Formation and stabilization of radical pairs in the quinone—pyrocatechol—polymer system

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The formation of radical pairs (RP) in solid mixtures of 3,6-di-*tert*-butyl-*o*-quinones (Q) and 3,6-di-*tert*-butylpyrocatechol (QH_2) under the action of shock-wave (SW) pulses was studied by ESR and IR spectroscopy. The radical pairs are formed only when a threshold value of SW power is achieved. The generation of RP is preceded by the formation of hydrogen-bonded associates QH_2...Q upon intimate mixing and fine dispergation of the reagents in a SW field. The incorporation of the reagents into a polymeric matrix favors the formation of associates and stabilization of the pairs, which leads to a decrease in the SW power threshold.

Key words: radical pairs, hydrogen bond; ESR, IR spectroscopy; shock wave.

It is established[1,2] that a)the action of a shock-wave (SW) pulse on polycrystalline mixtures of the 3,6-di-*tert*-butylpyrocatechol (QH_2)—3,6-di-*tert*-butyl-*o*-quinone (Q) type results in the formation of hydroxyphenoxyl radicals and radical pairs (RP) stable at room temperature; b)the generation of hydrophenoxyl radicals and radical pairs in the Q—QH_2 mixture has a threshold character, *i.e.*, the formation of radical products in the samples studied begins only after the SW power attains a critical value; c)as the dispergation increases, the concentration of radical pairs and hydroxyphenoxyl radicals increases; and d)a polymeric matrix (polystyrene) decreases the threshold value of the SW power for the formation of paramagnetic products.

The preparation of the initial polycrystalline material by evaporation of combined toluene solutions of the quinone and pyrocatechol was a specific feature of the Q—QH_2 systems studied previously.[1,2] In this process, Q and QH_2 molecules form complexes with a hydrogen bond that breaks under the action of a SW pulse. When this bond breaks the radical products remain in the cage, resulting in the formation of RP. Preliminary studies showed that RP are also generated when SW act on mechanical mixtures of Q and QH_2, *i.e.*, without preformation of complexes. In this case, reagent molecules contact one another directly under the action of the SW pulse. Several fundamental aspects need to be clarified: first, the extent to which mechanical treatment causes the formation of the initial structures needed (quinone—pyrocatechol complexes) for the formation of RP; second, the causes and mechanism for the influence of a polymeric matrix on the course of the generation of RP. This work is devoted to the solution of these problems.

Experimental

3,6-Di-*tert*-butyl-*o*-quinone, 3,6-di-*tert*-butylpyrocatechol (Q and QH_2, respectively), and their solid-phase mixtures were used. Solutions of these compounds and their mixtures in CCl_4, solid-phase mixtures of Q with QH_2 and of Q—QH_2 with KBr, and polyethylene (PE) films containing Q and QH_2 were studied. The latter were obtained from a melt that was rapidly cooled on a steel sheet to room temperature. The thickness of the films was 0.15—0.20 mm.

Solid-phase samples were subjected to the action of shock-wave pulses (SWP) in a device described previously.[1] The sample was simultaneously subjected to SW action and to uniaxial compression in a closed volume between two steel waveguides. Shock waves were generated by explosive breakage of polypropylene plates under pressure. Shock waves were conveyed to samples through a steel waveguide.

The samples obtained after these actions were studied by ESR on 3 cm-range Varian E-12A and SE/X-2547

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† Deceased.

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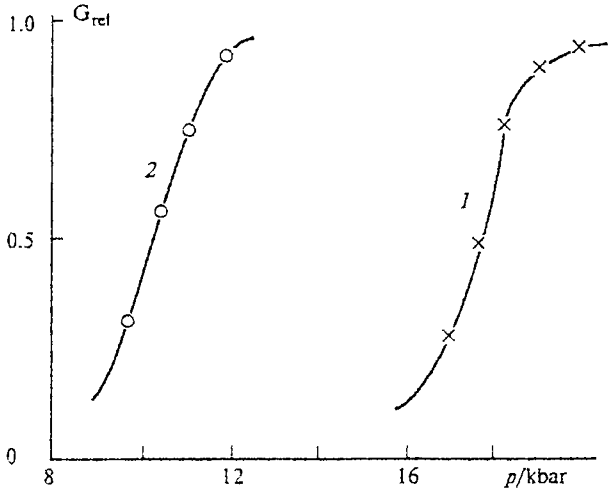


Fig. 1. Dependence of the yield of radical pairs (rel. units, determined from the intensity of the ESR spectra) on the threshold pressure of SW pulses for samples of mechanical Q—QH$_2$ (*1*) and Q—QH$_2$—PE (*2*) mixtures.

radiospectrometers at 77 and 300 K. The quinone, QH$_2$, and their mixtures in KBr, on a polyethylene matrix, and in solutions in CCl$_4$ were studied by IR spectroscopy. The measurements were performed at 300 K on a Specord M-80 spectrometer attached to a computer.

Results and Discussion

Radical pairs with D_1 = 280 G are observed when a SW pulse acts on a molded pellet of Q—QH$_2$ (1 : 1) powder. This coincides with the results of previous works.[1,2] The threshold value of the pressure at which RP begin to form in this system is p_{th} = 17.4 kbar (Fig. 1, curve *1*).

The ESR spectra of the Q—QH$_2$ (1 : 1)—PE samples subjected to SW action (Fig. 2) contain not only components of the fine structure of RP with D = 250 G (4.8 Å), but also components with splittings of 125 G and 50 G, which are likely caused by pairs with distances between paramagnetic centers of 6 and 8.2 Å. The threshold value of the pressure at which all three types of RP appear in these samples is equal to 10 kbar (Fig. 1, curve *2*). Thus, both the spectroscopic (structural) and the mechanochemical parameters of the generation of RP in the Q—QH$_2$ and Q—QH$_2$—PE systems differ.

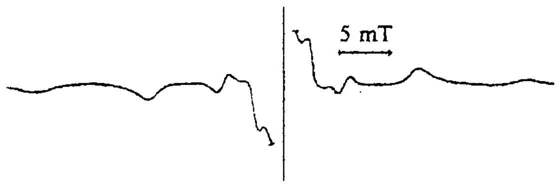


Fig. 2. ESR spectrum of the Q—QH$_2$—PE sample.

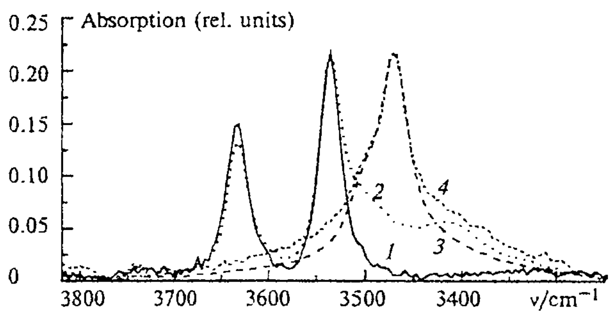
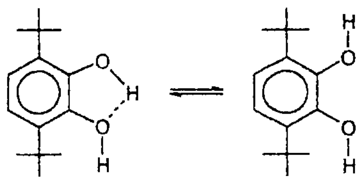


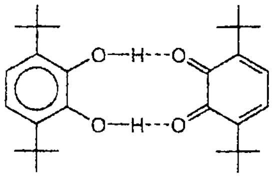
Fig. 3. IR spectra of the QH$_2$ (*1*) and Q—QH$_2$ (*2—4*) samples: liquid solutions in CCl$_4$ (*1, 2*), powder of the Q—QH$_2$ mixture before (*3*) and after (*4*) the SW action.

It was shown by the XDA method[3] that in the Q—QH$_2$ and Q—QH$_2$—PS systems, the solid formed after SW action is X-ray amorphous, *i.e.*, paramagnetic products are formed by the fine dispergation of crystals of the initial Q and QH$_2$ down to untradispersed particles or clusters (UDC), whose crystal lattices contain no long range order. The deformations caused by mechanical stresses occur on the scale of intermolecular distances and result in breakages of hydrogen bonds in the [QH$_2$...Q] complexes accompanied by the transfer of hydrogen and the formation of a pair of semiquinone radicals. The deformation-induced UDC structures are "frozen" after the SWP action so that the RP are stabilized for a long time (several weeks at room temperature). At the same time, the photolysis of samples containing UDC, *i.e.*, subjected to preliminary SWP action, results in the appearance of additional RP from the [QH$_2$...Q] complexes previously "prepared" from UDC, which decay over several minutes even at 77 K. This means that the transfer of hydrogen from pyrocatechol to quinone is not accompanied by deformation of the structure that stabilizes the generated RP.

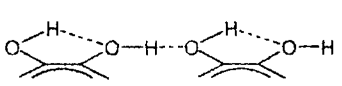
The role of hydrogen bonds in these processes was studied by IR spectroscopy. The spectrum of a dilute solution of QH$_2$ in CCl$_4$ contains (along with other bands) two narrow symmetric bands at 3536 and 3634 cm^{-1} (Fig. 3, curve *1*), which are absent in solutions of Q. These bands are assigned to stretching vibrations of OH groups bound by intramolecular hydrogen bonds (3536 cm^{-1}) and free OH groups (3634 cm^{-1}) of the QH$_2$ molecules.



When Q is added to a dilute solution of QH_2 in CCl_4, a broad band at 3415 cm^{-1} appears in the spectrum along with the bands of the monomeric QH_2. This band is assigned to the OH group bound to Q by an intermolecular H-bond (Fig. 3, curve *2*).



A band at 3472 cm^{-1} with a shoulder at 3500 cm^{-1} is observed in the region of stretching vibrations of OH groups in solid samples of QH_2 in KBr (Fig. 3, curve *3*). These bands can be assigned to vibrations of the OH groups bound by intermolecular bonds in planar or sandwich associates, which appear when the QH_2 molecules are packed in a solid.



In the spectra of the solid-phase mechanical Q—QH_2 mixture (not subjected to SWP action) incorporated into KBr, bands at 3500 and 3472 cm^{-1} are observed (*i.e.*, the spectrum is completely identical to the IR spectrum of QH_2 in KBr). In the spectrum of the solid-phase mechanical Q—QH_2 mixture subjected to SWP action and incorporated then into KBr to obtain IR spectra, an additional absorption is observed (Fig. 3, curve *4*) in the 3400 cm^{-1} region. This absorption is comparable to the corresponding band in Fig. 3, curve *2*. This fact allows one to conclude that SW action results in the formation of a new mixed Q—QH_2 phase. The width of the line of the additional absorption is likely caused by the formation of complexes with hydrogen bonds that differ in energy (and probably in length).

We also carried out an IR study of PE—Q—QH_2 and PE—QH_2 samples both subjected to SW action and not subjected to SW action. It was established that the IR spectra of QH_2 in PE (Fig. 4, curve *1*) contain bands with maxima at 3634, 3536, 3500, and 3472 cm^{-1} characteristic of a mixture of monomolecular and associated forms of QH_2. This allows one to conclude that in these samples, the QH_2 molecules exist as two ensembles: a solution of QH_2 in PE and an individual crystalline phase. This heterophase character is caused by preparing of the samples by incorporating QH_2 (or Q—QH_2) into a melt of PE followed by rapid cooling of the melt. When SW act on QH_2 in PE at pressures higher than the threshold of 10 kbar, an increase in the relative intensity of the bands corresponding to associated forms of QH_2 is observed (Fig. 4, curve *2*, this spectrum is normalized to that in Fig. 4, curve *1* by the band at 3472 cm^{-1}). When SW act on the Q—QH_2 system in PE, redistribution of the intensities of the bands in favor of associated forms is observed as well; however, it is less significant (Fig. 4, curves *3* and *4*), because extensive binding of Q and QH_2 in complexes occurs already at the stage of incorporation of the mixture into the melt. Changes in the IR spectra appear under the action of SW pulses at pressures higher than the threshold of 10 kbar, which corresponds exactly to the threshold of the appearance of RP (see Fig. 1, curve *1*) established by ESR.

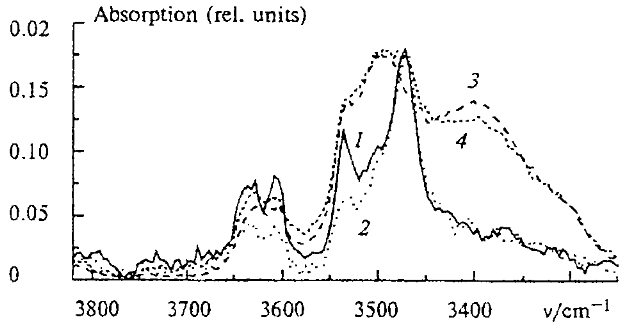


Fig. 4. IR spectra of the QH_2 (*1*, *2*) and Q—QH_2 (*3*, *4*) samples in PE before (*1*, *3*) and after (*2*, *4*) the SW action.

Thus, the results presented suggest the following conclusions.

a. Radical pairs are generated from hydrogen-bonded complexes in mixtures of Q—QH_2 powders and samples with the mixtures incorporated into a polymeric matrix under the action of a SW pulse:

$$[QH_2...Q] \rightarrow [QH...HQ].$$

At a certain threshold of SW pressure, the deformations reach the scale of intermolecular distances and result in breakages of hydrogen bonds accompanied by hydrogen transfer and the generation of a pair of semiquinone radicals, which are stabilized after removal of the stress.

b. The quinone—pyrocatechol complexes necessary for the generation of RP are formed from heterophase mixtures directly by the action of the SW pulse, which is evidence for intimate mixing and fine dispergation of the material leading to the formation of mixed associates of reagent molecules (ultradispersed clusters).

c. A polymeric matrix participates in the transportation and dissipation of elastic energy, which affects both the formation of UDC and their stabilization, by freezing deformations, and fixing RP.

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