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Complexes of tertiary amines with hindered quinones

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The generation of radical pairs by low-temperature photolysis of solutions of sterically hindered quinones in aliphatic amines has been studied by ESR. The process of stabilization of radical pairs is related to molecular complexes between amines and quinones in solution.

Key words: radical pairs, ESR spectrum; amines, quinones, molecular complexes.

It has been shown previously[1,2] that radical pairs (RP) are stabilized during photolysis of frozen (77 K) solutions containing 2,6-di-*tert*-butyl-1,4-benzoquinone (2,6-DTBB), trimethylamine, triethylamine, and some other aliphatic tertiary amines. It is known that RP exhibit the characteristic ESR spectrum caused by strong dipole-dipole interaction between unpaired electrons. RP, which are randomly oriented, have "perpendicular" and "parallel" components in spectra corresponding to the perpendicular and parallel orientation of RP in the magnetic field.[3,4] ESR spectra allow one to determine the value of the dipole-dipole interaction constant (D), which is related to the average distance between unpaired electrons (R_{av}) by the equation

$$D = \frac{3}{2}g^2\beta^2/R_{av}^3,$$

where g is the g-factor of a free electron and β is the Bohr magneton. The dependence of D on R_{av} is pronounced, and when $R_{av} > 1.5$ nm, $D < 12.0$ G, *i.e.*, the ESR spectrum of RP in solid samples looks like an unresolved signal. At the same time, scattering over average distances (±0.01 nm) results in a considerable broadening of the signal for well registered RP with R_{av} = 0.5 to 0.7 nm. Thus, the existence of well resolved ESR spectra of RP, which are stabilized after photolysis of frozen solutions, makes it possible to assume that photoreduction occurs in certain structural units, the complexes that existed in solutions before freezing. The distance between unpaired electrons determined from spectra allows one to draw a conclusion about the structure of complexes.

Two types of RP were observed during the photolysis of 2,6-DTBB in the presence of trimethylamine and triethylamine. It has been assumed[1,2] that RP are formed during the photoreduction of quinone in donor-acceptor complexes of two types. Some of them have the 1 : 1 composition, and amine is arranged above the quinone ring. Photoexcitation at the n,π absorption band of carbonyl groups results in the n,π* triplet excited state of quinone *via* intersystem conversion. In this state the quinone can abstract one electron from the unshared electron pair of the N atom. Further stabilization of the RP is accompanied by fast (10 to 20 ps) deprotonation of the amine radical cation. This RP **1** consists of the neutral semiquinone radical and the α-aminoalkyl radical. For the 2,6-DTBB—triethylamine system, RP **1** is characterized by a dipole-dipole interaction constant of D_1 = 118±2 G, and the average distance between unpaired electrons ($R_{av}{}^1$) is equal to 0.617±0.003 nm.

RP **2** for which D_2 = 57±2 G and $R_{av}{}^2$ = 0.787±0.002 nm were observed in the same system. It has been assumed that they are formed in a triple sandwich-type complex consisting of one quinone molecule and two amine molecules. The two-quantum photoreduction of quinone results in its transformation to a diamagnetic particle (hydroquinone or hydroquinone dianion), and RP **2** produce two α-aminoalkyl radicals or the amine radical cation. The ESR method does not allow one to determine whether RP **2** consists of neutral particles or radical ions. However, it has been assumed[1,2] that RP **2** consists of two amine radical cations, because the ability of RP **2** to be saturated when the power of the microwave radiation increases is considerably greater than that of RP **1**.

The question about the effect of the nonequivalence of carbonyl groups of 2,6-DTBB on the formation of the triple complex remained unclear. The possible structure of this complex was suggested only on the basis of data on the distance between unpaired electrons in RP **2** and taking into account sizes of molecules, which enter the complex.

The products of low-temperature photolysis of solutions of triethylamine and 2,5-di-*tert*-butyl-1,4-benzoquinone (2,5-DTBB), in which both of the carbonyl groups are equivalent, are studied in this work.

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Experimental

Reagents, 2,5-DTBB and 2,6-DTBB, were purified by sublimation. Triethylamine was distilled and dried prior to preparing samples. Photolysis was carried out at 77 K in quartz ESR tubes. A DRSh-1000 high-pressure mercury lamp and an argon ionic laser (488.0 nm), which provided highly polarized radiation, were used for irradiation.

ESR spectra were recorded at 77 K on Radiopan (Poland) and Bruker-220 (Germany) spectrometers.

Results and Discussion

Photolysis of a solution of 2,5-DTBB in pure triethylamine results in stabilization of radical pairs of only one type: RP **3**, which are similar to RP **1** considered above. For RP **3** the D_3 constant is equal to 128±2 G and $R_{av}{}^3$ = 0.600±0.003 nm. Like RP **1**, radical pairs **3** probably consist of α-aminoalkyl and semiquinone neutral radicals. The fact that the photolysis of quinone with equivalent carbonyl groups results in the stabilization of only type **3** RP casts some doubt on the previously suggested[1,2] mechanism of formation of RP **2** in triple complexes, because similar "triads" could also exist in the 2,5-DTBB—triethylamine system. However, no radical ion pairs with a large distance between unpaired electrons would be formed in this case. Therefore, the process of formation of RP **2** is likely related to the fact that 2,6-DTBB contains nonequivalent carbonyl groups, one of which is strongly shielded by bulky *tert*-butyl substituents. It is likely that only binary complexes are present in both systems.

Before discussing the possible mechanism of formation of RP **2** in the binary complex, it should be proved first that perpendicular components in the ESR spectrum of RP **2** (Fig. 1, *b*) belong in fact to the radical pair and are not components of the HFS of the α-aminoalkyl radical or the amine radical cation. In the previous works in which such radicals were studied[5,6] it has been shown that their ESR spectra consist of seven lines with the splitting constants $a_N \approx a_H \approx 21.6$ G and $g = 2.0028$. The superposition of this spectrum on the ESR spectrum of the RP (see Fig. 1, *b*) gave no coincidence between the lines of the HFS and the perpendicular components of RP **2**. All lines, except the central line, were of low intensity.

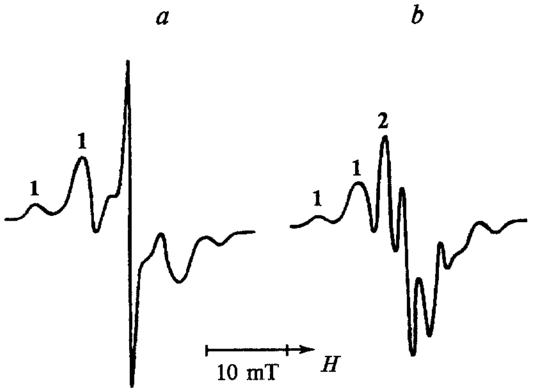

Fig. 1. ESR spectrum of solution of 2,6-DTBB ($5 \cdot 10^{-3}$ mol L^{-1}) in pure triethylamine irradiated and glazed at 77 K at various values of microwave power: *a*, 138 MW; *b*, 168 MW (signals of RP **1** and **2** are shown).

ESR spectra for RP **1** and RP **2** were also recorded on an ESR spectrometer with λ = 2 mm at 120 K. If the spectra of RP presented in Fig. 1, *b* were the superposition of the spectra of RP **1** and the amine radical cation, they would considerably diverge being recorded on a spectrometer with λ = 2 mm due to the difference in the values of their *g*-factors, and the total spectrum would have no single center of symmetry. However, the shape of the spectrum has become only somewhat more complicated, but remained symmetric. Therefore, the photolysis of the 2,6-DTBB—triethylamine system results in fact in the stabilization of RP of two types.

In addition, it should be explained how the formation of RP **1** and RP **2**, for which the mean values of distances between unpaired electrons differ substantially, can occur during photolysis of frozen solutions of 2,6-DTBB in triethylamine probably containing only binary complexes.

Ion pairs of 2,6-dimethyl-1,4-benzoquinone with Na^+ and K^+ have previously been studied[7] by the ESR method at room temperature. For the benzoquinone anion with two nonequivalent binding centers, the cation is localized predominantly near the O atom, which is sterically unshielded. However, the cation can also be localized near the screened oxygen atom, but the potential energy of such a state is somewhat higher. Cooling can result in the resolution of ESR spectra of two different ionic pairs.

It is reasonable to assume that binary complexes of two types, which differ in positions of the amine molecule relative to nonequivalent carbonyl groups of quinone, exist in the 2,6-DTBB—triethylamine as well. It has already been mentioned that RP **1** is formed in a more "rigid" contact complex, in which amine is shifted toward the unshielded oxygen atom of quinone. The photolysis is accompanied by very fast subsequent processes of electron and proton transfers.

RP **2** are stabilized in considerably "looser" structural units, and they are probably solvent-separated pairs. Since RP **2** are formed only with trimethylamine and triethylamine, it can be assumed that only these lower aliphatic amines succeed in sufficiently approaching the hindered carbonyl group of quinone. It is likely that the high shielding of the oxygen atom can result in the fact that only the first stage of photoreduction of quinone, the electron transfer, occurs during photolysis, while the subsequent proton transfer from the radical cation is sterically hindered, because the abstraction of the H atom is most efficient when alkyl substituents of the amine are mobile and the orbital of the unshared electron pair of the N atom can coincide with the direction of the broken α-C—H bond.[8] The amine radical cation formed is very active and can accept an electron from the neighboring neutral amine molecule arranged outside the complex in which the primary act of the photoprocess takes place. Then the radical pair separated by the neutral amine molecule is formed. One "shoulder" of this RP is the amine radical cation, and the second "shoulder" is the semiquinone radical anion. This conclusion is confirmed by data of a recent work (Ref. 9), in which processes of deprotonation of amine radical cations generated by the photolysis of triallylamines in the presence of triplet sensitizers containing carbonyl groups were studied by the Chemically Induced Dynamic Nuclear Polarization (CIDNP) technique. In particular, analysis of anomalous intensities of lines in ^{1}H NMR spectra of photoreaction products in the triethylamine—1,4-benzoquinone system in the magnetic field testifies that both neutral RP inside the reaction cage and radical ion pairs that have escaped from the cage can be precursors of these products.

To confirm the fact that RP **2** are in fact solvent-separated pairs, the experiments on diluting photolyzed solutions of 2,6-DTBB and triethylamine with decaline have been performed and it has been shown that the dilution results in a decrease in the yield of RP **2**. This testifies that in the deficient of amine in the system, when only one triethylamine molecule is localized near the hindered oxygen atom of quinone, no electron transfer of the "relay race" type occurs between two neighboring amine molecules and no stabilization of RP **2** is observed, and the excitation is quenched due to the direct and back electron transfers.

The use of polarized light for photoexcitation of solutions of 2,6-DTBB and triethylamine glazed at 77 K also allows one to obtain indirect evidence that the formation and stabilization of RP **2** occur *via* several stages of charge transfer. To observe the effect of magnetophotoselection, solutions of 2,6-DTBB in pure amine vitrified in an ESR tube were irradiated with linearly polarized light of an argon ionic laser (488.0 nm). The plane of light polarization was perpendicular to the axis of the tube. Some regular character of the orientation of randomly oriented RP is reached after irradiation of the fixed sample, and the intensity of components of the ESR spectra of RP is proportional to the polarization fraction of the populating n,π*-transition. When the sample is rotated in the resonator of the spectrometer, the intensities of components of the spectrum change as a function of the angle between the vector of light polarization (E) and the direction of the external magnetic field (H_0). For the system studied, the angular dependence of the intensity of components of RP **1** was observed, while components of RP **2** remained unchanged. This testifies that the formation of RP **2** is accompanied by the loss of polarization due to, for example, the electron transfer between two arbitrary oriented amine molecules, which comprise the solvate separated RP **2**.

Thus, comparison of the photochemical properties of these systems and use of linearly polarized light for photolysis makes it possible to draw the conclusion that solutions of both quinones in triethylamine contain binary complexes in which radical pairs are formed and stabilized.

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