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Triplet Exciplexes in the Photochemistry of Quinones

P.P.Levin and V.A.Kuz'min

The results of studies on the kinetics and mechanisms of reactions involving the transfer of an electron and a hydrogen atom to quinone molecules in triplet states are surveyed and the spectroscopic-kinetic characteristics of the triplet exciplexes of quinones and the role of the electron donor-acceptor interactions and hydrogen-bonded complexes in the photochemistry of quinonoid compounds are examined. Attention is concentrated on the experimental investigation of the kinetics and mechanisms of the primary photochemical processes by modern flash photolysis methods.
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INTRODUCTION

Under the influence of light, quinonoid compounds (Q) enter into a wide variety of chemical reactions. In most cases the primary step in the photochemical reactions of quinones is the transfer of an electron and a hydrogen atom to the molecules of quinones in triplet states (^{3}Q), electron donor–acceptor interactions and the formation of a hydrogen bond playing an important role in these processes.

A number of reviews have been devoted to the photochemistry of quinones[1-6] and the photochemical oxidation-reduction reactions of chloroquinones have been examined.[7] This review is devoted to the primary steps in the photochemical reactions of quinones, the transfer of an electron and a hydrogen atom to the molecules of quinones in triplet states, and also the properties of triplet exciplexes.

Important data on the kinetics of the elementary reactions and the mechanism of the transfer of an electron and a hydrogen atom with participation of ^{3}Q have been obtained in recent years, in many respects as a result of the development of methods for the investigation of fast reactions, especially flash photolysis with laser excitation sources in the nanosecond and picosecond ranges; the formation of triplet exciplexes in these chemical processes has been demonstrated.

II. ELECTRON DONOR–ACCEPTOR COMPLEXES OF QUINONES IN THE GROUND AND TRIPLET STATES

1. Electron Donor–Acceptor Complexes of Quinones in the Ground State

Quinonoid compounds are relatively strong electron acceptors and form electron donor–acceptor complexes (EDA complexes) with compounds having electron-donating properties.[8] The energy of the bond between the molecules in the EDA complexes is usually close to that characteristic of the van der Waals interaction and is comparable to or somewhat exceeds kT,[8] the nature of the interaction between the donor and acceptor in the complex being extremely varied.[9]

In the crystalline state and in the absence of a localised interaction, the planes of the rings of the quinone and of the aromatic molecule comprising the EDA complex are parallel and the distance between them is 3.1–3.55 Å.[8] In the presence of a hydrogen bond, the parallel arrangement breaks down; for example, when the donor is phenol, then the angle between the ring planes reaches 10°.[10] The energy of the hydrogen bond in the complex of *p*-benzoquinone (I) with phenol is 5.05 kcal mol^{-1} in the crystalline state, while the entropy is 15 cal mol^{-1} K^{-1}.[11]

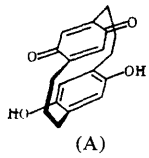
The study of the IR spectra of crystalline complexes of compound (I) with aniline derivatives demonstrated the presence of two non-equivalent carbonyl groups in the molecule of compound (I), which is due to the localised character of the interaction and the appreciable contribution by the ionic component.[2] The formation of complexes between compound (I) and donors having a primary or secondary amino-group is promoted additionally by the presence of a hydrogen bond between the NH and C=O groups to which the ionic component makes an appreciable contribution. The slight non-equivalence of the carbonyl groups in the molecule of compound (I) is also observed in the complex of this compound with *NN*-dimethylaniline and is caused by the localised charge transfer from the unshared pair of the N atom to one of the C=O groups. In the EDA complex of compound (I) with *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) the C=O groups are equivalent in the crystalline state; the complex is ionic with a delocalised interaction.

Quinones do not form EDA complexes with triethylamine and bipyridyl in solutions, apparently as a consequence of the steric hindrance generated by the alkyl substituents in the donor. The formation of EDA complexes with amines of the type of triethylenediamine and quinuclidine in solutions has been noted.[13]

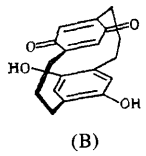
The formation of EDA complexes between quinones and electron donors is accompanied by the appearance in the IR spectrum of a charge-transfer (CT) band.[8] The energy of the CT band is a linear function of the one-electron half-wave potential for the reduction of the quinone in acetonitrile, i.e. $E_{1/2}(Q^-/Q)$, the slope being 0.95 for hexamethylbenzene and 0.8 for other donors.[14] The different slopes of the above relations for hexamethylbenzene compared with other donors may be explained by the steric influence of the methyl groups in the donor, which increases the distance between the donor and the quinone in the EDA complex.[15] The slopes of the analogous relations between the energy of the CT band and the ionisation potential of the aromatic electron donor are close to 0.9.[15,16] A slight deviation from the linear relation between the energy of the CT band and $E_{1/2}(Q^-/Q)$ has been observed for quinones with strong electron-accepting substituents [cyano-derivatives of the quinone (I)].[17]

The occurrence of a localised interaction influences significantly the position of the CT band. This is particularly pronounced for complexes of the quinhydrone type. Thus the formation of a relatively weak hydrogen bond in the EDA complexes of quinones with hydroquinones or *p*-phenylenediamines on passing from a solution to the crystalline state leads to a decrease of the energy of the CT transition by 5000–11000 cm^{-1}.[18–21] This shift is caused precisely by the formation of the hydrogen bond, since the position of the CT band in the spectra of complexes without a hydrogen bond depends only slightly on the state of aggregation.

The pronounced dependence of the interaction in the complexes of the quinhydrone type on the mutual orientation of the quinone and the donor has been demonstrated in a study of the paracyclophane derivatives (A) and (B):[22]



(A)



(B)

The CT band in the spectrum of compound (A) is observed at 462 nm, while the intensity of the absorption of compound (B) in this region is 30 times lower; its CT band has a maximum at 346 nm. The methoxy-derivatives of (A) and (B) behave analogously. Consequently, the hydrogen bonds in these structures do not play any role (the presence of the hydrogen bonds in the crystalline complexes shifts the CT band to the region of 600 nm[19]). The electron donor–acceptor interaction in the given structures is analogous to the interaction in the corresponding π-complexes formed in solution. A CT band has also been observed for multilayer structures analogous to those of compounds (A) and (B) but with an additional benzene ring between the quinone and the hydroquinone; however, the relative orientation of the donor and the acceptor in such structures does not play any role.[23]

The energy of the CT state in the EDA complexes of quinones depends significantly also on the molecular environment. The increase in solvent polarity on passing from cyclohexane to acetonitrile lowers the energy of the CT transition from 1.43 to 1.34 eV for the EDA complex of chloranil (II) with TMPD.[24]

Specific interaction with the medium may exert a strong influence on the formation of quinhydrone complexes in solution. The spectra of the EDA complexes of *ortho*-quinones with the corresponding hydroquinones contain a CT band with the maximum at 440 nm. However, on dissolution of the specimens in alcohols and ethers, the formation of complexes is not observed owing to the presence of hydrogen bonds to solvent molecules.[25]

Quinones are also capable of forming complexes with aromatic amines having an ionic structure.[8,26] The ionic complexes can exist simultaneously with the non-polar EDA complexes and can be detected only in relatively polar solvents or crystals. The dynamics of the system incorporating simultaneously the polar and non-polar EDA complexes has been investigated in detail for complexes of compound (II) with TMPD.[24,27–32] Apart from the absorption characteristic of the non-polar EDA complex, a 3:1 mixture of ethyl ether and isopropyl alcohol exhibits bands at 635, 520, and 434 nm due to the absorption by the corresponding radicals and there is an inverse CT band at 1100 nm.[29,30] The formation of radicals in this system has been demonstrated by EPR.[24] The equilibrium

$$Q + D \rightleftarrows Q \ldots D \rightleftarrows Q^- \ldots D^+. \qquad (1)$$

has been postulated.

Ionic complexes arise when the concentration of the non-polar EDA complex exceeds a specific value;[29,30] they are formed on aggregates of non-polar EDA complexes of the cluster type as a result of the increased polarity of the micro-environment in these aggregates, which promotes ionisation. However, the aggregation of neutral EDA complexes has not been observed by Staab and Herz[22] even at temperatures down to 185 K.

In polar solvents neutral EDA complexes of quinones with aromatic amines dissociate into free radical-ions,[8,26,27] whose presence in acetonitrile solutions of compound (II) with TMPD has been detected by EPR.[31] The kinetics of the dissociation reaction have been investigated by flash photolysis in acetonitrile solutions of TMPD and 2.6-diphenyl-1,4-benzoquinone (III);[34] the EDA complexes dissociate with a rate constant of 5.5×10^3 s^{-1} and the enthalpy and entropy of activation are 3.6 kcal mol^{-1} and −29 cal mol^{-1} K^{-1} respectively. The large negative entropy indicates a significant reorganisation of the molecules of the medium on dissociation of the non-polar EDA complex into radical ions. Comparison of the dissociation constants with $E_{1/2}(Q^-/Q)$ for a series of quinones showed that the experimentally observed free energy of electron transfer is below values calculated from the corresponding one-electron potentials.[34]

It is noteworthy that in the quinhydrone complexes thermal electron and hydrogen atom transfer reactions take place.[20,21,25]

Thus the structure of the molecular environment as well as the mutual orientation of the reactants in the complex and the specific features of the interactions between them influence significantly the energy of the state with total charge transfer and hence the kinetics of the reactions involving the charge transfer stage.

2. Triplet Exciplexes of Quinones

The electron affinity of the molecule in an electronically excited state is higher than in the ground state by an amount which is usually set equal to the excitation energy.[35] For this reason, EDA complexes in the triplet state—the triplet exciplexes (TE)—have a structure characterised by a higher contribution of the state with total charge transfer compared with the structure of the corresponding EDA complexes in the ground state. Like the EDA complexes in the ground state, the TE can also be divided on the basis of their structure into polar and non-polar depending on the contribution of the polar state with total CT.

The non-polar triplet states of the EDA complexes of quinones differ significantly in their characteristics from the corresponding ^3Q. For example, compound (I) and its derivatives virtually do not phosphoresce in frozen solutions in solvents without electron-donating properties. The introduction of weak electron donors (aromatic hydrocarbons) into these solutions leads to a significant increase of the phosphorescence intensity,[36–38] which is observed on photoexcitation at the wavelength in the region of the CT band. The phosphorescence bands of the EDA complexes of quinones are broadened and displaced to longer wavelengths compared with the phosphorescence spectra of the quinone and to a greater extent the higher the electron-donating capacity of the aromatic hydrocarbon.[38] The phosphorescence spectra of the EDA complexes of compound (I) and its derivatives with aromatic hydrocarbons are similar, as regards the position and form of the bands, to the phosphorescence spectrum of the initial quinone, which shows that the main contribution to the structure of the EDA complexes in the triplet state comes from the structure with excitation localised at the quinone molecule.

The triplet states of the EDA complexes with localised excitation, formed by compound (II) and weak electron donors, have been detected from their absorption by flash[39] and laser[40,41] photolysis methods. The triplet–triplet absorption spectra of solutions of compound (II) in benzene, acetone, and dioxan at room temperature or in a diethyl ether–isopentane–ethyl alcohol (EPA) mixture in the presence of methyl methacrylate at 77 K have weak bands in the range $\lambda > 550$ nm, there is virtually no absorption of compound (II) in the triplet state. The triplet exciplexes formed on quenching of duroquinone (IV) in the triplet state by weak electron donors in non-polar solvents and in acetonitrile have analogous absorption spectra.[42–44]

The photoexcitation of the EDA complexes of quinones in the region of the CT band in systems where the energy of the state with total charge transfer is below that of the triplet state does not lead to the formation of any intermediates.[38,45–48] The main channel leading to the deactivation of the polar electronically excited singlet state of the EDA complex is rapid non-radiative transition to the ground state. The rate of this process is determined by the rate of the vibrational relaxation and the relaxation processes in the molecular environment and amounts to $\geq 10^{11}$ s^{-1}, which is significantly higher than the rate of dissociation into radical-ions and the rate of the singlet–triplet transitions.[49]

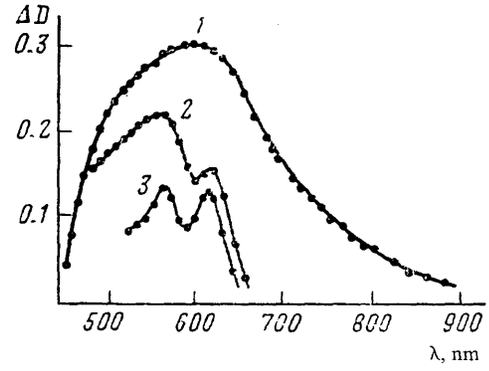


Figure 1. Absorption spectra of solutions of 2,6-diphenyl-1,4-benzoquinone and *NNN'N'*-tetramethyl-1,4-phenylenediamine in dibutyl phthalate (subjected to laser photolysis) obtained at the end of the laser pulse: *1*) ^3Q (obtained in the absence of TMPD); *2*) polar TE (obtained at a TMPD concentration of 0.15 M); *3*) absorption spectrum of TMPD radical-cation in acetonitrile.[46]

On quenching ^3Q by electron donors in the systems indicated, the formation of polar TE is observed.[43–46] The absorption spectra of the TE contain bands characteristic of the corresponding radical-ions, which is typical for exciplexes with total charge transfer. Absolute agreement between the absorption spectra of the polar TE in inert solvents and the absorption spectra of the corresponding radical-ions is not observed as a consequence of the pronounced overlap of the electron clouds of the radicals in complexes of the "sandwich" type. For example, the

absorption spectrum of the polar TE of compound (III) with TMPD contains bands characteristic of the TMPD radical-cation, but the ratio of the intensities of these bands in the spectra of TE and $TMPD^+$ is different (Fig. 1). The presence of hydrogen bonds between the radical-ions in the polar TE results in a greater similarity between the absorption spectra of the TE and the radical-ions. For example, the absorption spectrum of the TE of the compound (III)–diphenylamine (DPA) systems shown in Fig. 2 is virtually identical with the absorption spectrum of the DPA radical-cation.[45,50] The formation of a hydrogen bond reduces the electron overlap between the radicals as a consequence of the breakdown of the "sandwich" structure. Chemically induced nuclear polarisation (CINP), which arises in the course of photolysis via a triplet mechanism on geminal recombination of the radical-ion pairs, is observed in this system.[50] It has been noted for analogous systems involving compound (II) that the absorption spectrum of the radical-anion components of the hydrogen bonded TE agrees with the absorption spectrum of the radical-anion of compound (II) in alcoholic solutions, where hydrogen bands are formed with solvent molecules.[51,52]

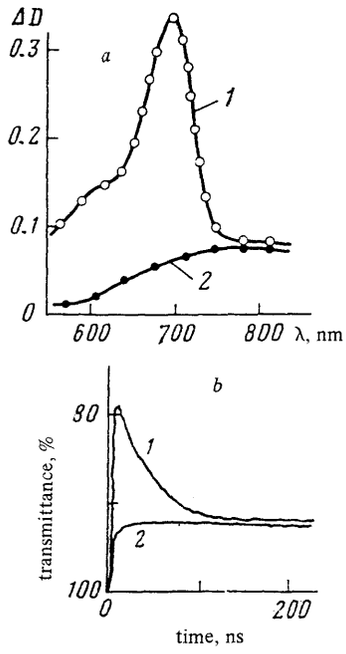


Figure 2. *a*) Absorption spectra of toluene solutions of 2,6-diphenyl-1,4-benzoquinone and Ph_2NH subjected to laser photolysis at −12 °C: *1*) obtained at the end of the laser pulse (superposition of TE and $Ph_2N^{\cdot}$ spectra); *2*) 150 ns after the laser pulse ($Ph_2N^{\cdot}$ spectrum); *b*) kinetics of the destruction of TE recorded from the absorption at 690 nm (curve *1*) and of the formation of $Ph_2N^{\cdot}$ at 830 nm (curve *2*).[50]

The introduction of solvating additives, for example, alcohols, induces a change in the absorption spectra of polar TE. When the methanol content in benzene is 10%, the absorption spectra of the TE virtually correspond to a superposition of the absorption spectra of the corresponding radical-ions.[43,44,53] The alcohol molecules form hydrogen bonds with the quinone radical-anion in the TE.[54] Solvated polar TE have the structure of a solvate-separated ion pair.

In systems characterised by close energies of the state with total CT and a localised excitation, solvation induces the most pronounced changes in the structure of the TE and shifts the equilibrium [a scheme of type (I) with participation of ^3Q] towards the formation of radical-ion pairs in a triplet state.[42–44] For example, the introduction of an insignificant amount of methanol into benzene (the dielectric constant of the solvent hardly changes under these conditions) or an increase of the dielectric constant of the medium to 5 by introducing the corresponding amount of acetonitrile into benzene leads to the formation of radical-ion pairs on photoexcitation of the quinone (IV) in the presence of triphenylamine (TPA) or even at relatively low TPA concentrations, where the formation of a polar TE in this system in benzene is hardly observed.[44] The influence of solvation and of the dielectric constant of the medium is caused by the change in the energy of the state with total CT.

The rate constant for the non-radiative conversion to the ground state (k_{TE}) of polar TE with an energy exceeding 1 eV [for example, the TE of the compound (III)–TPA system] depends only slightly on the polarity and viscosity of the solvent (Table 1). In the case of TE with a low energy, this constant diminishes with increasing polarity of the medium [the TE of the system compound (III)–TMPD (Table 1)]. Solvation by methanol increases or diminishes the k_{TE} of polar TE with high and low energies respectively. The value of k_{TE} increases as the energy of the state with total CT is reduced[43,54] and deviations from this relation are observed only for very low values of the energy indicated.

The kinetics of the non-radiative deactivation of the TE of quinones by transition to the ground state obey the energy gap rule for internal conversion processes, which indicates the important role of the Franck–Condon factor in processes involving the non-radiative deactivation of TE. The same factor is responsible for the increase of k_{TE} on formation of hydrogen bonds with the molecules of the medium or between the radicals in the TE. The constant k_{TE} diminishes slightly when the pressure is raised to 3 kbar.[55]

Triplet exciplexes participate as intermediate species in many photochemical reactions of quinones—photoaddition, photosubstitution, sensitised photoisomerisation, and photodecomposition. Thus p-benzoquinone is photochemically stable in benzene but 4-phenoxyphenol is formed in the presence of difluoroacetic acid.[56] It has been suggested that this reaction includes a stage in which a non-polar TE is formed as a biradical adduct in which acid catalysed proton transfer takes place. The existence of this adduct has been confirmed by the CINP method on photoexcitation of the EDA complex of fluoranil with benzene in the region of the CT band.[57] The TE consisting of a biradical adduct or having a structure with a significant contribution by the state with total charge transfer, also participates in the cycloaddition of olefins to quinones in the triplet state.[58–62] These exciplexes are quenched by O_2, SO_2, and nucleophiles and are protonated in the presence of acids with formation of various products. The simultaneous study by the CINP and picosecond laser photolysis methods of the nature of the intermediates arising in the photolysis of the chloranil–1,1-dimethylindene system in acetonitrile showed that the primary product of the interaction of ^3Q with the olefin is a radical-ion pair.†

† See P.M.Rentzepis, D.W.Steyert, H.D.Roth, and C.I.Abelt, J.Phys.Chem., 1985, **89**, 3955.

Table 1. The rate constants for the destruction of triplet exciplexes of quinones at room temperature.

Electron donor	Solvent	$10^{-6} k_{TE}$, s^{-1}	Refs.
	Duroquinone		
2-Methoxynaphthalene	Benzene	0.6	[42]
"	Acetonitrile	0.4	[42]
Triphenylamine	Benzene	0.5	[44]
	Benzene–methanol (20:1)	3.0	[44]
	2,6-Diphenyl-1,4-Benzoquinone		
Triphenylamine	Benzene	5.0	[53]
"	Toluene	5.1	[53]
"	Perfluorobenzene	5.0	[53]
"	1,4-Dioxan	8.6	[53]
"	Liquid paraffin	5.6	[53]
"	Dibutyl phthalate	7.2	[53]
"	Tetrahydrofuran	7.6	[53]
"	Tetrachloroethane	27	[53]
"	Pentyl alcohol	19	[53]
"	Benzene–methanol (20:1)	12	[53]
Diphenylamine	Toluene	28	[50]
"	Perfluorobenzene	11	[50]
"	Tetrahydrofuran	10	[50]
"	Dibutyl phthalate	68	[50]
"	Liquid paraffin	12	[50]
4-Phenylaniline	Dioxan	50	*
"	Benzene	25	*
"	Toluene	25	*
"	$CHCl_3$	22	*
"	CH_2Cl_2	35	*
"	1,1,2,2-Tetrachloroethane	19	*
"	1,2-Dichloroethane	32	*
"	Tetrahydrofuran	55	*
NN-Dimethyl-4-methoxyaniline	Toluene	23	[84]
NNN'N'-Tetramethyl-*p*-phenylenediamine	Toluene	$\geqslant$50	[45]
"	Dibutyl phthalate	26	[45]
"	Tetrahydrofuran	30	[45]
	3-Chloro-2,6-diphenyl-1,4-benzoquinone		
Naphthalene	Benzene	9.5	[43]
"	Benzene–methanol (20:1)	11	[43]
1,2,3-Trimethoxybenzene	Benzene	1.6	[43]
"	Benzene–methanol (20:1)	2.7	[43]
4-Phenylaniline	Toluene	42	*
"	1,1,2,2-Tetrachloroethane	51	*
Triphenylamine	Benzene	6.4	[43]
"	Benzene–methanol (20:1)	13	[43]
NN-Dimethyl-4-methoxyaniline	Benzene	12	[43]
"	Benzene–methanol (20:1)	18	[43]
NNN'N'-Tetramethyl-*p*-phenylenediamine	Benzene	$\geqslant$50	[43]
	3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone		
Triphenylamine	Benzene	10	[43]
"	Benzene–methanol (20:1)	21	[43]
4-Phenylaniline	Toluene	$\geqslant$140	*
	Chloranil		
Triphenylamine	Benzene	15	[43]
"	Benzene–methanol (20:1)	25	[43]
1-Methylimidazole	Dioxan	6.5	[51]
1-Methylbenzimidazole	Dioxan	5.0	[51]
2-Ethylindazole	Dioxan	$\geqslant$50	[51]
Indole	Dioxan	$\geqslant$50	[51]
1-Ethylindole	Dioxan	$\geqslant$50	[51]
4-Phenylaniline	Toluene	$\geqslant$140	*
Diphenylamine	1,2-Dichloroethane	110	[48]
Durene	1,2-Dichloroethane	20	[48]
"	Ethyl acetate	20	[48]
"	Dioxan	17	**
"	Benzene	22	**
"	Ether	40	**
"	Dichloromethane	21	**
"	CCl_4	31	***
Hexamethylbenzene	Benzene	21	***
"	CCl_4	26	***
Pentamethylbenzene	Benzene	20	***
"	CCl_4	23	***
p-Xylene	Benzene	10	***
"	CCl_4	6.2	***
Mesitylene	Benzene	11	***
"	CCl_4	7.6	***
m-Xylene	Benzene	1.8	***
"	CCl_4	2.1	***
Toluene	Benzene	0.52	***
"	CCl_4	0.56	***

*See P.P.Levin and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 2587.

**See H.Kobashi, T.Kondo, and M.Funabashi, Bull.Chem. Soc.Japan, 1986, 59, 2347.

***See P.P.Levin and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1986, 1435.

It has been suggested that the initial formation of polar TE is a universal process in many photochemical addition reactions involving quinones.[62] The study of the CINP in the photoisomerisation of olefins[63] and various cyclic hydrocarbons,[64–69] in the photodecomposition of thymine dimers,[70] and in the dimerisation of olefins and the dissociation of their cyclic dimers[71] and of the anthracene dimer,[72] all sensitised by quinones, has shown that all these reactions include a step in which radical-ion pairs are formed as a consequence of electron transfer from the reactant to ^3Q. The primary step in the nucleophilic substitution of sulpho-derivatives of 9,10-anthraquinone (V) in the presence of aliphatic amines is electron transfer from the amine to the quinone molecule in the triplet state with subsequent substitution in the radical-ion pair.[73] The photosubstitution of the hydroxy- and amino-derivatives of compound (V) takes place analogously.[74] In the decarboxylation of uric acid sensitised by quinones electron transfer to ^3Q also occurs.[75]

III. ELECTRON TRANSFER TO QUINONE MOLECULES IN TRIPLET STATES

1. Kinetics of the Quenching of Quinone Molecules in Triplet States by Electron Donors

The kinetics and mechanism of the quenching of the triplet states of quinones by electron donors in liquid solutions have been investigated by laser flash photolysis methods. The rate constants for the quenching of the triplet states of compounds (IV),[42,44,76–82] (II),[40,48,51,52,83] and III,[45,46,84] 2-methyl-1,4-naphthoquinone (VI),[85] 2-sulpho-9,10-anthraquinone (VII),[86–88] and anthanthrone (VIII),[89,90] by various electron donors have been obtained (Table 2). The kinetics of the quenching of the triplet state of compound (VIII) by free radicals, which serve as electron donors in this reaction, have also been studied.[91] The rate constants for the quenching of the triplet state of 2,6-disulpho-9,10-anthraquinone (or its solvate) in water by various anions have been estimated as 10^6–10^7 litre mol^{-1} s^{-1}.[92,93] The triplet state of 2-methanesulphonyl-9-10-anthraquinone is quenched by Cl^- in water with a rate constant of ~10^7 litre mol^{-1} s^{-1}.[94]

Table 2. The rate constants for the quenching of the triplet states of quinones by electron and hydrogen atom donors in liquid solutions at room temperature.

Quenching agent	Solvent	k_q, litre $mol^{-1}s^{-1}$	Refs.
	Duroquinone		
NN-Dimethyl-4-methoxyaniline	Benzene	$1.2 \cdot 10^{10}$	[42]
"	Acetonitrile	$1.3 \cdot 10^{10}$	[42]
"	Methanol	$1.4 \cdot 10^{10}$	[42]
NN-Dimethylaniline	Benzene	$7.7 \cdot 10^{9}$	[42]
"	Acetonitrile	$9.9 \cdot 10^{9}$	[42]
"	Methanol	$1.1 \cdot 10^{10}$	[42]
NN-Diethylaniline	Cyclohexane	$8.0 \cdot 10^{9}$	[77]
"	Acetonitrile	$9.4 \cdot 10^{9}$	[77]
Aniline	Water–methanol (4:1), pH 8	$3.0 \cdot 10^{9}$	[81]
$PhNH_3^+$	Water–methanol (4:1), pH 2.4	$5.0 \cdot 10^{7}$	[81]
"	Water–methanol (4:1), pH ~2	$< 10^{7}$	[81]
Diphenylamine	Benzene	$7.3 \cdot 10^{9}$	[42]
"	Acetonitrile	$7.5 \cdot 10^{9}$	[42]
"	Methanol	$8.4 \cdot 10^{9}$	[42]
"	Wather–ethanol (2:1)	$3.0 \cdot 10^{9}$	[78]
Tri-*p*-tolylamine	Benzene	$6.7 \cdot 10^{9}$	[42]
"	Acetonitrile	$1.0 \cdot 10^{10}$	[42]
"	Methanol	$1.0 \cdot 10^{10}$	[42]

Table 2 (cont'd)

Quenching agent	Solvent	k_q, litre mol^{-1}s^{-1}	Refs.
	Duroquinone		
Triphenylamine	Benzene	$6.5\cdot10^7$	[42]
"	Acetonitrile	$7.8\cdot10^9$	[42]
"	Methanol	$8.0\cdot10^9$	[42]
Tri-*p*-bromophenylamine	Benzene	$4.2\cdot10^8$	[42]
"	Acetonitrile	$6.4\cdot10^9$	[42]
"	Methanol	$8.0\cdot10^9$	[42]
Trimethylamine	Water–methanol (4 : 1), pH 11	$3.0\cdot10^9$	[81]
Me_3NH^+	Water–methanol (4 : 1), pH 7	$<10^7$	[81]
Triethylamine	Cyclohexane	$2.0\cdot10^9$	[77]
"	Acetonitrile	$6.0\cdot10^9$	[77]
Et_3NH^+	Water–methanol (4 : 1), pH 2	$<10^5$	[81]
Triethylamine	Isopropyl alcohol	$7.1\cdot10^8$	[76]
Et_3NH^+	Water–methanol (4 : 1), pH −2	$<10^6$	[81]
s-Butylamine	Isopropyl alcohol	$2.3\cdot10^8$	[76]
Diazabicyclooctane	Water–methanol (4 : 1), pH 2.1	$1.3\cdot10^7$	[81]
"	Water–methanol (4 : 1), pH 0	$3.0\cdot10^6$	[81]
$CH_3CH(CO_2^-)NH_2$	Water–methanol (4 : 1), pH 10.2	$1.0\cdot10^5$	[81]
$CH_3CH(CO_2^-)NH_3^+$	Water–methanol (4 : 1), pH 5.4	$5\cdot10^5$	[81]
$^-O_3SCH_2NH_2$	Water–methanol (4 : 1), pH 7.2	$2.7\cdot10^7$	[81]
$NCCH_2NH_2+NCCH_2NH_3^+$	Water–methanol (4 : 1), pH 5.3	$1\cdot10^6$	[81]
$NCCH_2NH_3^+$	Water–methanol (4 : 1), pH 3.3	$<10^5$	[81]
NH_3	Water–methanol (4 : 1), pH 10–11	$3.0\cdot10^6$	[81]
NH_4^+	Water–methanol (4 : 1), pH 4–5	$<10^5$	[81]
1,3,5-Trimethoxybenzene	Water–ethanol (2 : 1)	$3.3\cdot10^9$	[78]
1,2,3-Trimethoxybenzene	Benzene	$5.5\cdot10^7$	[42]
"	Acetonitrile	$2.2\cdot10^8$	[42]
"	Methanol	$3.0\cdot10^9$	[42]
2-Methoxynaphthalene	Benzene	$4.2\cdot10^7$	[42]
"	Acetonitrile	$1.0\cdot10^8$	[42]
"	Methanol	$2.2\cdot10^9$	[42]
Dibenzo-18-crown-6 ether	Benzene	$7.6\cdot10^6$	[42]
"	Acetonitrile	$5.5\cdot10^7$	[42]
"	Methanol	$9.5\cdot10^8$	[42]
2,3-Dimethylnaphthalene	Benzene	$3.2\cdot10^9$	[42]
"	Acetonitrile	$3.3\cdot10^8$	[42]
"	Methanol	$4.3\cdot10^7$	[42]
2,6-Dimethylnaphthalene	Benzene	$1.6\cdot10^8$	[42]
"	Acetonitrile	$3.3\cdot10^6$	[42]
"	Methanol	$1.1\cdot10^8$	[42]
Pentamethylbenzene, naphthalene	Benzene, acetonitrile, methanol	$<5\cdot10^4$	[42]
Cl^-	Water–methanol (4 : 1), pH 7	$1.0\cdot10^7$	[81]
"	Water–methanol (4 : 1), pH −2	$1.0\cdot10^9$	[81]
Br^-	Water–methanol (4 : 1), pH 7	$4.0\cdot10^9$	[81]
OH^-	Water–methanol (4 : 1), pH 10–12	$1.5\cdot10^9$	[81]
I^-	Water–methanol (4 : 1), pH 7	$9.0\cdot10^9$	[81]
"	Acetonitrile	$9.9\cdot10^9$	[82]
Ag^+	Water–methanol (2.3 : 1)	$1.5\cdot10^6$	[82]
"	Acetonitrile	$5\cdot10^5$	[82]
Fe^{2+}	Water–ethanol (2 : 1)	$1.3\cdot10^9$	[78]
$Fe(CN)_6^{4-}$	Water–ethanol (2 : 1)	$2.6\cdot10^9$	[78]
"	Water–methanol (2.3 : 1)	$4.3\cdot10^9$	[82]
$IrCl_6^{3-}$	Water–methanol (2.3 : 1)	$4.1\cdot10^9$	[82]
SCN^-	Water–methanol (2.3 : 1)	$4.6\cdot10^9$	[82]
"	Acetonitrile	$8.1\cdot10^9$	[82]
CO_3^{2-}	Water–ethanol (2 : 1)	$7.3\cdot10^7$	[78]
Durohydroquinone	Isopropyl alcohol	$2.1\cdot10^9$	[150]
"	Cyclohexane	$6.2\cdot10^9$	[149]
"	Ethanol	$3.9\cdot10^9$	[149]
4-Phenylphenol	Benzene	$1.2\cdot10^{10}$	[42]
"	Acetonitrile	$2.3\cdot10^9$	[42]
"	Methanol	$6.9\cdot10^9$	[42]
	Chloranil		
Naphthalene	Propionitrile	$7.0\cdot10^9$	[83]
Acrylonitrile	1,2-Dichloroethane	$3.1\cdot10^4$	[40]
Durene	1,2-Dichloroethane	$3.1\cdot10^9$	[48]
Methyl methacrylate	1,2-Dichloroethane	$5.1\cdot10^6$	[40]
"	Acetonitrile	$6.7\cdot10^8$	[40]
Styrene	1,2-Dichloroethane	$2.5\cdot10^9$	[40]
"	Acetonitrile	$8.0\cdot10^8$	[40]
Pyrazole	Dioxan	$4\cdot10^7$	[51]
"	Acetonitrile	$7\cdot10^7$	[51]
Imidazole	Dioxan	$2.0\cdot10^9$	[51]
"	Acetonitrile	$4.1\cdot10^9$	[51]
1-Methylimidazole	Dioxan	$2.6\cdot10^9$	[51]
"	Acetonitrile	$4.7\cdot10^9$	[51]
Benzimidazole	Dioxan	$1.4\cdot10^9$	[51]
"	Acetonitrile	$6.3\cdot10^9$	[51]

Table 2 (cont'd)

Quenching agent	Solvent	k_q, litre mol^{-1}s^{-1}	Refs.
	Chloranil		
1-Methylbenzimidazole	Dioxan	$1.1\cdot10^9$	[51]
"	Acetonitrile	$4.8\cdot10^9$	[51]
Indazole	Dioxan	$1.4\cdot10^9$	[51]
"	Acetonitrile	$5.3\cdot10^9$	[51]
2-Ethylindazole	Dioxan	$3.4\cdot10^9$	[51]
"	Acetonitrile	$9.6\cdot10^9$	[51]
Indole	Dioxan	$5.0\cdot10^9$	[51]
"	Acetonitrile	$1.3\cdot10^{10}$	[51]
1-Ethylindole	Dioxan	$5.4\cdot10^8$	[51]
"	Acetonitrile	$1.2\cdot10^{10}$	[51]
Tetrachlorohydroquinone	Dioxan	$1.7\cdot10^9$	[152]
"	1,2-Dichloroethane	$3.6\cdot10^9$	[152]
"	Acetonitrile	$4.7\cdot10^9$	[152]
	Fluoranil		
Tetrafluorohydroquinone	Benzene	$2.0\cdot10^9$	[57]
	2,6-Diphenyl-1,4-benzoquinone		
NNN'N'-Tetramethyl-*p*-phenylenediamine	Toluene	$1.8\cdot10^{10}$	[45]
	Dibutyl phthalate	$1.1\cdot10^9$	[45]
Triphenylamine	Toluene	$5.0\cdot10^9$	[45]
"	Dibutyl phthalate	$3.3\cdot10^8$	[45]
Diphenylamine	Toluene	$7.9\cdot10^9$	[45]
"	Dibutyl phthalate	$5.1\cdot10^8$	[45]
2,3,5-Trimethylphenol	Benzene	$1.1\cdot10^{10}$	[151]
2,4,6-Trimethylphenol	Benzene	$9.9\cdot10^9$	[151]
4-Phenylphenol	Benzene	$1.0\cdot10^{10}$	[151]
2,6-Diphenylhydroquinone	Benzene	$1.0\cdot10^{10}$	[151]
2,6-Diphenyl-4-diphenylmethylphenol	Benzene	$9.2\cdot10^9$	[151]
6-t-Butyl-2-phenyl-4-diphenylmethylphenol	Benzene	$5.6\cdot10^9$	[151]
2,6-Di-t-butyl-4-diphenylmethylphenol	Benzene	$3.4\cdot10^9$	[151]
2,4,6-Tri-t-butylphenol	Benzene	$2.3\cdot10^9$	[151]
2,3-Dichlorophenol	Benzene	$9.1\cdot10^9$	[151]
3-Nitrophenol	Benzene	$1.3\cdot10^{10}$	[151]
2,6-Di-t-butyl-4-nitrophenol	Benzene	$6.6\cdot10^9$	[151]
4-Nitrophenol	Benzene	$2.7\cdot10^9$	[151]
2,4-Dinitrophenol	Benzene	$4.2\cdot10^9$	[151]
2,6-Dinitrophenol	Benzene	$7.3\cdot10^8$	[151]
2,4,6-Trinitrophenol	Benzene	$9.7\cdot10^9$	[151]
	2-Methyl-1,4-naphthoquinone		
Thymine	Water	$2.7\cdot10^9$	[85]
Uracil	Water	$3.0\cdot10^9$	[85]
6-Methyluracil	Water	$3.2\cdot10^9$	[85]
	2-Sulpho-9,10-anthraquinone		
$NCSe^-$	Water	$3.7\cdot10^9$	[86]
NO_2^-	Water	$3.2\cdot10^9$	[86]
I^-	Water	$4.2\cdot10^9$	[86]
N_3^-	Water	$3.1\cdot10^9$	[86]
Br^-	Water	$3.8\cdot10^9$	[86]
NCS^-	Water	$3.9\cdot10^9$	[86]
OH^-	Water	$0.3\cdot10^9$	[86]
Cl^-	Water	$0.5\cdot10^9$	[86]
ClO_4^-, SO_4^{2-}	Water	$<10^6$	[86]
	Anthanthrone		
NN-Dimethyl-4-methoxyaniline	Benzene	$7.6\cdot10^9$	[89]
"	Acetonitrile	$9.2\cdot10^9$	[89]
Triphenylamine	Benzene	$4.6\cdot10^5$	[89]
"	Acetonitrile	$2.3\cdot10^9$	[89]
4-Aminobiphenyl	Benzene	$4.6\cdot10^9$	[89]
"	Acetonitrile	$5.3\cdot10^9$	[89]
4-Bromoaniline	Benzene	$4.8\cdot10^9$	[89]
"	Acetonitrile	$4.8\cdot10^9$	[89]
4-Methoxybiphenyl	Benzene	$3.5\cdot10^5$	[89]
"	Acetonitrile	$3.9\cdot10^5$	[89]
2,6-Diphenylhydroquinone	Benzene	$2.8\cdot10^9$	[151]
"	Acetonitrile	$2.1\cdot10^9$	[151]
2,4,6-Trimethylphenol	Benzene	$3.2\cdot10^9$	[151]
"	Acetonitrile	$5.8\cdot10^8$	[151]
2,6-Di-t-butyl-4-methylphenol	Benzene	$9.2\cdot10^7$	[151]
"	Acetonitrile	$2.2\cdot10^7$	[151]
2,3,5-Trimethylphenol	Benzene	$2.3\cdot10^9$	[151]
"	Acetonitrile	$4.8\cdot10^8$	[151]
4-Phenylphenol	Benzene	$2.3\cdot10^9$	[151]
"	Acetonitrile	$2.8\cdot10^7$	[151]
2,3-Dichlorophenol	Benzene	$5.3\cdot10^7$	[151]
"	Acetonitrile	$8.3\cdot10^6$	[151]
3-Nitrophenol	Benzene	$1.1\cdot10^7$	[151]
"	Acetonitrile	$1.9\cdot10^6$	[151]
2,6-Di-t-butyl-4-nitrophenol	Benzene	$7.2\cdot10^6$	[151]
"	Acetonitrile	$3.4\cdot10^6$	[151]
4-Nitrophenol	Benzene	$5.7\cdot10^6$	[151]
"	Acetonitrile	$1.0\cdot10^6$	[151]
2,6-Dinitrophenol	Benzene	$4.0\cdot10^5$	[151]
"	Acetonitrile	$8.1\cdot10^5$	[151]
2,4-Dinitrophenol	Benzene	$1.9\cdot10^5$	[151]
"	Acetonitrile	$2.7\cdot10^5$	[151]
2,4,6-Trinitrophenol	Benzene	$5.2\cdot10^4$	[151]
"	Acetonitrile	$1.5\cdot10^5$	[151]

The quenching of excited states by electron transfer is described by the scheme[95,96]

$$^3Q + D \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} (^3Q \cdots D) \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} {}^3(Q^- \cdots D^+) - \begin{cases} \xrightarrow{k_{30}} Q^- + D^+, \\ \xrightarrow{k_{31}} Q + D. \end{cases} \quad (2)$$

Subject to the condition $k_{31} \ll k_{30}$, which is usually fulfilled in polar solvents, the quenching rate constants k_q can be calculated within the framework of this scheme from the formula

$$k_q = \frac{k_{12}}{1 + (1/K_{23} + k_{30}/k_{23})\, k_{21}/k_{30}}. \quad (3)$$

The rate constants for the elementary steps of reaction (2) are calculated from the formulae

$$k_{23} = k^0 \exp(-\Delta G^*_{23}/RT), \quad (4)$$

$$k_{23}/k_{32} = K_{23} = \exp(-\Delta G_{23}/RT), \quad (5)$$

where k^0 is the frequency factor and ΔG^*_{23} and ΔG_{23} are the free energy of activation and the standard free energy of electron transfer. It is assumed in the above model[95,96] that $k^0 = k_{30}$ and that k_q in acetonitrile can be calculated from the formula

$$k_q, \text{ litre mol s}^{-1} = 2 \cdot 10^{10} \{1 + 0.25 [\exp(\Delta G^*_{23}/RT) + \exp(\Delta G_{23}/RT)]\}^{-1}, \quad (6)$$

ΔG^*_{23} is then related to ΔG_{23} by the equation

$$\Delta G^*_{23} = \frac{1}{2}\Delta G_{23} + \left[\left(\frac{1}{2}\Delta G_{23}\right)^2 + (\Delta G_{23}(0))^2\right]^{1/2}, \quad (7)$$

where $\Delta G_{23}(0)$ is the internal barrier to the electron transfer process, amounting to 2.4 kcal mol^{-1} in acetonitrile. Other relations between ΔG^*_{23} and ΔG_{23} have also been proposed—within the framework of parabolic energy surfaces:[97,98]

$$\Delta G^*_{23} = \Delta G_{23}(0)\,[1 + 0.25\Delta G_{23}/\Delta G_{23}(0)]^2, \quad (8)$$

and a formula analogous to the corresponding expression for the energy transfer process:[99]

$$\Delta G^*_{23} = \Delta G_{23} + \Delta G_{23}(0) \ln\{1 + \exp[-\Delta G_{23} \ln 2/\Delta G_{23}(0)]\} (\ln 2)^{-1}. \quad (9)$$

ΔG_{23} can be calculated from the oxidation-reduction potentials and the energy of the triplet state.[95,96,100]

The relations between k_q and ΔG_{23}, calculated by Eqn.(6) using Eqns.(7)–(9), are presented in Fig.3, which also includes experimental data on the quenching of the triplet states of compounds (IV) and (VII) by inorganic ions in water as well as compound (IV) in the triplet state in acetonitrile and benzene by aromatic electron donors (Table 2). The relations corresponding to Eqns.(7) and (9) describe satisfactorily the experimental results in a polar medium. The relation corresponding to Eqn.(8) predicts a decrease of k_q for high negative values of ΔG_{23}, which has not been observed experimentally. The causes of the discrepancy between the theory and experiment (the presence of other reaction channels, the characteristic features of the organisation of the medium around the pair of charged and neutral reactants, and the forms of the energy surface) have been discussed.[101,102]

The satisfactory correlation between k_q and ΔG_{23} is not by itself proof that total charge transfer takes place in the course of the quenching process. Thus, whereas in the quenching of compound (IV) in the triplet state by certain inorganic ions and aromatic donors in hydroxylated solvents yields radical-ions even for low values of k_q,[42,78,80] in acetonitrile radical-ions are formed only for values of k_q close to the diffusional limit.[42] In quenching with low constants k_q, the reaction can be achieved via the formation of a non-polar TE, which dissociates slowly into radical-ions. The protonation of ^3Q leads to an increase of the electron-accepting capacity. In the protonation of compound (IV) in the triplet state, k_q for the anions increases and that for the cation diminishes (Table 2).[81]

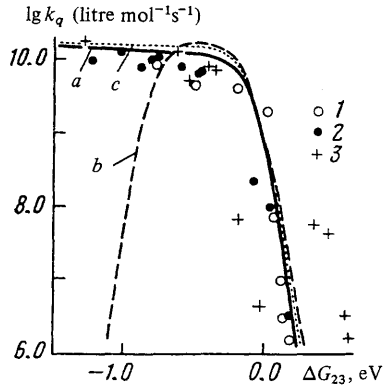


Figure 3. Dependence of lg k_q on ΔG_{23} calculated by Eqn. (6) using Eqns.(7) (*a*), (8) (*b*), and (9) (*c*) and experimental values of k_q obtained in the quenching of quinone molecules in the triplet state by electron donors in different solvents: *1*) water; *2*) acetonitrile; *3*) benzene.

If the intermediate TE is non-polar in both polar and non-polar solvents, then k_q does not change on passing from benzene to acetonitrile (Table 2). Such TE have low dipole moments and their energy depends only slightly on the dielectric constant of the medium ε. The change in the nature of the TE (a transition from non-polar to polar nature) if ε increases entails a sharp break in the relations between k_q and ε, as has been observed in the quenching of certain ^3Q by triphenylamine.[44,89] The introduction of solvating additives, which form complexes with TE, is also accompanied by an appreciable increase in k_q (Table 2) as a consequence of the change in the nature and energy of the TE.[42,44,89]

Thus the kinetics and mechanism of the quenching of the triplet states of quinones by electron donors are determined by the properties of the intermediate TE, which are also responsible for the characteristics of the formation reaction of radical-ions in polar media.

2. The Formation of Radical-Ions in Reactions of Quinones in Triplet States

Electron transfer to a quinone molecule in the triplet state in polar media is accompanied by the formation of the quinone radical-anion and the oxidised form of the electron donor, which is frequently the solvent molecule. The radical-ions have been detected by flash and laser photolysis methods in the quenching of the triplet states of compound (IV) by aromatic amines,[34,42,44,54,77–79,82,103,104] aromatic hydrocarbons,[42,78,80] acetone,[78] and inorganic anions;[78,79,81] the triplet state of compound (II) by aromatic amines,[34,48,54,105] heterocyclic compounds,[51,52] aromatic hydrocarbons,[41,42,83,106–108] cyclic hydrocarbons,[64] methyl methacrylate,[40] and

certain polar solvents;[39,83,105,108–110] the triplet states of other derivatives of compound (I) by aromatic amines and hydrocarbons;[33,34,45,46,53–55] the triplet state of 1,4-naphthoquinone (IX) by triphenylamine;[54] the triplet state of compound (VI) by pyrimidines,[85] the triplet state of compound (V) and its derivatives by amines[54,111] and inorganic anions;[86,87,92,93,112] the triplet state of compound (VIII) by aromatic amines,[89] and the triplet states of diphenoquinone derivatives by triphenylamine.[54] The formation of radical-ions follows unambiguously from CINP data on the photolysis of compound (II) in polar solvents in the presence of olefins[63,71] and certain cyclic hydrocarbons.[65–69] The formation of radical-ion pairs in the photolysis of t-butyl-substituted derivatives of compound (I) and o-benzoquinone in frozen diethylamine and triethylamine has been observed by EPR,[113,114] but in another study[115] it was concluded that a pair of neutral radicals is formed.

On the basis of chemically induced electron polarisation (CIEP) and CINP data, it has been suggested that the main process in the quenching of ^3Q by aliphatic amines in alcohols is the formation of quinone radical-anions.[116,117] The radical-anion can be formed in the course of secondary proton transfer processes.[118] Thus the formation of quinone radical-anions has been detected by the CIEP method in the photolysis of alcoholic solutions of quinones in the presence of aliphatic amines,[76,119–122] but it has been noted in experimental laser photolysis that the formation reaction of these radicals is slower than the destruction of the initial triplet state.[76] In experiments on picosecond laser photolysis, it was possible to demonstrate unambiguously that the quenching of the triplet state of compound (V) and its chlorinated derivatives by triethylamine in alcohol entails electron transfer.[111] The conclusion, reached on the basis of EPR and CIEP data, that radical-ions are formed in the course of the primary step, in quinone–organometallic donors[118,123–127] and vitamin K_1–vitamin C[128] systems also appears to be fairly unambiguous. In the 9,10-phenanthrenequinone (X)–$Me_3SnSnMe_3$ system, radicals are formed on photoexcitation of the EDA complexes in the region of the CT band.[118] An EPR signal, which was assigned to a radical-ion pair, has been detected in the photolysis of crystalline specimens of 3,6-di-t-butylcatechol with added 3,6-di-t-butyl-1,2-benzoquinone.[129–130]

The formation of radical-ions on interaction of quinones in triplet states with electron donors in polar media usually takes place with yields close to 1.0 in systems where ΔG_{23} is negative and k_q is close to the diffusional limit.[42,78,83] Donors having a radical fragment are an exception, since in this case an ion pair in a doublet spin state is formed. In this state (in contrast to the triplet state) there is no prohibition of the transition to the ground (also doublet) state of the initial reactant.[91] In systems with positive ΔG_{23} and k_q below the diffusional limit, high yields of radicals were observed only in hydroxylated solvents.[42]

Radical-ions are formed in high yields on quenching of ^3Q by electron donors in micellar solutions and microemulsions, where the reactants can be present in both the same and in different phases.[78,79,80,103,104,131] In the latter case electrons are transferred from the surface of the micelle (the site where the donor is located) through the interface to the quinone molecule in the triplet state located within the micelle. This process is very rapid, for example occurring in 40 ns between the molecule of compound (IV) in an anionic micelle and Fe^{2+} [78] and even faster between the same molecule in a cationic micelle and CO_3^{2-},[79] which is due to the operation of a tunnel mechanism. The radicals are not formed in micelles containing Cl^- and Br^- anions owing to the quenching of the triplet state by the latter. This effect is not quite so pronounced in microemulsions, where the molecule in the triplet state is present in the benzene phase and is separated from the ions of the surfactant.[103]

In many cases the quenching of ^3Q by inorganic anions (for example, NO_2^-, CO_3^{2-}, and SO_3^{2-}) is accompanied by the formation of radicals with a high yield.[86,87,92,93,112,132] However, radicals are not formed on interaction with N_3^-, NCS^-, Cl^-, Br^-, and I^-.[81,86,87,92,94] The contribution of quenching due to the heavy atom effect is insignificant, since Cs^+ ions do not quench effectively the triplet state of compound (IV).[81] The dependence of the yield of radicals on the nature of the inorganic anion can be accounted for in terms of the extent of the spin–orbital coupling in the inorganic radical. If the multiplet splitting of the energy levels of the radical, determined by the orbital momentum, exceeds 100 cm^{-1} then the intersystem crossing in the radical pair is accelerated so much that this process becomes the main channel leading to the destruction of the triplet radical pair.[87] The quenching by the NO_2^- anion, which has a triplet state with an energy of 56 kcal mol^{-1}, should be specially mentioned. The quenching by this anion leads to the formation of radicals, i.e. in the presence of two possible reaction channels (energy transfer and electron transfer), both of which are exothermic, the process proceeds via the pathway most favoured by energy factors. It is quite likely that electron transfer is preceded in this instance by energy transfer.

A low quantum yield in the formation of radicals is characteristic also of the quenching by the OH^- anion [in the compound (IV)—OH^- system, the yield of radicals is 10%[77]] as a consequence of the existence of rapid chemical channels leading to the destruction of TE (hydroxylation).[86] Exactly the same adduct formation reaction, competing with dissociation into radical-ions, is responsible for the low efficiency of the formation of radicals on quenching of the triplet state of compound (II) by vinyl monomers.[40]

Low yields of radical-ions have been recorded in the photolysis of quinones in polar solvents without hydroxy-groups [thus the quantum yield is 0.08 in the photolysis of compound (II) in acetonitrile and is smaller by a factor of 3 in propyl cyanide,[40,83] while in the photolysis of compound (IV) in acetone it amounted to 0.08[78]], which is due to the low value of the electron transfer rate constant. The low (0.15) yield of radical-anions in the photolysis of compound (IV) in micellar solutions of sodium lauryl sulphate (the sulphate group is the electron donor) can be explained analogously.[78]

Detailed studies by flash photolysis with measurement of the absorption and electrical conductivity in binary mixtures and viscous alcohols at different pressures have shown that, in the quenching of the triplet states of quinones by aromatic electron donors in media of moderate polarity, radicals are formed as a result of the dissociation of the TE in accordance with the scheme[34,53–55]

$$3Q + D \rightleftarrows TE \begin{cases} \xrightarrow{k_2} Q^- + D^+, \\ \xrightarrow{k_1} Q + D. \end{cases} \qquad (10)$$

The rate constant for the dissociation of polar TE into radical-ions (k_2) depends on the viscosity of the medium and can be calculated satisfactorily from the formula for the rate constant for the diffusion-controlled dissociation of ion pairs:

$$k_{dis} = 3e^2D\{\sigma^3\varepsilon kT[\exp(e^2/\sigma\varepsilon kT) - 1]\}^{-1}, \qquad (11)$$

where e is the electronic charge, D the mutual diffusion coefficient, and σ the average distance between the ions in the pair.

The values of σ (Table 3), obtained from the dependence of k_{TE} or the yield of radicals on the dielectric constants ε of the binary mixtures (Fig. 4) in most cases significantly exceed the sum of the van der Waals radii of the reactants and

also the distance between the unpaired electrons in the analogous radicals pairs in frozen solutions (amounting to 6.0–6.5 Å[38,113]), where the reaction proceeds via EDA or hydrogen-bonded complexes). The presence of a hydrogen bond between the radicals, for example, in the 3-chloro-2,6-diphenyl-1,4-benzoquinone–DPA system, is accompanied by a decrease of σ which is more pronounced the stronger the hydrogen bond. High values of σ reflect the fact that the radicals are formed from solvate-separated radical-ion pairs.

Table 3. The distances (σ/Å) between the radical-ions in triplet exciplexes.*

Quinone	Donor	Solvent		Refs.
		benzene–methanol	benzene–benzonitrile	
9,10-Anthraquinone	Triphenylamine	16.7	—	[54]
1,4-Naphthoquinone	"	17.3	—	[54]
Duroquinone	"	19.2	11.9 (19.7)	[54]
2,6-Diphenyl-1,4-benzoquinone	"	16.0	11.4	[54]
1,4-Benzoquinone	"	15.3	—	[54]
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	"	14.2	—	[54]
Chloranil	"	13.4	10.5	[54]
Bromanil	"	12.9	10.9	[54]
4,4'-Diphenoquinone	"	17.0	—	[54]
3,3',5,5'-Tetrachloro-4,4'-diphenoquinone	"	15.1	11.6	[54]
3,6-Di-t-butyl-1,2-benzoquinone	"	13.6	—	[54]
3-Chloro-2,6-diphenyl-1,4-benzoquinone	"	14.7	—	[54]
"	Naphthalene	15.3	—	[54]
"	1,2,3-Trimethoxybenzene	15.6	—	[54]
"		13.8	—	[54]
3-Chloro-2,6-diphenyl-1,4-benzoquinone	*NN*-Dimethylaniline	14.6	—	[54]
"	*NN*-Dimethyl-4-methoxyaniline	15.7	—	[54]
"	*NNN'N'*-Tetramethylbenzidine	15.0	—	[54]
"	*NNN'N'*-Tetramethyl-*p*-phenylenediamine	—	7.5	[34]
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	Diphenylamine	—	8.5	[34]
Chloranil	"	—	10.5	[34]
Bromanil	"	—	11.5	[34]
	"			

*The value for the benzene–benzonitrile mixture + 5 vol.% methanol is given in brackets.

In the absence of specific interactions of the radicals with one another or with the molecules of the medium, the values of σ are almost independent of the structure of the quinone and the donor (Table 3), but the introduction of alcohols into the system induces an increase of σ which is greater the stronger the hydrogen bond between the radical-anion of the quinone and the alcohol molecule.

The study of the dynamics of the processes in the radical-ion pair in the picosecond time range in electron transfer from aromatic donors to a molecule of compound (II) in the triplet state in acetonitrile showed that the electron transfer is accompanied by the establishment of equilibrium in the cation–anion–molecular environment system over a period of approximately 0.1–0.5 ns.[106] It has been suggested that this thermodynamic equilibrium is attained due to diffusional processes. In the analysis of the spectral changes in the course of the establishment of equilibrium, it was concluded that the distance over which the electron is transferred is less than the equilibrium distance between the radicals in the pair. Analogous experiments in the compound (V)—triethylamine system in alcohol and acetonitrile also indicate the primary formation of a contact radical-ion pair.[111]# However, studies on the benzophenone–amine system have led the authors[133,134] to the conclusion that the radicals formed after electron transfer come closer together.

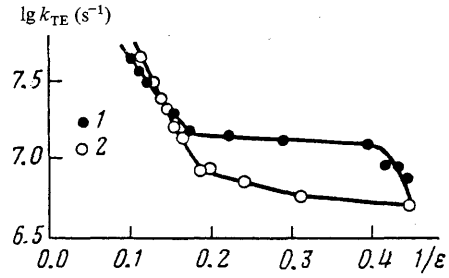


Figure 4. Dependence of lg k_{TE} on $1/\varepsilon$ for the solvent obtained by laser photolysis of solutions of 2,6-diphenyl-1,4-benzoquinone in the presence of triphenylamine in binary benzene–methanol (1) and benzene–benzonitrile (2) mixtures.[53]

IV. HYDROGEN ATOM TRANSFER TO QUINONE MOLECULES IN TRIPLET STATES

The reaction involving the transfer of a hydrogen atom to the molecules of quinones in triplet states can be achieved via three mechanisms. In the two extreme cases their reaction takes place in two stages where an electron is transferred initially followed by a proton [Scheme (12)] or conversely [Scheme (13)]:

$$\begin{array}{l} {}^3Q + RH \rightleftarrows ({}^3Q \cdots RH) \rightleftarrows {}^3(Q^- \cdots RH^+) \begin{cases} \longrightarrow Q^- + RH^+, \\ \longrightarrow Q + RH, \end{cases} \\ \qquad\qquad\qquad\qquad \uparrow\downarrow \\ \qquad\qquad\qquad\qquad {}^3(QH^\cdot \cdots R^\cdot) \begin{cases} \longrightarrow QH^\cdot + R, \\ \longrightarrow Q + RH. \end{cases} \end{array} \qquad (12)$$

$$\begin{array}{l} \qquad\qquad\qquad\quad Q + RH \\ \qquad\qquad\qquad\quad \uparrow \\ {}^3Q + RH \rightleftarrows {}^3(Q \cdots RH) \rightleftarrows {}^3(QH^+ \cdots R^-) \rightleftarrows {}^3(QH \cdots R^\cdot) \begin{cases} \longrightarrow QH^\cdot + R^\cdot, \\ \longrightarrow Q + RH. \end{cases} \end{array} \qquad (13)$$

In the intermediate case the hydrogen atom is transferred more or less as a single whole:

$$^3Q + RH \rightleftarrows (^3Q \cdots RH) \rightleftarrows {}^3(QH^\cdot \cdots R^\cdot) \begin{cases} \longrightarrow QH^\cdot + R^\cdot, \\ \longrightarrow Q + RH. \end{cases} \qquad (14)$$

Generally speaking the processes enumerated may compete with one another, but the situation where the reaction cannot be assigned to any one of three types is more probable since the intermediate CT stage is described by a superposition of states of different nature and the hydrogen-bonded complex can be characterised by a potential surface with a single minimum for the position of the proton.

#See K.Hamanoue, T.Nakayama, K.Sugiura, H.Teranishi, M.Washio, S.Tagawa, and Y.Tabatu, Chem.Phys.Letters, 1985, 118, 503, and K.Hamanoue, M.Kimoto, Y.Kajiwara, T.Nakayama, and H.Teranishi, J.Photochem., 1985, 31, 143.

The transfer of a hydrogen atom to carbonyl compounds in triplet $n\pi^*$ states has much in common with the analogous process involving alkoxy-radicals and has been considered theoretically as a reaction within the framework of valence bond methods,[135] correlation diagrams,[136] and perturbation theory.[137,138] Furthermore, Formosinho[139,140] carried out calculations for the transfer of a hydrogen atom to carbonyl compounds in triplet states, including quinones, as a tunnel process within the framework of the theory of non-radiative transitions; this approach makes it possible to calculate satisfactorily the rate constants for the transfer of a hydrogen atom in systems with electron donor–acceptor interactions.

1. The Transfer of a Hydrogen Atom in the Interaction of Quinones in Triplet States with Amines

The interaction of quinones in triplet states with secondary and primary aromatic amines in liquid solutions is accompanied by the formation of both radical-ions and neutral radicals as a consequence of electron and hydrogen atom transfer respectively.[34,42,45,50,141] An increase in the temperature of the solution leads to an increased yield of neutral radicals, while the overall yield of radicals does not change. The quenching process takes place with a diffusional rate constant (Table 2); deuteriation of the amino-groups does not cause an appreciable change in the ratio of the yields of radicals of different nature.

Table 4. The equilibrium constant K_H, the enthalpy ΔH_H, and the entropy ΔS_H of the prototropic equilibrium in radical pairs in toluene and acetonitrile.[141]

Quinone	Amine	K_H		ΔH_H, kcal mol^{-1}		ΔS_H, cal mol^{-1} K^{-1}	
		toluene	CH_3CN	toluene	CH_3CN	toluene	CH_3CN
Duroquinone	Diphenylamine	50	2.7	—	5.0	—	19
2,6-Dimethoxy-1,4-benzoquinone	"	34	3.1	8.0	4.8	34	19
2,6-Diphenyl-1,4-benzoquinone	"	25	1.8	9.4	4.5	39	16
3-Chloro-2,6-diphenyl-1,4-benzoquinone	"	8.1	1.0	10.0	4.3	38	15
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	"	1.2	0.25	10.4	3.8	36	10
2,5-Dichloro-1,4-benzoquinone	"	0.52	0.17	10.6	3.5	35	9
Chloranil	"	0.04	0.08	11.4	3.3	32	6
3-Chloro-2,6-diphenyl-1,4-benzoquinone	4-t-Butyldiphenylamine	2.8	0.62	9.9	2.7	36	8
"	4,4'-Di-t-butyldiphenylamine	1.4	0.37	10.1	1.6	35	3
"	4,4'-Bis(1,1,3,3-tetramethylbutyl)-diphenylamine	1.1	0.28	10.2	1.0	35	1
3,5-Dichloro-2,6-diphenyl-1,4-benzoquinone	4,4'-Di-t-butyldiphenylamine	0.25	0.16	10.8	0.5	34	−2

The above features are characteristic of reactions proceeding via scheme (12). ΔG_{23} is negative and electron transfer is therefore the fastest of the possible reactions. Next, prototropic equilibrium is established in the radical pair and the process also takes place very rapidly in the course of thermodynamic relaxation as a consequence of the presence of a hydrogen bond. Table 4 presents the thermodynamic parameters for the prototropic equilibrium in the radical pairs formed on quenching of the triplet states of quinones by secondary aromatic amines. The reorganisation of the molecules of the medium in the vicinity of the ion pair, which has a significantly higher dipole moment than the pair of neutral radicals, leads to an extremely high ΔS_H. The weakening of the electrostatic field with increase of solvent polarity is accompanied by a decrease of ΔS_H and ΔH_H. The equilibrium shifts towards the ion pair with increase of the acidity of the semiquinone and the basicity of the aminyl radical. A linear relation is observed between the free energy of proton transfer in toluene and acetonitrile, on the one hand, and the free energy of the acid–base equilibrium in water, calculated from the corresponding pK,[141] on the other. U-shaped relations between K_H and ε for the binary toluene–acetonitrile mixture have been obtained, which can be accounted for by the different course of the decrease of ΔS_H and ΔH_H with increase of ε.[141]

The quenching of ^3Q by primary and secondary aromatic amines in the case where ΔG_{23} is positive [for example in systems incorporating compound (IV) or (VIII) and DPA, 4-aminobiphenyl, or 4-bromoaniline] is accompanied by the formation of neutral radicals and takes place with rate constants exceeding significantly the analogous constants obtained for electron donors with the same oxidation potentials but without NH groups in their structure (Table 2).[42,89,90] It has been suggested that the quenching proceeds in accordance with Scheme (14), which includes the formation of a hydrogen-bonded TE ensuring very rapid transfer of a hydrogen atom.[42,89] The question of the degree of charge transfer in the hydrogen-bonded TE remains open; one must take into account the fact that the hydrogen bond reduces significantly the energy of the states with total charge transfer. The quenching rate constants increase with increase of ε of the medium or after the introduction of a solvating additive.[89] In a polar medium or under the conditions of specific solvation, the ΔG_{23} are lower and the reaction therefore proceeds in accordance with Scheme (12).

In certain cases the transfer of a hydrogen atom takes place also on quenching of ^3Q by tertiary aromatic amines, for example, in the compound (IV)—*NN*-diethylaniline system in benzene.[77] The existence of a fairly mobile proton in the amine radical-cation results in the appearance of a channel leading to the destruction of the polar TE—a proton transfer process. Direct observations by picosecond laser photolysis have shown that the proton transfer in the polar TE arising as a result of electron transfer from *N*-methylacridine to a molecule of compound (V) in the triplet state in benzene proceeds over a period of 140 ps. §

The formation of neutral radicals is frequently observed in the interaction of quinones in triplet states with aliphatic amines having a mobile hydrogen atom at the α-carbon atom. On quenching of the triplet state of compound (IV) by triethylamine, neutral radicals are formed in both non-polar and polar solvents.[77] In CINP experiments, it has been shown[117] that the photoinitiated transfer of a hydrogen atom in the compound (I)—triethylamine system in acetonitrile takes place in two stages.[117] This mechanism has been confirmed by direct observations for the systems compound (V)—triethylamine in toluene[111] and benzophenone—triethylamine system in acetonitrile.[142] When electron transfer is thermodynamically unfavourable, an effective transfer of a hydrogen atom as a whole can be achieved provided that the α-CH bond can be arranged parallel to the orbital of the unshared electron pair of the nitrogen atom.[143]

§ See L.E.Manring and K.S.Peters, J.Amer.Chem.Soc., 1985, **107**, 6452.

The photolysis of quinones in the presence of aliphatic and secondary aromatic amines in frozen non-polar solvents is accompanied by the appearance of an EPR signal due to the pairs of neutral radicals formed on phototransfer of a hydrogen atom in the EDA complex.[144–146] The distance between the unpaired electrons in the radical pairs is 5–9 Å.

On the basis of the analysis of the temperature dependence of the yields of radicals of different nature in quinone–amine systems, one may expect that predominantly radical-ion pairs should be formed at low temperatures. However, this is true only in liquid solutions. In frozen solutions the formation of an ion pair may be difficult, since the rotational and translational mobilities of the solvent molecules are restricted, which hinders the reorganisation of the medium necessary for the stabilisation of the ion pair.

2. Interaction of Quinones in Triplet States with Phenols

The photoexcitation of quinonoid compounds in the presence of phenols is accompanied by the formation of semiquinone and phenoxy-radicals both in the liquid state and in a solid matrix. The kinetics and mechanism of the interaction of quinones in triplet states with phenolic compounds as well as the nature of the radicals formed have been investigated by flash photolysis,[41,42,84,89,90,147–165] EPR,[113,114,166] the CIEP method,[116,167–173] and the CINP method.[57,170,172,174–176] The steric structure and dynamics of the radical pairs formed in the photolysis of frozen solutions or crystals of quinones and phenols have been studied by EPR.[113,114,130,177–184]

(a) Kinetics of the reactions of quinones in triplet states with phenols. The quenching of the triplet states of quinones with a fairly high triplet energy by phenolic compounds takes place with high rate constants approaching the diffusional limit (65; see also Table 2).[42,57,84,149,150–152,163,167] As the electron-donating capacity of the phenol decreases, k_q initially falls but subsequently it begins to rise (Fig.5), which indicates a change in the reaction mechanism. The values of k_q diminish following the introduction of t-butyl groups in the *ortho*-position in the phenol owing to the shielding of the reaction centre.[151] Fig.5 shows that the quenching of the triplet state of anthanthrone, which has a low triplet energy, proceeds mainly with lower k_q (see also Table 2).[89,90,151] We may note that, although k_q diminishes as the electron-donating properties of the phenol are weakened, nevertheless the slope of the corresponding relations is significantly smaller than the value expected for electron transfer reactions and the k_q exceed the rate constant for electron transfer in the given systems. The observed set of characteristic features of the influence of the structure of the reactants and of the properties of the medium may be accounted for within the framework of three possible mechanisms [Schemes (12)–(14)].

The reactions between quinones in a high energy triplet state and phenols having fairly strong electron-donating properties (for example, hydroquinones) proceeds in accordance with Scheme (12); the protropic equilibrium in the radical pair is then fully displaced towards the formation of a pair of neutral radicals as a consequence of the extremely high acidity of the phenol radical-cations.

In the case where the free energy of the electron transfer from the phenol to the quinone molecule in the triplet state is large and positive, quenching takes place in accordance with Scheme (14). Hydrogen-bonded TE, in which the transfer of a hydrogen atom takes place, is formed in the first stage of the reaction. Since the triplet state is electrophilic, k_q diminishes as the electron-donating capacity of the phenol is reduced. An increase in the polarity of the medium weakens the hydrogen bond between the reactants in the TE, which is accompanied by a decrease of the rate constant for the transfer of a hydrogen atom.

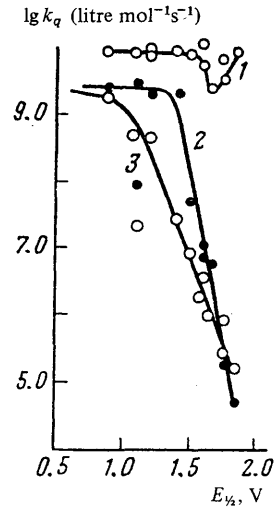


Figure 5. Dependence of lg k_q on the one-electron oxidation potentials $E_{1/2}$ of phenols in the quenching of the triplet states of 2,6-diphenyl-1,4-benzoquinone (energy of the triplet state ~2.3 eV) in benzene (curve *1*) and anthanthrone (energy of the triplet state ~1.6 eV) in benzene (curve *2*) and acetonitrile (curve *3*).[151]

It is noteworthy that the formation of a hydrogen bond in the TE can lead to a significant decrease in the energy of the state with total charge transfer (by approximately 1 eV and even more), which can be explained by the fact that the displacement of a proton from the donor to the acceptor is accompanied by an increase of the electron-donating capacity of the donor and of the electron-accepting capacity of the acceptor. For this reason, in hydrogen-bonded systems, where the free energy of the electron transfer calculated from the oxidation-reduction potentials of the reactants is positive, there is also a possibility of the transfer of a hydrogen atom via Scheme (12). The two-stage transfer of a hydrogen atom in certain analogous systems, where the reaction proceeds with participation of singlet hydrogen-bonded exciplexes, has been demonstrated experimentally as a result of direct observations by the method of picosecond laser photolysis.[185,186]

The quenching of ^{3}Q by phenols with very pronounced acid properties (picric acid, dinitrophenols) is described by Scheme (13). When this mechanism obtains, k_q can increase with increase of the acidity of the phenol and the polarity of the solvent as a consequence of the displacement of the prototropic equilibrium towards the ion pair.

The study of the influence of the viscosity of the medium on the kinetics of the quenching of the triplet state of anthanthrone by phenols made it possible to separate the stages involving the formation of a hydrogen-bonded TE and the transfer of a hydrogen atom in the TE.[90] The constants k_q

for certain phenols are significantly lower than the rate constant for the reaction occurring in each encounter of the reactants in solution, but they depend on the viscosity in the same way as the rate constant for a diffusion-controlled reaction (Fig. 6). The rate-limiting stage of the reaction in these systems is the formation of a hydrogen-bonded TE. This process is controlled by the molecular mobility but takes place with a relatively low rate constant, since the formation of a hydrogen bonded complex requires a rigorous relative orientation of the reactants. An increase in the acidity of the phenol diminishes the rate constant for the formation of the intermediate hydrogen-bonded TE,[90] which can be explained by the fact that, in systems where a hydrogen atom is transferred in complexes with a stronger hydrogen bond, the reactants in these complexes are more rigorously oriented relative to one another and such "rigid" orientation hinders the formation of the complex.

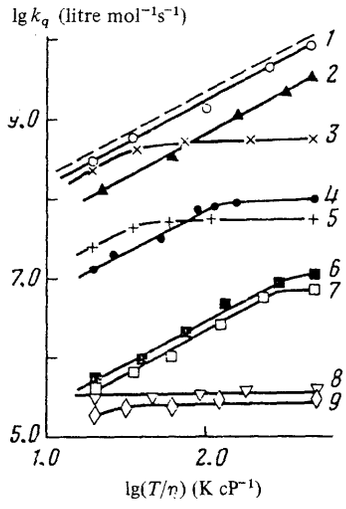


Figure 6. Dependence of lg k_q on lg (T/η) obtained in the quenching of the triplet state of anthanthrone in binary toluene–dinonyl phthalate and toluene–hexadecane mixtures by various compounds: *1*) *NN*-dimethyl-4-methoxyaniline; *2*) 2,4,6-trimethylphenol; *3*) 4-bromoaniline; *4*) 2,6-di-t-butyl-4-methylphenol; *5*) 2,3-dichlorophenol; *6*) 3-nitrophenyl; *7*) 4-nitrophenol; *8*) 4-methoxybiphenyl; *9*) 2,6-dinitrophenol. The dashed line has been calculated from the Debye formula ($8RT/3000\eta$).[90]

The nature of the rate-limiting stage and the mechanism of the quenching of ^{3}Q by phenols determine the observed kinetic isotope effect. The transfer of a hydrogen atom in the TE is characterised by an appreciable kinetic isotope effect, but when the rate-limiting stage of the quenching process involves the formation of an intermediate TE, no isotope effects are observed.[90,151] Low values (close to unity) of the kinetic isotope effect are characteristic also of quenching processes via Scheme (12) and (13), since the rates of these reactions are determined by stages involving charge transfer or the establishment of protropic equilibrium.[89,151]

(b) The formation of radicals in the photolysis of quinones in the presence of phenols. In most systems, the interaction of quinones in triplet states with phenols leads to the formation of semiquinone and phenoxy-radicals in yields close to 100%,[42,89,149,151] but CINP studies on the photolysis of quinones in the presence of phenols indicate an insignificant contribution to the geminal radical pair recombination process,[57,170–172,174–176] which should reduce the yield of radicals. Furthermore, if the process is described by Scheme (12), the decrease in the yield of radicals may be caused by rapid intersystem crossing in the non-equilibrium TE. Thus relatively low yields of radicals in the quenching of the triplet state of chloranil (II) by tetrachlorohydroquinone can be explained in this way.[41,152]

Very low yields of radicals have been observed in the quenching of the triplet state of anthanthrone by picric acid and dinitrophenols in benzene.[151] The reaction in these systems is described by Scheme (13) and the main channel leading to the destruction of the radical pair, formed after proton transfer, is the intersystem transition to the ground state. If the proton transfer reaction in the primary TE competes with the hydrogen atom transfer, then the yield of phenoxy-radicals increases with increase of temperature as a consequence of the shift of the prototropic equilibrium towards the primary TE in which the hydrogen atom is transferred.[151] The existence of the prototropic equilibrium also explains the low yields of radicals (which increase with increase of temperature) in the quenching of polar TE by phenols.[163] The transfer of a hydrogen atom results in the formation of a complex incorporating the phenoxy- and semiquinone radicals and also a molecule of the electron donor (amine). The prototropic equilibrium in this complex is determined by the proton transfer between the amine and the semiquinone.

It has been noted that, in the quenching of ^{3}Q having non-equivalent oxygen atoms, the formation of two types of semiquinone radicals may be expected, their ratio of their yields depending on the reaction mechanism.[151]

Photolysis of frozen solutions of phenols and quinones leads to the formation of radical pairs from phenoxy- and semiquinone radicals.[113,177] The phototransfer of a hydrogen atom takes place in EDA complexes, which are also present in aqueous solutions, this being indicated by the slight scatter of the distance between the unpaired electrons in the radical pair (≤0.1 Å).[177,179] Estimation of the formation constant for these complexes yields 0.2–3 litre mol^{-1} at −90 °C.[181] Analysis of the EPR spectra yielded geometrical parameters characterising the relative disposition of the radicals in the pair—the planes of their rings are parallel and are located at a distance of 1.6 Å.[180] At a low temperature the radical pairs rotate as a whole with characteristic times in the range 0.1–1.0 ms.[182]

Two types of radical pairs with different distances between the unpaired electrons have been detected for *o*-benzoquinone derivatives, which has been explained by the migration of the proton in the semi-quinone between two non-equivalent oxygen atoms.[177–180,182,184] The formation of two types of radical pairs can also be caused by the existence of EDA complexes of different composition.[183]

Two types of EPR signals of the radical pairs have been recorded in the photolysis of single crystals in polycrystalline specimens of 3,6-di-t-butyl-1,2-benzoquinone and the corresponding catechol.[129,130] One type has been assigned to the radical ion pair and the other to the pair of neutral radicals. These radical pairs are formed and are destroyed independently of one another. Presumably the protropic equilibrium in the crystal is frozen and the hydrogen atom and electron transfer processes therefore proceed in parallel within donor

and acceptor pairs, whose structure and molecular environment favour either the transfer of a hydrogen atom or the transfer of an electron. Electron transfer has been postulated in the photoexcitation of the EDA complex of duroquinone and hydroduroquinone in the region of the CT band in alcohol.[187]

3. The Abstraction of a Hydrogen Atom by Molecules of Quinones in The Triplet State from Other Organic Compounds

The transfer of a hydrogen atom to ^3Q is a very common reaction and is observed in interactions with hydrocarbons, ketones, ethers, aldehydes, anhydrides, and amides—virtually with participation of all organic compounds.[4-6]

The molecules of quinones in the triplet state can abstract a hydrogen atom even from benzene, although the quantum yield in the formation of radicals is very low.[39,188-191] The rate constant for the quenching of the triplet state of compound (V) by benzene in CCl_4 is 7.2×10^5 litre mol^{-1} s^{-1} and increases to 2.2×10^6 litre mol^{-1} s^{-1} on passing to acetonitrile.[192] The nature of the triplet state is very important in the reaction with benzene; thus the rate constants for the interaction of derivatives of compound (V) having a triplet state of the $n\pi^*$ type with benzene are significantly lower.[192] The transfer of a hydrogen atom from benzene takes place in a non-polar TE (of the type of a biradical adduct[57]) and is a side channel leading to the destruction of this species.

The photochemical reduction of quinones in a mixture with saturated hydrocarbons is relatively ineffective;[78,150,193] nevertheless, it has been possible to detect radicals by EPR[194] and flash photolysis.[39,149,195-198] The quantum yield of the radicals in the photochemical reduction of compound (IV) in cyclohexane is only 0.09[149] and is even lower in hexane.[78,150] In the case of compound (V), which has a triplet state of the $n\pi^*$ type with a higher energy, the quantum yield of the radicals in hexane is 0.11,[196] while $k_q = 8.6 \times 10^5$ litre mol^{-1} s^{-1}.[199]

The reactivity of ^3Q in relation to alkylbenzenes, fluorene, and 9,10-dihydroanthracene has been investigated in detail.[200-206] The rate of disappearance of 9,10-phenanthrenequinone (X) increases in the sequence benzene < t-butylbenene < toluene < ethylbenzene < cumene (0.33, 0.42, 1.00, 1.27, and 2.33 respectively).[200] It has been established by the CINP method that the primary step involves the abstraction of a hydrogen atom in α-position in the alkyl substituent with formation of radical pairs, which give rise to adducts on formation of C–C or C–O bonds.[201-206]

Experiments on picosecond laser photolysis demonstrated that a hydrogen atom is transferred from durene to a molecule of chloranil in the triplet state via Scheme (12) in a non-equilibrium polar TE.[48] A small contribution by a slow proton transfer process in the equilibrium TE has also been observed.

In the photolysis of frozen solutions of *p*-benzoquinone and alkylbenzenes on irradiation in the region of the CT band, the formation of radical pairs in the triplet state, incorporating neutral radicals with the distance between the unpaired electrons in the range 5.8–6.1 Å has been noted.[38] The radical pairs are also formed in the compound (I)–α-methylnaphthalene system but not in the system with β-methylnaphthalene, which is due to the different relative positions of the reacting groups (for example, the greater distance of the methyl group from C=O in the EDA complex with β-methylnaphthalene).

It has been shown by flash photolysis that radicals are formed in the photolysis of compound (IV) in chloroform[197] and of compound (II) in 1,2-dichloroethane; the quantum yield is 0.19.[40] It follows from CINP data that the reaction of fluoroanil in the triplet state with chloroform includes a stage in which a radical pair is formed. The latter then recombines to the initial reactants and dissociates into radicals.[57,175,176] A study of the reaction by EPR showed that the effectiveness of the formation of the radicals increases in the presence of traces of acid.[207] Presumably the transfer of a hydrogen atom includes a proton transfer stage.

The formation of semiquinone radicals has been observed in the photolysis of compound (II) in acetonitrile and propionitrile together with charged radicals;[39,40,83,108,110] the yield of radicals in propionitrile is then higher than in acetonitrile.[83] However, it has been concluded that semiquinone radicals are not products of the reaction of compound (II) in the triplet state with solvent molecules but are formed in photochemical side reactions.[108,110]

A hydrogen atom is transferred extremely effectively in the reactions of ^3Q with olefins. The rate constant for the quenching of the triplet state (X) by 2-methylpropene, *trans*- and *cis*-but-2-enes, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene in benzene increases from 1.0×10^8 to 1.3×10^9 litre mol^{-1} s^{-1} in this series of compounds.[208] The quantum yield of the reaction then increases from 0.21 to 0.79 and there is a simultaneous increase of the contribution of the R–H addition process, which includes a hydrogen atom transfer stage. A hydrogen atom is transferred in the TE and this process competes with the other TE destruction channel—the formation of cycloaddition products. The formation of various adducts in the TE and in the pair of neutral radicals leads to a low yield of radicals. The quantum yields of semiquinone radicals when the triplet stage of chloranil is quenched by acrylonitrile and methyl methacrylate in 1,2-dichloroethane are 0.2 and 0.08, while radicals were not detected in the quenching by styrene.[40] The quenching rate constants are determined by the ionisation potential of the donor (Table 2).

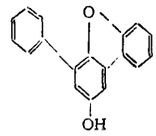
In the interaction of ^3Q with ethers, a hydrogen atom is transferred from the α-position. Radicals have been detected by EPR,[172,190,207,209-216] and flash photolysis.[39,41,215] According to CINP data, the radical pair recombines to adducts.[172,202,203,205,206,217-220] The reactivity of ethers is higher than that of alkylbenzenes. The rates of disappearance of compound (X) in tetrahydrofuran, dioxan, and diethyl ether are 1.78, 2.47, and 3.44 respectively (relative to toluene),[200] which is due to the presence of the oxygen atom with the unshared electron pair participating in the electron donor–acceptor interaction with ^3Q in the TE. A hydrogen atom may be transferred on irradiation with light in the region of the CT band in the spectrum of the EDA complex in the triplet state, as has been observed in systems of the type $R-X-CH_2CO_2H$ (X = O, S, or NH)[221] or in the compound (II)—dioxan system.[41] The yield of radicals in the latter case is 0.13, the rate constant for the formation of radicals from the TE is 3.8×10^4 s^{-1}, and the rate constant for other TE deactivation processes is 2.6×10^5 s^{-1}.

Semiquinone radicals have been recorded by EPR[190,207,209,212,214,222] and by flash photolysis[39,105,110] on photoexcitation of quinones in acetone. The yield of radicals increases in the presence of traces of acids.[207] It has been suggested that semiquinone radicals are formed in a photochemical reaction with participation of the products of a dark reaction between the reactants.[108,110]

The molecules of quinones in triplet states abstract a hydrogen atom from the aldehyde group.[4] The reaction has been investigated by the CINP method and it has been shown that its mechanism is the same as for processes involving the participation of ethers and alkylbenzenes.[206] The reactions involving the abstraction of a hydrogen atom from anhydrides

and amides are also known.[4] In the case of amides[4] and phosphates[190,210,212,214] semiquinone radicals have been detected by EPR. Semiquinone radicals are formed on photoexcitation of quinones in microemulsions[104] and in micellar solutions[223–227] as a consequence of the transfer of a hydrogen atom from the surfactant.

There exist numerous photochemical reactions of quinonoid compounds with participation of their substituents. It has been frequently suggested that the primary process is the transfer of a hydrogen atom from the substituent to the carbonyl oxygen atom, but this mechanism is still controversial.[4] A solvent molecule can participate in reactions of this type. For example, the formation of the final product of the photolysis of compound (III), i.e.



can also be accounted for within the framework of the mechanism involving intramolecular transfer of a hydrogen atom, but CINP data showed that the primary step is electron or hydrogen atom transfer from the medium with subsequent abstraction of a hydrogen atom from the substituent in the quinone by a solvent radical.[228,229]

V. PRIMARY PROCESSES IN THE PHOTOCHEMICAL REDUCTION OF QUINONES BY ALCOHOLS

Numerous studies have been devoted to the mechanism of the photochemical reduction of quinones in alcohols; the problem of the nature of the primary step, whether it is electron transfer or the transfer of a hydrogen atom as a whole, has been discussed in many of them.

The photolysis of frozen alcoholic solutions of quinones leads to the formation of semiquinone radicals, detected by UV absorption or by EPR.[38,222,230–235] The study of the nature of the alcohol radicals has shown that alkoxy-radicals are formed initially.[230,232] The primary step is electron transfer with subsequent proton transfer from the hydroxy-group. Hydroxyalkyl radicals are formed in secondary reactions. There exists a second reaction channel—the abstraction of a hydrogen atom from a carbon atom; the contribution of this pathway is 10% in the compound (I)—ethanol system.[222]

The intermediates in the photochemical reduction of quinones in the presence of alcohols in liquid solutions have been investigated by flash photolysis.[39,78,81,93,105,149,150,215,229,236–248] Scheerer and Grätzel[78] concluded that a molecule of compound (IV) in the triplet state abstracts an electron from an alcohol molecule in the 2:1 water–ethanol mixture. The formation of radical-anions derived from compound (IV) with a quantum yield of 0.2 is observed simultaneously with the destruction of the triplet. The photolysis of compound (II) in ethanol takes place analogously.[7] The interaction of compound (IV) in the triplet state with the solvent in ethanol and isopropyl alcohol leads to the formation of semiquinone radicals with a yield of 0.4.[149,150] Semiquinone radicals are formed in high yields (up to 1.0) in many other systems, but a hydrogen atom can then be transferred via a two-stage mechanism.[229]

Convincing conclusions concerning the mechanisms of the interaction of compound (V) and its halogeno-derivatives with ethanol have been reached in a study[192]¶ of the influence of added acid on the isotope effect in the photochemical reaction. Simultaneous formation of a radical-anion and the semiquinone radical was observed. Deuteriation of the alcohol reduces the yield of the photochemical reduction reaction by a factor of 1.5. The introduction of CF_3COOH does not influence the isotope effects in the case of compound (V) but reduces the isotope effect in reactions involving the halogeno-derivatives, which have a lowest triplet state of the $\pi\pi^*$ type. Thus the molecule of compound (V) in the triplet $n\pi^*$ state abstracts a hydrogen atom from an ethanol molecule, while the halogeno-derivatives of compound (V) in the triplet $\pi\pi^*$ state abstract an electron with subsequent proton transfer. Comparison of the quantum yields in the photochemical reduction in C_2H_5OD and C_2D_5OH showed that the proton is transferred from the α-carbon atom of the alcohol radical-cation.

The rate constant for the quenching of the triplet state of compound (IV) by ethanol and isopropyl alcohol is 3×10^4 litre mol^{-1} s^{-1},[78,249] while that for the quenching by benzyl alcohol is 8×10^5 litre mol^{-1} s^{-1} and increases to 2.7×10^7 litre mol^{-1} s^{-1} on protonation of a molecule of compound (IV) in the triplet state,[81] which suggests electron transfer. A significant increase in the rate constant for the quenching of ^3Q by alcohols has been observed on passing from quinones with lowest triplet states of the $\pi\pi^*$ type [compounds (II), (III), and (IV)] or of the CT type (2-piperidino-9,10-anthraquinone) to quinones with triplet states of the $n\pi^*$ type [compounds (I) and (V)]. In the quenching of compound (V) in the triplet state, the constant k_q ranges from 3×10^6 to 2×10^7 litre mol^{-1} s^{-1},[199,250] while an estimate of k_q for the quenching of compounds (I) in the triplet state by methanol in water yielded a value in excess of 10^8 litre mol^{-1} s^{-1}.[242] This feature indicates a radical mechanism of the reaction, on the basis of which the activity series of alcohols in their photochemical dehydrogenation, which is determined by the mobility of the hydrogen atom in the α-position, has been explained.[251]

The mechanism of the photochemical reduction of quinones by alcohols has been investigated by the CIEP[116,119,167,169,171,173,252–260] and CINP[170,228,229,253,261–264] methods, which in most cases do not yield an unambiguous answer as to the nature of the primary radicals. The conclusion that the primary step is electron transfer was reached in a CINP study in the compound (I)—CCl_3COOH–t-butyl alcohol[263] and compound (III)—n-propyl alcohol[228,229] systems in which CINP arises via a triplet mechanism whose manifestation is possible by virtue of the short electronic relaxation time of the alcohol radical-cation. The study of the latter system simultaneously by the CINP and flash photolysis methods showed that, although the primary step is electron transfer, ultimately neutral radicals emerge from the solvent "cage" owing to the subsequent proton transfer.

The nature of the radicals formed in the photolysis of alcoholic solutions of quinones has been investigated in detail by EPR.[187,189,190,207,210,212,214,215,265–276] Using spin-trapping agents, it has been possible to detect primary (very short-lived) alkoxy-radicals derived from the alcohol.[187,271,272,276] It was concluded that the primary step is in many cases electron transfer. In the case of very distinct triplet states of the $n\pi^*$ type there exists a second reaction pathway—the transfer of a hydrogen via a radical mechanism. The transfer of an electron or a hydrogen atom takes place in a hydrogen-bonded

¶ See also K.Hamanoue, K.Yokoyama, Y.Kajiwara, K.Nakajima, T.Nakayama, and H.Teranishi, Chem.Phys.Letters, 1984, **110**, 25.

EDA complex in the triplet state and is induced by the electron donor–acceptor interaction with participation of the unshared electron pair localised on the oxygen atom of the alcohol molecule and the electron located in the n orbital of the quinone molecule in the triplet state.

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Analysis of the literature data permits the conclusion that the electron transfer processes and the formation of triplet electron donor-acceptor complexes with a particular degree of charge transfer and with a hydrogen bond play an important role in the photochemistry of quinonoid compounds. The kinetics and mechanism of the formation of triplet exciplexes and the processes occurring in them constitute a basis which determines the course of the subsequent chemical reaction. The study of the physicochemical properties of triplet exciplexes constitutes an important field in photochemistry.

Triplet exciplexes are not formed as intermediate species in many photochemical and photobiological systems alone. Modern approaches to the creation of new methods for the recording of information on non-silver materials can also include exciplex systems in which triplet exciplexes play a key role. By virtue of the progress in the field of new methods based on laser techniques, this field is developing rapidly at the present time.

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Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow