociation energies. The problem of estimation of $D_{O-H}(YROOH)$ for such hydroperoxides was solved recently by using **MIP** in application to kinetic experimental data on co-oxidation of hydrocarbons with compounds YRH including functional groups (Denisova & Denisov, 2004). From kinetics of co-oxidation of YRH with hydrocarbon (RH) ratios of rate constants $k_Y(YROO^\bullet + RH)/k(ROO^\bullet + RH)$ were calculated and then estimated the differences in activation energies: $\Delta E = E(YROO^\bullet + RH) - E(ROO^\bullet + RH) = RT\ln(k/k_Y)$. These values of ΔE opened the way to estimate the O−H bond dissociation energies in hydroperoxides with functional groups (see Eqn. 13 and Table 10).
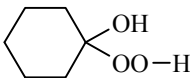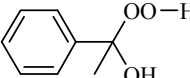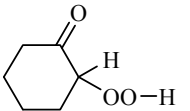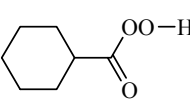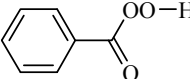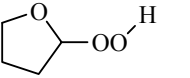
ROO–H	D, kJ/mol	ROO–H	D, kJ/mol
R^1R^2CHOO–H	365.5	$R^1R^2R^3COO$–H	358.6
(cyclohexane ring with OH and OO–H)	362.1	(benzene ring with OO–H and OH)	358.7
(cyclohexanone ring with O, H and OO–H)	369.8	(cyclohexane ring with C(=O)OO–H)	376.9
$R^1C(O)OO$–H	387.1	(benzene ring with C(=O)OO–H)	403.9
$R^1OCH(OO$–H$)R$	367.3	(tetrahydrofuran ring with OO–H)	367.6
$R^1R^2CHOC(OO$–H$)R^1R^2$	358.4	$R^1OCH(OOH)Ph$	374.8
$R^1C(O)CH(OO$–H$)R$	369.8	$AcOCH(OOH)Ph$	378.0
$R^1R^2NC(OO$–H$)CHMe$	364.1	CCl_3CCl_2OO–H	413.1

Table 10. The O−H bond dissociation energies in hydroperoxides with functional groups (Denisova & Denisov, 2004)

There were measured the rate constants for reactions of haloid substituted methyl and ethyl peroxyl radicals with nonsaturated fatty acids (Huie & Neta, 1997). These data can be used for evaluation of D_{O-H} of substituted hydroperoxides in the scope of **MIP**. The ratios of rate constants $k_i(R_iO_2{}^\bullet + RH)/k_1(R_1O_2{}^\bullet + RH)$ at T = 298 K and values of ΔD and D of O−H bonds of ROOH calculated by Eqns. 10 and 13 are presented in Table 11. The following parameters were used for calculation: α = 0.814, br_e = 15.21 (kJ/mol)$^{1/2}$, A_0 = 1.0 × 10^7 l/mol s (Denisov & Denisova, 2000), $E_{e1}(HO_2{}^\bullet +$ linoleic acid) = 36.3 kJ/mol and $E_{e1}(CCl_3O_2{}^\bullet +$ linolenic acid) = 25.1 kJ/mol.

$R_1O_2{}^\bullet$	$R_iO_2{}^\bullet$	RH	k_1/k_i	ΔD, kJ/mol	D, kJ/mol
$HO_2{}^\bullet$	$CCl_3O_2{}^\bullet$	Linoleic acid	0.012	40.1	409.1
$CCl_3O_2{}^\bullet$	$CF_3O_2{}^\bullet$	Linolenic acid	0.16	19.5	428.6
$CCl_3O_2{}^\bullet$	$CBr_3O_2{}^\bullet$	Linolenic acid	0.92	0.9	410.0
$CCl_3O_2{}^\bullet$	$CF_3CHClO_2{}^\bullet$	Linolenic acid	3.67	−12.7	396.4

Table 11. Dissociation energies of O−H bonds in haloid substituted hydroperoxides calculated by **MIP**

Recently these values were used for calculation of enthalpy of exchange equilibrium reaction (Denisova, 2007):
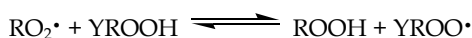
$$RO_2{}^\bullet + YROOH \rightleftharpoons ROOH + YROO^\bullet$$

where $\Delta H = D_{O-H}(YROOH) - D_{O-H}(ROOH)$ in nonpolar solvent. The reactions and values of ΔH for reactions of exchange between $Me_3CO_2^\bullet$ and YROOH are listed in Table 12.
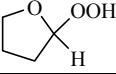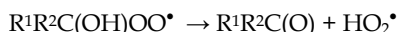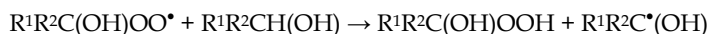
YROOH	D_{O-H}, kJ/mol	ΔH, kJ/mol	K ($T = 300$ K)	K ($T = 350$ K)
HOOH	369.0	10.4	1.55×10^{-2}	2.80×10^{-2}
sec-ROOH	365.5	6.9	6.29×10^{-2}	9.34×10^{-2}
tert-ROOH	358.6	0.0	1.00	1.00
cyclo-C_6H_{10}(OH)OOH	362.1	3.5	2.46×10^{-1}	3.00×10^{-1}
RPhC(OH)OOH	359.8	1.2	0.62	0.66
ROC(OOH)R	367.3	8.7	3.06×10^{-2}	5.03×10^{-2}
R_2CHOC(OOH)R_2	358.4	−0.2	1.08	1.07×10^{-2}
ROCH(OOH)Ph	374.8	16.2	1.51×10^{-3}	3.82×10^{-3}
	367.6	9.0	2.71×10^{-2}	4.54×10^{-2}
RC(O)OOH	387.1	28.5	1.09×10^{-5}	5.58×10^{-5}
R_3CC(O)OOH	376.9	18.3	6.51×10^{-4}	1.86×10^{-3}
cyclo-C_6H_{11}C(O)OOH	376.9	18.3	6.51×10^{-4}	1.86×10^{-3}
PhC(O)OOH	403.9	45.3	1.30×10^{-8}	1.73×10^{-7}
RC(O)CH(OOH)R	369.8	11.2	1.12×10^{-2}	2.13×10^{-2}
RC(O)CH(OOH)Ph	376.4	17.8	7.06×10^{-4}	2.21×10^{-3}
CCl_3CCl_2OOH	413.1	54.5	3.51×10^{-10}	7.35×10^{-8}
$CHCl_2CCl_2$OOH	411.6	53.0	5.92×10^{-10}	1.23×10^{-8}

Table 12. The values of ΔH for reactions of exchange: $Me_3CO_2^\bullet + YROOH \rightleftarrows$
$Me_3CO_2H + YROO^\bullet$ (Denisova, 2007)

4.2 Decomposition of α-hydroxyhydroperoxides and α-hydroxyperoxyl radicals

The oxidation of alcohols, their co-oxidation with other organic compounds, and deep steps of hydrocarbon oxidation yield α-hydroxyperoxyl radicals (Denisov & Afanas'ev, 2005). The last participate in the following reactions:

$$R^1R^2C(OH)OO^\bullet + R^1R^2CH(OH) \rightarrow R^1R^2C(OH)OOH + R^1R^2C^\bullet(OH)$$

$$R^1R^2C(OH)OO^\bullet \rightarrow R^1R^2C(O) + HO_2^\bullet$$

The formed α-hydroxyhydroperoxide decomposes into carbonyl compound and hydrogen peroxide.

$$R^1R^2C(OH)OOH \rightarrow R^1R^2C(O) + H_2O_2$$
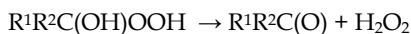
The thermodynamics and kinetic of these reactions were analysed recently in paper (Denisov & Denisova, 2006). Hydroxyhydroperoxides are labile compounds and are not amenable to thermochemical measurements of their enthalpy of formation (Denisov et al.,

2003). Earlier, comparing the enthalpies of formation of hydroperoxides ROOH with $\Delta H(RH)$ and $\Delta H(ROH)$, we observed a symbatic change in these values, namely, the correlations: $\Delta H(ROOH) = a + \Delta H(RH)$ and $\Delta H(ROOH) = b + \Delta H(ROH)$ (Denisov & Denisova, 1988). This regularity was extended to the enthalpy of formation of α-hydroxyhydroperoxides. The following procedure was used to estimate $\Delta H(R^1R^2C(OH)OOH)$. First, the difference of the formation enthalpies of R_2CHOOH and R_2CH_2 was determined, and then the enthalpy of formation of $R^1R^2C(OH)OOH$ was calculated as the algebraic sum: ΔH_f^0

$$\Delta H_f^0(R^1R^2C(OH)OOH) = \Delta H_f^0(R^1R^2CHOH) + \{\Delta H_f^0(R^1R^2CHOOH) - \Delta H_f^0(R^1R^2CH_2)\} \quad (16)$$

The results of calculation of the enthalpies of formation for fourteen α-hydroxyhydroperoxides by Eqn. (16) are given in Table 13. This calculation implies that the replacement of H by OOH varies the enthalpy of formation of the corresponding alcohol by the same value as in the case of this substitution in RH. The validity of this approach was qualitatively verified by comparing the enthalpies of two equilibrium reactions of cyclohexanone with ROOH and H_2O_2 (Denisov & Denisova, 2006). The values of decomposition enthalpies of α-hydroxyhydroperoxides are listed in Table 13.

α-Hydroxyhydroperoxide	$-\Delta H_f^0(R^1R^2C(O))$, kJ/mol	$-\Delta H_f^0(R^1R^2C(OH)OOH)$, kJ/mol	ΔH, kJ/mol
$CH_2(OH)OOH$	108.8	261.1	15.9
$MeCH(OH)OOH$	165.7	320.0	17.9
$EtCH(OH)OOH$	187.4	336.8	13.0
$Me_2C(OH)OOH$	217.1	366.1	12.6
$PrCH(OH)OOH$	207.5	353.5	9.6
$EtMeC(OH)OOH$	240.6	385.8	8.8
$MePrC(OH)OOH$	259.0	401.7	6.3
$PhCH(OH)OOH$	37.7	190.0	15.9
$PhMeC(OH)OOH$	86.6	231.8	8.8
$cyclo$-$C_6H_{11}CH(OH)OOH$	235.1	389.5	18.0
$cyclo$-$C_5H_8(OH)OOH$	192.5	349.2	20.3
$cyclo$-$C_6H_{10}(OH)OOH$	225.9	377.7	22.4
$cyclo$-$C_{12}H_{22}(OH)OOH$	351.5	495.7	7.8
α-Tetralyl-(OH)OOH	90.8	246.0	18.8

Table 13. Enthalpies (ΔH) of decomposition of α-hydroxyhydroperoxides in nonpolar solvents

According data presented in Table 10 the strength of the OO–H bond in α-hydroxycyclohexyl hydroperoxide is equal to 362.1 kJ/mol. Therefore, using the expression for the strength of the OO–H bond:

$$D_{O-H} = \Delta H_f^0(R_2C(OH)OO^{\bullet}) + \Delta H_f^0(H^{\bullet}) - \Delta H_f^0(R_2C(OH)OOH) \quad (17)$$

and supposing D_{O-H} = 362.1 kJ/mol for all hydroxyhydroperoxides we obtain the following thermochemical equation for the enthalpy of formation of the α-hydroxyperoxyl radical (ΔH_f^0(H$^•$) = 218.0 kJ/mol (Luo, 2005)):

$$\Delta H_f^0(R_2C(OH)OO^•), \text{kJ/mol} = \Delta H_f^0(R_2C(OH)OOH) + 144.1 \qquad (18)$$

The ΔH_f^0 (>C(OH)OO$^•$) values calculated for decomposition of fifteen radicals by Eq. (18) are given in Table 14. The enthalpy (ΔH) of decomposition of the α-hydroxyperoxyl radical was calculated by the Eqn. 19:

$$\Delta H(\text{decay}), \text{kJ/mol} = \Delta H_f^0(R_2C(O)) + \Delta H_f^0(HO_2^•) - \Delta H_f^0(R_2C(OH)OO^•) \qquad (19)$$

where ΔH_f^0(HO$_2$$^•$) = 14.6 kJ/mol (Lide, 2004). The results of calculation of the enthalpies of degradation of the α-hydroxyperoxyl radicals are presented in Table 14.

α-Hydroxyperoxyl radical	$-\Delta H_f^0$(>C(OH)OOH)), kJ/mol	$-\Delta H_f^0$(>C(OH)OO$^•$), kJ/mol	ΔH, kJ/mol
CH$_2$(OH)OO$^•$	261.1	117.0	22.8
MeCH(OH)OO$^•$	320.0	175.9	24.8
EtCH(OH)OO$^•$	336.8	192.7	20.0
Me$_2$C(OH)OO$^•$	366.1	222.0	19.5
PrCH(OH)OO$^•$	353.5	209.4	16.5
EtMeC(OH)OO$^•$	385.8	241.7	15.7
MePrC(OH)OO$^•$	401.7	257.6	13.2
Me$_2$CHMeC(OH)OO$^•$	401.7	257.6	9.9
PhCH(OH)OO$^•$	190.0	45.9	22.8
PhMeC(OH)OO$^•$	231.8	87.7	15.7
cyclo-C$_6$H$_{11}$CH(OH)OO$^•$	389.5	245.4	25.0
cyclo-C$_5$H$_8$(OH)OO$^•$	349.2	205.1	27.2
cyclo-C$_6$H$_{10}$(OH)OO$^•$	377.7	233.4	22.4
cyclo-C$_{12}$H$_{22}$(OH)OO$^•$	495.7	351.6	15.0
α-Tetralyl-(OH)OO$^•$	246.0	101.9	25.7

Table 14. Enthalpies of decomposition of α-hydroxyperoxyl radicals

4.3 Enthalpies of reactions of peroxyl radicals with phenols

As was written earlier, the reaction of peroxyl radicals with phenols is the main reaction of action of phenols as antioxidants. The enthalpy of this reaction is equal to difference of bond dissociation energies of two O−H bonds:

$$\Delta H = D_{O-H}(ArOH) - D_{O-H}(ROOH) . \qquad (20)$$

The values of ΔH calculated for 108 reactions of different R$_i$O$_2$$^•$ with phenols (Ar$_j$OH) are presented in Table 15. It is seen from Table 15 that enthalpy of reaction strongly depends on D_{O-H}(ArOH) as well as on D_{O-H}(ROOH).

Ar$_j$OH/R$_i$O$_2^\bullet$	ΔH, kJ/mol					
	tert-ROO$^\bullet$	*sec*-ROO$^\bullet$	HO$_2^\bullet$	AcCH(OO$^\bullet$)Me	AcOO$^\bullet$	PhC(O)OO$^\bullet$
PhOH	10.4	3.5	0.0	1.7	−18.1	−34.9
4-Me-C$_6$H$_4$OH	3.0	−3.9	−7.4	−5.7	−25.5	−42.3
4-OMe-C$_6$H$_4$OH	−8.7	−15.6	−19.1	−17.4	−37.2	−54.0
4-OH-C$_6$H$_4$OH	−3.5	−10.4	−13.9	−12.2	−32.0	−48.8
4-NH$_2$-C$_6$H$_4$OH	−36.4	−43.3	−46.8	−45.1	−64.9	−81.7
4-COMe-C$_6$H$_4$OH	12.9	6.0	2.5	4.2	−15.6	−32.4
2,4-(Me)$_2$-C$_6$H$_3$OH	1.9	−5.0	−8.5	−6.8	−26.6	−43.4
2,6 -(Me)$_2$-C$_6$H$_3$OH	−4.0	−10.9	−14.4	−12.7	−32.5	−49.3
Ionol	−15.6	−22.5	−26.0	−24.3	−44.1	−60.9
α-Tocopherol	−28.6	−35.5	−39.0	−37.3	−57.1	−73.9
β-Tocopherol	−23.3	−30.2	−33.7	−32.0	−51.8	−68.6
δ-Tocopherol	−17.1	−24.0	−27.5	−25.8	−45.6	−62.4
Ubiquinol-0	−13.3	−20.2	−23.7	−22.0	−41.8	−58.6
Quercetin	−15.6	−22.5	−26.0	−24.3	−44.1	−60.9
Chrysin	−1.5	−8.4	−11.9	−10.2	−30.0	−46.8
Morin	5.0	−1.9	−5.4	−3.7	−23.5	−40.3
Campherol	−9.7	−16.6	−20.1	−18.2	−38.2	−55.0
Myricetin	−17.7	−24.6	−28.1	−26.4	−46.2	−63.0

Table 15. Enthalpies (kJ/mol) of reactions R$_i$O$_2^\bullet$ + Ar$_j$OH $\rightarrow$ R$_i$OOH + Ar$_j$O$^\bullet$ (Eqn. 20)

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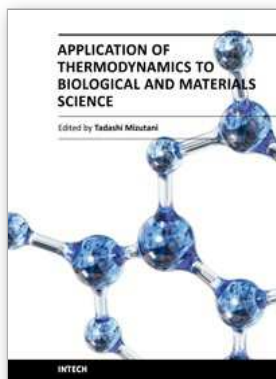
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