The N—H and O—H bond dissociation energies in 4-hydroxydiphenylamine and its phenoxyl and aminyl radicals

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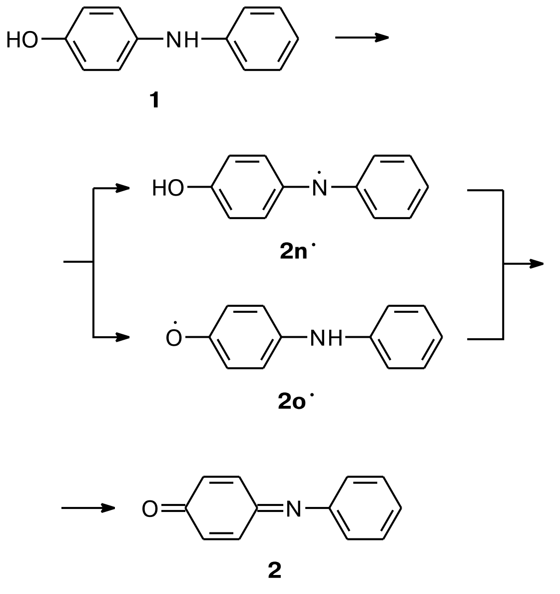
The N—H and O—H bond dissociation energies in 4-hydroxydiphenylamine Ph—NH—C_6H_4—OH (D_{NH}= 353.4, D_{OH}=339.3 kJ mol^{-1}) and its semiquinone radicals D_{NH}(Ph—NH—C_6H_4—O$^•$) = 273.6, D_{OH}(Ph—N$^•$—C_6H_4—OH) = 259.5 kJ mol^{-1} were first estimated using the parabolic model and experimental data (rate constants) on two elementary reactions with participation of *N*-phenyl-1,4-benzoquinonemonoimine (**2**). One of the reactions, namely, that of **2** with aromatic amines, was studied in this work using a specially developed method.

Key words: 4-hydroxydiphenylamine, 4-hydroxydiphenylaminyl and 4-anilinophenoxyl radicals, bond dissociation energies, parabolic model of radical reactions; *N*-phenyl-1,4-benzoquinonemonoimine, aromatic amines, rate constants.

4-Hydroxydiphenylamine (**1**) possesses the properties of a strong antioxidant and is used for stabilization of rubbers, fuels, lubricants, and other materials.[1] Hydrogen abstraction from molecule **1** can result in 4-hydroxydiphenylaminyl (**2n$^•$**) or 4-anilinophenoxyl (**2o$^•$**) radicals depending on which group (NH or OH) is involved in the reaction.

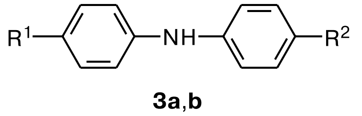


Further oxidation of both radicals (reaction with yet another radical) results in the same compound, *N*-phenyl-1,4-benzoquinonemonoimine (**2**).

The N—H and O—H bond dissociation energies (D_{NH} and D_{OH}, respectively) for molecule **1** and for the semiquinone radicals **2n$^•$** and **2o$^•$** have not been determined as yet. Because of this, some problems concerning the reactivities of these species are still to be solved. These are, in particular, (i) which group (OH or NH) in molecule **1** is mainly attacked by free radicals and (ii) which atom (O or N) is more reactive in the hydrogen abstraction reaction during dehydrogenation of organic compounds with quinonemonoimine **2** and is thus to the greatest extent involved in the reaction.

In this work we first estimated the parameters D_{NH} and D_{OH} for molecule **1** and the aminyl and phenoxyl radicals derived from this molecule. They were calculated using the intersecting paraboles (IP) method,[1] some published data, and the rate constants for two elementary reactions involving quinonemonoimine **2** (the last-mentioned parameters were determined in this work).

Among them, there are the reactions of quinoneimine **2** with 4,4´-dimethoxydiphenylamine (**3a**) and 4,4´-dimethyldiphenylamine (**3b**). The rate constants for these and related reactions are unavailable as yet because no relevant methods of their determination were proposed. Such a procedure was developed in this work. It is based on the use of the kinetic laws of an initiated chain reaction of quinonemonoimine **2** with 2,5-di-*tert*-butylhydroquinone (**4**), catalyzed by aromatic amines.



3a,**b**

$R^1 = R^2$ = OMe (**a**), Me (**b**)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 293—299, February, 2004.

Experimental

The synthesis and purification of reactants and solvent (chlorobenzene) were reported earlier.[2] Experiments were carried out in an argon atmosphere in a thermostatted quartz cell reactor of bubbling type (the volume was 8.5 mL, the optical path length was 2.0 cm), incorporated into a Specord UV-VIS spectrophotometer. The experiments involved monitoring of the optical density at λ = 450 nm (ε = 2950 at 321.5 K and 2920 L mol^{-1} cm^{-1} at 340.0 K); our previous experiments showed that only the absorbance of quinoneimine **2** was detected in this spectral region. To minimize the experimental errors, quinoneimine **2** and the initiator (tetraphenylhydrazine) were simultaneously introduced into a preheated cell containing solutions of both hydroquinone and aromatic amine. To this end, we used co-solutions of quinoneimine **2** and tetraphenylhydrazine with a prescribed concentration of each component.

The products accumulated affect the rate of the reaction;[2,3] therefore, the reaction kinetics was studied using the initial rates (w_2) of the quinoneimine consumption (in this case, the effect of the products can be ignored). To increase the accuracy, the w_2 values were calculated using the results of approximation of the kinetic curves of the quinonemonoimine consumption by an empirical equation

$$\ln(a + \ln[\mathbf{2}]) = b + ct,$$

where a, b, and c are constants determined using an iterative procedure. In this case, one has

$$w_2 = -c\,[\mathbf{2}]_0(\ln[\mathbf{2}]_0 + a).$$

Results and Discussion

The most correct estimate of the N—H bond dissociation energy ($D_{\rm NH}$/kJ mol^{-1}) for molecule **1** can be obtained from the correlation equation proposed[4] for substituted diphenylamines:

$$D_{\rm NH} = (363.6\pm0.24) + (11.93\pm0.42)\sigma^{+} \ (r = 0.995),$$

where σ^{+} is the Brown constant of the substituent in *p*-position of the benzene ring of diphenylamine. Using the same system of σ^{+}-constants as that employed in Ref. 4 ($\sigma^{+}_{\rm OH} = -0.853$ [5]), we get $D_{\rm NH}(\mathbf{1}) = 353.4\pm0.6$ kJ mol^{-1}.

Hereafter, this value will be considered as a preferred one.

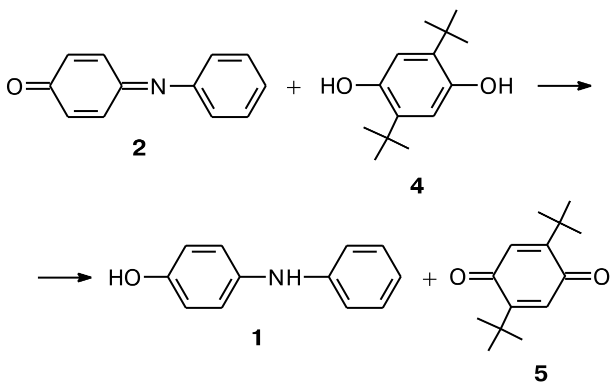
Method of investigation and determination of the rate constants for the reactions of quinoneimine 2 with aromatic amines. For brevity, let us write the equation of this reaction in the form

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathbf{2}^{\bullet} + \mathbf{3}^{\bullet}, \qquad (1)$$

where $\mathbf{2}^{\bullet}$ are the phenoxyl or aminyl radicals formed from quinoneimine **2**. Reaction (1) cannot be studied immediately by following the consumption of the starting compounds because the reactant concentrations remain virtually unchanged over a rather long period after mixing. This is due to the fact that the rate constant for the strongly exothermic reverse reaction (k_{-1}) is 12 to 13 orders of magnitude greater than k_1.

The k_1 value can be determined reliably if reaction (1) plays the role of an initiation stage for some chain process. In this case, provided that all the radicals formed are accepted, the reaction (1) can contribute largely to the total rate of the process. This contribution can be measured experimentally with ease, because an increase in the rate of the process will be ν times greater than the rate of the elementary reaction (1), where ν is the chain length.

A convenient example is provided by the chain reaction of quinonemonoimine **2** with 2,5-di-*tert*-butylhydroquinone (**4**), resulting in 4-hydroxydiphenylamine (**1**) and 2,5-di-*tert*-butylquinone **5** [2,3]:



This reaction proceeds by the mechanism presented below:

Chain initiation*

$$\mathbf{2} + \mathbf{4} \longrightarrow \mathbf{2}^{\bullet} + \mathbf{5}^{\bullet} \qquad (2)$$

Chain propagation

$$\mathbf{2} + \mathbf{5}^{\bullet} \longrightarrow \mathbf{2}^{\bullet} + \mathbf{5} \qquad (3)$$

$$\mathbf{2}^{\bullet} + \mathbf{4} \longrightarrow \mathbf{1} + \mathbf{5}^{\bullet} \qquad (4)$$

Chain termination

$$\mathbf{2}^{\bullet} + \mathbf{2}^{\bullet} \longrightarrow \mathbf{2} + \mathbf{1} \qquad (5)$$

$$\mathbf{2}^{\bullet} + \mathbf{5}^{\bullet} \longrightarrow \begin{cases} \mathbf{2} + \mathbf{4} \\ \mathbf{1} + \mathbf{5} \end{cases} \qquad (6)$$

$$\mathbf{5}^{\bullet} + \mathbf{5}^{\bullet} \longrightarrow \mathbf{5} + \mathbf{4} \qquad (7)$$

The reaction mechanism is significantly complicated in the presence of aromatic amines. The amine

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* Radical $\mathbf{5}^{\bullet}$ is the 2,5-di-*tert*-butyl-4-hydroxyphenoxyl radical formed upon hydrogen abstraction from hydroquinone **4** or upon hydrogen addition to quinone **5**.

admixtures act as catalysts and the reaction mechanism scheme is augmented by the following elementary reactions[6]:

Chain initiation

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathbf{2}^{\cdot} + \mathbf{3}^{\cdot} \qquad (1)$$

Radical exchange

$$\mathbf{3}^{\cdot} + \mathbf{4} \rightleftharpoons \mathbf{3} + \mathbf{5}^{\cdot} \qquad (8), (-8)$$

$$\mathbf{2}^{\cdot} + \mathbf{3} \longrightarrow \mathbf{1} + \mathbf{3}^{\cdot} \qquad (9)$$

Chain termination

$$\mathbf{2}^{\cdot} + \mathbf{3}^{\cdot} \longrightarrow \mathbf{2} + \mathbf{3} \qquad (-1)$$

$$\mathbf{5}^{\cdot} + \mathbf{3}^{\cdot} \longrightarrow \mathbf{5} + \mathbf{3} \qquad (10)$$

$$\mathbf{3}^{\cdot} + \mathbf{3}^{\cdot} \longrightarrow \text{Products} \qquad (11)$$

The expression for the consumption rate of quinoneimine in the presence of a catalyst can be written as follows:

$$w_2{}^2 = \frac{k_3^2 k_8^2 [\mathbf{4}]^2 [\mathbf{2}]^2 A^2 B}{k_3^2 [\mathbf{2}]^2 C + k_3[\mathbf{2}]AD + A^2 E}\,, \qquad (\mathrm{I})$$

where

$$A = k_4[\mathbf{4}] + k_9[\mathbf{3}],$$

$$B = k_2[\mathbf{4}][\mathbf{2}] + k_1[\mathbf{3}][\mathbf{2}],$$

$$C = k_5 k_8{}^2[\mathbf{4}]^2 + k_{-1}k_8k_9[\mathbf{4}][\mathbf{3}] + k_9{}^2k_{11}[\mathbf{3}]^2,$$

$$D = k_6 k_8{}^2[\mathbf{4}]^2 + k_8(k_{-1}k_{-8} + k_9k_{10})[\mathbf{4}][\mathbf{3}] + 2k_{-8}k_9k_{11}[\mathbf{3}]^2,$$

$$E = k_7 k_8{}^2[\mathbf{4}]^2 + k_8k_{-8}k_{10}[\mathbf{4}][\mathbf{3}] + k_{-8}{}^2k_{11}[\mathbf{3}]^2.$$

In expression (I), the factor B equals the sum of the rates of the reactions (1) and (2) in which radicals are formed in the system. Let us rewrite expression (I) in the form:

$$w_2{}^2 = \Phi(i)B = \Phi(i)(k_1[\mathbf{2}][\mathbf{3}] + k_2[\mathbf{2}][\mathbf{4}]), \qquad (\mathrm{II})$$

where $\Phi(i)$ is the function of the concentrations of the compounds **2** and **4**, catalyst **3**, and of the rate constants of all the elementary reactions, except for the initiation stages (1) and (2). Expressions (I) and (II) show that the dependence of $w^2{}_2$ on the concentration of amine **3** cannot be used to determine k_1 because the factor $\Phi(i)$ changes as the parameter $[\mathbf{3}]_0$ varies. However, if an initiator capable of generating free radicals at a preset rate w_i is introduced into the amine-containing system, the k_1 value can be determined by following the reaction kinetics. Indeed, in the presence of an initiator one has

$$\begin{aligned} w_2{}^2 &= \Phi(i)(k_1[\mathbf{2}][\mathbf{3}] + k_2[\mathbf{2}][\mathbf{4}] + 0.5w_i) = \\ &= \Phi(i)(k_1[\mathbf{2}][\mathbf{3}] + k_2[\mathbf{2}][\mathbf{4}]) + \Phi(i)0.5w_i, \end{aligned} \qquad (\mathrm{III})$$

where $\Phi(i)$ is the same function as that appeared in expression (II). The function $\Phi(i)$ is independent of w_i, and therefore its value remains constant in a series of runs at constant concentrations of compounds **2**, **4**, and **3** and at variable w_i. Then, by plotting a straight line ($w^2{}_2$ *vs.* $0.5w_i$) one can determine $a = \Phi(i)(k_1[\mathbf{2}][\mathbf{3}] + k_2[\mathbf{2}][\mathbf{4}])$ from the Y-intercept while the slope gives $b = \Phi(i)$. The ratio $a/b = k_1[\mathbf{2}][\mathbf{3}] + k_2[\mathbf{2}][\mathbf{4}]$ gives the sum of the rates of the reactions (1) and (2). Now, it is possible to determine k_1 provided the known k_2 value and the concentrations of the reagents **2** and **4**.

This method, which is based on the double mixed initiation of a chain reaction, was employed in this work to determine the k_1 values for the reactions involving compounds **3a** and **3b**. The linear dependence (III) between $w_2{}^2$ and the initiation rate is quite reasonable (Fig. 1). The experimental data and the calculated the rate constants are listed in Table 1.

Calculations of the N—H and O—H bond dissociation energies for the semiquinone radicals 2n˙ and 2o˙. Method 1. The O—H and N—H bond dissociation energies in radicals **2n˙** and **2o˙**, respectively, can be calculated from the rate constant for the elementary reaction (2) of the mechanism of the chain reaction between compounds **2** and **4** (see above). The experimental k_2 values at 298.2 and 340.0 K are $3.22 \cdot 10^{-3}$ and $8.61 \cdot 10^{-2}$ L mol^{-1} s^{-1}, respectively.[2]

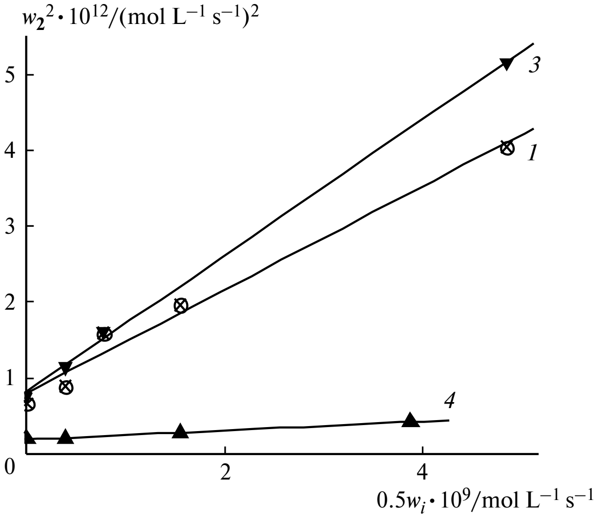


Fig. 1. The rate of the chain reaction of quinoneimine **2** with hydroquinone **4** catalyzed by aromatic amines plotted *vs.* the radical initiation rate due to decomposition of the initiator (tetraphenylhydrazine). The straight lines are enumerated exactly in the same manner as the series of runs (see Table 1).

Table 1. Rate constants k_1 (L mol^{-1} s^{-1}) obtained using double mixed initiation method[a]

Compound	Series of runs	T/K	$[\mathbf{4}]_0\cdot10^4$	$[\mathbf{3}]_0\cdot10^3$	$0.5w_i\cdot10^{10}$	$w_2\cdot10^7$	$k_1\cdot10^3$	$k_1^{av}\cdot10^3$ [b]
			mol L^{-1}		mol L^{-1} s^{-1}		L mol^{-1} s^{-1}	
3a	*1*	340	4.75	0.57	0	8.12	3.60±0.90	
					3.88	9.44		
					7.76	12.6		
					15.5	14.0		4.10±1.40
					48.5	20.1		
	2	340	2.38	0.57	0	4.20	4.80±2.00	
					3.88	6.05		
					7.76	8.18		
					48.5	13.0		
3b	*3*	340	2.38	5.70	0	5.53	0.50±0.23	
					7.76	10.1		
					15.5	13.0		
					48.5	17.9		0.38±0.15
	4	340	4.75	1.90	0	8.68	0.35±0.11	
					3.88	10.7		
					7.76	12.7		
					48.5	22.7		
6[c]	*5*	340	2.38	1.90	0	4.5	7.35±1.50	
					3.88	4.4		
					15.5	5.2		4.00±1.60[d]
					38.8	6.5		
	6	340	4.75	1.90	0	9.6	9.10±4.90	
					7.76	8.6		
					15.5	9.6		
					38.8	12.3		
	7	321.5	2.44	5.85	0	3.9	1.38±0.40	
					1.504	4.2		
					4.63	4.4		0.66±0.20[d]
	8	321.5	2.44	11.7	0	4.5	1.25	
					11.1	5.4		

[a] With tetraphenylhydrazine as the initiator; k_i (s^{-1}) = $1.475\cdot10^{14}\exp(-E_a/RT)$[2] and E_a = 117.5 kJ mol^{-1}. The concentration of **2** was $1.9\cdot10^{-4}$ at 340.0 K and $1.95\cdot10^{-4}$ mol L^{-1} at 321.5 K. The k_2 values at 321.5 and 340.0 K are $2.23\cdot10^{-2}$ (calculated from the temperature dependence) and $8.61\cdot10^{-2}$ L mol^{-1} s^{-1}.[2]

[b] k_1^{av} denotes the average value.

[c] Dimethyldi-(4-anilinophenoxy)silane (**6**).

[d] Per NH group.

However, the reaction

$$\mathbf{2} + \mathbf{4} \longrightarrow \mathbf{2}^{\bullet} + \mathbf{5}^{\bullet} \tag{2}$$

proceeds involving two channels:

$$\mathbf{2} + \mathbf{4} \longrightarrow \mathbf{2o}^{\bullet} + \mathbf{5}^{\bullet}, \tag{2a}$$

$$\mathbf{2} + \mathbf{4} \longrightarrow \mathbf{2n}^{\bullet} + \mathbf{5}^{\bullet}, \tag{2b}$$

where $k_2^{\exp} = k_{(2a)} + k_{(2b)}$.

To calculate the D_{OH} and D_{NH} values for radicals $\mathbf{2n}^{\bullet}$ and $\mathbf{2o}^{\bullet}$ by the IP method, one should know not only $k_2^{\exp}$ but also the exact value of the O—H bond dissociation energy in the molecule of hydroquinone **4**, $D_{\mathrm{OH}}(\mathbf{4})$. Earlier,[7] we estimated this parameter at $D_{\mathrm{OH}}(\mathbf{4})$ = 345.1±1 kJ mol^{-1} by data averaging over four dependences between the logarithm of the rate constants for elementary reactions of 4,4´-substituted diphenylaminyl radicals $\mathbf{3}^{\bullet}$ with sterically unhindered phenols and the thermal effects, q, of the reactions ($q = D_{\mathrm{NH}} - D_{\mathrm{OH}}$). In turn, these dependences were plotted using the results of a laser flash photolysis study of the reactions of four radicals $\mathbf{3}^{\bullet}$ ($R^1 = R^2$ = H, Me, Br; R^1 = OMe, R^2 = H) with eight different phenols including **4**. The characteristics of the phenols, D_{OH}, used in calculations were somewhat different from the recommended values[1].

Phenol	D_{OH}/kJ mol^{-1}	
	Earlier values	Recommended values[1]
C_6H_4OH	369.0	367.0
4-MeC_6H_4OH	362.2	359.8
4-$MeOC_6H_4OH$	345.8	349.3
2,6-$Me_2C_6H_3OH$	354.6	356.1
2,4,6-$Me_3C_6H_2OH$	347.5	352.3
2,6-$(MeO)_2C_6H_3OH$	347.9	354.0

In this work, we consider the D_{OH}(**4**) value as a reference. Because of this, as well as trying to use the data from the same source, we revised the experimental data[7] and accepted the recommended[1] values of D_{OH} in phenols. As a consequence, the following new value was obtained:

$$D_{OH}(\mathbf{4}) = 337.3 \pm 2.3 \text{ kJ mol}^{-1}.$$

This value of D_{OH}(**4**) is used hereafter in all calculations.

The activation energies of strongly endothermic reactions (2a) and (2b) nearly coincide with the corresponding enthalpies:

$$E_a(2a) = D_{OH}(\mathbf{4}) - D_{NH}(\mathbf{2o}^\bullet) - 0.5RT =$$
$$= 337.3 - D_{NH} - 0.5RT,$$

$$E_a(2b) = D_{OH}(\mathbf{4}) - D_{OH}(\mathbf{2n}^\bullet) - 0.5RT =$$
$$= 337.3 - D_{OH} - 0.5RT.$$

According to the IP method,[1] for the classes of reactions similar to those described by Eqns. (2a) and (2b), the averaged pre-exponential factors $A_{(2a)}$ and $A_{(2b)}$ are $1 \cdot 10^7$ and $1 \cdot 10^9$ L mol^{-1} s^{-1}, respectively. In the case in hand, they should be doubled, because molecule **4** contains two equivalent OH groups. For strongly endothermic processes (enthaply of reaction exceeds some threshold value ΔH_e^{max}), one should take into account the change in the collision cross-section using the following coefficients[1]:

$$\gamma_{(2a)} = \left[1 + 1.3\left(\sqrt{337.3 - D_{NH} + \eta_{(2a)}} - \sqrt{\Delta H^{max}_{(2a)}}\right)\right]^2, \quad (IV)$$

$$\gamma_{(2b)} = \left[1 + 1.3\left(\sqrt{337.3 - D_{OH} + \eta_{(2b)}} - \sqrt{\Delta H^{max}_{(2b)}}\right)\right]^2, \quad (V)$$

where $\eta = 0.5hN_A(v_i - v_f)$ is the zero-point vibrational energy difference between the cleaved O—H bond, v_i, in molecule **4** and the forming bond (N—H or O—H) v_f in radicals $\mathbf{2o}^\bullet$ or $\mathbf{2n}^\bullet$ (h is the Planck constant, N_A is the Avogadro constant, and v is the vibrational frequency). In the case in hand, we have $\eta_{(2a)} = 0.5hN_A(v_{OH} - v_{NH}) = 1.5$ kJ mol^{-1}, $\eta_{(2b)} = 0.5hN_A(v_{OH} - v_{OH}) = 0$, $\Delta H_e^{max}{}_{(2a)} = 21.9$, and $\Delta H_e^{max}{}_{(2b)} = 42.1$ kJ mol^{-1}.

The relationship for calculating the rate constant for the overall reaction (2) by the IP method has the form:

$$k_2^{exp} = \{2 \cdot 10^7 e^{-1/2} \gamma_{(2a)} \exp[-(337.3 - D_{NH})/RT]\} +$$
$$+ \{2 \cdot 10^9 e^{-1/2} \gamma_{(2b)} \exp[-(337.3 - D_{OH})/RT]\}. \quad (VI)$$

Expresion (VI) was used for processing the experimental data for k_2^{exp} at $T = 298.2$ and 340.0 K. When calculating, the bond dissociation energies were determined iteratively. The following values were obtained (in kJ mol^{-1}): $D_{NH}(\mathbf{2o}^\bullet) = 273.89$ and $D_{OH}(\mathbf{2n}^\bullet) = 259.55$ ($\Delta = 14.34$).

The results of comparison of the calculated temperature dependence of k_2 and the experimental data are presented in Fig. 2.

Method 2. The D_{NH} and D_{OH} values for radicals $\mathbf{2o}^\bullet$ and $\mathbf{2n}^\bullet$ can be calculated using the rate constants (see Table 1) for the reactions:

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathbf{2}^\bullet + \mathbf{3}^\bullet, \quad (1)$$

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathbf{2o}^\bullet + \mathbf{3}^\bullet, \quad (1a)$$

$$\mathbf{2} + \mathbf{3} \longrightarrow \mathbf{2n}^\bullet + \mathbf{3}^\bullet, \quad (1b)$$

$k_1^{exp} = k_{(1a)} + k_{(1b)}$. The expression for calculating k_1^{exp} is similar to Eq. (VI), $\eta_{(1a)} = 0.5hN_A(v_{NH} - v_{NH}) = 0$, $\eta_{(1b)} = 0.5hN_A(v_{NH} - v_{OH}) = -1.5$ kJ mol^{-1}, and the threshold values are $\Delta H_e^{max}{}_{(1a)} = 31.2$, $\Delta H_e^{max}{}_{(1b)} = 16.7$ kJ mol^{-1}, $A_{(1a)} = A_{(1b)} = 1 \cdot 10^8$ L mol^{-1} s^{-1}.[1] The N—H bond dissociation energies (D_{NH}) for **3a** and **3b** are respectively 348.6 and 357.5 kJ mol^{-1}. The D_{NH} value in molecules **3a,b** was used as independent variable, while the $D_{NH}(\mathbf{2o}^\bullet)$ and $D_{OH}(\mathbf{2n}^\bullet)$ values were fitted. The dissociation energies found are as follows: $D_{NH}(\mathbf{2o}^\bullet) = 273.23$ and $D_{OH}(\mathbf{2n}^\bullet) = 259.44$ kJ mol^{-1} ($\Delta = 13.79$).

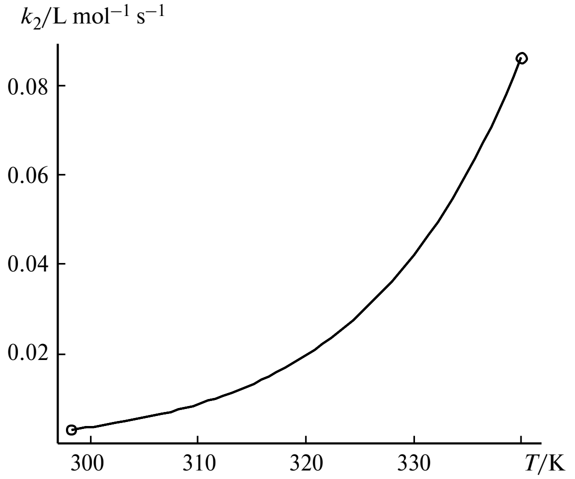


Fig. 2. Results of calculations of the temperature dependence of the rate constant k_2 using Eq. (VI) (solid line) compared with the experimental data (points).

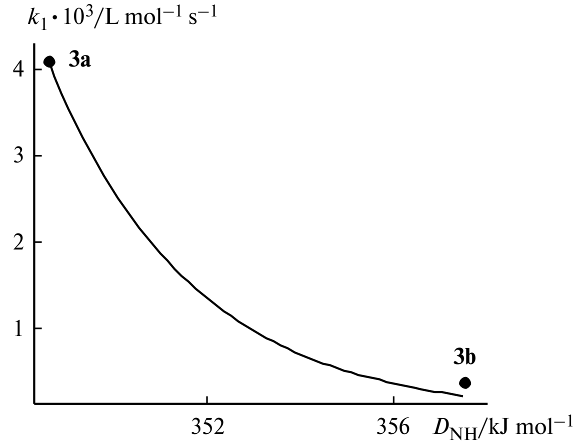


Fig. 3. Rate constant for reaction (1) at 340.0 K plotted *vs*. the N—H bond dissociation energy in secondary aromatic amines. The experimental data for 4,4′-dimethoxydiphenylamine (**3a**) and 4,4′-dimethyldiphenylamine (**3b**) are shown as full circles. Results of calculations by the IP method are shown by a solid line (see text).

These estimates are in good agreement with the values listed above. The results of approximation with these D_{NH} and D_{OH} values are shown in Fig. 3.

The averaged values of the N—H and O—H bond dissociation energies in radicals $\mathbf{2}^\bullet$ (D_{NH} = 273.6, D_{OH} = 259.5 kJ mol^{-1}) can be used for evaluating the N—H bond dissociation energy in diamine $(PhNHC_6H_4O)_2SiMe_2$ (**6**), for which only unreliable data are known. Calculations using Eq. (VI) and the rate constants k_1 for the reactions of **6** with **2** at 340.0 and 321.5 K (see Table 1) gave D_{NH}(**6**) = 349.1 kJ mol^{-1}.

As can be seen, calculations of the D_{NH} and D_{OH} values for the radicals $\mathbf{2o}^\bullet$ and $\mathbf{2n}^\bullet$ from the rate constants for two different elementary reactions give very similar results. Taken altogether with the estimate of D_{NH} for **1** (see above), these data are sufficient for assessing the last unknown parameter, namely, the OH bond dissociation energy for molecule **1**. This is possible because the D_{NH} and D_{OH} values for compound **1** and the radicals formed from molecule **1** are not independent. From the equality of the thermal effects of the reactions of successive hydrogen addition to quinoneimine **2** to give compound **1** as the end product

$$\mathbf{2} + \mathrm{H} \longrightarrow \mathbf{2o}^\bullet\ (+\mathrm{H}) \longrightarrow \mathbf{1},$$

$$\mathbf{2} + \mathrm{H} \longrightarrow \mathbf{2n}^\bullet\ (+\mathrm{H}) \longrightarrow \mathbf{1},$$

it follows that

$$D_{NH}(\mathbf{2o}^\bullet) + D_{OH}(\mathbf{1}) = D_{OH}(\mathbf{2n}^\bullet) + D_{NH}(\mathbf{1})$$

or

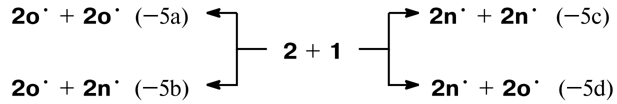
$$D_{NH}(\mathbf{1}) - D_{OH}(\mathbf{1}) = D_{NH}(\mathbf{2o}^\bullet) - D_{OH}(\mathbf{2n}^\bullet).$$

The last equality shows that the N—H bond dissociation energy for molecule **1** exceeds the O—H bond dissociation energy for this molecule by the same value as that by which the N—H bond dissociation energy for radical $\mathbf{2o}^\bullet$ exceeds the O—H bond dissociation energy for radical $\mathbf{2n}^\bullet$, *i.e.*, by 14.1 kJ mol^{-1}.

Test of the results obtained. Estimation of the O—H bond dissociation energy for molecule 1 from the rate constant for reaction of quinoneimine 2 with 4-hydroxydiphenylamine (1). The bond dissociation energies D_{NH} and D_{OH} for compound **1** and radicals $\mathbf{2o}^\bullet$ and $\mathbf{2n}^\bullet$ can also be calculated from the rate constant for the reaction

$$\mathbf{2} + \mathbf{1} \longrightarrow \mathbf{2}^\bullet + \mathbf{2}^\bullet. \qquad (-5)$$

This reaction proceeds concurrently involving a total of four channels:



The experimental rate constant for the reaction, k_{-5}, equals the sum of the rate constants for the stages (−5a), (−5b), (−5c), and (−5d).

Based on the aforesaid, only three rather than four unknown parameters D_{OH} and D_{NH} should be determined from the experimental k_{-5}^{exp} values. The experimental values of k_{-5}^{exp}/(L mol^{-1} s^{-1}) are $(6.23\pm0.72)\cdot10^{-3}$ at 298.2 K and $(1.19\pm0.14)\cdot10^{-1}$ at 340.0 K.[2]

These data are insufficient for correct estimation of three D_{OH} and D_{NH} values simultaneously. Therefore, we evaluated only the O—H bond dissociation energy for molecule **1** D_{OH}(**1**), while the averaged values $D_{NH}(\mathbf{2o}^\bullet)$ = 273.6 and $D_{OH}(\mathbf{2n}^\bullet)$ = 259.5 kJ mol^{-1} (see above) were considered constant. The parameters of the elementary reactions necessary to perform the IP calculations are available in the literature.[1] The equation for calculating the rate constant k_{-5}^{exp} is similar to Eq. (VI) and contains four terms in accord with the number of concurrent reactions (see above):

$$\begin{aligned}
k_{-5}^{exp} = {} & \{6.065\cdot10^{6}\left[1+1.3(\sqrt{D_{OH}-273.6+1.5}-\sqrt{21.9})\right]^2\cdot \\
& \cdot\exp(-(D_{OH}-273.6)/RT)\} + \\
& + \{6.065\cdot10^{7}\left[1+1.3(\sqrt{(D_{OH}+14.1)-273.6}-\sqrt{31.2})\right]^2\cdot \\
& \cdot\exp(-((D_{OH}+14.1)-273.6)/RT)\} + \{6.065\cdot10^{7}\cdot \\
& \cdot\left[1+1.3(\sqrt{(D_{OH}+14.1)-259.5-1.5}-\sqrt{16.7})\right]^2\cdot \\
& \cdot\exp(-((D_{OH}+14.1)-259.5)/RT)\} + \\
& + \{6.065\cdot10^{8}\left[1+1.3(\sqrt{(D_{OH}-259.5)}-\sqrt{42.1})\right]^2\cdot \\
& \cdot\exp(-(D_{OH}-259.5)/RT)\}. \qquad \text{(VII)}
\end{aligned}$$

Processing of the data on the temperature dependence of $k_{-5}^{\exp}$ using relationship (VII) with iterative fitting of the optimum D_{OH} value gave $D_{OH}(\mathbf{1})$ = 334.06±0.04 kJ mol^{-1}. Since $\Delta = D_{NH} - D_{OH}$ = 14.1 kJ mol^{-1}, one gets $D_{NH}(\mathbf{1})$ = 334.06 + 14.1 = 348.16 kJ mol^{-1}, which differs from the preferred estimate of $D_{NH}(\mathbf{1})$ by ~5 kJ mol^{-1} only. Such a good agreement between the results simultaneously points to correctness of the N—H and O—H bond dissociation energies in the semiquinone radicals $\mathbf{2o}^{\bullet}$ and $\mathbf{2n}^{\bullet}$, respectively (see above), which were used in the last-mentioned calculations.

Thus, the N—H and O—H bond dissociation energies for molecule **1** and radicals $\mathbf{2o}^{\bullet}$ and $\mathbf{2n}^{\bullet}$ are as follows: $D_{NH}(\mathbf{1}) = 353.4$, $D_{OH}(\mathbf{1}) = 339.3$, $D_{NH}(\mathbf{2o}^{\bullet}) = 273.6$, and $D_{OH}(\mathbf{2n}^{\bullet}) = 259.5$ kJ mol^{-1}.

These data allow, *e.g.*, the rate constants for the reactions of **1** with alkylperoxide radicals $RO_2^{\bullet}$ to be calculated, which is of particular interest taking into account the fact that compound **1** is used as antioxidant. For definiteness sake, we will consider the reactions of secondary peroxy radicals $RO_2^{\bullet}$ with compound **1** at 333 K (60 °C). Using the recommended[1] value of the O—H bond dissociation energy in secondary hydroperoxides (D_{OH}(ROOH) = 365.5 kJ mol^{-1}) and the parameters of the elementary reactions mentioned above, the IP method gives (k/L mol^{-1} s^{-1}):

$$k_{NH} = k(RO_2^{\bullet} + \mathbf{1}) = 5.83 \cdot 10^5,$$

$$k_{OH} = k(RO_2^{\bullet} + \mathbf{1}) = 7.16 \cdot 10^5,$$

$$k_{\Sigma} = k_{NH} + k_{OH} = 1.30 \cdot 10^6.$$

As can be seen, the k_{NH} and k_{OH} values are close to each other. Among other things, this means that 4-hydroxydiphenylamine can be considered as an antioxidant of two classes of compounds (phenols and secondary aromatic amines) simultaneously.

It should be pointed out that the k_{NH} and k_{OH} values differ only slightly, whereas the thermal effects, Q, of these reactions are significantly different, namely, $Q_{NH} = D(\text{ROOH}) - D_{NH}(\mathbf{1}) = 365.5 - 353.4 = 12.1$ and $Q_{OH} = D(\text{ROOH}) - D_{OH}(\mathbf{1}) = 365.5 - 339.3 = 26.2$ kJ mol^{-1}. These results demonstrate that the reactions in question proceed involving an apparent violation of the Polanyi—Semenov rule, which relates the activation energy and, hence, the rate constants to the thermal effect of the reaction*. Mention may be made that a rather large number of reactions are currently known, which proceed with violation of the Polanyi—Semenov rule. Thorough analysis of this problem allowed nearly ten factors governing the E_a value to be established, the heat of reaction being only one of them (though one of the most important).[1] To reveal the role of the other factors, one should compare the activation energy, E_{e0}, of thermally neutral reactions (the case where the contribution Q to E_a is included and has no effect on E_a). For the classes of reactions under study, $E_{e0\,(NH)} = 39.0$ and $E_{e0\,(OH)} = 43.3$ kJ mol^{-1}.[1] As can be seen, the activation energy of the thermally neutral reaction following the first route (the transition state geometry is O...H...N) is 4.3 kJ mol^{-1} lower compared to the reaction following the second route (the transition state geometry is O...H...O). The reason for the lower E_{e0} value for the reaction between $RO_2^{\bullet}$ and **1** involving the N—H bond as compared to the reaction involving the O—H bond was determined earlier[8]: this is the electronegativity difference between the O and N atoms in the transition state.

The author expresses his deep gratitude to E. T. Denisov for helpful discussions.

This work was financially supported by the Chemistry and Materials Science Branch of the Russian Academy of Sciences (a grant in the framework of the Program "Theoretical and experimental investigations on the nature of the chemical bonding and mechanisms of the most important chemical reactions and processes").

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Received February 5, 2003;
in revised form May 20, 2003

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* The activation energies of the reactions, calculated by the IP method are as follows: $E_{NH} = 14.2$ and $E_{OH} = 10.5$ kJ mol^{-1}.