===== **PHOTOCHEMISTRY** =====

Effect of Solvent Nature on the Photoreduction Kinetics of Substituted Benzoquinones

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Abstract—Effect of the solvent nature on the kinetics of photoreduction of substituted benzoquinones in the presence of hydrogen donors has been studied. It has been found that the effective photoreduction rate constant (k_H) for quinones decreases with an increase in solvent polarity. For the 3,6-di-*tert*-butylbenzoquinone−1,2-*N*,*N*-dimethylaniline pair, the dependence of ln k_H on the difference of the reciprocals of optical and static solvent permitivities ($1/\varepsilon_\infty - 1/\varepsilon_0$) is stepwise with a break point corresponding to CH_2Cl_2. A similar relationship $\ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$ is observed for the *p*-chloranil−mesitylene pair. In the study of the photoreduction kinetics for a series of seven *o*-benzoquinones in the presence of *p*-derivatives of *N*,*N*-dimethylaniline in CH_2Cl_2, it has been found that the dependence of k_H on the free energy of electron transfer (ΔG_e) has a maximum for the 3,6-di-*tert*-butylquinone-1,2−*N*,*N*-dimethylaniline pair at $\Delta G_e = 0.11$ eV.

Keywords: *o*-benzoquinones, *p*-chloranil, *N*,*N*-dimethylanilines, mesitylene, solvent dielectric properties, photoinduced hydrogen transfer, free energy of electron transfer

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Substituted *o*-benzoquinones in combination with H-donating compounds compose systems used for photoinitiation of radical polymerization [1, 2]. The operation of these systems is based on the photoreduction reaction of quinones, during which a photoexcited quinone molecule Q abstracts a hydrogen atom from a donor molecule (DH) to give the semiquinone radical QH˙ and the radical D˙. The latter can initiate radical reactions [3, 4]. Other carbonyl compounds (benzophenones, fluorenones, thioxanthones, camphoroquinone) initiate photopolymerization via a similar mechanism [5−8]. The introduction of organic solvents into photopolymerizing compositions based on *o*-quinone photoinitiators makes it possible to synthesize porous polymeric monoliths [9], to obtain light-induced gradient refractive index structures [10], and to control the viscosity of a polymerization medium. Note that the solvent nature and concentration affect both the polymer formation process and the kinetics of photogeneration of initiating radicals, which is determined by the *o*-benzoquinone photoreduction kinetics. The necessity to predict the effect of solvent on each of these processes, in particular, on the photoinitiation of polymerization makes studying the dependence of the *o*-benzoquinone photoreduction kinetics a quite important task. In this work, we examined the effect of the dielectric parameters of the reaction medium on the photoreduction kinetics of hindered *o*-benzoquinones. For comparison, the photoreduction kinetics of *p*-benzoquinone (*p*-chloranil) was also studied.

EXPERIMENTAL

Absorption spectra were recorded on Specord M-40 and SF-56 spectrophotometers. A KGM-24-150 lamp with a focusing system was used as a light source. In the study of quinone photoreduction kinetics for separation of the light wavelength, ZhS-16 ($\lambda \geq$ 500 nm) and SS-4 ($300 < \lambda < 420$ nm) light filters were used in the cases of *o*-benzoquinone in the presence of *p*-substituted *N*,*N*-dimethylanilines and the *p*-chloranil−mesitylene pair, respectively. The quinone/H-donor reactant molar ratio was 1 : 50. Organic solutions of the reactants were deaerated, saturated with Ar, and poured into a spectrophotometric cell, and the dynamics of evolution of the quinone absorption spectra during irradiation was recorded. Current quinone concentrations were determined by measuring the change in the intensity of the quinone absorption band due to the $S(\pi \rightarrow \pi^*)$ electronic transition. Under experimental conditions at the initial reaction stage until a quinone conversion of 30%, the photoreduction obeys the first-order rate law. The effective rate constant of the quinone photoreduction was determined graphically as the slope of the linear portion of the $\ln([A_0]/[A_\tau]) - \tau$ curve.

o-Benzoquinones were synthesized according to the procedures described elsewhere [11−14]. 2,3,5,6-Tetrachloro-1,4-benzoquinone (*p*-chloranil) was purified by recrystallization from hexane. *N,N*-Dimethylanilines (*N,N*-dimethylaniline (Aldrich), *N,N*-dimethyl-*p*-toluidine (Aldrich), 4-(*N,N*-dimethylamino)benzaldehyde (Fluka), and *N,N*-dimethyl-*p*-methoxyaniline synthesized by a published procedure [15]), mesitylene, and the solvents were purified according to standard procedures [16].

RESULTS AND DISCUSSION

3,6-Di-*tert*-butyl-4-nitro-1,2-benzoquinone (**1a**), 3,6-di-*tert*-butyl-4,5-difluoro-1,2-benzoquinone (**1b**), 3,6-di-*tert*-butyl-4-fluoro-1,2-benzoquinone (**1c**), 3,6-di-*tert*-butyl-4-chloro-1,2-benzoquinone (**1d**), 3,6-di-*tert*-butyl-1,2-benzoquinone (**1e**), 3,6-di-*tert*-butyl-4-methyl-1,2-benzoquinone (**1f**), 3,6-di-*tert*-butyl-4-*n*-propyl-1,2-benzoquinone (**1g**), and 2,3,5,6-tetrachloro-1,4-benzoquinone (*p*-chloranil) (**2**) were examined as photoacceptors. *p*-Substituted *N,N*-dimethylanilines (**3**) and mesitylene (**4**) were used as hydrogen donors.
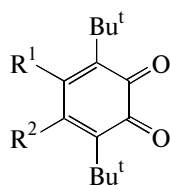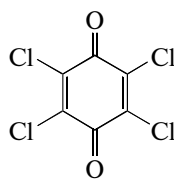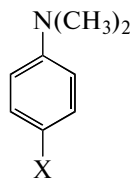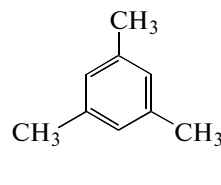

(1)   (2)   (3)   (4)

R^1 = H, R^2 = NO$_2$ (**1a**); R^1 = F (**1b**); R^1 = H, R^2 = F (**1c**); Cl (**1d**); H (**1e**); CH$_3$ (**1f**); Pr^n (**1g**).

X = CH$_3$O (**3a**); CH$_3$ (**3b**); H (**3c**); C(O)H (**3d**).

The effect of solvent nature on the photoreduction rate constant (k_H) was studied for two pairs of the reactants, 3,6-di-*tert*-butyl-1,2-benzoquinone (**1e**)−*N,N*-dimethylaniline (**3c**) and *p*-chloranil (**2**)−mesitylene (**4**). The results are listed in Table 1. The limited set of solvents for the **2−4** pair was due to the fact that some solvents, such as benzene, toluene, diethyl ether, chlorobenzene, and THF, themselves act as an H donor in the *p*-chloranil photoreduction reaction.

As follows from the data presented in Table 1, k_H for the test benzoquinones monotonically decreases with an increase in solvent polarity, with the response of k_H to the polarity of the medium being significantly higher for the *p*-chloranil−mesitylene pair; on passing from CCl$_4$ to DMSO, the value of k_H decreases twelvefold. At the same time, k_H for *o*-quinone **1e** in the presence of **3c** decreases only threefold on passing from benzene to DMSO. Similar results were obtained earlier in a study of the influence of solvent on the rate of photoreduction of 3,6-di-*tert*-butyl-1,2-benzoquinone in the presence of *p*-bromo-*N,N*-dimethylaniline [17].

Although the photoreduction of carbonyl compounds, in particular, *o*- and *p*-benzoquinones is well documented [18], kinetic investigations have been largely focused on elementary steps, such as the formation of the encounter complex [19] and electron [20] and proton [21] transfer, and on the effect of the nature of the reactants and the solvent on the kinetics of these processes [19, 22, 23]. Consider how the

experimental data correspond to the dependence of k_H on the solvent nature predicted within the framework of the model of photoinduced proton transfer proposed in [24−26] as applied to the photoreduction of carbonyl compounds. The essence of this model is as follows. Photoinduced proton transfer involves the

Table 1. Effective rate constants of photoreduction k_H of 3,6-di-*tert*-butyl-1,2-benzoquinone (**1e**) in the presence of *N,N*-dimethylaniline (**3c**) and *p*-chloranil (**2**) in the presence of mesitylene (**4**) in different solvents

Solvent	ε	1e−3c	2−4
		$k_H \times 10^3$ (s^{-1})	$k_H \times 10^4$ (s^{-1})
CCl$_4$	2.23	–	3.20
PhH	2.28	5.16	–
PhCH$_3$	2.38	5.20	–
Et$_2$O	4.34	3.70	–
CHCL$_3$	4.70	4.53	1.48
PhCl	5.62	4.45	–
THF	7.32	4.28	–
CH$_2$Cl$_2$	8.90	4.61	0.12
CH$_2$ClCH$_2$Cl	10.4	–	1.45
CH$_3$CN	36.2	1.76	–
DMF	36.7	2.27	–
DMSO	49.0	1.43	0.16

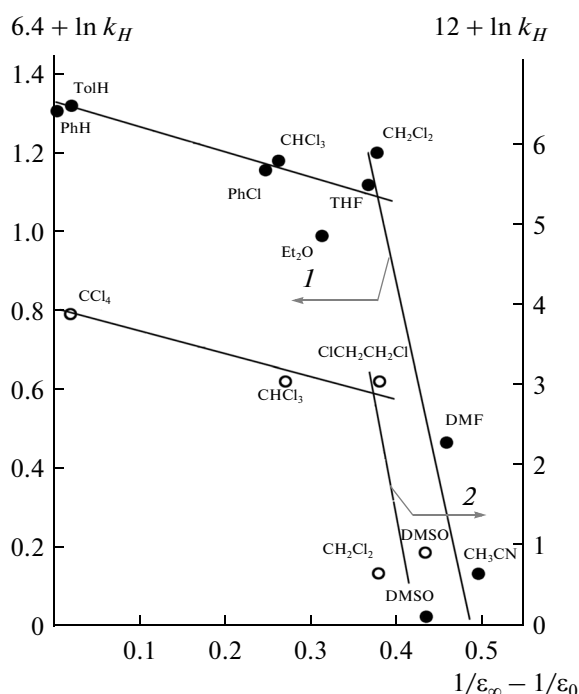$6.4 + \ln k_H$ $12 + \ln k_H$

Fig. 1. Effect of dielectric parameters of the medium on the effective rate constant of photoreduction of (**1**) 3,6-di-*tert*-butyl-1,2-benzoquinone (**1e**) in the presence of *N,N*-dimethylaniline (**3c**) and (**2**) *p*-chloranil (**2**) in the presence of mesitylene (**4**) at 298 K.

successive steps of the formation of the encounter complex (EC), electron transfer to give a radical—ion pair (RIP), and proton transfer to give a radical pair (RP). Each reactant pair (A—DH) is characterized by EC, RIP, and RP energies. On passing from one reactant pair to another in a narrow set of reactants of the same type, when A or DH = const, the position of the RIP energy level changes relative to constant levels of EC and RP. Thus, it follows that the activation energy of the overall process is equal either to the activation energy of electron transfer or that of proton transfer, depending on the redox parameters of A and DH. In accordance with the rate-limiting step, k_H is equal to either electron transfer or proton transfer rate constant k_e or k_{H^+}, respectively. The reaction rate-limiting step changes when the electron and proton transfer activation energies become equal to one another. The dependence of k_H on the free energy of electron transfer (ΔG_e) is nonmonotonic, a behavior that is due to the change in the position of the energy level of the intermediate state (RIP) of the system relative to the fixed energy levels of the initial and final states (EC and RP). The $k_H = f(\Delta G_e)$ curve has two branches, the right branch is determined by the dependence of the electron transfer rate constant k_e on ΔG_e, and the left one is determined by the dependence of the proton transfer rate constant k_{H^+} on $f(\Delta G_e)$. The position of the maximum of the function $k_H = f(\Delta G_e)$ on the ΔG_e scale is determined by the difference Δ of the energies

of the final (RP) and initial (EC) states of the system. The expression for k_H is written as a function of ΔG_e, hydrogen atom transfer energy Δ, and reorganization energy λ (1):

$$k_H = k_0 \exp\left(-\left(\lambda + |\Delta G_e - \Delta|\right)^2\right)\big/ 4\lambda RT. \qquad (1)$$

As follows from Eq. (1), the value of k_H should decrease with an increase in λ. At $\Delta G_e \to \Delta$, Eq. (1) is simplified to Eq. (2), according to which k_H is a function of λ only:

$$\ln k_{H(\Delta G_e \to 0)} = A - \lambda/4RT. \qquad (2)$$

The reorganization energy that accompanies electron transfer is an additive quantity and consists of two parts λ_{In} and λ_{out}. The former refers to internal oscillations of the two reactants ("inner-sphere" interaction), and the latter refers to solvent repolarization causing electron transfer ("outer-sphere" contribution). Within the same pair of reactants, the value of λ_{In} should be constant and should not depend on the solvent. The energy required for the reorganization of the solvation shell outside the coordination sphere of the reactants λ_{out} is associated with a change in atomic and orientation polarization of the medium and is defined by Eq. (3):

$$\lambda_{out} = e^2 \left(1/\varepsilon_\infty - 1/\varepsilon_0\right)\left(1/2a_A + 1/2a_{DH} - 1/d\right), \qquad (3)$$

where e is the electron charge; ε_∞ is the optical (high-frequency) dielectric permittivity equal to the squared refractive index n_D^2; ε_0 is the static dielectric permittivity (dielectric permittivity in constant field); a_A and a_{AD} are the acceptor and donor radii, respectively; and d is the distance between the centers in the encounter complex during electron transfer. From Eq. (3) it follows that λ_{out} should increase with an increase in solvent polarity. The dependence of $k_{H(\Delta G_e \to 0)}$ on the solvent dielectric parameters can be found by substitution Eq. (3) into Eq. (2). Thus, Eqs. (4) and (5) are obtained, which define $\ln k_{H(\Delta G_e \to 0)}$ is a linear function of $(1/\varepsilon_\infty - 1/\varepsilon_0)$ at values of ΔG_e close to Δ:

$$\ln k_{H(\Delta G_e \to 0)} = A - \lambda_{In}/4RT - e^2\left(1/\varepsilon_\infty - 1/\varepsilon_0\right) \\ \times \left(1/2a_A + 1/2a_{DH} - 1/d\right)/4RT \qquad (4)$$

$$\text{or } \ln k_{H(\Delta G_e \to 0)} = A - B\left(1/\varepsilon_\infty - 1/\varepsilon_0\right). \qquad (5)$$

Equation (5) suggests that for the same pair of reactants with $\Delta G_e \to \Delta$, the decrement in $\ln \ln k_{H(\Delta G_e \to 0)}$ should be proportional to the increment in $(1/\varepsilon_\infty - 1/\varepsilon_0)$. According to previously published data [26], the value of Δ calculated for the 3,6-di-*tert*-butylbenzoquinone—*N,N*-dimethylaniline system is +0.12 eV. For the pair of reactants **1e**—**3c**, $\Delta G_e = +0.11$ eV. The experimental relationships $\ln k_H = \ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$ for **1e**—**3c** are shown in Fig. 1. The value of $\ln k_H$ for pair **1e**—**3c** (Fig. 1, curve *I*) decreases proportionally to $(1/\varepsilon_\infty - 1/\varepsilon_0)$ in the $(1/\varepsilon_\infty - 1/\varepsilon_0)$ range of 0.005 (ben-

zene) to 0.381 (dichloromethane). At $(1/\varepsilon_\infty - 1/\varepsilon_0) > 0.38$ (acetonitrile, DMF, DMSO), the values of $\ln k_H$ dramatically drops. The relationship for the *p*-chloranil–mesitylene pair is similar (Fig. 1, curve *2*).

In order to determine the cause of deviation from linearity in the experimental relation $\ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$, it is necessary to compare the $k_H = f(\Delta G_e)$ curves for the *o*-benzoquinones–*p*-substituted *N,N*-dimethylanilines system in three ranges of the function $\ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$, namely, in the break point at $(1/\varepsilon_\infty - 1/\varepsilon_0) \approx 0.38$ and on each side of this point. The relationships $k_H = f(\Delta G_e)$ in toluene and acetonitrile, for which the parameter $(1/\varepsilon_\infty - 1/\varepsilon_0)$ is 0.02 and 0.49, respectively, were obtained earlier [27]. The results of the study of the photoreduction kinetics of *o*-benzoquinones in the presence of **3a–3d** in dichloromethane are presented in Table 2. The reduction potentials for *o*-benzoquinones are taken as given in [28]. The value of ΔG_e for each pair of the reactants was calculated by Eq. (6) [29]:

$$\Delta G_e = -\Delta E_{00} - E\left(A^{\cdot-}/A\right) + E\left(DH/DH^{\cdot+}\right) - T\Delta S_e + 0.13 \text{ eV}, \quad (6)$$

where ΔE_{00} is the energy of the $0 \rightarrow 0$ transition triplet of the lowest excited state of a carbonyl compound; $E(A^{\cdot-}/A)$ and $E(DH/DH^{\cdot+})$ are the redox potentials of the acceptor and the donor, respectively; and ΔS_e is the entropy change in the formation of the charge transfer complex. The value $T\Delta S_e \approx -0.23$ eV was used [30].

Figure 2 shows the $k_H = f(\Delta G_e)$ *o* relations for *o*-benzoquinones in toluene (*1*), (k_H maximum is at $\Delta G_e = 0.09$ eV), dichloromethane (*2*) (k_H maximum is at $\Delta G_e = 0.11$ eV), and acetonitrile (*3*) (k_H maximum is at $\Delta G_e \sim 0.15$ eV). The experimental data points form three similar pike-shaped curves embedded in one another. The "intensity" of the peaks decreases with an increase in solvent polarity. It interesting that on passing from one solvent to another, the right and left branches of the $k_H = f(\Delta G_e)$ curves behave differently. The left branch successively shifts to the right on passing from toluene to dichloromethane and further to acetonitrile. On the contrary, the right branch of the curve shifts significantly to the left only on passing from toluene to dichloromethane. The difference between the right branches of the curves in dichloromethane and acetonitrile is insignificant. The asymmetry of the shift for the branches of the $k_H = f(\Delta G_e)$ curves upon the solvent replacement can result from the difference in the reaction rate-limiting step for the reactant pairs in the different branches of the curve. The main changes of the right branch of the $k_H = k_H = f(\Delta G_e)$ curve (electron transfer is the reaction rate-limiting step) must occur on passing from toluene to dichloromethane. This is due to the fact that k_e depends on $(1/\varepsilon_\infty - 1/\varepsilon_0)$, and the difference of the values of $(1/\varepsilon_\infty - 1/\varepsilon_0)$ for dichloromethane and toluene is

Table 2. Effective rate constants of photoreduction k_H for *o*-benzoquinones **1a–1g** in the presence of *p*-substituted *N,N*-dimethylanilines **3a–3d** and calculated values of ΔG_e

Quinone–Amine	ΔG_e, EV	$k_H \times 10^3$, s^{-1}
1a–3c	−0.18	0.35
1e–3a	−0.11	0.89
1a–3d	−0.05	1.60
1g–3a	0.01	0.82
1e–3b	0.05	2.30
1b–3c	0.06	1.69
1c–3c	0.06	3.46
1c–3b	0.09	1.10
1d–3c	0.09	3.17
1e–3c	0.11	4.61
1f–3b	0.15	1.17
1g–3b	0.17	0.48
1c–3d	0.19	0.73
1d–3d	0.22	0.28

two times that for acetonitrile and dichloromethane (0.354 and 0.145, respectively). The nonuniform "countercurrent" motion of the right and left
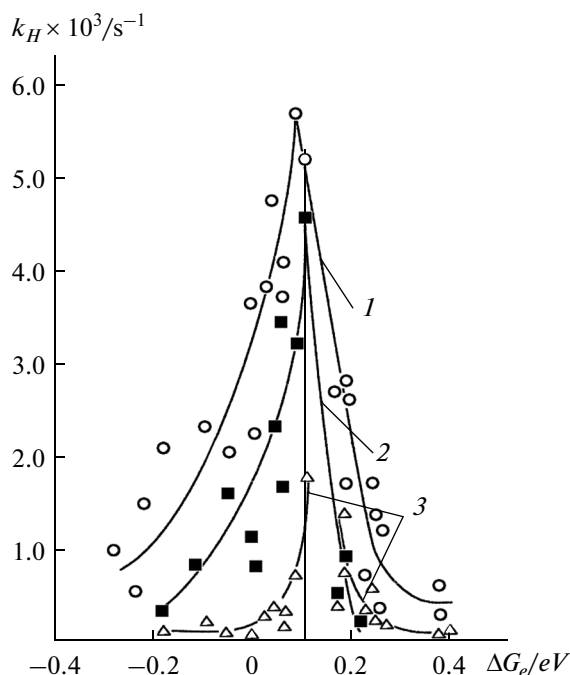

Fig. 2. Effective rate constant k_H as a function of ΔG_e for the photoreduction of *o*-benzoquinones (**1a–1g**) in the presence of *p*-substituted dimethylanilines (**3a–1d**) in (*1*) toluene [27], (*2*) dichloromethane, and (*3*) acetonitrile [27] at 298 K.

branches of the $k_H = f(\Delta G_e)$ curve with an increase in solvent polarity results in the shift of the k_H maximum to the endothermic range of ΔG_e. The point corresponding to k_H for pair **1e–3c** (**1e–3c** ($\Delta G_e = 0.11$ eV) in toluene lies on the right branch of the $k_H = f(\Delta G_e)$ curve. In dichloromethane, this point is in the maximum of the curve; i.e. it also belongs to the right branch of the curve; but in the case of acetonitrile, it is already in the left branch of the curve (for clearness, this metamorphosis is illustrated in Fig. 2 by a vertical line corresponding to $\Delta G_e = 0.11$ eV). It may be assumed that this crossover from one branch to the other accounts for the break on the linear dependence $\ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$ (Fig. 1)., Since the rate of photoreduction of **1e** in the presence of **3c** is determined by proton, rather than electron transfer at $(1/\varepsilon_\infty - 1/\varepsilon_0) > 0.38$, the function $\ln k_H = (1/\varepsilon_\infty - 1/\varepsilon_0)$ losses its meaning and the dependence of k_H on the dielectric parameters of the medium should be different. Regarding the stepwise relationship $\ln k_H = f(1/\varepsilon_\infty - 1/\varepsilon_0)$ for the reaction pair **2–4**, it may be assumed that the reason for its appearance is the same as for the **1e–3c** pair.

In summary, the following conclusions can be made. An increase in solvent polarity results in a decrease in k_H of photoreduction of *o*-benzoquinones and *p*-chloranil. For 3,6-di-*tert*-butylbenzoquinone-1,2 and chloranil, the dependence of k_H on the dielectric permittivity of the medium is stepwise. At $\varepsilon \sim 10$, k_H abruptly decreases, a fall that is presumably due to the change of the rate-limiting step.

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