Solvent effect on the equilibrium constant of the chain reversible reaction of *N*,*N*′-diphenyl-1,4-benzoquinonediimine with 2,5-dichlorohydroquinone

S. Ya. Gadomsky and V. T. Varlamov★

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (496) 515 5420. E-mail: varlamov@icp.ac.ru

The temperature dependences of the equilibrium constant K of the reversible chain reaction of *N*,*N*′-diphenyl-1,4-benzoquinonediimine with 2,5-dichlorohydroquinone in benzene, chlorobenzene, anisole, benzonitrile, and CCl_4 were studied. The enthalpies and entropies of the reaction in these solvents were determined, and a linear dependence between them in aromatic solvents was found. The equilibrium constant depends on the solvent nature: the replacement of CCl_4 by benzene at $T = 298$ K increases K from 13.6 to 140. The solvation effects are caused by several types of intermolecular interactions of participants of equilibrium with the medium. The decrease in K in the benzene—anisole—benzonitrile series is related, to a great extent, to complex formation with hydrogen bonding between 2,5-dichlorohydroquinone and the solvents. In anisole a charge-transfer complex is formed between the solvent and reaction product (2,5-dichloroquinone). The constant and enthalpy of the complexation were estimated.

Key words: *N*,*N*′-diphenyl-1,4-phenylenediamine, 2,5-dichlorohydroquinone, *N*,*N*′-diphenyl-1,4-benzoquinonediimine, 2,5-dichloroquinone, reversible chain reactions, equilibrium constant, reaction enthalpy and entropy, hydrogen bonding, complexation.

Quinoneimines are nitrogen anologs of quinones and, hence, reactions of quinoneimines with hydroquinones proceed analogously to the reactions of quinones with hydroquinones. In this case, one of the components (quinoneimine or quinone) is reduced due to the oxidation of the second component (hydroquinone). In aprotic organic solvents (chlorobenzene) quinoneimines react with hydroquinones *via* the chain mechanism.[1,2] It has recently[3,4] been confirmed experimentally that in the general case these reactions are chain reversible processes.[5] This implies that the equilibrium can be achieved *via* the chain route from the side of both the reactants and products and in equilibrium the forward and backward chain reactions have equal rates.

The reversible character of the chain reactions of quinoneimines with hydroquinones is caused by a small change in the free energy during these reactions. They are characterized by equilibrium constants K low in absolute values, which can reliably be measured experimentally. The available data indicate that the K values are very sensitive to the reactant structure.[2,5,6] It could be assumed that the K values also depend on the solvent nature. No experimental research in this area was carried out, although these data are of doubtless interest. This is explained by the fact that the semiquinone radicals are involved in the reactions of quinoneimines with hydroquinones and, therefore, the observed effect of the medium on the equilibrium constant of the overall reaction evidences for the dependence of the redox reactivity of the semiquinone radicals on the solvation effects. These data are important for understanding of the mechanism of action of lipid-soluble bioantioxidants of the quinone type (ubiquinones, K group vitamins).[7]

In the present work, we studied the effect of the solvent nature on the equilibrium constant of one of the reversible chain reactions in a quinoneimine—hydroquinone system, namely, the reaction of *N*,*N*′-diphenyl-1,4-benzoquinonediimine (**1**) with 2,5-dichlorohydroquinone (**2**), whose chain mechanism has been established earlier.[6]

Experimental

Compound **1** was synthesized by the oxidation of *N*,*N*′-diphenyl-1,4-phenylenediamine Ph—NH—C_6H_4—NH—Ph (**3**) with PbO_2.[2] Compound **1** was purified by liquid chromatography on SiO_2 (benzene with additives of chloroform (5%) as eluent) and recrystallization from methanol. Compound **3** (analytically pure grade) was purified from mechanical and strongly polar admixtures by passing a solution of compound **3** (in a concentration close to saturation) in a benzene (95%) + chloroform (5%) mixture through a column (10×2.5 cm) packed with silica gel L (Chemapol, 40—100 μm). The eluate was evaporated

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2296—2302, December, 2007.

at room temperature by ~95%, the crystals were separated, washed with benzene, and dried *in vacuo*. Sample **3** was recrystallized from a mixture of methanol with chloroform (3—5%) and then from toluene.

2,5-Dichloroquinone (**4**) (Aldrich) was purified by double sublimation *in vacuo*. A portion of purified quinone **4** was used for the synthesis of hydroquinone **2** by reduction with sodium dithionite $Na_2S_2O_4$ according to an earlier described procedure.[8] After the synthesis hydroquinone **2** was purified by recrystallization from methanol and then from toluene.

Special attention was given to the purity of solvents because of a prolong duration of experiments and small reactant concentrations. At the initial stages, the solvents were purified according to commonly accepted procedures[9,10] and then using the treatment with tetraphenylhydrazine, distillation, and passing through a column with a special packing.[6] In the case of anisole and benzonitrile, *N*,*N*′-diphenyl-1,4-phenylenediamine (**3**) (~150 mg L^{-1}) was added to the solvents purified according to standard procedures, and the mixtures were heated to ~370 K. After 15—20 min Ar was bubbled through the hot solvent, displacing air completely. During this procedure the solvents were orange-colored due to quinonediimine **1**, which was formed from compound **3** in the reactions with oxidizing admixtures and due to the oxidation of compound **3** with air oxygen. Then the solvent was distilled in an Ar atmosphere in a vacuum of a water-jet pump in the presence of a **1** + **3** mixture. Owing to the presence of the latter, residues of both oxidizing and reducing admixtures were removed from the solvents during distillation. Compounds **3** (~2 mg L^{-1}) were added again to the obtained solvents, the mixtures were heated, air was replaced by argon, and the mixtures were heated and again distilled in an Ar atmosphere under reduced pressure. The bottom residues had only a slight orange shade, indicating a very low content of compound **1**.

The spectrophotometric method was used to determine the equilibrium constants. The experiments were carried out in a temperature-controlled quartz cell, being a bubbling-type reactor (volume 6.0 mL, optical path length 2.0 cm), built-in into a Specord UV—Vis spectrophotometer. The consumption or accumulation of quinonediimine was continuously monitored by its absorption in the visible region at one of the following wavelengths: λ/nm: 449 (band maximum), 500, or 526 (ν = 22260, 20000, or 19000 cm^{-1}, respectively), depending on the concentration. Usually the experiments were started at T = 298 K, and we waited for the equilibration of the system. Then the temperature was increased to a new specified value, the experiment was continued to equilibration at the new temperature, *etc.* Since the experiments were prolong, the intensity of Ar bubbling was sharply decreased ~15 min after the beginning of the experiment at T = 298 K to decrease the error due to solvent evaporation.

When calculating the K equilibrium constant, the correction for thermal expansion (β_T) of the solvent was taken into account (Table 1). The temperature dependences of specific volumes (V_{sp}) of the solvents were determined from the data[11] on their densities.

The experimental molar absorptivities of quinonediimine **1** at the experimental temperature were calculated using the formula

$$\varepsilon_T^{\lambda}(\mathbf{1}) = D_T^{\lambda}(\mathbf{1})_{exp}\beta_T/([\mathbf{1}]_0^{298}l), \quad (1)$$

where l is the cell thickness. The results obtained are given in Table 2.

Table 1. Corrections for the thermal expansion (β_T) of solvents at temperatures 298—383 K*

Solvent	$\beta_T = V_{sp}^T/V_{sp}^{298}$			
	321	343	364	383
Benzene	1.029	1.059	—	—
CCl_4	1.030	1.060	—	—
Benzonitrile**	1.023	1.043	1.064	1.085
Chlorobenzene	1.023	1.045	1.068	1.090
Anisole	1.022	1.045	1.067	1.088

* At T = 298 K β_T = 1 for all solvents.
** Calculated by the formula $\beta_T = 1 + 0.001(T - 298)$.

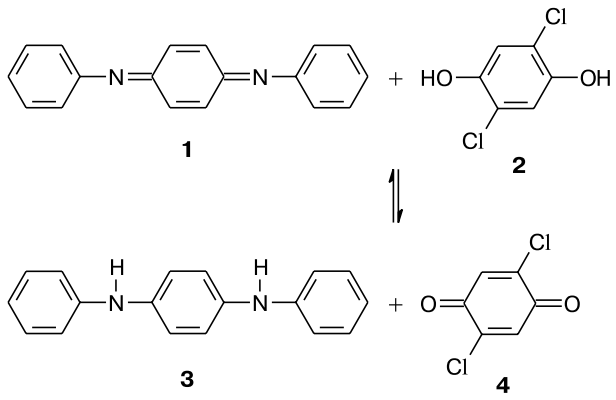
Table 2. Molar absorptivities (ε^{λ}_T) of quinonediimine **1** at temperatures 298—383 K

Solvent	λ/nm	ε_T^{λ}(**1**)/L mol^{-1} cm^{-1}				
		298	321	343	364	383
Benzene	449	7133	6993	6928	—	—
	500	3842	3714	3630	—	—
	526	1567	1531	1517	—	—
CCl_4	449	7096	6953	6833	—	—
Benzonitrile	449	6831	6677	6542	6401	6280
	500	3767	3688	3634	3591	3533
	526	1617	1633	1652	1635	1654
Chlorobenzene	449	7025	6881	6726	6598	—
	500	3919	3845	3755	3686	—
	526	1763	1708	1690	1710	—
Anisole	449	6792	6634	6534	6422	6312
	500	3692	3602	3554	3487	3428
	526	1517	1363	1389	1383	

Results and Discussion

The reaction of quinonediimine **1** with hydroquinone **2** is presented in Scheme 1.

Scheme 1



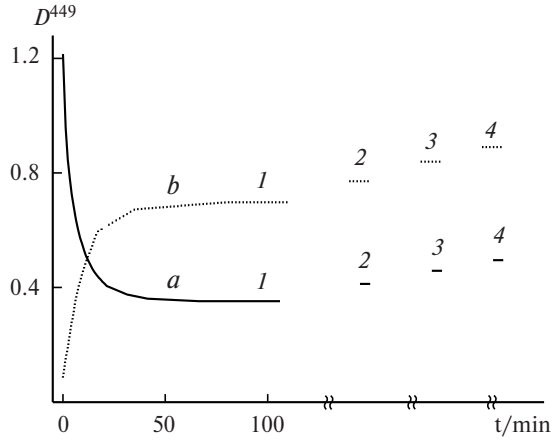


Fig. 1. Changes in absorbance at λ = 449 nm during equilibration in chlorobenzene: from the forward reaction **1** + **2** ($[\mathbf{1}]_0^{298} = 9.12 \cdot 10^{-5}$ mol L^{-1}, $[\mathbf{2}]_0^{298} = 2.70 \cdot 10^{-4}$ mol L^{-1}) in the presence of the initial additive of **3** ($[\mathbf{3}]_0^{298} = 7.20 \cdot 10^{-3}$ mol L^{-1}) (*a*) and from the the backward reaction **3** + **4** ($[\mathbf{3}]_0^{298} = [\mathbf{4}]_0^{298} = 3.60 \cdot 10^{-4}$ mol L^{-1}) (*b*). The limiting absorbance values at equilibration at 298 (*1*), 321 (*2*), 343 (*3*), and 364 K (*4*). Argon bubbling, cell thickness 2.0 cm.

The results of experiments on equilibration from the sides of the forward and backward reactions in chlorobenzene are presented in Fig. 1. When calculating the K equilibrium constant, it was taken into account that the initial concentrations of the substances were specified at $T_0 = 298$ K, and at higher T temperatures the concentrations decreased due to the thermal expansion of the solvent, for instance, $[\mathbf{2}]^T_0 = [\mathbf{2}]^{298}_0/\beta_T$. The equilibrium concentrations of quinonediimine $[\mathbf{1}]^T_e$ were determined experimentally from the absorbance and molar absorptivity calculated by Eq. (1).

In all chosen solvents, except for anisole, the absorbance of quinone **4** could be neglected at all analytical wavelengths (ε ≈ 20 L mol^{-1} cm^{-1} at λ = 449 nm). A charge-transfer complex between quinoline **4** and the solvent is formed in anisole. In this case, a rather intense absorption band of the complex appears in the visible region (λ_{max} ~400 nm). This band is overlapped with the absorption band of quinonediimine **1**. Therefore, necessary corrections were applied for the calculation of the composition of equilibrium reaction mixture. The effective molar absorptivity of the complex based on the analytical concentration of quinone **4** is given in Table 3.

If the absorbance of quinone **4** could be neglected, the K equilibrium constant was determined by the formula

$$K = \frac{[\mathbf{3}]^T_e[\mathbf{4}]^T_e}{[\mathbf{1}]^T_e[\mathbf{2}]^T_e} = \frac{([\mathbf{3}]^{298}_0 + [\mathbf{1}]^{298}_0 - \beta_T[\mathbf{1}]^T_e)([\mathbf{4}]^{298}_0 + [\mathbf{1}]^{298}_0 - \beta_T[\mathbf{1}]^T_e)}{\beta_T[\mathbf{1}]^T_e([\mathbf{2}]^{298}_0 - [\mathbf{1}]^{298}_0 + \beta_T[\mathbf{1}]^T_e)}. \quad (2)$$

Table 3. Effective molar absorptivities of the complex of quinone **4** with anisole based in the analytical concentration of quinone **4** at λ = 449 (I) and 500 nm (II)

T/K	$(\varepsilon^\lambda_T)_{eff}$/L mol^{-1} cm^{-1}	
	I	II
298	438	90
321	392	74
343	352	65
364	317	61
383	280	50

If the equilibrium is achieved from the side of the backward reaction **3** + **4**, then

$$K = \frac{[\mathbf{3}]^T_e[\mathbf{4}]^T_e}{[\mathbf{1}]^T_e[\mathbf{2}]^T_e} = \frac{([\mathbf{3}]^{298}_0 - \beta_T[\mathbf{1}]^T_e)([\mathbf{4}]^{298}_0 - \beta_T[\mathbf{1}]^T_e)}{\beta_T[\mathbf{1}]^T_e([\mathbf{2}]^{298}_0 + \beta_T[\mathbf{1}]^T_e)}. \quad (3)$$

The results obtained are given in Table 4. The solvent nature strongly affects K: when CCl_4 is substituted for benzene, at $T = 298$ K the equilibrium constant increases from 13.6 to 140, *i.e.*, by an order of magnitude. On the contrary, the temperature exerts a weak effect on K. This could be expected on the basis of a complex chain reaction mechanism. The linear dependence of the averaged equilibrium constants on the inverse temperature is presented in Fig. 2. Based on these data, the thermodynamic parameters of the reaction were determined

$$\ln K = \Delta S/R - \Delta H/(RT),$$

and presented in Table 5. As can be seen from the data in Fig. 3, in aromatic solvents ΔH and ΔS are related by a

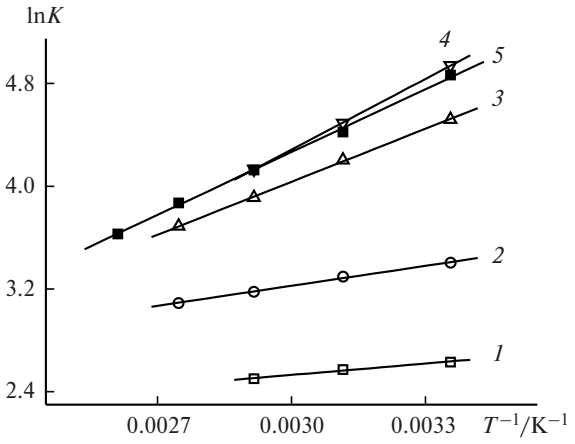


Fig. 2. Temperature dependence of the equilibrium constants of the reversible reaction of quinonediimine **1** with hydroquinone **2** in the ln$K$—T^{-1} coordinates when using CCl_4 (*1*), benzonitrile (*2*), chlorobenzene (*3*), benzene (*4*), and anisole (*5*) as solvent.

Table 4. Experimental data on the temperature dependence of the equilibrium rate constant in different solvents

$C^* \cdot 10^5$/mol L^{-1}				K at various T/K			
1	**2**	**3**	**4**	298	321	343	364
			CCl_4				
9.00	27.0	180	—	11.8	10.9	10.1	—
9.00	9.00	113	—	15.7	13.9	12.0	—
—	—	45.0	45.0	14.5	13.5	12.7	—
9.02	27.1	359	—	13.9	13.4	13.0	—
—	—	31.7	31.7	13.8	13.5	13.2	—
—	36.0	45.0	45.0	12.8	11.9	11.0	—
9.02	27.0	127	—	12.4	11.9	11.5	—
	Average			13.6±1.3	12.7±1.1	11.9±1.1	
			Benzonitrile				
9.00	27.0	540	—		31.2	26.8	23.5
8.45	33.2	332	—	29.4	26.2	23.6	20.7
—	—	72.0	72.0	37.8	33.5	30.6	28.3
9.00	27.0	—	540	33.1	30.6	28.2	26.1
45.2	45.0	—	180	26.4	24.6	23.2	20.0
—	—	36.0	36.0	35.7	30.9	27.8	24.9
9.00	27.00	360		28.8	26.0	22.1	18.9
	Average			31.9±4.4	29.0±3.4	26.0±3.1	23.2±3.5
			Chlorobenzene				
9.00	27.0	450	—	82.8	59.0	46.3	37.0
9.00	9.00	126	—	116	84.8	63.2	48.3
9.00	27.0	540	—	92.5	65.0	48.0	38.7
—	—	36.0	36.0	94.2	69.3	52.1	41.4
—	—	54.0	54.0	97.1	70.7	52.7	42.1
9.00	27.0	720	—	87.6	64.5	49.2	39.5
45.0	45.0	180	—	74.9	53.4	42.0	35.3
	Average			92±13	67±10	50±7	40±4
			Benzene				
9.00	9.00	900	0.00	139	91.4	62.9	—
9.00	9.00	225	0.00	133	84.1	56.2	—
9.00	27.0	720	0.00	126	80.7	55.7	—
9.00	9.00	0.00	900	152	96.0	62.6	—
9.82	29.5	0.00	589	136	89.2	65.1	—
0.00	0.00	90.0	90.0	134	83.9	—	—
45.0	45.0	—	540	139	84.5	61.2	—
45.0	45.0	—	90.0	160	105	73.1	—
	Average			140±11	89.4±8.0	62.4±5.9	
			Anisole**				
9.00	9.00	—	—	139	91.7	65.9	45.5
9.00	18.0	180	—	115	83.5	63.2	48.9
9.00	27.0	540	—	117	85.4	64.9	50.1
9.00	9.00	450	—	133	95.5	65.0	48.8
—	—	73.8	73.8	—	74.2	59.9	50.2
14.4	28.8	540	—	—	70.0	50.6	43.8
	Average			126±12	83.4±9.8	62.0±5.8	48.0±2.6

* Initial concentrations of the reactants at $T = 298$ K.

** At 383 K $K = 40.7$ and 34.7 at the initial concentration of compounds **3** and **4** equal to $73.8 \cdot 10^{-5}$ and compound **3** equal to $540 \cdot 10^{-5}$ mol L^{-1}, respectively ($K_{av} = 37.7 \pm 4.3$).

Table 5. Thermodynamic parameters of the reaction of quinonediimine **1** with hydroquinone **2**

Solvent	ΔS	$-\Delta H$	$-\Delta G = RT\ln K^{298}_{av}$
	/J mol^{-1} K^{-1}	kJ mol^{-1}	
CCl_4	13.3±0.03	2.5±0.1	6.5
Benzonitrile	14.4±1.1	4.3±0.1	8.6
Chlorobenzene	−0.2±0.05	11.3±0.1	11.2
Benzene	−10.2±0.5	15.3±0.2	12.2
Anisole	−5.3±1.0	13.6±0.3	12.0

distinct linear dependence. The data for CCl_4 do not fall on this plot and are much closer to the parameters of the reaction in polar benzonitrile than in nonpolar benzene. This indicates, most likely, that the nature of solvation interactions in CCl_4 and aromatic solvents differs substantially.

As mentioned above, quinone **4** forms a complex with anisole. The formation of donor-acceptor complexes with electron-releasing molecules is characteristic of quinones, especially for quinones with electron-withdrawing substituents in the cyclohexadiene ring.[12–14] The complex formation is visually manifested by the fact that solutions of quinone **4** in anisole are brightly yellow—orange rather than weakly yellowish as in other solvents. Solutions of quinone **4** in decane are almost colorless: λ_{max} ~330 nm, ε^{330} = 230 L mol^{-1} cm^{-1}. The absorption of quinone **4** in anisole has $\lambda_{max} \approx 400$ nm and the effective molar absorptivity (based on the analytical concentration of **4**) $\varepsilon^{400} \approx 670$ L mol^{-1} cm^{-1}. The formation of a complex of **4** with anisole is an exothermic process decreasing the apparent enthalpy and entropy values of the reaction of quinonediimine with 2,5-hydroquinone.

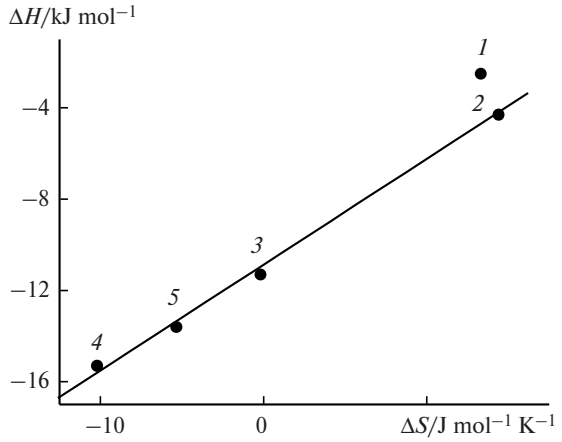


Fig. 3. Plots of the enthalpy (ΔH) *vs* entropy (ΔS) of the reversible reaction of quinonediimine **1** with hydroquinone **2** in CCl_4 (*1*), benzonitrile (*2*), chlorobenzene (*3*), benzene (*4*), and anisole (*5*).

To estimate the contribution of complexation to the thermodynamics of the reaction, we considered the reaction in the simplest form

$$\mathbf{4} + \text{Solv} \rightleftharpoons \mathbf{4}\ldots\text{Solv} \quad (K_{Solv}),$$

where Solv is anisole. At [Solv] >> $[\mathbf{4}]_0$ the following equations are valid:

$$[\mathbf{4}\ldots\text{Solv}]_e = \frac{K_{Solv}[\text{Solv}][\mathbf{4}]_0}{K_{Solv}[\text{Solv}]+1}, \quad (4)$$

$$D^{\lambda} = (\varepsilon^{\lambda} l)\frac{K_{Solv}[\text{Solv}][\mathbf{4}]_0}{K_{Solv}[\text{Solv}]+1}, \quad (5)$$

$$\frac{1}{D^{\lambda}} = \frac{1}{(\varepsilon^{\lambda} l)[\mathbf{4}]_0} + \frac{1}{(\varepsilon^{\lambda} l)K_{Solv}[\mathbf{4}]_0[\text{Solv}]}. \quad (6)$$

According to Eqs (5) and (6), two series of experiments were carried out at T = 298 K, and each series the anisole concentration was measured at $[\mathbf{4}]_0$ = const. Decane was used as the inert solvent. The obtained dependences of the absorption intensity of the complex on the anisole concentration are shown in Fig. 4, and their rectification in the coordinates of Eq. (6) is shown in Fig. 5. Based on these data, we calculated the $K_{Solv(298)}$ and ε^{500} values given below (average values (6.8±1.0) · 10^2 L mol^{-1} and 246±39 L mol^{-1} cm^{-1}, respectively).

$[\mathbf{4}] \cdot 10^4$ /mol L^{-1}	$K_{Solv(298)} \cdot 10^2$ /L mol^{-1}	ε^{500} /L mol^{-1} cm^{-1}
4.5	6.6±1.3	252±36
16.8	7.0±0.6	241±16

Using the determined $K_{Solv(298)}$ value, we obtained the ratio $[\mathbf{4}\ldots\text{Solv}]_e/[\mathbf{4}]_0$ = 0.38 using Eq. (4), *i.e.*, in anisole at T = 298 K ~40% quinone **4** exist as a complex with the solvent.

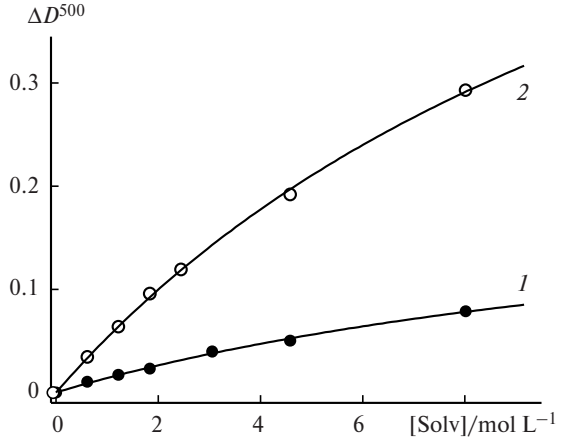


Fig. 4. Influence of the anisole (Solv) concentration on the absorbance of the complex at λ = 500 nm (ΔD^{500}); T = 298 K, cell thickness 2.0 cm, and concentration of compound **4**: 4.5 · 10^{-4} (*1*) and 16.8 · 10^{-4} mol L^{-1} (*2*).

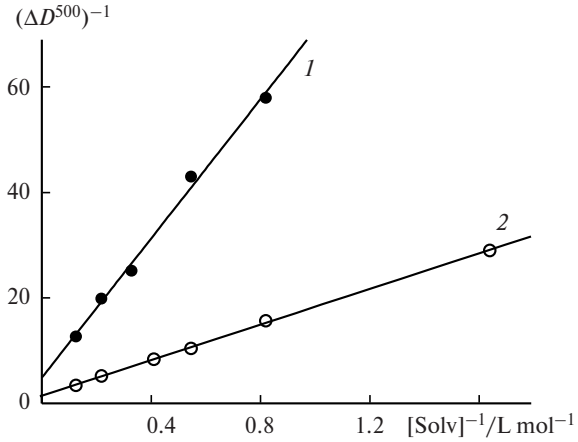


Fig. 5. Processing of the experimental data (see Fig. 4) in the coordinates of Eq. (6).

The intensity of the absorption band of the **4**...Solv complex decreases strongly with the temperature rise. The temperature effect on ε^{λ} is much stronger than that in the case of quinonediimine **1** when the absorption intensity decreases mainly because of dilution due to the thermal expansion of the solvent. The decrease in the absorption band intensity of the complex with the temperature rise is mainly caused by a decrease in the concentration of the complex because of its thermal instability.

Using the temperature dependences of D^{500} of quinone **4** solutions in anisole under the assumption that ε^{500} is temperature-independent being 246 L mol^{-1} cm^{-1}, we obtained a tentative estimate of the enthalpy of formation of a complex of quinone **4** with anisole. For this purpose we used the data for the solution: $[\mathbf{4}]_0^{298} = 1.98 \cdot 10^{-3}$ mol L^{-1}. The $K_{Solv(T)}$ value was calculated by the formula

$$K_{Solv(T)} = \frac{\beta_T[\mathbf{4}...Solv]_e}{[Solv]_{298}(1.98 \cdot 10^{-3} - [\mathbf{4}...Solv]_e)},$$

and $[Solv]_{298} = 9.16$ mol L^{-1}. The results of calculations are presented below.

T/K	$[\mathbf{4}...Solv]_e \cdot 10^5$ /mol L^{-1}	$K_{Solv(T)} \cdot 10^2$ /L mol^{-1}
298.2	7.54	6.72
321.5	6.50	5.45
343.7	5.52	4.41
364	4.86	3.79

Based on these data, we derive the dependence of $\ln K_{Solv(T)}$ on T^{-1}

$$\ln K_{Solv(T)} = -(5.89 \pm 0.08) + (954 \pm 27)T^{-1},$$

from which

$$\Delta H \approx -7.9 \pm 0.2 \text{ kJ mol}^{-1}.$$

Although the obtained estimate of ΔH is only tentative, it is rather high and comparable with the thermal effect of the reaction under study and, hence, the complexation of **4** with anisole contributes substantially to the experimental enthalpy of the reaction of **1** with **2** in this solvent.

The solvation effects (enthalpy of the reaction ΔH) in benzonitrile, anisole, and benzene are determined to a great extent by the thermal effect of formation of hydrogen-bonded complexes of hydroquinone **2** with the solvent molecules as proton acceptors. This follows from the data in Fig. 6 showing the dependence of the experimental ΔH values of the reaction on the estimated values of the enthalpy of formation of the H-complex (ΔH_{bond}) between the solvent and hydroquinone **2**. The estimates of ΔH_{bond} were obtained in the framework of the multiplicative approach to the thermodynamics of hydrogen bonding.[15,16] In this method, the following formula was used for the calculation of ΔH_{bond}:

$$\Delta H_{bond} \text{ (kJ mol}^{-1}) = 4.96 E_a E_d,$$

where E_a and E_d are the enthalpy factors of the H-acceptor (a) (solvent) and H-donor (d) (hydroquinone **2**), respectively. The E_a and E_d factors characterize the relative ability to H-bonding formation with respect to the standard substances, namely, unsubstituted phenol ($E_d = -2.50$ kJ$^{0.5}$ mol$^{-0.5}$) and hexamethylphosphotriamide ($E_a = 2.50$ kJ$^{0.5}$ mol$^{-0.5}$). For other compounds the E_a and E_d values determined from the experimental data are tabulated.[15,16] For CCl_4 $E_a = 0$ (by definition), and for benzene, chlorobenzene, anisole, and benzonitrile $E_a = 0.66$, 0.30, 1.00, and 1.19 kJ$^{0.5}$ mol$^{-0.5}$, respectively; the proton-donating ability of hydroquinone **2** being $E_d = -2.60$ kJ$^{0.5}$ mol$^{-0.5}$.[16]

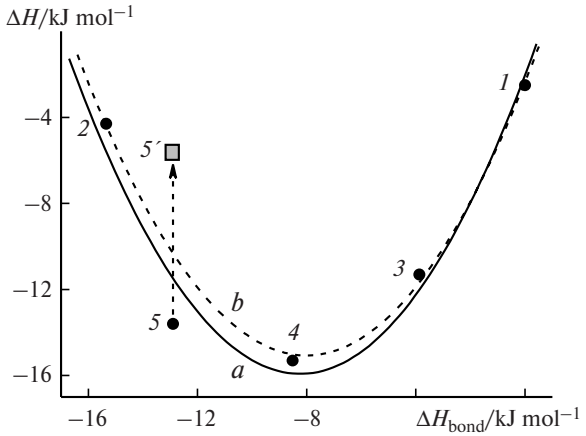


Fig. 6. Plots of ΔH of the reaction **1** + **2** $\rightleftharpoons$ **3** + **4** *vs* enthalpy of hydrogen bonding of hydroquinone **2** with various solvents: *1*, CCl_4; *2*, benzonitrile; *3*, chlorobenzene; *4*, benzene; *5*, anisole (experimental value); *5′*, with allowance for the enthalpy of formation of a donor-acceptor complex of quinone **4** with anisole (−7.9 kJ mol^{-1}); *a* is the parabolic curve $y = 0.205x^2 + 3.37x - 2.03$ approximating all experimental points, and *b* is the parabola $y = 0.198x^2 + 3.18x - 2.35$ constructed ignoring the data on ΔH of the reaction in anisole.

As can be seen from the data in Fig. 6, the experimental data are described by a parabolic function, especially if the results of measurements in anisole are omitted (*cf.* parabolas *a* and *b* in Fig. 6). The vertex of the parabola lies near the values for benzene. The left descending branch contains the values for benzonitrile and anisole (in these solvents the heteroatoms of the substituents are proton acceptors[16]), and the right ascending branch includes the values for chlorobenzene (in which, as in benzene, a system of π-electrons is the proton acceptor[16]) and CCl_4 (in the multiplicative approach, CCl_4 was accepted as the standard "non-solvating" solvent). The dependence of ΔH on ΔH_{bond} for the series of solvents benzonitrile—anisole—benzene agrees with the assumption that in the case of relatively strong hydrogen bonding the reaction enthalpy ΔH depends mainly on the heat of formation of the H-complex of hydroquinone **2** with the solvents (ΔH_{bond}).

The reaction of **1** with **2** proceeds *via* the mechanism of chain reversible reactions. The *K* equilibrium constant of these reactions is equal to the product of the equilibrium constants of the both chain propagation steps,[4] *i.e.*, the *K* value is determined by the rate constants of four elementary reactions. Therefore, it is not surprising that no simple correlations are observed between $\ln K$ and parameters of the solvents. This is exemplified in Fig. 7 by the plots of $\ln K_{298}$ *vs* donor (*DN*) and acceptor (*AN*) numbers of the solvents. The *DN* values were borrowed from Ref. 17, and *AN* were calculated* using the known[18] E_T parameters by the formula[17]

$$AN = -40.52 + 1.29E_T.$$

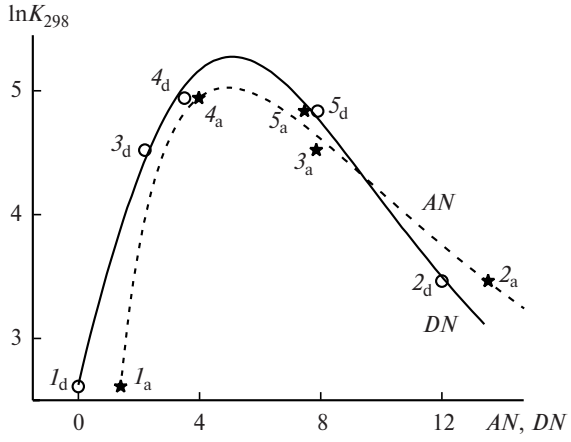


Fig. 7. Plots of $\ln K_{298}$ *vs* donor (*DN*) and acceptor (*AN*) numbers of the solvents: *1*, CCl_4; *2*, benzonitrile; *3*, chlorobenzene; *4*, benzene; *5*, anisole.

* No reliable data on the *AN* values are available for CCl_4.

Note that the plots of $\ln K_{298}$ *vs* dielectric functions (lnε, 1/ε, Kirkwood´s function $(\varepsilon - 1)/(2\varepsilon + 1)$) are also nonlinear and qualitatively resemble the dependence of $\ln K_{298}$ on *DN*. It is seen from the data in Fig. 7 that in a rough approximation one can speak about a weak linear dependence of $\ln K_{298}$ on *AN* for the aromatic solvents, whereas no linear dependence of $\ln K_{298}$ on *DN* is observed for these solvents. The data for CCl_4 deviate strongly from the both dependences. This agrees with the assumption on a substantial difference in the mechanisms of solvation of participants of equilibrium in CCl_4 and aromatic solvents (see Fig. 3).

Thus, this study revealed that the solvent nature exerts rather strong effect on the equilibrium constant and thermodynamic parameters of the chain reversible reaction of quinonediimine **1** with hydroquinone **2**. The solvation effects are caused by several types of intermolecular interactions of participants of equilibrium with the medium. The results obtained indicate that the reactivity of the semiquinone radicals depends on the solvation interactions with the solvent and indicate a possibility of the existence of a strong dependence of the rate constants of elementary steps of chain reversible reactions in quinoneimine—hydroquinone systems on the solvent nature.

This work was financially supported by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (Program No. 1 "Theoretical and Experimental Investigation of the Chemical Bond Nature and Mechanisms of Most Important Chemical Reactions and Processes") and the Project "Development of Mechanisms of Integration of the Bashkir State University, the Institute of Organic Chemistry (Ufa Research Center of the Russian Academy of Sciences), and the Institute of Problems of Chemical Physics (Russian Academy of Sciences)."

References

1. V. T. Varlamov, *Dokl. Akad. Nauk*, 1993, **332**, 457 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
2. V. T. Varlamov, *Kinet. Katal.*, 2001, **42**, 836 [*Kinet. Catal.*, 2001, **42** (Engl. Transl.)].
3. A. V. Antonov and V. T. Varlamov, *Dokl. Akad. Nauk*, 2006, **408**, 63 [*Dokl. Chem.*, 2006 (Engl. Transl.)].
4. V. T. Varlamov, *Dokl. Akad. Nauk*, 2006, **408**, 627 [*Dokl. Chem.*, 2006 (Engl. Transl.)].
5. A. V. Antonov and V. T. Varlamov, *Kinet. Katal.*, 2006, **47**, 541 [*Kinet. Catal.*, 2006, **47** (Engl. Transl.)].
6. A. V. Antonov, S. Ya. Gadomskii, and V. T. Varlamov, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1661 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1723].
7. E. T. Denisov and I. B. Afanas´ev, *Oxidation and Antioxidants in Organic Chemistry and Biology*, Taylor and Francis Group, Boca Raton, Florida, 2005, 981 pp.

8. M. G. Dolson and J. S. Snenton, *J. Am. Chem. Soc.*, 1981, **103**, 2361.
9. A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, *Organic Solvents*, Interscience Publishers, Inc., New York—London, 1955.
10. A. J. Gordon and R. A. Ford, *The Chemist´s Companion*, J. Wiley and Sons, New York—London, 1972.
11. G. A. Krestov, V. N. Afanas´ev, and L. S. Efremova, *Fiziko-khimicheskie svoistva binarnykh rastvoritelei* [*Physicochemical Properties of Binary Solvents*], Khimiya, Leningrad, 1988, 688 pp. (in Russian).
12. L. G. Andrews, *Chem. Rev.*, 1954, **54**, 713.
13. S. P. McGlynn, *Chem. Rev.*, 1958, **58**, 1113.
14. R. Foster, *Organic Charge-Transfer Complexes*, Acad. Press, New York, 1969, 389.
15. O. A. Raevsky, V. Yu. Grigor´ev, D. B. Kireev, and N. S. Zefirov, *Quant. Struct.-Act. Relat.*, 1992, **11**, 49.
16. O. A. Raevsky, V. Yu. Grigor´ev, and S. V. Trepalin, *HYBOT Program Package*, *Registration № 990090 of Russian State Department of Patents and Trade Marks of 10.02.99*, 1999.
17. R. Shmid and V. N. Sapunov, *Neformal´naya kinetika* [*Non-formal Kinetics*], Mir, Moscow, 1985, 263 pp. (in Russian).
18. Yu. Ya. Fialkov, *Rastvoritel´ kak sredstvo upravleniya khimicheskim protsessom* [*Solvent As a Tool for Controlling the Chemical Process*], Khimiya, Leningrad, 1990, 240 pp. (in Russian).

Received April 18, 2007