Determination of dissociation energies of N—H bond in the 4-anilinodiphenylaminyl radical and O—H bond in the 2,5-dichloro-4-hydroxyphenoxyl radical from the equilibrium constants of chain reactions in quinoneimine—hydroquinone systems

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The temperature dependences of the equilibrium constants of two chain reversible reactions in quinonediimine (quinonemonoimine)—2,5-dichlorohydroquinone systems in chlorobenzene were studied. The enthalpy of equilibrium of the reversible reaction of quinonediimine with 4-hydroxydiphenylamine was estimated from these data ($\Delta H = -14.4\pm1.6$ kJ mol^{-1}) and a more accurate value of the N—H bond dissociation energy in the 4-anilinodiphenylaminyl radical was determined ($D_{NH} = 278.6\pm3.0$ kJ mol^{-1}). A chain mechanism was proposed for the reaction between quinonediimine and 2,5-dichlorohydroquinone, and the chain length was estimated ($v = 300$ units) at room temperature. Processing of published data on the rate constant of the reaction of styrylperoxy radicals with 2,5-dichlorohydroquinone in the framework of the intersecting parabolas method gave the O—H bond dissociation energy in 2,5-dichlorohydroquinone: $D_{OH} = 362.4\pm0.9$ kJ mol^{-1}. Taking into account these data, the O—H bond dissociation energy in the 2,5-dichlorosemiquinone radical was found: $D_{OH} = 253.6\pm1.9$ kJ mol^{-1}.

Key words: *N,N´*-diphenyl-1,4-benzoquinonediimine, *N*-phenyl-1,4-benzoquinonemonoimine, 2,5-dichlorohydroquinone, 4-anilinodiphenylaminyl radical, 2,5-dichloro-4-hydroxyphenoxyl radical, bond dissociation energies, reversible chain reaction, enthalpy of reaction.

The values of dissociation energies of X—Y bonds (D_{X-Y}) make it possible to conclude about the reactivity of molecules and radicals. The methods for determination of D_{X-Y} are known[1-3] but, in each particular case, this finding is associated with considerable experimental difficulties. Special difficulties appear for the determination of D_{X-Y} in highly reactive radicals, although these data are of unambiguous interest. For instance, *N,N´*-diphenyl-1,4-phenylenediamine (**1**) is one of the strongest synthetic antioxidants and widely used for stabilization of rubber and other materials.[4,5] During oxidation inhibited by diamine **1** the latter forms unstable 4-anilinodiphenylaminyl radicals **2** as intermediates, which possess dual redox activity and are capable of both H atom abstracting and regenerating to form compound **1** and donating the H atom to transform into *N,N´*-diphenyl-1,4-benzoquinonediimine (**3**).

The dissociation energy of the N—H bond in radical **2** ($D_{NH}(\mathbf{2})$) characterizes both its reduction and oxidation
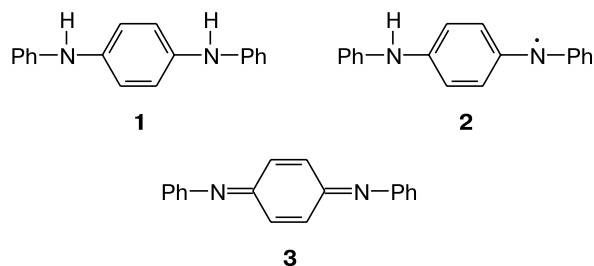

reactivities of diimine **3**, *i.e.*, the ability of the latter to abstract the H atom from molecules and radicals. The $D_{NH}(\mathbf{2})$ value is of great interest for analysis of the mechanism of the inhibition effect of diamine **1** and prediction of the efficiency of its use for stabilization of specific substrates. Data on $D_{NH}(\mathbf{2})$ are also very important for understanding the kinetic regularities of reversible chain reactions in quinoneimine—hydroquinone systems,[6-8] because diimine **3** reacts with hydroquinones with their dehydration *via* a chain mechanism (see below) and el-

ementary reactions involving this diimine are rate-deter-mining for the whole process.

We have recently[9] attempted to determine $D_{NH}(2)$. The experimental estimate of $D_{NH}(2)$ (274.7 ± 3.3 kJ mol^{-1}) is lower than the value calculated by the quantum chemical methods (290.6 kJ mol^{-1}). In the present work, we again attempted to determine experimentally the $D_{NH}(2)$ value. For this purpose we proposed a new approach based on the use of temperature dependences of the equilibrium constants of two auxiliary reversible chain reactions in quinonenimine—hydroquinone systems.

Experimental

In experiments special attention was given to the purity of reagents and solvent. Diamine **1** and 4-hydroxydiphenylamine (**4**) were purified as follows. To remove mechanical and strongly polar admixtures, a solution (close to saturation) of compound **4** (~5 g) in benzene (or compound **1** (~5 g) in a benzene (95%)—chloroform (5%) mixture) was passed through a glass column (10×2.5 cm) packed with silica gel L (Chemapol, 40—100 micron). The eluate was evaporated by ~95% at ~20 °C, the mother liquor was rejected, and the crystals that precipitated were washed with small portions of benzene and dried *in vacuo*. Then compounds **4** and **1** were recrystallized from methanol or a methanol—chloroform (3—5%) mixture, respectively, and then recrystallized additionally from pure toluene.
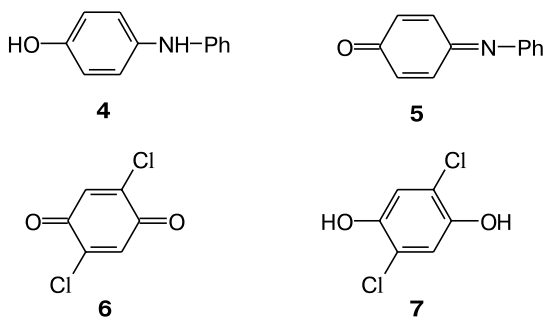
Quinonediimine **3** and *N*-phenyl-1,4-benzoquinonemonoimine (**5**) were synthesized from reduced forms of compounds **1** and **4**, respectively, by the oxidation of the latter with PbO$_2$ and purified by liquid chromatography on SiO$_2$ and recrystallization from methanol.[7]

2,5-Dichloroquinone (**6**) (Aldrich) was purified by double sublimation *in vacuo*. 2,5-Dichlorohydroquinone (**7**) was synthesized by the reduction of purified quinone **6** using Na$_2$S$_2$O$_4$ by a known procedure[10] and recrystallized two times from methanol.

Chlorobenzene was used as the solvent. Chlorobenzene purified by a standard procedure[11] (treatment with concentrated H$_2$SO$_4$, washing with water and soda solution, drying with CaCl$_2$, and distillation) turned out to be inappropriate for work, because solutions of compounds **1** and **4** in this solvent after several hours at ~20 °C gained a noticeable orange tint due to the formation of quinoneimines. The following purification procedure was used. Initial chlorobenzene (high-purity grade) was distilled, treated with concentrated H$_2$SO$_4$, washed with water,

and treated with a saturated solution of KMnO$_4$ in 20% aqueous NaOH until resistance to oxidation was attained (unchanged color after 30 min of shaking), again washed with water, dried with CaCl$_2$, and distilled. Tetraphenylhydrazine (~1 g L^{-1}) was added, argon was purged through the mixture for 15 min, and the mixture was heated to 70—80 °C and kept for 2 h at this temperature. Then the temperature was slowly raised, and the mixture was distilled under argon. The bottoms were orange-colored due to the formation of quinoneimine and diphenyl-nitroxide radical.[12] Repeated distillation was carried out in the presence of tetraphenylhydrazine (0.2—0.3 g L^{-1}) under the same conditions. Now the bottoms were not orange but weakly green-yellowish due to the formation of semidines.[13—15] After distillation chlorobenzene was passed through a glass column (70×2.5 cm) packed in layers with the following powders (layer length from the inlet of the column/cm): concentrated H$_2$SO$_4$ on SiO$_2$ (3), SiO$_2$ (2), KMnO$_4$ on Al$_2$O$_3$ (7), SiO$_2$ (2), CaCl$_2$ (8), KOH (10), and activated Al$_2$O$_3$ was the rest. Chlorobenzene purified using this procedure behaves as quite inert solvent. It should be mentioned that upon prolong storage (for 1 year at ~20 °C under Ar) small amounts of admixtures are accumulated, which accept, in particular, stable 2,4,6-tri-*tert*-butyl-phenoxyl radicals. To remove the admixtures, it is enough to pass this chlorobenzene through a column packed as described above.

Equilibrium constants of quinoneimines **3** and **5** with hydroquinone **7** were determined by spectrophotometry. Quinoneimines are orange-colored ($\lambda_{max} \approx 450$ nm), while the other species are colorless or very weakly absorb in the visible region (for quinone **7** $\varepsilon_{450} \approx 20$ L mol^{-1} cm^{-1}). Experiments were carried out in temperature-controlled quartz cells, which served as bubble reactors, 8.5 and 6.0 cm^3 in volume and 2.0 cm optical path incorporated into a Specord UV VIS spectrophotometer. Experiments were started at 298 K. At this temperature the consumption of quinoneimines were continuously monitored by the absorption of the latter at a chosen wavelength in the visible region. The experiments were continued until equilibration. Then the controlling thermometer in the thermostat was changed and, continuing the experiment, the temperature in the thermostat and reactor was raised to a new specified value, the experiment was continued at a new specified temperature until equilibration, *etc*. After measurements at all chosen temperatures, the reactor was cooled to 298 K and the solution was equilibrated at this temperature to compare the result with that obtained at the onset of the experiment. Taking into account that at prolong duration of entries the results can be distorted because of evaporation of the solvent, relatively vigorous argon bubbling (4—5 bubbles per second) was carried out only during the first ~15 min at 298 K, after which the argon flow was sharply decreased to 1—2 bubbles per minute, remaining at this level within the whole experiment.

Results and Discussion

The sum of the dissociation energies of the N—H bonds in diamine **1** and its radical **2** can be determined from the enthalpy ΔH of the reaction of quinonediimine **3** with 4-hydroxydiphenylamine (**4**), because the dissociation enthalpies of the N—H and O—H bonds in amine **4**
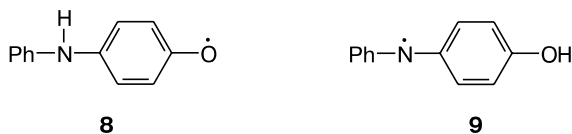
and 4-anilinophenoxyl (**8**) and 4-hydroxydiphenylaminyl (**9**) radicals formed from compound **4** are known[16]: $D_{NH}(\mathbf{4}) = 353.4$, $D_{OH}(\mathbf{4}) = 339.3$, $D_{NH}(\mathbf{8}) = 273.6$, and $D_{OH}(\mathbf{9}) = 259.5$ kJ mol^{-1}.

$$\Delta H = [D_{NH}(\mathbf{4}) + D_{OH}(\mathbf{9})] - [D_{NH}(\mathbf{1}) + D_{NH}(\mathbf{2})] =$$
$$= [D_{OH}(\mathbf{4}) + D_{NH}(\mathbf{8})] - [D_{NH}(\mathbf{1}) + D_{NH}(\mathbf{2})]$$

The $D_{NH}(\mathbf{1})$ value necessary for calculations can be obtained independently from the correlation between D_{NH} in 4-substituted diphenylamines and σ^+ constants of the substituents[9] ($D_{NH}(\mathbf{1}) = 348.7 \pm 1.4$ kJ mol^{-1}) or after processing the data on the rate constants of the reactions of the peroxide radicals with amine **1** in the framework of the parabolic model ($D_{NH}(\mathbf{1}) = 346.9$ kJ mol^{-1})[17]. Then

$$D_{NH}(\mathbf{2}) = 612.9 - 348.7 \pm 1.4 - \Delta H =$$
$$= (264.2 - \Delta H) \pm 1.4 \text{ kJ mol}^{-1}. \tag{1}$$

The ΔH value can experimentally be determined from the temperature dependence of the equilibrium constant (K) of the reversible reaction

$$\mathbf{3} + \mathbf{4} \rightleftharpoons \mathbf{1} + \mathbf{5}, \tag{a}$$

for which

$$\frac{d\ln K_{(a)}}{d(1/T)} = -\frac{\Delta H_{(a)}}{R}.$$

This method, with the use of spectrophotometric recording of the absorbance D^{∞}_{450}, where quinoneimines **3** and **5** absorb, have been used previously.[9] The found value $D_{NH}(\mathbf{2}) = 274.7 \pm 3.3$ kJ mol^{-1}, as mentioned above, differs strongly from the results of quantum chemical calculations. The main source of errors could be strong overlapping of the absorption bands of quinoneimines **3** and **5** decreasing the accuracy of analysis, because the equilibrium concentrations of each quinoneimine (**3** and **5**) cannot be determined directly from experiment and they are calculated from the solution of a system of two equations with two unknown quantities (material balance and the total D^{∞}_{450} value in the two-component spectral system).

In the present work, we propose a new approach devoiding of this drawback to determine $\Delta H_{(a)}$. This approach uses the temperature dependences of the equilibrium constants of two reversible reactions

$$\mathbf{3} + \mathbf{7} \rightleftharpoons \mathbf{1} + \mathbf{6}, \tag{b}$$

$$\mathbf{5} + \mathbf{7} \rightleftharpoons \mathbf{4} + \mathbf{6}. \tag{c}$$

Reactions (b) and (c) can be treated as half-reactions of reaction (a). When the initial and/or resulting species of reactions (b) and (c) are mixed, then the concentrations of all the six components will take with time values that would be equilibrium simultaneously for reversible reactions (a)—(c). In this case, $K_{(a)} = K_{(b)}/K_{(c)}$ and

$$\Delta H_{(a)} = \Delta H_{(b)} - \Delta H_{(c)}. \tag{2}$$

Quinoneimines **3** and **5** are the only components absorbing in the visible region at $\lambda \geq 450$ nm in each reaction (b) and (c), due to which their equilibrium concentrations can experimentally be determined directly from the absorbance.

The mechanism of reactions (a)—(c) needs special consideration. It has experimentally been proved for the first time for reaction (c) as an example[8] that the processes in quinoneimine—hydroquinone systems proceed *via* the reversible chain mechanism. These reactions reach equilibrium by the chain pathway from both the side of the initial substances and reaction products, and the forward and backward reactions proceed to the equilibrium toward each other with equal rates. It was found in the present work that reaction (b) also proceeds *via* the chain mechanism. This follows from the data on the dependence of the initial rate of reaction (b) ($w_{(b)}$) determined from the kinetics of consumption of quinonediimine **3** on the initiation rate w_i (tetraphenylhydrazine was used as the initiator, $k_i^{298} = 3.92 \cdot 10^{-7}$ s^{-1}).[7] At the initial concentrations $[\mathbf{3}]_0 = [\mathbf{7}]_0 = 9.0 \cdot 10^{-5}$ mol L^{-1} the increase in the w_i initiation rate by $\sim 10^{-11}$ mol L^{-1} s^{-1} induces an increase in the reaction rate by $\sim 0.3 \cdot 10^{-8}$ mol L^{-1} s^{-1}. This indicates that the chain length, under the experimental conditions, is ~ 300 units. Taking into account the aforesaid about the mechanism of reactions (b) and (c), we conclude that reaction (a) also has the chain mechanism.

Using published data[18] on the density of chlorobenzene, we found the temperature dependence of its specific volume (V_{sp}). The obtained results are presented below.

T/K	298	321	343	364	381
$\beta_T = V_{sp}^T/V_{sp}^{298}$	1	1.023	1.045	1.068	1.090

These data were used to determine the molar absorption coefficients (ε) of quinoneimines **3** and **5** at the temperature of experiment. For example,

$$\varepsilon^{\lambda}_T(\mathbf{3}) = [D^{\lambda}_T(\mathbf{3})_{exp} \cdot \beta_T]/([\mathbf{3}]_0^{298} \cdot l),$$

where l is the cell thickness. The experimental results are given in Table 1. Using the ε^{λ}_T values found from the absorbance at equilibrium, we determined the equilibrium concentrations of quinoneimine $[\mathbf{3}]^T_{eq}$ and $[\mathbf{5}]^T_{eq}$ and calculated the equilibrium constants. For instance, if

Table 1. Molar absorption coefficients of quinoneimines **3** and **5** in chlorobenzene

λ/nm	298 K		321 K		343 K		364 K	
	3	**5**	**3**	**5**	**3**	**5**	**3**	**5**
449.2	7243	3015	7111	2956	6928	2899	6796	2844
500.0	4040	1631	3967	1577	3868	1526	3797	1477
526.3	1817	—	1774	—	1741	—	1761	—

Table 2. Results of studying the temperature dependence of the equilibrium constants (K) of reversible reactions (b) and (c) in chlorobenzene

$[C]_0{}^* \cdot 10^4$/mol L^{-1}				K at T/K				$\ln K(T) = a + b/T$		ΔH^{**} /kJ mol^{-1}
3 (5)	**7**	**1 (4)**	**6**	298	321	343	364	a	b	
				Reaction 3 + 7 $\rightleftarrows$ 1 + 6 (b)						
0.91	2.70	45.0	—	82.8	59.0	46.3	37.0	−0.008±0.08	1318±26	−11.0±0.2
0.95	0.90	12.6	—	116.0	84.8	63.2	48.3	−0.06±0.17	1440±57	−12.0±0.5
0.90	2.70	54.0	—	92.5	65.0	48.0	38.7	−0.33±0.07	1450±22	−12.0±0.2
—	—	3.6	3.6	94.2	69.3	52.1	41.4	−0.002±0.09	1360±29	−11.3±0.2
—	—	5.4	5.4	97.1	70.7	52.7	42.1	−0.06±0.07	1390±23	−11.5±0.2
9.12	2.7	72	—	87.6	64.5	49.2	39.5	0.07±0.05	1320±17	−10.9±0.1
4.50	4.50	18.0	—	74.9	53.4	42.0	35.3	0.14±0.15	1240±51	−10.3±0.4
				Reaction 5 + 7 $\rightleftarrows$ 4 + 6 (c)						
1.88	2.00	1.60	—	0.252	—	0.313	0.323	0.056±0.19	−426±62	3.5±0.5
1.88	12.0	3.20	—	—	0.351	0.370	0.394	−0.077±0.09	−313±31	2.6±0.3
2.01	12.0	0	—	—	—	0.352	0.367	−0.321	−248	2.06
1.91	12.0	0.80	—	—	0.340	0.355	0.367	−0.431±0.015	−208±5.3	1.7±0.04
—	8.0	2.40	12.0	—	0.327	0.342	0.371	−0.068±0.22	−339±74	2.8±0.6
—	16.0	2.40	12.0	—	0.322	0.345	0.387	0.40±0.28	−495±97	4.1±0.8
—	—	3.20	4.0	0.365	0.382	0.462	0.482	0.66±0.32	−502±107	4.2±0.9

* Initial concentrations of the reactants at 298 K.

** Average values: $\Delta H_{(b)} = -11.3\pm0.8$ kJ mol^{-1} and $\Delta H_{(c)} = 3.1\pm1.0$ kJ mol^{-1}.

equilibrium (b) is attained from the side of the forward reaction **3 + 7**, then

$$K_{(b)} = \frac{([1]_0^{298} + [3]_0^{298} - \beta_T[3]_{eq}^T) \cdot ([6]_0^{298} + [3]_0^{298} - \beta_T[3]_{eq}^T)}{\beta_T[3]_{eq}^T \cdot ([7]_0^{298} - [3]_0^{298} + \beta_T[3]_{eq}^T)},$$

and from the side of the backward reaction **1 + 6**,

$$K_{(b)} = \frac{([1]_0^{298} - \beta_T[3]_{eq}^T) \cdot ([6]_0^{298} - \beta_T[3]_{eq}^T)}{\beta_T[3]_{eq}^T \cdot ([7]_0^{298} + \beta_T[3]_{eq}^T)}.$$

The results of studying reactions (b) and (c) are given in Table 2. Based on these data and using formula (2), we find the enthalpy of reaction (a)

$$\Delta H_{(a)} = \Delta H_{(b)} - \Delta H_{(c)} = (-11.3\pm0.6) - (3.1\pm1.0) =$$
$$= -14.4\pm1.6 \text{ kJ mol}^{-1}.$$

The found $\Delta H_{(a)}$ value is somewhat higher than $\Delta H_{(a)} = 10.5\pm1.9$ kJ mol^{-1} obtained earlier[9] from the temperature dependence of the equilibrium constant of direct reaction (a). As mentioned above, the direct study of reaction (a) by spectrophotometry is associated with consid-

erable difficulties for determination of the equilibrium concentrations of compounds **3** and **5** because of strong overlapping of their absorption spectra. Therefore, we believe that the $\Delta H_{(a)}$ value obtained in the present work is more accurate.

Substituting the $\Delta H_{(a)}$ value into Eq. (1), we obtain the estimate of the dissociation energy of the N—H bond in radical **2**

$$D_{NH}(2) = (264.2 - \Delta H_{(a)})\pm1.4 = 278.6\pm3.0 \text{ kJ mol}^{-1}.$$

This estimate is somewhat higher than the earlier[9] determined $D_{NH}(2)$ value (274.7±3.3 kJ mol^{-1}) and closer to the value calculated by the quantum chemical methods (290.6 kJ mol^{-1}). For more correct comparison of the experimental and calculated $D_{NH}(2)$ values one should take into account the solvation of the reactants and products of reaction (a). These PCM quantum chemical calculations[9] of E_{solv} indicate that the difference between the experimental and calculated $D_{NH}(2)$ values decreases by 3.7 kJ mol^{-1} when taking into account the solvation of the reactants and products.

Using the data in Table 2, one can estimate the dissociation energy of the O—H bond in 2,5-dichloro-4-hydroxyphenoxyl semiquinone radical **10**. In fact, when ignoring the contribution of the solvation of the reactants and products, the enthalpy of reaction (c) is equal to the difference between the sum of the dissociation energies of the dissociated O—H bonds in hydroquinone **7** and its radical **10** ($D_{OH}(\mathbf{7}) + D_{OH}(\mathbf{10})$) and the sum of the dissociation energies of the bonds formed in 4-hydroxydiphenylamine and its radicals ($D_{NH}(\mathbf{4}) + D_{OH}(\mathbf{9})$ or $D_{OH}(\mathbf{4}) + D_{NH}(\mathbf{8})$). Then we can write
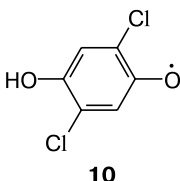
$$D_{OH}(\mathbf{7}) + D_{OH}(\mathbf{10}) = \Delta H_{(c)} + [D_{NH}(\mathbf{4}) + D_{OH}(\mathbf{9})] =$$
$$= (3.1\pm1.0) + 612.9 = 616.0\pm1.0 \text{ kJ mol}^{-1}.$$

The necessary estimate of the dissociation energy of the O—H bond in hydroquinone **7** can be obtained by processing the experimental data[19] on the inhibition effect of hydroquinones on the chain reaction of styrene oxidation in the framework of the intersecting parabolas method.[20] The rate constants of the reactions of styrylperoxy radicals with hydroquinones at 310 K were determined.[19]

According to the intersecting parabolas method,[20] the reaction rate constants are calculated by the equation

$$k = nA_0 \cdot e^{-E/RT}, \tag{3}$$

where n is the number of equivalent OH groups (for hydroquinone $n = 2$), and A_0 is the pre-exponential factor $(3.2 \cdot 10^7 \text{ L mol}^{-1} \text{ s}^{-1})$. In this case, to calculate the activation energy of the reaction E, the following expression is used:

$$E = \left\{ \frac{b_i r_e}{1-\alpha^2} \left[1 - \alpha \sqrt{1 - \frac{1-\alpha^2}{(b_i r_e)^2} \Delta H_e} \right] \right\}^2 - 0.5hLv_i + 0.5RT,$$

where h is Planck´s constant, L is Avogadro´s number, and v_i is the zero-point vibrational frequency of the OH bond in hydroquinone. The enthalpy of the reaction

$$\Delta H_e = D_i - D_f + 0.5hL(v_i - v_f)$$

is calculated as the difference of the dissociation energies of the dissociated OH bond in hydroquinone ($D_i = D_{OH}(\mathbf{7})$ (desired value)) and formed OH bond in hydroperoxide ($D_f = D_{OH}(\text{ROOH}) = 365.5 \text{ kJ mol}^{-1}$)[20]; the correction $0.5hL(v_i - v_f) = 0.3 \text{ kJ mol}^{-1}$ takes into account the difference in the zero-point vibrational energies of the dissociated and formed bonds. For the considered class of reactions, the parameters $b_i r_e = 12.5 \text{ (kJ mol}^{-1})^{1/2}$, $\alpha = 1.014$, and $0.5hLv_i = 21.5 \text{ kJ mol}^{-1}$ were accepted.[21,22]

The experimental k values at 310 K and the $D_{OH}(\mathbf{7})$ values calculated from k by Eq. (3), as well as the k and D_{OH} values for other studied[19] symmetric hydroquinones are presented below.

Hydroquinone	$k(\text{RO}_2{}^\bullet + \text{Ar(OH)}_2) \cdot 10^5$ /L mol^{-1} s^{-1} [19]	D_{OH} /kJ mol^{-1}
7	0.90±0.15	362.4±0.9
4-HOC$_6$H$_4$OH	5.54±0.34	352.6±0.5
2,5-Me$_2$,4-HOC$_6$H$_2$OH	11.9±0.5	348.3±0.2
2,3-Me$_2$,4-HOC$_6$H$_2$OH	18.8±1.4	345.6±0.5

Using the obtained results, we find

$$D_{OH}(\mathbf{10}) = (616\pm1) - (362.4\pm0.9) =$$
$$= 253.6\pm1.9 \text{ kJ mol}^{-1}.$$

Thus, the present study of the temperature dependence of the equilibrium constants of reversible chain reactions (b) and (c) in quinonediimine **3** (quinonemonoimine **5**)—2,5-dichlorohydroquinone (**7**) systems in chlorobenzene gave a new, more accurate estimate of the enthalpy of equilibrium of reversible reaction (a) of quinonediimine **3** with 4-hydroxydiphenylamine (**4**): $\Delta H_{(a)} = -14.4\pm1.6 \text{ kJ mol}^{-1}$. This made it possible to find a more accurate value of the dissociation energy of the N—H bond in 4-anilinodiphenylaminyl radical **2**: $D_{NH}(\mathbf{2}) = 278.6\pm3.0 \text{ kJ mol}^{-1}$. Using the approach of direct introduction of the initiator, we proved the chain mechanism of reaction (b) between quinonediimine **3** and 2,5-dichlorohydroquinone (**7**) and obtained the estimate of the reaction chain length ($v \approx 10^3$ units). The sum of the dissociation energies of the O—H bonds in 2,5-dichlorohydroquinone (**7**) and its semiquinone radical **10** was determined from the enthalpy of equilibrium of reversible reaction (c) of quinonemonoimine **5** with 2,5-dichlorohydroquinone (**7**) and the known values of the dissociation energies of the bonds in 4-hydroxydiphenylamine (**4**) and its radicals: $D_{OH}(\mathbf{7}) + D_{OH}(\mathbf{10}) = 616\pm1 \text{ kJ mol}^{-1}$. Processing of published data on the rate constants of the reactions of the styrylperoxy radicals with 2,5-dichlorohydroquinone (**7**) in the framework of the intersecting parabolas method made it possible to calculate the dissociation energy of the O—H bond in 2,5-dichlorohydroquinone (**7**): $D_{OH}(\mathbf{7}) = 362.4\pm0.9 \text{ kJ mol}^{-1}$. This allowed us to estimate for the first time the dissociation energy of the O—H bond in 2,5-dichlorosemiquinone radical **10**: $D_{OH}(\mathbf{10}) = 253.6\pm1.9 \text{ kJ mol}^{-1}$.

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