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O—H Bond dissociation energies in hydroquinones and 4-hydroxyphenoxyl radicals and effect of solvation on the kinetics of reactions involving hydroquinones and semiquinone radicals

V. T. Varlamov,* B. E. Krisyuk, and A. V. Antonov

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 524 9676. E-mail: varlamov@icp.ac.ru

The O—H bond dissociation energies (D_{OH}) in the molecules of 2,5-dimethylhydroquinone (**1**) and 2,5-di-*tert*-butylhydroquinone (**2**) and in the corresponding semiquinone radicals (**5** and **8**, respectively) were estimated by the method of intersecting parabolas (IP) from experimental data on the rate constants for the reactions of these compounds with *N*-phenyl-1,4-benzoquinonemonoimine (**3**) and using the density functional B3LYP/6-31+G* quantum chemical calculations. When calculating the D_{OH} values by the IP method, solvation of reactants and transition states should be taken into account. The energies of solvation of quinones, semiquinone radicals, and hydroquinones were evaluated by the PCM method. The results of quantum chemical calculations obtained with inclusion of the effects of solvation and the D_{OH} estimates obtained by the IP method are in good agreement, being equal to 337.9±1.6, 242.5±1.4, and 242.7±3.4 kJ mol^{-1} for molecule **1** and radicals **5** and **8**, respectively.

Key words: hydroquinones, 4-hydroxyphenoxyl (semiquinone) radicals, bond dissociation energies, quantum chemical calculations, method of intersecting parabolas, rate constants, solvation.

The X—Y bond dissociation energies (D_{XY}) are important thermochemical parameters. Based on these data, it is possible to evaluate the stabilities of compounds and to assess the rates and routes of reactions involving them. Although the D_{XY} values are of great interest, at most three or four thousands of them are available from handbooks.[1—4] A considerable body of such data were obtained only recently by analyzing the rate constants for reactions using the method of intersecting parabolas (IP).[2,5]

Information concerning the bond dissociation energies in unstable 4-hydroxyphenoxyl (semiquinone) radicals that are formed from hydroquinones and their *N*-substituted analogs upon abstraction of a proton is scarce. The D_{OH} energies for unsubstituted and four chlorine-substituted semiquinone radicals were estimated[5] from thermochemical data and the O—H bond dissociation energies in hydroquinones. The D_{OH} and D_{NH} values for 4-hydroxydiphenylaminyl and 4-anilinophenoxyl radicals resulting from 4-hydroxydiphenylamine were determined from kinetic data.[6] The D_{NH} value for 4-anilinodiphenylaminyl radical formed from *N*,*N*′-diphenyl-1,4-phenylenediamine antioxidant was obtained.[7]

The O—H bond dissociation energies of semiquinone radicals characterize both the reducing ability of these radicals (their proton donor activity) and the oxidizing ability of the corresponding quinones (their activity in dehydrogenation reactions). Knowledge of D_{OH} values is of great importance for establishment of the mechanism of action of liposoluble quinone-type bioantioxidants (*e.g.*, ubiquinones and K group vitamins)[8] and for studies of the kinetics of chain reversible reactions in the quinone—hydroquinone systems.[9,10]

In this work we first estimated the D_{OH} energies for 2,5-dimethylhydroquinone (**1**) and for two semiquinone radicals, one of which is formed from hydroquinone **1** while the other from a close analog, 2,5-di-*tert*-butylhydroquinone (**2**). We showed that the solvent affects the experimental D_{OH} values and the rate constants for the reactions involving hydroquinones and semiquinone radicals.

Calculation Procedure

The D_{OH} values were estimated by the IP method from the experimental rate constants for elementary reactions of hydroquinones and semiquinone radicals and using density functional B3LYP quantum chemical calculations with the 6-31+G*, 6-31+G**, 6-311+G*, and 6-311+G** basis sets, which were

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carried out using the GAMESS [11] and GAUSSIAN-94/03 [12,13] programs. The B3LYP approximation gives reasonable estimates of the O—H and N—H bond strengths.[7,14] The energies of solvation were calculated using the PCM method;[15—17] here, the environment of the molecule is simulated by a polarizable continuum with a preset dielectric constant.

The semiempirical IP method employed in this work was proposed recently[18] and now we will dwell on some details of the technique. It is based on the experimental kinetic data. The energy profile of the reaction

$$\mathrm{X + H{-}Y \longrightarrow [X...H...Y]^{\neq} \longrightarrow X{-}H + Y}$$

is approximated by two parabolas. One of them describes the vibrations of the atoms involved in the cleaving bond H—Y and the other describes the vibrations of the atoms involved in the forming X—H bond. The parabolas can move along the vertical and horizontal axes (energy and distance axes, respectively). This assumption made it possible to divide all elementary reactions into classes (total of a hundred classes are known to date).[19] Each reaction class is characterized by a set of specific parameters (activation energy of thermally neutral reaction (E_{e0}), pre-exponent per attacked bond (A_0), *etc.*), which were calculated from experimental data and tabulated. The expression for the rate constant of the reaction is written in the Arrhenius form

$$k = nA_0 \cdot \exp[-E/(RT)], \qquad (1)$$

where n is the number of equivalent atoms (bonds) involved in the reaction. Relationships for activation energy (E) calculations include parameters, which were determined from experimental data and tabulated (see, *e.g.*, Refs 2 and 5). Particular form of the expressions for E and k depends on the enthalpy of reaction (ΔH_e), which is calculated with inclusion of zero-point vibrational energy correction for the cleaving (i) and forming (f) bonds

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f). \qquad (2)$$

Here D and ν are the bond dissociation energies and vibrational frequencies, respectively; h is the Planck constant, and L is the Avogadro constant. For each reaction class there are two threshold ΔH_e values, namely, $\Delta H_{e,min}$ (exothermic reactions) and $\Delta H_{e,max}$ (endothermic reactions). If $\Delta H_e < \Delta H_{e,min}$, the activation energy of the reaction is given by $E = 0.5RT$. If $\Delta H_e > \Delta H_{e,max}$, then

$$E = \Delta H + 0.5RT = D_i - D_f + 0.5RT.$$

In both cases the A_0 value characteristic of a given reaction class is multiplied by a coefficient $\gamma > 1$

$$\gamma = [1 + 1.3(|\Delta H_e|^{1/2} - |\Delta H_{e,min}|^{1/2})]^2, \qquad (3)$$

or

$$\gamma = [1 + 1.3(\Delta H_e^{1/2} - \Delta H^{1/2}_{e,max})]^2. \qquad (4)$$

The $\Delta H_{e,min}$ and $\Delta H_{e,max}$ values were calculated from experimental data and tabulated.[2] If the enthalpy of reaction, ΔH_e, is in the range $\Delta H_{e,min}$—$\Delta H_{e,max}$, the parameters E and k are calculated without applying corrections given by Eqs (3) or (4). These expressions were published[2,5] along with the corresponding values of the reaction parameters obtained by the IP method.

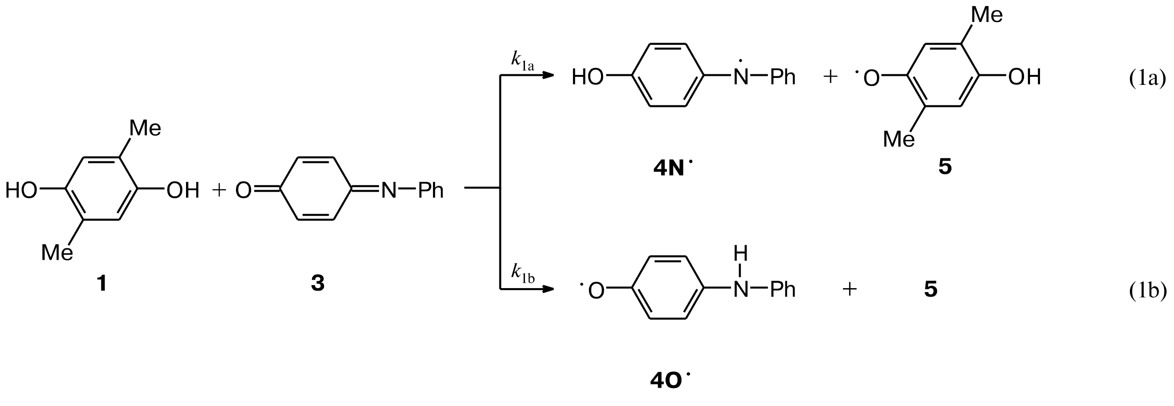
Results and Discussion

To calculate the D_{OH}(**1**) value by the IP method, we used the rate constant for the reaction of this compound with *N*-phenyl-1,4-benzoquinonemonoimine (**3**) in PhCl, which results in 4-hydroxydiphenylaminyl (**4N**$^\bullet$) and 4-anilinophenoxyl (**4O**$^\bullet$) radicals while hydroquinone **1** is oxidized into 2,5-dimethyl-4-hydroxyphenoxyl semiquinone radical **5** (Scheme 1).

The experimental values of the rate constant $k_1 = k_{1a} + k_{1b}$ are $(3.39\pm0.52) \cdot 10^{-3}$ (298.2 K) and $(4.83\pm0.92) \cdot 10^{-2}$ L mol^{-1} s^{-1} (340.0 K).[20]

The necessary D_{OH}(**4N**$^\bullet$) and D_{NH}(**4O**$^\bullet$) values are 259.5 and 273.6 kJ mol^{-1}, respectively.[6] Analysis of the published data on the D_{OH} energies for hydroquinones[2,4,5] suggests that the D_{OH}(**1**) value lies in the range 330—350 kJ mol^{-1}. Therefore, in the framework of the IP method the reactions (1a) and (1b) (see Scheme 1) should be treated as highly endothermic processes for which $\Delta H_e > \Delta H_{e,max}$.

Scheme 1



For reaction (1a)* one has $n = 2$, $A_0 = 1 \cdot 10^9$ L mol^{-1} s^{-1}, $\Delta H_{e,\max} = 42.1$ kJ mol^{-1}, and $0.5hL(\nu_i - \nu_f) = 0$. Correspondingly, for reaction (1b) one has $n = 2$, $A_0 = 1 \cdot 10^7$ L mol^{-1} s^{-1}, $\Delta H_{e,\max} = 21.9$ kJ mol^{-1}, and $0.5hL(\nu_i - \nu_f) = 1.5$ kJ mol^{-1}. The relationship for calculating the $k_1 = k_{1a} + k_{1b}$ value has the form

$$k_1 = 2 \cdot 10^9 e^{-1/2}[1 + 1.3(\sqrt{D_{OH} - 259.5} - \sqrt{42.1})]^2 \cdot \\ \cdot \exp[-10^3(D_{OH} - 259.5)/(RT)] + \\ + 2 \cdot 10^7 e^{-1/2}[1 + 1.3(\sqrt{D_{OH} - 273.6 + 1.5} - \sqrt{21.9})]^2 \cdot \\ \cdot \exp[-10^3(D_{OH} - 273.6)/(RT)], \quad (5)$$

where D_{OH} (kJ mol^{-1}) is the desired $D_{OH}(\mathbf{1})$ value. Iterative procedures using experimental k_1 values at two temperatures led to $D_{OH} = 336.9 \pm 0.6$ (298.2 K) and 338.9 ± 0.6 kJ mol^{-1} (340 K). Averaging gave $D_{OH}(\mathbf{1}) = 337.9 \pm 1.6$ kJ mol^{-1}.

For comparison,[6] $D_{OH}(\mathbf{2}) = 337.3 \pm 2.3$ kJ mol^{-1} (obtained using correlations and results of laser flash photolysis studies of the reactions of diarylaminyl radicals with phenols).

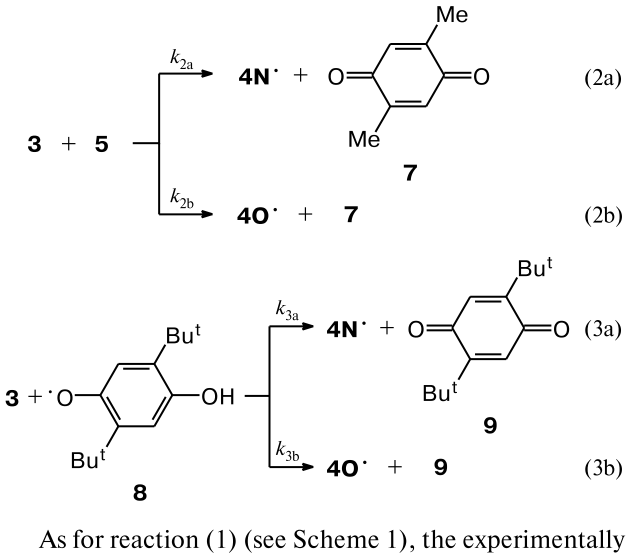
It is interesting to compare the $D_{OH}(\mathbf{1})$ and $D_{OH}(\mathbf{2})$ values with the O—H bond dissociation energy for unsubstituted hydroquinone **6** ($D_{OH} = 352.0$ kJ mol^{-1}, averaged value for alkylaromatic solvents).[2,5] As can be seen, introduction of two electron-donor substituents (Me or Bu^t) at positions 2 and 5 of the benzene ring causes the D_{OH} value to decrease by nearly the same increment (~14 kJ mol^{-1}). This is consistent with experimental data,[21] which point that the rate constants for the reactions of peroxy radicals with hydroquinones increase upon introduction of electron-donor substituents into the benzene ring.

The experimental values of $k_1 = k_{1a} + k_{1b}$ for a similar reaction **2** + **3** in PhCl are $3.22 \cdot 10^{-3}$ and $8.61 \cdot 10^{-2}$ L mol^{-1} s^{-1} at 298.2 and 340 K, respectively.[10] Similar values of the rate constants for the reactions **1** + **3** and **2** + **3** at the same temperatures are not unexpected, because only in this case one can obtain similar D_{OH} values for hydroquinones **1** and **2** (see Eq. (5)). But quite unexpected are significantly different temperature dependences of the k_1 constants of these reactions, namely, $8.22 \cdot 10^6 \exp[-53.6/(RT)]$ for the reaction **1** + **3** and $1.27 \cdot 10^9 \exp[-66.2/(RT)]$ for the reaction **2** + **3**.

The experimental E_1 value for the reaction **1** + **3** is smaller than the difference between the strengths of the cleaving and forming bonds. Indeed, using the $D_{OH}(\mathbf{1})$ and $D_{OH}(\mathbf{2})$ values and Eq. (5), we can find that route (1b) makes a nearly 80% contribution to the overall reaction (1) (see Scheme 1), *i.e.*, the nitrogen atom in molecule **3** is more reactive in the reactions with hydroquinones. Then, neglecting the contribution of route (1a), we can obtain the lower bound of E_1. Because $D_{NH}(\mathbf{4O^{\bullet}}) = 273.6$ kJ mol^{-1},[6] we get $E_1 \geq (337.9 \pm 1.6) - 273.6 = 64.3 \pm 1.6$ kJ mol^{-1} for reaction **1** + **3** and $E_1 \geq$ $\geq (337.3 \pm 2.3) - 273.6 = 64.7 \pm 2.3$ kJ mol^{-1} for reaction **2** + **3**. If the latter estimate is in reasonable agreement with the experimental data, the experimental E_1 value for reaction **1** + **3** is smaller than our estimate. Reaction **1** + **3** is also characterized by a smaller pre-exponent value. Thus, the reactions of hydroquinones **1** and **2** with quinoneimine **3** show a compensation effect, which is responsible for similar experimental values of k_1 in spite of different E_1 values.

The O—H bond dissociation energies for semiquinone radicals **5** and **8** were calculated using the published[10,20] rate constants for the reactions of these radicals with quinoneimine **3** (these reactions represent the chain propagation stages in the chain reactions **1** + **3** and **2** + **3**). Because molecule **3** has two reactive sites (O and N atoms), each reaction under study can follow two concurrent channels (Scheme 2).

Scheme 2



As for reaction (1) (see Scheme 1), the experimentally measured rate constants for reactions (2) and (3) equal the sums of the rate constants for the reactions following both channels

$$k_2 = k_{2a} + k_{2b},$$

$$k_3 = k_{3a} + k_{3b}.$$

For each term on the right side we obtained the expression in the framework of the IP method and then the $D_{OH}(\mathbf{5})$ and $D_{OH}(\mathbf{8})$ values were determined using numerical methods when comparing the calculated k_2 and k_3 values with experimental data.

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* Hereafter the numerical values of the parameters of the IP method for elementary reactions were taken from Ref. 2.

The parameters of the IP method for the reactions (2a) and (3a) are as follows: $n = 1$, $A_0 = 1 \cdot 10^9$ L mol^{-1} s^{-1}, $br_e = 12.61$ kJ$^{1/2}$ mol$^{-1/2}$, $\alpha = 1$, $\Delta H_{e,max} = 42.1$ kJ mol^{-1}, $\Delta H_{e,min} = -42.1$ kJ mol^{-1}, $0.5hL(\nu_i - \nu_f) = 0$, and $0.5hL\nu_i = 21.5$ kJ mol^{-1}. For the enthalpy one has $\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f) = D_{OH} - 259.5$ kJ mol^{-1}. The activation energy is calculated by the equation[2]

$$E = [br_e/2 + \Delta H_e/(2br_e)]^2 - 0.5hL\nu_i + 0.5RT. \qquad (6)$$

The parameters of the IP method for the reactions (2b) and (3b) are as follows: $n = 1$, $A_0 = 1 \cdot 10^7$ L mol^{-1} s^{-1}, $br_e = 11.30$ kJ$^{1/2}$ mol$^{-1/2}$, $\alpha = 1.079$, $\Delta H_{e,max} = 21.9$ kJ mol^{-1}, $\Delta H_{e,min} = -16.6$ kJ mol^{-1}, $0.5hL(\nu_i - \nu_f) = 1.5$ kJ mol^{-1}, $0.5hL\nu_i = 21.5$ kJ mol^{-1}. For the enthalpy one has $\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f) = D_{OH} - 273.6 + 1.5$ kJ mol^{-1}. If ΔH_e lies within the range $\Delta H_{e,min}$—$\Delta H_{e,max}$, the activation energy is calculated using the equation[2]

$$E = \left\{ \frac{b_i r_e}{1-\alpha^2} \left[1 - \alpha \sqrt{1 - \frac{1-\alpha^2}{(b_i r_e)^2} \Delta H_e} \right] \right\}^2 - 0.5hL\nu_i + 0.5RT. \qquad (7)$$

In Eqs (6) and (7), b_i and b_f are coefficients relating the potential energy to the vibrational amplitude of the cleaving (i) and newly forming (f) bonds, the force constant of the bond being $2b^2$; r_e is the distance between the vertices of the parabolas (sum of the vibrational amplitudes of the cleaving and forming bonds in the transition state); and $\alpha = b_i/b_f$. If $D_{OH} < 255.5$ kJ mol^{-1} (the case of D_{OH}(**8**) calculations), the rate constant for reaction (3b) should be calculated by the following equation

$$k = 1 \cdot 10^7 e^{-1/2} \left[1 + 1.3 \left(\sqrt{|D_{OH} - 273.6 + 1.5|} - \sqrt{|-16.6|} \right) \right]^2 .$$

The experimental k values and the results of calculations of the D_{OH} values for radicals **5** and **8** are listed in Table 1.

The higher O—H bond dissociation energy for semiquinone radical **5** compared to D_{OH}(**8**) is quite unexpected result (difference is nearly 10 kJ mol^{-1}), because one could assume that similar properties of substituents (Me and Bu^t) will lead not only to similar D_{OH}(**1**) and D_{OH}(**2**) (see above) but also D_{OH}(**5**) and D_{OH}(**8**) values.

In order to compare our estimates of D_{OH} for radicals **5** and **8** with experimental data for related compounds, we examined the available thermochemical data[22] on the standard enthalpies of formation ($\Delta_f H°$(s) and $\Delta_f H°$(g) for the solid and gas phases, respectively) and sublimation ($\Delta_{subl} H°$) of hydroquinones HQ_2 and corresponding quinones Q. Using these data, one can determine the sum of the O—H bond dissociation energies for hydroquinones and semiquinone radicals resulting from them

$$\begin{aligned} D_\Sigma &= D_{OH}(\text{molecule}) + D_{OH}(\text{radical}) = \\ &= D_{HH} - [\Delta_f H°(g)_{QH_2} - \Delta_f H°(g)_Q] = \\ &= D_{HH} - \{[\Delta_f H°(s) + \Delta_{subl} H°]_{QH_2} - \\ &\quad - [\Delta_f H°(s) + \Delta_{subl} H°]_Q\}, \end{aligned} \qquad (8)$$

where $D_{HH} = 436$ kJ mol^{-1} is the H—H bond dissociation energy for the H_2 molecule. The results of calculations are listed in Table 2.

Table 1. Experimental and calculated rate constants for reactions (2) and (3) (k/L mol^{-1} s^{-1}) at two temperatures and the results of calculations of the O—H bond dissociation energies (D_{OH}/kJ mol^{-1}) in radicals **5** and **8**

Parameter	298.2 K	340 K
	Radical **5**	
$k_2^{exp} \cdot 10^{-6}$	3.56	2.74
$k_{2a}^{calc} \cdot 10^{-5}$	4.22	6.21
$k_{2b}^{calc} \cdot 10^{-6}$	3.14	2.12
$k_2^{calc} \cdot 10^{-6}$ [a]	3.57	2.75
D_{OH} [b]	259.1	261.9
	Radical **8**	
$k_3^{exp} \cdot 10^{-7}$	3.47	1.28
$k_{3a}^{calc} \cdot 10^{-6}$	4.53	2.68
$k_{3b}^{calc} \cdot 10^{-7}$	3.02	1.00
$k_3^{calc} \cdot 10^{-7}$ [c]	3.47	1.27
D_{OH} [d]	246.8	253.6

[a] $k_2^{calc} = k_{2a}^{calc} + k_{2b}^{calc}$.

[b] Average value is 260.5±1.4 kJ mol^{-1}.

[c] $k_3^{calc} = k_{3a}^{calc} + k_{3b}^{calc}$.

[d] Average value is 250.2±3.4 kJ mol^{-1}.

Attention should be paid to the fact that the accuracy of the published calorimetric data is often rather low. For instance, the $\Delta_f H°$(s) and $\Delta_{subl} H°$ values obtained by different authors for unsubstituted quinone and hydroquinone vary within the range of 6—10 kJ mol^{-1} each.[22] This should be taken into account when analyzing the D_Σ(g) values.

Using the data listed in Table 2 and assuming that for unsubstituted hydroquinone D_{OH}(g) = 347 kJ mol^{-1} (see below), we obtained the estimate for the simplest semiquinone radical 4-$HOC_6H_4O^•$ (**11**), namely, $D_{OH} = 242.8$ kJ mol^{-1}. This is 8—18 kJ mol^{-1} lower than the D_{OH} estimates obtained for radicals **5** and **8**.

In order to independently evaluate the D_{OH} values for hydroquinones and semiquinone radicals, we carried out quantum chemical calculations by the B3LYP method, which earlier[7] led us to quite reasonable estimates of the N—H and O—H bond dissociation energies for 4-hydroxydiphenylamine. First, we calculated the O—H bond dissociation energies for a reference molecule **6** and semiquinone radical **11** using different basis sets (without and with inclusion of zero-point vibrational energy correc-

Table 2. Standard enthalpies of formation ($\Delta_f H°$(s) and $\Delta_f H°$(g) for the solid and gas phases, respectively) and sublimation ($\Delta_{subl}H°$) of quinones and hydroquinones[22] and the sums of the O—H bond dissociation energies for hydroquinone and corresponding semiquinone radical in the gas phase (D_Σ(g)) (in kJ mol^{-1}) calculated using Eq. (8)

Substituents	Hydroquinone			Quinone			D_Σ(g)
	$-\Delta_f H°$(s)	$\Delta_{subl}H°$	$-\Delta_f H°$(g)	$-\Delta_f H°$(s)	$\Delta_{subl}H°$	$-\Delta_f H°$(g)	
—*	—	—	277.0	186	62.8	123.2	589.8
Cl	393	102.9	290.1	231.0	69.0	162.0	564.1
2,6-Cl_2	433.9	92	341.9	254	69.9	184.1	593.8
2,3,5-Cl_3	451.5	101.3	350.2	280	88.7	191.3	594.9
2,3,5,6-Cl_4	463.2	88.7	374.5	298	98.7	199.3	611.2

* Unsubstituted hydroquinone **6** and quinone (**10**).

tion, ZPE). This made it possible to choose the basis set for other calculations. The results of total energy (E_{tot}) calculations are listed in Table 3.

Using these data, we calculated the D_{OH} values for molecule **6** and radical **11** (Table 4).

As in the case of 4-hydroxydiphenylamine,[7] the best agreement with experimental data, with respect to the sum of the D_{OH} values for the molecule and radical, was obtained in the B3LYP calculations with the 6-31+G* basis set without inclusion of zero-point vibrational energy. Apparently, this is a consequence of an even number of mutually cancelling errors due to (i) neglect of zero-point vibrations and (ii) finite number of functions in the basis set. The results obtained by other methods are in better agreement with one another rather than experimental data. Here, experimental data are best fitted by calculations with inclusion of zero-point vibrational energy. By and large, the results of quantum chemical calculations show that the B3LYP/6-31+G* approximation is more appropriate for estimating D_{OH} values for hydroquinone molecules and corresponding radicals.

The calculated geometric parameters of molecule **6** and semiquinone radical **11** are also of interest. Their values are almost independent of the size of the basis set and indicate that in molecule **6** the OH groups lie in the benzene ring plane, the C—O bond length (r_{CO}) is 1.356 Å

Table 3. Total energies (E_{tot}/hartree) of the reference molecule **6**, semiquinone radical **11**, and quinone **10** obtained from B3LYP quantum chemical calculations with different basis sets

Basis set	Molecule **6**		Radical **11**		Quinone **10**	
	$-E_{tot}$	$-E_{tot}$(ZPE)*	$-E_{tot}$	$-E_{tot}$(ZPE)*	$-E_{tot}$	$-E_{tot}$(ZPE)*
6-31+G*	382.6987821	382.590617	382.06938	381.97334	381.47045	381.385331
6-31+G**	382.7166460	382.608374	382.08128	381.98527	381.47649	381.391552
6-311+G**	382.8030563	382.695174	382.16641	382.07077	381.56178	381.477205
6-311++G**	382.8032078	382.695484	382.16654	382.07101	381.56187	381.477397

* With inclusion of zero-point vibrational energy correction.

Table 4. O—H bond dissociation energies (D_{OH}/kJ mol^{-1}) obtained for molecule **6** and radical **11** from B3LYP quantum chemical calculations with different basis sets

Basis set	D_{OH}(**6**)		D_{OH}(**11**)		D_Σ	
	without ZPE	with ZPE	without ZPE	with ZPE	without ZPE	with ZPE
6-31+G*	339.04	307.20	259.10	230.34	598.06	537.55
6-31+G**	354.69	322.49	274.40	245.35	629.09	567.83
6-311+G**	353.10	320.96	269.06	239.99	622.16	560.96
6-311++G**	352.90	320.89	268.88	239.85	621.77	560.74

Note. The values obtained from experimental data are as follows: D_{OH}(**6**) = 347 kJ mol^{-1}, D_{OH}(**11**) = 242.8 kJ mol^{-1}, and D_Σ = 589.8 kJ mol^{-1}.

while the O—H bond length (r_{OH}) is 0.940 Å. In radical **11**, the OH group geometry changes only slightly, namely, r_{CO} = 1.358 Å and r_{OH} = 0.972 Å; the O atom bearing the unpaired electron remains in the benzene ring plane but r_{CO} decreases to 1.259 Å.

We also calculated the D_{OH} values for hydroquinones **1** and **2** and radicals **5** and **8** by the B3LYP/6-31+G* method. The geometries of these compounds are similar to those of their unsubstituted analogs and the calculated O—H bond dissociation energies are 330.3 (**1**), 248.4 (**5**), 328.0 (**2**), and 245.7 kJ mol^{-1} (**8**).

Similar D_{OH} values obtained for hydroquinones **1** and **2** are in agreement with the results obtained by the IP method (see above); however, similar estimates of D_{OH} for radicals **5** and **8** contradict them.

Analysis of possible reasons for the differences between the D_{OH} estimates suggested that they are to a great extent due to neglect of the role of solvation of quinones, hydroquinones, and semiquinone radicals. For instance, it is known[23,24] that the extent of solvation of phenols and hydroquinones in aromatic solvents is rather high so they can form H-complexes. In this connection it is more correct to treat the estimates of the bond strengths obtained in this work as the estimates of the enthalpies of O—H bond dissociation (ΔH_{OH}) in PhCl, associating the O—H bond dissociation energies (D_{OH}) with the enthalpies of dissociation in the gas phase in the absence of solvation.

We calculated the energies of solvation (E_{solv}) of quinones, hydroquinones, and semiquinone radicals by chlorobenzene (and those of **6**, **10**, and **11** by benzene and toluene) by the B3LYP/6-31+G*/PCM method. The results are listed in Table 5. Calculations of the energies of solvation of hydroquinone **1** and quinone **7** by the PCM method failed. But even without these values it is possible to draw some definite conclusions based on the data listed in Table 5. As can be seen, in PhCl and PhMe the semiquinone radical is solvated to the greatest extent and the initial hydroquinone is solvated to somewhat less extent. The energy of solvation of quinone is about 10 kJ mol^{-1} lower than the energy of solvation of the corresponding hydroquinone. Comparison with the data for unsubstituted hydroquinone shows that introduction of two Me groups into the ring has a little effect on the energy of solvation of chlorobenzene, whereas two Bu^t groups cause the E_{solv} value to decrease by nearly 10 kJ mol^{-1} for both hydroquinone and quinone or radical.

Table 5. Solvation energies (E_{solv}) of quinones, hydroquinones, and semiquinone radicals obtained from quantum chemical calculations

Solvent	Ring substituents	$-E_{solv}$/kJ mol^{-1}		
		Hydroquinone	Radical	Quinone
PhH	—*	10.2	11.8	5.5
PhMe	—*	13.0	14.7	7.9
PhCl	—*	17.1	20.1	8.9
	2,5-Me$_2$	—	18.0	—
	2,5-Bu$^t_2$	6.9	7.5	<1.0

* Hydroquinone **6**, radical **11** and quinone **10**, respectively.

Based on the data listed in Table 5, one can make preliminary assumptions of the types of interactions occurring in the course of solvation of quinones, hydroquinones, and semiquinone radicals. Aromatic solvents differ in polarity (μ_{PhH} = 0, μ_{PhMe} = 0.4, μ_{PhCl} = 1.55 D).[25] Besides, the Me substituent in toluene serves as an electron donor, whereas the Cl atom in chlorobenzene is an electron acceptor. In this connection the aromatic ring in the PhMe molecule is a better proton acceptor compared to benzene while the aromatic ring in the PhCl molecule is a worse proton acceptor.[23,24] Then, comparing the E_{solv}(**6**) and E_{solv}(**11**) values in these solvents, one can assume that their solvation is due to both the dipole-dipole interaction and the formation of H-complexes with the solvent. Methyl substituents in radical **5** almost do not preclude its solvation and the E_{solv}(**5**) value in chlorobenzene is only slightly lower than the E_{solv}(**11**) value in the same solvent. Two bulky Bu^t substituents present much greater difficulties to solvation of hydroquinone **2**, radical **8**, and quinone **9**; therefore, the E_{solv} estimates for these compounds are lower than for the corresponding unsubstituted analogs by nearly the same increment value.

The data in Table 5 point that the kinetics of reactions involving hydroquinones and semiquinone radicals should be analyzed with allowance for solvation by the solvent. Taking into account this fact, we will return to the results of the determination of D_{OH} values for molecule **1** and semiquinone radicals **5** and **8** from the rate constants for reactions (1), (2), and (3) (see Schemes 1 and 2). The necessary (to complete the picture) energies of solvation of quinoneimine **3** and radicals **4O$^\bullet$** and **4N$^\bullet$** formed in chlorobenzene calculated by the B3LYP/6-31+G*/PCM method[7] are 9.9 (**3**), 21.6 (**4O$^\bullet$**), and 23.0 kJ mol^{-1} (**4N$^\bullet$**).

The compensation effect in the reactions of quinoneimine **3** with hydroquinones of the type **1** can be explained by participation of the solvent. These reactions are highly endothermic, they are characterized by a late transition state, and the activated complex is structurally similar to reaction products, that is, radicals. For the reaction to begin, the fragments of the reactant molecules, which enter the reaction, should be desolvated. The degree of solvation of the activated complex will mainly be determined by solvation of the almost formed semiquinone radical whose peripheral polar OH group is readily accessible to the solvent molecules. Although the activated complex also includes a nearly formed radical **4O$^\bullet$** (or **4N$^\bullet$**), its solvation makes a smaller contribution to the overall effect, because the polar NH (or OH) group of this nearly formed radical is blocked by the neighbor, semiquinone radical, which had no time to move away (*cf.* the effects of the Me and Bu^t groups in positions 2 and 5 on solvation of radicals **5** and **8**; see Table 5). In the reaction **3** + **2** (here, a moderately solvated radical **8** is formed from **2**) the gain in energy of solvation of the activated complex is slightly different from the energy expenditure for partial desolvation of reactants in the initial reaction stage; therefore, the activation energy for the reaction is similar to the difference between the strengths of the cleaving and forming bonds.

The energy balance for reaction **3** + **1** is different. In this case the activated complex is highly solvated and the heat (enthalpy) of solvation of the almost formed semiquinone radical **5** exceeds the energy expenditure for partial desolvation of reactants in the initial stage of reaction. The activation energy, which includes the difference between the energies of solvation of the initial reactants and the activated complex, can become lower than the difference between the strengths of the cleaving and forming bonds. High degree of solvation of the activated complex and corresponding orientation ordering of a fraction of solvent molecules cause the entropy of the system to decrease and the higher the degree of solvation of the activated complex, the higher the loss of entropy. Probably, this is the reason for experimentally observed compensation effect in the reactions under study.

Another situation is characteristic of reactions (2) and (3) (see Scheme 2). They are slightly exothermic or similar to thermally neutral reactions and the structure of the activated complex is intermediate between those of the initial reactants and products. Therefore, the extent of solvation of the activated complex is much lower than in the reactions of the type (1) (see Table 5). For the reaction to begin, quinoneimine **3** should be partially desolvated while semiquinone radicals **5** or **8** should be almost completely desolvated, because only in this case the OH group in these radicals can be involved in the reaction. If the energy expenditure for partial desolvation of molecule **3** in the initial stage of the reaction is to a great extent compensated by solvation of the activated complex, the D_{OH}(g) values for radicals **5** and **8** can be estimated using the ΔH_{OH} values for radicals found by the IP method and the E_{solv} values from Table 5 at 242.5±1.4 and 242.7±3.4 kJ mol^{-1}, respectively.

It is quite surprising that in spite of approximate character of calculations the estimates obtained in this work nearly coincide with the results of quantum chemical calculations.

The assumption of the need for preliminary desolvation of the OH group by the semiquinone radical to begin the reactions (2) and (3) can be confirmed by comparing these data with data for other reactions characterized by similar energy profiles and the structure of the reaction center (*e.g.*, with almost thermally neutral reactions between radicals and phenols). For instance, the rate constants for reactions of stable 1,1-diphenyl-2-picrylhydrazyl radical with phenols depend on the nature of the solvent. Namely, they decrease by about an order of magnitude for unshielded phenols and by a factor of 1.5—3 for sterically hindered 2,6-di-*tert*-butyl-4R-phenols upon replacement of CCl_4 by benzene.[26] In a laser flash photolysis study[27] of reactions of diphenylaminyl radicals with phenols at 293 K it was found that replacement of the solvent (decane → toluene) causes the rate constants for the reactions to decrease by about an order of magnitude almost irrespective of the nature of the substituent in position 4 of the phenol molecule. The decrease in k was explained by the formation of H-complexes of phenols with toluene (E_{solv} = 5—7 kJ mol^{-1}). Finally, studies of the reactions of α-tocopherol with 1,1-diphenyl-2-picrylhydrazyl, *tert*-butoxyl,[28] and ethylbenzylperoxy[29] radicals also revealed a strong dependence of the rate constants for the reactions on the solvent (here, $k = 2 \cdot 10^7$ (hexane), $1.4 \cdot 10^7$ (CCl_4), $3.4 \cdot 10^6$ (benzene), $3 \cdot 10^6$ (toluene), $2.7 \cdot 10^6$ (chlorobenzene) and $1.5 \cdot 10^6$ (anisole) L mol^{-1} s^{-1} at 298 K). The decrease in k in aromatic solvents was explained by the formation of H-complexes between phenol and the solvent.[28,29]

Taking into account the effect of solvent on the kinetics of reactions involving hydroquinones and semiquinone radicals, the D_{OH}(**6**) value of 352.0 kJ mol^{-1} recommended[2] based on analysis of experimental data on the kinetics of liquid-phase reactions involving hydroquinone in the framework of the IP method should seemingly be treated as the enthalpy of O—H bond dissociation (ΔH_{OH}) in aromatic solvents. The gas-phase D_{OH} value should be 4—6 kJ mol^{-1} lower, *i.e.*, $D_{\mathrm{OH}}(\mathbf{6})_{\mathrm{g}}$ = 347±1 kJ mol^{-1}.

Thus, in this work we estimated the O—H bond dissociation energies for the molecule of 2,5-dimethylhydroquinone and for 2,5-dimethyl- and 2,5-di-*tert*-butyl-4-hydroxyphenoxyl (semiquinone) radicals by analyzing kinetic data in the framework of the IP method and using quantum chemical calculations. We have shown that the kinetic data on the reactions involving hydroquinones and especially semiquinone radicals in the framework of the IP method should be analyzed only with allowance for solvation effect. Depending on the thermal effect of reaction, solvation can manifest itself in the compensation effect in a series of similar reactions (highly endothermic reactions of quinoneimine **3** with hydroquinones **1** and **2**) or in the overestimated value of the dissociation energy of the cleaving O—H bond (weakly exothermic reactions of quinoneimine **3** with semiquinone radicals **5** and **8**).

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