## Photoreduction of *ortho*-benzoquinones in the presence of *para*-substituted *N*,*N*-dimethylanilines

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Photoreduction of o-benzoquinones irradiated at the wavelengths  $\lambda_{max} \approx 400$  and 600 nm corresponding to the  $S(\pi \rightarrow \pi^*)$  and  $S(n \rightarrow \pi^*)$  electron transitions in the >C=O groups, respectively, in the presence of N.N-dimethylaniline and its derivatives was studied. The apparent rate constants of the photoreduction  $(k_H)$  of o-quinones are determined by the free energy of electron transfer from the amine molecule to a photoexcited o-quinone molecule  $(\Delta G_{e,1})$ . The  $\Delta G_{e,1}$  values are calculated as the sums of the energies of the 0 $\rightarrow$ 0 transitions of the lowest triplet excited state of o-quinones, the reduction energies of o-quinones, and the oxidation energies of amines (the last two terms are numerically equal to the corresponding redox potentials). The maximum rate of photoreduction was found for  $\Delta G_{e,1} \approx 0$ . The reaction mechanism is proposed, in which the reversible formation of a triplet exiplex is the rate-determining stage and hydrogen transfer proceeds in parallel with electron transfer within the exiplex.

Key words: ortho-quinones, N,N-dimethylanilines, photoreduction, free energy of electron transfer.

Photonitiated redox reactions of carbonyl-containing compounds (A) with H-donors (DH) follow a multistage mechanism. Initially, the reactions of low-excited triplet <sup>3</sup>A\* molecules with DH produce the so-called triplet exiplexes<sup>1-3</sup> (encounter complexes).<sup>4,5</sup> Quenching of triplet exiplexes affords two types of primary products, namely, radical ion pairs (A<sup>+-</sup>,DH<sup>++</sup>) and/or radical pairs (AH<sup>+</sup>,D<sup>+</sup>) (reaction (1)).

$${}^{3}A^{*} + DH \rightarrow {}^{3}[A^{*}, DH] \rightarrow (A^{**}, DH^{*+}), (AH^{*}, D^{*})$$
 (1)

The contact or solvent-separated radical ionic pairs relax to give the initial reactants, while the evolution of radical pairs leads to the products of photoreduction of A.

Published data on the effect of the nature of reagents on the kinetics of photoreduction of carbonyl-containing compounds (in particular, substituted benzoquinones) are contradictory. It has been reported that the rates of photoreduction of p-quinones (1) in the presence of diphenylamine increase as their electron-acceptor ability decrease from p-chloranil to duroquinone.<sup>6</sup> On the other hand, a general tendency has been found for o-quinones (2) toward increasing the rate of photoreduction in the presence of tertiary amines (3) with an increase in the electron-acceptor ability.<sup>7</sup> Based on recent advances in the synthesis of new o-benzoquinones,<sup>8</sup> in this work we performed a more systematic study of the effect of the nature of o-quinones 2 on the rate of their photoreduction.



2:  $R^1 = H$ ,  $R^2 = Pr'(a)$ ,  $Pr^n(b)$ , H(c), Cl(d), F(e),  $NO_2(g)$ , CN(h);  $R^1 = R^2 = F(f)$ 3: R = Me(a), H(b), C(O)H(c)

## Experimental

NMR spectra were recorded on a Varian Gemini-300 spectrometer operated at 300 MHz for <sup>1</sup>H and at 75 MHz for <sup>13</sup>C with hexamethyldisiloxane as internal standard. IR spectra were recorded on a Specord M-80 spectrophotometer. Electronic absorption spectra were measured on Specord M-40 and SF-14 spectrophotometers in toluene. The half-wave potentials of reversible one-electron reduction,  $E(A^* - /A)$ , of o-quinones were measured vs. s.c.e. in DMF. Absorption spectra of charge-transfer (CT) complexes were obtained using a difference procedure by comparing the absorption spectra of the o-quinone solutions in toluene and in toluene—N,N-dimethylaniline (1:1) mixture.

The light source used in the experiments was comprised of a KGM-24-150 lamp equipped with a focuser and a GS-16 light filter transmitting radiation with  $\lambda \ge 500$  nm. The *o*-quinone and amine solutions ([Q] = 5 \cdot 10^{-4} and [AmH] = 2.5 \cdot 10^{-2} mol L^{-1}, respectively) used in the kinetic studies were deaerated, saturated with Ar, and placed in a spectrophotometric cell

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(l = 1.0 cm) at a distance of 10 cm from the focuser. Changes in the *o*-quinone concentration were determined from the decrease in the intensity of the absorption band in the region 400 nm recorded on an SF-14 spectrophotometer.

Polarographic studies of  $5 \cdot 10^{-3}$  M solutions of o-quinones in DMF were carried out using a PU-1 polarograph with 0.1 M NaClO<sub>4</sub> as the supporting electrolyte (NaClO<sub>4</sub> was twice recrystallized from bidistilled water and dried *in vacuo* at 100 °C for 12 h). DMF was distilled *in vacuo* at a pressure of 5 to 10 Torr, stored for ~24 h over 4A molecular sieves, and repeatedly distilled *in vacuo* at 2 Torr in an Ar stream.

The solvents were purified following standard procedures.<sup>9</sup> N,N-Dimethyl-p-toluidine (3a) (Aldrich) and N,N-dimethyl-aniline (3b) (Aldrich) were purified by fractional distillation, and 4-(N,N-dimethylamino)benzaldehyde (3c) (Fluka) was recrystallized from hexane.

The syntheses of o-quinones 2a-f have been described earlier.<sup>10</sup>

3.6-Di-tert-butyl-4-nitrobenzoauinone-1.2 (2g). 3.6-Di-tertbutylbenzoquinone-1,2 (2.2 g) was dissolved in 50 mL of acetic acid and  $HNO_3$  (2 mL) was added. The reaction mixture was heated to 50 °C for 4-5 min and water (100 mL) was added. The organic layer was extracted with hexane  $(3 \times 30 \text{ mL})$ , washed until pH 7, and dried with Na<sub>2</sub>SO<sub>4</sub>. After concentration to ~10 mL the hexane solution was chromatographed on a column with silica gel (with a hexane-ether (100 : 1) mixture as eluent). The blue-emerald band was separated and green crystals were isolated after evaporation of the solvent. Recrystallization from hexane gave o-quinone 2g (0.61 g, 23%), m.p. 85-87 °C (from MeOH-H<sub>2</sub>O). Found (%): C, 62.62; H, 7.42. C14H19NO4. Calculated (%): C, 63.34; H, 7.22. IR (KBr). <sup>1</sup>: 1372, 1544 (NO<sub>2</sub>); 1680, 1660 (C=O). <sup>1</sup>H NMR v/cm<sup>-</sup> (CDCl<sub>3</sub>), δ: 1.19 (s, 9 H, Bu<sup>t</sup>); 1.23 (s, 9 H, Bu<sup>t</sup>); 6.52 (s, 1 H, H(5)), <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ : 28.5, 28.6 (CH<sub>3</sub>); 35.6, 36.4 (CMe<sub>3</sub>); 131.1 (C(5)H); 139.2 (ring C(3)); 151.8 (ring C(6)); 153.0 (C(4)NO<sub>2</sub>); 178.8 (C(1)=O); 182.5 (C(2)=O).

3,6-Di-tert-butyl-4-cyanobenzoquinone-1,2 (2h). 3,6-Ditert-butylbenzoquinone-1,2 (2.2 g) was dissolved in 50 mL of acetone and 5 mL of acetonecyanohydrin. Granulated KOH (0.6 g) was added to the mixture. After dissolution of the alkali and disappearance of the initial o-quinone (TLC monitoring on Silufol plates) the reaction mixture was diluted with water (100 mL). The organic layer was extracted with ether (3×30 mL), washed until pH 7, and dried with Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent the dry residue was dissolved in 10 mL of a hexane-ether (100 : 1) mixture and chromatographed under conditions described above. The blue-green band was separated and after evaporation of the eluent the dry residue was recrystallized from hexane to give red-brown crystals (0.46 g. 19%), m.p. 144-146 °C (MeOH-H<sub>2</sub>O). Found (%): C, 73.31; H, 7.54. C<sub>15</sub>H<sub>19</sub>NO<sub>2</sub>. Calculated (%): C, 73.44; H, 7.81. IR (KBr), v/cm<sup>-1</sup>: 2235 (CN); 1680, 1665 (C=O). <sup>1</sup>H NMR  $(CDCl_3)$ ,  $\delta$ : 1.20 (s, 9 H, Bu<sup>t</sup>); 1.40 (s, 9 H, Bu<sup>t</sup>); 6.70 (s, 1 H, H(5)), <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 28.7, 30.0 (CH<sub>3</sub>); 35.2, 37.6 (CMe<sub>3</sub>); 117.7 (CN); 118.0 (ring C(4)); 135.0 (C(5)H); 150.7 (ring C(6)); 158.2 (ring C(3)); 179.7 (C(1)=O); 182.5 (C(2)=O).

## **Results and Discussion**

A series of sterically hindered *o*-benzoquinones 2a-hwith different substituents in positions 4 and 5 of the quinoid ring was chosen for our study. Photoreduction of *o*-quinones 2a-h was carried out in the presence of *para*-substituted *N*,*N*-dimethylanilines 3a-c.

Table	1.	Positio	ns of	maxima	a of	the	absorption	bands	of
o-quir	one	s 2a—h	and t	heir CT	сотр	lexes	with amine	: 3 <b>b</b> in	the
visible	reg	ion and	the r	eduction	pote	ntials	of o-quino	nes 2a-	h

o-Quinone	$\lambda_{\pi\pi} / nm$ (c) <sup>a</sup>	λ <sub>nπ*</sub> /nm (ε) <sup>σ</sup>	$\frac{-\mathcal{E}(\mathbf{A}^{*-}/\mathbf{A})}{/V}$	VCTC /cm <sup>-1</sup>
2a	400	578 (130)	0.53	23550
2Ъ	404 (2100)	578 (76)	0.51	23550
2c	410 (2400)	598 (60)	0.39	21550
2d	398 (2150)	575 (86)	0.37	21400
2e	398 (2300)	566 (60)	0.34	21050
2f	387 (2200)	535 (66)	0.34	21090
2g	388 (2800)	592 (56)	0.10	18590
2h	388 (2500)	591 (58)	0.06 <sup>b</sup>	17680

" In L mol-1 cm-1.

<sup>b</sup> Calculated from the correlation between the  $E(A^{+-}/A)$  and  $v_{CTC}$  of o-quinones 2a-g.

The results of spectral and polarographic studies of oquinones 2a-h and the frequencies of maxima for the absorption bands of the CT complexes of o-quinones 2a-h with 3b (v<sub>CTC</sub>) are listed in Table 1.

Analysis of the data listed in Table 1 shows that the introduction of substituents in positions 4 (or 4 and 5) of the quinoid ring of 3,6-di-*tert*-butylbenzoquinone-1,2 leads to a blue shift of the maxima of the absorption bands corresponding to the  $S(\pi \rightarrow \pi^*)$  and  $S(n \rightarrow \pi^*)$  electron transitions of the carbonyl groups irrespective of the nature of substituents. The half-wave reduction potentials (*E*) of *o*-quinones are in the same range as the  $E(A^{*-}/A)$  values of *p*-quinones.<sup>11</sup> A linear relationship between the  $E(A^{*-}/A)$  values of *o*-quinones **2a**-*m* and the  $v_{CTC}$  values was found,  $E(A^{*-}/A) = 1.41 - (8.28 \cdot 10^{-5}) \cdot v_{CTC}$  (the correlation coefficient is 0.99). This relatioship was used for the determination of the half-wave reduction potential of *o*-quinone **2h**.

To investigate the effect of the nature of substrate and amine on the photoreduction of o-quinones, we studied spectrophotometrically the kinetics of this reaction in toluene and acetonitrile. The reaction, as applied to o-quinones 2a-h, is characterized by photochemical activity of both absorption bands in the visible region. This is due to the fact that the lowest triplet excited state of the o-quinones is a  $T(n \rightarrow \pi^*)$  state. Nearly 100% of photoexcited molecules undergo transitions into this state<sup>12</sup> from the  $S(\pi \rightarrow \pi^*)$  and  $S(\pi \rightarrow \pi^*)$  states.<sup>10</sup> To simplify calculations. we investigated the reaction initiated by radiation corresponding to the  $S(n \rightarrow \pi^*)$  transition. Since for o-quinones 2a-h the absorption bands corresponding to the  $S(n \rightarrow \pi^*)$  transitions are observed in the same spectral region, the kinetics of the photoreduction of all the o-quinones can be studied using the same source of polychromatic radiation and a light filter transmitting the radiation with  $\lambda \ge 500$  nm. At a [2] : [3] molar ratio of 1:50 the photoreduction obeys a firstorder kinetic law up to a ~40% conversion of the o-quinone. The apparent rate constants of photoreduction  $(k_{\rm H})$  of o-quinones were determined graphically from

the slope of the linear portion of the  $\ln([2]_0/[2]_{\tau})$  vs. time curve  $([2]_0 \text{ and } [2]_{\tau}$  are the initial concentration of substrate and its concentration at instant  $\tau$ , respectively). The dependence of the  $k_{\rm H}$  values found for the photoreduction of o-quinones 2a-h in the presence of amines 3a-c in toluene on the  $E(A^{-}/A)$  values of the substances are shown in Fig. 1. A curve with a clearly seen maximum for o-quinone 2d fits the points corresponding to the photoreduction of compounds 2a-h in the presence of amine 3b. The available data for the photoreduction in the presence of amine 3a only allow the plotting of descending branches of the curve, which also has a maximum. It seems likely that the position of the maximum lies in the  $E(A^{+}/A)$  range between -0.4 and -0.5 V. The same is also true for the curve for the dependence of the photoreduction of o-quinones in the presence of amine 3c on  $E(A^{-}/A)$ . In this case, the position of the maximum should lie near  $E(A^{+-}/A) \approx$ -0.2 V. The lack of o-quinones with  $E(A^{-}/A) =$ -0.1 - -0.3 V and -0.4 - -0.5 V precludes exact determination of the positions of maxima on the curves of photoreduction in the presence of amines 3a and 3c. From the aforesaid it follows that changes in the rate of the photoreduction of o-quinones in the presence of amines pass through an extremum rather than go in parallel with the electron-acceptor ability of o-quinones, as was assumed previously.<sup>6</sup> For the same amine, the  $k_{\rm H}$ value is maximum for that o-quinone which is characterized by a specified  $E(A^{+-}/A)$  value. The position of the maximum also depends on the nature of the amine, that is, the maximum shifts toward more negative reduction potentials of o-quinone as the electron-donor ability of the amine increases, and vice versa.



Fig. 1. Relationship between the rate constants of reduction  $(k_{\rm H})$  and the reduction potentials  $(E(A^{+-}/A))$  of *o*-quinones 2a--h in the presence of 4-(N,N-dimethylamino)benzaldehyde (1), N,N-dimethylaniline (2), and N,N-dimethyl-*p*-toluidine (3) in toluene at 298 K.

As was found previously in the studies of photoreduction of fluorenone in the presence of para-substituted dimethylanilines in benzene,13 the dependence of the quantum yield of photoreduction ( $\varphi_{\rm H}$ ) of fluorenone on the electron-donor ability of amine 3 passes through a maximum. Therefore, the profiles for the efficiency of photoreduction of electron acceptors in the presence of amines 3 as functions of the redox potentials of both components of the photoreaction pass through a maximum. Hence, a common parameter should exist which characterizes the reaction pair and controls the process of photoreduction. This can be, e.g., the free energy of electron transfer ( $\Delta G_{e_1}$ ) from the amine molecule to the photoexcited molecule of a carbonyl compound. In the 1960s, quantitative relationships between the kinetics of electron-transfer quenching of excited states of aromatic hydrocarbons in the presence of amines and the thermodynamic properties of the reaction pairs were first found<sup>14,15</sup> and a widely used (see Refs. 1, 3-6, 13) empirical equation (2) for calculating the  $\Delta G_{e,t}$  values, which characterize the electron phototransfer, was proposed:

$$\Delta G_{e,1} = -\Delta E_{00} - E(\mathbf{A}^{-}/\mathbf{A}) + E(\mathbf{D}/\mathbf{D}^{+}) - T\Delta S_e + 3 \text{ kcal mol}^{-1}.$$
(2)

Here,  $\Delta E_{00}$  is the energy of a singlet or triplet<sup>3,4</sup>  $0 \rightarrow 0$ transition for the lowest excited state of a carbonylcontaining compound;  $E(\mathbf{A}^{+-}/\mathbf{A})$  is the reduction energy of the acceptor and  $E(\mathbf{D}/\mathbf{D}^{++})$  is the oxidation energy of the donor (these values are numerically equal to the corresponding redox potentials); and  $\Delta S_e \approx$ -18 cal mol<sup>-1</sup> deg<sup>-1</sup>. By going from calories to more convenient (in this case) electron-volts, we get the equation for T = 298 K

$$\Delta G_{\rm c,t} = -\Delta E_{00} - E(\mathbf{A}^{*-}/\mathbf{A}) + E(\mathbf{D}/\mathbf{D}^{*+}) + 0.36 \text{ eV}.$$
 (3)

Only approximate calculations of  $\Delta G_{e,t}$  values for the system 2-3 are possible because of the lack of experimental  $\Delta E_{00}$  values for o-quinones 2a-h. The  $\Delta E_{00}$ value for unsubstituted o-benzoquinone is 1.44 eV.16 Comparison of the energies of triplet states of benzene and its derivatives (PhX, where X = OH, Me,  $NH_2$ , CN), benzophenone and 4,4'-dichlorobenzophenone, and naphthalene and its derivatives<sup>1,17</sup> indicates that the introduction of any atoms or groups into the molecule of unsubstituted benzene, benzophenone, or naphthalene causes a slight decrease in the  $\Delta E_{00}$  value irrespective of the nature of the substituent. Analysis of the absorption spectra of o-quinones 2a-h in the visible region (see Table 1) shows that for all these compounds the positions of the maxima of the bands corresponding to the  $S(n \rightarrow \pi^*)$  transition fall in the same region of width 0.1 eV. It is obvious that changes in the energies of the corresponding triplet states of molecules 2a-h should not exceed this value. This suggests that all the o-quinones under study have nearly the same  $\Delta E_{00}$  values (~1.35 eV)

o-Qui- none							3c		
	$k_{\rm H} \cdot 10^{3}/{\rm s}^{-1}$		$\Delta G_{\rm e,t}/{\rm eV}$	$k_{\rm H} \cdot 10^3 / {\rm s}^{-1}$		$\Delta G_{\rm e,t}/{\rm eV}$	k <sub>H</sub> ·I	$0^{3}/s^{-1}$	$\Delta G_{\rm e,u}/{\rm eV}$
	PhCH <sub>3</sub>	MeCN		PhCH <sub>3</sub>	MeCN		PhCH <sub>3</sub>	MeCN	
2a	0.3	0.1	0.28	0.35	0.25	0.15	1.7		0.09
2b	0.6	0.05	0.26	0.7	0.3	0.13	2.7	0.45	0.07
2c	1.2	0.2	0.14	5.2	1.8	0.01	4.7	0.4	-0.05
2d	1.7	0.6	0.12	5.7	0.7	-0.01	3.8	0.3	-0.07
2e	2.8	1.4	0.09	4.1	0.35	-0.06	3.6	0.1	-0.10
Zſ	2.6	0.9	0.09	3.7	0.15	0.06	2.3		-0.10
2g	2.1	0.1	-0.15	2.1	0.05	-0.28	0.5		-0.34
2h	2.3	0.2	-0.19	1.5	-	-0.32	1.0	-	-0.38

**Table 2.** Rate constants and calculated  $\Delta G_{e,1}$  values for the reactions of photoreduction  $(k_{\rm H})$  of o-quinones in the presence of amines **3a-c** in toluene and acetonitrile

and allows calculations of the  $\Delta G_{e,t}$  values for each *o*-quinone—amine pair. The experimental  $k_{\rm H}$  values for the photoreduction of *o*-quinones **2a**—**h** in the presence of amines **3a**—**c** in toluene and acetonitrile and the corresponding  $\Delta G_{e,t}$  values for each *o*-quinone—amine pair are listed in Table 2. The oxidation potentials of amines **3b,c** were taken from Ref. 11. Based on the linear dependence between the  $E(D/D^{++})$  value for amine **3** and the Hammett  $\sigma_p$  constants of substituents in molecule **3b** ( $E(D/D^{++}) = 0.70 + 0.637 \cdot \sigma_p$ , at a correlation coefficient of 0.99), we determined the  $E(D/D^{++})$  value for amine **3c** (0.85 eV).

The  $k_{\rm H}$  plots as functions of  $\Delta G_{\rm e,t}$  for all the *o*-quinone—amine pairs are shown in Fig. 2. As can be seen, passage from the  $E(\mathbf{A}^{+-}/\mathbf{A})$  coordinate (see Fig. 1) to  $\Delta G_{\rm e,t}$  leads to matching of the three curves (see



Fig. 2. Relationship between the rate constants of photoreduction  $(k_{\rm H})$  of *a*-quinones 2**a**—**h** and the free energy of electron transfer  $(\Delta G_{\rm e,l})$  in the presence of 4-(N,N-dimethylamino)benzaldehyde (I), N,N-dimethylaniline (2), and N,N-dimethyl*p*-toluidine  $(\mathcal{I})$  in toluene (a) and acetonitrile (b) at 298 K.

Fig. 1), which means that the  $\Delta G_{e,t}$  scale is common to the photoreduction of all *o*-quinones  $2\mathbf{a}-\mathbf{h}$  in the presence of amines  $3\mathbf{a}-\mathbf{c}$ . The  $k_{\rm H} = f(\Delta G_{e,t})$  curves display distinct maxima at  $\Delta G_{e,t} \approx 0.1$  eV (toluene) and at  $\Delta G_{e,t} \approx 0.15$  eV (acetonitrile). When moving along the  $\Delta G_{e,t}$  coordinate toward smaller  $\Delta G_{e,t}$  values (nearly down to zero), which corresponds to replacement of the reagents in the *o*-quinone—amine pairs by stronger electron acceptors and donors, respectively, the  $k_{\rm H}$  value monotonically increases and reaches a maximum, and then the rate of photoreduction decreases drastically on going to negative  $\Delta G_{e,t}$  values. Thus, the rate of photoreduction of *o*-quinone is determined by the free energy of electron transfer ( $\Delta G_{e,t}$ ) from the amine molecule to the photoexcited *o*-quinone molecule (see Eq. (3)).

Calculations of the rate constants of photoreduction of fluorenone  $(k'_{\rm H})$  in the presence of amines 3 in benzene using published data<sup>13</sup> followed by comparison of the  $k'_{\rm H}$  values with the corresponding  $\Delta G_{\rm e,t}$  values determined from Eq. (3) lead to an analogous dependence of  $k'_{\rm H}$  on  $\Delta G_{\rm e,t}$  with a maximum at  $\Delta G_{\rm e,t} \approx 0$ . The quantum yields and the rate constants of photoreduction of fluorenone in the presence of amines 3 as functions of both the oxidation potential of amine,  $E(\mathbf{D}/\mathbf{D}^{+})$ , and the calculated  $\Delta G_{e_1}$  values are listed in Table 3. The energy of the lowest triplet excited state of fluorenone (the  $\pi \rightarrow \pi^*$  state),  $\Delta E_{00}$ , is 2.3 eV<sup>18</sup> and  $E(A^{-}/A) =$ 1.35 eV.<sup>2</sup> The oxidation potentials of p-Cl- and p-Me<sub>2</sub>N-derivatives of **3** were taken from Ref. 11. The  $E(\mathbf{D}/\mathbf{D}^{++})$  values for p-CN-, p-Br-, and p-EtO-substituted amines 3 (1.12, 0.85, and 0.65 eV, respectively) were found from the linear relationship between the  $E(\mathbf{D}/\mathbf{D}^{++})$  values and Hammett  $\sigma_p$  constants of substituents in molecule 3, as was described above.

At the same time, no similar relationship with an extremum is observed for the *p*-quinone—diphenylamine system.<sup>6</sup> The rate of photoreduction of *p*-quinone, as well as that of the formation of radical products (QH<sup>+</sup>), increases as the electron-acceptor ability of quinones decreases on going from *p*-chloranil to duroquinone. According to the proposed reaction mechanism,<sup>6</sup> the first stage of the interaction of a photoexcited

**Table 3.** Quantum yield  $(\varphi_{\rm H})$  and the rate constant of photoreduction  $(k'_{\rm H})$  of fluorenone in the presence of *para*-substituted *N*,*N*-dimethylanilines (data taken from Ref. 13) as functions of the oxidation potential of amine,  $E({\rm D}/{\rm D}^{++})$ , and calculated  $\Delta G_{\rm e,i}$  values

Substituent in the amine	φн	k'H · 10 <sup>-8</sup> /L mol <sup>-1</sup> s <sup>-1</sup>	$\frac{E(\mathbf{D}/\mathbf{D}^{+})}{/\nabla}$	$\Delta G_{\rm e,t}$ /eV
p-Me <sub>2</sub> N	~0.02	3.2	0.016	-0.59
p-MeOCHN	~0.02	8.2		
p-ElO	0.35	35.0	0.55	-0.04
p-MeS	0.29	19.4	~	
p-Me	0.60	9.6	0.65	+0.06
н	0.44	3.1	0.71	$\pm 0.12$
p-Cl	0.31	0.93	0.84	+0.25
p-Br	0.23	0.92	0.85	+0.26
p-EtCO <sub>2</sub>	0.12	0.56		
p-CN	0.09	0.006	1.12	+0.53

quinone molecule  $({}^{3}Q^{*})$  with DH includes the formation of a triplet exiplex followed by electron transfer and establishment of a prototropic equilibrium,  $(Q^{-}, DH^{+}) \implies (QH^{+}, D^{-})$ , which is shifted toward the products of proton transfer as the electron-acceptor ability of quinone or the electron-donor ability of DH decreases. This suggests that the constant  $k'_{\rm H}$  should monotonically increase with increasing  $\Delta G_{e,t}$ , which was found previously.<sup>6</sup> However, calculations of  $\Delta G_{e,t}$  values using Eq. (3) show that the  $\Delta G_{e,1}$  values for all the pairs of compounds  $1-Ph_2NH$  lie between -0.95 and -0.12 eV. Therefore, an increase in  $k'_{\rm H}$ <sup>6</sup> with increasing  $\Delta G_{e,t}$  is similar to that found (i) in this work for the system 2-3 and (ii) previously<sup>13</sup> for the system fluorenone-3 at  $\Delta G_{e,t} \leq 0$ . Most likely, these examples are particular cases of a general relationship between the rate of photoreduction of carbonyl-containing compounds and  $\Delta G_{e,t}$ , which has an extremum. At  $\Delta G_{e,t} \ge 0$ , the  $k_{\rm H}$  values pass through a maximum (for the 2-3 and fluorenone-3 systems). This effect cannot be rationalized in the framework of the mechanism proposed earlier.6

We believe that the reason for such an extremal dependence of the rate of photoreduction of o-quinones and fluorenone on  $\Delta G_{e,i}$  can be established by analyzing the kinetics of phototransfer of electrons and hydrogen in the system 1-polymethylbenzene (ArH).<sup>4,5</sup> In these studies it was found that the equilibrium constant of the formation of a triplet exiplex  $K_{TE}$  (encounter complex<sup>4,5</sup>) [1\*, ArH] is determined by the nature of both the reagents and the solvent (the  $K_{TE}$  value reaches ~200 m<sup>-1</sup> for the reaction in CCl<sub>4</sub>)<sup>5</sup> and that the  $K_{TE}$  $(\Delta G_{e,t})$  curve passes through a maximum at  $\Delta G_{e,t} \approx 0$ (Fig. 3). The fact that the dependences of  $k_{\rm H}$  (for o-quinones),  $k'_{\rm H}$  (for fluorenone), and  $K_{\rm TE}$  (for p-quinones) on  $\Delta G_{e,t}$  belong to the same type (see Fig. 3) indicates that the rate of photoreduction of quinones and fluorenone in a medium of low polarity is determined by the stage of the formation of the triplet exiplex. In this case the rate constant for electron transfer, considered as a function of  $\Delta G_{e,t}$ , increases on going to negative  $\Delta G_{e,t}$  values until reaching a diffusion limit<sup>4,5</sup> rather than passing through an extremum. It is believed that hydrogen transfer occurs as a one-step process independently of the electron transfer; in other words, hydrogen transfer occurs concurrently with electron transfer rather than following it.<sup>5,6</sup> In a simplified form, the photoreduction of *o*-quinones can be described by the scheme shown below, which seems to be common to quinones and fluorenone.

$${}^{3}\mathbf{A}^{*} + \mathbf{D}\mathbf{H} \xrightarrow{\mathcal{K}_{\text{TE}}} {}^{3}[\mathbf{A}^{*}, \mathbf{D}\mathbf{H}] \xrightarrow{\mathbf{k}_{h}} (\mathbf{A}\mathbf{H}^{*}, \mathbf{D}^{*})$$

$$(4)$$

$$(4)$$

$$k_{\rm H} = K_{\rm TE} \cdot k_{\rm h} \cdot [\rm DH] \tag{5}$$

According to reaction (4), the molecule of carbonylcontaining compound  ${}^{3}A^{*}$ , which is in the lowest triplet excited state, and a molecule of hydrogen donor **DH** form a triplet exiplex. The reaction is reversible and the equilibrium constant  $K_{TE}$  is determined by the redox properties of  ${}^{3}A^{*}$  and **DH**, which are characterized by the parameter  $\Delta G_{e,t}$ . The maximum  $K_{TE}$  value is reached at  $\Delta G_{e,t} \approx 0$ . An explanation for this fact has been proposed recently<sup>4</sup> on the basis of Mulliken's theory. Here,<sup>4</sup> the stability of a triplet exiplex depends on the degree of "mixing" of the wave functions of two limiting states of the triplet exiplex, namely, the state with a



Fig. 3. Relationship between the rate constants of photoreduction  $(k_{\rm H}, k'_{\rm H})$  of *o*-quinones (1) (in toluene) and fluorenone (2) (calculated using data taken from Ref. 13, in benzene) in the presence of *p*-substituted N,N-dimethylanilines and the dependence of the constant for triplet exiplex formation  $(K_{\rm TE})$  in the *p*-quinone--polymethylbenzene system (3) (data taken from Ref. 4, in CH<sub>2</sub>Cl<sub>2</sub>) on  $\Delta G_{\rm e, f}$  at 298 K.

localized excited state and the state with complete charge transfer.  $[\mathbf{A}^*, \mathbf{D}\mathbf{H}] \iff (\mathbf{A}^{-}, \mathbf{D}\mathbf{H}^{++})$ . At  $\Delta G_{e,t} \approx 0$ , the states [A\*,DH] and (A<sup>\*+</sup>,DH<sup>\*+</sup>) are at equal energy levels and [A\*,DH] closely matches (A<sup>\*-</sup>,DH<sup>\*+</sup>), which means the greatest decrease in the energy of the triplet exiplex with respect to  ${}^{3}A^{*}$ ; hence, in this case  $K_{TE}$  is maximum. Hydrogen transfer occurs in the triplet exiplex, thus competing with electron transfer. Both  $k_h$  and  $k_{e,t}$ values are determined from the  $\Delta G_{e,t}$  value.<sup>4-6</sup> For a non-polar medium, we have  $k_h/k_{e,t} \approx 10^2$  at  $\Delta G_{e,t} \rightarrow 0, 6^{\circ}$ so that electron transfer can be ignored, the expression for  $k_{\rm H}$  is simplified to Eq. (5), and the  $\Delta G_{\rm e,t}$  profiles of  $k_{\rm H}$  and  $K_{\rm TE}$  coincide. It should be emphasized that this holds only for particular  $\Delta G_{e,t}$  values. For the 1-ArH system in a medium of low polarity  $(CH_2Cl_2)$ , the  $k_{e,t}$ value remains constant (~10<sup>6</sup> s<sup>-1</sup>) as  $\Delta G_{e,t}$  decreases down to 0.25 eV and then increases up to  $10^8$  s<sup>-1</sup> for  $\Delta G_{e,t}$  values in the range between 0.25 and -0.1 eV. It is in this range of the  $\Delta G_{e,t}$  values that the extremum dependence of  $K_{TE}$  on  $\Delta G_{e,t}$  is observed.<sup>4</sup> In acetonitrile, the  $k_{e,t}$  values (an increase by two orders of magnitude) change analogously as  $\Delta G_{e,t}$  decreases in a much more narrow region (from 0.25 to 0.2 eV), so this increase in  $k_{e,t}$  must affect the dependence of  $k_{H}$  on  $\Delta G_{e,t}$ . Since electron transfer begins to compete with hydrogen transfer, the range of  $\Delta G_{e,t}$  values in which a "burst" of  $k_{\rm H}$ occurs should be narrowed. Comparison of the experimental  $k_{\rm H} = f(\Delta G_{\rm e,i})$  curves for o-quinones in the presence of amines 3 in toluene and acetonitrile (see Fig. 2) shows that this is true. When moving from the positive to negative  $\Delta G_{e,t}$  values down to  $\Delta G_{e,t} \approx 0.2$  eV, the  $k_{\rm H} =$  $f(\Delta G_{e,t})$  curves in toluene and acetonitrile are close; however, after passing this value the constant  $k_{\rm H}$  in toluene is increased (see Fig. 2, a), whereas a sharp decrease in the  $k_{\rm H}$  values in acetonitrile occurs (see Fig. 2, b). In toluene, a "burst" of  $k_{\rm H}$  occurs in the range covering  $\Delta G_{e,t}$  values from 0.3 to ~-0.4 eV (a total of ~0.7 eV), whereas in acetonitrile it occurs in the  $\Delta G_{e,t}$ range from 0.3 to 0 eV (a total of 0.3 eV only).

Thus, we determined spectral characteristics and the half-wave potentials of one-electron reduction,  $E(\mathbf{A^{--}}/\mathbf{A})$ , of a series of substituted 3,6-di-*tert*butylbenzoquinones-1,2 and obtained a linear correlation between the  $E(\mathbf{A^{--}}/\mathbf{A})$  values and the frequencies of CT complexes of the corresponding o-quinones with N,N-dimethylaniline. It was found that the rate of photoreduction of o-benzoquinones in the presence of N,N-dimethylaniline derivatives depends on the redox potentials of both reagents, passes through a maximum, and is determined by the free energy of electron transfer  $(\Delta G_{e,1})$  from the amine molecule to photoexcited o-benzoquinone molecule.

The fact that an analogous dependence of the rate of photoreduction on  $\Delta G_{e,1}$  is also observed for the photoreactions of fluorenone with N,N-dimethylaniline derivatives suggests that there is a common regularity, which controls the reactions of photoreduction of car-

bonyl-containing compounds in the presence of amines. The formation of a triplet exiplex, in which hydrogen transfer occurs concurrently with electron transfer, is the limiting stage of the photoreduction.

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