Investigation of radical pairs produced upon pulse action of elastic waves on the 3,6-di-*tert*-butylcatechol—3,6-di-*tert*-butyl-*o*-benzoquinone—sulfur system

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The pulse action of elastic waves on polycrystalline mixtures of 3,6-di-*tert*-butylcatechol and 3,6-di-*tert*-butyl-*o*-benzoquinone produces radical pairs stable at room temperature, and the addition of polycrystalline sulfur considerably increases their yield. The dependences of formation and decay rates of paramagnetic centers on the composition of the mixture were studied. The threshold character of formation of paramagnetic centers at various powers of elastic wave pulse was established.

Key words: 3,6-di-*tert*-butylcatechol—3,6-di-*tert*-butyl-*o*-benzoquinone—sulfur system, elastic wave effect, ESR of radical pairs.

Mechanochemical actions (grinding and abrasion) on the 3,6-di-*tert*-butylcatechol (DTBC)—3,6-di-*tert*-butyl-*o*-quinone (DTBQ) system are characterized by the formation of radical pairs in high concentrations with such unusual properties as a positive sign of the splitting constant D in zero field and stability even at room temperature.[1—3] It is also known that elastic wave pulse (EWP) action on a DTBC + DTBQ mixture results in the formation of paramagnetic centers.[4] The purpose of the present work is to study this phenomenon in detail.

Experimental

A polycrystalline mixture DTBC + DTBQ was prepared from a solution of these compounds in toluene after evaporation, a powder of sulfur being added to several samples prior to evaporation.

Experiments on the EWP action were carried out on the setup shown in Fig. 1. EWP appeared due to the rheologic explosion of a polypropylene plate, which was subjected to high pressure upon one-axis compression in an apparatus of the type of modified Bridgman anvils. An EWP was introduced into a molded pellet of the mixture under study *via* a steel wave guide. Thin (<100 μm) samples were used in the experiments, which ensured the absence of scatter of the substance, even if several EWP acted on the same sample. The pellet of

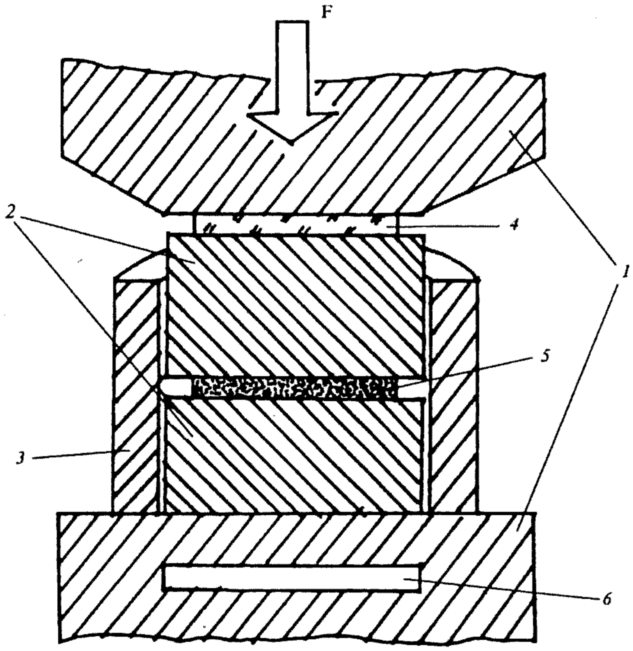

Fig. 1. Scheme of elastic wave pulse treatment of the mixture studied: *1*, steel anvils of the press; *2*, steel wave guides (steel ShKh-15); *3*, steel ring; *4*, polypropylene pellet; *5*, molded pellet of the mixture studied; *6*, piezodetector.

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the mixture studied was additionally fixed by a steel ring. A piezodetector attached to a S9-8 storage oscillograph, and an IBM PC/AT computer was used for the registration of EWP parameters. The time of increase in the front of edge of the pulse was ~20 μs.

It is known[5] that the *p* value of the static pressure at which the rheologic explosion occurs is a characteristic of the power of the elastic wave pulse, and the upper boundary of absorbed energy can be estimated from the formula

$$E = V\frac{p^2}{2G}, \qquad (1)$$

where *G* is the Young's modulus of steel and *V* is the volume of the steel wave guide. Using the typical parameters of the experiment ($p = 100$ kN cm^{-2}, $V = 3.17 \cdot 10^{-6}$ m^3) and the known[6] value $G = 2 \cdot 10^{11}$ Pa, we obtain $E \approx 8$ J. Using the characteristic value of the mass of the sample remaining between the wave guides after the EWP action ($m = 80$ mg), we find that in the experiments on the EWP action the dose of the single action was up to 100 J g^{-1} and the power was up to 10^7 W g^{-1}.

The ESR spectra of the substance remaining between the anvils were recorded on 3-cm-range Varian E12A and SE/X-2547 radiospectrometers. The concentrations of radical pairs and monoradicals were determined by the standard procedure.[7,8]

Results and Discussion

The EWP action on a molded pellet of a DTBC + DTBQ mixture results in the formation of radical pairs. The ESR spectrum of the sample treated by three consecutive EWP is presented in Fig. 2 (curve *1*). The mass ratio of components in the mixture was 1 : 1. The central signal in the spectrum corresponds to hydroxyphenoxyl monoradicals formed along with radical pairs. The doublet signal corresponds to radical pairs with D = 286 G (the splitting parameter in zero field D was determined by the known procedure,[7] $D_\perp = (D_1 + D_2)/2$). The studies performed using a 2-mm-range ESR spectrometer at low (5—10 K) temperatures show that $D > 0$ (the procedure of determination of the sign of the D constant from the high-field ESR spectra is well known[2,3]).

Three samples with mass ratios (and, hence, molar fractions) of DTBC + DTBQ equal to 2 : 1, 1 : 1, and 2 : 3 were used for the study of the dependence of the yields of paramagnetic products on the quantitative composition of the mixture. Each of the samples was subjected to triple consecutive EWP action of approximately the same power. The dependences are bell-shaped (Fig. 3). The maximum concentrations of paramagnetic centers are $6 \cdot 10^{18}$ spin (g of the mixture)$^{-1}$ for radical pairs and $5 \cdot 10^{18}$ spin (g of the mixture)$^{-1}$ for monoradicals and correspond to a molar ratio of components of 1 : 1. The yields (*G*) of paramagnetic centers (the number of particles formed per 100 eV of the admitted energy) are equal to 0.25 for hydroxyphenoxyl radicals and 0.3 for radical pairs in the maxima of the dependences in Fig. 3. The degree of chemical transformation is ~0.6 % of the total mass of DTBC and DTBQ. When

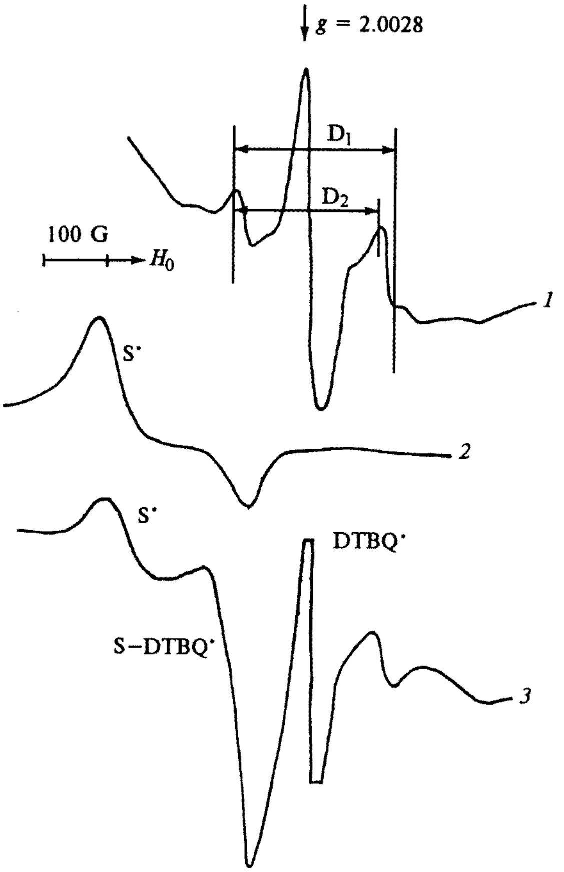

Fig. 2. ESR spectra of the DTBC + DTBQ mixture (*1*), elemental sulfur (*2*), and the DTBC + DTBQ + S mixture (*3*) after EWP action.

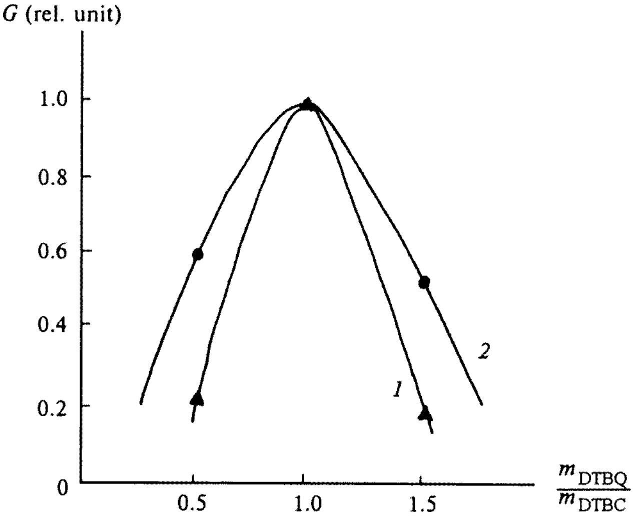

Fig. 3. Dependences of relative yields of radical pairs (*1*) and monoradicals (*2*) on the ratio of components of the mixture of DTBC and DTBQ.

the DTBC + DTBQ mixture was ground in a mortar, the maximum concentration of pairs reached (8—10) $\cdot 10^{18}$ spin g^{-1} (Refs. 1—3) and that of monoradicals was $6 \cdot 10^{18}$ spin g^{-1} (Ref. 9), which corresponds to a degree of transformation of up to 0.8 % of the total mass of DTBC and DTBQ. It should be mentioned, however, that when the mixture is ground in a mortar, the dose of mechanochemical action can be up to 10^4 J g^{-1} (Ref. 10), which is two orders of magnitude higher than that for the single action of an elastic wave pulse. However, since durations of grinding in the mortar are long (1 min and more), the yields of paramagnetic centers in this case do not exceed $0.9 \cdot 10^{-2}$ (hydroxyphenoxyl radicals) and $1.3 \cdot 10^{-2}$ (radical pairs). Thus, EWP action is a considerably more efficient method for the generation of radical products.

The formation of hydroxyphenoxyl radicals and radical pairs in the DTBQ : DTBC mixture (at their ratio of 1 : 1) has a threshold character: radical products in the samples studied appear only after the pulse power reaches a certain critical value p_{cr}: the relative yields (G_{rel}) of hydroxyphenoxyl radicals and radical pairs begin to increase at p_{cr} = 125 and 175 kN cm^{-2}, respectively (Fig. 4, curves *1* and *2*).

In order to elucidate the possibilities of an increase in the yield or a decrease in the critical pressure of formation of free-radical centers, we used elemental sulfur as a matrix-diluent, because the EWP action on this matrix results in the formation of radicals (S_n—S$^{\cdot}$) (see Fig. 2, curve *2*), and hydroxyphenoxyl radicals are formed under EWP action on the DTBC + S system even at p_{cr} = 50 kN cm^{-2}. Perhaps, the matrix of elemental sulfur plays the role of an additional reducing agent.

Study of the DTBQ + DTBC + S mixture (molar ratio is 1 : 1 : 2) made it possible to establish that considerable concentrations of hydroxyphenoxyl radicals and radical pairs appear upon single EWP action, the threshold parameters of formation of all products decrease, and p_{cr} in this system is 75 kN cm^{-2} for hydroxyphenoxyl radicals and 140 kN cm^{-2} for pairs (see Fig. 4, curves *3* and *4*, respectively).

The strong off-scale signal in the center of the ESR spectrum of the DTBC + DTBQ + S mixture is the spectrum of hydroxyphenoxyl monoradicals formed under EWP action (see Fig. 2, curve *3*). The broad singlet in the extreme left region of the spectrum with g = 2.1971 and the distance between peaks $\Delta H_m \approx 230$ G correspond to monoradicals of elemental sulfur (S_n—S$^{\cdot}$). The asymmetric signal between the two signals described above can likely be assigned to DTBQ monoradicals. Perpendicular and parallel components of the radical pair are also manifested in the right region of the spectrum. The downfield region of the spectrum of these pairs is masked by signals of monoradical products.

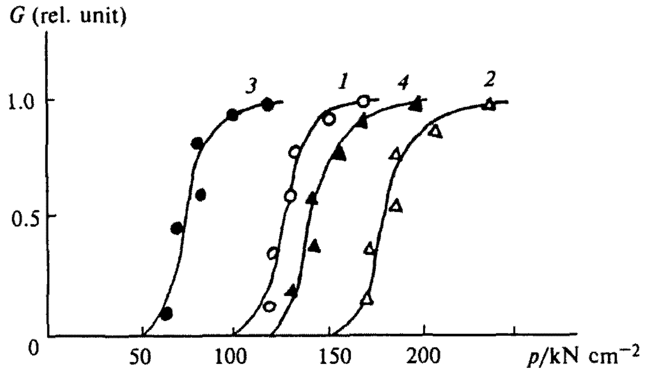

Fig. 4. Dependences of relative yields of radical products on the value of static pressure at the instant of EWP introduction: *1*, hydroxyphenoxyl radicals in the DTBQ + DTBC mixture ($m_{DTBC} : m_{DTBQ}$ = 1 : 1); *2*, radical pairs in the DTBQ + DTBC mixture ($m_{DTBC} : m_{DTBQ}$ = 1 : 1); *3*, hydroxyphenoxyl radicals in the DTBC + DTBQ + S mixture ($m_{DTBC} : m_{DTBQ} : m_S$ = 1 : 1 : 2); *4*, radical pairs in the DTBC + DTBQ + S mixture ($m_{DTBC} : m_{DTBQ} : m_S$ = 1 : 1 : 2).

The dependences of the yields of paramagnetic products on the quantitative composition of the (DTBC + DTBQ) : S mixture (mass ratios 1 : 4, 2 : 3, 1 : 1, 3 : 2, and 4 : 1; mass ratio of DTBC : DTBQ in all samples 1 : 1) have a typical bell-shaped character (Fig. 5). The maximum concentrations of paramagnetic centers are $4 \cdot 10^{17}$ spin (g of the mixture)$^{-1}$ for pairs, $2 \cdot 10^{18}$ spin (g of the mixture)$^{-1}$ for hydroxyphenoxyl monoradicals, and $6 \cdot 10^{18}$ spin (g of the mixture)$^{-1}$ for monoradicals of elemental sulfur. The yields of paramagnetic centers in the maxima of the dependences per 100 eV of the admitted energy are 2.9 for hydroxy-

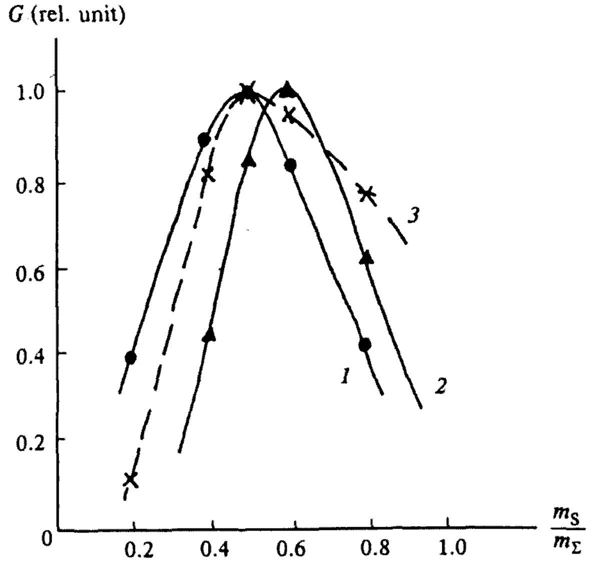

Fig. 5. Dependences of yields of radical pairs (*1*), hydroxyphenoxyl radicals (*2*), and radicals of elemental sulfur (*3*) in the DTBC + DTBQ + S mixture on the mass fraction of sulfur.

phenoxyl radicals and 0.6 for radical pairs. The degree of chemical transformation is ~0.2 % of the total mass of DTBC and DTBQ. A probable reason for the decrease in the yield of radical pairs and the degree of chemical transformation is the possibility of the formation of radical products involving sulfur.

This assumption is confirmed by the fact that at a mass fraction of sulfur equal to 0.5—0.6 the concentration of hydroxyphenoxyl radicals DTBC$^\cdot$ decreases as the concentration of sulfur gradually increases, and there is an intersection point where [S$^\cdot$] = [DTBQ$^\cdot$] (see Fig. 5). These results can be explained by the following scheme[11]: the action of an elastic wave pulse at the first stage of the mechanochemical reaction results in the formation of a mobile electron that enters competing reactions of the following type:

$$e^- + \mathrm{DTBQ\ (DTBC)} \longrightarrow \mathrm{DTBQ^\cdot\ (DTBC^\cdot)}\ , \qquad (1)$$

$$e^- + \mathrm{S} \longrightarrow \mathrm{S}^\cdot\ . \qquad (2)$$

It is evident that the pair e^- + H$^+$ should be formed to retain the electroneutral character of the chemical reaction. Thus, mobile particles e^- and H$^+$ can form at the first stage of EWP action in the reaction:

$$\mathrm{DTBC} + \mathrm{DTBQ} + \mathrm{S} \xrightarrow{\mathrm{EWP}} \longrightarrow e^- + \mathrm{H}^+ + \text{radical products}. \qquad (3)$$

However, the addition of sulfur can change the kinetic parameters of the free-radical centers. The decay kinetics of radical pairs obeys the logarithmic dependence $N = N_0 - A\log(t/t_0)$, where N_0 is the number of pairs at the initial moment t_0, N is the number of pairs at the moment t, and t_0 is time constant (in the given case, 1 h). An increase in the content of sulfur in the system accelerates the decay of radical pairs at a mass fraction of sulfur lower than 0.4 (Fig. 6). In this range, the decay rate constants of pairs are proportional to mass fractions of the sulfur content in the system. This is confirmed by the existence of two competing reactions (1) and (2). An increase in the mass fraction of sulfur higher than 0.4 does not result in the acceleration of decay of pairs. Radical pairs formed in the DTBC + DTBQ system without the addition of sulfur are stable at room temperature.

Thus, the results obtained make it possible to suppose that the radical products are generated in the solid-phase system in the formation of electron-hole pairs. The reaction occurs on the contacting surfaces of different solid components during the formation of ultradisperse particles, whose surface is metastable due to the considerable number of inherent surface ionic defects. This assumption agrees with the observed logarithmic dependence of the decay kinetics of radical pairs, because similar dependences can take place if the pairs are distributed over the solid and possess different stabilization energies. In addition, positive values of the *D* constant and the high thermal stability of the pairs testify to the specific packing of molecular structures during EWP action. Probably, this packing results in the generation of radical pairs, whose molecules are arranged in a different way than in the case of photochemical initiation,[12] for example, as molecular aggregates with stronger dipole-dipole and exchange interactions.

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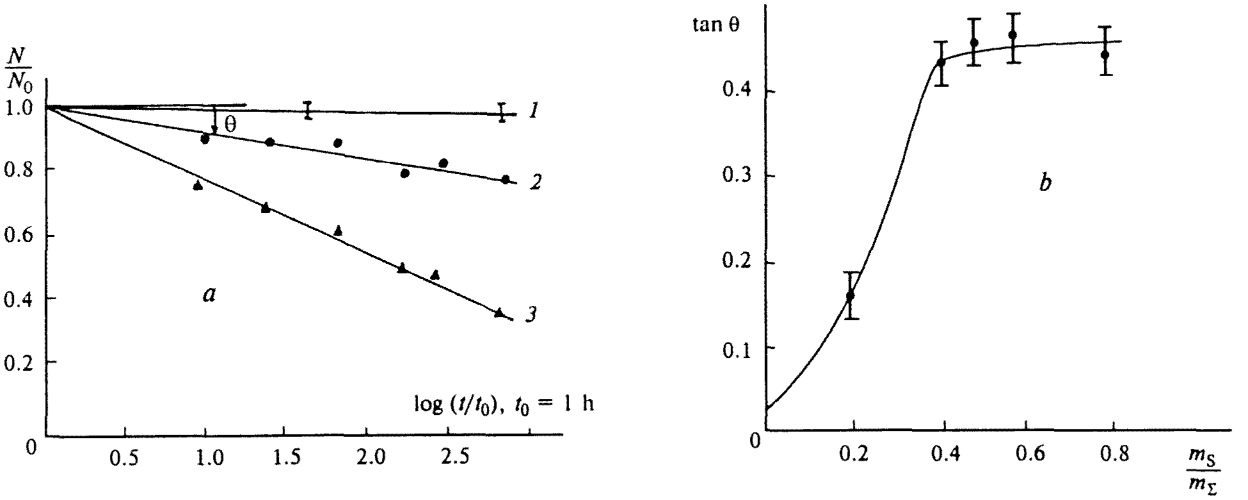

Fig. 6. *a*. Decay kinetics of radical pairs in the mixtures: *1*, DTBC + DTBQ ($m_{\mathrm{DTBC}} = m_{\mathrm{DTBQ}}$); *2*, DTBC + DTBQ + S (($m_{\mathrm{DTBC}} + m_{\mathrm{DTBQ}}$) : m_{S} = 4 : 1; $m_{\mathrm{DTBC}} = m_{\mathrm{DTBQ}}$); *3*, DTBC + DTBQ + S (($m_{\mathrm{DTBC}} + m_{\mathrm{DTBQ}}$) : m_{S} = 3 : 2; $m_{\mathrm{DTBC}} = m_{\mathrm{DTBQ}}$). The plots corresponding to ($m_{\mathrm{DTBC}} + m_{\mathrm{DTBQ}}$) : m_{S} = 1 : 1, 2 : 3, and 1 : 4 almost coincide with plot *3* and are not shown in the figure. *b*. Dependence of tanθ on the sulfur content in the mixture.

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