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Mechanism of the Photochemical Reactions of Substituted Benzoquinones

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Abstract—Photoreactions of 2,6-dimethyl-, 2,6-di-*tert*-butyl-, and 2,6-diphenyl-1,4-benzoquinones with alcohols, organic acids, thioalcohols, amines (primary, secondary, and tertiary), cyclic ethers, tri- and tetraethoxysilanes are accompanied by the effect of chemical polarization of nuclei (CINDP) and lead, along with the formation of hydroquinones, to bicyclic and tricyclic structures and the products of radical substitution in the aromatic ring. The mechanisms of elementary photoreactions were elucidated. The intermediate excited states and radical structures were considered. For the first time permanent generation of radio waves in the course of the reversible photochemical reaction of substituted 1,4-benzoquinones with alcohols was detected.

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1. Photoexcited states of 1,4-benzoquinoid systems. The 1,4-benzoquinoid systems include: 1,4-benzoquinone, 1,4-benzoquinone diazides, 1,4-benzomethylenquinones, 1,4-benzoquinone imines, 1,4-cyclohexaspirodienones, and diphenoquinones. Structure and reactivity of some representatives of 1,4-benzoquinoid systems have been considered in a series of monographs and review papers [1–4]. However, due to intensive development of physicochemical and chemical methods, in recent years appeared an opportunity to look afresh and, in some cases, change the point of view on some issues related to the structure, reactivity and mechanism of reactions of 1,4-benzoquinoid systems.

The 1,4-benzoquinone molecule includes conjugated chromophore groups: >C=C< and >C=O. Therefore the molecular orbitals of 1,4-benzoquinones are of three types: σ, π, and *n*. After absorption of a photon, the molecule can exist in different electronic states ($S_{\pi\pi^*}$, S_{nn^*}, $T_{n\pi^*}$, and $T_{n\pi^*}$), to which correspond the levels of different energy. In the case of 1,4-benzoquinone [5, 6] the bands corresponding to σ–π* transitions lie in the region of vacuum ultraviolet and requires much energy consumption, and these states do not play a significant role in photochemical reactions. The bands of π–π* transitions lie in the ultraviolet region, and the bands corresponding to the *n*–π* transition are in the visible region of the spectrum.

The occupation of 1,4-benzoquinone levels is a result of π–π* and *n*–π* singlet-singlet transitions, to which correspond the bands in the absorption spectrum with the maxima at 240, 276, 456 nm and extinction coefficients 19 500, 340, and 20, respectively. In the absorption spectrum also a very weak band is observed at λ = 539 nm, which is due to the forbidden singlet-triplet transition. Hence, it is clear that the triplet state of 1,4-benzoquinone is populated mainly due to the $S_n\pi^* \rightsquigarrow T_n\pi^*$ intercombinatory conversion.

The transitions to the opposite direction are also possible [7]. This leads to an equilibrium between two states of the system even when a chemical reaction proceeds. The relative populations of the singlet and triplet states can be approximated by the $\exp(\Delta E_{ST}/KT)$, where ΔE_{ST} is the difference in the electronic energies of the singlet and triplet states [8]. The lifetime and energy of the lowest excited level T_1 of 1,4-benzoquinones are dependent on the substituents in the ring. For 1,4-benzoquinone this energy is 0.25 eV, so at room temperature the ratio of steady-state concentrations of singlet and triplet states is 1:1000.

The electronic spectrum of 1,4-benzoquinone is affected significantly by solvents: The increase in the solvent polarity shifts the *n*–π band to the region of shorter wavelengths; the π–π bands, as a rule, are weakly sensitive to the solvent polarity. 1,4-Benzoquinones dissolved in an aromatic hydrocarbon form π-complexes with the solvent, and in the absorption spectra appear charge transfer bands. The electron-withdrawing substituents in 1,4-benzoquinone increase the π-complex strength [8]. The chloranil π-complex was also observed in the solution of chloranil in tetrahydrofuran.

Thus, in substituted 1,4-benzoquinones essential influence of the substituents with different donor-acceptor properties (due to their inductive, resonance and steric effects) should be expected on the spectral characteristics of the 1,4-benzoquinone itself and the nature and behavior of the intermediate species.

Reaction of photoreduction of 1,4-benzoquinones are widely used in biology, medicine and technology. This class of reactions include the transfer of electron and hydrogen atom as elementary acts. The donors of the hydrogen atom in the photoreduction reactions may be organic compounds of various classes, the donors of the electron are heteroatoms (O, N, P, S) and inorganic ions. The photoreduction reaction proceed in parallel with other photochemical reaction of 1,4-benzoquinone discussed above. Electron or hydrogen atom transfer, or occurrence of the both processes simultaneously, largely depend on the presence of donor-acceptor complexes of 1,4-benzoquinones either with the quinone itself, or with solvent molecules or the molecule of electron (or H atom) donor. A specific role of the donor-acceptor complexes in biochemical objects, where they are widely spread, has been stressed in [9, 10]. The interaction of proteins with carbonyl compounds is primarily responsible for important aspects of the manifestations of life: reflex and secretion. Formation of charge transfer complexes may be a cause of biological evolution. The decisive role of the complexes in quinone-hydroquinone tautomerism both in crystalline phase and in solutions of substituted diphenoquinones was shown in [11]. The processes of complexation of spirane cyclohexadienones with heavy metal ions in alcohol medium were also studied [12].

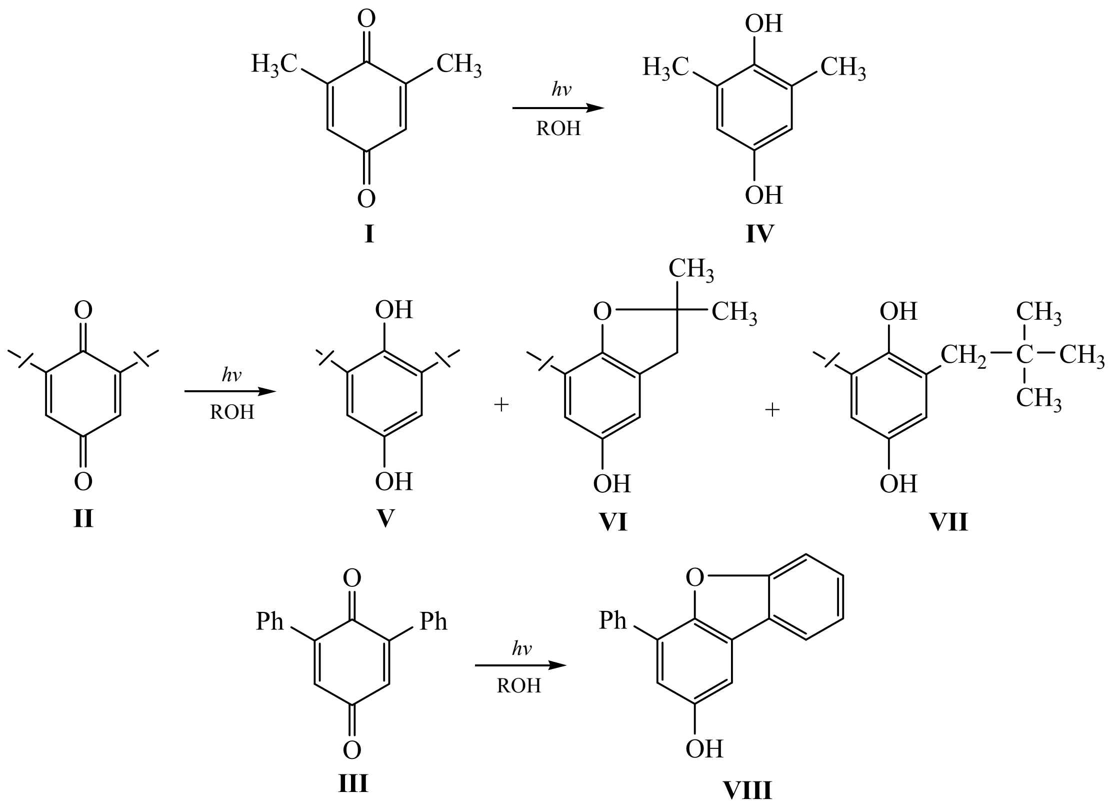
Structure and properties of the quinone donor-acceptor complexes and their photoreactions are studied effectively using various physicochemical methods (UV, IR, NMR spectroscopy, measuring the dielectric constant and dipole moments, fluorescence, pulsed and laser photolysis), but the real breakthrough in these studies was reached using the effects of chemically induced dynamic nuclear polarization (CIDNP).

The very fact of the CIDNP detection evidences that the reaction proceeds through an intermediate formation of paramagnetic ion-radicals or radicals. From the sign of the integral or multiplet polarization one can judge about the spin multiplicity of the reacting species, which is the most important characteristic of the reaction mechanism. The CINDP is the only kinetic method which allows distinguishing competition of the radical and non-radical reaction mechanisms and quantifying their contributions. The CINDP allows detection of unstable intermediates of the reaction. Registration of CIDNP has become a powerful tool for studying photoreactions, because its sensitivity toward the radicals and radical stages significantly exceeds the sensitivity of ESR spectroscopy. The CIDNP effects can determine the magnitude and signs of hyperfine coupling constants in radicals, *g*-factors of radicals, the exchange interaction energy in a pair, the magnitude and sign of spin–spin interaction in a molecule.

2. Photochemical reactions of 1,4-benzoquinone in alcohols. The photochemical reaction of 1,4-benzoquinones in alcohols have been considered partially in [1, 2, 11–14]. However, due to the non-adequacy of the photolysis conditions, it is impossible to estimate comparatively the influence of structural factors on the characteristic of photochemical reactions. In this regard, we investigated photolysis of 2,6-disubstituted 1,4-benzoquinones under equal conditions to study the effect of the nature of substituents on the photochemical behavior of 2,6-disubstituted 1,4-benzoquinones **I**–**III**. Photolysis of these quinones in aliphatic alcohols leads to different products of photoreduction (Table 1). The photochemical transformations of 2,6-dimethyl- (**I**), 2,6-di-*tert*-butyl- (**II**), and 2,6-diphenyl-1,4-benzoquinone (**III**) in methanol, ethanol, isopropyl alcohol (**VI**), and *tert*-butyl alcohol (**IX**) proceed along the scheme bellow.

As seen from Table 1, the nature of the substituents in the 1,4-benzoquinones **I**–**III** affects significantly both the character and yield of the products of photochemical reduction by alcohol. Thus, replacing the CH_3 groups by the *tert*-butyl leads to an increase in the number of the final reaction products: mainly the compounds with the isomerized *tert*-butyl group are formed.

Photolysis of quinone **III** in aliphatic alcohols affords only one product of the photoreduction in a high yield, the dibenzofuran derivative **X**. Note that at the



photolysis of quinones **III** and **I** the yield of the only one product formed does not depend or little depends on the alcohol nature (see Table 1) and is determined only by the exposure duration, which is maximal in the case of *tert*-butyl alcohol. The composition and ratio of the photolysis products of quinone **II** depend on the nature of alcohol. The appearance of significant quantitiy of di-*tert*-butylhydroquinone increasing in parallel with the alcohol acidity was noted. In *tert*-butyl alcohol up to 40% of furan derivative **VII** is formed, which is absent in all other cases.

2,6-Dimethyl-1,4-benzoquinone **I** is reduced effecttively with the alcohols containing α-hydrogen, but slowly with *tert*-butyl alcohol, with the formation of dimethylhydroquinone **IV**. The photolysis of 2,6-diphenyl-1,4-benzoquinone **III** to dibenzofuran **X** occurs equally well in all the alcohols.

Table 1. Photolysis of 2,6-disubstituted-1,4-benzoquinones **I–III** in alcohols

Solvent	**I**		**II**		**III**	
	time, h	products of the photolysis (yield)	time, h	products of the photolysis (yield)	time, h	products of the photolysis (yield)
CH_3OH	1	**IV** (100%)	2.5	**V** (92%)	3	**X** (92%)
C_2H_5OH	0.5	**IV** (100%)	3	**V** (40%) **VII** (58%)	2	**X** (100%)
$(CH_3)_2CHOH$	0.5	**IV** (100%)	3.5	**V** (25%) **VII** (62%)	7.5	**X** (95%)
$(CH_3)_3COH$	2	**IV** (100%)	6.5	**V** (10%) **VII** (42%) **VIII** (48%)	15	**X** (90%)

At the photoreduction of quinone **I**, along with hydroquinone **IV** the products are formed of alcohol oxidation (aldehydes or acetone). These substances are not formed (or formed with low quantum yield) at the reduction of quinone **III**.

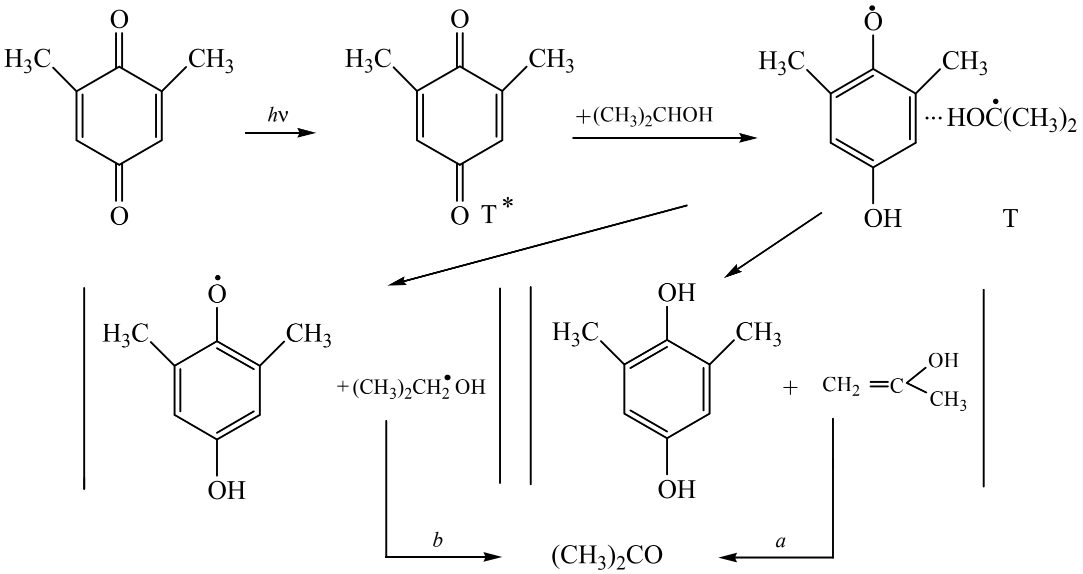
Quinones **III** and **I** react with alcohols in the triplet excited state, as evidenced by inhibition with the pyrene additives. A similar pattern observed at the photoreduction in air (the triplets quencher is oxygen).

At the photoreduction of quinone **I,** the polarized protons were those contained in the initial quinone, hydroquinone **IV,** and the oxidation products of alcohols (aldehydes and ketones). At the photolysis of quinone **I** both in pure alcohol and in the solutions diluted with deuteroacetone or C_6F_6 the polarization of the protons of the final products of alcohol oxidation is observed.

At the irradiation of quinone **III** in dilute solutions in addition the signals of polarized protons of an unstable product were observed. The signals disappeared after the irradiation was finished. In the case of 2-propanol this product was the acetone enol (Fig. 1, regions of 1.8 and 4 ppm) [14]. The width of the proton signals of the quinone and hydroquinone in the CIDNP spectrum depends essentially on the properties of the medium.

At the photolysis of quinone **I** in an alcohol solution diluted with CD_3OH the quinone as well as hydrquinone protons are polarized, the polarization is of A/E and A+A/E type for quinone and hydroquinone, respectively (Fig. 1).

The observed polarization effects at the photoreduction of quinone **I** in the presence of aliphatic alcohols (by the example of 2-propanol) correspond to the following scheme:



The acetone enol is formed in the cage at the disproportionation of radicals, and acetone is a result of the enol isomerization in the reactions of the radicals $(CH_3)_2C^{\cdot}OH$ leaving the cage with the parent quinone. The peaks of polarized acetone and respective enol are observed separately in the alcohol solution diluted with CD_3CN. In pure 2-propanol alcohol the acetone enol lifetime is very short, it rapidly isomerizes into acetone. The polarization of the acetone is composed of two contributions compensating each other: in cage (disproportionation in the cage and the subsequent isomerization, path *a*) and in out-of-cage (path *b*). The observed polarization of the acetone protons is positive, due to the large contribution of the out-of-cage component. This is confirmed by the observation that the sign of the acetone polarization at the photolysis of alcohol solution of quinone **I** depends on the presence of an acceptor of alcohol radicals, a good acceptor is oxygen. In the reaction of oxygen with $(CH_3)_2COH$ the nuclei of the latter are depolarized due to fast relaxation in the paramagnetic adduct. Therefore, upon decrease in the content of quinone **I** in the reaction mixture containing oxygen the out-of-cage contribution to the acetone polarization

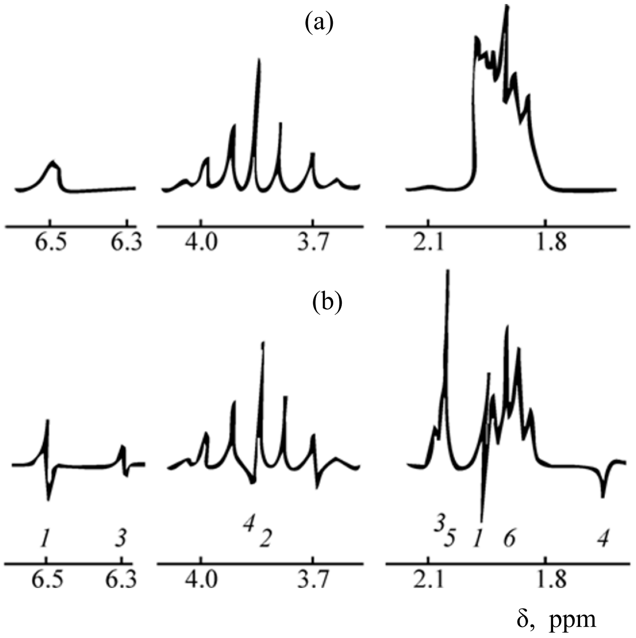


Fig. 1. ^{1}H NMR spectra of 2,6-dimethyl-1,4-benzoquinone (2×10^{-2} M) and 2-propanol (10^{-2} M) in CD_3CN: (a) before irradiation, (b) after irradiation of the solution. The lines correspond to the protons of: (*1*) quinone, (*2*) alcohol, (*3*) 2,6-dimethylhydroquinone, (*4*) acetone enol, (*5*) acetone, (*6*) protons of the undeuterated acetonitrile.

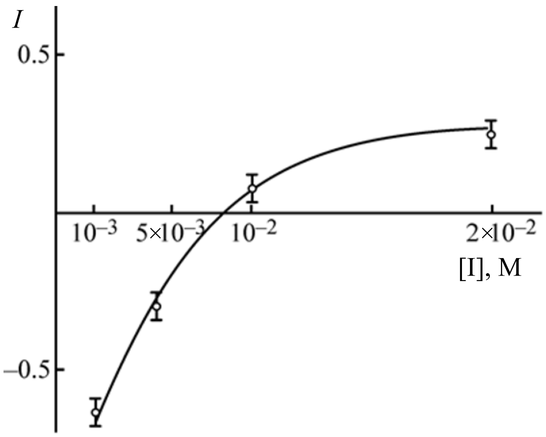


Fig. 2. The dependence of signal intensity of the polarized acetone CH_3 protons vs. the concentration of 2,6-dimethyl-1,4-benzoquinone **I** at its photolysis in the 2-propanol containing oxygen.

should be significantly reduced. This is actually observed in the experiment as a change in the proton polarization of acetone at the photolysis of the quinone solution in alcohol at the concentration 10^{-3} M without removing residual oxygen (Fig. 2).

At the photolysis of quinone **III** in the presence of an alcohol the polarization was observed of the protons of original quinone (protons of both quinoid and aromatic rings, Fig. 3, peaks *1* and *2*, respectively), of the resulting dibenzofuran (peaks *7* and *8*) and, finally, the protons of the starting alcohol also proved to be polarized (in ethanol, the protons of CH_3, CH_2, and OH; peaks *4*, *3* and *5*, respectively). As in the photolysis of quinone **I**, the signals in the ^{1}H NMR spectrum of quinone **III** at the photolysis in pure alcohol are broadened, and, in addition, at the increase in the alcohol concentration the polarization of protons of dibenzofuran falls. From the relation between the intensities of the polarized signals and the signs of polarization of the reaction products and the initial reactants we can deduce the structure of the radicals prior to formation of the polarized molecules. According to the theory of CIDNP, the intensity of polarized proton signal of a molecule is proportional to the hyperfine interaction constants of the unpaired electron with the corresponding proton in the parent radical.

The intense polarization of the protons of OH and CH_2 observed in the CIDNP spectrum (Fig. 3) and the weak polarization of the protons of CH_3 of alcohol cannot be a result of reaction of the $R\dot{C}HOH$ radical, as it is not consistent with the ratio of the values of the

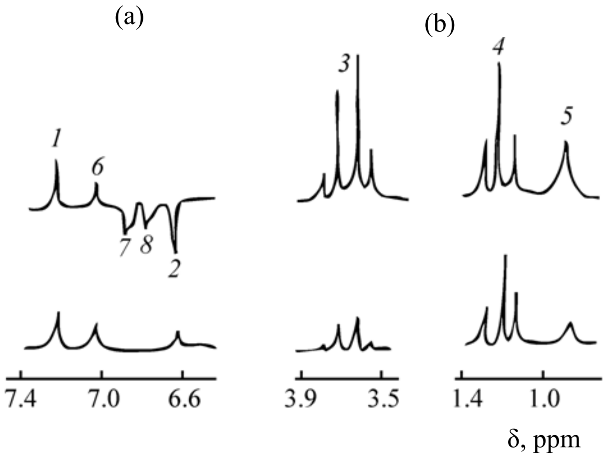


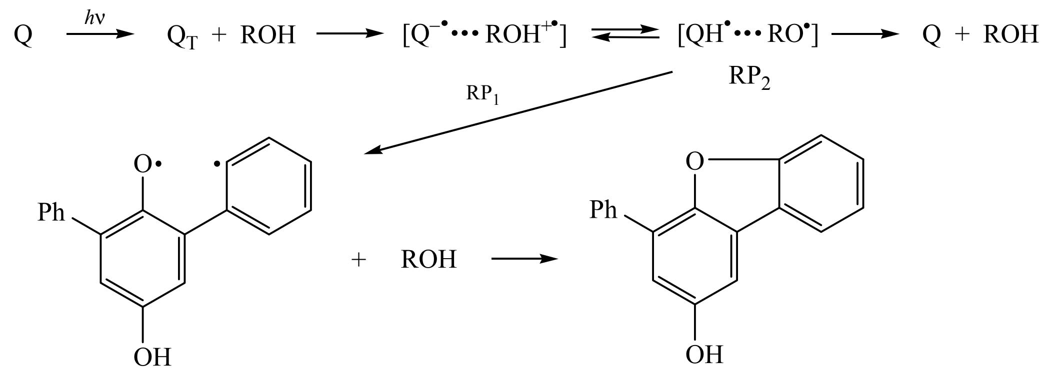
Fig. 3. ^{1}H NMR spectra of 2,6-diphenyl-1,4-benzoquinone (**III**) and C_2H_5OH in a mixture with C_6F_6 and C_6D_6 before (bottom) and after (top) irradiation of the solution. The alcohol concentration (a) 10^{-1} M and (b) 10^{-2} M, quinone 4×10^{-3}, M. Peaks (*1*) and (*2*) correspond to the aromatic and cyclohexanone, respectively, protons of quinone, (*3*–*5*) corresponds to the CH_2, CH_3 and OH protons, respectively, of alcohol, (*6*) the residual protons in C_6D_6; (*7*, *8*) the protons of dibenzofuran.

hyperfine interaction constants at its protons: The constants are large for α- and δ-protons (15 and 22 Oe, respectively) and small for hydroxyl (~1 Oe) [11]. Therefore, to explain the observed polarization of alcohol is necessary to assume that the polarization is created at the S–T_0 transition in the radical pair with the participation of neutral alkoxy radical or radical cation.

A partner of the alcohol radical in the radical pair should be neutral semiquinone or its anion-radical, since only these species satisfy the correspondence required by theory between the signs of the hyperfine interaction constant and the signs of the polarized peaks of the related quinone and dibenzofuran nuclei.

Indeed, the constants of hyperfine interaction with the *meta*-protons of phenoxyl ring in the semiquinone radical are positive. The sign of the hyperfine interaction on the protons of phenyl substituents of the semiquinone radical can be easily estimated: on the *o*- and *p*-protons they are negative, while on *m*-protons positive. The overall sign of the hyperfine interaction on the protons of the phenyl ring is negative, because the negative constants on *o*- and *p*-protons far exceed by magnitude the positive hyperfine coupling constants on the *m*-protons. Opposite signs of the hyperfine coupling with the ring protons of the semiquinone phenoxyl and phenyl radicals correspond to opposite signs of polarization of the cyclohexadiene and aromatic protons of the quinone. Thus, at the photolysis of quinone **III** in alcohol, in contrast to the analogous reaction of quinone **I**, the radical pair creating polarization of the protons of initial quinone **III** and dibenzofuran **X** must include both the alkoxyl and the semiquinone radicals.

The data obtained from the polarization at the photoreduction of quinone **III** in alcohols is consistent with the following mechanism of photolysis:

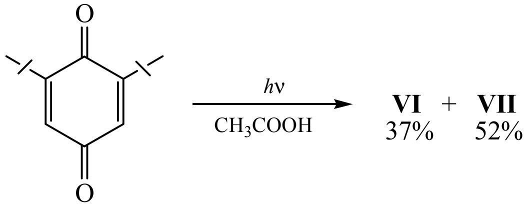


The primary act of the reaction is apparently the electron transfer from the alcohol oxygen atom to the excited diphenylquinone to form a pair of charged radicals RP_1. This assumption is based primarily on the fact that the polarization intensity of the protons of reaction product (dibenzofuran) depends strongly on the medium polarity. The increase in the mediun polarity should decrease the lifetime of the ion-radical pair (the pair effectively dissociates) and, conesquently, it decreases the time of selection of radicals according to the nuclear spin states, which should result in the polarization weakening of the protons in the product. Just this is observed in the experiment.

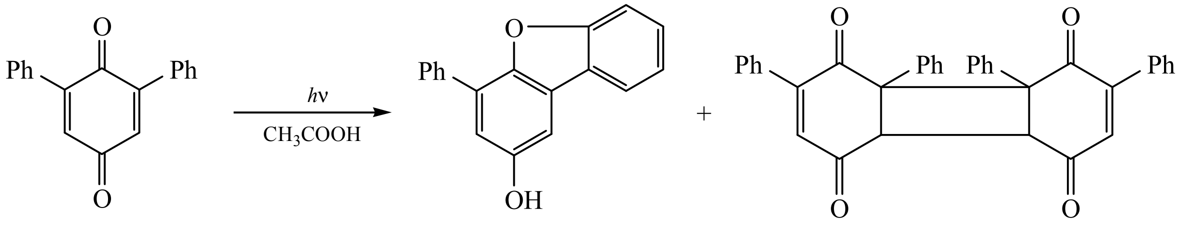
The radical pair RP_1 is transformed to RP_2 through proton transfer, with retention of the spin correlation. The disproportionation of this pair (the alkoxy radical takes H atom from the phenyl substituent in the semiquinone radical) results in the polarized alcohol and a biradical, whose internal recombination gives the polarized dibenzofuran.

From the data on the polarization of the quinone and alcohol protons we may derive the reliable estimates of the parameters of Zeeman and hyperfine interactions in alkoxyl radicals. Indeed, for the cyclohexadienone and aromatic protons of quinone **III** and the alcohol OH proton a sufficient set of parameters is known defining their integral polarization. The spin multiplicity of the radical pair is triplet. The polarized molecules are the products of the cage reaction, since otherwise it would be impossible to explain the polarization of the alcohol OH proton. If we assume that the cleavage by alkoxyl radical of either *o*-, or *m*-, or *p*-H from the substituent in the quinone is statistically equally probable, then the observed positive polarization of the alcohol OH proton matches the negative sign of the hyperfine coupling constant of *ortho*- and *para*- protons of the phenyl ring in the semiquinone radical. Then, according to the Captain rules, from the three known parameters defining integral polarization and using the experimental data we can determine the fourth parameter, namely, the ratio of the *g*-factors in the radical pair. The *g*-factor of the alkoxyl radical is higher than the *g*-factor of semiquinone radical (g = 2.0040). At this relation of the *g*-factor values in the radical pair the signs of the observed polarization of the CH_2 and CH_3 protons of alcohol are consistent with the theoretical estimation for the case of positive hyperfine coupling constant on α-proton ($a_\alpha > 0$) and negative on the β-protons ($a_\beta < 0$) of the alkoxyl radicals. Therewith, the absolute values of the hyperfine coupling constants on α- and β-protons are connected through the relation: $|a_\alpha| >> |a_\beta|$.

The features of the photolysis of quinones in acids were considered in [12]. Since a crucial role in the ratio of the products of quinones photoreduction with alcohols have the reducing properties of the solvent (alcohol, which is simultaneously a reagent), at the photolysis of a quinone in acid the main product of the reaction should be the product of reduction. However, the data obtained evidence that not only the reductive properties of the solvent affect the ratio and composition of the photolysis products. Thus, the photolysis of quinone **II** in acetic acid gave a mixture of products, but hydroquinone **V** was not detected among them.



The photolysis of quinone **III** in acetic acid also affords two products: dibenzofuran derivative **X**, which can be considered as a product of photoreduction, and dimer of original quinone **XI**. Noteworthy that the irradiation of the photodimer results in a mixture of original quinone **III** and dibenzofuran **VIII**. Therefore we can assume that the formation of a significant amount of dibenzofuran is due to the low photostability of the dimer.



VIII
78%

IX
12%

3. Photochemical reactions of 1,4-benzoquinones with mercaptans [15–18]. As known, the triplet and singlet energy levels of substituted 1,4-benzoquinones lie respectively above and below the corresponding levels of pyrene and anthracene. When any of these compounds is added to a mixture of quinone with thiol, the CIDNP effects disappear and the products of the quinone photoreduction are not detected. This shows that in the photoreaction only triplet quinone molecules are involved. The quinones are stable under irradiation of their solutions in acetone, acetonitrile, hexafluorobenzene, and less stable in benzene and toluene. At the pulsed photoexcitation of solutions of quinones **II** and **III** with ethyl and propyl mercaptan (solvent hexane) the formation and disappearance was observed of short-living intermediate, the triplet quinone Q^T. The Q^T lifetime in an oxygen-free solution equals 10^{-5} s that is comparable to the duration of the light pulse. In this case the following reactions occur:

$$Q + h\nu \rightarrow Q^S \rightarrow Q^T \rightarrow, \tag{1}$$

$$Q^T \rightarrow Q, \tag{2}$$

$$Q^T + RH \rightarrow QH^{\cdot} + R^{\cdot}. \tag{3}$$

In 5×10^{-6} s after the light pulse were registered absorption spectra of the solutions indicating the formation of the semiquinone radicals formed in the reaction (3), and the kinetics of their quenching (Fig. 4).

Analysis of the oscillograms of semiquinone radicals quenching shows the second-order reaction with the rate constant 5×10^8 l mol^{-1} s^{-1} for quinone **III**, and 1.2×10^8 l mol^{-1} s^{-1} for quinone **II**.

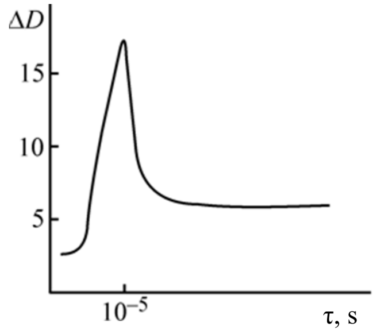


Fig. 4. Oscillogram of the spectral changes at λ = 640 nm caused by formation and disappearance of Q^T and formation of semiquinone radical $QH^\bullet$.

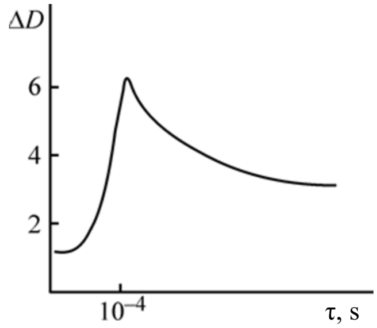


Fig. 5. Oscillogram caused by the formation and termination of the $QH^\bullet$ radical and formation of the $Q^{-\bullet}$ radical anion. Region of 450 nm.

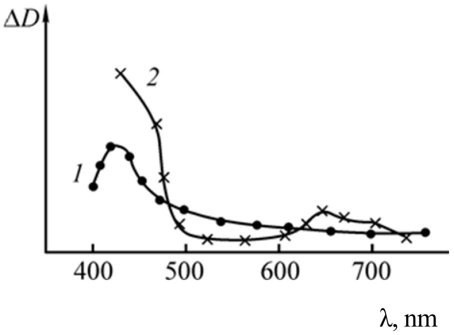


Fig. 6. The absorption spectrum of (*1*) $Q^{-\bullet}$ and (*2*) $QH^\bullet$ in the course of the pulse irradiation of the quinone mixture with ethyl mercaptan (10^{-5} M).

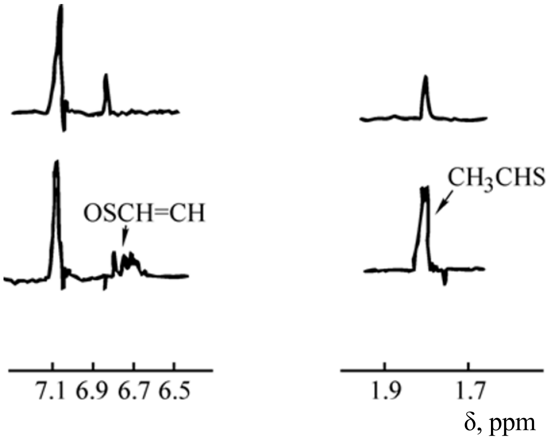


Fig. 7. Fragments of the ^1H NMR spectra in the course of photolysis of quinone **I** mixture with ethyl mercaptan. (bottom) photolysis and (top) after photolysis.

The semiquinone radical lifetime is of the order of magnitude 10^{-4} s. During this time after the flash a product with an absorption maximum at 450 nm is accumulated (Fig. 5). This long-living component is probably the quinone radical anion formed in the reaction: $QH \rightarrow Q^{-\bullet} + H^+$.

The kinetics of accumulation of the radical anion $Q^{-\bullet}$ corresponds to the first order, with the rate constant of 5×10^8 s^{-1}.

Figure 6 shows the absorption spectrum of $Q^{-\bullet}$. The $Q^{-\bullet}$ absorption maximum is shifted to longer wavelengths compared to the semiquinone radical.

While the flash photolysis allows us to study the kinetics of the disappearance and accumulation of intermediates leaving the solvent cage, the CIDNP method can be used to investigate the processes in the cage. Quinones **I** and **II** in solutions of C_6F_6, cyclohexane, and hexane are reduced actively with ethyl mercaptan and isopropyl mercaptan at the action of light (350 nm) with the formation of the corresponding hydroquinones. Figure 7 shows a fragment of the NMR spectrum recorded at the irradiation of ethyl mercaptan with quinone **I**. The spectrum contains the signals of thioacetaldehyde and hydroquinone. Photolysis of quinones **I** and **II** in isopropyl mercaptan gives rise to CIDNP effect on the *meta*-protons of the starting quinone, *meta*-protons of the corresponding hydroquinone, as well as on the groups CH_3 of thioacetone.

Based on the CIDNP data, it is presumable that the product molecules from both quinones **I** and **II** are formed from the radicals of the same structure. These radicals can only be the α-thioethanol radicals, in which the hyperfine coupling constants of α- and β-protons are of the opposite signs, while their absolute values are close. Along with thioethanol radicals the semiquinone radicals are formed. The *g*-factors of the semiquinone (g_s = 2.0057) and alcohol radicals relate as $g_s > g$. It is obvious that thioacetaldehyde is formed in the out-of-cage reactions, as indicates the coincidence of the theoretical signs of CIDNP on the β-protons of thioacetaldehyde with experimental data. The hydroquinone molecules are formed in the cage reactions, as evidences the coincidence of theoretical and experimental signs of the effect on the ring *meta*-protons.

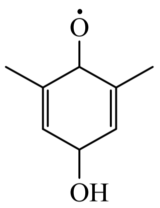
$$T = + + - + = E \text{ for thiovinyl alcohol,}$$
$$T = + - - + = A \text{ for thioacetaldehyde,}$$
$$T_{ring} = + + + + = A \text{ for the hydroquinone ring } meta\text{-protons.}$$

These data can be represented by the following scheme:

$$\begin{tikzcd}
Q^T + CH_3CH_2SH \arrow[r] & {[QH^\bullet CH_3CH^\bullet SH]^T} \arrow[dl] \arrow[dd] \\
QH + CH_3CH^\bullet SH + Q \arrow[d] & \\
QH^\bullet + CH_3CH^\bullet SH \arrow[r] & QH_2 + CH_2{=}CHSH
\end{tikzcd}$$

According to the scheme, quinone in the triplet state abstracts from the mercaptan its α-H atom. The oxidation products of ethyl mercaptan are formed from thioethanol radicals, thioacetaldehyde is formed in the reaction of α-thioethanol radicals with the parent quinone.

Di(*tert*-butyl)-subsrituted quinone **II** is reduced like the methyl-substituted quinone but less effectively. The corresponding hydroquinones are positively polarized, that indicates their formation at the cross-disproportionation of semiquinone and thiol radicals in the solvent cage. Primary radical pairs have the same multiplicity, and in both pairs the semiquinone *g*-factor exceeds the *g*-factor of α-thioalkyl radical. Since the sign of effective hyperfine coupling constants for ring protons of the unsubstituted semiquinone is negative and is defined by the greater absolute value at the *ortho*-protons, in the substituted quinones the sign of the hyperfine coupling at the ring protons must be positive, that is, they should be the *meta*-protons. It is possible when the substituted semiquinone radicals have the following structure:

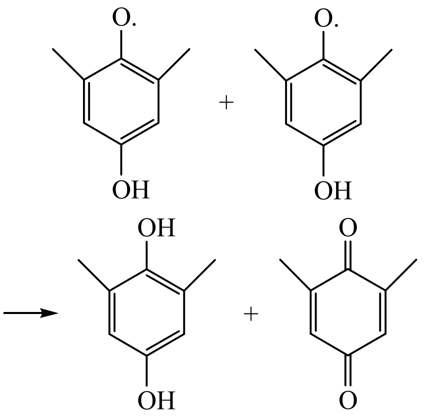


The weak multiple AE polarization on the quinone ring protons can be explained as follows. It is known [17] that at the flash photolysis of unsubstituted quinone with alcohols occurs the termination of the semiquinone radicals when they met each other after leaving the solvent cage, according to the scheme:

$$QH^\cdot + QH^\cdot \rightarrow QH_2 + Q.$$

Since the difference of the radicals *g*-factors in these pairs is zero, then, according to the model of S–T_0 transitions, in such pairs can only be produced multiple polarization, which can be detected only in the products with the multiple NMR spectrum. Therefore, the protons of methyl-substituted quinone and hydroquinone with multiple NMR spectrum should display the multiple polarization. According to the Captain rule, on the methyl and ring protons of methyl-substituted quinone and hydroquinone formed in the reaction (4) the theoretical phase of multiple effect agrees with the experiment:

$$T = CH_3 + + + + - + A = E, \ GK = + + + + - + = AE$$



(4)

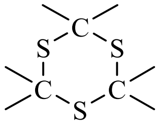
At the photolysis of a dilute solutions of quinone **III** in mercaptan the CIDNP effects occur on the protons of the parent quinone, hydroquinone, the oxidation products of mercaptans (thioacetone, thioaldehyde), initial mercaptan, and the dibenzofuran derivative. So we obtain the pattern similar to that obtained at the photoreduction of quinones **I** and **II**, except for appearance of a new negative polarized signal of the protons of the dibenzofuran hydroxy-substituted ring. The CIDNP effect appears on the latter only in the case of low concentrations of ethyl mercaptan. Estimates of the benzofuran yield compared with that of hydroquinone support this conclusion.

The prevailing formation of hydroquinone at the photolysis of quinone **III** in ethyl mercaptan and isopropyl mercaptan allows a conclusion on the preferential formation of α-thioalkyl and semiquinone radicals and their further interaction according to the scheme:

$$Q^T + CH_3CHSHCH_3 \rightarrow [QH^{\cdot}\ CH_3C^{\cdot}SHCH_3]$$
$$\rightarrow QH_2 + CH_3CSCH_3$$

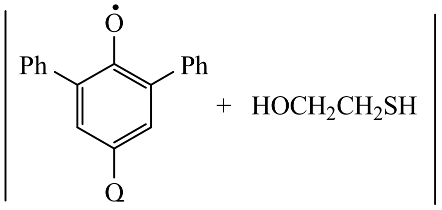
This process is analogous to the reactions of quinones **I** and **II** (H-atom transfer). A trace amount of dibenzofuran can be formed either intramolecularly (in favor of this says the comparable yield with ethyl, isopropyl, and propyl mercaptan), or intermolecularly, but in this case should occur the electron transfer from the mercaptan molecule to the triplet excited quinone, and then proton transfer from the SH group. Consequently, we can assume the existence of alkylthio radical and the formation of a new radical pair RP_2 (Fig. 8).

Although this path is not the main one, it cannot be excluded. An indirect proof of the existence of alkylthio radicals is the relative decrease in CIDNP effects in the case of increasing content of ethyl mercaptan in the reaction mixture, which leads to an increase in the medium polarity. Consequently, the increase in the rate of dissociation of radical ion pairs reduces the probability of proton transfer with the conversion of ion-radical pair into a pair of neutral radicals. The mercaptan itself being an active radical trap can also prevent the out-of-cage formation of oxybenzofuran. As noted above, at the photoreduction of quinones **I, II,** and **III** with isopropyl mercaptan polarization occurs of the thioacetone CH_3 groups at δ 2.55 ppm. After irradiation near this area a signal was recorded with the maximum corresponding to CH_2 groups of thioacetone trimer.

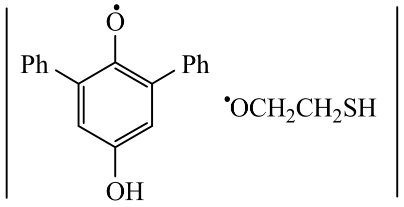


Photolysis of benzyl mercaptan with quinone **III** does not show an effective CIDNP effect. The signal corresponding to the CH group decreases under the influence of light with a simultaneous increase in the signals of hydroquinone. UV spectrum shows the presence of thiobenzaldehyde with a maximum absorption at λ = 577 nm at room temperature. This suggests that thiobenzaldehyde does not form trimers. Apparently, this is a general tendency for the aromatic thioketones, which is defined by the inclusion of thiocarbonyl group in the system of conjugation.

At the photolysis directly in the probe of the NMR spectrometer of quinone **III** with 2-mercaptoethanol $HOCH_2CH_2SH$ in a polar solvent CD_3CN or $(CD_3)_2CO$, the CIDNP effects are observed for the *meta*-protons of the initial quinone at δ 6.85 (negative polarization). In the case of hydroquinone **IV** a positive polarization occurs at δ 6.66 on the *meta*-protons. The mercaptoethanol OH group is polarized positively. At the photolysis of this quinone in ethyl alcohol, the formation of its photoreduction product, a dibenzofuran derivative, is not observed. These effects can be explained assuming that the formation of CIDNP occurs at $S–T_0$ transitions in radical pairs RP_1 and RP_2.



RP_1



RP_2

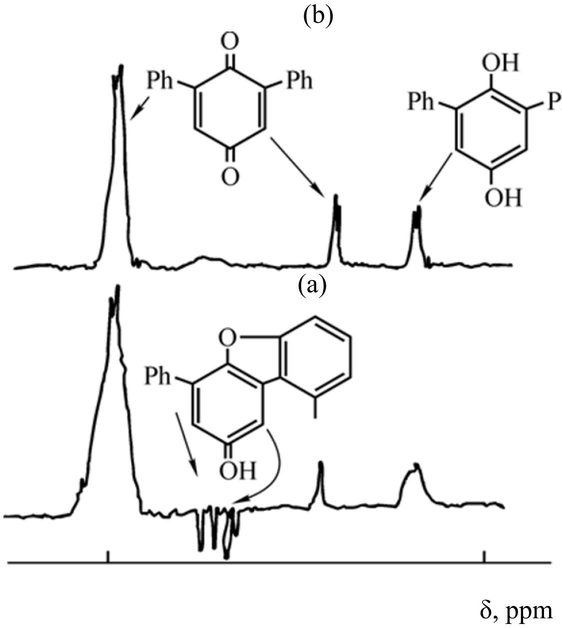


Fig. 8. A fragment of the downfield part of ^1H NMR spectrum at the photolysis of quinone **III** in a mixture with ethyl mercaptan (negatively polarized *meta*-protones of the dibenzofuran derivative).

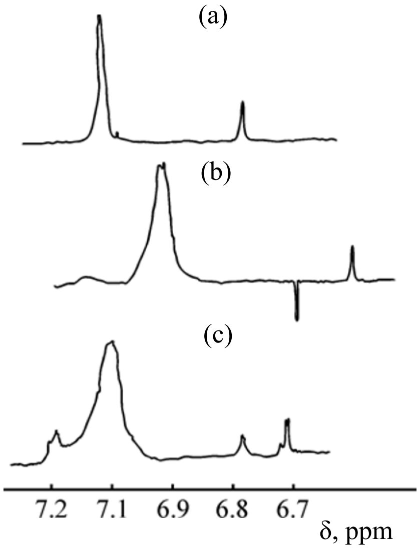


Fig. 9. Downfield part of the ^{1}H NMR spectra (CD_3CN) of quinone **III** mixture with 2-mercaptoethanol (5×10^{-3} M): (a) before irradiation, (b) during irradiation, and (c) after irradiation.

Since the signs of hyperfine coupling constants for the *meta*-protons of the semiquinone radical and ion radical coincide and both are positive, hence the initial 2-mercaptoethanol and quinone are formed inside the cage. On the contrary, hydroquinone, the product of the photoreduction, is formed out-of-cage. The spin multiplicity of the pair is observed as a triplet. Then, by the Captain rule, the theoretical value of the sign of the integral polarization on the *meta*-protons of the initial quinone is: T = + + – + < 0, and for the hydroxy protons of mercaptoethanol T = + + + +> 0, and coincide with the experimental observations under the condition that the quinone anion radical *g*-factor is less than the *g*-factor of the radical cation of alcohol. The out-of-cage product is hydroquinone. Its *meta*-protons are polarized positively, which is confirmed experimentally (Fig. 9).

The CIDNP spectrum on the ^{13}C nuclei indicates the in-cage formation of quinone molecules. Signs of the integral polarization on the quaternary atoms of quinone C^1 188.2, C^2 147.4, C^4 186.8 ppm are:

$$T_{C1} = + + - - + > 0;\ T_{C2,C2} = + + - + < 0.$$

If we assume that the molecule of quinone **III** is formed in the cage reactions of triplet and diffuse pairs under the condition of $g_x < g_c$, there will be a complete correspondence of theoretical and experimental signs of polarization as the hyperfine coupling constants with the carbon nuclei in the position 1 in the semiquinone radicals are negative, while in the positions 2 and 4 positive. Thus, the scheme of photoreducion of quinone with mercaptoethanol in a polar solvent looks as follows:

$$\begin{aligned}&Q + h\nu \rightarrow Q^{T} + M \rightarrow (Q^{-\cdot}M^{\cdot+})\mathrm{RP}_1\\&\rightarrow (QH^{\cdot}, M^{\cdot})\mathrm{RP}_2 \rightarrow Q + M,\end{aligned} \tag{5}$$

$$QH^{\cdot} + M^{\cdot} \rightarrow \text{Reaction products}, \tag{6}$$

$$QH^{\cdot} + M \rightarrow \text{F-pairs}, \tag{7}$$

$$QH^{\cdot} + Q \rightleftarrows Q + QH^{\cdot}. \tag{8}$$

Another pattern of polarization is observed in the photolysis of the same reagents in nonpolar solvents C_6D_6 or C_6F_6. The quinone **III** *meta*-protons (δ 6.58 ppm) are poalrized negatively as in the polar solvents. But the *meta*-protons of respective hydroquinone (δ 6.73) change sign from positive to the negative. As shown above, integral polarization of the *meta*-protons of quinone formed during the disproportionation of the radicals in RP_1 and RP_2 by $S–T_0$ mechanism should have a negative sign, the photoreduction product hydroquinone formed out-of-cage must be polarized positively. According to scheme (8), semiquinone radicals exchange H atoms with the parent molecules. This reaction causes transfer of the nuclear polarization to the diamagnetic molecules from diffusing semiquinone radicals competing with the relaxation destruction of polarization in the radicals. The rate of this exchange reaction depends on the quinone concentration in the solution. Therefore, at the increase in its concentration a decrease in the CINDP effects at the quinone is expected within the model of $S–T_0$ transitions.

This is explained also by the fact that the reaction (8) leads to an increase in the proportion of the out-of-cage components in the observed overall effect, which should compensate the cage polarisation of opposite sign. However, the 10-fold increase (up to 1.10 M) in the concentration of the starting quinone does not lead to a noticeable decrease in the negative CIDNP on the *meta*-protons. Explanation of this fact, as well as of negative CIDNP on the *meta*-protons of hydroquinone is difficult in the framework of the model of radical pairs. Therefore, we can assume that triplet mechanism is also involved in the polarization, and its efficiency grows with increasing rate of the exchange reaction. Thus, the have to involve the triplet mechanism of the CIDNP formation due to CIDNP signs mismatch and the independence of the quinone nuclei polarization scale on its concentration. In the experiment on the photolysis of quinone and mercaptoethanol in non-polar solvents a negative polarization is

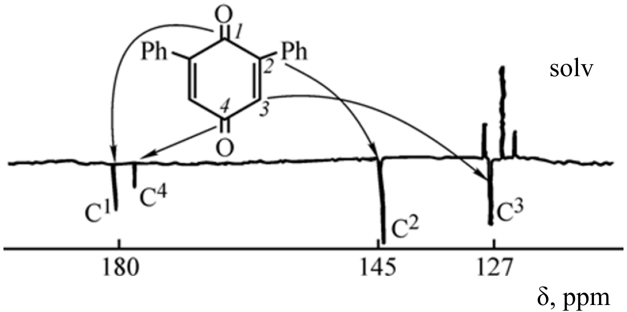


Fig. 10. A fragment of the ^{13}C NMR spectrum (C_6D_6) with the effects of CIDNP of quinone **III** at the irradiation in a mixture with 2-mercaptoethanol.

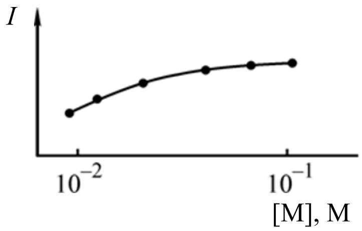


Fig. 11. The dependence of CIDNP on the quinone *meta*-protons (concentration 10^{-2} M) on the concentration [M] of 2-mercaptoethanol. Solvent deuterobenzene.

also observed at all four quaternary carbon atoms. It can serve as a direct evidence of the triplet mechanism involvement, as the CIDNP signs do not correspond to the alternating positive and negative signs of hyperfine coupling constants on the carbon nuclei in the semiquinone radical ring (Fig. 10).

At the triplet mechanism the signs of nuclear polarization are known to depend strictly on the signs of the electron polarization in radicals and the cross-relaxation transitions. From the ^{1}H and ^{13}C CIDNP spectra it is seen that quinone polarization in polar and nonpolar media is different. In acetonitrile, the positive and negative polarization at the ring carbon atoms of quinone alternates in full accordance with the sign of hyperfine coupling constant on these atoms. In nonpolar solvent C_6D_6 this is not observed. This can be explained by the features of the mechanism in the nonpolar solvents where the nuclear polarization in the not dissociating radical ion pairs can be generated by the triplet mechanism. The sign of the nuclear polarization in the radicals at the photolysis of quinones is known to be negative when the electron-nuclear polarization is induced by a time-dependent com-ponent of the anisotropic hyperfine interaction, and positive if the relaxation is induced by the isotropic hyperfine interaction. Consequently, the negative polarization on the protons, as well as ^{13}C nuclei of quinone and its photoreduction product hydroquinone in nonpolar media are formed in the process of the relaxation transitions resulting from the anisotropic dipole interaction whose modulation is caused by molecular rotation. The magnitude of the electron polarization in radicals should increase with increasing concentration of donor molecules, thereby increasing the nuclear polarization, as is observed in the experiment.

The magnitude of electron polarization vs. the donor concentration is expressed by the formula (9).

$$\gamma = (\gamma_0/W)k + k[\mathrm{M}]. \tag{9}$$

Here k[M] is the rate of chemical quenching; $T_3 \sim \{W\}^{-1}$ is the rate of intercombinatorial transitions, which is proportional to the reciprocal average lifetime of the triplet state and the concentration of triplet-excited molecules.

The magnitude of nuclear polarization is expressed similarly (10).

$$I = I_0(k[\mathrm{M}])/(W + k[\mathrm{M}]), \tag{10}$$

where I is intensity of the experimentally observed CIDNP.

After appropriate transformations we obtain:

$$1/I = 1/I_0 + 1/(I_0W^{-1}k[\mathrm{M}]. \tag{11}$$

From the dependence of $1/I$ slope on the reciprocal concentration of mercaptoethanol (Fig. 12), we obtain that the constant K of electron transfer from triplet mercaptan molecules to quinones is close to the diffusion constant, 6×10^8 s^{-1}.

At high concentrations of donor the anamorphosis deviates from a straight line. This is explainable by the increase in the medium polarity with increasing mercaptoethanol concentration, and preferential formation of CIDNP in the framework of the radical pairs model. As far as the magnitude of CIDNP in this model depends on the quenching quantum yield rather than the process rate, the intensity of the CIDNP in the region of high donor concentrations should not be changed, in contrast to the triplet mechanism of CIDNP.

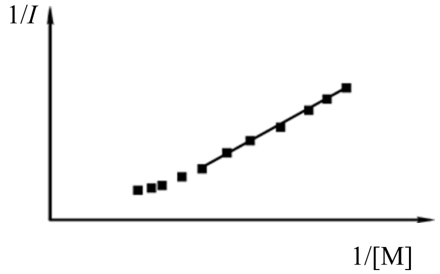


Fig. 12. Anamorphosis of the curve of CIDNP magnitude on the quinone *meta*-protons (*I*) vs. the 2-mercaptoethanol concentration [M]. The rate of spin-dependent intercombined transitions $W = 10^9$ mol l s^{-1}.

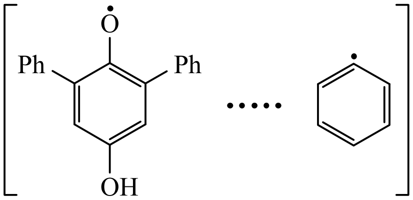
Mercaptans are widely used as traps of various unstable radicals. Therefore, to maximize the cage effect of the mercaptans they were used to accept excited quinone in a solvent cage. Based on the CIDNP data we can conclude that the mechanism of photoreduction includes competing routes of transfer of either H atom, or electron and then proton from the mercaptan to the excited quinone in the primary act. At the photolysis of 2,6-dimethyl- and 2,6-di-*tert*-butyl-1,4-benzoquinones in mercaptans, the CIDNP effects do not depend on the polarity of the medium, that is, the formation of primary radical pair occurs at the transfer of the α-H atom from the alcohol. In the case of 2,6-diphenyl-1,4-benzoquinone the competing mechanism with the electron transfer was detected. This can be explained by the introduction of powerful electron-withdrawing groups in 2 and 6 positions, and by increase of the oxidation potential of the quinone triplet molecules over the reduction potential of mercaptans.

At the photolysis of quinone **III** the nuclear polarization is formed both along the model for radical pairs with the transfer of α-H atom, and the triplet mechanism. In nonpolar solvents prevails the contribution of the triplet mechanism induced by dipole-dipole interaction. In polar solvents the CIDNP is a result of the S–T_0 transitions. Noteworthy that similar by structure ethylene glycol under the same conditions gave no CIDNP effects. At illumination of its mixture with quinone the ^{1}H NMR signals broadened considerably, and after illumination they narrowed with the characteristic relaxation times. Probably ethylene glycol forms a very stable complex with unexcited quinone that exists also at the quinone excitation. This suppresses completely the diffusion of radicals required for the efficient S–T_0 conversion, resulting in turn in the CINDP.

4. Mechanisms of complexation of substituted benzoquinones and their photolysis in aromatic hydrocarbons. Currently, the primary act of the photochemical reactions of substituted benzoquinones with the reagents not containing a heteroatom, that is, not electron donors, is the less studied. It was shown [19, 20] that at the photolysis of 2,6-diphenyl-1,4-benzoquinone **III** in aromatic hydrocarbons the main product is a dimeric derivative. At the irradiation of the quinone in deuterobenzene and deuterotoluene in the NMR spectrometer probe with the light at 400 nm, the signal of *meta*-protons of the initial quinone (δ 6.89 ppm) increases indicating its positive polarization. In the process of irradiation appears negatively polarized signal at 6.72 ppm corresponding to the *meta*-protons of 2,6-diphenyl-1,4-hydroquinone. Prolonged irradiation results in a large yield of a dimer of cyclobutane structure.

In aromatic hydrocarbons the photoreduction product, hydroquinone, is observed in small quantities (in benzene less than in toluene). Reactions of this type are characteristic of the triplet states of quinones of *n*π* nature.

On the basis of CIDNP spectra it is possible to suggest that quinone **III** in its triplet excited state capures H from benzene or CH_3 of toluene resulting in a triplet radical pair:



At the disproportionation of radicals in the solvent cage or at a random collisions in the bulk are registered the molecules of quinone and benzene (toluene). In favor of this attests the positive integral polarization of the *meta*-protons of quinoid ring in the above structure.

In the bulk, the semiquinone radicals disproportionate at the random collisions forming diphenylhydroquinone and the corresponding hydroquinone.

Since the total CINDP on the quinone *meta*-protons is positive, then the value of the out-of-cage contribution to the quinone CIDNP is negligible due to relaxation destruction in the freely diffusing semiquinone radicals. The polarization of the hydroquinone ring protons is opposite, that is, negative, since hydroquinone is formed out-of-cage. According to the Captain rule, for the integral polarization: $T = \mu \cdot \varepsilon \cdot \Delta g \cdot a$, T = + + + + > 0 for quinone and T = + – + + < 0 for hydroquinone.

Noteworthy that increase in the medium pH leads to broadening of the NMR signals.

Flash photolysis of quinone **I** in aromatic solvents leads to the formation of a short-living intermediate with the absorption maximum at 630 nm, and a long-living one, with the two absorption bands, at 450 and 650 nm, at the quinone concentration 5×10^{-5} M. The rate constants of disappearance (K, s^{-1}) of the short-living compound in various solvents varies as follows: 1.2×10^4 (C_6F_6); 0.67×10^4 (C_6H_5Cl); 3.2×10^5 ($C_6H_4CH_3$); 0.9×10^4 (C_6H_6).

With an increase in the quinone concentration, the K value increases. Similar absorption spectrum was obtained at the flash photolysis of quinone in carbon tetrachloride. The saturation with air oxygen leads to a drastic reduction in the lifetime and reduces the signal intensity of the intermediate. Apparently, the intermediate is the triplet state of quinone. With increasing quinone concentration or at adding a proton donor (alcohol) the rate constant of quenching increases due to the following reactions.

$$Q^T + ROH \rightarrow \text{Reaction products},$$
$$Q^T + Q \rightarrow \text{Dimer}.$$

The long-living intermediate is the semiquinone radical $QH^{\cdot}$. Its concentration increases in the series of solvents from C_6F_6 to $C_6H_5CH_3$. Kinetics of its disappearance in these solvents is of the second order. Using the values of the extinction coefficients $\sim 2\times10^3$ l mol^{-1} cm^{-1} and 2×10^4 l mol^{-1} cm^{-1} the rate constant was obtained of $QH^{\cdot}$ termination in benzene: $K = 1.2\times10$ l mol^{-1} s^{-1} in the reaction $QH^{\cdot} + QH^{\cdot} \rightarrow Q + QH_2$. Thus, the presence of labile hydrogen atom promotes the formation of the reduction product hydroquinone. But this route is not the main in the reaction.

As noted above, the main reaction product is the stable dimeric derivative, while hydroquinone is found in a trace amount. This is due to the difference in the ways of their formation. It was shown in [19, 20] that quinone **I** in crystal has stacking packing with the distance 3.48 Å between the parallel planes of the quinone rings. In the case of halodiphenoquinones, such packing was retained in the liquid phase [21, 22]. Therefore, the photolysis of quinone **I** in aromatic hydrocarbons is possible by two parallel directions of the quinone consumption: through the formation of either excimers, or exciplexes. The quinone triplet state quenching by an electron donor such as triphenylamine leads in benzene to the formation of triplet exciplexes. The quencing of the latter, as is known, occurs by the mechanism of radiationless intercombination conversion into the ground state.

The consumption of quinone Q through exciplexes in our case is responsible for the formation of the photoreduction products. In the absence of a good electron donor, the formation of excimers is preferable, as is known that in aromatic hydrocarbons the distance between the excimer molecules is 3–4 Å, which corresponds to the distance between the parallel planes of the quinone rings in the stack. The excimer route of quinone **I** consumption can lead to the fomation of the dimer in a high yield. By changing the medium polarity or pH it is possible to increase the contribution of a particular direction. In alcohols and acids the quinone photolysis proceeds by exciplex mechanism, leading predominantly to the formation of the products of photoreduction.

5. Photochemical reactions of the quinones complexes with amines. Among the most important elementary processes in chemical reactions is a change of electron distribution followed by a change in the nuclear configuration during the reaction. Such changes occur upon photoexcitation of complexes of amines with quinones.

The complexes of quinones with aliphatic amines in the excited state can be regarded as a typical model system for studying the elementary processes in chemical reactions. A similar situation occurs in the case of molecular interactions at the molecular collisions in excited states, as well as in the complexes that exist before illumination (excimers) and then are excited by light (exciplexes).

The complexes of various 1,4-benzoquinones with aliphatic amines were considered in [23–25].

An essential parameter for obtaining the thermodynamic characteristics in the experimental conditions was the equilibrium constant K of the complexation reaction, which was determined by ^{1}H NMR spectroscopy. Then the thermodynamic parameters were obtained. For example, the constant K of the complex of 1,4-diazabicyclo-2,2,2-octane with quinone **III** in CCl_4 can be expressed through the concentration of donor, acceptor and the complex itself (Fig. 13).

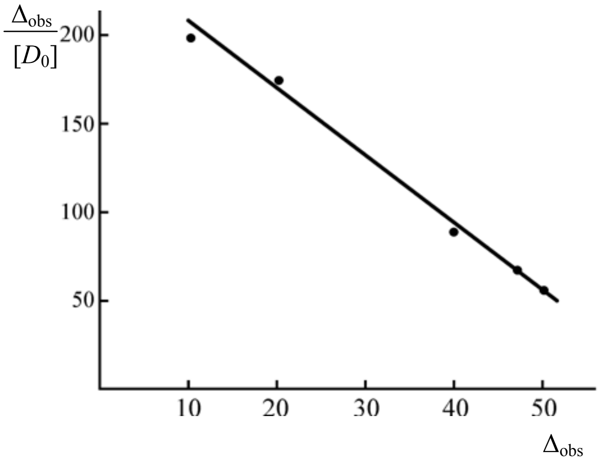


Fig. 13. The Foster–Fife coordinates for determining the chemical characteristics of the complex of 1,4-diazabicyclo-2,2,2-octane (10^{-1} M) with quinone **III** in CCl_4.

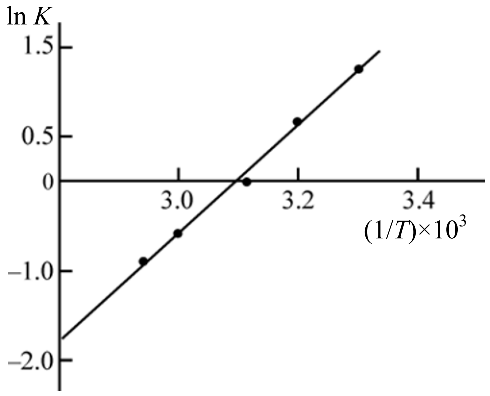


Fig. 14. The graph for finding the thermodynamic characteristics ΔG, ΔH, and ΔS of the quinone···1,4-diazabicyclo[2,2,2]complex (data in Table 3).

Table 2 shows the kinetic and spectral characteristics of the complex at 300 K. In a similar way were calculated the parameters of the quinone complexes with the amines.

Thus, virtually all the studied mono- and diamines are electron donors and form complexes with quinone **III** with various thermodynamic parameters: The equilibrium constant *K* increases in going from the tertiary diamines to secondary and primary, the absolute value of ΔH therewith increases significantly.

Consequently, the parameters of the complex formation may serve as a numerical evaluation of the depth of photochemical reaction of quinone reduction.

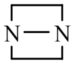
Interesting that at replacement of 2,6-diphenyl-1,4-benzoquinone **III** by 2,6-di-*tert*-butyl-1,4-benzoquinone **II** the above mentioned effects do not occur. Apparently, large steric hindrance, as well as the presence of stronger electron-donor *tert*-butyl groups do not allow to create the charge transfer complexes. Thus, the absence of an excited complex (exciplex) has a decisive influence on the course of the photoreaction.

The choice, using CIDNP, between the mechanism that includes intermediate electron transfer with the participation of radical ion pairs, and the mechanism of one-step transfer of hydrogen atoms with the formation of neutral radicals is based on the assumption that electrons of the amine nitrogen atom are transferred to the carbonyl group with the formation of the ammonium cation radicals, and the hydrogen atom cleavage occurs from the α-carbon atom of the amine resulting in the formation of neutral aminoalkyl radicals. The *g*-factors and hyperfine interaction constants a_i of these radicals may differ considerably, which should lead to different polarization effects (registered with NMR spectrometer) in the systems involving radical cations or neutral radicals. Thus, it is possible to determine reliably the elementary act of the reaction.

Table 2. The parameters for the complexation constant of quinone **III** with 1,4-diazabicyclo[2,2,2]octane

Donor concentration, $[D_0]$ M	Frequency shift, Δ_{obs}	$\frac{\Delta_{obs}}{[D_0]}$	*K*
0.050	9.9	198	3.75
0.125	20.7	162	
0.400	37.9	95	
0.650	46.0	70	
1.000	50.0	50	

Table 3. Thermodynamic characteristics of the complexes of various electron-donors with quinone **III**

Electron donor	$-\Delta H$, kcal mol^{-1}	$-\Delta S$, J deg^{-1}	$-\Delta G$, kcal mol^{-1}	*K*
	6.66	13.4	2.58	3.75
NEt_3	7.40	13.6	3.35	8.00
$HNEt_3$	12.20	23.5	5.20	10.20
$H_2N(CH_2)_2NH_2$	38.00	9.3	10.10	15.50

Consider the phototransformation of 2,6-dimethyl-1,4-benzoquinone **I**, 2,6-di-*tret*-butyl-1,4-benzoquinone **II** and 2,6-diphenyl-1,4-benzoquinone **III** in a mixture with triethylamine. At the irradiation of quinone **I** with triethylamine dissolved in C_6F_6, CCl_4 directly in the NMR probe, the protons of the formed diethylvinylamine (δ 3.98 ppm) are polarized positively. The value of the ^{1}H NMR signal corresponding to α-protons suggests that they are not polarized. In a polar solvent CD_3CN a positive polarization of both α- and β-protons occurs, although the intensity of the polarization peak is much lower.

These polarizations can be explained assuming the out-of-cage formation of diethylvinylamine. To its polarization contribute the ion-radical pairs and the pairs of neutral radicals.

Initially, the quinone triplet form an exciplex with the amine. After the electron transfer the radical ion pair RP_1 appears, which due to protonation transforms into a pair of neutral radicals RP_2. Both the pairs contribute to the polarization. Polarization on the diethylvinylamine β-protons is observed only for the pair of neutral radicals, and the hyperfine coupling constant on β-protons in the radical-ion pair is close to zero. The hyperfine coupling on the α-protons in the radical ion pairs and the pairs of neutral radicals are of opposite sign. Therefore, their total contribution to the polarization is insignificant and the signal corresponding to α-proton of the vinyl group is not observed. With increasing medium polarity stabilization of radical ion pairs occurs, which leads to preferential formation of diethylvinylamine from the radical ion pairs with positive polarization of the vinyl protons.

$$RP_1 \xrightarrow{H^+} RP_2 \rightarrow CH_2{=}CHN(C_2H_5)_2 + QH.$$

A completely different pattern occurs at the photolysis of quinone **II** with triethylamine. The corresponding hydroquinone is formed in trace amounts. The *meta*-protons (δ 6.51 ppm) of the initial quinone are positively polarized. A weak positive polarization is observed at the α-protons of the initial amine, while its β-protons are negatively polarized. If we assume that the chemical polarization of nuclei is formed inside the cage in a pair of neutral radicals, and the *g*-factor of the semiquinone radical is higher than that of aminoalkyl radical, the signs of CIDNP can be completely explained. The theoretical signs of polarization ($T = \mu\varepsilon\Delta g a$) found by the Captain rule coincide with the experimental ones:

$$T_m = {+}{+}{+}{+} > 0 \text{ (\textit{meta}-protons)},$$

$$T_\alpha = {+}{+}{-}{-} > 0 \text{ (α-protons)},$$

$$T_\beta = {+}{+}{-}{+} < 0 \text{ (β-protons)}.$$

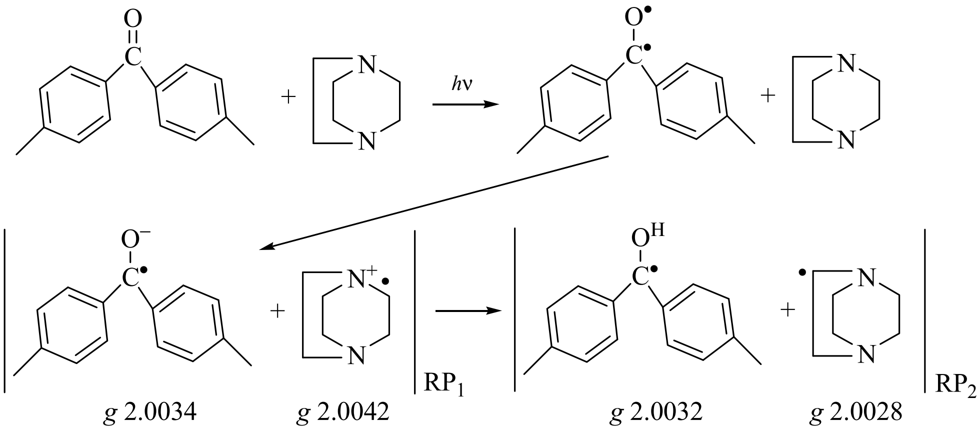
The polarization of nuclei of the initial reagents is a result of inside the cage disproportionation of a pair of neutral radicals. Large steric hindrances and the presence of electron-donating groups do not allow the creation of the charge-transfer complexes.

In the process of photolysis of quinone **III** with triethylamine there is a very strong negative polarization of the β-protons of initial quinone, while its α-protons are not polarized. In diethylvinylamine both α- and β-protons are polarized positively. The *meta*-protons of the initial quinone (δ 6.85 ppm) are also polarized positively. This pattern is similar to the photolysis of quinone **I** with triethylamine, but with stronger CIDNP. The main difference in the patterns of the photolysis of quinone **III** and **I** is retaining in the former of the CIDNP sign in polar and nonpolar solvents. Apparently the phenyl substituents greatly increase the oxidation potential of the quinone, thus increasing the stability of ion-radical pair RP_1 for the effective singlet-triplet conversion.

Photoreaction mechanism of amine was also studied with compounds containing a carbonyl group. *p,p*'-Dimethylbenzophenon was chosen as acceptor. Its photoreduction with 1,4-diazabicyclo-2,2,2-octane may proceed with an intermediate electron transfer or one-step transfer of the hydrogen atom. The scheme below shows the *g*-factors of the generated ion radicals and neutral radicals. It is important to emphasize that the values of Δ*g*-factors (the difference between the *g*-factors) in the pairs of neutral radicals and radical ions are of opposite sign. Consequently, the products generated by them have opposite polarization of the signals in the CIDNP spectra.

At low concentrations of amine the photoreduction is known to occur with the participation of the triplet state of ketone, and the hyperfine coupling constants of the protons of phenyl rings in the radicals and radical anions of the ketones alternate ($a_{orto} < 0 < a_{meta}$), because these species are the π-radicals. The initial quinone regeneration obviously occurs inside the cage.

According to the experimental data obtained, the *ortho*-protons of the initial *p,p*'-dimethylbenzophenone are polarized positively in the process of photoreduction, while the *meta*-protons, as well as the protons of methyl groups, negatively. According to the



Captain rule, we have: T_m = ++–+ < 0 (for *meta*-protons), T_o = ++— > 0 (for *ortho*-protons).

These signs correspond to the appearance of CIDNP in pairs with $\Delta g < 0$, that is, in the pairs with the participation of the ion-radicals formed by the electron transfer from amine to benzoquinone. The data obtained suggest the two-stage mechanism of hydrogen transfer: first electron and then proton. Thus, the parameters of the CIDNP effect allow reliable determining the elementary act of the photoreaction.

6. Elementary processes of photochemical reactions of 2,6-diphenyl-1,4-benzoquinone with cyclic ethers. Knowledge of the photoreduction mechanism of 1,4-benzoquinones compounds containing no OH and NH groups is of interest for studying the electron-donor properties of heteroatoms in photochemical reactions [26, 27].

As the donors we used tetrahydrofuran (THF), dioxane, and 12C4 crown ether. The ^{1}H NMR spectra of 2,6-diphenyl-1,4-benzoquinone with THF in C_6F_6 and CCl_4 solutions showed no complex formation in a wide range of temperatures and the reactants concentration. In the case of dioxane the chemical shift of the quinone *meta*-protons correlates with the donor

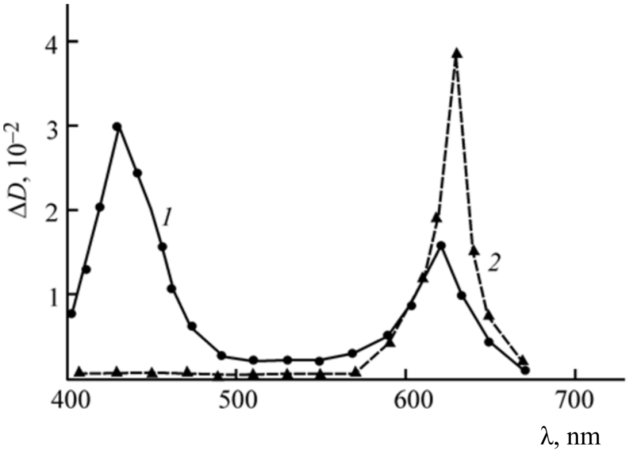


Fig. 15. Electron absorption spectra of intermediates at the flash photolysis of 2,6-diphenyl-1,4-benzoquinone in C_6F_6 and CCl_4. (*1*) long-living product (second order disappearance), (*2*) short-living product (first order disappearance).

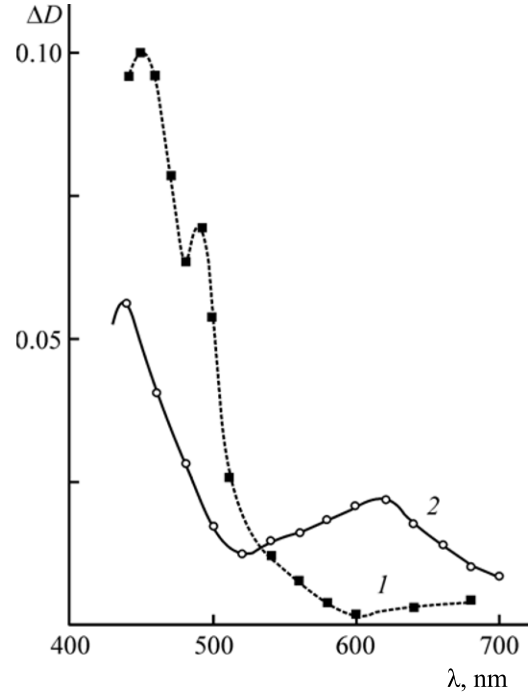


Fig. 16. The absorption spectrum of the intermediates at the flash photolysis of 2,6-diphenyl-1,4-benzoquinone Q (c 10^{-5} M): (*1*) in CCl_4 + 5×10^3 M, (*2*) in dioxane.

concentration and temperature. Study of interaction of 12C4 crown ether with quinone gave a similar picture, with a larger correlation coefficient (the presence of the complex was detected in the ^1H NMR spectra at room temperature), which is associated with the greater electron-donor properties of oxygen atoms. Below we show that the presence of such donor-acceptor complexes plays fundamental role in elementary acts of the photochemical processes.

At the flash photolysis of quinone in non-polar solvent (C_6F_6, CCl_4) in a time of 10^{-5} s the absorption spectrum of the mixture indicates formation of semiquinone radical $QH^{\cdot}$, whose kinetics of the radical termination at a wavelength of 620 nm corresponds to the second order (Fig. 15).

The flash photolysis of quinone in the medium with a heterocyclic compound allowed us to fix the intermediates absorbing in the regions of 450 and 480 nm. They are formed from a short-living product absorbing at 630 nm, since kinetics of its disappearance coincides with the kinetics of accumulation of the long-living product.

Introducing THF into the solution does not lead to noticeable change in the absorption spectrum. Only quinone underwent excitation that leds to traces of respective hydroquinone, as confirmed by photometric studies.

Flash photolysis of quinone in the same solvents but with dioxane and 12C4 crown ether gives a completely different pattern. Both short-living and long-living intermediates were registered that give rise in the spectra to the bands with the absorption maxima at 420 and 620 nm (Fig. 16). In [3] it was indicated that the intermediate absorbing at 480 and 620 nm was $QH^{\cdot}$ radical, and that absorbing in the region of 480 nm was the radical $Q^{-\cdot}$. According to [19], the absorption band at 620 nm refers to different compounds, because the flash photolysis of quinone Q in an inert solvent in 5×10^{-6} s fixed a short-living intermediate with maximum absorption at 630 nm. According to our opinion, the intermediates in this case are the triplet excimers disappearing in a first-order reaction and the triplet exciplexes whose disappearance occurs in a second-order reaction. They both can exist in the reaction mixture simultaneously, but in different proportions, resulting in an intermediate order of the reaction.

The flash photolysis of quinone Q in a medium containing ethers allows fixation of the intermediates absorbing in the regions of 450 and 480 nm (Fig. 16). They are formed from the short-living intermediate absorbing at 630 nm, since the kinetics of its disappearance coincides with the kinetics of accumulation of long-living intermediate (Fig. 17). Evidently, the triplet excimers (the exciplexes) are precursors of radical intermediates $Q^{-\cdot}$ and QH^{+}, which are in equilibrium with each other.

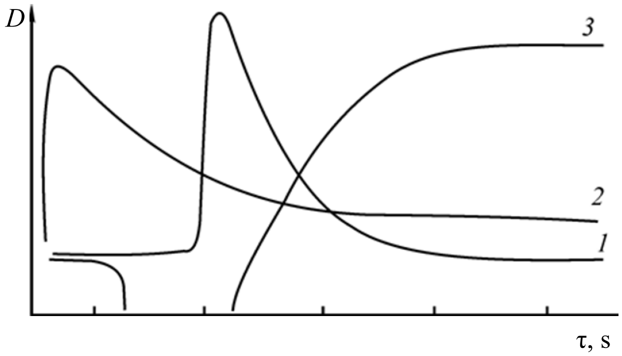


Fig. 17. The total oscillogram of the change in the optical density *D* of the intermediates formed at the flash photolysis of quinone in C_6F_6 containing 10^{-2} M of the crown ether 12C4. (*1*) λ = 630 nm, the scale 2×10^{-5} s, (*2*) 450 nm, the scale 4×10^{-5} s, (*3*) 450 nm, the scale 5×10^{-5} s. Kinetics of disappearance is of the second order.

The rate constants and activation energies of the complexes with different oxygen-containing electron donors were determined. In the photoreaction of 2,6-diphenyl-1,4-benzoquinone with dioxane the rate constant $k = 1.1\times10^5$ mol l^{-1} s^{-1}, the activation energy $E = 6.2$ kcal mol^{-1}, in the reaction with the crown ether $k = 3.2\times10^5$ M s^{-1}, $E = 8.48$ kcal mol^{-1}. Comparing the ratio of the rate constants and activation energies a conclusion is possible that ethers form complexes with the excited state of quinone and behave as a bulky substituent. Moreover, the activation energy of the complex increases in the order dioxane < 12C4 < 15C5 < 18C6, and the reaction rate constants are reduced in the same order. Thus, the heterocycles do not form a complex with unexcited quinone. Formation of donor-acceptor complexes occurs at the collision of excited triplet quinone with the heterocycle. The latter inhibits reactions of semiquinone radicals due to creation of steric hindrances for disproportionation and dimerization.

The mechanism of photolysis of quinone in ether includes several elementary acts of two reactions occurring simultaneously, but with different efficiency.

The final product is formed by the H atom abstraction from the α-carbon atom in the radical cation of the

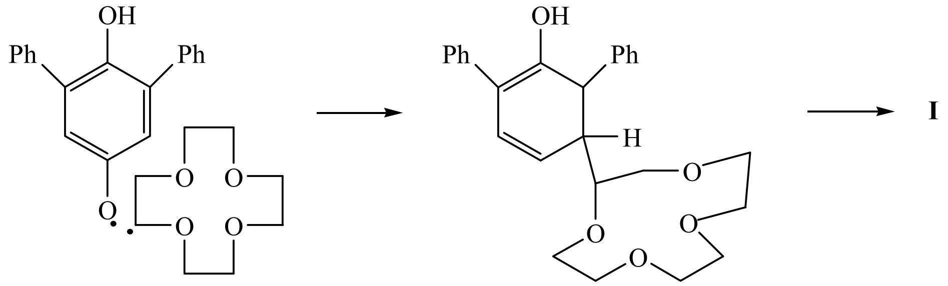
$$QQ \longrightarrow \text{Eximer} \longrightarrow Q^{\bullet}\cdots Q^{+\bullet} \overset{H^+}{\rightleftarrows} QH^{\bullet}\cdots Q^{\bullet} \longrightarrow \text{Products}$$

$$QD \longrightarrow \text{Eximer} \longrightarrow \underset{\substack{\text{short-loving}\\ \text{absorption}\\ \text{at 630 nm}}}{Q^{\bullet}\cdots D^{+\bullet}} \overset{H^+}{\rightleftarrows} \underset{\substack{\text{long-licing}\\ \text{absorption}\\ \text{at 480, 450 nm}}}{QH^{\bullet}\cdots D^{\bullet}} \longrightarrow \text{Products}$$

D is donor of electrons.

crown ether and the subsequent recombination of radicals in the radical pair.

Noteworthy that the decrease in electron-donor properties of the oxygen atom in the series leads to a sharp increase in the required duration of preparative photolysis, resulting in the secondary photochemical reactions leading to the opening of the hydroquinone macroheterocycle.



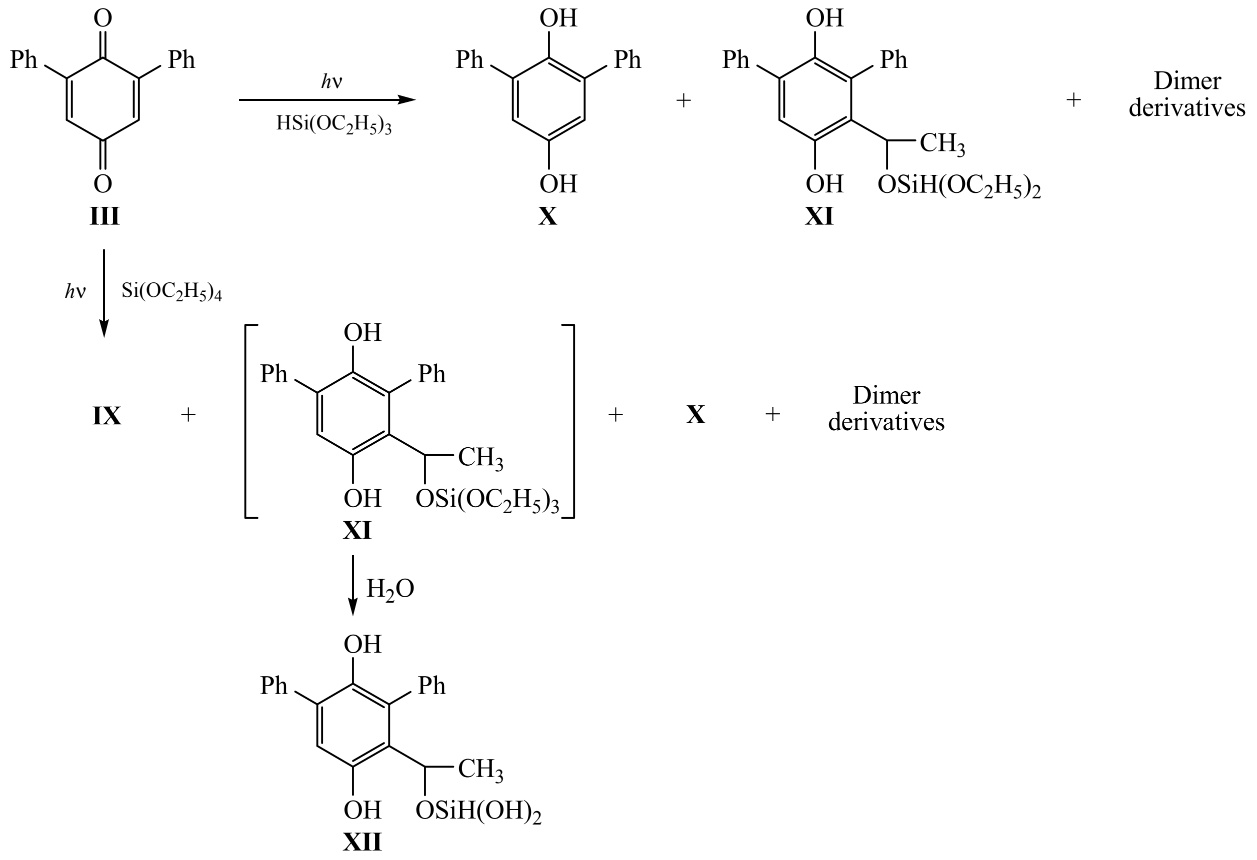
7. Photochemical reactions of 2,6-diphenyl-1,4-benzoquinone in tri- and tetraethoxysilane. Photolysis of 2,6-diphenyl-1,4-benzoquinone **III** in tri- and tetraethoxysilane [29] leads to the same reaction products, but in different ratios. In both cases, the yield of silanohydroquinones **XI** and **XII** is 10%. Triethoxysilane is a strong reducing agent, and the main product of the reaction is diphenylhydroquinone **X**, yield of photodimer **IX** is 10%. In tetraethoxysilane the main reaction product is photodimer **IX**, the yield of compound **X** is about 10%.

Theoretically, not only the structure **IX** can be formed in the photolysis of these quinones. To prove the formation of dimers of different nature the reaction mixture composition was investigated at the photolysis of quinone **III** using mass-spectrometric method with a system of direct inlet, and the technique of molecular distillation in a vacuum.

The peaks of molecular ion corresponding to the dimeric form **IX** were not recorded in the mass spectra. Ions with the highest *m*/*e* values 260 and 262 formally correspond to molecular masses of the initial quinone and hydroquinone **X**. A study of evaporation of these compounds, and photodimers **IX** showed that their evaporation temperatures differ sharply. Dimer **IX** treated with acetone when heated in a sealed ampule at 180°C affords hydroquinone **X**. At the mass spectrometry of the heated sample the maximum of the total ion current is shifted to the temperature near 90°C. Consequently, the dimer **IX** shows not only photochromism, but thermochromism. In the direct inlet unit at a temperature of 170°C the dimer **IX** suffers thermodestruction, and in the spectra only the molecular ions of quinone **III** and diphenylhydroquinone **X** are recorded; the latter is a result of the transfer of two hydrogen atoms from one quinone fragment **IX** to another.

Also noteworthy the fact that in the mass spectra of the initial quinone **III** at higher temperatures a formation is fixed of some quantity of hydroquinone **X**, that is, an intermolecular abstraction of two hydrogen atoms occurs by one quinone molecule from identical another molecule, which is typical for the case of stack packaging. The result of this supramolecular structure of donor–acceptor complexes of quinone **III** is the migration of two hydrogen atoms at elevated temperature. A similar migration of two hydrogen atoms was observed in the diphenoquinone stacks [11].

When the temperature of evaporation of the reaction mixture was increased to 190°C and above, in the spectra the peaks appeared of molecular ions at



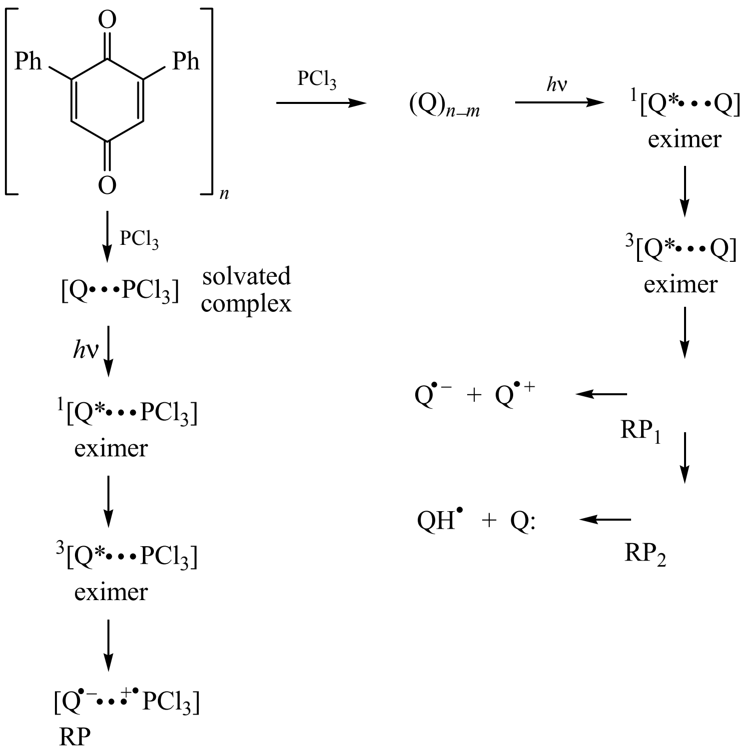
516, 518, 520, and 522. Their intensity increases simultaneously with the decrease in the total ion current and the ion currents with *m/e* 260 and 262. Hence, these molecular masses cannot be attributed to dimer **IX**. Thus, the considered photochemical reactions in triethoxysilane lead mainly to diphenylhydroquinone, while in tetraethoxysilanes the main product is the photodimer.

8. The mechanism of photolysis of 2,6-diphenyl-1,4-benzoquinone in phosphorus trihloride. According to the data of NMR spectroscopy, photolysis in phosphorus trihloride [30] proceeds with the quinone consumption in the zero-order reaction with the rate constant of 6.4×10^{-2} mol l s^{-1}. At the flash photolysis of quinone in phosphorus trichloride two intermediates are formed: the short-living $QH^{\cdot}$ and the long-living $QH^{\cdot-}$, absorbing at λ_{max} 630 and 450 nm, respectively. Kinetics of the neutral radical $QH^{\cdot}$ termination in the absence of oxygen obeys the first order with k = 2.5×10^{3} s^{-1}.

Formation of the $QH^{\cdot}$ radical in this reaction is of particular interest, since PCl_3 is aprotic solvent. Therefore, the donor of the hydrogen atom can be quinone itself either in the ground state as exciplex, or in excited state at the escape to the bulk of the components of the pair $(Q^{\cdot-}\cdots PCl_3^{+\cdot})$ or $(Q^{-\cdot}\cdots Q^{+\cdot})$. Thus, the data of the flash photolysis and NMR spectroscopy, and high yield of phosphonium quinone ylide (up to 95% in a preparative photolysis) are consistent with the reaction scheme.

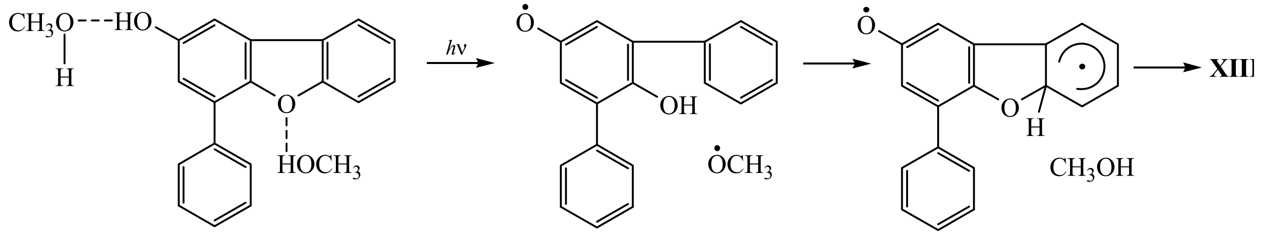
It was shown previously that photolysis of quinones in aprotic solvent CCl_4 leads to the formation of a dimeric derivative by the mechanism similar to the case of C_6F_6 and to the photochemical rupture of carbon–chlorine bond with theformation of a wide range of products.

Thus, it follows from the above said that the composition and ratio of final products of photochemical reactions of 1,4-benzoquinoid systems is largely defined by the nature of the donor–acceptor complexes in the ground state. The role of steric factors in substituents is associated with the ability of quinoid system to packing in a nano-stacks causing formation of either excimers, or exciplexes at the excitation of the quinoid system with a quantum of light.



9. Forced generation of radio emission at the photolysis of the 8-hydroxy-6-phenyldibenzofuran–deuteromethanol system. Photolysis of 8-hydroxy-6-phenyldibenzofuran was carried out in deuteruated benzene, acetonitrile, or water medium, directly in the NMR spectrometer probe. The ^{1}H NMR spectra in these solvents did not differ from the spectra taken in the dark. When methanol was added to the reaction mixture, a strong negative polarization of the *meta*-protons (δ = 7.9 ppm) of the parent compound (δ^7 = 7.46 ppm; δ^9 = 7.18 ppm) was observed. The polarization reaches its maximum (factor 700 to 750) at the alcohol concentration 20% by volume, and after the transition period (15–20 s), the signal remains at the same level for many hours. Thus, there is almost a constant radio-frequency radiation in the process of reversible photochemical reactions. After turning off the light, the polarization of the protons of initial 8-hydroxy-6-phenylbenzofuran disappears [31].

The observed effects can be explained by the reversible photoreaction in the system of 8-hydroxy-6-phenylbenzofuran–methanol associate **XIII**. Under photoexcitation, in the system radical pair **XIV** in the triplet state is formed. As a result of the triplet-singlet conversion, the *meta*-protons (δ = 7.9 ppm) are polarized negatively. This is confirmed by the Captain rule: T = + + – + < 0.



The radical pair **XIV** formed (it is in this pair the nuclear polarization occurs due to the singlet–triplet transition) is reorganized into the original methanol and transitive biradical structure **XV**, in which one unpaired electron is distributed over the polynuclear radical-like conjugated complex, that provides the transition of a hydrogen atom and the formation of the initial associate **XIII** with the polarized protons of 8-hydroxy-6-phenylbenzofuran.

When water is used instead of methanol, these processes are not observed, due to another structure of the associative complexes in the dense solvate shell in the system 8-hydroxy-6-phenylbenzofuran–water.

The observed effects belong to the unusual examples of generation of a high-power stationary radio emission in the course of the photoreaction, and may have practical implementation to create targets with orientable nuclei, as well as for producing industrial magnetometers.

10. Features of interaction of *p*-benzoquinone radicals with iron salts. This section presents the results of study of the interaction of *para*-benzosemiquinone radicals with $Fe_2(SO_4)_3$ and Mohr salt under the flash photolysis [32]. These reactions were carried out in a water–alcohol solution (the water–propanol ratio is 9:1 by volume) at the neutral and acidic (pH = 4.6) medium. To avoid the influence of varying ionic strength, 1 M solutions of sodium sulfate were used in the work. To prevent further dark oxidation and reduction reactions, *p*-benzoquinone and hydroquinone were used as a source of semiquinone radicals in the reactions with $Fe_2(SO_4)_3$ and Mohr salt, respectively. The pulse photoexcitation of hydroquinone or *p*-benzoquinone in the presence of hydrogen donor (alcohol) through the UFS-2 filter (280–350 nm) leads to the formation of *p*-semiquinone radicals. At pH = 4.6 formed semiquinone anion radical $Q^{\bullet -}$. The termination of these radicals occurs not only as a result of disproportionation, but also in the reaction with ferrous iron to form hydroquinone and ferric iron:

$$QH^{\bullet} + QH^{\bullet} \rightarrow Q + QH_2,$$

$$Q^{\bullet -} + Fe^{2+} \xrightarrow{+2H^+} QH_2 + Fe^{3+}.$$

At high concentrations of the Mohr salt the kinetics of $Q^{\bullet -}$ loss corresponds to the first-order equation. From the linear dependence of the effective constants on the Mohr salt concentration the value of $K_2 = 4.3 \times 10^5$ l mol^{-1} s^{-1} was obtained. In a neutral environment the semiquinone radicals $QH^{\bullet}$ are generated, which disproportionate and undergo the reactions with ferrous and ferric ions:

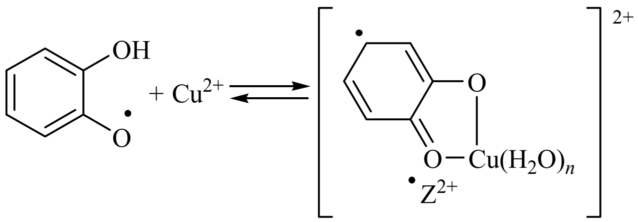
$$QH^{\bullet} + Fe^{2+} \xrightarrow{+H^+} QH_2 + Fe^{3+},$$

$$QH^{\bullet} + Fe^{3+} \xrightarrow{-H^+} Q + Fe^{2+}.$$

These reactions are of pseudo-first order at the salts concentration 10^{-4} M and above, with the constants $K_3 = 10^5$ l mol^{-1} s^{-1}, $K_4 = 7 \times 10^5$ l mol^{-1} s^{-1}.

The redox reaction between iron salts and the radicals $QH^{\bullet}$ proceeds through the formation of complexes, which are destroyed by interaction with hydrogen ions.

11. Complexation of benzosemiquinone radicals with bivalent copper ions. We have examined [33] a complexation of benzosemiquinone radicals with copper ions [33]. The radicals were generated from pyrocatechol BH_2 through the flash photolysis in the presence of copper dichloride. Under the experimental conditions (pH = 2) the absorption spectrum without the flash was a sum of spectra of the parent compounds. However, under pulsed photoexcitation of the BH_2 solution (10^{-3} M) in the presence of $CuCl_2$ (2×10^{-2} M), the bands characteristic of $BH^{\bullet}$ disappear and simultaneously the spectrum appears of the intermediate with a considerably longer lifetime. This change is due to the formation of complexes of $BH^{\bullet}$ and Cu^{2+} in the reaction:



Extinction coefficients of the formed $^{\bullet}Z^{2+}$ were obtained from the relation:

$$\varepsilon_{380}^{\bullet Z^{2+}} = \varepsilon_{380}^{BH^{\bullet}} \frac{\Delta D_{380}^{\bullet Z^{2+}}}{\Delta D_{380}^{BH^{\bullet}}} = 4.1\times10^{2}\ \text{l mol}^{-1}\ \text{cm}^{-1}.$$

At lower concentrations of $CuCl_2$ (10^{-3} M) the disappearance of the intermediates occurred in two directions:

$$BH^{\bullet} + Cu^{2+} = {}^{\bullet}Z^{2+} \text{ (fast conversion)},$$

$${}^{\bullet}Z^{2+} + {}^{\bullet}Z^{2+} = \text{Products (slow conversion)}.$$

The linear relationship between $^{\bullet}Z^{2+}$ and Cu^{2+} at the determination of the equilibrium constants indicates that the ratio of the components in the complex is equimolar. The constant of the complex decay is 10^{-4} s^{-1}. The complexes of Cu^{2+} ion are the strongest among the similar complexes of bivalent transition metals [2]. Hence, in this case an inner-sphere complex of Cu^{2+} with neutral short-living $BH^{\bullet}$ radical is formed.

Thus, in the course of investigations it was shown that the photoreactions of substituted 2,6-dimethyl-, 2,6-di-*tert*-butyl-, and 2,6-diphenyl-1,4-benzoquinones with alcohols, organic acids, thioalcohols, amines (primary, secondary and tertiary), cyclic ethers, tri- ant tetraethoxysilanes were accompanied by the effects of chemically induced dynamic nuclear polarization (CIDNP) and led to the formation, alongside hydroquinones, of bi- and tricyclic structures and the products of radical substitution in aromatic ring.

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