Kinetics of photoreduction of 9,10-phenanthrenequinone in the presence of amines and polymethylbenzenes

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A study of the kinetics of photoreduction of 9,10-phenanthrenequinone in the presence of hydrogen donors (*para*-substituted *N*,*N*-dimethylanilines and polymethylbenzenes) showed that plots of the quantum yield of photoreduction (φ_H) and apparent reaction rate constant (k_H) vs. oxidation potential of hydrogen donors are extreme. In the presence of amines, k_H and φ_H increase, as a whole, whereas they decrease in the presence of polymethylbenzenes. In coordinates $\varphi_H - \Delta G_e$ (ΔG_e is the change in the free energy of electron transfer) for pairs quinone—H donor, φ_H increases with ΔG_e approaching to zero. For the amine series, this effect is mainly in the exothermic region of ΔG_e ($\Delta G_e > 0$).

Key words: 9,10-phenanthrenequinone, hydrogen phototransfer, free energy of electron transfer, N, N-dimethylanilines, polymethylbenzenes.

Operation of various technical and biological photosensitive systems is based on the photoinduced electron and hydrogen transfer involving carbonyl-containing compounds.^{1,2} However, only few systematic studies of the influence of the nature of reactants on the kinetics of photoreduction reactions are known, and their results are ambiguous. For instance, it has been found by the nanosecond laser photolysis technique for the kinetics of photoreduction of a series of *p*-benzoquinones in the presence of 4-phenylaniline³ that the rate constant of quinone photoreduction $k_{\rm H}$ decreases with an increase in the electron-acceptor ability of the quinones. Similarly, for the *p*-benzoquinone—diphenylamine system,⁴ the calculated $k_{\rm H}$ values decrease with an increase in the reduction potential of the quinone in the duroquinone—*p*-choloranil series. At the same time, when the triplet state of anthanthrone is quenched with anilines or phenols, ${}^{5}k_{\rm H}$ increases with a decrease in the oxidation potential of amine and phenol, and the $\log k_{\rm H} = f(E_{1/2(\rm DH)})$ plots are linear in both cases. As follows from these examples, the facilitation of an electron transfer due to an enhancement of the electron-withdrawing^{3,4} or electron-releasing⁵ properties of reactants can change $k_{\rm H}$ in opposite directions. A study of the plots of the quantum yield ($\varphi_{\rm H}$) of fluorenone photoreduction in the presence of a wide series of p-substituted N,N-dimethylanilines (from 4-nitrile-N,N-dimethylaniline to N, N, N', N'-tetramethyl-p-phenylenediamine) showed⁶ that φ_H changed extremely with a change in the electron-releasing properties of the amine. A study of the photoreduction of similar in structure o-benzoquinones in the presence of N, N-dimethylanilines found⁷ that the plot of the apparent rate constant of photoreduction $k_{\rm H}$ vs. half-wave potential $E_{1/2}$ of the polarographic reduction of the quinones also has an extreme. Researchers are interested in studying the kinetics of photoreduction of other photoacceptors because of extreme plots of $\varphi_{\rm H}$ or $k_{\rm H}$ vs. redox characteristics of reactants in systems containing fluorenone and o-benzoquinones—N, N-dimethylanilines.

In this work, we studied the kinetics of photoreduction of 9,10-phenanthrenequinone in the presence of various hydrogen donors: *p*-substituted *N*,*N*-dimethylanilines and polymethylbenzenes.

Experimental

Electronic absorption spectra were recorded on Perkin—Elmer Lambda-25 and SF-14 spectrophotometers in benzene. NMR spectra were obtained on a Bruker DPX-200 spectrometer.

9,10-Phenanthrenequinone (1) (Aldrich) was recrystallized from methanol. Toluene (2a) (Reakhim), 1,2-dimethylbenzene (o-xylene) (2b) (Reakhim), 1,4-dimethylbenzene (p-xylene) (2c) (Reakhim), 1,3,5-trimethylbenzene (mesitylene) (2d) (Reakhim), 1,2,4,5-tetramethylbenzene (durene) (2e) (Reakhim), hexamethylbenzene (2f) (Aldrich), and benzene used as solvent were purified according to standard procedures.⁸ N, N, N', N'-Tetramethyl-p-phenylenediamine (3a) (Fluka) and 4-nitrile-N, N-dimethylaniline (3g) (Fluka) were purified by double sublimation. 4-Methyl-N, N-dimethylaniline (3c) (Aldrich) and N, N-dimethylaniline (3d) (Aldrich) were distilled.

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4-Formyl-N,N-dimethylaniline (**3e**) (Fluka) and 4-bromo-N,N-dimethylaniline (**3f**) (Aldrich) were recrystallized from hexane. 4-Methoxy-N,N-dimethylaniline (**3b**) was synthesized by a known procedure.⁹

9-Hydroxy-9-(3',5'-dimethylbenzyl)-10-oxo-9,10-dihydrophenanthrene was synthesized according to a previously described procedure.¹⁰ ¹H NMR (CDCl₃), δ : 2.19 (s, 6 H, CH₃); 2.92, 3.00 (both d, 1 H each, CH₂, J = 13 Hz); 3.99 (s, 1 H, OH); 6.43 (s, 2 H, CH(2'), CH(6')); 6.81 (s, 1 H, CH(4')); 7.38–7.95 (m, 8 H, CH(1), CH(2), CH(3), CH(4), CH(5), CH(6), CH(7), CH(8)).

9-Hydroxy-9-[(*N*-phenyl-*N*-methyl)-aminomethyl]-10-oxo-**9,10-dihydrophenanthrene.** ¹H NMR (C_6D_6), δ : 2.55 (s, 3 H, NCH₃); 3.47 and 3.62 (both d, 1 H each, C(9)CH₂N, J = 15 Hz); 4.53 (br.s, 1 H, OH), signals of aromatic protons overlap with the corresponding signals of the starting substances.

Quantum yields of photoreduction of 9,10-phenanthrenequinone in the presence of polymethylbenzenes and p-substituted N,N-dimethylanilines were determined using a standard actinometer (potassium ferrioxalate). A benzene solution (4.4 mL) containing 9,10-phenanthrenequinone $(1 \cdot 10^{-3} \text{ mol } L^{-1})$ and a hydrogen donor $(5 \cdot 10^{-2} \text{ mol } L^{-1})$ was deaerated, saturated with argon, and placed in a quartz cell 1 cm thick. The solution was irradiated with a monochromatic light of $\lambda = 412$ nm, which was isolated from the full light flux of an KGM-24-150 lamp using an interference light filter no. 10. The intensity measurement of the monochromatic light and experimental runs were carried out according to a known procedure.² The intensity of irradiation with the monochromatic light $\lambda = 412$ nm was $1.53 \cdot 10^{-9}$ Einstein s⁻¹. Quantum yields were measured from a decrease in the intensity of the absorption band of 9,10-phenanthrenequinone ($\lambda = 410 \text{ nm}, \epsilon = 2200 \text{ L mol}^{-1} \text{ cm}^{-1}$).

Apparent rate constants of photoreduction of 9,10-phenanthrenequinone in the presence of p-substituted N,N-dimethylanilines and polymethylbenzenes were determined spectrophotometrically. A benzene solution (5 mL) containing 9,10-phenanthrenequinone $(4.2 \cdot 10^{-4} \text{ mol } \text{L}^{-1})$ and a hydrogen donor $(2.1 \cdot 10^{-2} \text{ mol } \text{L}^{-1})$ was deaerated, saturated with argon, placed in a spectrophotometric cell 0.5 cm thick, and exposed at a distance of 6 cm from the collimator of an illuminator with an KGM-24-150 lamp. The radiation with $\lambda < 430$ nm was isolated from the light flux of the illuminator with an SS-5 light filter. Current concentrations of 9,10-phenanthrenequinone were detected by a change in the intensity of the absorption band of quinone ($\lambda = 412$ nm. $\varepsilon = 2200$ L mol⁻¹ cm⁻¹) according to the Lambert-Bouger-Beer law. Under experimental conditions. the photoreduction obeys a first-order kinetic equation in the initial reaction step until a conversion of quinone of ~30%. The apparent rate constant of quinone photoreduction was determined from the slope ratio of the linear region of the $\ln([A_0]/[A_\tau]) - \tau$ plot, where τ is the total time of irradiation of the solution. The numerical value of the apparent rate constant was averaged by three measurements with convergence of results within 5%.

Results and Discussion

The visible light irradiation of benzene solutions of 9,10-phenanthrenequinone (1) and polymethylbenzenes (2) or *para*-substituted N,N-dimethylanilines (3) changes



Fig. 1. Spectral changes upon irradiation with the light $\lambda < 430$ nm at equal time intervals (40 s) of a solution of 9,10-phenanthrenequinone (4.2 · 10⁻⁴ mol L⁻¹) and mesitylene (2.1 · 10⁻² mol L⁻¹) in benzene (deaerated solution was saturated with Ar, 298 K).



Fig. 2. Spectral changes upon irradiation with the light $\lambda < 430$ nm at equal time intervals (40 s) of a solution of 9,10-phenanthrenequinone ($4.2 \cdot 10^{-4} \mod L^{-1}$) and *N*,*N*-dimethylaniline ($2.1 \cdot 10^{-2} \mod L^{-1}$) in benzene (deaerated solution was saturated with Ar, 298 K).

the color of solution due to the photoreduction of **1**. The changes in the spectral characteristics of **1** and **2d**, as well as **1** and **3a**, in benzene upon irradiation with the light $\lambda < 430$ nm at equal time intervals are presented in Figs. 1 and 2, respectively, as typical examples. It is seen that a decrease in the absorption band intensity of the quinone at 410 nm is accompanied by an increase in the absorbance of the solutions in the UV spectral region, and distinct isosbestic points are observed in both cases.

The main product of photoreduction of phenanthrenequionone 1 in the presence of arenes 2 is the corresponding ketol,¹⁰ which was confirmed by the analysis of the products of photointeraction of compounds 1 and 2d (see Experimental). The NMR study of the products of reaction of 1 with 3d showed the formation of ketol 9-hydroxy-



n = 1 (2a), 2 (2b, *o*-xylene), 2 (2c, *p*-xylene), 3 (2d, mesitylene), 4 (2e, durene), 6 (2f)

 $R = NMe_2$ (3a), OMe (3b), Me (3c), H (3d), C(O)H (3e),

Br (3f), CN (3g)

9-[(*N*-phenyl-*N*-methyl)aminomethyl]-10-oxo-9,10-dihydrophenanthrene. Protons of the methylene group linked with the asymmetric C(9) atom are nonequivalent. In the NMR spectrum, the methylene group looks like an AB multiplet with the center at 3.54 ppm and a spin-spin coupling constant characteristic of geminal protons of 15 Hz.

For the photoreduction of 9,10-phenanthrenequinone, as in the case of other carbonyl-containing compounds,^{2,11,12} the lowest excited triplet state is active (quinone molecule transits to this state from the $S(\pi\pi^*)$ and $S(n\pi^*)$ states).¹³ In the electronic absorption spectrum of 9,10-phenanthrenequinone, the bands corresponding to electron transitions $S(\pi \rightarrow \pi^*)$ and $S(n \rightarrow \pi^*)$ have maxima at 410 and 510 nm.¹ It is convenient to monitor the reaction course by a decrease in the intensity of the absorption band of 1 ($\lambda_{max} = 410 \text{ nm}$), whose molar absorption coefficient in benzene is 2200 L mol⁻¹ cm⁻¹. Ketols have light yellow color.¹⁰ For instance, the electronic absorption spectrum of the product of the reaction of compounds 1 and 2d (9-hydroxy-9-(3',5'-dimethylbenzyl)-10-oxo-9,10-dihydrophenanthrene) in benzene contains an unresolved band in the visible region with the red boundary at 500 nm. The molar absorption coefficient of this absorption band at $\lambda = 410$ nm is equal to $12 \text{ L} \text{ mol}^{-1} \text{ cm}^{-1}$. This value is two orders of magnitude lower than the molar absorption coefficient of 9,10-phenanthrenequinone, which makes it possible to study spectrophotometrically the kinetics of photoreduction of phenanthrenequinone 1 in the presence of polymethylbenzenes 2 and 3 from a decrease in the absorption band of **1** at $\lambda_{max} = 410$ nm.

The photoreduction of phenanthrenequinone 1 in the presence of compounds 2 and 3 was studied using irradiation of reactant solutions with the light $\lambda < 430$ nm (see Experimental). The oxidation potentials of H donors and the quantum yields and apparent rate constants of photoreduction of 1 in the presence of 2a–f and 3a–g for each pair of reactants are presented in Table 1 (oxidation potentials of dimethylanilines 3a–d,g against saturated calomel electrode were taken from Ref. 14). The $E_{1/2(DH/DH^{+})}$ value for compound 3e was calculated from

Table 1. Oxidation potentials of polymethylbenzenes 2 and *para*-substituted *N*,*N*-dimethylanilines 3 ($E_{1/2(DH/DH^{+}+)}$) and experimental values of the quantum yield (φ_H) and apparent rate constant of photoreduction (k_H) of 9,10-phenanthrene-quinone 1 in the presence of the hydrogen donors

Hydrogen donor	$E_{1/2(\text{DH/DH}^{+})}/\text{V}$	$\boldsymbol{\phi}_{H}$	k_{H} · 10 ³ /s ⁻¹
2a	2.28	0.03	0.27
2b	1.87	0.10	0.75
2c	1.86	0.15	0.67
2d	1.85	0.14	0.91
2e	1.59	0.34	1.37
2f	1.46	0.43	3.30
3g	1.12	0.70	4.37
3f	0.86	0.41	3.20
3e	0.84	0.63	3.24
3d	0.71	0.53	1.90
3c	0.65	0.41	1.55
3b	0.49	~0	0.04
3a	0.16	~0	0.003

Note. Exposure conditions are given in the text, C_6H_6 , 298 K.

linear plots of $E_{1/2(DH/DH^{++})}$ vs Hammett σ_p constants for the substituents in an N,N-dimethylaniline molecule.⁷ The oxidation potentials of polymethylbenzenes were obtained by reducing the tabulated $E_{1/2(DH/DH^{++})}$ values¹⁴ to the potential against SCE in an 0.5 *M* solution of NaClO₄ in acetonitrile.

In Table 1, hydrogen donors are arranged in an order of increasing their electron-donor ability: from toluene to hexamethylbenzene in the series of compounds 2 and from *p*-nitrile-N, N-dimethylaniline to N, N, N', N'-tetramethyl-*p*-phenylenediamine in the series of compounds 3. For polymethylbenzenes, the $\varphi_{\rm H}$ and $k_{\rm H}$ values increase successively on going from toluene to hexamethylbenzene. This can be caused by an increase in the number of hydrogen atoms in molecules of compounds of the studied series of H donors. For instance, the quantum yields of photoreduction of 2,3,5,6-tetrachloro-1,4-benzoquinone in the presence of 1-methylnaphthalene and 1,4-dimethylnaphthalene differ by ~2 times.¹⁵ However, the $\phi_{\rm H}$ and $k_{\rm H}$ values normalized to the number of hydrogen atoms in a polymethylbenzene molecule also increase by 2.4 and 2 times on going from 2a to 2f, respectively. It is most likely that for the reaction under study $\varphi_{\rm H}$ and $k_{\rm H}$ depend on both the number of hydrogen atoms in a hydrogen donor molecule and its redox characteristics. When the oxidation potential of compound 2 decreases, the efficiency of polymethylbenzenes as H donors increases.

In *N*,*N*-dimethylanilines, on going from one amine to another, the reaction center (dimethylamino group) remains unchanged, providing a more correct analysis of the plots of $\varphi_{\rm H}$ and $k_{\rm H}$ vs. electron-donor ability of amines **3**. It follows from the data presented that a de-

crease in the oxidation potential $E_{1/2(DH/DH^{+})}$ of amine is accompanied by a decrease in the $\varphi_{\rm H}$ and $k_{\rm H}$ values. The φ_H value for **3f**, which is lower than the expected value likely due to the influence of the Br atom on the lifetime of an excited complex between reactant molecules, does not obey the monotonic plot $\varphi_{\rm H}$ = $f(E_{1/2(DH/DH^{+})})$. As a whole, the plots $\varphi_{H} =$ $f(E_{1/2(\text{DH/DH}^{+})})$ and $k_{\text{H}} = f(E_{1/2(\text{DH/DH}^{+})})$ are S-like. For $E_{1/2(DH/DH^{+})} < 0.5$ V and $E_{1/2(DH/DH^{+})} > 0.8$ V, the $\varphi_{\rm H}$ and $k_{\rm H}$ values are minimum and maximum, respectively, and they change sharply in the interval 0.5 < $E_{1/2(\mathrm{DH/DH}^{+})}$ < 0.8 V. The plots ϕ_{H} = $f(E_{1/2(\text{DH/DH}^{+})})$ and $k_{\text{H}} = f(E_{1/2(\text{DH/DH}^{+})})$ are close for both systems 1-2 and 1-3, which makes it possible to use both experimentally determined parameters ϕ_H and $k_{\rm H}$ to describe the kinetic relations of 9,10-phenanthrenequinone photoreduction.

If $\varphi_{\rm H}$ is considered as a function of $E_{1/2(\rm DH/DH^{+})}$, ignoring differences in the nature of H donors, then the resulting experimental data form, as a whole, a wave-like relation $\varphi_{\rm H} = f(E_{1/2(\rm DH/DH^{+})})$. The plots $\varphi_{\rm H} = f(E_{1/2(\rm DH/DH^{+})})$ are inverse in two regions of values of the oxidation potentials of H donors. At $E_{1/2(\text{DH/DH}^{+})} < +1.12$ V the quantum yield of photoreduction of 1 increases with an increase in $E_{1/2(DH/DH^{+})}$, and at $E_{1/2(DH/DH^{+})} > +1.46 \text{ V} \varphi_{\text{H}}$ decreases. For the systems of reactants 1-2 and 1-3, the change in the character of the $\varphi_{\rm H} = f(E_{1/2(\rm DH/DH^{+})})$ plot coincides with a change in the nature of the H donor and can be explained by this fact. At the same time, for the fluorenone-3 system, this change is observed within the series of N, N-dimethylanilines in an interval of $E_{1/2(\text{DH/DH}^{+})}$ from +0.16 to +1.12 V;⁶ the plot of φ_{H} vs. $E_{1/2(DH/DH^{+})}$ is extreme with a maximum at $E_{1/2(DH/DH^{+})} = +0.65 \text{ V}$ (3c). A similar curve $k_{\text{H}} =$ $f(E_{1/2(DH/DH^{+})})$ was obtained for the photoreduction of 2,3,5,6-tetrachloro-1,4-benzoquinone in the presence of **2**: with an increase in $E_{1/2(DH/DH^{+})}$ from +1.46 V (**2f**) to +1.85 V (2d), $k_{\rm H}$ increase, whereas further they decrease sharply on going to xylenes and toluene,¹⁶ and the maximum of $k_{\rm H}$ corresponds to $E_{1/2(\rm DH/DH^{+})} \approx +1.85$ V. Thus, the plots of $\varphi_{\rm H}$ and/or $k_{\rm H}$ vs. $E_{1/2({\rm DH}/{\rm DH}^{+})}$ for 9,10-phenanthrenequinone, fluorenone, and 2,3,5,6-tetrachloro-1,4-benzoquinone are extreme. The position of the maximum is determined by the photoacceptor nature. For 9,10-phenanthrenequinone, it lies at $E_{1/2(DH/DH^{+})} \approx$ +1.12 V; for fluorenone, in a region of $E_{1/2(\text{DH/DH}^{+})} \approx$ +0.65 V; for 2,3,5,6-tetrachloro-1,4-benzoquinone, in a region of $E_{1/2(\text{DH/DH}^{+})} \approx +1.85 \text{ V}.$

As found by numerous studies, carbonyl-containing compounds are characterized, on the one hand, by efficient photoreduction and, on the other hand, by the "Rehm—Weller dependence" ¹⁷ between the logarithm of the quenching rate constant of ³A* and the free energy of electron transfer $\log kq = f(\Delta G_e)^{18-20}$ (A is benzoquinone

and its analogs, *viz.*, *o*- and *p*-quinones, including 1). This indicates that the hydrogen phototransfer reaction involving these photoacceptors proceeds through the photoinduced electron transfer from DH to ${}^{3}A^{*}$ to form intermediate radical ion products. Direct proofs for the stepwise character of the photoreduction were obtained from the picosecond photolysis study of the "classical" system benzophenone—*N*,*N*-dimethylaniline (BP—DMA).^{21,22} This mechanism of hydrogen transfer for the photoreduction of carbonyl-containing compounds was proposed and discussed in earlier studies.^{6,15,18,19,23}

It seems reasonable to consider a relation between the kinetic parameters of photoreduction and $\Delta G_{\rm e}$ due to the presence of an electron transfer step. The $\Delta G_{\rm e}$ value includes the energy of the excited state of a photoacceptor E_{00} and redox characteristics of a photoacceptor and H donor^{24,25}

$$\Delta G_{\rm e} = -\Delta E_{00} - E_{1/2(\rm A} \cdot -_{\rm /A}) + E_{1/2(\rm DH/DH} \cdot +_{\rm)} - - T\Delta S_{\rm e} + 0.13 \text{ eV}, \qquad (1)$$

where ΔE_{00} is the energy of the triplet $0 \rightarrow 0$ transition of the lowest excited state of a carbonyl-containing compound, $E_{1/2(A^{*}-/A)}$ is the redox potential of an acceptor, and ΔS_e is the entropy change upon the formation of a charge-transfer complex (contact radical ion pair). The following characteristics of 9,10-phenanthrenequinone were used for the calculation of ΔG_e : $\Delta E_{00} = 2.12 \text{ eV}$,²⁶ $E_{1/2(A^{*}-/A)} = -0.66 \text{ eV}$,¹⁴ and $T\Delta S_e \approx -0.23 \text{ eV}$ obtained²⁴ for quenching excited states of aromatic hydrocarbons in the presence of *N*,*N*-diethylaniline.

The plot $\varphi_{\rm H} = f(\Delta G_{\rm e})$ is presented in Fig. 3. The $\Delta G_{\rm e}$ value varies from -0.96 eV to +1.17 eV. Reaction pairs **1**-3 exist in the endothermic region of $\Delta G_{\rm e}$ values,



Fig. 3. Quantum yield ($\varphi_{\rm H}$) of photoreduction of 9,10-phenanthrenequinone in the presence of *N*,*N*-dimethylanilines (*1*) and polymethylbenzenes (*2*) as a function of the free energy of electron transfer ($\Delta G_{\rm e}$) (irradiation with the light $\lambda = 412$ nm, benzene, 298 K).

while the exothermic region contains reaction pairs 1–2. As $\Delta G_{\rm e}$ increases (*i.e.*, on going from negative to positive $\Delta G_{\rm e}$), the $\varphi_{\rm H}$ values increase, reach a maximum at $\Delta G_{\rm e} = +0.01$ eV (reactant pair 1–3f), and then decrease (system 1–2).

It has previously been shown⁷ that for the fluorenone-3 system $\Delta G_{\rm e}$ changes from -0.44 eV to +0.53 eV; the plot $\varphi_{\rm H} = f(\Delta G_{\rm e})$ is also extreme, and the $\varphi_{\rm H}$ maximum is observed at $\Delta G_{\rm e} = +0.06$ eV. For the system 2,3,5,6-tetrachloro-1,4-benzoquinone-2, $\Delta G_{\rm e}$ varies from -0.30 to +0.52 eV; with an increase in $\Delta G_{\rm e}$, the $k_{\rm H}$ values increase, reach a maximum at $\Delta G_{\rm e} = +0.09$ eV, and then decrease.¹⁶ A similar result was obtained⁷ for the photoreduction of a series of eight similar in structure o-benzoquinones in the presence of N, N-dimethylanilines 3d, 3e, and 3f. In this case, the redox characteristics of both photoacceptors and H donors changed. Three extreme plots $k_{\rm H} = f(E_{1/2({\rm A} \cdot -/{\rm A})})$ were obtained, and on going to coordinates $k_{\rm H} = f(\Delta G_{\rm e})$ they ran into one plot with a maximum at $\Delta G_{\rm e} = +0.09$ eV. A comparison of the obtained data shows that for all reaction systems under study the maximum values of $\varphi_{\rm H}$ and/or $k_{\rm H}$ correspond to pairs of reactants, whose ΔG_e is close to zero. On going from zero to the endothermic or exothermic region of $\Delta G_{\rm e}$, the $\varphi_{\rm H}$ and/or $k_{\rm H}$ values decrease.

Thus, the study of the kinetics of 9,10-phenanthrenequinone photoreduction in the presence of hydrogen donors (*p*-substituted *N*,*N*-dimethylanilines and polymethylbenzenes) showed that the quantum yield of photoreduction and apparent reaction rate constant exhibit an extreme change with an increase in the oxidation potential of hydrogen donors. In the presence of amines, the $\varphi_{\rm H}$ and $k_{\rm H}$ values increase as a whole, while they decrease in the presence of polymethylbenzenes. In the coordinates $\varphi_{\rm H} - \Delta G_{\rm e}$ (change in the free energy of electron transfer), for pairs quinone—H donor, $\varphi_{\rm H}$ increases as the $\Delta G_{\rm e}$ values approach to zero in both cases: this occurs in the exothermic region of $\Delta G_{\rm e}$ ($\Delta G_{\rm e} < 0$) for the series of amines and in the endothermic region ($\Delta G_{\rm e} > 0$) for the polymethylbenzene series.

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