Effect of solvation on the kinetic parameters of the reactions of phenoxyl radicals with phenols and semiquinone radicals with hydroquinones

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Experimental rate constants of the reactions of semiquinone radicals with hydroquinones in chlorobenzene at ~300 K are by almost an order of magnitude higher than the rate constants of the reactions of phenoxyl radicals with phenols, which are equivalent to the former ones by heat effects. To reveal differences in the rate constants of these groups of reactions, we performed quantum chemical calculations of the energy profiles of the reactions and dissociation energies by the B3LYP density functional theory using the GAMESS and GAUSSIAN-03 programs in the 6-31+G* basis set. The solvation energies were calculated in all stationary points on the reaction coordinate by the method of polarized continuum model. In terms of the intersecting parabolas method, the reactions of semiquinone radicals with hydroquinones and phenoxyl radicals with phenols can be attributed to the same class of reactions only in the gas phase. In solvents this class of reactions is divided into two subclasses due to differences in solvation energies of the preliminary complexes and transition states of these reactions.

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

Rate constants of the reactions of phenoxyl and hydroxyphenoxyl (semiquinone) radicals with phenols and hydroquinones are necessary for description of the kinetic regularities of processes involving phenols, hydroquinones, and quinones that occur in many systems, for instance, when mixtures of these compounds are used as antioxidant additives (to oils, lubricants, fuels, polymers, *etc.*),[1—4] and in biological systems, whose lipids usually contain mixtures of bioantioxidants (α-tocopherol, ubiquinones, and K group vitamins).[5]

The kinetics of the reactions of phenoxyl radicals with phenols was repeatedly studied.[6,7] Analysis and generalization of the experimental data by the intersecting parabolas method (IPM) made it possible to find the IPM parameters of these reactions.[4,8] Presently, the rate constants of the reactions of the phenoxyl radicals with phenols can be calculated if the strengths of the H—O bonds in the corresponding phenols are known. No experimental data have been available up to recently for the reactions of the semiquinone radicals with hydroquinones and, therefore, the IPM parameters of the close class of the reactions of the phenoxyl radicals with phenols[4] are recommended for use to estimate the rate constants of these reactions.

When studying the kinetics of the chain reactions of *N*-phenyl-1,4-benzoquinonemonoimine with 2,5-di-*tert*-butyl- and 2,5-dimethylhydroquinone in chlorobenzene, the rate constants of elementary steps were determined, some of which can be attributed to the class of reactions of the semiquinone radicals with hydroquinones.[9,10] We analyzed these data by the IPM and found that the reactions of the semiquinone radicals with hydroquinones occur much more rapidly than it can be expected if these reactions would be approximated in calculations by the corresponding by heat effects of the reactions of the phenoxyl radicals with phenols. In the present study, we performed the quantum chemical analysis of the higher values of the rate constants of the semiquinone radicals with hydroquinones than the rate constants of the phenoxyl radicals with phenols having the same heat effects.

Calculation procedure

The intersecting parabolas method[11] was used. In this method, all elementary reactions are classified according to the nature of atoms in the reaction center and the type of the reaction. The reaction centers of the reaction of the semiquinone radicals with hydroquinones and phenoxyl radicals with phenols have the same structure, namely, H...O...H. Each class of reactions in the IPM is characterized by a certain set of parameters (activation energy of

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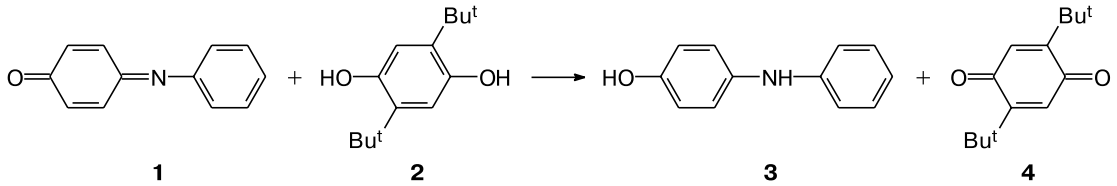
Scheme 1



1 **2** **3** **4**

the thermally neutral reaction E_{e0}, pre-exponential factor per attacked bond A_0, *etc.*). The numerical values of the parameters were obtained from the experimental data and tabulated.[1,4] The equations for calculation of the activation energy E and the rate constant k depend on the enthalpy of the reaction ΔH_e, whose calculation takes into account the zero-point vibrational energies of dissociated (initial) (D_i) and formed (D_f) bonds,

$$\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f),$$

where D and ν are the dissociation energies and vibrational frequencies of the bonds, h is the Planck constant, and N_A is Avogadro´s number.

Each class of reactions is characterized by two threshold values, which were calculated by experimental data and tabulated: $\Delta H_{e,min}$ (exothermic reactions) and $\Delta H_{e,max}$ (endothermic reactions). The E and k parameters are calculated by the standard IPM formulas only when $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$. For $\Delta H_e < \Delta H_{e,min}$, the activation energy of the reaction is $E = 0.5RT$; if $\Delta H_e > \Delta H_{e,max}$, then $E = \Delta H + 0.5RT = D_i - D_f + 0.5RT$. In the both cases, the pre-exponential factor A_0 is multiplied by the coefficient $\gamma > 1$, whose value is calculated using a special formula.

The quantum chemical calculations of the energy profiles of the reactions and dissociation energies of the bonds were performed by the B3LYP density functional method using the GAMESS [12] and GAUSSIAN-03 [13] programs in the 6-31+G* basis set. The normal vibrational frequencies and the zero-point vibrational energies (ZPE) were calculated in extremes of the potential energy surface. The parameters of the states corresponding to minima on the potential surface were determined for complete optimization of all variables. The transition states (TS) were found from the geometry of the states before and after the TS on the reaction coordinate. The solvation energy was calculated in the framework of the polarized continuum model (PCM)[14] using the geometry obtained for isolated molecules in the gas phase.

Results and Discussion

In the present work, we used the kinetic data[15] for the chain reaction of *N*-phenyl-1,4-benzoquinonemonoimine **1** with 2,5-di-*tert*-butyl-1,4-hydroquinone **2** in which quinoneimine **1** is reduced to 4-hydroxydiphenylamine **3** due to the oxidation of hydroquinone **2** to 2,5-di-*tert*-butyl-1,4-quinone **4** (Scheme 1).

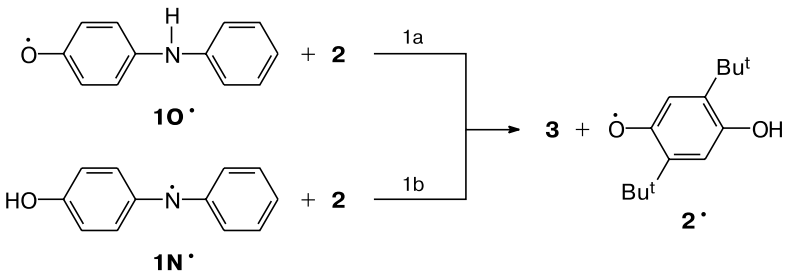
In the total process, two parallel reactions (1a) and (1b) of semiquinone radicals **1O**$^{\bullet}$ and **1N**$^{\bullet}$ with 2,5-di-*tert*-butylhydroquinone are the chain propagation steps (Scheme 2).

The reaction center of reactions (1a) and (–1a) has the structure H...O...H and, therefore, these reactions are of interest as model reactions of the semiquinone radical with hydroquinone.

The experimental kinetic data from Ref. 9 used in our further calculations are given in Table 1.

Using these data, one can calculate the dissociation energy of the H—O bond D_{O-H} in hydroquinone **2** by the IPM and compare the result with the earlier obtained value $D_{O-H}(\mathbf{2}) = 337.3 \pm 2.3$ kJ mol^{-1} (see Ref. 16). If the necessary (for these calculations) assignment of elementary steps (1a), (–1a), (1b), and (–1b) to the IPM classes of reactions is correct, then the obtained $D_{O-H}(\mathbf{2})$ value is close to the indicated one.

Scheme 2



1O$^{\bullet}$ **1N**$^{\bullet}$ **2**$^{\bullet}$

Table 1. Rate constants of the total forward (k_1) and reverse (k_{-1}) reactions in chlorobenzene and the mole fractions of radicals **1O**$^{\bullet}$ (x) and **1N**$^{\bullet}$ ($1-x$) for the reaction between **1** and **2**

T/K	k_1	k_{-1}	x	$1-x$
	L mol^{-1} s^{-1}			
298.2	$1.65\cdot10^7$	$3.52\cdot10^6$	0.967	0.033
340.0	$1.75\cdot10^7$	$3.03\cdot10^6$	0.936	0.064

Let us calculate D_{O-H}(**2**) assuming that reactions (1a) and (−1a) are reactions of the phenoxyl radicals with phenols, reaction (1b) is attributed to the reaction class of the diarylaminyl radicals with phenols, and reaction (−1b) is related to the reaction class of the phenoxyl radicals with diarylamines. The following values of the dissociation energies of the H—O and H—N bonds in 4-hydroxydiphenylamine **3** will be used (see Ref. 16): D_{O-H}(**3**) = 339.3 and D_{N-H}(**3**) = 353.4 kJ mol^{-1}. Let us take into account that the experimental k_1 values are related to k_{1a} and k_{1b} by the equation

$$k_1 = xk_{1a} + (1 - x)k_{1b}.$$

The experimental data in Table 1 were processed by the formulas of the parabolic model using the iteration procedure to give the rate constants of reactions (1a) and (1b). These values and the estimated D_{O-H}(**2**) values are presented in Table 2 along with the kinetic data obtained for the chain reaction of quinoneimine **1** with 2,5-dimethylhydroquinone **2**′, which is a close analog of 2,5-di-*tert*-butyl-1,4-hydroquinone **2** (see Ref. 10).

For hydroquinone **2** the found estimate D_{O-H} = 325.7±1.6 kJ mol^{-1} is by ~12 kJ mol^{-1} lower than the obtained[14] value D_{O-H}(**2**) = 337.3±2.3 kJ mol^{-1}. This result corresponds to the fact that the experimental k_1 value at T = 298.2 K is by an order of magnitude higher than it can be expected from the calculation by the IPM formulas for D_{O-H}(**2**) = 337.3 kJ mol^{-1}.

A similar result is obtained by analysis of the kinetic data for the reaction of quinoneimine **1** with 2,5-dimethylhydroquinone **2**′ (see Table 2). The dissociation energy of the H—O bond in this hydroquinone is D_{O-H} = 337.9±1.6 kJ mol^{-1} (calculated from the rate constant of the elementary reaction of quinoneimine with 2,5-dimethylhydroquinone).[17] Thus, in this case, the estimate of D_{O-H} by the rate constant of reaction (1) is by ~11 kJ mol^{-1} lower.

Finally, another estimate of D_{O-H}(**2**) can be obtained by the rate constant of reverse reaction (−1). This reaction proceeds *via* two parallel routes (−1a) and (−1b), and

$$k_{-1} = k_{-1a} + k_{-1b}.$$

Substituting the numerical values of the IPM parameters into the calculation formulas and using the above experimental k_{-1} values at 298.2 and 340.0 K, we have the k rate constant values (Table 3).

The determined D_{O-H} value is by 10—11 kJ mol^{-1} higher than the experimental value D_{O-H}(**2**) = 337.3±2.3 kJ mol^{-1}. As can be seen, the calculation of D_{O-H} in hydroquinone **2** from the k_1 rate constant of forward reaction (1) and the k_{-1} rate constant of reverse reaction (−1) gives different D_{O-H} values. One of them is by 10—11 kJ mol^{-1} higher and the second one is by the same value (10—11 kJ mol^{-1}) lower than D_{O-H} = 337.3±2.3 kJ mol^{-1}. In other words, both forward (1) and reverse (−1) reactions at 298.2 K occur by an order of magnitude more rapidly than it can be expected from the IPM calculations at the above assignment of the reactions to the corresponding classes.

Analysis of the obtained calculated values of the k_{1a}, k_{-1a}, k_{1b}, and k_{-1b} reaction rate constants is of certain interest even despite their estimation character. The numerical values of these constants show that forward and reverse reactions (1) and (−1) proceed mainly *via* two routes (1a) and (−1a) with the transition state O...H...O. The contribution of parallel reactions (1b) and (−1b) with the N...H...O transition state is low and almost constant,

Table 2. Rate constants (k/L mol^{-1} s^{-1}) of the reaction *via* routes (1a) and (1b) and the estimated values of the dissociation energies of the O—H bonds (D_{O-H}/kJ mol^{-1}) in hydroquinones **2** and **2**′

Hydroquinone	T/K	$xk_{1a}\cdot10^{-7}$	$(1-x)k_{1b}\cdot10^{-7}$	$k_1^{calc}\cdot10^{-7}$ *	$k_1^{exp}\cdot10^{-7}$	D_{O-H}**
2	298.2	1.39	0.26	1.65	1.65	324.1
	340.0	1.40	0.36	1.76	1.75	327.2
						(325.7±1.6)
2′	298.2	1.00	0.22	1.22	1.23	325.8
	340.0	1.34	0.35	1.69	1.68	327.5
						(326.7±0.9)

* $k_1^{calc} = xk_{1a} + (1-x)k_{1b}$.
** The average value is given in parentheses.

Table 3. Rate constants (k/L mol^{-1} s^{-1}) of the reverse reaction involving 2,5-di-*tert*-butylsemiquinone radicals **2**$^{\cdot}$ and the calculated from them dissociation energies of the O—H bond (D_{O-H}/kJ mol^{-1}) in hydroquinone **2**

T/K	$k_{-1a} \cdot 10^{-6}$	$k_{-1b} \cdot 10^{-6}$	$k_{-1}^{calc} \cdot 10^{-6}$ *	$k_{-1}^{exp} \cdot 10^{-6}$	D_{O-H}
298.2	2.74	0.77	3.51	3.52±0.26	349.3±0.4
340.0	2.46	0.59	3.05	3.03±0.38	344.7±0.8
					(347±3)**

* $k_{-1}^{calc} = k_{-1a} + k_{-1b}$.
** The average value is given in parentheses.

being ~20% of the total k_1 and k_{-1} values. This route can be neglected in the first approximation. Then the reaction shown in Scheme 2 can be written as

$$\mathbf{1O}^{\cdot} + \mathbf{2} \overset{K_{1a}}{\rightleftharpoons} \mathbf{3} + \mathbf{2}^{\cdot}. \qquad (1a, -1a)$$

The values of the K_{1a} equilibrium constant for this reaction at T = 298.2 and 340.0 K are given in Table 4.

It can be seen that K_{1a} has a small absolute value, which changes insignificantly with the temperature increase. The weak temperature dependence of the K_{1a} equilibrium constant indicates that $\Delta H_{1a} \approx 0$, *i.e.*, it can be expected that $D_{O-H}(\mathbf{3}) \approx D_{O-H}(\mathbf{2})$. The values $D_{O-H}(\mathbf{3})$ = 339.3 (see Ref. 16) and $D_{O-H}(\mathbf{2})$ = 337.3±2.3 kJ mol^{-1} (see Ref. 17) are presented above. Thus, the assumption that $D_{O-H}(\mathbf{3}) \approx D_{O-H}(\mathbf{2})$ agrees with the experimental data.

No results consistent with experiment can be obtained by the IPM applied to the estimation of $D_{O-H}(\mathbf{2})$ from the rate constants of forward and reverse reactions (1) and (−1) (*i.e.*, mainly from k_{1a} and k_{-1a}) if the kinetic IPM parameters of the reactions of the unhindered phenoxyl radicals with phenols are used in the calculations. Therefore, we can assume that the reactions of the semiquinone radicals with hydroquinones in terms of the IPM should be considered as a special subclass of the indicated class of reactions.

The main IPM characteristics of this subclass (parameter br_e and activation energy of a thermally neutral reaction E_{e0}) can be calculated and compared with similar characteristics of the reactions of the phenoxyl radicals with phenols. The IPM formulas[4] will be used in the calculations

$$br_e = \sqrt{E_e - \Delta H_e} + \sqrt{E_e},$$

$$E_{e0} = \left(\frac{br_e}{2}\right)^2.$$

In our case, $E_e = RT\ln(nA_0/k_{exp}) + 0.5hN_A\nu_I - 0.5RT$ and $\Delta H_e = D_i - D_f$. Let us use the above indicated values D_{O-H} = 337.3 (**2**), 337.9 (**2**′), and 339.3 kJ mol^{-1} (**3**), and the pre-exponential factor will be considered the same as that for the class of reactions of the phenoxyl radicals with phenols, namely, $A_0 = 10^9$ L mol^{-1} s^{-1} (see Ref. 4). Thus obtained br_e parameters are given in Table 5.

Table 4. Equilibrium constant K_{1a} and the rate constants of reactions (1a) and (−1a)

T/K	$k_{1a} \cdot 10^{-7}$	$k_{-1a} \cdot 10^{-6}$	K_{1a}
	L mol^{-1} s^{-1}		
298.2	1.65	3.52±0.26	4.7±0.4
340.0	1.75	3.03±0.38	5.8±0.7

Table 5. Parameter br_e ((kJ mol^{-1})$^{1/2}$) and the activation energy of the thermally neutral reactions (E_{e0}/kJ mol^{-1}) of the semiquinone radicals with hydroquinones calculated by the IPM from the rate constants of reactions (1a) and (1b)

T/K	$br_e(k_{1a})$*	$br_e(k_{1a})$	$br_e(k_{-1a})$	$E_{e0}(k_{1a})$*	$E_{e0}(k_{1a})$	$E_{e0}(k_{-1a})$
298.2	11.59	11.52	11.53	33.6	33.1	33.3
340.0	11.71	11.74	11.91	34.3	34.5	35.5

* For the reaction of **1O**$^{\cdot}$ with 2,5-dimethylhydroquinone.

The results obtained show that br_e and E_{e0} calculated for forward and reverse reactions (1) and (−1) coincide within the experimental error. This is a substantial argument in favor of the fact that the reactions of the semiquinone radicals with hydroquinones in chlorobenzene can be considered as a particular subclass of reactions with the following averaged IPM parameters:

br_e = 11.67±0.06 (kJ mol^{-1})$^{1/2}$,

E_{e0} = 34.0±0.4 kJ mol^{-1}.

These characteristics differ noticeably from the IPM parameters of the reactions of the phenoxyl radicals with unhindered phenols[4]

br_e = 12.61 (kJ mol^{-1})$^{1/2}$,

E_{e0} = 39.7 kJ mol^{-1}.

It is seen that the E_{e0} activation energy of the thermally neutral reaction of the semiquinone radicals with hydroquinones is by 5.7 kJ mol^{-1} lower than E_{e0} of the

reactions of the phenoxyl radicals with phenols. This scale of decreasing E_{e0} can be caused by two factors. First, the decrease in E_{e0} can be a result of a stronger interaction (complexation) of the reactants in the O...H...O transition state in the reactions of the semiquinone radicals with hydroquinones. In this case, it can be expected the r_e distance at which the H atom is transferred in the O...H...O transition state in the reaction of the semiquinone radicals with hydroquinones is shorter than the corresponding distance in the transition state of the reactions between the phenoxyl radicals and phenols. Second, it cannot be excluded that the solvation effects of the initial reactants and transition state affect the reactions of the semiquinone radicals with hydroquinones to much greater extent compared to the reactions of the phenoxyl radicals with phenols. This also can be a reason for the considerable difference in activation energies and rate constants of the thermally neutral reactions.

To reveal the role of these two factors, we performed quantum chemical calculations for the two simplest thermally neutral reactions: of phenol (**5**) with the corresponding phenoxyl radical (**5**$^{\bullet}$) (1c) and of unsubstituted hydroquinone (**6**) with the forming from it 4-hydroxyphenoxyl radical (**6**$^{\bullet}$) (1d). For completeness, similar calculations were also carried out for the crossing reaction between the indicated reactants (1e, −1e). According to the calculations, all the three reactions in the gas phase pass through a series of extremes on the potential surface. In all cases, the formation of the transition state is preceded by the step of formation of a preliminary complex, which is well known for the radical reactions involving phenols and phenoxyl radicals.[18—22]

Reactants ⇌ Complex of reactants ⇌ Transition state ⇌ Complex of reaction products ⇌ Reaction products

According to this, the reactions under study can be written as shown in Scheme 3.

The complexes and TS for all the reactions have similar structures: the benzene rings lie in the same plane, and the reacting atoms O...H...O are arranged on the same line. The structures of the complex and TS for the reaction **6** + **6**$^{\bullet}$ are shown in Fig. 1. The calculated values of the total electronic energy E_{tot} in the extreme points of the potential surface, including those taking into account the zero-point vibrational energy (ZPE), and the lengths of the reacting O—H bonds are presented in Table 6.

The vibrational frequencies of the reacting O—H bonds in phenols and hydroquinones are very close (3754 and 3756 cm^{-1}, respectively, and 3737 cm^{-1} in radical **6**$^{\bullet}$). It is seen that the O...H bond lengths in the TS of the reaction of the semiquinone radical with hydroquinone are almost the same as those in the reaction of the phenoxyl radical with phenol. This implies that in the gas phase the reactions considered from the viewpoint of the IPM belong to one reaction class, and the same set of reaction parameters can be used in calculations of their rate constants.

However, this conclusion poorly agrees with the experimental data on the reactions in chlorobenzene when the rate constants of the reactions of the semiquinone radical with quinone are by almost an order of magnitude

Scheme 3

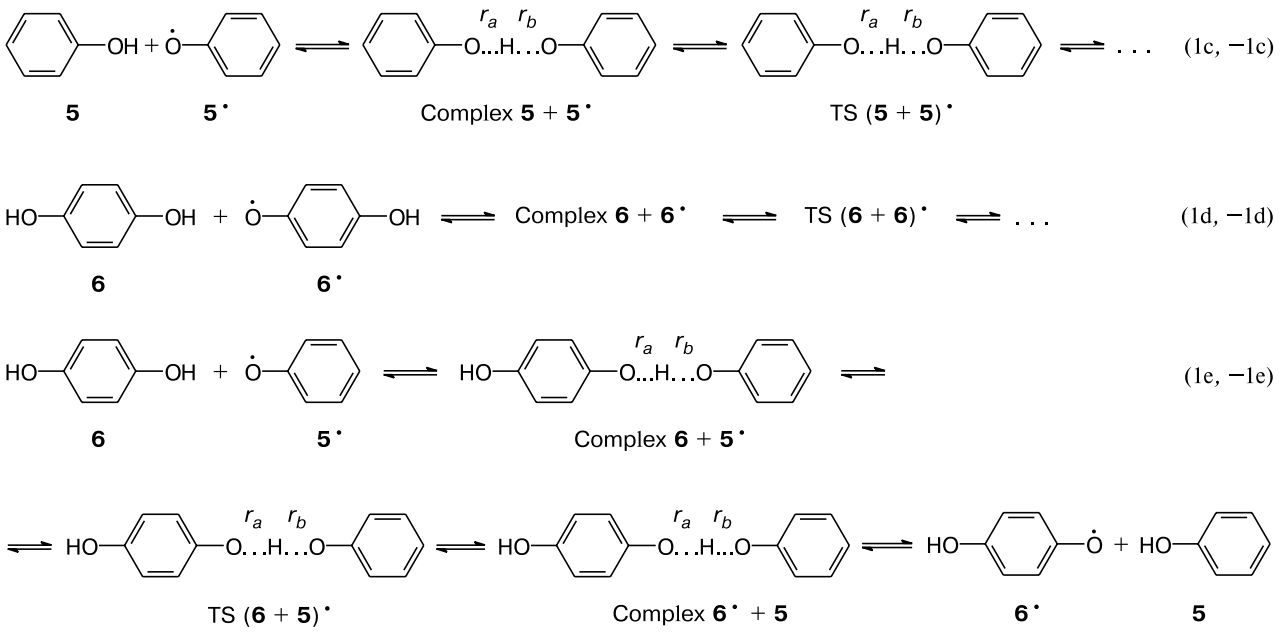


Table 6. Calculated values of the total electronic energy (E_{tot}) in the extreme points of the potential surface, including taking into account zero-point vibrational energies (ZPE), and the lengths of reacting O—H bonds for reactions (1c)—(1e)

Compound	$-E_{tot}$	$-(E_{tot} + ZPE)$	Distance O—H/m·10^{10}	
	hartree		r_a	r_b
5	307.4803097	307.37583	0.970	—
5$^{\cdot}$	306.84242	306.75082	—	—
Complex **5** + **5**$^{\cdot}$	614.3361012	614.138132	0.984	1.824
TS (**5** + **5**)$^{\cdot}$	614.3219784	614.128891	1.200	1.200
6	382.6987821	382.59062	0.970	—
6$^{\cdot}$	382.0693768	381.973339	0.968	—
Complex **6** + **6**$^{\cdot\cdot}$	764.782469	764.576304	0.985	1.803
TS (**6** + **6**)$^{\cdot}$	764.7692001	764.567935	1.201	1.201
Complex **6** + **5**$^{\cdot}$	689.563784	689.352878	0.984	1.805
TS (**6** + **5**)$^{\cdot}$	689.545926	689.348733	1.156	1.250
Complex **6**$^{\cdot}$ + **5**	689.5641491	689.361588	1.800	0.986

higher than those calculated by the IPM assuming that these reactions belong to the class of reactions of the phenoxyl radicals with phenols. Therefore, we considered a problem about the solvent effect on the reactions of the semiquinone radicals with hydroquinones and phenoxyl radicals with phenols. For this purpose, the solvation energies were calculated for all extreme points on the reaction coordinate using the polarized continuum model.[14] The solvation energy (E_{sol}) implies the difference of the total energies taking into account the zero-point vibrational energies of the corresponding state in the solvent and vacuum: $E_{sol} = (E_{tot} + ZPE)_{sol} - (E_{tot} + ZPE)_{vac}$. The solvation energy values in the extreme points of the potential surface are given in Table 7.

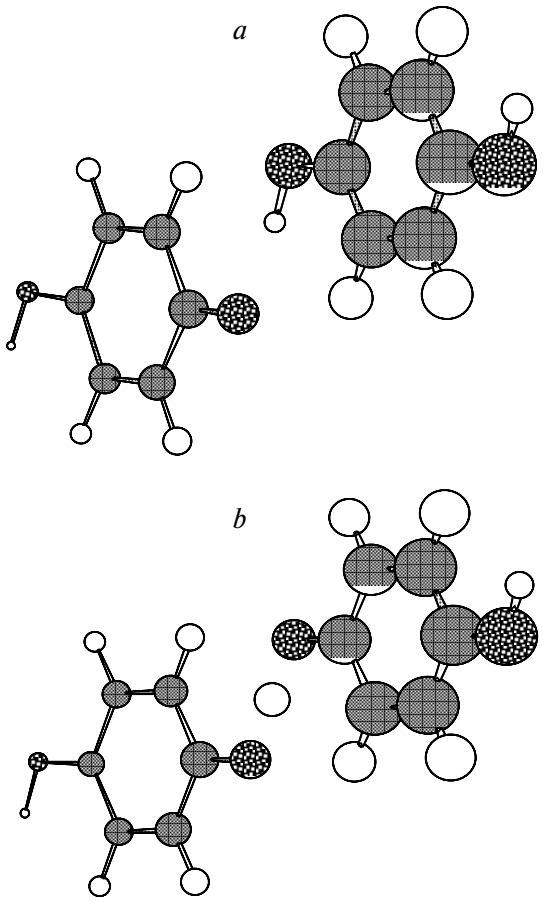


Fig. 1. Structures of the preliminary complex (*a*) and transition state (*b*) in the reaction of the semiquinone radical with hydroquinone.

Using the solvation energy of the initial reactants **5** + **5**$^{\cdot}$, **6** + **6**$^{\cdot}$, and **6** + **5**$^{\cdot}$ as the origin of energies in calculation of the relative energies of the stationary points (E_{rel}) on the coordinate of reactions (1c—1e), we obtained the results presented in Table 8. These data show that the solvation with the solvent substantially affects the

Table 7. Solvation energy in the extreme points on the potential surface

Compound	E_{sol}/kJ mol^{-1}	
	Benzene	Chlorobenzene
	Reactions (1c) and (−1c)	
5	−6.8	−16.1
5$^{\cdot}$	−5.8	−14.6
Complex **5** + **5**$^{\cdot}$	−1.8	−4.9
TS (**5** + **5**)$^{\cdot}$	2.3	2.6
	Reactions (1d) and (−1d)	
6	−11.3	−17.1
6$^{\cdot}$	−11.8	−20.1
Complex **6** + **6**$^{\cdot}$	−10.8	−22.5
TS (**6** + **6**)$^{\cdot}$	−7.85	−15.4
	Reactions (1e) and (−1e)	
Complex **6** + **5**$^{\cdot}$	−8.7	−17.1
TS (**6** + **5**)$^{\cdot}$	−3.2	−7.7
Complex **6**$^{\cdot}$ + **5**	−8.3	−16.3

Table 8. Relative energies of stationary points (E_{rel}) on the coordinate of reactions (1c)—(1e) in different media

Compound	E_{rel}/kJ mol^{-1}		
	Vacuum	Benzene	Chlorobenzene
	Reactions **5** + **5**$^{\bullet}$ (1c) and (−1c)		
Complex **5** + **5**$^{\bullet}$	−30.1	−19.3	−4.3
TS (**5** + **5**)$^{\bullet\bullet}$	−5.9	9.0	27.4
	Reactions **6** + **6**$^{\bullet}$ (1d) and (−1d)		
Complex **6** + **6**$^{\bullet}$	−32.3	−20.0	−17.6
TS (**6** + **6**)$^{\bullet}$	−10.4	4.9	11.4
	Reaction **6** + **5**$^{\bullet}$ (1e)		
Complex **6** + **5**$^{\bullet}$	−34.6	−25.8	−19.2
TS (**6** + **5**)$^{\bullet}$	−19.1	−5.2	4.8
Complex **6**$^{\bullet}$ + **5**	−60.0	−51.2	−44.6
6$^{\bullet}$ + **5**	−22.3	−23.8	−26.7

reaction kinetics. For the reactions **5** + **5**$^{\bullet}$ and **6** + **6**$^{\bullet}$ in the both solvents, the solvation energy of the TS is lower than the sum of solvation energies of the initial substances, which is related to partial screening of the reacting O—H polar groups (see the configuration of the TS in Fig. 1). This results in an increase in the activation energies of the reactions and a decrease in the rate constants in the solvent compared to the gas phase. On going from the gas phase to the solution, the rate constants of the thermally neutral reactions **5** + **5**$^{\bullet}$ and **6** + **6**$^{\bullet}$ decrease to different extents. For instance, in chlorobenzene and benzene the sum of the solvation energies of phenoxyl radical **5**$^{\bullet}$ and phenol **5** is 30.7 and 12.6 kJ mol^{-1}, respectively, and those of semiquinone radical **6**$^{\bullet}$ and hydroquinone **6** are 37.2 and 23.1 kJ mol^{-1}. The solvation energy of the TS (**5**+**5**)$^{\bullet}$ in chlorobenzene and benzene is +2.6 and +2.3 kJ mol^{-1}, respectively; for the TS (**6**+**6**)$^{\bullet}$ E_{sol} = −15.4 and −7.85 kJ mol^{-1}, respectively. The solvation energies of the weakly polar intermediate complex (**5**+**5**$^{\bullet}$) and strongly polar intermediate complex (**6**+**6**$^{\bullet}$) differ considerably (by almost 5 times).

It is of interest to compare the relative energies of the final reaction products (1e) in vacuum, benzene, and chlorobenzene (see the last row in Table 8). The data presented are in fact the enthalpies of the reaction of phenoxyl radical **5**$^{\bullet}$ with hydroquinone **6** calculated by the quantum chemical methods in different media, *i.e.*, difference in dissociation energies of the O—H bonds in hydroquinone and phenol. According to published data,[4] D_{OH}(**6**) = 352.0 kJ mol^{-1} and D_{OH}(**5**) = 369.0 kJ mol^{-1}, *i.e.*, ΔH_{1e} = 17.0 kJ mol^{-1}, which differs from the value for the gas phase presented in Table 8 by only 5.3 kJ mol^{-1}. It seems more important that ΔH_{1e} is inconstant on going from the gas phase to benzene and chlorobenzene: this value decreases by 1.5 and even by 4.4 kJ mol^{-1}, respectively. Evidently, ΔH_{1e} is inconstant because of differences in the solvation ability of the reactants and products.

Thus, the quantum chemical calculations show that in the gas phase the reactions of the semiquinone radicals with hydroquinones and phenoxyl radicals with phenols in the framework of the IPM can be attributed, in fact, to the same class of reactions. However, in the liquid phase (in solutions) this reaction class should be divided into two subclasses. The differentiating effect of solvents is caused by the difference in solvation energies of the preliminary complex and transition state of these reactions. Due to the peripheral polar OH groups, the preliminary complexes and transition states of the reactions of the semiquinone radicals with hydroquinones are strongly solvated by even such weak proton acceptors as molecules of aromatic solvents.

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