Effect of Donor and Acceptor on the Mechanism of a Photochemical Reaction in Doped Single Crystals for Radical Pairs in 4-Bromo-2,6-Di-*tert*-Butylphenol Single Crystal Doped with 2,6-Di-*tert*-Butyl-*p*-Quinone

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Abstract—Radical pairs produced by the photolysis of 4-bromo-2,6-di-*tert*-butylphenol single crystals doped with 2,6-di-*tert*-butyl-*p*-quinone are studied by EPR spectroscopy. The mechanism of radical pair generation changes from hydrogen-atom transfer to electron transfer (without proton transfer). The reasons for this change are discussed.

INTRODUCTION

Photochemical reactions in binary systems involving various phenols and quinones acting as donors and acceptors have attracted increasing attention in recent years [1, 2]. A typical study of such systems includes growing a phenol or pyrocatechol single crystal doped with quinone and registering radical pairs formed under exposure to light using EPR. Taking into account that radicals obtained on crystal photolysis are spatially ordered in the crystal lattice, one can easily determine their hyperfine structure and, hence, the dipole–dipole interaction in a radical pair. These data allow one to identify these products and to carefully determine the elementary steps of a photochemical reaction, such as electron or proton transfer. Earlier studies of the systems based on 2,6-di-*tert*-butyl-4-methylphenol (ionol) with various dopants [1, 2] showed that radical pairs are formed via hydrogen-atom transfer. In this work, we examined the systems based on 4-bromo-2,6-di-*tert*-butylphenol.

EXPERIMENTAL AND RESULTS

4-Bromo-2,6-di-*tert*-butylphenol (**1**) single crystals doped with 2,6-di-*tert*-butyl-*p*-quinone (**2**) were grown in the dark at room temperature from the saturated solutions that were prepared beforehand by dissolving small amounts of **1** and **2** in ethanol ([quinone]/[pyrocatechol] = 10^{-2}–10^{-3}). This procedure was described in [1, 2] in more detail. Two types of radical pairs with the values of dipole–dipole splitting D of 15.0 and 12.5 mT were recorded upon UV irradiation at a wavelength of up to 300 nm. Figure 1 presents the EPR spectra of these radical pairs. Spectrum (a) refers to the single crystal orientation corresponding to the broadest spectrum. In this case, the distance between the pair components, described by the equation $D = D_\perp(1 - 3\cos^2\theta)$ [3], corresponds to the angle between the pair axis and the direction of the external magnetic field when $\theta = 0°$. The A_1, A_2, A_1', and A_2' components may be assigned to one radical pair (with $D = 15.0$ mT), and the B and B' components refer to another radical pair (with $D = 12.5$ mT).

Spectrum (b) in Fig. 1 corresponds to a polycrystalline powder. It consists of the parallel components ($\theta = 0°$) $A_\parallel$, $A_\parallel'$ ($D = 15.0$ mT) and $B_\parallel$, $B_\parallel'$ ($D = 12.5$ mT) (corresponding to the position shown in Fig. 1a) and the perpendicular ones ($\theta = 90°$) $A_\perp$, $A_\perp'$, $B_\perp$, and $B_\perp'$. For both types of radical pairs, the splitting of these components occurs because of a substantial hfs on one proton (2 mT).

This hfs is especially pronounced in the signal obtained in the half-field (Fig. 2). Figure 3 illustrates the splitting of one component into two, observed upon rotating the crystal through 15°.

Special experiments using deuterium confirmed that, not being observed for deuterated phenol, splitting may be attributed to the presence of a mobile proton in the phenol molecule and that the EPR signals may be attributed to the existence of two rather than three types of radical pairs. The pairs with D of 15.0 and 12.5 mT become saturated in a different manner and, in contrast to the B components, the A_1 and A_2 components change in the same manner. Moreover, heating to room temperature for 2–3 s allowed us to eliminate one pair (namely, the one with a higher D value). In all the
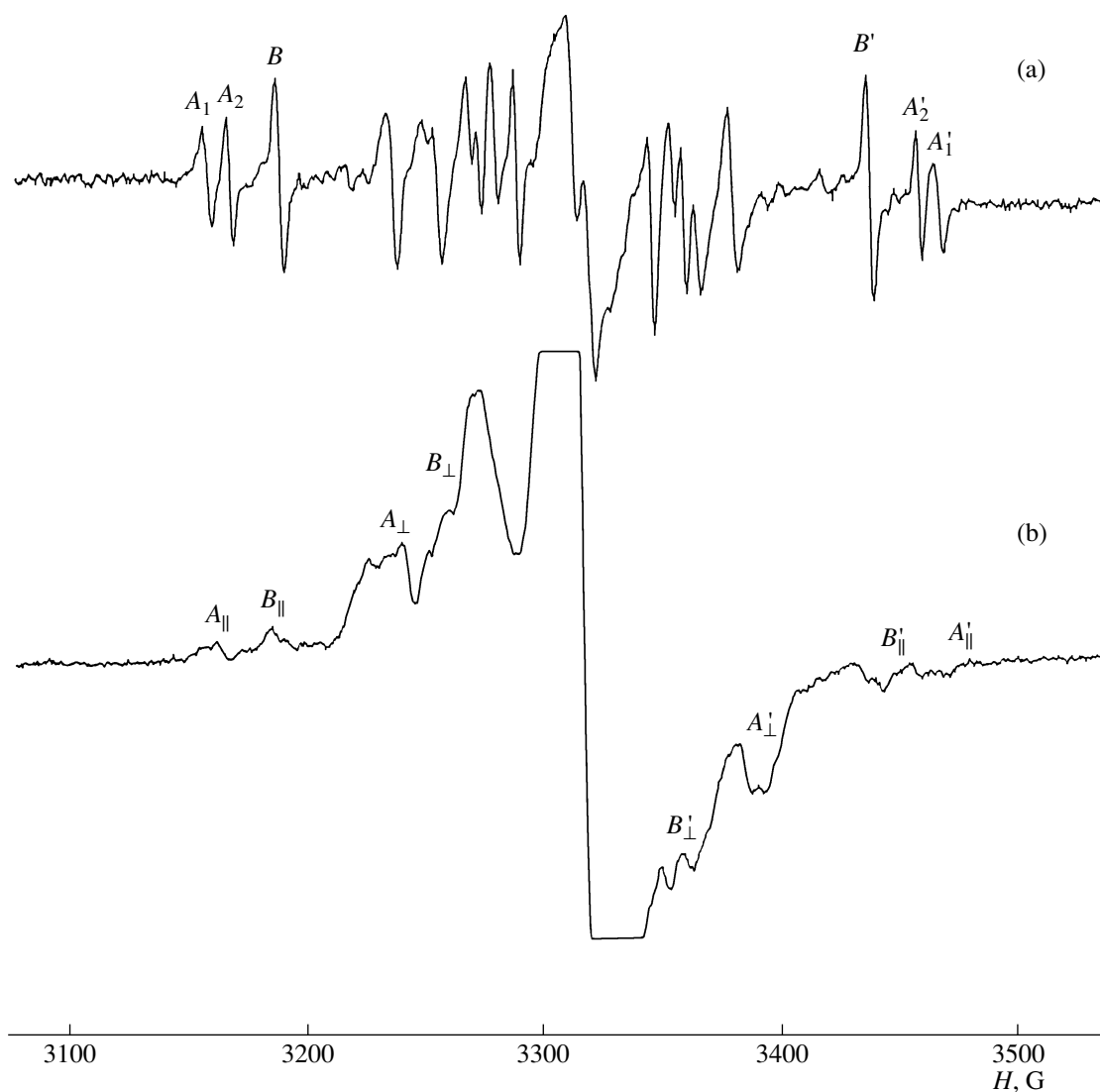
Fig. 1. (a) EPR spectrum of **1** single crystal doped with **2** upon irradiation at a chosen orientation (see the text). Lines A_1, A_2, A'_1, and A'_2 correspond to the radical pair with $D = 15.0$ mT, whereas B and B' lines correspond to the radical pair with $D = 12.5$ mT. Both line sets refer to the parallel components. (b) EPR spectrum of polycrystalline powder **1** doped with **2**. Lines $A_\parallel$, $A'_\parallel$ and $A_\perp$, $A'_\perp$ correspond to the parallel and perpendicular components of the radical pair with $D = 15$ mT, respectively.

experiments, we failed to detect three types of radical pairs.

The generation of radical pairs of both types occurs upon exposure to light with a wavelength of 370 nm. For quinone **2**, the long-wave absorption boundary is at 510 nm and the second absorption band appears at 375 nm. The long-wave absorption boundary of phenol **1** is at 440 nm. Most likely, the primary quantum is absorbed by quinone **2**, which is excited in its second absorption band because the long-wave boundary of radical pair formation (370 nm) virtually coincides with the second absorption band of quinone (375 nm).

We also studied the EPR spectrum of the single crystal of **1** upon irradiating it with UV at $T = 77$ K.

Analysis of this spectrum is complicated by the presence of both the g-tensor without axial symmetry and the hfs tensor (the splitting of certain lines changes after rotating the single crystal). Moreover, the radical in the single crystal may be oriented in different directions. Therefore, no comprehensive analysis was performed. In this case, no radical pairs are observed (the EPR signal half-field is not recorded).

Upon exposure to only visible light, the D value for radical pairs in a frozen ethyl benzene solution of **1** and **2** at $T = 77$ K is 10.8 mT. The generation of these radical pairs may be attributed to hydrogen-atom transfer between two molecules (a donor and an acceptor), which form a complex even in the solution. This com-
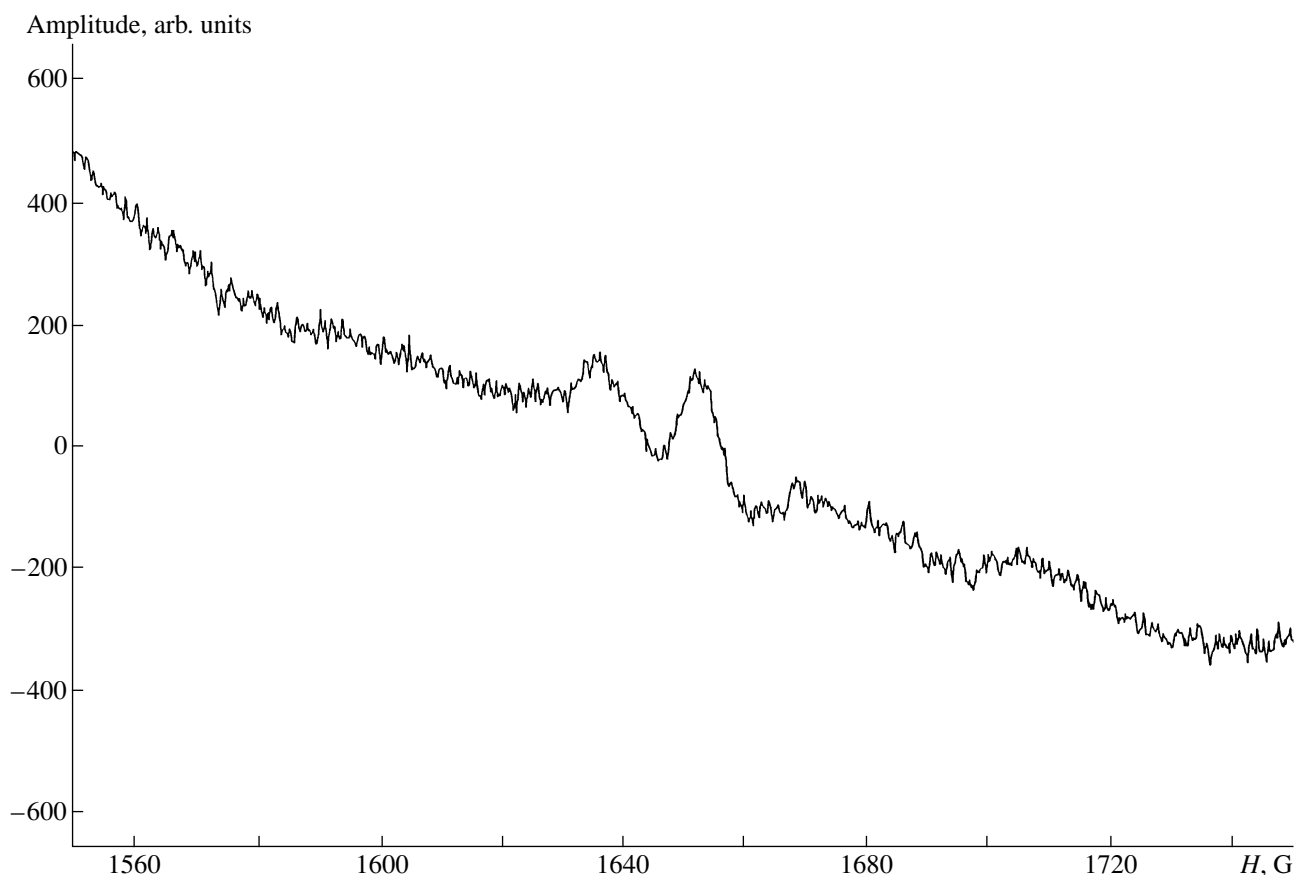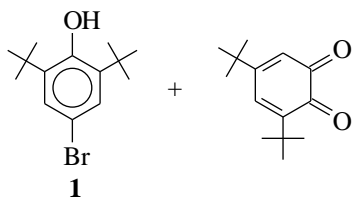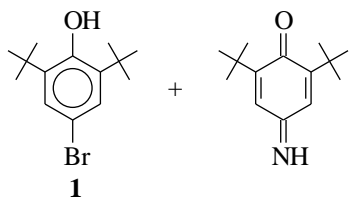
Amplitude, arb. units

Fig. 2. EPR spectrum of the **1**–**2** system upon UV irradiation ($\lambda < 300$ nm) recorded in a half-field at $T = 77$ K.

plex remains unchanged on freezing, thus ensuring radical pair formation upon irradiation [4].

Radical pairs are also generated in some other systems (where the phenol single crystal is doped with an acceptor):
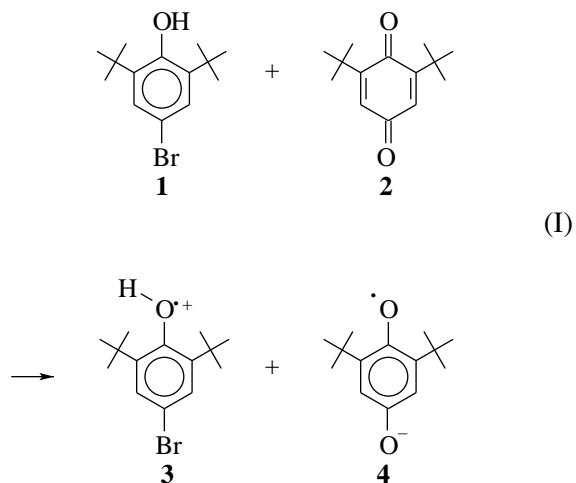

and

Radical pairs with the D values of 10.5 and 16.0 mT are formed in the **1** + 3,5-di-*tert*-butyl-*o*-quinone and **1** + 2,6-di-*tert*-butyl-1-imino-*p*-quinone systems, respectively.

DISCUSSION

The presence of the doublet hyperfine splitting suggests that an ion–radical pair consisting of radical cation **3** and semiquinone radical **4** is produced by electron transfer via the following mechanism:

(I)

This reaction differs from those described in [1, 2], which imply hydrogen-atom transfer from phenol to
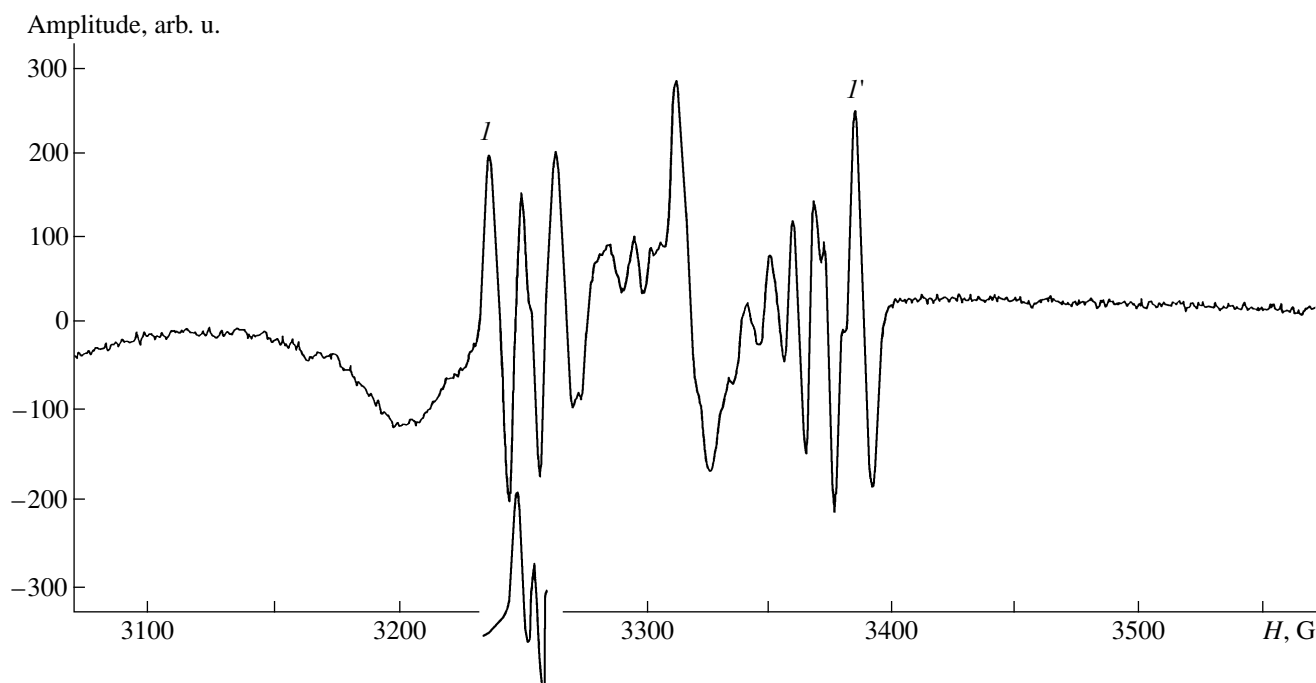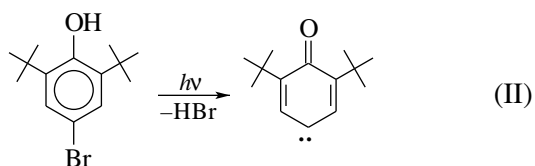
Fig. 3. EPR spectrum of the single crystal oriented with respect to the external magnetic field differently than that in Fig. 1. Lines *1* and *1'* correspond to the radical pair located at a certain angle in the laboratory system of coordinates. At the bottom: the transformation of line *1* upon single crystal rotation about the axis, which is perpendicular to the external magnetic field, through 15 °.
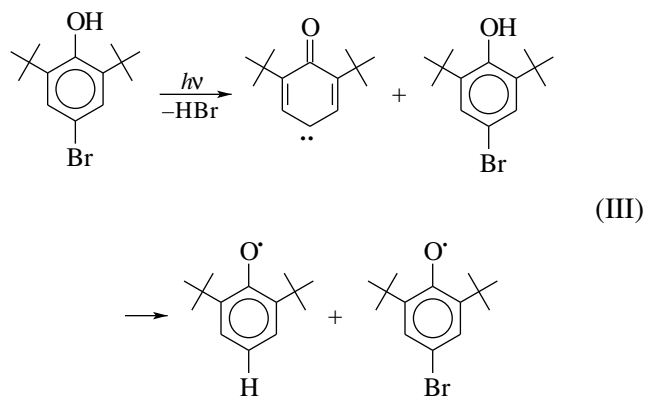
quinone. Reaction (I) seems to be the only possible reason for a hyperfine splitting of 2 mT. Indeed, this hfs value on one proton was not observed for the photochemical reaction of ionol with 2,6-di-*tert*-butyl-*p*-quinone [1]. The absence of an hfs from one proton of 2 mT was also confirmed for the radical cation produced by H⁺-transfer from phenol to quinone [5]. This rules out the presence of the semiquinone radical cation. Therefore, mechanism (I) is the only one possible.

Some other mechanisms are also considered that imply carbene generation during the photolysis of **1**. For example, the mechanism that is obviously responsible for carbene generation from 4-chlorophenol was described in [6]. As applied to our case, it can be represented as follows:

(II)

We failed to register the signal at 460 mT (the EPR region of 3 cm) that should accompany carbene generation [1]. However, any carbene formed can undergo further transformations to give a radical pair consisting of 4-bromo-2,6-di-*tert*-butylphenoxy and 2,6-di-*tert*-butylphenoxy radicals:

(III)

In this case, the hyperfine structure should differ from that observed in our experiments: a splitting of 2 mT seems to be too high for the resulting phenoxy radicals. Moreover, we failed to register any radical pairs in the single crystal of pure **1**, where they should have appeared in accordance with reaction (III). Therefore, reaction (I) is the most likely mechanism of radical pair generation. Proton transfer in the process involving 4-chlorophenol is described in [7].

In principle, both the ion–radical (electron transfer) and neutral radical pairs (hydrogen-atom transfer) can be generated in certain systems (e.g., 3,6-di-*tert*-butylpyrocatechol + 3,6-di-*tert*-butyl-*o*-quinone) under

exposure to light [8]. However, the process involving 2,6-di-*tert*-butyl-4-methylphenol (ionol), which is very much like 4-bromo-2,6-di-*tert*-butylphenol, doped with the same quinone (2,6-di-*tert*-butyl-*p*-quinone) is accompanied by only hydrogen-atom transfer to stabilize the neutral radical pair. In this case, the mechanism of the chemical reaction, induced by using one phenol (ionol) instead of the other (**1**), changes. However, this explanation is satisfactory only if the mechanism of hydrogen-atom transfer is not considered in detail. In principle, two mechanisms are possible: (i) electron transfer followed by proton transfer and (ii) hydrogen-atom transfer [8]. The former is more likely in the reaction with ionol, thus ensuring the stabilization of the intermediate radical cation in the process involving **1** (see below). However, this fact also suggests a change in the mechanism because the proton is not further transferred to stabilize a neutral radical pair. Interestingly, the distances in the crystal lattice between the relevant reactants change only slightly upon phenol substitution. In both cases, the values of the dipole–dipole splittings in radical pairs are close to 15 mT, that is, the distances between the radicals in the ion–radical and neutral pairs are nearly the same. The position of ion–radical pairs stabilized in the crystal lattice of 4-bromo-2,6-di-*tert*-butylphenol was determined by the procedure described in detail in [9]. In both cases, the crystal lattices are identical (orthorhombic) and their crystal lattice parameters are close (the relevant values for compounds **1** and ionol are given in [10] and [11], respectively). The stabilization of the radical cations may be attributed to the mesomeric + M effect [12] in the 4-bromo-2,6-di-*tert*-butylphenol molecule due to the substitution of the bromine atom for the CH_3 group. By contrast to the CH_3 group, the bromine atom apparently can partially donate its electron to the benzene ring, thus stabilizing the radical cation.

CONCLUSION

Thus, we found a new system, in which radical pairs may be generated by UV irradiation. In contrast to the system with ionol [1], this system of the single crystal of phenol **1** doped with quinone **2** is characterized by an abnormally high anisotropic hfs constant. This can be due to a change in the photochemical reaction mechanism: electron transfer to form an ion–radical pair occurs instead of hydrogen-atom transfer (as in the case of ionol).

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