Russian Chemical Reviews **68** (9) 727 – 736 (1999) © 1999 Russian Academy of Sciences and Turpion Ltd

UDC 541.515

Radical pairs in redox reactions involving sterically hindered quinones and phenols †

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Abstract. The review summarises the results of studies on the redox reactions involving sterically hindered quinones and pyrocatechols (phenols) occurring in glassy and single-crystal matrices. Exposure of these systems to light results in the transfer of a hydrogen atom or an electron from the phenol to the quinone accompanied by the formation of radical pairs, *viz*., two paramagnetic species existing in the triplet state. Studies of the transformations in single-crystal matrices enabled separation of the mechanisms of electron and hydrogen atom transfer. Synchronous transfer of two hydrogen atoms from two sterically hindered phenol molecules to *o*-benzoquinone is also possible. The bibliography includes 39 references.

I. Introduction

The simplest quinones can be considered as model systems that mimic biologically important quinoid compounds (plastoquinones, ubiquinones, vitamin K, flavin adenine dinucleotide, *etc*.). Therefore, studies of the photochemistry of quinones are of undeniable interest due to elucidation of their role as electron acceptors in photosynthesis. For example, photoreduction of quinones results in semiquinone radicals, which are active species in electron transfer reactions in biological systems. Studies of photoreduction reactions in the liquid phase make use of methods of flash photolysis with optical detection of intermediate products and chemically induced dynamic polarisation of electrons and nuclei, while studies of these reactions in the solid state are carried out with the use of ESR spectroscopy. Although the ESR data obtained in the solid state are essentially depleted due to unaveraged rotational dipole – dipole electron – nucleus interactions, studies of solid-state processes and the identification of the radical species formed in these processes are still of special interest.

The present review generalises the results of studies dealing with the solid-state photoreduction of quinones and quinone-like systems with sterically hindered phenols.

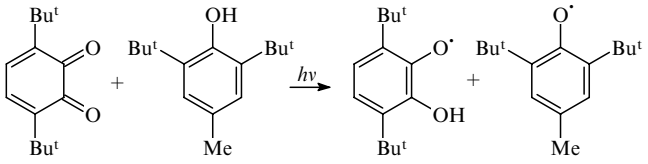
A characteristic feature of sterically hindered phenols and their derivatives is that they are readily involved in redox reactions to give relatively stable radicals. The application of radio-frequency spectroscopic methods gave strong impetus to the studies on the structure and reactivity of phenoxyl-type radicals and promoted progress in the chemistry of this class of compounds; this resulted in the synthesis of metal complexes with paramagnetic ligands.[1,2] The rather high stability of phenoxyl radical species and the relative simplicity of their ESR spectra made it possible to solve diverse structural and kinetic problems based on the analysis of the hyperfine structure (HFS) of the spectra.[2–4] Taken together, all this has made the sterically hindered phenols – quinones system a convenient model for studying the photooxidation by the ESR method.

UV irradiation of aromatic ketones in the presence of hydrogen or electron donors results in the reduction of carbonyl groups.[5–7] In a discussion of the elementary act of transfer of an H atom from a hydrogen donor (AH) to an excited quinone (Q*), Porter suggested in 1958 two possible variants of this process: (1) transfer of a hydrogen atom as a whole (one-step process) and (2) transfer of an electron followed by transfer of a proton (two-step process).[8]

$$Q \xrightarrow{h\nu} Q^*,$$
$$Q^* + AH \longrightarrow QH^{\bullet} + A^{\bullet},$$
$$Q^* + AH \longrightarrow Q^{-\bullet} + AH^{+\bullet} \longrightarrow QH^{\bullet} + A^{\bullet}.$$

In certain cases, it was possible to detect the formation of both neutral and radical-ion intermediates in these systems and to demonstrate the independence of their formation and dark decay. This fact implies that the solid-state reactions of this type are quite unusual.

Irradiation of a solution of 3,6-di-*tert*-butyl-1,2-benzoquinone (**1**, 3,6-Q) and 2,6-di-*tert*-butyl-4-methylphenol (**2**) in toluene or CCl_4 results in the phototransfer of an H atom from the phenol **2** to the quinone **1** accompanied by the formation of 2,6-di-*tert*-butyl-4-methylphenoxyl (**3**) and 3,6-di-*tert*-butyl-2-hydroxyphenoxyl (**4**, 3,6-SQH$^{\bullet}$) radicals, as indicated unambiguously by the HFS of the spectra of these species (Fig. 1 *a*).



1 **2** **4** **3**

† In memory of Professor Ya S Lebedev.

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Received 15 January 1999
Uspekhi Khimii **68** (9) 806 – 816 (1999); translated by S S Veselyi

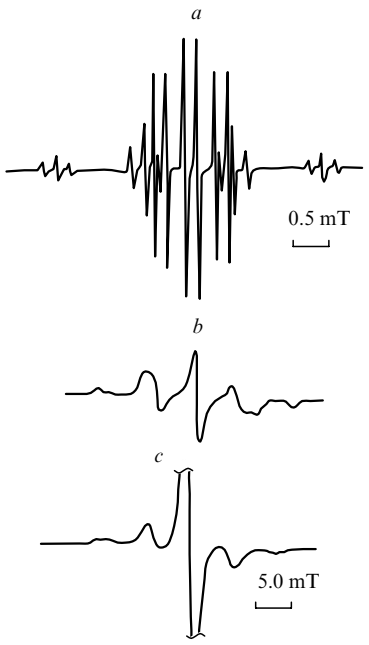


Figure 1. ESR spectra of a solution of 3,6-di-*tert*-butyl-1,2-benzoquinone (1,3,6-Q) and 2,6-di-*tert*-butyl-4-methylphenol (**2**) in CCl_4 (UV irradiation, 30 °C) (*a*) and of radical pairs (3,6-Q + NEt_3) (*b*) and (3,6-Q + phenol **2**) (*c*) in solid phase (toluene, 77 K).

On the other hand, irradiation of quinone **1** in the presence of amines results in semiquinone (SQ) radical anions.[9]

HFS of the ESR spectra of biradicals formed upon photolysis of the quinone **1** – phenol **2** system at 77 K points to their triplet state (Fig. 1 *b*,*c*). A similar pattern is also observed for the efficient dipole – dipole interaction of unpaired electrons of two monoradical species located in a solid phase at a distance of up to 7 – 10 Å from each other (radical pairs).

A theoretical consideration of systems in a triplet state enables an experimental determination of the zero splitting parameters (D and E) from the lines of the fine structure corresponding to the allowed transitions ($\Delta m_S = 1$).[10] The parameter D (in mT) in the point dipole approximation depends on the distance between the radical centres: $D = 3g\beta/r_{av}^3$, where g is the spectroscopic splitting factor, β is the Bohr magneton, and r_{av} is the average distance between the unpaired electrons. In this approximation, r is defined as r_{av}(Å) = 14.06 $D^{-1/3}$. As regards the parameter E, $E \neq 0$ in the absence of axial symmetry, while $E = 0$ in the case of axial symmetry where the system should have, at least, a three-fold axis.

The recorded absorption ($\Delta m_S = 1$, $g = 2$) due to reorientation of one electron spin in the external magnetic field (H) and in the field of the other electron of the radical pair (RP) is anisotropic in principle. Therefore, two components are distinguished for chaotically oriented RP, which correspond to RP oriented along the direction of H, *i.e.*, parallel ($D_\parallel$) and perpendicular ($D_\perp$); in this case, $D_\parallel \approx 2D_\perp$.

In addition, the ESR spectra of triplet systems often display forbidden transitions ($\Delta m_S = 2$) in the range $g = 4$ (half-field signal); the intensity of these increases with a decrease in the distance between the electron spins. The signal with $\Delta m_S = 2$ is intrinsically isotropic, as it originates from simultaneous reorientation of two electrons of the RP in the field H.

Detailed analysis of the ESR spectra of single crystals of phenols doped with quinones and similar compounds and subjected to photolysis made it possible to reveal fundamentally new types of solid-state reactions, *viz*., synchronous transfer of two hydrogen atoms from a single-crystal phenol matrix to a quinone, relay transfer of a hydrogen atom in the system 2,6-di-*tert*-butylphenol – 2,6-di-*tert*-butyl-1,4-quinonediazide, and tunnel transfer of a hydrogen atom in the dark decay of RP in a single crystal of 2,6-di-*tert*-butylphenol doped with 2,6-di-*tert*-butylquinoneimine.

The effects of abnormal relaxation of RP detected due to the different saturation of certain lines of the fine structure proved to be useful in the study on the chemical polarisation of nuclei in liquid solutions of the above systems. In certain cases, X-ray diffraction analysis of single crystals of phenols made it possible to determine specific ways of reverse transfer of a hydrogen atom in the dark decay of the RP. Analysis of kinetic curves of the RP decay showed the possibility of intramolecular migration of a hydrogen atom in semiquinone radicals.

Thus, detailed investigations into the spectral and relaxation characteristics of RP can provide additional information regarding the nature of the RP and the mechanism of processes resulting in their formation.

II. Radical pairs of phenoxyl radicals in frozen solutions

Specific features of solid-state phototransfer of a hydrogen atom in frozen solutions have been studied for the system 2,4,6-tri-*tert*-butylphenol (**5**) – 3,6-di-*tert*-butyl-1,2-benzoquinone (**1**) as an example.[11] The ESR spectra of the radical pairs formed upon photolysis of the phenol **5** and the quinone **1** in Nujol at 77 K (Fig. 2) attest to the formation of two types of RP, *viz*., RP_1 with $r_{av} = 5.4$ Å and RP_2 with $r_{av} = 6.3$ Å. The lines corresponding to the $D_\perp$ component of RP_1 coincide with the lines of the $D_\parallel$ component of RP_2. A study of the static saturation of these types of RP showed that the RP_1 lines are saturated with much greater difficulty than the RP_2 lines (Fig. 3) because of efficient relaxation in RP_1 due to stronger spin – spin interaction of unpaired electrons. It was shown that the accumulation of RP_1 and RP_2 during photolysis by filtered light ($\lambda = 365 - 460$ nm) occurs in parallel, but the ratio of their maximum concentrations at 77 K is 1 : 4. The presence of two types of RP in this system is due to the formation of 'sandwich' donor – acceptor complexes (Fig. 4) between the quinone **1** and the phenol **5** (NMR data) in which

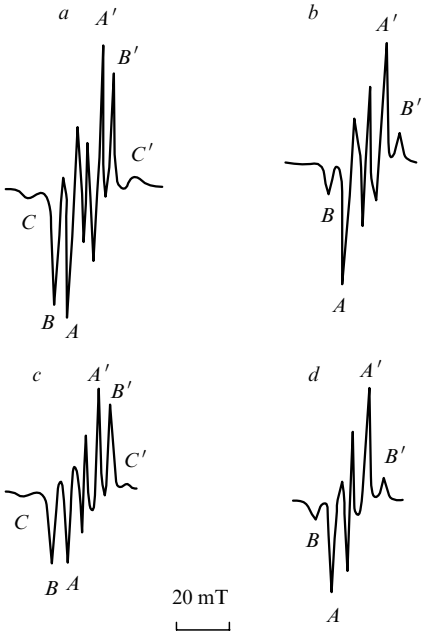


Figure 2. ESR spectra of radical pairs formed after 10-min irradiation of frozen solutions of 3,6-Q and 2,4,6-tri-*tert*-butylphenol (**5**) in Nujol at 77 K with light at a wavelength of 365 – 450 nm (*a*, *b*) and after 6 min of annealing the samples at 133 K (*c*, *d*).
The spectra were recorded at a microwave irradiation power of 150 (*a*, *c*) and 0.2 mW (*b*, *d*).

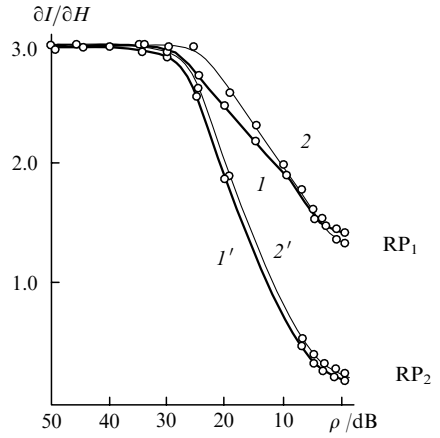


Figure 3. Dependence of saturation of RP_1 (*1*, *2*) and RP_2 (*1′*, *2′*) formed upon irradiation of solutions [3,6-Q + 2,4,6-tri-*tert*-butylphenol (**5**)] (*1*, *1′*) and (3,6-Q + OH-deuterated 2,4,6-tri-*tert*-butylphenol) (*2*, *2′*) in Nujol on the microwave irradiation power (ρ).

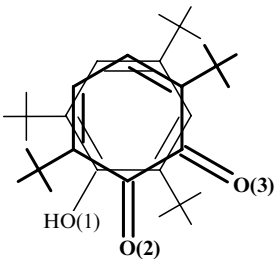
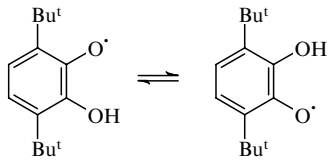


Figure 4. Tentative structure of the complex of the quinone **1** with the phenol **5**.

the distances between the oxygen atoms of the OH group of the phenol **5** and two carbonyl groups of the quinone **1** [O(1)...O(2) and O(1)...O(3)] differ noticeably. In addition, account of the electric dipole interaction between the oxygen atoms of the OH group of the phenol **5** and the carbonyl groups of the quinone **1** in the sandwich complex (Fig. 4) shows that the relative depth of the proton trap at the O(2) atom is greater than that at the O(3) atom by 0.2 kcal mol^{-1}. As a result, the ratio between the equilibrium concentrations of RP_1 and RP_2 is approximately equal to 1 : 4, which is consistent with the experimental data. The hydroxyphenoxyl radical **4** formed is characterised by intramolecular migration of a hydrogen atom between the oxygen atoms at a frequency of $\nu \simeq 10^9$ s^{-1} (at 300 K) or $\nu \simeq 10^3$ s^{-1} (at 77 K), which is much slower than the ESR time scale (10^{-6}–10^{-10} s).[12]



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As a result, the spectra of RP_1 and RP_2 are recorded separately.

Studies of the dark decay of RP_1 and RP_2 showed that both types of pairs decay in the same way and that the kinetics of this process is stepwise, which is probably caused by the heterogeneity of the matrix. The similarity of the character of accumulation and decay of RP_1 and RP_2 is apparently due to intramolecular migration of the H atom in the hydroxyphenoxyl radical, which causes the kinetic interrelation between the states determining the existence of both pairs. It should be noted that multiple cycles of generation and subsequent dark decay of the pairs do not result in the consumption of the starting reagents, which suggests that only two processes occur in these and similar systems, *viz*., photo-

Table 1. The values of fine structure constants D (mT) for neutral and radical-ion (D^i) pairs formed upon irradiation of the system quinone **1**–pyrocatechol **6** with light at $\lambda = 480$–650 nm in various solvents.

Solvent	D_1 (C,C') [a]	D_2 (B,B') [a]	D^i	ΔD^i (see [b])
3-Methylhexane	25.7	14.6	22.5	0.5
1,1,2,2-Tetrachloroethane	24.2	14.2	21.1 [c]	0.9
Toluene	24.9	14.3	–	0.5
Carbon tetrachloride	23.1	12.5	22.9	–
Pentane	25.5	14.2	22.0	0.9
Hexane	24.5	13.4	21.5	1.6
Heptane	24.7	13.9	20.9	0.9
Octane	23.5	12.4	21.4	0.7
Nonane	23.5	13.1	20.3	0.7
Decane	23.2	12.3	21.3	1.2
Tridecane	23.8	13.1	20.5	1.4
Benzene	23.3	13.2	21.0	0.6
Chlorobenzene	23.0	13.4	21.7	1.1
Bromobenzene	24.5	13.9	21.0	0.5
Dichloroethane	24.1	13.8	20.5	0.8
m-Ethyltoluene	21.5	12.1	22.4	1.2
Tetramethylsilane	23.8	13.3	20.9	1.3
Decalin	23.3	12.6	–	0.9

[a] D_1 and D_2 are dipole–dipole coupling constants for neutral RP with the perpendicular components C,C' and B,B'. [b] ΔD^i is the change in D^i after 30 min of dark annealing at 77 K. [c] In this case it was possible to measure E, which was found to be 0.47 mT.

transfer of the hydrogen atom from the phenol to the quinone and its reverse transition in the dark process.

A detailed study of the dependence of the structure of RP formed in the system quinone **1**–3,6-di-*tert*-butyl-1,2-dihydroxybenzene (**6**, 3,6-QH_2) in glassy frozen solutions at 77 K on the solvent nature (Table 1) and the wavelength of the incident light was carried out.[13,14] Irradiation of this system with light at $\lambda = 365$–500 nm results in the phototransfer of a hydrogen atom with formation of three types of neutral RP,‡ which differ in their fine structure parameters. The kinetic characteristics of accumulation and decay of all of these types of RP are identical due to the intramolecular migration of the H atom in the phenoxyl radical 3,6-$SQH^{\bullet}$, and hence, the difference between the accumulation and decay curves of the RP disappears.

However, irradiation of this system with light at $\lambda = 480$–650 nm gives, in addition to the types of pairs specified above, one more type which has an intermediate D value and corresponds to a radical-ion pair formed due to the phototransfer of an electron:

$$3,6\text{-Q} + 3,6\text{-QH}_2 \longrightarrow 3,6\text{-Q}^{-\bullet} + 3,6\text{-QH}_2^{+\bullet}.$$

The kinetic stability of this type of RP is much smaller (Fig. 5) than that of neutral ones.

An important feature of radical-ion pairs is the absence of an induction period in their accumulation curves; this made it possible to draw the conclusion that the formation of the neutral and radical-ion pairs occurs independently, *i.e*. the two processes occur in parallel.[14,15] The main argument for the suggested mechanism of the formation of neutral and radical-ion pairs is the increase in the relative photoyield of ionic RP in comparison

‡ In solution, the quinone **1** and the pyrocatechol **6** give donor–acceptor complexes;[13] in this case, the phototransfer of an H atom formally results in four types of RP (generally, four localisation variants of two H atoms on four O atoms are possible in each hydroxyphenoxyl radical; however, the parameters D of two of these variants are equal).

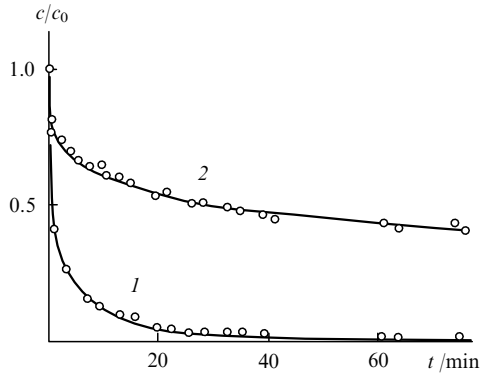


Figure 5. Kinetic curves of decay of ionic (*1*) and neutral (*2*) radical pairs in 3-methylhexane.

with that of the neutral ones (Fig. 6) with an increase in the wavelength of the incident light (λ). Similar results were obtained for the photoreduction of *p*-benzoquinone in an ethanolic solution at room temperature.[16] The long-wave threshold for the generation of neutral semiquinone radicals is 450±10 nm, while that of radical ions is 580±10 nm.[16] Hence, the transfer of a hydrogen atom requires irradiation in a shorter wavelength range than that required for the electron transfer. This feature of ionic RP is apparently due to the formation of donor – acceptor complexes in which the single-electron phototransfer is facilitated.[17]

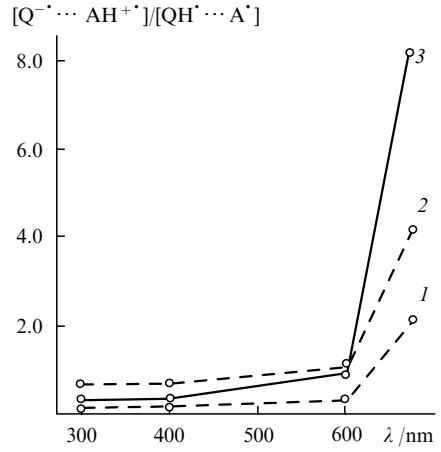


Figure 6. Dependence of the relative photoyield of radical-ion pairs [$Q^{-\bullet} \cdots AH^{+\bullet}$]/[$QH^{\bullet} \cdots A^{\bullet}$] in different solvents on the wavelength of the exciting light. The abscissa axis represents the value of λ corresponding to the maximum of the transmission band of a set of light filters (the half-width of the transmission band was 50 nm);
(*1*) toluene; (*2*) 1,1,2,2-tetrachloroethane; (*3*) 3-methylhexane.

III. Characteristic features of photoreduction of quinones in single crystals of organic hydrogen donors

Doping of single-crystalline phenolic compounds with sterically hindered quinones enabled the development of new interesting systems characterised by specific behaviour when exposed to photoirradiation. Single crystals of 3,6-QH_2 doped with 3,6-Q (10^{-2} mol litre^{-1}) were obtained[18] and the ESR spectra of radical pairs formed upon irradiation of this system (λ = 425 – 475 nm) at 77 K were studied. Figure 7 shows the ESR spectra of single-crystalline 3,6-QH_2 doped with 3,6-Q (Fig. 7 *a*) and a polycrystalline sample obtained from a melt of

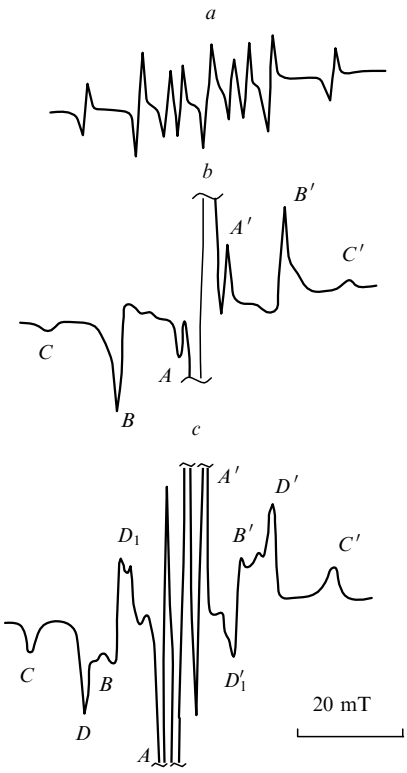


Figure 7. ESR spectra of a single crystal of 3,6-QH_2 doped with 3,6-Q (10^{-2} mol litre^{-1}) (*a*) and a polycrystalline sample obtained from a melt of the corresponding single crystals (*b*, *c*);
(*a*) is the single-crystal sample 10 min after irradiation with light at a wavelength of 425 – 475 nm; (*b*) is the polycrystalline sample 10 min after the irradiation; (*c*) is the polycrystalline sample during irradiation in the ESR spectrometer resonator.
The components *A* and *A*′ can be assigned to RP with D = 7.5±0.2 mT and r_{av} = 7.2 Å; *B* and *B*′, to the perpendicular components $D_{\perp}$; *C* and *C*′, to the parallel components $D_{\parallel}$. The additional short-lived components *D*, *D*′ and D_1, D_1' belong to RP with E = 0. The parallel components of the short-lived RP coincide with those for the stable RP.

the corresponding single crystals (Fig. 7 *b*,*c*). The calculated value of parameter D = 28.6±0.4 mT for this system corresponds to the mean distance between the unpaired electrons, r_{av} = 4.6 Å.

The equality between the $D_{\parallel}$ components of short-lived and stable RP suggests that their r_{av} are approximately equal to 4.6 Å. The essential difference in the stability of the RP in question enables one to assign the short-lived RP to radical-ionic ones ($AH^{+\bullet} + Q^{-\bullet}$) formed upon phototransfer of an electron. Stable RP ($A^{\bullet} + SQH^{\bullet}$) result from the phototransfer of an H atom. As in glassy frozen solutions (see Section II), the long-wave threshold of the formation of stable RP is 460±15 nm, while that of radical-ionic RP is 560±15 nm. It should be noted that irradiation of a sample with light at λ = 475 nm for 2 h virtually does not give stable RP. Analysis of the ESR spectra of radical pairs shows that the fraction of the radical-ion pairs is 99.9%, and their subsequent dark decay occurs without conversion into stable neutral RP.[15] These data confirm the conclusions on the independence of two photoreduction mechanisms of excited 3,6-Q made for glassy frozen solutions.

Single crystals of 3,6-QH_2 were studied by the X-ray diffraction method.[19] They were found to have a tetragonal structure (space group $I4_1/a$). Analysis of packing of the 3,6-QH_2 molecules in the crystal indicates that they form a helix relative to a four-fold axis (4_1) (Fig. 8) with a rotation angle of 90° relative to each other.

The X-ray diffraction data were compared with those of ESR spectroscopy by calculating the zero splitting parameters (D and E) for the case where one 3,6-QH_2 molecule is replaced by 3,6-Q

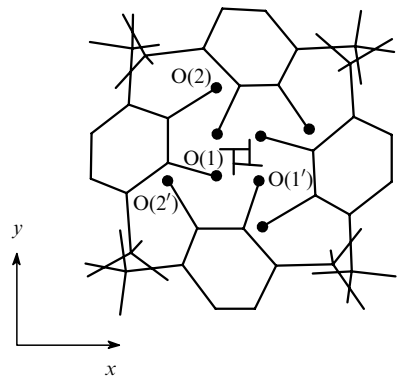
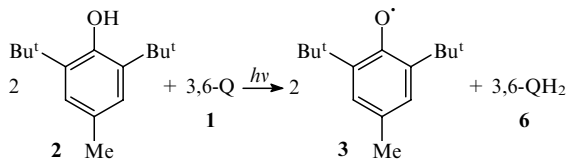


Figure 8. Fragment of a projection of the unit cell of 3,6-QH_2 on the *xy* plane.

and two identical 3,6-SQH$^{\bullet}$ radicals are formed upon irradiation. The values of *D* were calculated for various pairs of adjacent molecules using the method described in Ref. 20. The spin densities on various atoms in the 3,6-SQH radical were taken from Ref. 21 where they are given with an accuracy of 15%. The transfer of the H atom (Fig. 8) can occur through the channels O(1)–O(1′) and O(1)–O(2′). The calculated values of *D* are 33.55 mT for the channel O(1)–O(1′) and 33.4 mT for the channel O(1)–O(2′). These values are virtually identical and differ from the experimental one by 14% (D_{exp} = 28.6 mT). Since the spin density distribution in 3,6-SQH$^{\bullet}$ was estimated to the same accuracy, the agreement between the theoretical and experimental *D* values may be considered as satisfactory. By comparing the theoretical and experimental angular dependences $D(\theta)$, where θ is the angle between the axis *x* (Fig. 8) and the direction of the external magnetic field *H* (the crystal rotates around a four-fold axis), it was shown that the O(1)–O(2′) channel of the transfer of the H atom is more efficient.[19]

The interest in the photoprocesses in single-crystal matrices is caused by the fact that single crystals of sterically hindered phenols doped with quinones have diverse crystal structures and unit cell parameters, which depend on the structure of the phenol. In turn, this determines the specific features of the photo- and dark processes of the H atom transfer in each particular case.

It is known that in some redox processes, the transfer of two electrons can occur within one elementary act.[22] Studies [13, 23, 24] of the transfer of H atoms in single crystals of sterically hindered phenols doped with quinones showed the possibility of synchronous transfer of two H atoms from the phenol single-crystal matrix to quinones. The ESR spectra that appear upon photoirradiation (λ = 285–470 nm) of single-crystalline 2,6-di-*tert*-butyl-4-methylphenol doped with 3,6-Q are given in Fig. 9. Visually, the single crystals of the phenol **2** have a two-fold axis (axis *z*) and two faces parallel to this axis; the axis *y* is chosen along these faces. The spectral pattern shown in Fig. 9 *a* corresponds to the direction of the external magnetic field *H* along the axis *z*. Six groups of lines of the fine structure of the RP formed comprise HFS lines, which indicates unambiguously the interaction of the unpaired electrons with the protons of two equivalent methyl groups in the phenoxyl radicals **3** present in the pair. Each component of the fine structure contains seven lines with a binomial intensity distribution, a_H^{Me} = 0.53 mT. Such a pattern can only be caused by the transfer of two H atoms from two matrix molecules of the phenol **2** to the quinone **1**:



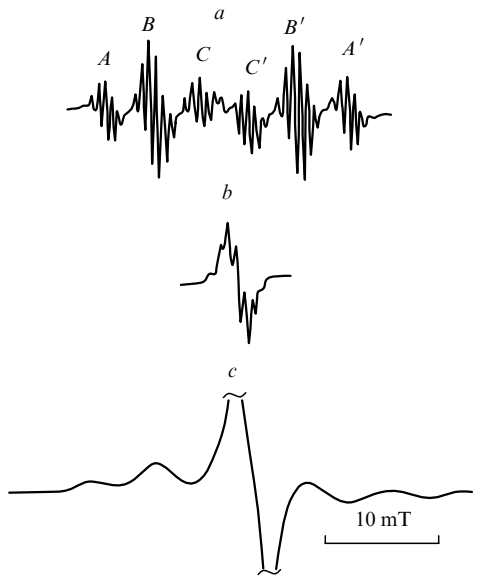


Figure 9. ESR spectra of a single crystal of the phenol **2** doped with 3,6-Q (10^{-3} mol litre^{-1}) (*a*) (*b* is the forbidden signal of single-crystalline phenol **2** (Δm_S = 2) in half-field) and polycrystalline sample (*c*).

The isotropic forbidden signal (Δm_S = 2) also contains seven lines (Fig. 9 *b*) from two equivalent methyl groups. The HFS constant in this system is half that in the original radical existing in solution (a_H^{Me} = 10.7 mT), which also proves the existence of two phenoxyl radicals **3** in the triplet state. In other words, along with the dipole–dipole interaction of two unpaired electrons giving fine structure lines, their strong isotropic exchange interaction due to overlapping of the wave functions of the unpaired electrons is observed.[25] The presence of six groups of fine structure lines (*A*,*A*′, *B*,*B*′ and *C*,*C*′) in the single-crystalline phenol **2** suggests the possibility of three orientations of the three RP with respect to the external magnetic field *H*; on the other hand, only one type of RP with *D* = 15.8±0.3 mT (r_{av} = 5.4 Å) is observed in the polycrystalline matrix of this sample (Fig. 9 *c*).

The spectral pattern is completely the same in the system phenol **2**–3,5-di-*tert*-butyl-1,2-benzoquinone (3,5-Q). Thus, one can state that the transfer of two H atoms from two molecules of the phenol **2** to the quinone 3,5-Q accompanied by the formation of two phenoxyl radicals **3** existing as a pair also occurs in this case.

The photoirradiation of the same single-crystalline phenol matrix doped with 2,6-di-*tert*-butyl-1,4-benzoquinone (**7**, 2,6-Q) results in a spectral pattern where the fine structure components of the three types of RP contain HFS from only one methyl group (a quadruplet with a 1:3:3:1 intensity ratio, a_H^{Me} = 0.53 mT) (Fig. 10). This indicates unambiguously that the transfer of only one H atom occurs.

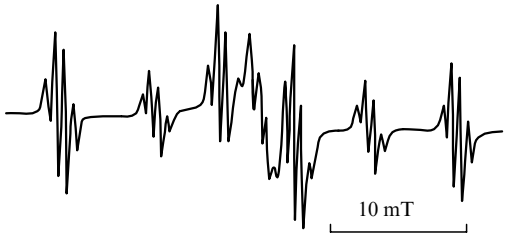
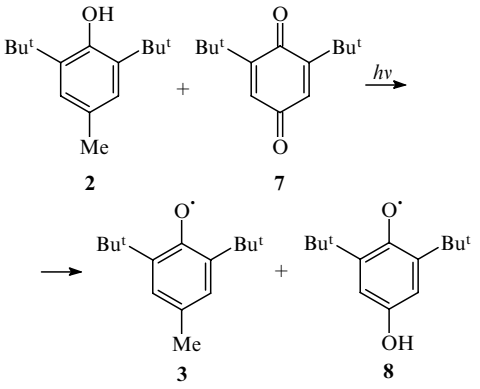


Figure 10. ESR spectrum of irradiated single crystal of the phenol **2** doped with 2,6-di-*tert*-butyl-1,4-benzoquinone.



It should be noted that the D parameter (13.4 mT) in this polycrystalline sample is noticeably smaller than that in the sample doped with 3,6-Q; this suggests that the relative arrangement of molecules of the corresponding quinones and the phenol **2** in these systems is different in principle.

The question arises as to the mechanism of phototransfer of two H atoms in the system phenol **2**–3,6-Q. It was shown that the RP accumulation in this system is proportional to the radiation intensity, *i.e.*, the transfer of two H atoms is not a two-quantum process. In addition, the long-wave threshold frequency of the RP formation in the single-crystalline phenol **2** doped with 3,6-Q is in the range from 290 to 330 nm, while in glassy frozen solutions where the transfer of one H atom occurs the long-wave threshold frequency of the RP formation is 560–630 nm; this indicates that a much smaller energy (by a factor of 1.7–2.2) is required for the phototransfer of one H atom. Let us note that the long-wave threshold frequency of the RP formation in the system single crystal of the phenol **2**–2,6-Q where phototransfer of one H atom occurs is noticeably higher: λ = 390–445 nm. These data altogether support the one-quantum mechanism of phototransfer of two H atoms in the system single crystal of phenol **2**–3,6-Q (or 3,5-Q). Nevertheless, the principal proof of a one-quantum process is that the RP yields, or, in other words, the efficiencies of phototransfer of one and two H atoms in all three systems (phenol **2**–3,6-Q, phenol **2**–3,5-Q and phenol **2**–2,6-Q) are all almost the same. In the case of the two-quantum process, the efficiency of phototransfer of two H atoms would be much lower.

It was found in a study of the kinetics of RP decay in all the three systems that it is exponential and is the same in the systems phenol **2**–3,6-Q and phenol **2**–3,5-Q ($k = 10^4$ s^{-1}, E_a = 23.8 kJ mol^{-1}) but differs strongly from the kinetics of RP decay in the system phenol **2**–2,6-Q ($k = 10^8$ s^{-1}, E_a = 22.8 kJ mol^{-1}). Apparently, the decay of RP occurs due to the reversible dark transfer of H atoms.

Thus, is has been shown that the phototransfer of two H atoms requires much higher excitation energy and that this act occurs due to the absorption of one quantum of light.

IV. Other quinoid systems in hydrogen atom transfer reactions in single-crystalline phenols

The interest in the use of 2,6-di-*tert*-butyl-1,4-quinonediazide (2,6-QN) as a potential acceptor of an H atom from phenolic hydrogen donors is due to the fact that the photoirradiation of 2,6-QN results in its dissociation into a carbene **9** (2,6-SQN) and molecular nitrogen.[26–28]

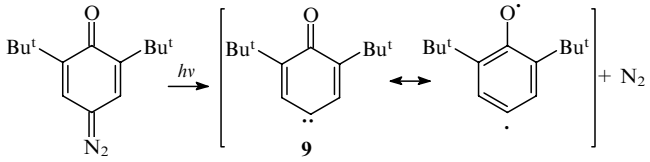


Figure 11 *a* shows a part of the ESR spectrum of the carbene **9** in single-crystalline phenol **2** doped with 2,6-QN upon irradiation with light at a wavelength of λ = 530±20 nm at 77 K. In this case, two triplets (1 : 2 : 1) are observed which correspond to the interaction of unpaired electrons with benzene ring protons.§ This spectrum corresponds to the high-field transition $\Delta m_S = \pm 1$. Depending on the sample rotation angle, four sets of triplets, which reflect four orientations of the 2,6-QN molecules in a single crystal, are observed.[27] Depending on the conditions, it is possible to observe two types of radical pairs in the system phenol **2**–2,6-QN, *viz.*, RP_1 (D = 13.2 mT, r_{av} = 6.0 Å) and RP_2 (D = 3.9 mT, r_{av} = 8.9 Å) (Fig. 11 *b*,*c*). The fine structure parameters were determined from the spectra of polycrystalline samples.

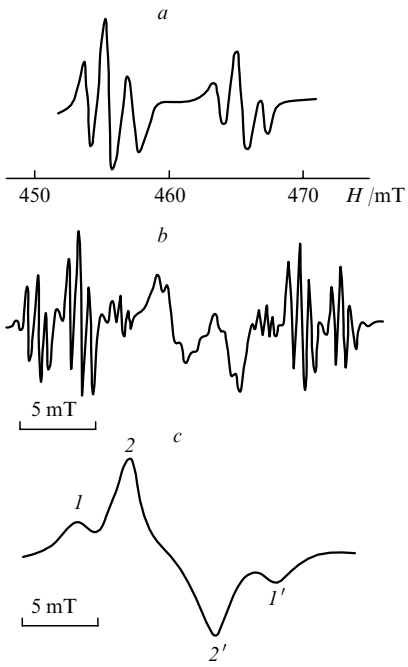
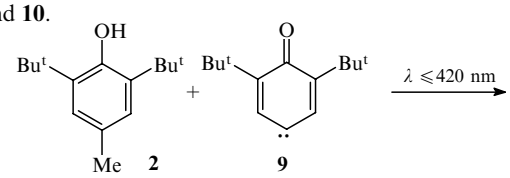


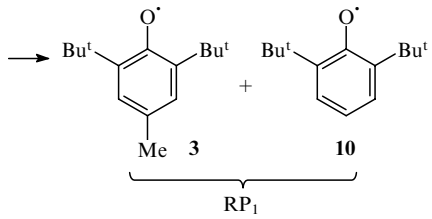
Figure 11. ESR spectra of the carbene **9** (*a*), the radical pair appearing upon irradiation of a single crystal of the phenol **2** doped with 2,6-QN (77 K) (*b*) and a polycrystalline sample obtained from a melt of single crystals of the phenol **2** and 2,6-QN (*c*);
(*1*, *1′*) are perpendicular components of RP_1; (*2*, *2′*) are perpendicular components of RP_2.

The radical pairs RP_1 and RP_2 appear upon irradiation with light at $\lambda \leqslant 420$ nm and $\lambda \leqslant 350$ nm, respectively.

In the short-term (30 s) irradiation at 77 K, only the spectrum of RP_2 and the carbene is observed. After a period of three days, the signal of the carbene disappears, but the intensity of the signal of RP_2 (D = 3.9 mT) increases. The rate of RP_1 formation at the beginning of photolysis with light at $\lambda \geqslant 310$ nm at 77 K is practically zero and its increase is observed after some time; this is apparently due to the transfer of an H atom from the phenol **2** to the carbene **9** with the formation of two phenoxyl radicals, *viz.*, **3** and **10**.

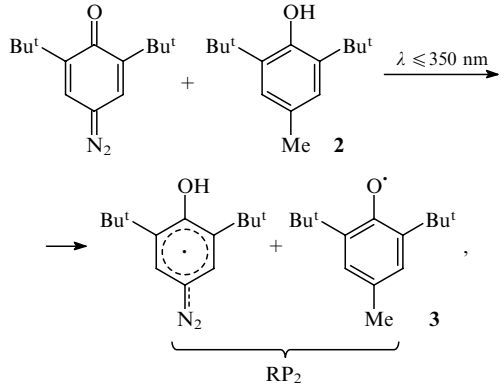


§ The magnitude of D for the system phenol **2**–2,6-Q is comparable with the magnetic field strength in the ESR spectrometer.



The characteristic time of RP_1 accumulation (D = 13.2 mT) is 30 min at 110 K. As the temperature is increased to 300 K, the RP_2 species disappear and only the RP_1 species remain.

These data suggest that there are two different processes of the H atom phototransfer. Specifically, these include the phototransfer itself (the formation of RP_2) resulting in the formation of a 'primary' pair,



and the reaction of the carbene with the matrix (the formation of RP_1).

The eight groups of lines containing a multiplet (1 : 4 : 6 : 4 : 1) correspond to different orientations of RP_1 relative to the external magnetic field H in the single crystal. The relative intensity of the lines corresponding to each type of pairs depends on the photoreaction efficiency, *i.e.* on the orientation of the 2,6-QN molecules relative to the direction of the incident light.

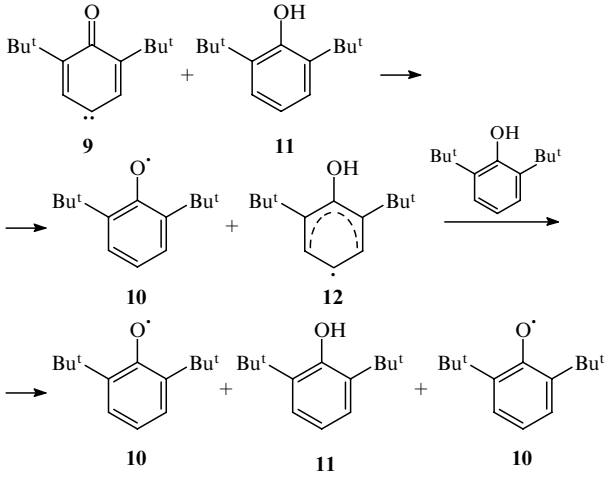
The photoselection effect in the photolysis of 2,6-QN has been studied in detail.[28] The line positions vary as the crystal is rotated relative to the external magnetic field, but the hyperfine coupling (HFC) remains unchanged and corresponds to the interaction of the unpaired electrons of the carbene **9** with four equivalent protons (a_H = 0.6 mT). The hyperfine structure (multiplet) originates from the interaction of the unpaired electrons of RP_1 with three protons of the methyl group in the radical **3** and the H atom at the *para* position of 2,6-di-*tert*-butylphenoxyl (radical **10**).

This conclusion was confirmed by a study of photoreactions that occur in the matrix of the phenol **2** with a deuterated OH group. In this case the multiplet is transformed into a quadruplet due to the HFC only with the hydrogen atoms of the methyl group.[28]

The particular channels of the H atom phototransfer were determined from X-ray diffraction data [24] on the phenol **2** crystal structure and with consideration of the spin density distribution in the phenoxyl radicals formed.

The experimental results obtained allow one to assume a different mechanism of the RP_1 and RP_2 formation as well. The radical pair RP_2 (the 'primary' RP) eliminates N_2 to give the 'secondary' RP_1; the difference between the r_{av} of the unpaired electrons is due to the change in the spin density distribution in the radical partners of the phenoxyl radical **3** and the relative change in the distances between the radicals in the corresponding pairs.

The formation of symmetric RP was observed in the photolysis of single-crystalline 2,6-di-*tert*-butylphenol (**11**) doped with 2,6-QN.[29] Two types of RP were detected in the ESR spectra of this system due to different orientations of the RP in the crystal. Owing to the specific features of the 2,6-di-*tert*-butylphenol crystal lattice, the phototransfer of an H atom can involve two possible different RP orientations relative to the external magnetic field. The small magnitude of the fine structure parameter D (4.3 mT) in this case suggests a large distance between the radical centres. X-Ray diffraction data and calculations of the D and E hyperfine structure parameters and data on the spin density distribution in phenoxyl radicals suggest that the RP are formed in this case through a two-step (relay) process.[30, 31]



The carbene **9** formed in the photolysis abstracts the *para*-hydrogen atom from the nearest 2,6-di-*tert*-butylphenol molecule to give a phenoxyl radical (**10**) and a phenyl radical (**12**). In turn, the phenyl radical abstracts an H atom from the nearest 2,6-di-*tert*-butylphenol molecule. In this manner, an RP is formed from rather remote phenoxyl radicals. Experiments with OH-deuterated single crystals confirmed the formation of such RP with identical hyperfine structures, which proves the validity of the suggested relay scheme of the H atom transfer.

The ESR spectra of the radical pairs formed upon photolysis of single-crystalline phenol **2** doped with 2,6-di-*tert*-butyliminoquinone (λ = 350 nm) and those of the corresponding polycrystalline sample are given in Fig. 12. The spectrum of the polycrystal (Fig. 12*b*) implies the formation of only one type of RP (D = 12.2±0.2 mT). The observed combination of the fine structure lines suggests different orientation of radical pairs relative to the external magnetic field due to the crystal structure of the phenol **2**.[28]

The nature of the radicals that form RP in a single crystal of the phenol **2** doped with 2,6-di-*tert*-butylquiononeimine was established using computer modelling based on the set of HFS

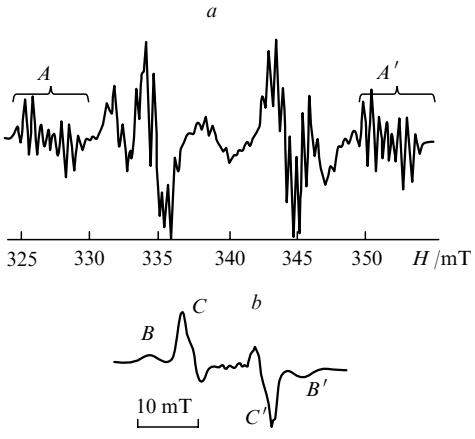
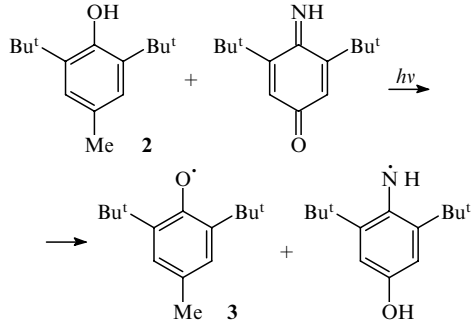


Figure 12. ESR spectra of the radical pairs formed upon photolysis of a single crystal of the phenol **2** doped with 2,6-di-*tert*-butyliminoquinone (*a*) and the corresponding polycrystalline sample (*b*).

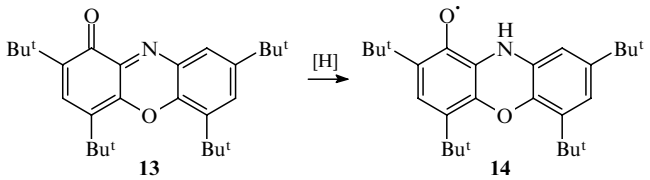
lines (Fig. 12 *a*).[30,31] It was found that the HFS is due to the interaction between the unpaired electrons and four equivalent protons, which implies the phototransfer of the H atom and formation of the corresponding phenoxyl and aminyl radicals.



The multiplet is formed by three protons of the methyl group and the proton of the aminyl radical. The long-wave threshold frequency of the RP formation in this system is 430±10 nm, which corresponds to the quinoneimine absorption band. The interpretation of the RP spectra was confirmed completely by experiments with single crystals of deuterated phenol **2**.[30]

The exponential character and an unexpectedly large kinetic isotope effect ($k_H/k_D = 10^3$) of the dark RP decay allow one to assume the tunnel character of the H atom reverse transfer.[32]

The redox properties of 2,4,6,8-tetrakis-*tert*-butylphenoxazin-1-one (**13**) are rather similar to those of sterically hindered *o*-quinones. The phenoxazinyl radical **14** formed in the reduction of phenoxazinone **13** manifests high stability and very characteristic ESR spectrum with a hyperfine coupling constant $a_N = 0.9$ mT.[33]



The high spin density on the nitrogen nucleus makes it possible to obtain additional information on the structure of paramagnetic complexes incorporating this ligand and on the structural changes in RP formed upon phototransfer of the hydrogen atom in single crystals of 3,5-QH_2 doped with the phenoxazinone **13**.[34]

Figure 13 presents the optical absorption spectra of 3,5-QH_2 and the phenoxazinone **13**. The ESR spectra of single-crystalline 3,5-QH_2 doped with the phenoxazinone **13** contain only a combination of lines of the original pyrocatechol and phenoxazinone, *i.e.*, no additional bands are present.

On irradiation of single-crystalline phenol **2**, RP of various types appear in the absorption band of the phenoxazinone (Fig. 14 *a*, *b*). Analysis of the spectral pattern obtained suggests

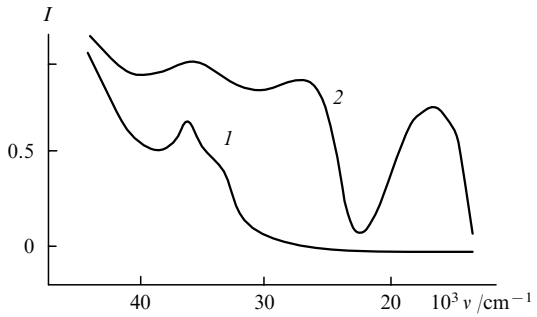


Figure 13. Optical absorption spectra of 3,5-QH_2 (*1*) and phenoxazinone **13** (*2*).

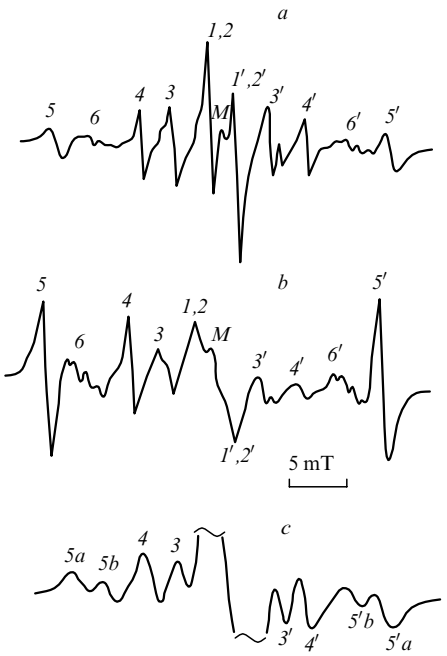
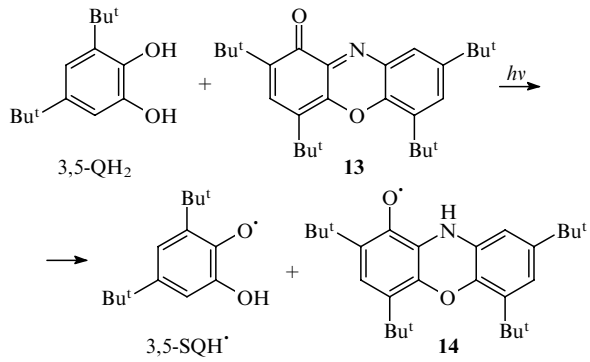


Figure 14. ESR spectra of the radical pairs formed upon photolysis of a single-crystalline 3,5-QH_2 doped with the phenoxazinone **13** (*a*, *b*) and polycrystalline sample (*c*).
Microwave power /mW: (*a*) 1, (*b*) 50.

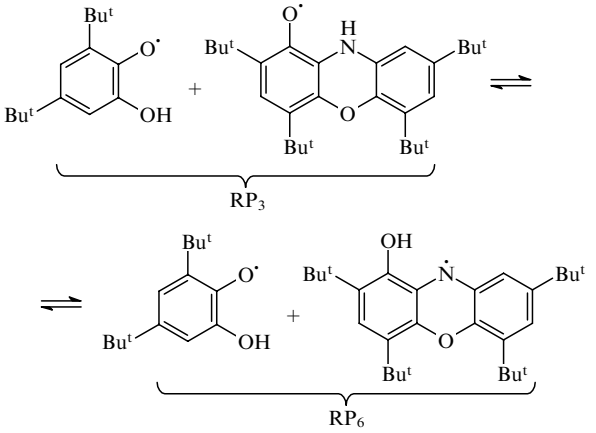
that there are six types of RP with different spectral characteristics (*D*) and hence with different distances between the radical centres. The radical pairs $RP_1 - RP_4$ appear upon irradiation with light at $\lambda \leqslant 600\pm20$ nm, RP_5 at $\lambda \leqslant 520\pm20$ nm and RP_6 at $450 \leqslant \lambda \leqslant 550$ nm. The observed RP have the following dipole–dipole coupling constants: $D_1 = D_2 = 1.6$, $D_3 = 8.0$, $D_4 = 13.0$, $D_5 = 25.0$ and $D_6 = 0.7$ mT. The values of D_3, D_4 and D_5 were determined from the spectra of polycrystalline samples (Fig. 14 *c*), and those of D_1 and D_2, from studies of the dependence of these parameters on the angle relative to the external field.

Studies of the dark decay of $RP_1 - RP_6$ at 77 K showed that the kinetic curves are satisfactorily linearised in the $I/I_0 - \log(t/t_0)$ coordinates,[34] which indicates that there is a set of different rates of reverse transfer of the H atom from the radical **14** to the 3,5-$SQH^{\cdot}$ radical. This situation is typical of processes occurring in solids and is determined by the structural features of the RP formed in this system. In the case under consideration, the distribution of the RP decay rates can be determined by the small changes (~ 0.1 Å) in the position of the phenoxazinone **13** in the crystal lattice of 3,5-QH_2. Moreover, the presence of six types of RP and, hence, the difference in their kinetic behaviour can be due to different arrangement of hydrogen atoms at the oxygen atoms of the 3,5-$SQH^{\cdot}$ radical (non-equivalent shielding of the oxygen atoms by the *tert*-butyl groups) and in the radical **14**.



Photolysis of the system 3,5-QH_2 – phenoxazinone **13** in the region from 450 to 550 nm at 77 K gives rise to RP_6 with additional HFS caused by the nitrogen nucleus of the radical **14** (Fig. 14); the intensity of the signal is small under these conditions.

The existence of reversible temperature evolution of RP_3 and RP_6 in the temperature range from 20 to 77 K has also been shown.[34] Only the ESR spectrum of RP_3 (Fig. 15 *a*) was observed during irradiation of a single crystal at 55 K. The spectrum of RP_6 was observed when the irradiation was terminated and the temperature was decreased to 20 K (Fig. 15 *b*); the components of this spectrum contain HFS from the ^{14}N nucleus (a_N = 0.9 mT). This temperature-reversible transformation is caused by spin density redistribution in the radical **14** as a result of H atom intramolecular transfer between the nitrogen and oxygen atoms (Fig. 16).



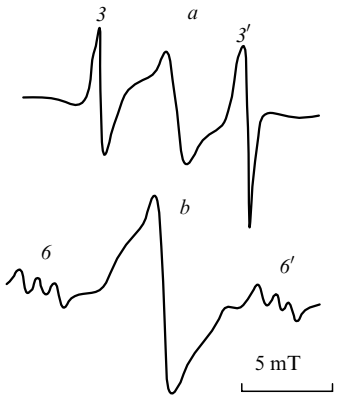


Figure 15. ESR spectra of the radical pairs RP_3 and RP_6 at 55 K (*a*) and 20 K (*b*).

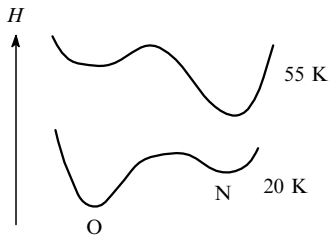


Figure 16. Potential energy curve for the migration of an H atom between the oxygen and nitrogen atoms in the radical **14**.

V. Anomalous relaxation in the ESR spectra of radical pairs

The ESR spectra of radical pairs sometimes show anomalies which can provide additional information on the interaction of the spin centres.

For example, anomalies have been reported [35] such as changes in the widths of the fine structure lines for the RP formed upon the hydrogen atom phototransfer in single-crystalline 3,5-QH_2 doped with 3,5-Q (system A) and in single-crystalline 3,3′,5,5′-tetrakis-*tert*-butyl-6,6′-dihydroxydiphenylmethane doped with 2,6-Q (system B). Figure 17 shows the ESR spectra of the system A obtained upon irradiation with light at $\lambda > 720$ nm. It can be seen that at low power of the microwave field (0.02 mW), the fine structure components have identical intensities, while at high power (2 mW), the high-field component has a considerably higher intensity implying shorter relaxation time.

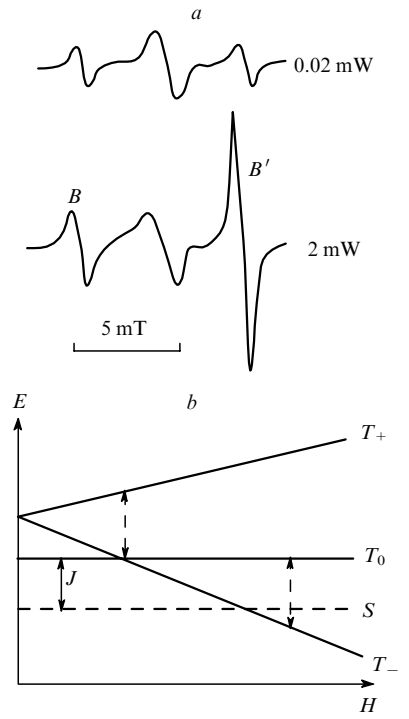


Figure 17. ESR spectra (*a*) and diagram of magnetic levels of the radical pair energy (*b*) for the system 3,5-QH_2 – 3,5-Q.

The times of spin – lattice (T_1) and spin – spin (T_2) relaxations for the low- and high-field components were determined from the saturation curves using the technique described in Ref. 36 and based on a model of non-interacting Bloch packets:

$T_1 = 5.7 \times 10^{-4}$, $T_2 = 6.6 \times 10^{-7}$ s (low-field component);

$T_1 = 1.2 \times 10^{-4}$, $T_2 = 2.8 \times 10^{-7}$ s (high-field component).

The system B was found to behave similarly.

In the systems studied, the ESR spectra at low power of the microwave field are centrosymmetric at any orientations of single crystals relative to the external magnetic field. Therefore, a mechanism of interaction of triplet levels was suggested [39] which dictated nonsymmetrical relaxation of the fine structure components but did not result in their asymmetry relative to the centre of the spectrum. Additional relaxation channels according to the scheme shown in Fig. 17 *b* were considered:

$T_0 \rightarrow S \rightarrow T_-$ (high-field component) — channel *1*;

$T_+ \rightarrow S \rightarrow T_0$ (low-field component) — channel *2*.

For these channels, the distances between the levels $S - T_-$ and $S - T_+$ are different. In the cases $J \ll g\beta H$ or $J \gg g\beta H$ (J is the distance between the T_0 and S levels), this difference is insignificant, and the rates of relaxation through the channels *1* and *2* are

the same. However, if the magnitudes of J and $g\beta H$ are comparable (Fig. 17), differences in the relaxation $S \rightarrow T_-$ and $T_+ \rightarrow S$ can be expected and, hence, the rates of relaxation through the channels *1* and *2* should differ.

The rates of the spin–lattice relaxation can be represented as:

$$\frac{1}{T_1(B)} = \frac{1}{T_0(B)} + \frac{1}{\tau_1},$$

$$\frac{1}{T_1(B')} = \frac{1}{T_0(B')} + \frac{1}{\tau_2},$$

where T_0(B) and T_0(B′) are the times of spin–lattice relaxations through the channels *1* and *2*, respectively; τ_1 and τ_2 are the times of relaxation through the channels *1* and *2*, respectively. The difference between $1/\tau_1$ and $1/\tau_2$ can explain the effect of abnormal asymmetrical relaxation provided that $1/T_0(B) \leqslant 1/\tau_1$ and $1/T_0(B') \leqslant 1/\tau_2$, *i.e.*, where the relaxation channels *1* and *2* under consideration contribute significantly to the relaxation rate.

Thus, the asymmetrical relaxation effect can take place if the singlet–triplet coupling is comparable with the Zeeman coupling, but is still different from the latter. These results can be useful in studies of the effect of a magnetic field on the rates of chemical reactions involving radical pairs as transition states.[37]

VI. Conclusion

The processes of solid-state hydrogen and electron transfer under photoirradiation considered above provide unique information on the nature of the elementary act in organic matrices which represent potential hydrogen donors. The advantage of studying solid-state systems, particularly single crystals, is that it provided the possibility of ESR in-depth studies of the structural features and kinetic behaviour of radicals which exist as radical pairs as a function of the features of the matrix and its crystal structure.

It was found that solid-state transfer of a hydrogen atom and an electron is possible not only under photoirradiation but also under elastic-wave impact on mechanical mixtures of the corresponding pyrocatechols and quinones or on the same mixtures in the presence of polymeric materials.[38, 39]

The results summarised in this work were obtained with direct participation of Professor Ya S Lebedev, whose top professionalism, authority, and sharp scientific intuition much favoured the development of chemical physics of solid-state processes in general and of the hydrogen atom and electron transfer in particular.

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