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Estimation of the bond dissociation energies from the kinetic characteristics of liquid-phase radical reactions

E T Denisov, V E Tumanov

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Abstract. Three methods used in the kinetics of liquid-phase radical reactions for estimating the dissociation energies of individual bonds in polyatomic molecules are described. The first approach is based on the study of the equilibrium in radical abstraction reactions involving stable radicals and measurements of the equilibrium constants. The second method is based on the study of the kinetics of homolytic decomposition of molecules. Measuring the activation energy of these reactions makes it possible to estimate the dissociation energies of the weakest bonds, *e.g.*, the O – O bonds in various peroxides. The essence of the third approach developed in the framework of the model of intersecting parabolas is calculations of the bond dissociation energy from the activation energy of a radical reaction involving the molecules under consideration. This method allowed the dissociation energies of the C – H, N – H, O – H and S – H bonds in a large number of organic compounds to be estimated. The scope and the specific features of application of each method are discussed and the bond dissociation energies determined by these methods are given. The bibliography includes 78 references.

I. Introduction

The dissociation energies of individual bonds in a molecule and the enthalpies of formation of a molecule or radical are the most important energy characteristics of such species, which are widely used in science and technology. Every year brings tens of studies presenting the results of measurements of these parameters. The first review summarising data on the bond dissociation energies in molecules was reported five decades ago.[1] In the USSR, collection, systematisation and publication of such data were initiated by academician V N Kondrat'ev.[2,3] Publication of a multivolume handbook of the thermal properties of molecules and atoms[4] became a great scientific event. A recently published handbook[5] by Luo contains a considerable body of information on the bond dissociation energies in polyatomic molecules.

A broad spectrum of physicochemical methods developed for measuring the bond dissociation energies comprises low-pressure pyrolysis, kinetic studies of gas-phase bromination and iodination of hydrocarbons, spectral methods (these are used for estimating the bond energy in diatomic molecules), electron impact mass spectrometry, photoelectron spectroscopy, electrochemical methods and recently elaborated photoacoustic calorimetry. Each method has its own field of application, specific features and limitations.[6–15]

The last two decades have been characterised by the widespread use of kinetic methods for studying and analysing liquid-phase radical reactions. Such methods allow one to estimate the strengths of individual bonds in polyatomic molecules and considerably extend the range of compounds with known bond strengths. They include:

(1) studies of equilibrium bimolecular reactions involving stable free radicals;

(2) investigations on the kinetics of monomolecular decomposition of compounds involving homolysis of one (the weakest) bond;

(3) measurements of the absolute or relative rate constants for radical abstraction reactions or the activation energies of such reactions followed by calculations of the dissociation energy of a particular bond involved in the rearrangement.

The aim of this review is to consider these methods and the values of the strengths of individual bonds in various organic compounds obtained using these approaches. The methods mentioned above made it possible to significantly extend the range of complex polyatomic molecules for which the bond dissociation energies were determined from experimental data.

E T Denisov, V E Tumanov Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax (7-096) 515 54 20, tel. (7-096) 522 19 14, e-mail: edenisov@icp.ac.ru (E T Denisov), tel. (7-096) 522 13 66, e-mail: tve@icp.ac.ru (V E Tumanov)

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II. Chemical equilibrium $X^{\bullet} + HY \rightleftharpoons HX + Y^{\bullet}$

The chemical equilibrium

$$X^{\bullet} + HY \underset{(a)}{\overset{K}{\rightleftharpoons}} XH + Y^{\bullet},$$

where $X^{\bullet}$ and $Y^{\bullet}$ are reactive free 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 ($X^{\bullet}$ and $Y^{\bullet}$) are stable and do not enter the recombination reaction. In this case the equilibrium concentrations of both radicals can be determined by EPR spectroscopy or spectrophotometrically. The equilibrium constant (K) is calculated from the ratio of the equilibrium concentrations of the molecules and radicals:

$$K = \frac{[Y^{\bullet}]_{\infty}[XH]_{\infty}}{[X^{\bullet}]_{\infty}[YH]_{\infty}}, \quad (1)$$

and the equilibrium enthalpy (ΔH) is calculated from the temperature dependence of $\ln K$. On the other hand, the equilibrium enthalpy of this reaction is equal to the difference between the dissociation energies (D) of the bonds involved in the reaction

$$\Delta H = D_{Y-H} - D_{X-H} \quad (2)$$

provided that solvation of reactants makes an insignificant contribution to the equilibrium. This can be attained by carrying out experiments in non-polar solvents.

The approach was employed in a number of studies [16–18] for estimating the dissociation energies of the O–H bonds in phenols. Belyakov *et al.*[16] measured the equilibrium of the type

$$Ar^1O^{\bullet} + Ar^iOH \rightleftharpoons Ar^1OH + Ar^iO^{\bullet},$$

with galvinoxyl as the reference phenoxyl radical $Ar^1O^{\bullet}$ and *para*-substituted 2,6-di-*tert*-butylphenols as the second reactants Ar^iOH. Changes in the galvinoxyl and phenoxyl $Ar^iO^{\bullet}$ concentrations were monitored by EPR spectroscopy (benzene, 298 K). Calculations of the equilibrium constant

$$K = \frac{[Ar^iO^{\bullet}][Ar^1OH]}{[Ar^1O^{\bullet}][Ar^iOH]}, \quad (3)$$

from the reactant concentration ratio were followed by calculations of the Gibbs free energy of equilibrium (ΔG):

$$\Delta G = -RT\ln K. \quad (4)$$

The equilibrium enthalpy was determined using the temperature dependence of the equilibrium constant. Experience showed that in such reactions one has $\Delta H \approx \Delta G$ within the limits of error in measurements. An analogous conclusion was also drawn by authors of other studies.[17,18] 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 characterised by recombination of phenoxyl radicals formed. Here, the reaction conditions are chosen in such a fashion that an equilibrium between reactants is attained and the phenols are consumed slowly, so it is possible to monitor each reactant and calculate the equilibrium constant.[17,18] 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} = 339.7 kJ mol^{-1} (see Ref. 19), which is in good agreement with the D value for unsubstituted phenol (D_{O-H} = 369.0 kJ mol^{-1}).[5,21] Both these phenols were used as reference compounds for calculating the absolute values of D_{O-H} of some other phenols (see Table 1). The error in estimating ΔH values is only ±1.1 kJ mol^{-1} (see Ref. 17).

In order to evaluate the dissociation energies of O–H bonds in various phenols, Mahoney and DaRooge[22] measured the equilibrium constant $K = k_1/k_{-1}$ for the reactions

$$ROO^{\bullet} + ArOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROOH + ArO^{\bullet}.$$

To this end, 9,10-dihydroanthracene (RH) was oxidised with oxygen in the presence of corresponding hydroperoxide (ROOH) and phenol (ArOH) in chlorobenzene at 333 K with 2,2,3,3-tetraphenylbutane as initiator. The experimental conditions were chosen in such a manner that the equilibrium (see above) was established in the system and the chain termination step was limited by the recombination of $ArO^{\bullet}$ and $ROO^{\bullet}$ radicals. In this case the rate, (v_v), of the chain oxidation process is satisfactorily described by the following equation [21]

$$v_v = k_p[RH]\sqrt{\frac{k_{-1}v_i[ROOH]}{2k_1k_t[ArOH]}}, \quad (5)$$

where k_p and k_t are the rate constants for the reactions of $ROO^{\bullet}$ with RH and $ROO^{\bullet}$ with $ArO^{\bullet}$, respectively, and v_i is the initiation rate.[21] The dependence of the chain oxidation rate $v_v = v - v_i$ (v is the overall reaction rate) on the ROOH and ArOH concentrations was used to determine the $k_p^2/(2Kk_t)$ ratio and then the equilibrium constant $K = k_1/k_{-1}$ was calculated using known values of k_p and $2k_t$. The $\Delta H = D_{ArO-H} - D_{ROO-H}$. values were determined assuming that $\Delta H = \Delta G = -RT\ln K$. The D_{ArO-H} calculated relative to the O–H bond dissociation energy in PhOH (369.0 kJ mol^{-1}) are listed in Table 1. Analysis of the data from Table 1 shows that differences between D_{O-H} values for the same phenol, reported by different authors, are small, being on average 1.2 ± 0.7 kJ mol^{-1}.

The equilibrium

$$Ar^iO^- + ClO_2^{\bullet} \underset{(a)}{\overset{K}{\rightleftharpoons}} Ar^iO^{\bullet} + ClO_2^-,$$

was studied by pulse radiolysis.[20] Here, the equilibrium constant was used to calculate the redox potential (E_0) of the aroxyl radical in aqueous solution. The Gibbs energy (ΔG°, in kJ mol^{-1}) of the reaction

$$Ar^iOH\,(aq) \longrightarrow Ar^iO^{\bullet}\,(aq) + 0.5\,H_2\,(gas)$$

was calculated as follows

$$\Delta G^{\circ} = 96.5\,E_0 + 5.70\,pK_a \quad (6)$$

(pK_a characterises acid dissociation of phenol) and used for calculating the O–H bond dissociation energy of phenol in water. This energy was estimated to be 12 ± 4 kJ mol^{-1} higher than in the gas phase due to solvation.[20] Table 1 lists the O–H bond dissociation energies for monosubstituted phenols (corrected for solvation effects in water), obtained based on the D_{O-H} = 369.0 kJ mol^{-1} value for phenol.

Reactions of aminyl radicals with phenols are extremely fast. The reverse reactions of phenoxyl radicals with amines also proceed at a high rate.[23–25] The interaction of a stable phenoxyl radical $ArO^{\bullet}$ with amine (AmH) in the presence of phenol (ArOH) can be considered as a two-step process:[23]

$$ArO^{\bullet} + AmH \underset{(a)}{\overset{K}{\rightleftharpoons}} ArOH + Am^{\bullet},$$

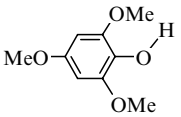
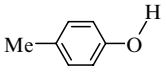
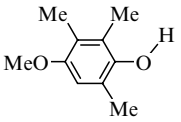
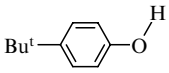
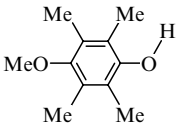
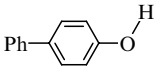
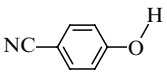
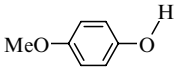
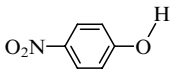
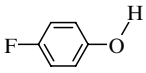
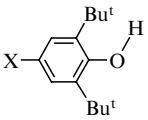
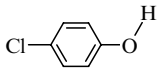
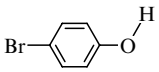
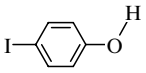
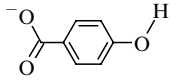
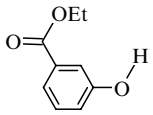
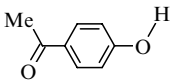
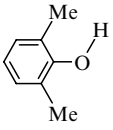
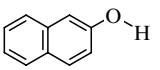
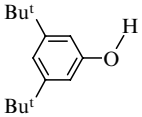
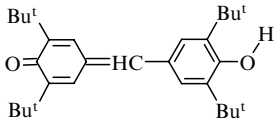
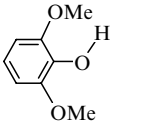
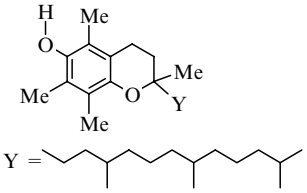
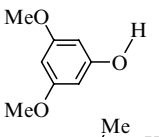
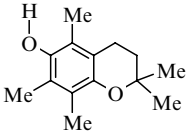
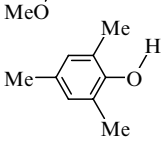
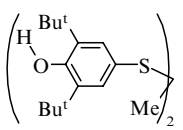
$$Am^{\bullet} + Am^{\bullet} \underset{(b)}{\overset{k}{\longrightarrow}} \text{products},$$

with the total rate given by

$$v_v = k[Am^{\bullet}]^2 = kK^2\left(\frac{[ArO^{\bullet}][AmH]}{[ArOH]}\right)^2. \quad (7)$$

The kinetics of the reactions of 2,4,6-tri-*tert*-butylphenoxyl radical with eleven amines (AmH) were studied [23] under the conditions

Table 1. Dissociation energies of O–H bonds in phenols calculated from the equilibrium constants.

Phenol	D_{O-H} /kJ mol^{-1}	Ref.	Phenol	D_{O-H} /kJ mol^{-1}	Ref.
PhO–H	369.2	18		334.5	18
	360.5 361.8 360.2	18 19 20		331.2	18
	356.7 361.5	18 19		342.4	18
	355.4	19		388.7	20
	346.3 351.3 345.6	18 19 20		394.1	20
	365.6	20			
	366.4	20	X = H	346.2	18
	368.6	20	X = Me	342.8 337.2 338.8	16 17 18
	367.7	20	X = CH_2Ph	335.1	16
	376.1	20	X = Ph	337.9	16
	375.7	19	X = Cl	344.5	16
			X = OMe	325.5 324.3 327.5	16 17 18
			X = OBu^t	330.2	16
	377.8	20	X = Ac	352.3	16
			X = CN	356.9	16
	353.3 355.7	18 19		361.6	19
	362.2 363.4	18 19		328.2 329.3	16 17
	350.0	18		330.0 327.1	17 18
	362.6	18		327.2	18
	345.9	18		338.0	17

Note. Hereinafter the attacked bonds are shown.

of fast establishment of the equilibrium between the ($ArO^{\bullet}$) radical involved in the reaction and the forming ($Am^{\bullet}$) radical. The equilibrium constants K (in CCl_4 at 298 – 340 K) were calculated from the reagent concentration ratio [see Eqn (7)]. The equilibrium enthalpies were determined from the temperature dependence of K

$$\Delta H = -R\frac{d\ln K}{d(1/T)}. \quad (8)$$

As mentioned above, the entropy of equilibrium in exchange radical reactions varies only slightly and can be set to zero; in these cases, one has $\Delta H = \Delta G$. Then the enthalpy of reaction can be determined from the equilibrium constant [see Eqn (4)].

The D_{N-H} values were calculated using two procedures:[23] (1) from the equilibrium constant measured at the same temperature (298 K),

$$D_{N-H} = 339.7 - RT\ln K\ (\text{kJ mol}^{-1}); \quad (9)$$

and (2) from the equilibrium enthalpy determined using expression (8). In this case the N – H bond strength was calculated as follows:

$$D_{N-H} = 339.7 + \Delta H\ (\text{kJ mol}^{-1}). \quad (10)$$

The first term in Eqns (9) and (10) is the dissociation energy of the O – H bond in the newly forming phenol. The dissociation energies of the N – H bonds in amines thus obtained are listed in Table 2. These D_{N-H} values are in agreement with the D_{O-H} values for phenols (see Table 1).

Jonsson *et al.*[26,27] reported a flash radiolysis study of two equilibrium reactions involving a number of substituted anilines

$$Ar^iNH_2 + N_3^{\bullet}\ (\text{or } Br_2^{-\bullet}) \overset{K}{\rightleftharpoons} Ar^iNH_2^{+\bullet} + N_3^-\ (\text{or } 2\,Br^-),$$

each of them being followed by the equilibrium deprotonation reaction

$$Ar^iNH_2^{+\bullet} \rightleftharpoons Ar^iNH^{\bullet} + H^+.$$

The equilibrium constant of one reaction was used to calculate the redox potential E_0 of aminyl radical in aqueous solution. The N – H bond strength (in kJ mol^{-1}) in aniline was calculated as follows:

$$D_{N-H} = 96.48\,E_0 + 5.70\,pK_a + 238.5. \quad (11)$$

The D_{N-H} values thus obtained for eighteen anilines studied are listed in Table 2 along with the dissociation energies of the N – H bonds in substituted anilines determined using the recommended[5] value $D_{N-H}(PhNH_2) = 375.3$ kJ mol^{-1}.

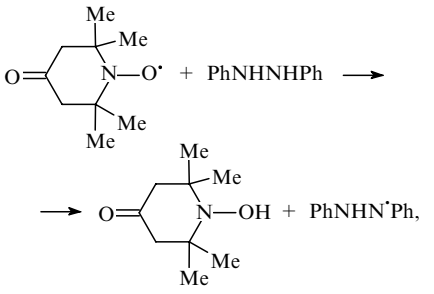
The composition of radicals produced upon photolysis of di-*tert*-butylperoxide in a benzene solution in the presence of phenol and amine was studied by EPR spectroscopy.[28] The radical ratio established in the system after fast exchange reaction is characteristic of the equilibrium (*a*).

The phenoxyl-to-aminyl radical concentration ratio was determined by EPR spectroscopy and the equilibrium constant of this reaction,

$$K = \frac{[Am^{\bullet}][ArOH]}{[ArO^{\bullet}][AmH]}. \quad (12)$$

was calculated. 2,6-Di-*tert*-butyl-4-methoxyphenol was used as the reference phenol. The D_{N-H} thus obtained for ten amines are listed in Table 2.

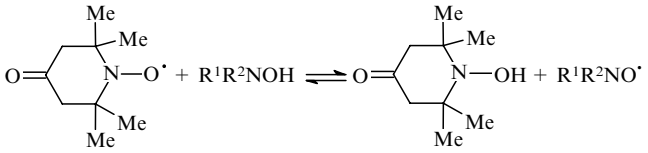
A number of EPR studies on the equilibrium between stable iminoxyl radicals and various hydroxylamines and oximes are available.[29–32] A calorimetric study of the reactions of such radicals with 1,2-diphenylhydrazine[29]



$$Bu^t_2C{=}NO^{\bullet} + PhNHNHPh \longrightarrow Bu^t_2C{=}NOH + PhNHN^{\bullet}Ph$$

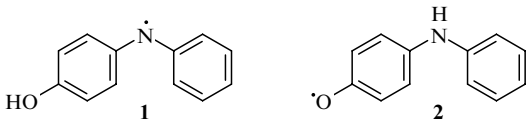
made it possible to determine their enthalpies of formation and use this parameter for calculating the O – H bond strengths in the corresponding hydroxylamines and oximes (Table 3).

The D_{O-H} value for 2,4,6-tri-*tert*-butylphenol was determined analogously.[19] Thus, it was found that the equilibrium-based D_{O-H} scale for hydroxylamines is consistent with the D_{O-H} scale for phenols and D_{N-H} scale for amines (see Tables 1 and 2). The D_{O-H} for various hydroxylamines calculated from the equilibrium constants of the following reactions

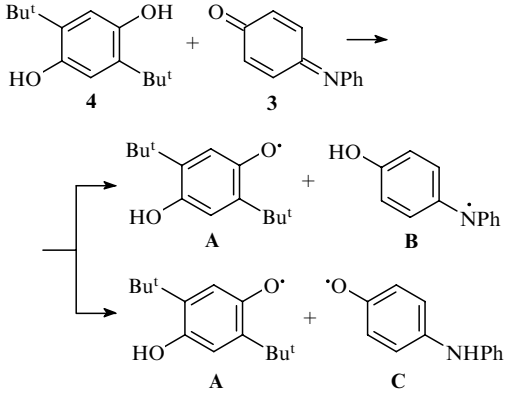


are listed in Table 3.

Determination of the dissociation energy of the attacked bond in various semiquinone radicals is a rather complicated task. For instance, a radical attack on *p*-hydroxydiphenylamine produces two radicals, namely, *p*-hydroxyphenylaminyl radical **1** and *p*-(phenylamino)phenoxyl radical **2**:



The strengths of the O – H bond in radical **1** and the N – H bond in radical **2** were estimated by Varlamov[33] in a recent detailed study of a reversible exchange reaction between *N*-phenyl-1,4-benzoquinoneimine (**3**) and 2,5-di-*tert*-butylhydroquinone (**4**). As was shown earlier, this reaction proceeds by a chain mechanism,[34] the chain initiation following two pathways:



The chain propagation step involves four very fast reactions of radicals **A** – **C** with quinoneimine **3** and quinone **5**.

Table 2. N–H bond dissociation energies in aromatic amines calculated from the equilibrium constants.

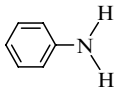
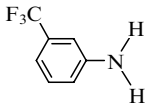
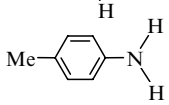
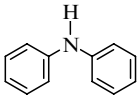
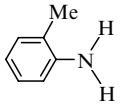
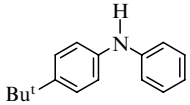
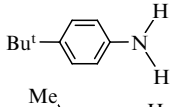
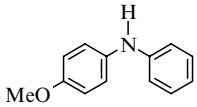
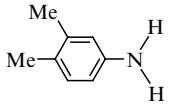
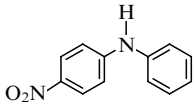
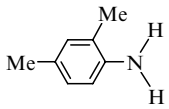
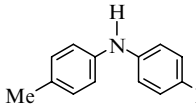
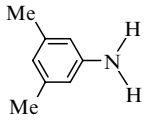
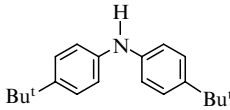
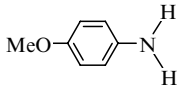
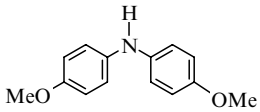
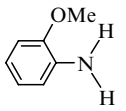
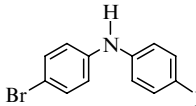
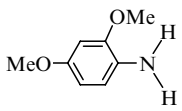
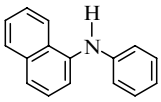
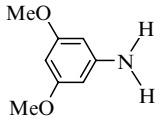
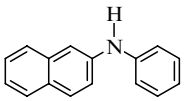
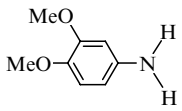
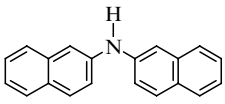
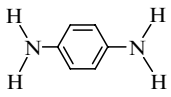
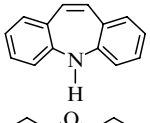
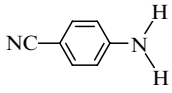
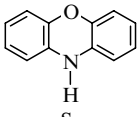
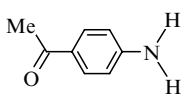
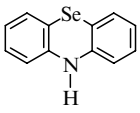
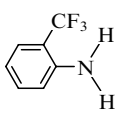
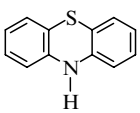
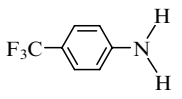
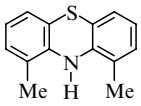
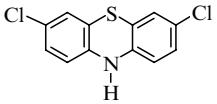
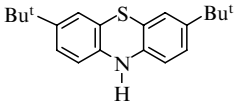
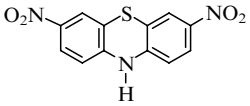
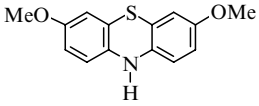
Amine	D_{N-H} /kJ mol^{-1}	Ref.	Amine	D_{N-H} /kJ mol^{-1}	Ref.
	375.3	26		392.3	27
	373.3	26		362.5 [a] 364.7 [b] 359.0	23 23 28
	361.3	27		361.6 [a] 360.0 [b]	23 23
	374.3	26		353.3 [a] 355.7 [b] 347.9	23 23 28
	373.3	27		378.8 [a] 372.6 [b]	23 23
	370.3	27		357.5 [a] 357.2 [b]	23 23
	380.3	27		355.1 [a] 358.5 [b]	23 23
	367.3	26		342.5 [a] 348.3 [b]	23 23
	373.3	27		358.9 [a] 363.9 [b]	23 23
	369.3	27		352.8 [a] 356.8 [b]	23 23
	385.3	27		362.3 [a] 362.6 [b]	23 23
	372.3	27		360.5 [a] 359.9 [b]	23 23
	362.3	26		344.8	28
	386.3	26		323.0	28
	381.3	26		336.4	28
	389.3	27		331.8	28
	387.3	26			

Table 2 (continued).

Amine	D_{N-H} /kJ mol^{-1}	Ref.	Amine	D_{N-H} /kJ mol^{-1}	Ref.
	325.1	28		333.9	28
	326.8	28		338.9	28
	318.8	28			

[a] D_{N-H} value was calculated based on ln K (at 298 K). [b] D_{N-H} value was calculated based on the enthalpy of equilibrium, ΔH.

Table 3. O–H bond dissociation energies in hydroxylamines and oximes calculated from the equilibrium constants.

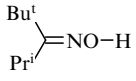
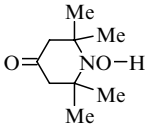
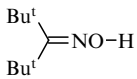
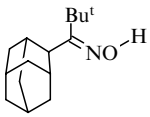
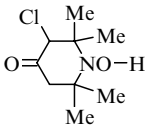
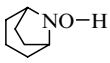
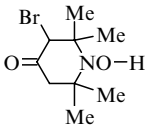
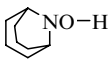
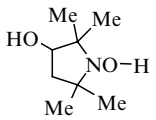
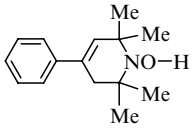
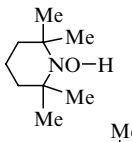
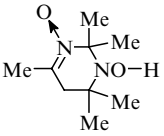
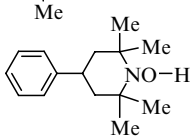
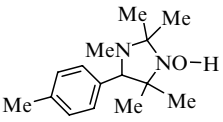
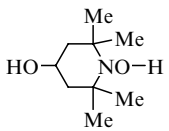
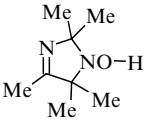
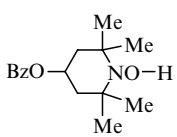
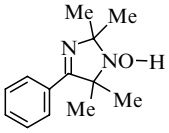
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	338.5	29			
	334.7	29		307.9	21, 31
	322.2	29		303.4	21, 31
	318.8	29			
	287.3	30		295.0	32
	297.7 292.6	29 30		308.8	21, 31
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	302.2	21, 31		295.2	21, 31
	300.3	21, 31		294.2	21, 31

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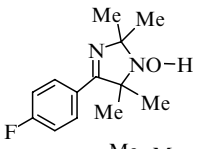
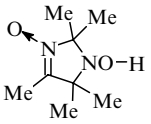
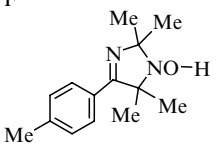
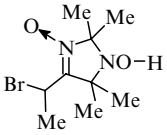
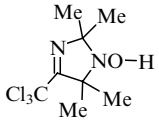
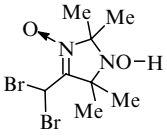
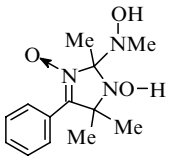
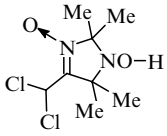
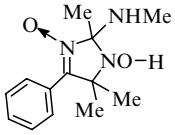
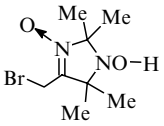
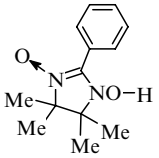
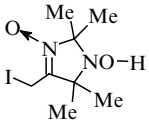
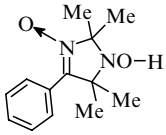
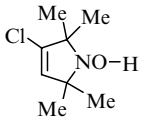
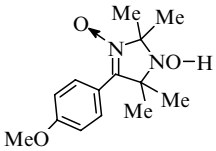
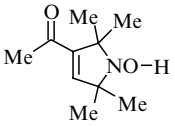
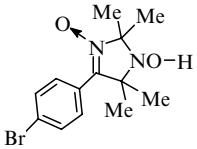
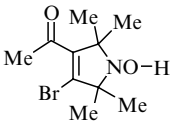
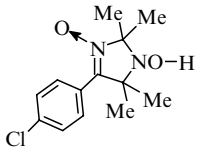
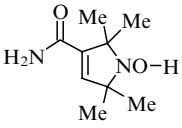
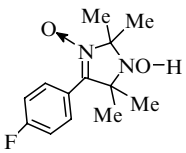
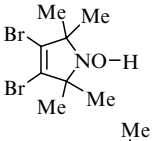
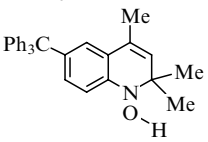
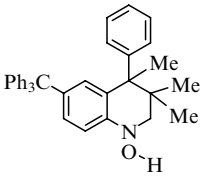
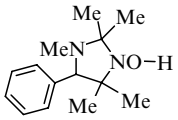
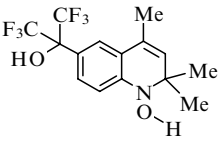
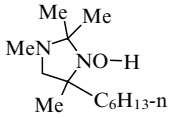
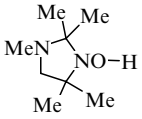
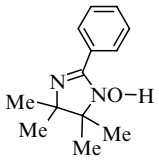
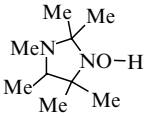
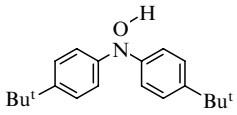
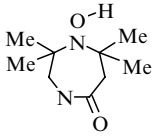
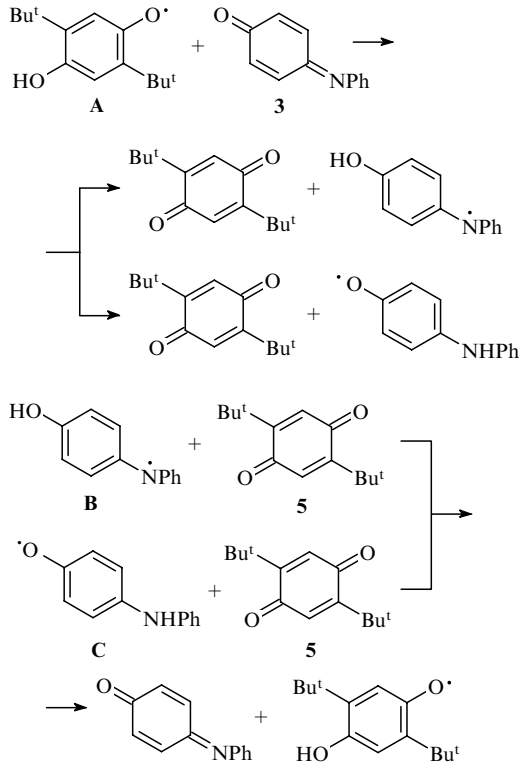
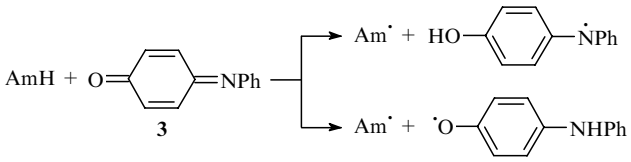
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	296.9	31		305.8	21, 31
	297.1	31		311.4	21, 31
	310.0	31		309.8	21, 31
	309.5	21, 31		306.3	31
	297.1	31		306.8	21, 31
	304.5	21, 31		293.3	21, 31
	303.2	31		294.3	31
	306.0	31		294.5	21, 31
	306.3	31		293.1	31
	305.8	31		293.9	31
				289.5 291.3	32 30

Table 3 (continued).

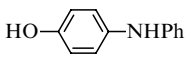
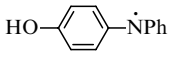
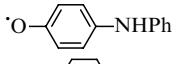
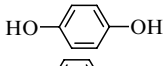
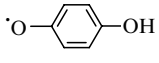
Compound	D_{O-H} /kJ mol^{-1}	Ref.	Compound	D_{O-H} /kJ mol^{-1}	Ref.
	292.8	32		292.6	21, 31
	295.0	30, 31		282.5	30
	286.6	30		312.2	21, 31
	290.8 288.7	21, 31 30		296.5 303.7	32 30
				304.3	21, 31



The chain termination step involves six disproportionation reactions of the three radicals involved in the chain reaction. In order to obtain an additional chain initiation, an amine (AmH), namely, di-*p*-tolylamine or 4-methoxyphenyl-*p*-tolylamine was introduced into the system. The amine reacted with quinoneimine, which accelerated the process.[35]



The overall rate of the additional initiation was measured from the dependence of the initial reaction rate of quinoneimine reduction on the initiation rate (with tetraphenylhydrazine as initiator, mixed initiation technique). Based on the kinetic data, the overall initiation rate constants were calculated for the reactions involving amines. Experiments were carried out at different temperatures. The D_{O-H} and D_{N-H} values for the radicals mentioned above were calculated using the intersecting parabolas method (see Section V). These parameters were also calculated from experimental values of the activation energies for these reactions. The O−H and N−H bond strengths in *p*-hydroxydiphenylamine were estimated using the Hammett correlation equations. Their values (in kJ mol^{-1}) are listed below[35] (for comparison, we also present the D_{O-H} values in hydroquinone and in semiquinone radical[21]):

Compound (radical)	D_{O-H}	D_{N-H}
	339.3	353.4
	259.5	–
	–	273.6
	352.0	–
	223.0	–

III. The kinetics of homolytic decomposition of molecules

Consider decomposition of a molecule into two radicals involving cleavage of a single bond, *e.g.*, the O—O bond in a peroxide

$$R^1OOR^2 \longrightarrow R^1O^{\bullet} + R^2O^{\bullet} \text{ (see }^{\dagger}\text{)}.$$

The activation energy (E_a) for this reaction is very similar to the dissociation energy of the bond being cleaved. In the framework of the Rice–Ramsperger–Kassel–Marcus (RRKM) theory in accord with the harmonic model the activation energy for the decomposition of a molecule differs from the dissociation energy by only $0.5RT$.[36]

$$D_{O-O} = E_a - 0.5RT. \quad (13)$$

This holds for gas-phase decomposition of substances at high pressures and, apparently, for liquid-phase decomposition (in solution) in non-polar solvents.

The rate constant for decomposition:

$$k = -\frac{d\ln[R^1OOR^2]}{dt}, \quad (14)$$

is determined from the kinetics of decomposition of the initial compound and the activation energy:

$$E_a = -\frac{R\,d\ln k}{d(T^{-1})}, \quad (15)$$

is found from the temperature dependence of k in a series of experiments carried out at different temperatures.

The rate constants for decomposition of various peroxides can be found in the literature;[37] they were used [38, 39] for estimating the D_{O-O} values. Analysis of experimental data on the kinetics of peroxide decomposition revealed a large error in measuring the activation energies for the decomposition of these compounds.[37] To improve the accuracy in determining this chararacteristic, the following procedure was employed. Experimental data for the structurally similar group in peroxides were used to calculate the average pre-exponent A

$$\ln A = \frac{1}{n}\sum_i \ln A_i$$

and then the activation energy was calculated from the rate constant for the reaction at each temperature using the Arrhenius relation:

$$E_a = RT\ln\left(\frac{A}{k}\right). \quad (16)$$

Listed below are the average A values for various peroxides:[38, 39]

Peroxide	ROOR	$PhR^1R^2COOCR^1R^2Ph$	RC(O)OOC(O)R
$10^{-15}\,A\,/s^{-1}$	2.4	1.4	0.63

Knowing the O—O bond dissociation energy and the enthalpy of formation of the initial ROOR molecule, it is possible to calculate the standard enthalpy of formation of $RO^{\bullet}$ radical:

$$2\Delta H_f^{\circ}(RO^{\bullet}) = \Delta H_f^{\circ}(ROOR) - D_{O-O}. \quad (17)$$

Such calculations were performed using the experimental values of the standard enthalpies of formation of peroxides and the enthalpies of vaporisation or sublimation of these compounds (see Ref. 37). In turn, the enthalpy of formation of the $RO^{\bullet}$ radical allows the dissociation energies of the RO—H, RO—Alk, RO—Acyl bonds, *etc.* to be calculated. This was done for a series of alkoxyl and acyloxyl radicals using the kinetic characteristics of decomposition of corresponding peroxides.[38, 39] The results of calculations of D_{O-H} values for alcohols and organic acids are presented in Table 4.

† Hereafter R (R^1, R^2) denotes alkyls.

In addition to the D_{O-H} values calculated from the peroxide decomposition kinetics, Table 4 lists the published [5] D_{O-H} values for a number of alcohols and acids (figures in parentheses). The differences between them lie within the range of scatter for similar values. Usually, the D_{O-H} values calculated using the procedure mentioned above are smaller than those obtained by other methods.

Aliphatic acids $C_nH_{2n+1}COOH$ are characterised by similar O—H bond strengths, the average D_{O-H} value being equal to 441.0 ± 3.3 kJ mol^{-1}. The D_{O-H} values (in kJ mol^{-1}) for alicyclic carboxylic acids cyclo-$C_nH_{2n-1}COOH$ depend on the ring strain energy, $E_{rsc}(n)$

$$D_{O-H} = (441.9 \pm 1.0) + (5.0 \pm 1.2)\cdot 10^{-2}\,E_{rsc}(n), \quad (18)$$

where n is the number of carbon atoms in the ring (Fig. 1).[38]

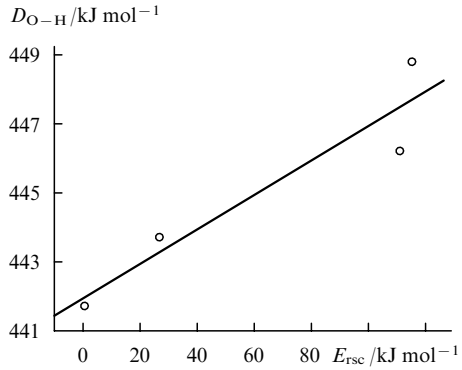


Figure 1. O—H bond dissociation energies (D_{O-H}) in cyclocarboxylic acids $C_nH_{2n-1}C(O)OH$ plotted *vs.* ring strain energy (E_{rsc}).

Limitations of the method for estimating the O—O bond strength (D_{O-O}) are as follows.

1. The technique is applicable only to the compounds which decompose *via* homolysis of a single (the weakest) bond. If the decomposition occurs as concerted cleavage of two bonds, the activation energy for the process does not characterise the cleavage of the single bond. This is the case for, *e.g.*, the decomposition of many peracid esters.[37] For instance, the decomposition of the peroxy ester $PhCH_2C(O)OOBu^t$ involves simultaneous cleavage of two bonds:

$$PhCH_2C(O)OOBu^t \longrightarrow PhC^{\bullet}H_2 + CO_2 + Bu^tO^{\bullet}.$$

Experiments showed that in this case one has $E_a < D_{O-O}$ and, at the same time, $E_a > \Delta H(r)$ [$\Delta H(r)$ is the enthalpy of reaction].

2. Radicals produced from solvent molecules and capable of attacking the initial peroxide molecule must not initiate an additional decomposition of the peroxide by the chain mechanism. For instance, the decomposition of dibenzoyl peroxide in alcohol (RCH_2OH) is described by the following chain reaction:[37]

$$PhC(O)OOC(O)Ph \longrightarrow 2\,PhC(O)O^{\bullet},$$

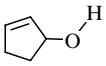
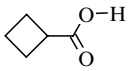
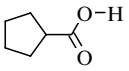
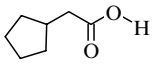
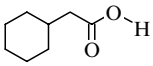
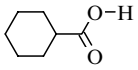
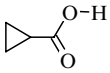
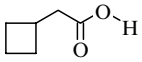
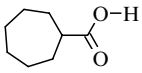
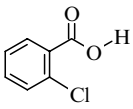
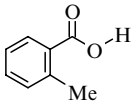
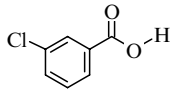
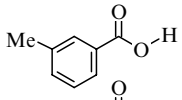
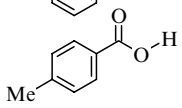
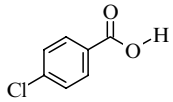
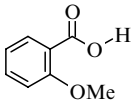
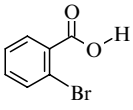
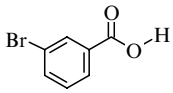
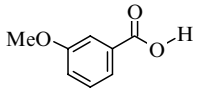
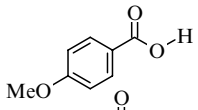
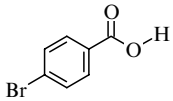
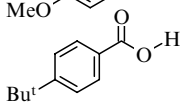
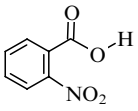
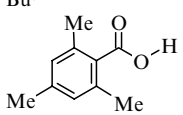
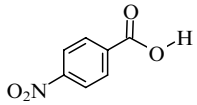
$$PhCO_2^{\bullet} + RCH_2OH \longrightarrow PhC(O)OH + RC^{\bullet}HOH,$$

$$RC^{\bullet}HOH + PhC(O)OOC(O)Ph \longrightarrow$$

$$\longrightarrow RC(O)H + PhC(O)OH + PhC(O)O^{\bullet}.$$

As a result, the rate of peroxide consumption becomes much higher than the peroxide homolysis rate and the activation energy for the decomposition no longer characterises the homolysis reaction. To exclude the chain decomposition of peroxide, an acceptor of free radicals, which does not react with the initial peroxide, is introduced into the solvent.

Table 4. O–H bond dissociation energies in alcohols and acids calculated from kinetic data on peroxide decompositions.[38, 39]

Compound	D_{O-H} /kJ mol^{-1}	Compound	D_{O-H} /kJ mol^{-1}
Alcohols			
MeO–H	431.7 (436–439)	Pr^nCMe_2O-H	435.4
EtO–H	432.4 (436–440)	Pr^iCMe_2O-H	434.4
Pr^nO-H	431.9 (433–443)	Bu^tCMe_2O-H	433.6
Pr^iO-H	431.9 (438–443)		434.8
Bu^nO-H	432.3 (426)		
Bu^tO-H	434.9 (440–446)		
Bu^sO-H	434.8 (441)	$PhCH_2CMe_2O-H$	435.8
$EtCMe_2O-H$	436.0	F_3CO-H	451.3 (456–497)
Bu^tCH_2O-H	436.1	$ClCH_2CMe_2O-H$	445.6
$Et_2^{\circ}MeO-H$	431.1		
Aliphatic acids			
AcO–H	445.8 (443–445)		446.2
EtC(O)O–H	439.3 (445)		
$Pr^nC(O)O-H$	439.8 (443)		
$Bu^nC(O)O-H$	442.1		443.7
$n\text{-}C_5H_{11}C(O)O-H$	439.3		
$n\text{-}C_6H_{13}C(O)O-H$	444.4		
$n\text{-}C_7H_{15}C(O)O-H$	438.5		447.7
$n\text{-}C_8H_{17}C(O)O-H$	443.0		
$n\text{-}C_9H_{19}C(O)O-H$	437.8		
$n\text{-}C_{11}H_{23}C(O)O-H$	445.8		447.7
$Pr^iC(O)O-H$	435.2		
$ClCH_2C(O)O-H$	458.9		
$PhCH_2C(O)O-H$	448.0		441.7
	448.8		
	448.3		441.8
Benzoic acids			
PhC(O)O–H	438.0 (439.3)		445.3
	444.2		
			448.9
	448.6		
	451.1		442.1
	443.5		445.5
			449.6
	447.8		
	447.0		449.1
	448.2		448.5
	445.4		448.3

Note. Data taken from handbook [5] are given in parentheses.

3. The decomposition of a molecule must follow a homolytic pathway only. The introduction of radical acceptor excludes a concurrent heterolytic decomposition of the peroxide. If only homolysis occurs, the rate of consumption of the radical acceptor equals the rate of peroxide decomposition within the accuracy to the escape probability (e) of radicals from the cage to the bulk ($e \approx 0.3-0.8$ for conventional solvents [37]).

IV. Linear correlations

Evans and Polanyi [40] were the first who found an empirical linear correlation between the activation energy and the enthalpy of reaction taking the reactions

$$R^iX + Na \longrightarrow R^{i\bullet} + NaX$$

as examples.

Semenov [41] extended this correlation to abstraction reaction involving various molecules and radicals and obtained the following averaged expression for such reactions:

$$E_a = A' + \alpha'\Delta H, \tag{19}$$

where $\alpha' = 0.25$ and $A' = 48$ kJ mol^{-1}. More recently, it was shown that this correlation equation correctly describes 'narrow' reaction series with the same reaction centre for each series characterised by its own coefficients α' and A'. Listed below are the X–H bond dissociation energies [5] and the α' and A' coefficients for a number of reaction series of X$^\bullet$ radical (X atom) reacting with the C–H bonds of paraffin hydrocarbons:[42]

$$X^\bullet + R^iH \longrightarrow XH + R^{i\bullet}$$

X$^\bullet$ (X)	D_{X-H} /kJ mol^{-1}	α'	A' /kJ mol^{-1}
HO$^\bullet$	499.1	0.25	31.6
H$^\bullet$	436.0	0.38	46.0
O	427.5	0.52	64.0
$H_3C^\bullet$	440	0.52	62.0
MeO$^\bullet$	436.2	0.59	49.0
$F_3C^\bullet$	449.4	0.66	60.0
$MeC^\bullet H_2$	422	0.70	53.0
$Cl_3C^\bullet$	392.5	0.94	67.0
Br$^\bullet$	366.3	0.86	16.0
I$^\bullet$	298.4	0.97	9.7

In these ten reaction series the α' coefficient varies from 0.25 to 0.97. The α' and D_{X-H} values vary in antiparallel fashion, namely, the higher the D_{X-H} value, the smaller the α' coefficient. The enthalpies of the investigated reactions of hydroxyl radical ($D_{X-H} = 499.1$ kJ mol^{-1}) vary in the range from -60 to -100 kJ mol^{-1} at $\alpha' = 0.25$. In contrast, similar reactions of iodine atoms ($D_{I-H} = 298.4$ kJ mol^{-1}) are highly endothermic ($\Delta H \approx 100-140$ kJ mol^{-1}) and the α' coefficient approaches unity. Naturally, one can assume that the E_a-*vs.*-ΔH dependence is nonlinear and therefore the $\alpha' = dE_a/d(\Delta H)$ parameter depends on the range of changes in ΔH in each reaction series. This issue was considered in a review.[43]

Linear dependence (19) is often used for estimating the bond dissociation energy. To this end, it is written as follows:

$$D_i = D_1 + \frac{E_{ai} - E_{a1}}{\alpha'} \tag{20}$$

or

$$D_i = D_1 + \frac{RT}{\alpha'}\ln\left(\frac{n_i k_1}{n_1 k_i}\right), \tag{21}$$

where k_1, E_{a1} and D_1 are respectively the rate constant for, the activation energy for and the bond strength corresponding to the reaction of the X$^\bullet$ radical with the compound R^{1}H with known strength of the X–H bond being formed, n_1 is the number of equally reactive bonds in the R^{1}H molecule involved in the reaction; and k_i, n_i, E_{ai} and D_i are the corresponding parameters of the reaction between the X$^\bullet$ radical and R^{i}H compound. Calculations give $\Delta D_i = \pm 2/\alpha'$ kJ mol^{-1} provided that the error in determination of the activation energy is 2 kJ mol^{-1}. The accuracy of calculations can be improved by considering the partial rate constant, k, for the reaction per equally reactive C–H bond involved in the reaction of the X$^\bullet$ radical with R^{i}H rather than the activation energy. The method is applicable to any reaction which belongs to the same series characterised by the α' coefficient and lies within the difference $\Delta H_{min} - \Delta H_{max}$ for this reaction series.

The kinetics of heterolytic reactions widely uses linear correlations based on linear relations for the free energy.[44,45] Correlations of the type

$$\log k_i = \log k_0 + \rho\sigma, \tag{22}$$

where ρ is the correlation coefficient, σ is the Hammett constant [or analogous Brown constants (σ^+) and Taft constants (σ^*)] are also used in radical chemistry.[46,47] Equation (22) can be reduced to the Polanyi–Semenov equation (19) at a constant pre-exponent for a given reaction series. Seemingly, Eqn (22) can also be employed for estimating the bond strength from the kinetic data for corresponding series of compounds using the following transformation:

$$D_i = D_0 + \rho\sigma, \tag{23}$$

where $D_i = D_0$ for the compound characterised by $\sigma = 0$. However, special care must be taken when using such correlations. Figure 2 shows the O–H bond strengths in monosubstituted phenols (the data for twenty-seven phenols were taken from handbook [21]) plotted *vs.* Hammett constants. Although we do observe a trend towards an increase in the D_{O-H} values as the σ constant increases, the correlation is very poor, because the correlation coefficient is only 0.75. The correlation equation of the straight line shown in Fig. 2 has the form

$$D_{O-H}\,(\text{kJ mol}^{-1}) = (364.8 \pm 1.4) + (19.22 \pm 3.44)\,\sigma. \tag{24}$$

For eight phenols the D_{O-H} values differ from the predicted results by more than 10 kJ mol^{-1}. Apparently, the reasons for poor correlation consist in fundamentally different stabilising effects of certain substituents Y on the acid anion $YC_6H_4CO_2^-$ and the aroxyl radical $YC_6H_4O^\bullet$ and in an additional solvation effect of the polar solvent on the benzoic acid anion, whereas the phenoxyl radical is generated in the non-polar solvent characterised by weaker solvation of reactants and transition state. Clearly, this type of correlation cannot serve as a reliable procedure for evaluating the bond strengths in molecules.

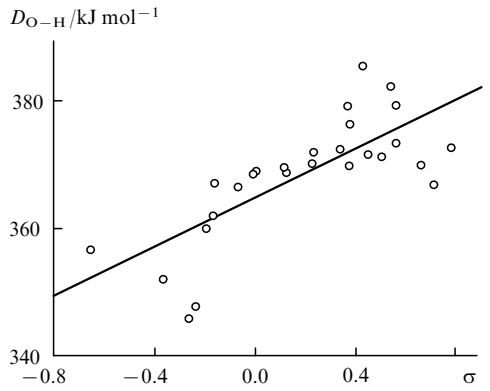


Figure 2. O–H bond dissociation energies (D_{O-H}) in phenols 4-YC_6H_4OH plotted *vs.* Hammett constants (σ).

V. Parabolic model for radical reactions

In the framework of the intersecting parabolas (IP) model the transition state of a radical reaction

$$X^{\bullet} + RH \longrightarrow XH + R^{\bullet}$$

is treated as a result of intersection of two potential energy curves.[21, 37, 43, 45, 48] One of them characterises the potential energy of the stretching vibration of the attacked R–H bond (U_{R-H}) as a function of the vibration amplitude while the other characterises the potential energy of the vibration of the X–H bond being formed (U_{X-H}). The stretching vibrations of the bonds are considered harmonic:

$$U_{R-H}^{1/2} = b\Delta r_{R-H},$$

$$U_{X-H}^{1/2} = b_f\Delta r_{X-H},$$

where Δr_{R-H} and Δr_{X-H} are the corresponding bond elongations in the transition state; b and b_f are the coefficients of proportionality ($2b^2$ and $2b_f^2$ are the force constants of the bond being cleaved and the bond being formed, respectively):

$$b = 2\pi\nu_{R-H}\,\mu_{R-H}^{1/2},$$

$$b_f = 2\pi\nu_{X-H}\,\mu_{X-H}^{1/2},$$

ν_{R-H} and ν_{X-H} are the corresponding vibrational frequencies and μ_{R-H} and μ_{X-H} are the reduced masses of the atoms involved in the C–H and X–H bonds. Figure 3 presents the transition state diagram of the $ROO^{\bullet}$ + RH reaction in the framework of the intersecting parabolas model.

A radical abstraction reaction is characterised by the following parameters:

(1) 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;

(5) parameter α (α^2 is the force constant ratio of the bond being cleaved to the bond being formed);

(6) pre-exponent A_0 per equally reactive bond (in the molecule) involved in the reaction.

The parameters listed above are interrelated as follows:[48]

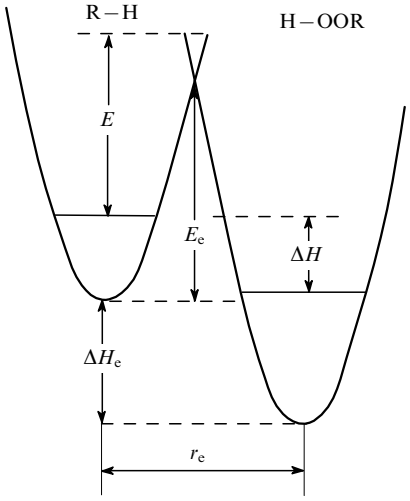


Figure 3. 'Bond stretch – potential energy' diagram for the $ROO^{\bullet}$ + HR reaction in the framework of the intersecting parabolas model.

$$\Delta H_e = D_{R-H} - D_{X-H} + 0.5\,hN_A(\nu_{R-H} - \nu_{X-H}), \qquad (25a)$$

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}\,. \qquad (25b)$$

Knowing the parameter br_e, one can calculate the classical potential barrier E_{e0} to a thermally neutral reaction characterised by $\Delta H_e = 0$:

$$E_{e0} = \frac{(br_e)^2}{(1+\alpha)^2}\,. \qquad (26)$$

The rate constant for the reaction is related to the activation energy, E_a, and the pre-exponent, A_0, by the Arrhenius relation:

$$k = nA_0\exp\left(-\frac{E_a}{RT}\right), \qquad (27)$$

where n is the number of equally reactive bonds in the reactant molecule.

The IP 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: α, br_e, $0.5hN_A\nu_{RH}$ (h is the Planck constant, N_A is the Avogadro constant) and A_0 and an individual reaction belonging to a certain class is characterised by the enthalpy, ΔH_e, and activation energy, E_e.

A method for estimating the bond strengths from the kinetic data, developed in the framework of the IP model, involves a number of versions.[43, 49–51]

1. With the measured rate constants k_i or the k_i/k_1 ratios for a reaction class of the type $X^{\bullet} + R^iH$ it is possible to estimate the bond strengths between the R^i–H and R^1–H compounds. The rate constant ratio, k_i/k_1, allows the activation energy difference, ΔE_{ei}, between these reactions to be calculated:

$$\Delta E_{ei} = E_{ei} - E_{e1} = RT\ln\left(\frac{n_ik_1}{n_1k_i}\right), \qquad (28)$$

where n_1 and n_i are respectively the numbers of equally reactive bonds in the R^1H and R^iH molecules attacked by the $X^{\bullet}$ radical. From Eqns (25b) and (28) it follows that the relation between the ΔE_{ei} value and the enthalpy difference $\Delta(\Delta H_i)$ between these reactions has the form:[49]

$$\Delta(\Delta H_i) = 2br_e\alpha^{-2}\left(\sqrt{E_{ei}} - \sqrt{E_{e1}}\right) - (\alpha^{-2} - 1)\Delta E_{ei}\,. \qquad (29)$$

On the other hand the enthalpy difference $\Delta(\Delta H_i) = D_i - D_1$ and the energy of the R^i–H bond can be calculated using the equation

$$D_i = D_1 + 2br_e\alpha^{-2}\left(\sqrt{E_{ei}} - \sqrt{E_{e1}}\right) - (\alpha^{-2} - 1)\Delta E_{ei}\,. \qquad (30)$$

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 (br_e and α). Experience showed that the error in ΔD measurements is 2–3 kJ mol^{-1} (see Ref. 49). At low ΔE_{ei} values ($\Delta E_{ei} \ll E_{e1}$), Eqn (30) can be simplified:[43]

$$D_i = D_1 + \frac{1+\alpha}{\alpha^2}\left(\sqrt{\frac{E_{e0}}{E_{e1}}} - 1 + \alpha\right)\Delta E_{ei}\,. \qquad (31)$$

This approach was used for estimating D_{C-H} values in hydrocarbons,[49, 50, 52] oxygen-containing compounds,[51, 53–55] amines and amides,[56, 57] nitriles and nitro compounds;[58] D_{O-H} values in phenols[59, 60] and hydroxylamines;[61] D_{N-H} values in aromatic amines;[62] D_{S-H} values in thiophenols[63, 64] and D_{Si-H} values in silanes.[65]

2. Using different radicals $X^{\bullet}$ (*e.g.*, $X^i = R^iOO^{\bullet}$) in a series of radical reactions $X^{\bullet}$ + RH belonging to the same class allows the approach to be employed for evaluating the X^i–H bond strengths. In this case Eqn (30) takes the form:

$$D_i = D_1 + 2br_e\alpha^{-2}(\sqrt{E_{e1}} - \sqrt{E_{ei}}) + (\alpha^{-2} - 1)\Delta E_{ei}. \quad (32)$$

This version of the technique was used in estimating the D_{O-H} values in hydroperoxides,[66] alcohols and acids.[67]

3. The D_i value for a reaction $X^{\bullet} + R^iH$ can also be evaluated from the absolute value of the rate constant k_i. Since, according to the Arrhenius relation,

$$k_i = n_i A_0 \exp\left(-\frac{E_{ai}}{RT}\right),$$

the energy E_{ei} is calculated using the following equation

$$E_{ei} = RT \ln\left(\frac{A_0 n_i}{k_i}\right) + 0.5hN_A\nu_{R-H} - 0.5RT, \quad (33)$$

and ΔH_e is calculated using the equation

$$\Delta H_e = E_{ei} - \alpha^{-2}(br_e - \sqrt{E_{ei}})^2, \quad (34)$$

from which after substituting expression (34) in Eqn (25a) we get:

$$D_i = D_{H-X} + E_{ei} - \alpha^{-2}(br_e - \sqrt{E_{ei}})^2 - \\ - 0.5hN_A(\nu_{R-H} - \nu_{X-H}). \quad (35)$$

In this case the error in the determination of D_i is usually higher than in the estimation using Eqn (32).

The parameters used for evaluating the D_i values in the radical abstraction reactions are listed in Table 5.

The limitation imposed on the method is associated with the enthalpy of reaction, ΔH_e (see Refs 43 and 49). The case in point is that Eqn (26) is valid for reactions belonging to the same reaction class and characterised by enthalpies lying in the interval $\Delta H_{e\,min} < \Delta H_e < \Delta H_{e\,max}$. The activation energy for a highly exothermic reaction ($\Delta H_e < \Delta H_{e\,min}$) is nearly zero (more correctly, $E = 0.5RT$) and independent of ΔH. Therefore, the enthalpies, ΔH_e, of such reactions cannot be estimated from the E_e values. The $\Delta H_{e\,min}$ value depends on the br_e and α parameters and on the zero-point vibrational energy of the R—H bond being cleaved:

$$\alpha^2\Delta H_{e\,min} = -(br_e)^2 + 2br_e\sqrt{0.5hN_A\nu_{R-H}} + \\ + 0.5hN_A\nu_{R-H}(\alpha^2 - 1). \quad (36)$$

The activation energies of highly endothermic reactions ($\Delta H_e > \Delta H_{e\,max}$) approximately equal ΔH_e, also being independent of the br_e and α parameters:

$$E_e = \Delta H_e + 0.5RT. \quad (37)$$

The threshold value, $\Delta H_{e\,max}$, depends on the α and br_e parameters and on the zero-point vibrational energy of the bond being formed

$$\Delta H_{e\,max} = (br_e)^2 - 2br_e\sqrt{0.5hN_A\nu_{X-H}} + \\ + 0.5hN_A\nu_{X-H}(\alpha^2 - 1). \quad (38)$$

An analogous method for evaluating the ΔD values for two reactants from kinetic data (ΔE) was elaborated in the framework of the reaction model using two intersecting Morse curves.[68,69] The results obtained by this technique and using the IP model are very similar.

Table 5. Parameters of the intersecting parabolas model used for calculating ΔD values from experimental data.[21,37,43,48]

Reaction	α	br_e /(kJ mol^{-1})$^{1/2}$	E_{e0} /kJ mol^{-1}	$0.5\,hN_A(\nu - \nu_f)$ /kJ mol^{-1}	A /litre mol^{-1} s^{-1}
$H^{\bullet} + R^1H$	0.901	14.50	58.2	−8.9	1.0×10^{11}
$H^{\bullet} + R^2H$	0.901	15.80	69.1	−8.9	1.0×10^{10}
$H^{\bullet} + R^3H$	0.901	15.00	62.3	−8.9	1.0×10^{10}
$R^{1\bullet} + R^1H$	1.00	17.30	74.8	0	1.0×10^{9}
$R^{1\bullet} + R^2H$	1.00	18.60	86.5	0	1.0×10^{8}
$R^{1\bullet} + R^3H$	1.00	17.80	79.2	0	1.0×10^{8}
$R^{2\bullet} + R^2H$	1.00	19.25	92.6	0	1.0×10^{8}
$R^{2\bullet} + R^3H$	1.00	18.45	85.1	0	1.0×10^{8}
$R^{3\bullet} + R^3H$	1.00	18.05	81.4	0	1.0×10^{8}
$Ph^{\bullet} + R^1H$	0.945	16.88	75.3	−1.0	1.0×10^{9}
$Ph^{\bullet} + R^2H$	0.945	18.15	87.1	−1.0	1.0×10^{8}
$Ph^{\bullet} + R^3H$	0.945	17.37	79.7	−1.0	1.0×10^{8}
$RO^{\bullet} + R^1H$	0.796	12.73	50.2	−4.3	1.0×10^{9}
$RO^{\bullet} + R^2H$	0.796	13.96	60.4	−4.3	1.0×10^{8}
$RO^{\bullet} + R^3H$	0.796	13.54	56.8	−4.3	1.0×10^{8}
$RO_2^{\bullet} + R^1H$	0.814	13.62	56.14	−3.8	1.0×10^{8}
$RO_2^{\bullet} + R^2H$	0.814	15.20	70.2	−3.8	1.0×10^{7}
$RO_2^{\bullet} + R^3H$	0.814	14.32	62.3	−3.8	1.0×10^{7}
$R^{1\bullet} + HSiR^4_3$	0.772	13.18	55.3	−4.3	1.0×10^{9}
$R^{1\bullet} + HGeR^4_3$	0.747	13.82	62.6	−4.8	1.0×10^{9}
$R^{1\bullet} + HSnR^4_3$	0.721	13.67	63.1	−5.3	1.0×10^{9}
$R^{1\bullet} + HSR^4$	0.808	11.80	42.6	−3.6	2.0×10^{7}
$R^{1\bullet} + Ar^1OH$	1.246	17.61	61.5	4.1	1.0×10^{8}
$R^{1\bullet} + Ar^2OH$	1.246	20.58	84.0	4.1	1.0×10^{8}
$R^{1\bullet} + AmOH$	1.246	17.82	63.0	4.1	1.0×10^{8}
$R^{1\bullet} + AmH$	1.150	18.46	73.7	2.6	1.0×10^{9}
$H^{\bullet} + HPR^4_2$	0.736	12.61	52.8	−12.4	2.0×10^{10}
$RO_2^{\bullet} + Ar^1OH$	1.014	13.16	42.7	0.3	3.2×10^{7}
$RO_2^{\bullet} + Ar^2OH$	1.014	14.30	50.4	0.3	3.2×10^{7}
$RO_2^{\bullet} + AmOH$	1.014	13.50	44.9	0.3	3.2×10^{7}
$RO_2^{\bullet} + AmH$	0.936	12.12	39.2	−1.2	1.0×10^{8}

Table 5 (continued).

Reaction	α	br_e /(kJ mol^{-1})$^{1/2}$	E_{e0} /kJ mol^{-1}	$0.5hN_A(\nu - \nu_f)$ /kJ mol^{-1}	A /litre mol^{-1} s^{-1}
$R_s^{\bullet}$ + R^4CH_2CN	0.955	16.29	69.4	−0.81	1.0×10^9
$R^{\bullet}$ + R^4CH_2CN	1.000	14.29	51.0	0	1.0×10^9
$H^{\bullet}$ + R^1CH_2CN	0.904	15.16	63.4	−2.27	1.0×10^{10}
$R_s^{\bullet}$ + R^1NO_2	0.955	16.88	74.5	−0.55	1.0×10^9
$R^{1\bullet}$ + $R^1CH_2NO_2$	1.000	17.65	77.9	0	1.0×10^9
$H^{\bullet}$ + R^1Cl	0.838	14.98	66.4	−12.95	6.0×10^{10}
$H^{\bullet}$ + R^1Br	0.672	11.36	46.2	−12.56	4.0×10^9
$H^{\bullet}$ + R^1I	0.502	9.22	3.7	−11.52	1.0×10^{11}
$R^{1\bullet}$ + CCl_3Br	1.000	10.65	28.4	0	3.0×10^9
$H^{\bullet}$ + R^3Cl	0.835	14.51	62.5	−12.93	6.0×10^9
$H^{\bullet}$ + R^3Br	0.672	11.56	47.8	−12.56	8.0×10^9
$H^{\bullet}$ + R^1SO_2Cl	1.906	27.18	87.5	−9.66	1.0×10^9
$R_s^{\bullet}$ + R^3I	1.000	4.77	5.7	0	4.0×10^9
$R^{\bullet}$ + R^1I	1.000	10.60	28.1	0	4.0×10^9
$R^{\bullet}$ + R^1SH	0.808	13.45	55.3	−3.6	1.0×10^9
$RO^{\bullet}$ + R^1SH	0.717	11.82	47.4	−6.3	1.0×10^9
$RO_2^{\bullet}$ + R^1SH	0.733	11.82	46.5	−5.8	1.0×10^9
$R^{3\bullet}$ + ArSH	0.904	13.45	49.9	−2.0	1.0×10^9

Note. In this Table, R^1H, R^2H and R^3H denote paraffin, olefinic and alkylaromatic hydrocarbons, respectively.

VI. Structure of molecular fragments and the C−H bond dissociation energies

The dissociation energies of the C−H bonds in hydrocarbon molecules were estimated from the experimental rate constants for abstraction reactions of the following radicals (the bond strengths were taken from Ref. 12): $H_3C^{\bullet}$ (D_{C-H} = 440 kJ mol^{-1}), $RC^{\bullet}H_2$ (D_{C-H} = 422 kJ mol^{-1}), $Me_3C^{\bullet}$ (D_{C-H} = 400 kJ mol^{-1}), $Ph^{\bullet}$ (D_{C-H} = 474 kJ mol^{-1}), $PhC^{\bullet}H_2$ (D_{C-H} = 375 kJ mol^{-1}), $RO_2^{\bullet}$ (D_{O-H} = 365.5 kJ mol^{-1} for the secondary and D_{O-H} = 358.6 kJ mol^{-1} for the tertiary alkylperoxy radicals).[21] The parameters for calculating the bond dissociation energies using the IP model are listed in Table 5 and the results of D_{C-H} calculations are presented in Tables 6–8.

The results obtained by this technique make it possible to significantly increase the number of hydrocarbons with known strengths of individual bonds.[5]

Attempts at evaluating the D_{C-H} values for various oxygen-containing compounds were found to be successful. In this case the limitation imposed on the IP method is as follows. All oxygen-containing molecules are polar and the reaction of a polar radical with a polar molecule leads to manifestation of the polar effect, which affects the activation energy.[70–74] Therefore, the C−H bond strengths in such compounds can be estimated only from the rate constants for reactions of non-polar alkyl radicals and hydrogen atom. The experimental D_{C-H} values for various alcohols, ketones and other oxygen-containing compounds are listed in Table 9.

Table 6. Dissociation energies (in kJ mol^{-1}) of C−H bonds in linear and cyclic alkanes calculated using the intersecting parabolas model.[37, 49, 50]

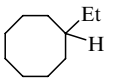
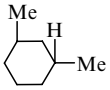
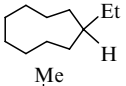
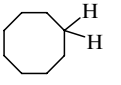
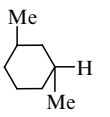
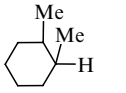
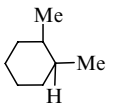
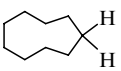
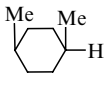
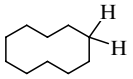
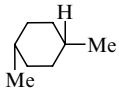
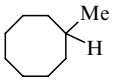
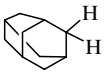
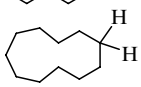
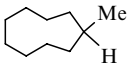
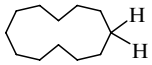
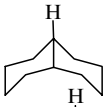
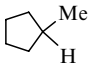
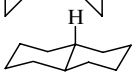
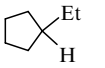
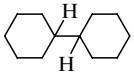
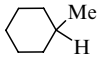
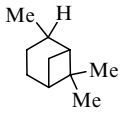
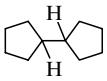
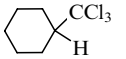
Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}
Linear alkanes							
$Bu^n(C-H)H_2$	422.0 [a]	Et(C−H)HEt	414.5	$Pr^n(C-H)MeEt$	397.1	Me_3C-H	400.0 [a]
$n\text{-}C_5H_{11}(C-H)H_2$	422.0 [a]	$Pr^n(C-H)HEt$	414.5	$n\text{-}C_5H_{11}(C-H)MeEt$	396.6	$Me_2(C-H)Et$	402.0
$n\text{-}C_6H_{13}(C-H)H_2$	422.0 [a]	$Bu^n(C-H)HEt$	414.5	$Bu^i(C-H)H_2$	422.0 [a]	$Me_2(C-H)Pr^n$	399.3
$Pr^n(C-H)HMe$	413.0 [a]	$n\text{-}C_5H_{11}(C-H)HEt$	414.5	$Bu^t(C-H)H_2$	422.0 [a]	$Me_2(C-H)Pr^i$	396.4
$Bu^n(C-H)HMe$	413.0 [a]	$Pr^n(C-H)HPr^n$	415.7	$Bu^t(C-H)HMe$	410.2	$Me_2(C-H)Bu^i$	400.0
$n\text{-}C_5H_{11}(C-H)HMe$	413.0 [a]	$Bu^n(C-H)HPr^n$	415.7	$Bu^t(C-H)Me_2$	399.6	$Me_2(C-H)C_5H_{11}$-neo	400.0
$n\text{-}C_6H_{13}(C-H)HMe$	413.0 [a]	Et(C−H)MeEt	399.7	$Bu^t(CH_2)_2(C-H)Me_2$	399.1	$Me_2(C-H)C_5H_{11}$-sec	405.4
						$[Me_2(C-H)CH_2]_2$	400.0
Cycloalkanes							
	429.0		392.3		403.9		393.0
	418.5		392.2		401.9		390.3
	408.4		392.8				
	408.8		407.7		402.9		392.0

Table 6 (continued).

Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}
Cycloalkanes							
	404.5		396.8		395.0		412.0
	404.7		395.5		394.8		393.1
	410.0		387.6				
	392.2		400.0		392.2		386.3
	395.5		377.4		382.2		391.1
	390.0		411.7		392.4		

Note. From this point on the C–H bond for which the dissociation energy is calculated is given in parentheses. [a] The bond dissociation energies were taken from Ref. 12.

Table 7. Dissociation energies (in kJ mol^{-1}) of C–H bonds in unsaturated hydrocarbons calculated using the intersecting parabolas model.[37, 49, 50]

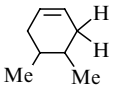
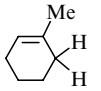
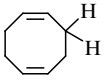
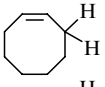
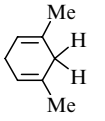
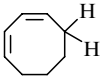
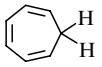
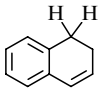
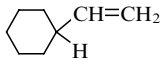
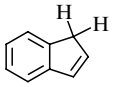
Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}
Linear compounds					
$CH_2=(C-H)H$	464.0 [a]	(*E*)-MeCH=CH(C–H)H_2	356.8	(*E*)-MeCH=CH(C–H)Me_2	333.9
$CH_2=CH(C-H)H_2$	368.0 [a]	$CH_2=CEt(C-H)H_2$	367.7	$CH_2=CH(C-H)HC_5H_{11}$-n	348.8
$MeCH=(C-H)H$	459.0 [a]	$CH_2=CMe(C-H)HMe$	347.2	$CH_2=CMe(C-H)Me_2$	351.1
$CH_2=CH(C-H)HMe$	348.8	(*Z*)-MeCH=CH(C–H)HMe	344.0	(*Z*)-MeCH=CH(C–H)HC_5H_{11}-n	344.0
		$MeCH=CMe(C-H)H_2$	352.4	$Me_2C=CMe(C-H)H_2$	352.8
H(C–H)–CH=CHMe-(*E*) | $(CH_2)_3CH=CHMe$-(*E*)	341.6	(*E*)-MeCH=CH(C–H)HMe	346.2	$CH_2=CHCH=CH(C-H)HPr^n$	331.9
		$CH_2=CHCHMe(C-H)H_2$	422.1	(*E*)-$Me_2(C-H)CH=CHPr^i$	336.1
		$MeCH=C=CH(C-H)H_2$	365.0	HC≡C–H	556.0 [a]
$CH_2=CHCH_2(C-H)H_2$	410.9	$CH_2=CH(C-H)Me_2$	339.7	HC≡C(C–H)H_2	359.8
$CH_2=CH(C-H)H(CH_2)_4CH=CH_2$	349.8	$CH_2=CH(C-H)HCH=CH_2$	318.0	MeC≡C(C–H)H_2	354.7
(*Z*)-MeCH=CH(C–H)H_2	355.8	$Me_2C=CH(C-H)HMe$	332.0	HC≡C(C–H)HMe	346.8
$CH_2=CMe(C-H)H_2$	357.9	$CH_2=CH(C-H)HPr^n$	348.8	$Bu^nC\equiv C(C-H)HPr^n$	348.2
Cyclic compounds					
	381.1		326.2		329.3
	338.9		346.6		331.8
	342.5		295.6		288.8
	332.7		357.2		336.4
	341.5		347.1		330.9

Table 7 (continued).

Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}	Hydrocarbon	D_{R-H}
Cyclic compounds			312.6		301.0
	336.5		341.8		339.9

[a] The bond dissociation energies were taken from Ref. 12.

Table 8. Dissociation energies (in kJ mol^{-1}) of C–H bonds in aromatic hydrocarbons, pyridines and quinolines calculated using the intersecting parabolas model.[37, 49, 52]

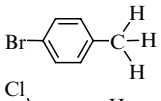
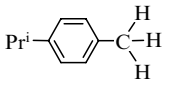
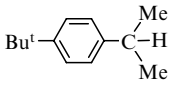
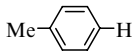
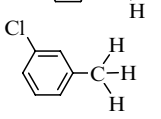
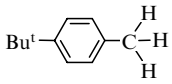
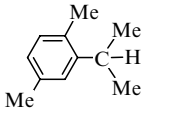
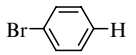
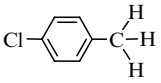
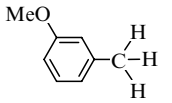
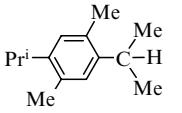
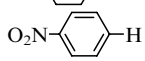
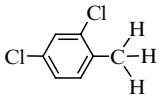
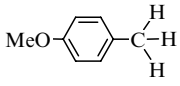
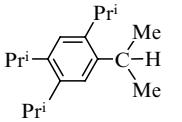
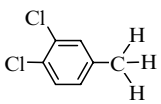
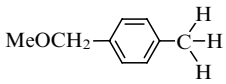
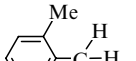
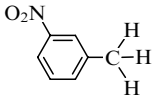
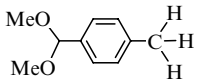
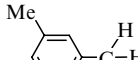
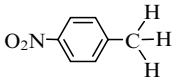
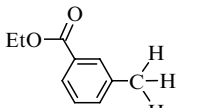
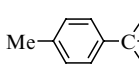
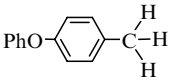
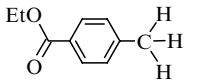
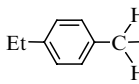
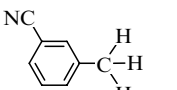
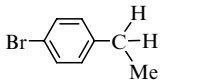
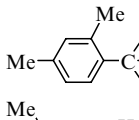
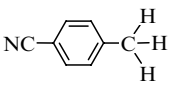
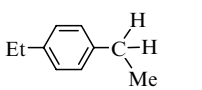
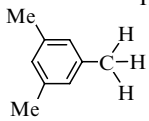
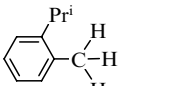
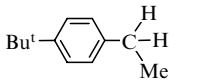
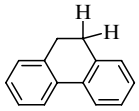
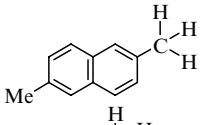
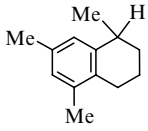
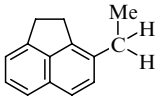
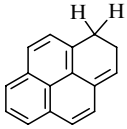
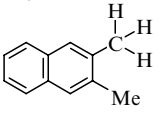
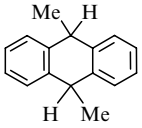
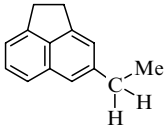
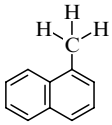
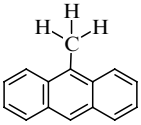
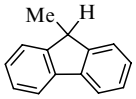
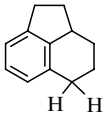
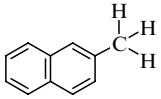
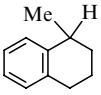
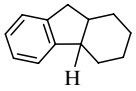
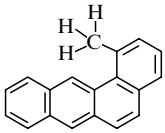
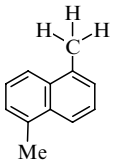
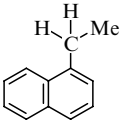
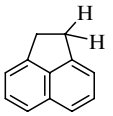
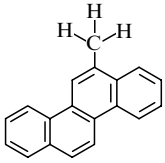
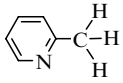
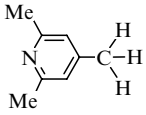
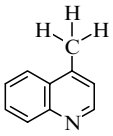
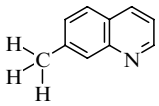
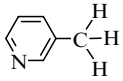
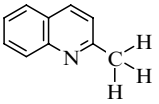
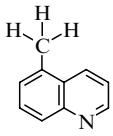
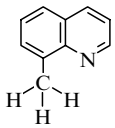
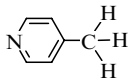
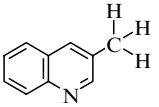
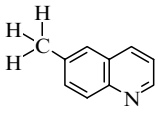
Compound	D_{C-H}	Compound	D_{C-H}	Compound	D_{C-H}	Compound	D_{C-H}
Aromatic hydrocarbons							
Ph–H	474.0 [a]		380.1		353.0		349.3
	474.8		376.1		373.8		362.9
	483.1		375.3		378.8		367.8
	490.7		370.9		362.5		375.3
Ph(C–H)H_2	375.0 [a]		369.6		357.5	$PhCH_2(C-H)HPh$	364.1
	374.6		375.0		353.2	Ph(C–H)HEt	366.2
	374.3		371.4		372.7	Ph(C–H)HMe	364.1
	372.5		377.3		374.1	$Ph(C-H)Me_2$	351.6
	363.9		371.2		364.6	$PhCMe_2(C-H)H_2$	412.6
	373.0		368.0		362.0	$Ph_2(C-H)H$	356.8
	373.9		366.6		362.1	Ph_3C-H	357.3
	374.3		363.2		380.2	$Ph_2(C-H)Me$	348.8
	370.9						357.0
	371.0						345.6
	373.0						316.9
							368.2
							356.4
							332.6

Table 8 (continued).

Compound	D_{C-H}	Compound	D_{C-H}	Compound	D_{C-H}	Compound	D_{C-H}
Aromatic hydrocarbons							
	341.6		363.2		338.4		352.7
	341.4		363.3		326.7		352.7
	365.1		366.9		328.5		317.0
	358.3		336.4		332.0		370.8
	363.1		364.4		351.3		358.7
Pyridines, quinolines							
	365.0		381.2		360.1		371.0
	378.2		366.6		366.3		377.8
	362.1		372.1		371.0		

[a] The bond dissociation energies were taken from Ref. 12.

In Table 10 we compare the D_{C-H} values obtained using the IP method with the published data. By and large, the results obtained are in reasonable agreement with one another, the differences between them lying within the scatter of the data that are also characteristic of other methods. Comparison of the two lists of compounds given in Tables 10 and 9 shows how the IP method made it possible to increase the number of compounds with known D_{C-H} values.

The strengths of the most reactive C—H bonds in aliphatic amines, nitriles, nitro compounds and sulfides (information on these parameters is scarce) were determined analogously. The results of calculations are listed in Table 11.

Empirical analysis of the effect of the structure of molecular fragments on the D_{C-H} values using the C—H bond strengths in various molecules (see Tables 6–11) makes it possible to draw some conclusions.

1. The presence of α-C=C bonds causes the D_{C-H} value to decrease. Owing to stabilisation of the allyl radical the α-C—H bonds in olefins are much weaker than in paraffins. The effect of the neighbouring methyl groups on the allyl C—H bond is illustrated below (see also Table 7; the D values are given in kJ mol^{-1}).

Compound	D_{C-H}	ΔD
$MeCH_2(C-H)H_2$	422	0
$CH_2=CH(C-H)H_2$	368	−54.0
$CH_2=CH(C-H)HMe$	349.8	−72.2
$CH_2=CH(C-H)Me_2$	339.6	−82.4

As can be seen, not only the double bond but also the neighbouring methyl groups strongly affect the strength of the C—H bond in the α-position with respect to the double bond. Replacement of a hydrogen atom at the carbon atom involved in the double bond by a methyl group also leads to reduction of D_{C-H} values, although to a somewhat lesser extent (see Table 4; the D_{C-H} values are given in kJ mol^{-1}).

Table 9. Dissociation energies of C – H bonds in oxygen-containing compounds calculated using the intersecting parabolas model.[51, 53–55]

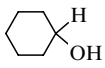
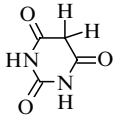
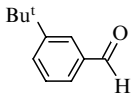
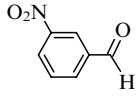
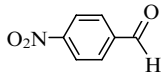
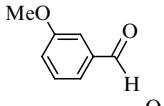
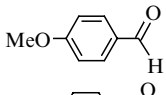
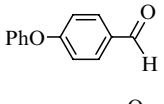
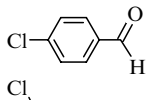
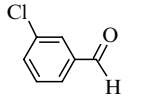
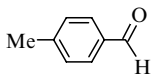
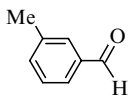
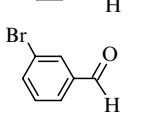
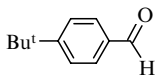
Compound	D_{C-H} /kJ mol^{-1}	Compound	D_{C-H} /kJ mol^{-1}
Alcohols			
H – CH_2OH	411.0 [a]	MeCH(OH)(C – H)(OH)Me	383.1
Me(C – H)(OH)H	399.8	n-C_9H_{19}(C – H)(OH)H	395.5
Et(C – H)(OH)H	399.5	CH_2 = CH(C – H)(OH)H	356.2
	388.4		330.7
Pr^n(C – H)(OH)H	397.2	Me_2(C – H)OH	390.5
H – CH_2(OH)CH_2OH	401.5	Ph(C – H)(OH)H	366.9
EtMe(C – H)OH	389.7	Bu^t(C – H)(OH)H	395.2
HO$(CH_2)_3$(C – H)(OH)H	404.2	Ph(C – H)(OH)Me	366.4
n-C_5H_{11}(C – H)(OH)H	391.4	H – CH_2(OH)CMe_2CH_3OH	408.3
$HOCH_2CH_2$(C – H)(OH)Me	387.7	H – CH_2CMe_2OH	417.4
n-C_8H_{17}(C – H)(OH)H	395.8		
Ketones			
MeC(O)(C – H)H_2	411.8	Me_2(C – H)C(O)Pr^i	387.5
MeC(O)C(O)(C – H)H_2	411.6	PhC(O)CH_2(C – H)Me_2	385.2
MeC(O)(C – H)HMe	392.6		
MeC(O)(C – H)HC(O)Me	399.1		401.2
MeC(O)(C – H)Me_2	383.8		
MeC(O)(C – H)HC(O)OEt	396.5		
MeC(O)(C – H)HEt	397.2	PhC(O)(C – H)HC_8H_{17}-n	394.3
PhC(O)(C – H)H_2	402.8		394.1
Me(C – H)HC(O)Et	396.5		
PhC(O)(C – H)HMe	394.4		
Et(C – H)HC(O)Pr^n	394.6		397.8
PhC(O)(C – H)Me_2	385.3		
Pr^n(C – H)HC(O)Bu^n	395.8		
PhC(O)(C – H)HEt	394.3		
MeC(O)CH_2(C – H)Me_2	388.7		
PhC(O)CMe_2(C – H)H_2	413.3		
Aldehydes			
HC(O) – H	377.8 [a]		345.4
H – CH_2C(O)H	394.3 [a]		
MeC(O) – H	373.8 [a]		343.7
	373.8		
Pr^nC(O) – H	371.2		
Pr^iC(O) – H	364.5		340.4
Bu^nC(O) – H	372.0		
Bu^iC(O) – H	362.6		
Bu^sC(O) – H	360.8		350.9
Bu^tC(O) – H	375.1		
Et_2CHC(O) – H	367.2		346.4
n-C_9H_{19}C(O) – H	373.3		
PhC(O) – H	348.0		347.1
$PhCH_2$C(O) – H	362.0		
$PhCMe_2$C(O) – H	362.9		
H – C(O)CO_2H	375.3		352.3
$HOCH_2$(CHOH)$_3$C(O) – H	370.0		
$HOCH_2$(CHOH)$_4$C(O) – H	371.4		353.6
	345.8		
	347.0		353.8
	337.1		

Table 9 (continued).

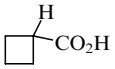
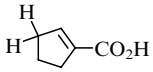
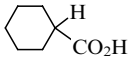
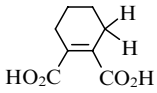
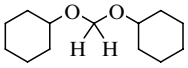
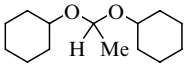
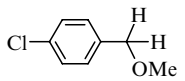
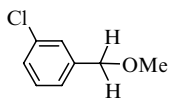
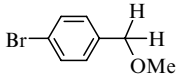
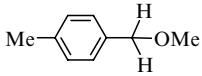
Compound	D_{C-H} /kJ mol^{-1}	Compound	D_{C-H} /kJ mol^{-1}
Acids			
$H-CO_2H$	392.7	n-$C_5H_{11}(C-H)HCO_2H$	399.1
$H-CH(CO_2H)_2$	400.1	$Ph(C-H)HCO_2H$	367.0
$H-CH_2CO_2H$	414.1	n-$C_8H_{17}(C-H)HCO_2H$	399.0
$HO_2C(C-H)HCH_2CO_2H$	397.8	$Cl(C-H)HCO_2H$	398.9
$Me(C-H)HCO_2H$	398.9		399.0
$[(C-H)(OH)CO_2H]_2$	392.7		
$Me_2(C-H)CO_2H$	388.3		
$NC(C-H)HCO_2H$	398.4		359.8
$Et(C-H)HCO_2H$	398.7		
$MeC(O)NH(C-H)HCO_2H$	402.2		
$H-CH_2CMe_2CO_2H$	415.2		388.2
$MeC(O)NH(C-H)MeCO_2H$	393.0		
$Pr^n(C-H)HCO_2H$	399.4		
$Bu^n(C-H)HCO_2H$	397.1		370.0
$H-C(OH)(CO_2H)H$	397.8		
$H-C(OH)(CO_2H)Me$	386.0		
Esters			
$MeCO_2(C-H)H_2$	404.0 [a]	$Bu^nCO_2(C-H)HC_7H_{15}$-n	391.9
$MeC(O)(CH_2)_6(C-H)HCO_2Me$	392.6	$Bu^tCO_2CMe_2(C-H)H_2$	415.0
$Et(C-H)HCO_2Me$	394.9	$Bu^tO_2CCH_2(C-H)HCO_2H$	393.1
$EtO_2CCO_2(C-H)HMe$	396.2	$Bu^tO_2C(CH_2)_2(C-H)HCO_2H$	391.0
$Pr^n(C-H)HCO_2Me$	394.9	$Bu^tO_2C(CH_2)_3(C-H)HCO_2H$	391.5
$Bu^n(C-H)HCO_2Me$	394.5	$Bu^tO_2C(CH_2)_4(C-H)HCO_2H$	391.3
$Pr^iO_2CCO_2(C-H)Me_2$	396.2	$Bu^tO_2C(CH_2)_7(C-H)HCO_2H$	391.3
$Pr^iO_2C(CH_2)_2CO_2(C-H)Me_2$	395.5	$MeO_2C(C-H)HCO_2Me$	391.7
$Pr^iO_2C(CH_2)_3CO_2(C-H)Me_2$	391.7	$MeO_2CCO_2(C-H)H_2$	403.9
$Pr^iO_2C(CH_2)_5CO_2(C-H)Me_2$	391.2	$MeO_2CCH_2(C-H)HCO_2Me$	404.8
$Pr^iO_2C(CH_2)_8CO_2(C-H)Me_2$	391.1	$MeO_2C(CH_2)_2(C-H)HCO_2Me$	393.1
$Bu^nCO_2(C-H)HMe$	392.3	$MeO_2C(CH_2)_4(C-H)HCO_2Me$	393.2
$Bu^nCO_2(C-H)HEt$	392.1	$PhCO_2(C-H)H_2$	418.4
$Bu^nCO_2(C-H)Me_2$	387.9	$PhSiMe_2(C-H)H_2$	410.1
Ethers and acetals			
$MeO(C-H)H_2$	411.9	$(EtO)_2(C-H)Pr^i$	380.5
$PhO(C-H)H_2$	385.0	$(iso\text{-}C_5H_{11}O)_2(C-H)Me$	378.3
$EtO(C-H)HMe$	399.5	$(Pr^nO)_2(C-H)Pr^i$	379.5
$Bu^tOCMe_2(C-H)H_2$	402.1	$(Pr^iO)_2(C-H)Pr^i$	381.4
$Pr^iO(C-H)Me_2$	390.8	$(Bu^nO)_2(C-H)Pr^i$	379.0
$Bu^nO(C-H)HPr^n$	392.2	$(Bu^sO)_2(C-H)Pr^i$	380.5
$MeO(C-H)HPh$	359.0	$(Pr^iO)_2(C-H)Me$	382.9
$MeO(C-H)Ph_2$	354.1	$(Bu^nO)_2(C-H)Me$	379.0
$PhCH_2O(C-H)HPh$	359.0	$(MeO)_2(C-H)Pr^n$	378.8
$(MeO)_2(C-H)H$	391.0	$(EtO)_2(C-H)Pr^n$	378.3
$(MeO)_2(C-H)Me$	381.2		384.3
$(Bu^nO)_2(C-H)H$	390.2		
$(EtO)_2(C-H)H$	390.1		380.2
$(MeO)_2(C-H)Ph$	353.9		
$(EtO)_2(C-H)Me$	380.2		
$(MeO)_2(C-H)Pr^i$	381.4		359.5
$(Pr^nO)_2(C-H)H$	391.8		
$(EtO)_2(C-H)Ph$	376.5		
$(Pr^nO)_2(C-H)Me$	379.6		360.9
$(Pr^iO)_2(C-H)Pr^n$	379.6		
$(Pr^iO)_2(C-H)H$	390.5		
$(Pr^iO)_2(C-H)Me$	380.7		
$(Bu^nO)_2(C-H)Me$	378.9		357.9
$(Bu^iO)_2(C-H)Me$	380.1		
$(Bu^iO)_2(C-H)H$	389.5		
$(n\text{-}C_5H_{11}O)_2(C-H)Pr^i$	378.3		
$(sec\text{-}C_5H_{11}O)(C-H)Pr^i$	379.6		357.3
$[iso\text{-}C_5H_{11}O]_2(C-H)H$	388.4		
$(Bu^sO)_2(C-H)H$	391.5		
$(n\text{-}C_5H_{11}O)_2(C-H)Me$	378.3		
$(sec\text{-}C_5H_{11}O)_2(C-H)H$	390.2		

Table 9 (continued).

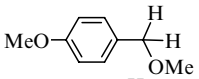
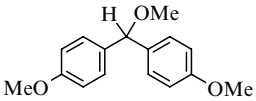
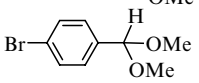
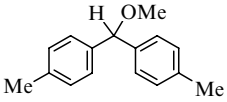
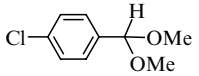
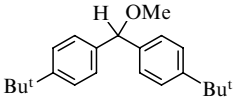
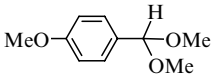
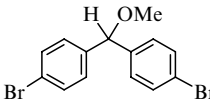
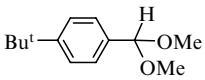
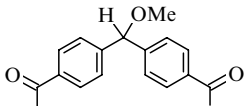
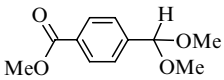
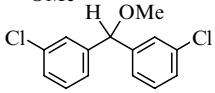
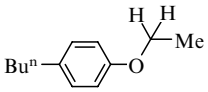
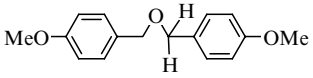
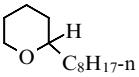
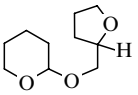
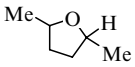
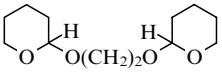
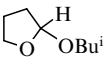
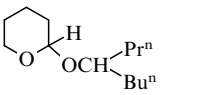
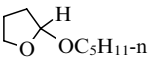
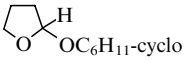
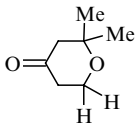
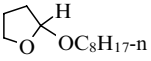
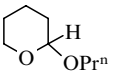
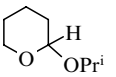
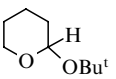
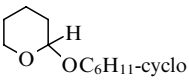
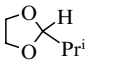
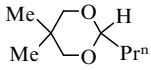
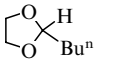
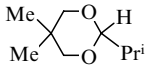
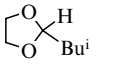
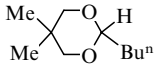
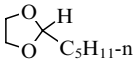
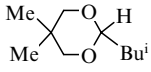
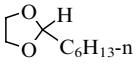
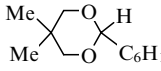
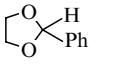
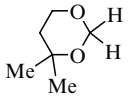
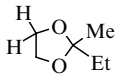
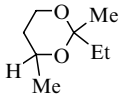
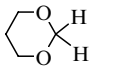
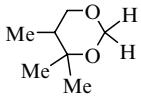
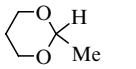
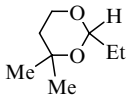
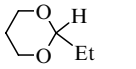
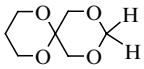
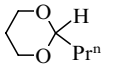
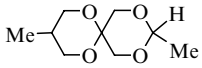
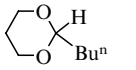
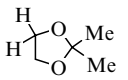
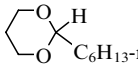
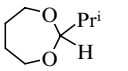
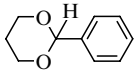
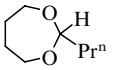
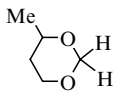
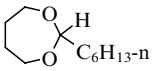
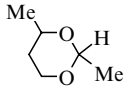
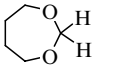
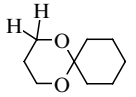
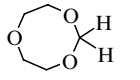
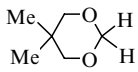
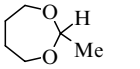
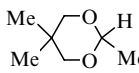
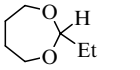
Compound	D_{C-H} /kJ mol^{-1}	Compound	D_{C-H} /kJ mol^{-1}
Ethers and acetals			
	354.5		342.8
	354.3		346.6
	354.3		347.6
	353.2		350.1
	353.1		353.5
	355.2		352.4
	357.7		
	350.0		
Cyclic ethers and acetals			
	391.6		380.5
	384.1		377.1
	387.5		383.7
	381.4		380.5
	378.5		376.0
	374.3		389.6
	375.3		405.7
	401.7		381.2
	386.0		373.4
	385.0		372.5
	386.0		
	381.8		

Table 9 (continued).

Compound	D_{C-H} /kJ mol^{-1}	Compound	D_{C-H} /kJ mol^{-1}
Cyclic ethers and acetals			
	373.1		379.4
	372.2		380.1
	371.3		379.1
	373.6		378.5
	371.6		378.1
	373.2		389.8
	381.7		389.7
	388.0		388.4
	378.0		381.4
	381.7		390.8
	377.7		375.5
	377.0		404.8
	376.5		377.4
	378.4		378.1
	383.6		373.6
	378.9		385.5
	396.2		400.9
	388.7		380.8
	380.3		379.2

[a] The bond dissociation energies were taken from Ref. 12.

Table 10. Dissociation energies of C–H bonds in oxygen-containing compounds calculated using the intersecting parabolas model as compared with published data.

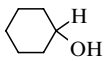
Compound	D_{C-H}/kJ mol^{-1}	
	IP model	Published data
H–CH_2OH	411.0	401.9,[5] 402.1,[10] 411.0,[12] 384.9,[13] 401.8 [75]
Me(C–H)(OH)H	399.8	401.3,[5] 389.1,[9] 384.9,[13] 389.2,[75] 392.5 [76]
Et(C–H)(OH)H	399.5	392.0,[12] 394.6 [76]
Me_2(C–H)OH	390.5	381.2,[5] 380.7,[9] 372.4,[13] 383.7 [76]
H–CH_2CMe_2OH	417.4	418.4,[5] 414.2,[13] 383.3 [76]
	388.4	386.6 [5]
H–CH_2(OH)CH_2OH	401.5	376.6,[13] 385.4 [76]
CH_2=CH(C–H)(OH)H	356.2	341.4 [5]
H–C(O)H	377.8	368.2,[10] 376.0,[12] 386.4 [75]
MeC(O)–H	373.8	372.0,[12] 373.8 [75]
H–CH_2C(O)H	394.3	394.6,[12] 394.3 [75]
MeC(O)(C–H)H_2	411.8	389.1,[76] 411.3 [75]
MeC(O)(C–H)HMe	392.6	386.2 [9]
EtO(C–H)HMe	399.5	386.2,[9] 384.9 [13]

Table 11. Dissociation energies of C–H bonds in nitrogen- and sulfur-containing compounds calculated from experimental data using the intersecting parabolas model.

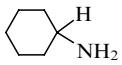
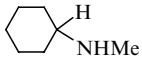
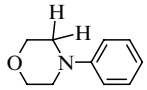
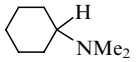
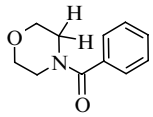
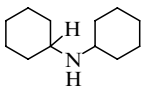
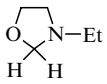
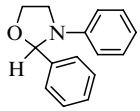
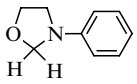
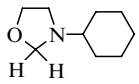
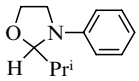
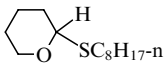
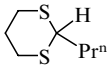
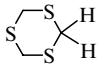
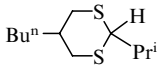
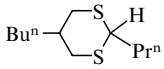
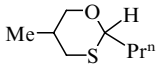
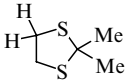
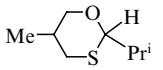
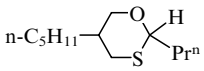
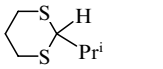
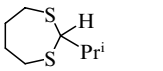
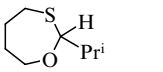
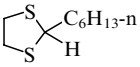
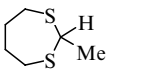
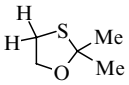
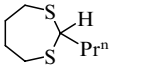
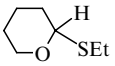
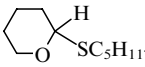
Compound	D_{C-H}/kJ mol^{-1}	Compound	D_{C-H}/kJ mol^{-1}
Amines and amides [56, 57]			
H_2N(C–H)H_2	400.0		385.6
MeNH(C–H)H_2	389.0		
Me_2N(C–H)H_2	376.6		
H_2N(C–H)HMe	389.6		
EtNH(C–H)HMe	384.6	CH_2=CH(C–H)HN(CH_2CH=CH_2)$_2$	345.6
Et_2N(C–H)HMe	379.5	CH_2=CH(C–H)HN(CH_2CH=CH_2)Ph	339.3
H_2N(C–H)Me_2	379.5	H_2N(C–H)HPh	368.0
Pr^iNH(C–H)Me_2	375.0	Me_2N(C–H)HPh	370.8
Pr^i_2N(C–H)Me_2	370.0	$(PhCH_2)_2N$(C–H)HPh	372.8
		PhMeN(C–H)H_2	383.7
	395.9	PhEtN(C–H)HMe	383.2
		Ph_2N(C–H)H_2	379.5
	388.0		361.0
	381.0		401.0
	387.3		
		AcNH(C–H)HMe	399.2
		AcNH(C–H)Me_2	395.5
		AcMeN(C–H)H_2	386.9
Nitriles [58]			
NC(C–H)H_2	401.7 [a]	$NCCH_2$(C–H)HCO_2Me	383.8
NC(C–H)HMe	387.2	NCCMePh(C–H)H_2	408.7
NC(C–H)Me_2	372.2	NCCH=(C–H)H	439.8 [a]
$NCCMe_2$(C–H)H_2	402.9	NCC≡C–H	471.3 [a]
[NCCMe(C–H)H_2]$_2$	404.4	N≡C–H	518.0 [a]

Table 11 (continued).

Compound	D_{C-H} /kJ mol^{-1}	Compound	D_{C-H} /kJ mol^{-1}
Cyclic aminoethers [55]			
	371.2		362.6
	369.9		370.1
	364.8		
Nitro compounds [58]			
$H-CH_2NO_2$	415.4	$Me(C-H)HNO_2$	402.4
$Me_2(C-H)NO_2$	394.0	O_2N-H	327.6 (D_{N-H}) [a]
Thio- and dithioacetals [53, 55, 64]			
$(EtS)_2(C-H)H$	390.2		378.0
$(EtS)_2(C-H)Me$	376.1		373.1
$(EtS)_2(C-H)Pr^i$	376.5		388.8
$(n\text{-}C_5H_{11}S)_2(C-H)Pr^i$	385.6		373.9
	367.3		371.5
	369.1		374.2
	404.0		374.7
	378.3		374.6
	370.8		388.0
	371.1		370.1
	370.6		384.7
	367.5		369.4
	394.7		369.8
	377.8		
	374.6		
	374.1		

[a] The bond dissociation energies were taken from Ref. 12.

Compound	D_{C-H}	ΔD
$CH_2=CH(C-H)H_2$	368.0	0
$CH_2=CMe(C-H)H_2$	357.9	−10.1
(*E*)-$MeCH=CMe(C-H)H_2$	356.8	−11.2
$Me_2C=CMe(C-H)H_2$	350.2	−17.8

Two double bonds have an even more pronounced effect on the α-C−H bond (see Table 4; the D_{C-H} values are given in kJ mol^{-1}).

Compound	D_{C-H}	ΔD_{C-H}
$CH_2=CH(C-H)H_2$	368.0	0
$CH_2=CHCH=CH(C-H)H_2$	343.0	−25.0
$(CH_2=CH)_2(C-H)H$	318.0	−50.0
$(CH_2=CH)_2(C-H)Me$	321.1	−46.9
	408.4	0
	342.5	−65.9
	329.3	−79.1
	288.8	−119.6
	408.8	0
	341.5	−67.3
	330.9	−77.9
	312.6	−96.2
	338.9	−69.9

2. The benzene ring has a similar effect on the α-C−H bond (see Table 8; the D_{C-H} values are given in kJ mol^{-1}).

Compound	D_{C-H}	ΔD_{C-H}
$Me(C-H)H_2$	422	0
$Ph(C-H)H_2$	375.0	−47.0
$Ph(C-H)HMe$	364.1	−57.9
$Ph(C-H)Me_2$	354.2	−67.8
$Ph_2(C-H)H$	356.8	−65.2

3. The C−H bond weakens if a nitrogen-containing functional group X–NH_2, NH_2 or CN is in the α-position with respect to this bond (see Table 11; the D_{C-H} values are given in kJ mol^{-1}).

Compound	X	D_{C-H}	ΔD_{C-H}
$X(C-H)H_2$	Me	422.0	0
	NH_2	400.0	−22.0
	NHR	398.0	−33.0
	CN	401.7	−20.3
	NO_2	415.4	−6.6
$X(C-H)HMe$	Me	412.0	0
	NH_2	389.6	−22.4
	NHR	384.6	−27.4
	CN	387.2	−24.8
	NO_2	402.4	−9.6
$X(C-H)Me_2$	Me	400.0	0
	NH_2	379.5	−20.5
	NHR	375.0	−25.0
	CN	372.2	−27.8
	NO_2	394.9	−5.1

This is due to stabilisation of free valence caused by the neighbouring group containing p- or π-electrons. With respect to their ability to stabilise the free valence on the neighbouring carbon atom the groups considered are in the same order: $NO_2 < CN < NH_2 < NHR$. Replacement of a hydrogen atom by a methyl group in the $X(C-H)H_2$ fragment reduces the D_{C-H} value by 10.5 ± 3.4 kJ mol^{-1} (*cf.* 19.2 ± 2.6 kJ mol^{-1} for replacement of two molecules).

4. Oxygen-containing groups X have a similar effect on the α-C−H bond (see Table 9; the D_{C-H} values are given in kJ mol^{-1}).

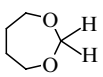
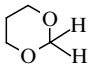
Compound	X	D_{C-H}	ΔD_{C-H}
$X(C-H)H_2$	Me	422.0	0
	OH	411.0	−11.0
	OR	411.9	−10.1
	C=O	411.8	−10.2
	C(O)OH	414.1	−7.9
$X(C-H)HMe$	Me	412.0	0
	OH	399.8	−12.2
	OR	399.5	−12.5
	C=O	397.2	−14.8
	C(O)OH	398.9	−13.1
$X(C-H)Me_2$	Me	400.0	0
	OH	390.5	−9.5
	OR	390.8	−9.2
	C=O	387.6	−12.4
	C(O)OH	388.3	−11.7

With respect to their ability to stabilise the free valence the oxygen-containing groups can be ordered as follows: OH > OR > C=O > CO_2H. The increments characterising the effect of one and two methyl groups on the D_{C-H} value are similar to those of hydrocarbons and N-containing groups:

$$D_{C-H}(XC-H)H_2 - D_{C-H}(XMeC-H)H = \\ = 13.3 \pm 1.6 \text{ kJ mol}^{-1};$$

$$D_{C-H}(XC-H)H_2 - D_{C-H}(XMeC-H)H = \\ = 15.9 \pm 3.0 \text{ kJ mol}^{-1}.$$

5. The C−H bond strengths in cyclic acetals are affected by the ring strain energy. Table 9 shows that the smaller the E_{rsc} (see Ref. 55) the larger the D_{C-H} value.

Cyclic acetal	D_{C-H} /kJ mol^{-1}	E_{rsc} /kJ mol^{-1} (see Refs 6, 7)
	381.2	29.16
	385.5	25.52
	388.0	13.09

The C−H bond dissociation energies in 1,3-dioxolane, 1,3-dioxane and 1,3-dioxepane are related to the ring strain energy E_{rsc} (in kJ mol^{-1}) by the following correlation equation:

$$D_{C-H} = 393.17 - 0.37\,E_{rsc}\,. \quad (39)$$

The C—H bond strength difference between 1,3-dioxane and diethoxymethane is −2.4 kJ mol^{-1}, *i.e.*, at minimum ring strain energy the C—H bond strength in 1,3-dioxane is similar to that of acyclic acetals (390.4 kJ mol^{-1}).

6. In the text below the C—H bond dissociation energies in SCHR (R = H, Me, Pr^i) fragments are compared with the C—H bond strengths in similar hydrocarbons [12] (the D_{C-H} values are given in kJ mol^{-1}).

Compound	$(EtX)_2(C-H)H$	$(EtX)_2(C-H)Pr^i$	$(EtX)_2(C-H)Me$
D_{C-H} for X = S	390	389	376
D_{C-H} for X = CH_2	412	400	396
ΔD	−22	−11	−20

As can be seen, the sulfur atoms lead to an appreciable (by 11–22 kJ mol^{-1}) decrease in the strength of the neighbouring C—H bond.

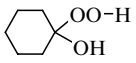
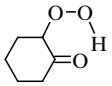
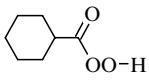
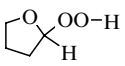
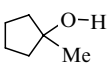
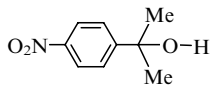
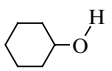
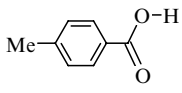
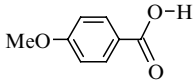
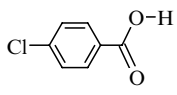
VII. Dissociation energies of O—H bonds in alcohols, acids, hydroperoxides, hydroxylamines and phenols

The O—H bond strengths in various hydroperoxides were first calculated [66] from experimental data (parameters of co-oxidation). The estimates of the ΔD_{O-H} values were obtained using the ratio of the rate constants for reactions of two different peroxyl radicals with the same hydrocarbon. The parameters of the IP model used in the ΔD_{O-H} calculations are listed in Table 5. Dimethylethyl hydroperoxide (D_{O-H} = 358.6 kJ mol^{-1}) [76] was used as a reference hydroperoxide. The results of calculations are presented in Table 12.

As can be seen from the data in Table 12, the D_{O-H} values vary over a wide range from 360 to 413 kJ mol^{-1} depending on the hydroperoxide structure. The hydroperoxides studied can be ordered as follows with respect to the O—H bond strength (D_{O-H}, in kJ mol^{-1}): $R_2CHOC(OO-H)R_2$ (358.4) < RPhC(O-H)OO—H (359.8) < 1-hydroxycyclohexyl 1-hydroperoxide (362.1) < ROCH(OO—H)R (367.3) < 2-hydroperoxytetrahydrofuran (367.6) < α-ketocyclohexyl peroxide (369.8) < ROCH(OO—H)Ph (374.8) < α-RC(O)OCH(OO—H)Ph (376.4) < cyclohexylperacid (376.9), $R_3CC(O)(OO-H)$ (376.9) < RC(O)(OO—H) (387.1) < PhC(O)(OO—H) (403.9) < $Cl_2CH.CCl_2(OO-H)$ (411.6) < $Cl_3CCCl_2(OO-H)$ (413.1). The highest D_{O-H} values were obtained for peracids and chlorine-containing hydroperoxides.

The D_{O-H} values in alcohols (dimethylethoxyl radical with D_{O-H} = 439.4 kJ mol^{-1} was used as a reference alkoxyl radical) [38] and acids (benzoyloxyl radical with D_{O-H} = 439.3 kJ mol^{-1} was used as a reference radical) [5] were estimated in a similar fashion.[67] The results of evaluation of the O—H bond strength are given in Table 12. As can be seen, the D_{O-H} values vary only slightly on going from one alcohol to another. As was mentioned above, the O—H bond strengths of various acids are also similar (see Table 4). The EtX compounds form the following sequence with respect to the O—H bond dissociation energy (in

Table 12. Dissociation energies of O—H bonds in hydroperoxides, alcohols and acids calculated from experimental data using the intersecting parabolas model.

Compound	D_{O-H} /kJ mol^{-1}	Compound	D_{O-H} /kJ mol^{-1}
Hydroperoxides [66] [$D_{O-H}(Bu^tOO-H)$ = 358.6 kJ mol^{-1} (see Ref. 76)]			
HOO—H	369.0		362.1
RCH_2OO-H	365.5		
$R_2CHOO-H$	365.5		
R_3COO-H	358.6		369.8
RPhC(OH)OO—H	359.8		
$R_3CC(O)OO-H$	376.9		
ROCH(OO—H)R	367.3		
PhC(O)OO—H	403.9		376.9
$R_2CHOC(OO-H)R_2$	358.4		
RC(O)CH(OO—H)R	369.8		
ROCH(OO—H)Ph	374.8		
RC(O)OCH(OO—H)Ph	376.4	$Cl_2CHCCl_2(OO-H)$	411.6
		$Cl_3CCCl_2(OO-H)$	413.1
	367.6	RC(O)(OO—H)	387.1
Alcohols [67] [$D_{O-H}(Bu^tO-H)$ = 439.4 kJ mol^{-1} (see Ref. 5)]			
$EtMe_2CO-H$	439.7		425.1
$PhMe_2CO-H$	438.2		
	437.6		438.5
Acids [67] {D_{O-H}[PhC(O)O—H] = 439.3 kJ mol^{-1} (see Ref. 5)}			
$Pr^nOC(O)O-H$	432.5		
$Bu^sOC(O)O-H$	431.9		
$PhC\equiv CC(O)O-H$	436.9		
	437.0		438.5
			432.2

kJ mol^{-1}): EtOO—H (365.5) < EtO—H (432.4) < EtC(O)O—H (439.3). It was found that the O—H bond strengths in *para*-substituted benzoic acids 4-$YC_6H_4CO_2H$ are independent of the substituent Y and only at Y = Cl is the D_{O-H} value 7 kJ mol^{-1} lower than in unsubstituted benzoic acid.

Y	σ	D_{O-H} /kJ mol^{-1}
MeO	−0.268	438.5
Me	−0.170	437.0
H	0.0	439.3
Cl	0.227	432.2

Tables 13 and 14 list the D_{O-H} values for phenols, calculated from experimental data in the famework of the IP model. The ΔD_{O-H} values were estimated from the rate constant ratio for the reactions of the same peroxyl radical with two phenols. The reference compounds were unsubstituted phenol (D_{O-H} = 369.0 kJ mol^{-1}) and 2,4,6-tri-*tert*-butylphenol (D_{O-H} = 339.7 kJ mol^{-1}).[19] The parameters of the IP model used in calculations are given in Table 5.

Comparison shows that in most cases the O—H bond strengths thus obtained are in good agreement with the D_{O-H} values found from the chemical equilibrium (see Table 1). The D_{O-H} values (in kJ mol^{-1}) for phenols 4-YC_6H_4OH, calculated from the equilibrium constants and from the kinetic data using the IP model are listed below.

Y	D_{O-H} (equilibrium)	D_{O-H} (IP model)
MeO	346.3	347.5
Me	360.5	362.2
H	369.2	369.0
Bu^t	356.7	360.1

An analogous picture is also observed for *para*-substituted 4-Y-2,6-di-*tert*-butylphenols (D_{O-H} values are given in kJ mol^{-1}).[21]

Y	D_{O-H} (equilibrium)	D_{O-H} (IP model)
H	346.2	347.4
Me	338.8	339.7
MeO	327.5	331.4
Ph	337.9	338.4
Cl	344.5	345.2
CN	356.9	353.1

Table 13. Dissociation energies of O—H bonds in phenols calculated from experimental data using the intersecting parabolas model, [D_{O-H}(PhO—H) = 369.0 kJ mol^{-1}].[59,60]

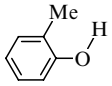
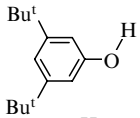
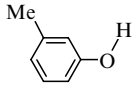
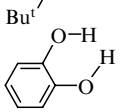
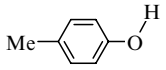
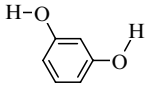
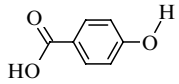
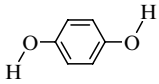
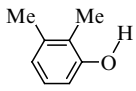
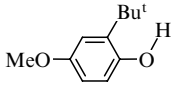
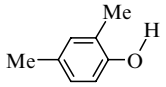
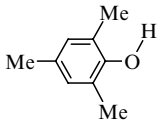
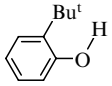
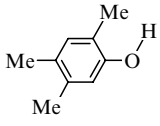
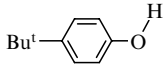
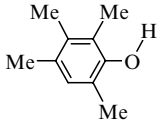
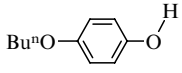
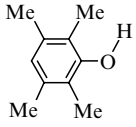
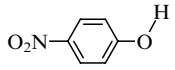
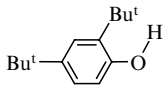
Phenol	D_{O-H} /kJ mol^{-1}	Phenol	D_{O-H} /kJ mol^{-1}
	359.9		362.4
	366.7		339.6
	362.2		369.1
	371.7		352.0
	355.5		343.4
	360.5		347.5
	353.8		356.8
	360.1		347.4
	347.8		351.2
	372.8		
	359.5		

Table 13 (continued).

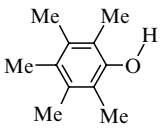
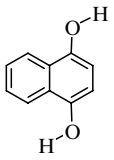
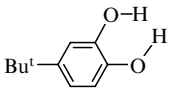
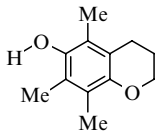
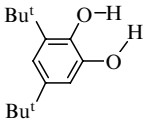
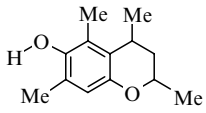
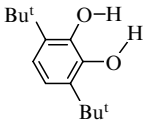
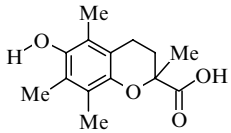
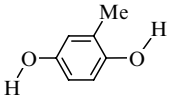
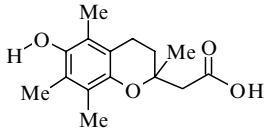
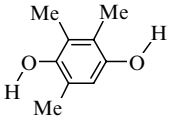
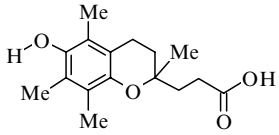
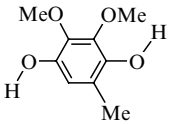
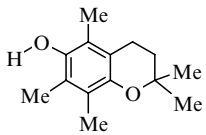
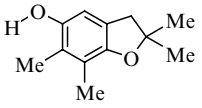
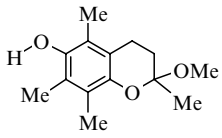
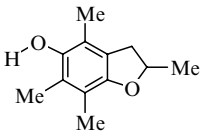
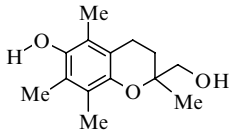
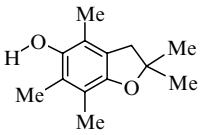
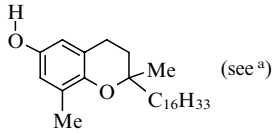
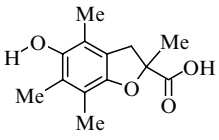
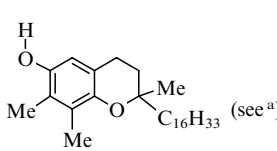
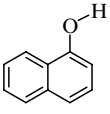
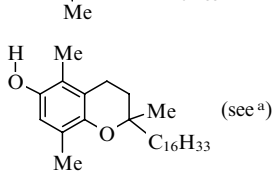
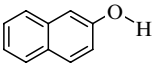
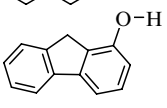
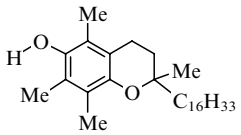
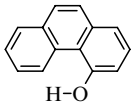
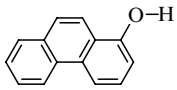
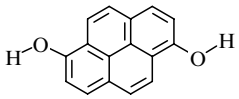
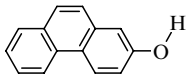
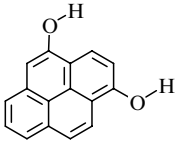
Phenol	D_{O-H} /kJ mol^{-1}	Phenol	D_{O-H} /kJ mol^{-1}
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	342.4		330.8
	340.3		326.4
	339.5		328.9
	349.8		333.3
	344.7		329.7
	343.8		328.4
	329.7		334.7
	326.4		331.0
	326.0		342.8
	334.0		335.1
	343.4		335.6
	353.8		
	338.3		

Table 13 (continued).

Phenol	D_{O-H} /kJ mol^{-1}	Phenol	D_{O-H} /kJ mol^{-1}
 (see [a])	330.0		356.2
	354.7		315.9
	367.0		317.7

[a] $C_{16}H_{33}$ = $[(CH_2)_3CHMe]_3Me$.

Table 14. Dissociation energies of O–H bonds in sterically hindered phenols calculated from experimental data using the intersecting parabolas model [D_{O-H}(2,4,6-$Bu^t_3C_6H_2O-H$) = 339.7 kJ mol^{-1}].[59, 60]

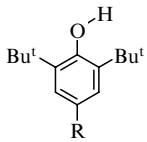
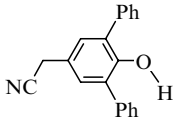
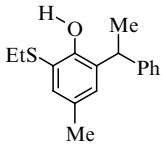
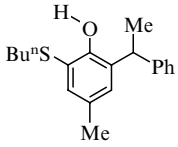
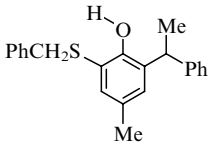
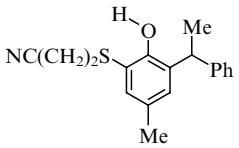
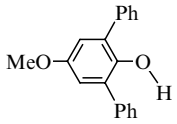
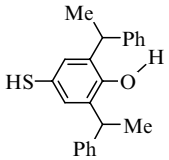
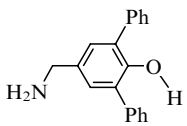
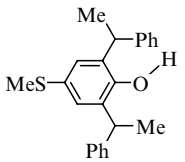
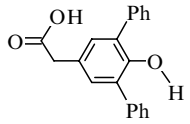
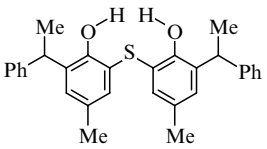
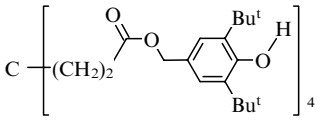
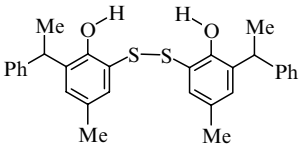
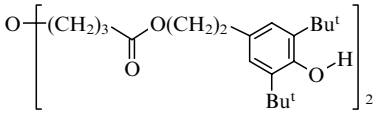
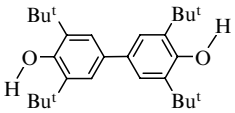
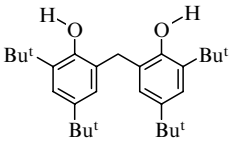
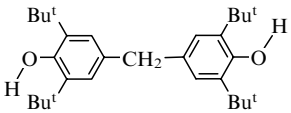
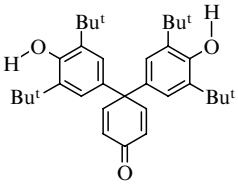
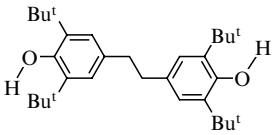
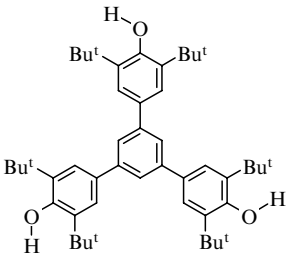
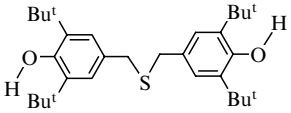
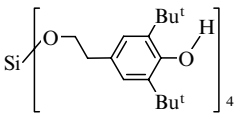
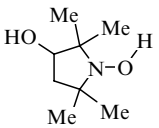
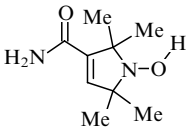
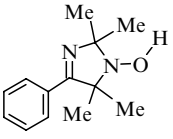
Phenol	D_{O-H} /kJ mol^{-1}	Phenol	D_{O-H} /kJ mol^{-1}
			312.0
R = H	347.4		339.4
R = Me	339.7		
R = CH_2Ph	340.4		
R = Ph	338.4		
R = Me_2PhC	340.8		
R = Ph_2CH	343.0		
R = OMe	331.4		339.2
R = OBu^t	332.0		
R = Cl	345.2		
R = NO	346.7		
R = NO_2	358.7		
R = CH_2NH_2	335.5		338.7
R = NHAc	327.4		
R = HCO	348.5		
R = Ac	346.2		
R = CN	353.1		
R = CO_2H	349.5		
R = CO_2Bu^t	348.5		
R = CH_2CO_2H	337.6		346.2
R = CH_2CO_2Me	343.5		
R = $CH_2CH_2CO_2C_{18}H_{37}$-n	340.3		
R = SPh	347.1		
	328.7		340.7
	323.6		341.1
	326.6		

Table 14 (continued).

Phenol	D_{O-H} /kJ mol^{-1}	Phenol	D_{O-H} /kJ mol^{-1}
	335.9		341.7
	335.3		339.6
	343.3		341.2
	340.9		347.0
	339.4		345.6
	340.6		
	341.6		

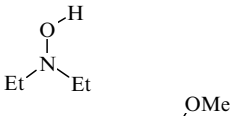
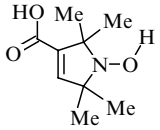
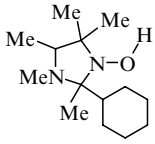
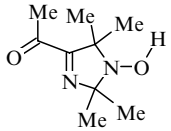
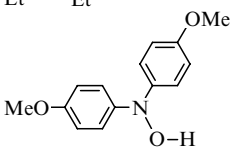
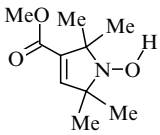
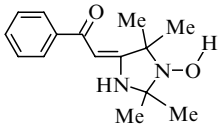
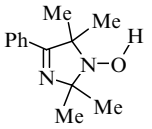
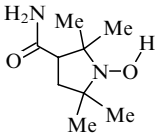
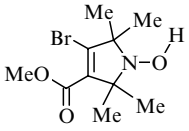
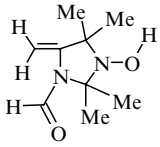
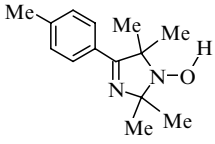
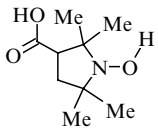
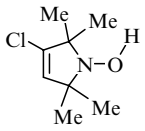
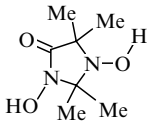
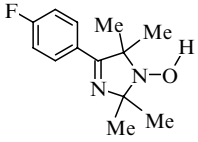
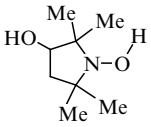
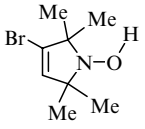
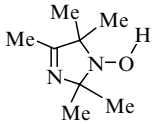
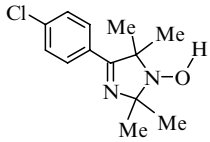
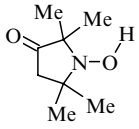
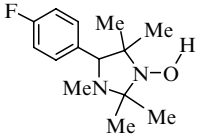
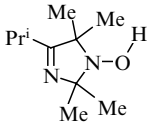
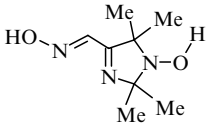
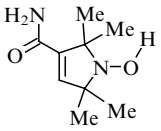
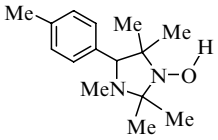
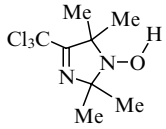
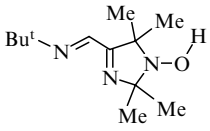
The O—H bond strengths in hydroxylamines were calculated using the IP model from the characteristics of reactions of various iminoxyl radicals with 1,2-diphenylhydrazine[61] using 1-hydroxy-2,2,6,6-tetramethylpiperidin-4-one (D_{O-H} = 300.4 kJ mol^{-1}) as the reference hydroxylamine. The results of calculations are listed in Table 15. They are in good agreement with the data presented in Table 3 and obtained from the equilibrium constants (D_{O-H} values are given in kJ mol^{-1}).

Hydroxylamine	D_{O-H} (equilibrium)	D_{O-H} (IP model)
	287.3	289.1
	293.1	292.6
	294.2	294.0
	296.1	295.1

Comparison of the D_{O-H} values in alcohols, phenols, hydroperoxides and hydroxylamines indicates that the O—H bond strength is strongly affected by conjugation of free valence of the oxygen atom with adjacent π-bonds and p electrons of heteroatoms (N, O).

Bond	Compound	D_{O-H} /kJ mol^{-1}	ΔD_{O-H} /kJ mol^{-1}
AlkO—H	Bu^{t}OH	439.4	0
ArO—H	PhOH	369.0	70.4
AlkOO—H	EtOOH	365.5	73.9
Alk_2NO—H	Et_2NOH	304.3	135.1

Table 15. Dissociation energies (in kJ mol^{-1}) of O–H bonds in hydroxylamines and oximes calculated from experimental data using the intersecting parabolas model [D_{O-H}(1-OH-2,2,6,6-Me$_4$-piperidin-4-one) = 300.4 kJ mol^{-1}].[61]

Compound	D_{O-H}	Compound	D_{O-H}	Compound	D_{O-H}	Compound	D_{O-H}
	304.3		291.2		286.9		296.9
	300.4		293.4		298.6		294.0
	291.0		293.4		298.6		295.7
	290.1		292.7		300.9		295.1
	289.1		293.1		295.4		294.8
	298.7		292.0		294.9		296.1
	292.6		291.2		295.9		294.9

VIII. Dissociation energies of N–H bonds in amines and S–H bonds in thiols

The dissociation energies of the N–H bonds in aromatic amines are listed in Table 16. They were calculated using the IP method from experimental rate constants for the reactions of peroxyl radicals with amines[62] with diphenylamine (D_{N-H} = 364.7 kJ mol^{-1})[21] as the reference amine. The parameters used in calculations are given in Table 5.

The D_{N-H} value calculated for 1-naphthylphenylamine using the IP model (352.5 kJ mol^{-1}) is nearly the same as the value obtained by the chemical equilibrium method (352.8 kJ mol^{-1}, see Table 2).

The dissociation energies of the S–H bonds in aliphatic and aromatic thiols are presented in Table 17. They were calculated in the framework of the IP model using the experimental rate constants for reactions between alkyl radicals and the S–H bonds of the corresponding compounds.[63,64] As can be seen, the structure of the hydrocarbon fragment in thiols has little effect on the D_{S-H} value.

IX. Dissociation energies of Si–H, Ge–H, Sn–H, Se–H and P–H bonds

The Y–H bond dissociation energies in organoelement compounds using the IP model were estimated[77] from the experimental rate constants for the reactions of hydrogen abstraction by the following radicals (the D_{C-H} values in kJ mol^{-1} taken from Ref. 12 are given in parentheses): RC$^{\cdot}$H$_2$ (422), Me$_3$C$^{\cdot}$ (400), PhC$^{\cdot}$H$_2$ (375), PhC$^{\cdot}$HR (364.1), *tert*-RO$_2^{\cdot}$ (356.8), Bu^{t}O$^{\cdot}$ (439.4). The parameters used for calculating D_{C-H} values are listed in Table 5. The reference compounds with known Y–H bond strengths were Et$_3$Si–H (398.0), Bu$^n_3$Ge–H (347.3), Bu$^n_3$Sn–H (309.6), n-C$_8$H$_{17}$PH$_2$ (375.3) (D_{Y-H} in kJ mol^{-1} are given in parentheses). The results of calculations are presented in Table 18.

Comparison shows that the weaker the Y–H bond, the longer is this bond and the lower is the corresponding stretching vibration frequency (ν_{Y-H}).

Compound	D_{Y-H} /kJ mol^{-1}	$r_{Y-H} \times 10^{10}$ /m	ν_{Y-H} /cm^{-1}
H$_3$C–H	440.0	1.093	2914
H$_3$Si–H	384.1	1.480	2200
H$_3$Ge–H	348.9	1.525	2150
H$_3$Sn–H	346.0	1.711	2067
Me$_3$C–H	400	–	–
Et$_3$Si–H	398.0	–	–
Bu$^n_3$Ge–H	347.3	–	–
Bu$^n_3$Sn–H	309.6	–	–

Table 16. Dissociation energies of N–H bonds in aromatic amines calculated from experimental data using the intersecting parabolas model [$D_{N-H}(Ph_2N-H)$ = 364.7 kJ mol^{-1}].[62]

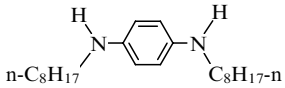
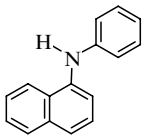
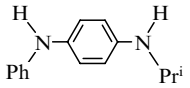
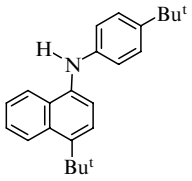
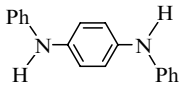
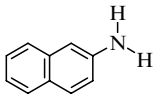
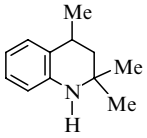
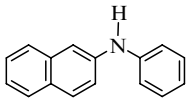
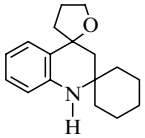
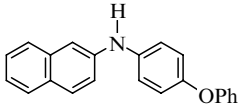
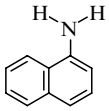
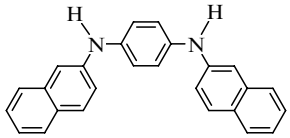
Amine	D_{N-H} /kJ mol^{-1}	Amine	D_{N-H} /kJ mol^{-1}
	352.2		352.5
	340.2		352.1
	346.9		379.5
	359.5		353.9
	360.8		349.5
	374.7		346.6

Table 17. Dissociation energies of S–H bonds in thiols calculated from experimental data using the intersecting parabolas model.[63,64]

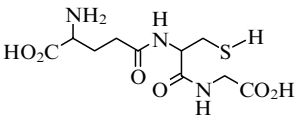
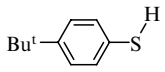
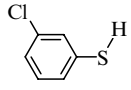
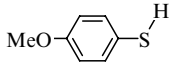
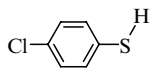
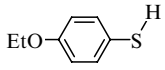
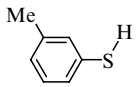
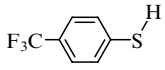
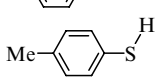
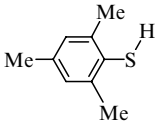
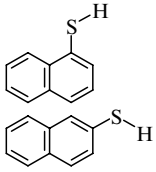
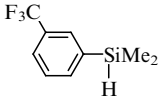
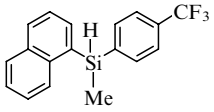
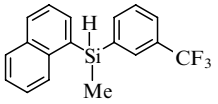
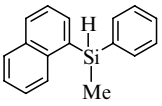
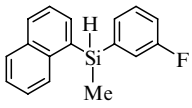
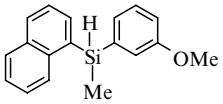
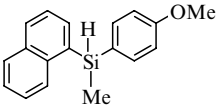
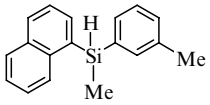
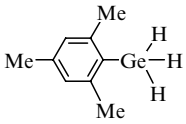
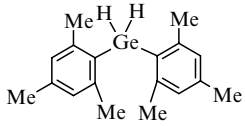
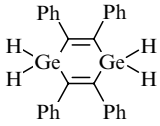
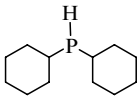
Thiol	D_{S-H} /kJ mol^{-1}	Thiol	D_{S-H} /kJ mol^{-1}
HS–H	382.0 [a]	HSS–H	325.0
Aliphatic thiols			
MeS–H	366.0 [a]		360.3
EtS–H	366.0		
Pr^nS–H	367.3		
Pr^iS–H	366.9		
Bu^nS–H	366.0		
PhC(S)S–H	367.9	cyclo-[CH(S–H)$(CH_2)_5$]	364.4
n-$C_{10}H_{21}$S–H	368.6	n-C_6H_{11}CHMeS–H	369.3
n-$C_{12}H_{25}$S–H	367.7	Me_2C(S–H)CH$(NH_2)CO_2$H	363.1
$Bu^tCH_2CMe_2CH_2CMe_2$S–H	367.9	H–SCH_2CH$(NH_2)CO_2$H	360.0
		HOCH_2C(S)S–H	368.2
Aromatic thiols			
PhS–H	330.0		329.6
	327.7		321.2
	326.0		321.5
	330.0		330.5
	326.7		

Table 17 (continued).

Thiol	D_{S-H} /kJ mol^{-1}	Thiol	D_{S-H} /kJ mol^{-1}
Aromatic thiols			
	328.5		320.3 318.7

[a] The bond dissociation energies were taken from Ref. 12.

Table 18. Dissociation energies (in kJ mol^{-1}) of X−H (X = Si, Ge, Sn, P) bonds calculated from experimental data using the intersecting parabolas model.[65, 77]

Compound	D	Compound	D	Compound	D	Compound	D
Silanes (R_3SiH)							
Ph_3Si-H	371.0		373.4		379.9		378.8
$PhMe_2Si-H$	380.2						
$Ph_2MeSi-H$	375.4						
$PhMeFSi-H$	394.6						
$PhMeClSi-H$	385.8						
$Ph(C_6F_5)MeSi-H$	384.7		374.2		378.4		375.4
$Ph(Ph_3Si)MeSi-H$	356.9						
$(Bu^tCH_2)PhMeSi-H$	375.4						
			371.6		372.8		
Germanes (R_3GeH)							
Ph_3Ge-H	322.5		337.5		336.8		319.9
$(PhCH_2)_3Ge-H$	324.9						
$Ph(PhCH_2)(Ge-H)H$	324.9						
$(Me_3Si)_3Ge-H$	305.2						
Stannanes (R_3SnH)							
Me_3Sn-H	318.5	Ph_3Sn-H	296.9	Bu_3Sn-H	309.6	H_3Sn-H	346.0
Phosphines (R_2PH)							
Et_2P-H	377.8	Bu^n_2P-H	375.0	$NC(CH_2)_3(P-H)H$	373.4		360.6
$(n\text{-}C_8H_{17})_2P-H$	375.3	$[NC(CH_2)_3]_2P-H$	369.5				

X. Dissociation energies of C−Hal bonds

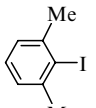
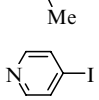
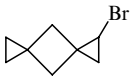
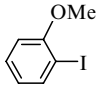
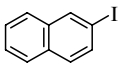
The dissociation energies of the C−halogen (Hal) bonds in halogen-containing compounds were estimated[78] by the IP method from the experimental rate constants for the reactions of halogen abstraction by hydrogen atom and by Ph$^{\cdot}$ and Me$^{\cdot}$ radicals (D_{C-H} = 474 and 440 kJ mol^{-1}, respectively).[12, 13] The S−Cl bond dissociation energy was also estimated for two compounds. The following halides were used as reference compounds with known C−Hal and S−Cl bond strengths (the D_{C-Hal} and D_{S-Cl}/kJ mol^{-1} values are given in parentheses): $BrCH_2CO_2H$ (270.9), MeBr (290.0), MeCl (354.0), MeI (240.0), PhI (281.0), $PhCH_2Cl$ (309.7), $PhCH_2Br$ (252.9), $MeSO_2Cl$ (292.9).[5] The parameters used for the IP model calculations are given in Table 5. The results of calculations are listed in Table 19.

Analysis of the data from Table 19 shows the following (on the average) decreasing order of the bond strengths: $D_{C-Cl} > D_{C-Br} > D_{C-I}$.

XI. Conclusion

Thus, the use of kinetic methods for estimating the Y−H (Y = C, O, N, P, Si, Ge, Sn) bond strengths makes it possible to considerably extend the range of compounds with known values of this important characteristic. Indeed, earlier only two hydroperoxides, namely, H_2O_2 and *tert*-ROOH were characterised by D_{O-H} values. Carrying out calculations based on experimental data on co-oxidation of organic compounds made it possible to determine the O−H bond strength values for nineteen different hydroperoxides (see Table 12). The number of alcohols and acids for which the D_{O-H} values were calculated (see Tables 4 and 12), and the number of oxygen-containing compounds with known D_{C-H}

Table 19. Dissociation energies (in kJ mol^{-1}) of C–Hal (Hal = Cl, Br, I) and S–Cl bonds calculated from experimental data using the intersecting parabolas model.[78]

Compound	*D*	Compound	*D*	Compound	*D*	Compound	*D*
Hal = Cl		Hal = I		Hal = I		Hal = I	
Et–Cl	346.3	Et–I	231.9		278.5		281.8
$PhCH_2CH_2$–Cl	319.8	Pr^i–I	230.6				
$EtSO_2$–Cl	285.6	Bu^t–I	217.4				
Pr^nSO_2–Cl	285.6						
Hal = Br			281.0		273.9		277.4
$PhCH_2CH_2$–Br	268.3						
n-C_6H_{13}–Br	296.6						
Br–$CHMeCO_2H$	256.3						
Br–$CH_2CH_2CO_2H$	276.3		280.2		281.6		278.6
Br–CH_2CO_2H	269.0						
	297.9		284.7		294.3		288.0
	304.4						287.4
	292.4		284.6		276.8		280.9
			281.9				279.5

values (see Table 9) increased similarly. A salient feature of the methods considered above is that they are applicable to various organic compounds of complex structure. This opens up prospects for estimating the bond dissociation energies in fragments constituting polymers and biopolymers. This review shows that the results obtained using various kinetic methods are in good agreement with one another.

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