The mechanism of formation of free-radical states upon the pulsed action of elastic waves on solid mixtures of donor-acceptor compounds

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The action of a pulse of elastic waves on polycrystalline mixtures of donors and acceptors (for example, 3,6-di-*tert*-butylcatechol and 3,6-di-*tert*-butyl-1,2-benzoquinone with the addition of sulfur and polystyrene) results in the formation of monoradicals and radical pairs. The study of the products by ESR spectroscopy and X-ray analysis shows that the solid powder is dispersed to submicroscopic particles, including those of the mixed composition.

Key words: elastic waves; radical pairs, ESR spectra; X-ray analysis.

In the previous works,[1,2] the possibility of initiating electron and hydrogen atom transfer reactions by the pulsed action of elastic waves was demonstrated for powder-like mixtures of organic compounds. These processes result in the formation of radical pairs (RP) that are extremely stable at room temperature in the systems of the type 3,6-di-*tert*-butylpyrocatechol—3,6-di-*tert*-butyl-*o*-quinone (DTBP—DTBQ), and the addition of polycrystalline sulfur to the solid-phase mixture increases considerably the yield of all free-radical products. It has been supposed[2] that the chemical transformations occur on the contacting surfaces of different solid components in the process of their deep dispersion to submicroscopic particles, whose surface is metastable due to the considerable number of defects. The purpose of this work is to check this suggestion using the data of X-ray powder diffraction analysis and ESR spectroscopy.

Experimental

The DTBQ—DTBP mixtures, which were introduced into polystyrene (PS), or the same mixtures with additions of sulfur were chosen as model objects. The compositions were obtained from a solution of organic substances in toluene, and sulfur was introduced as a finely dispersed powder. After evaporation of toluene, the ratio of dry components DTBQ : DTBP : PS was 45 : 45 : 10, and DTBQ : DTBP : S : PS = 35 : 35 : 20 : 10 (here and hereinafter in wt. %). The samples used were pellets 15 mm in diameter and 0.15—0.20 mm in width.

Experiments were carried out in such a way that the sample was simultaneously subjected to both uniaxial compression in the closed volume and the action of elastic wave (EW) pulses (Fig. 1). Elastic waves were generated by an explosion under pressure (upon the uniaxial compression in the open volume) of polypropylene (PP) plates and conveyed to the samples *via* a steel waveguide (see Fig. 1). The experimental conditions allowed one to exclude the effect of the shift deformation and plastic flow of the material of the sample (*i.e.*, to prevent its heating) before the EW action. In addition, massive steel shells favored the heat rejection from the sample. Thus, the "pure" mechanical EW action on the sample thermostated at room temperature was provided.

The samples subjected to the EW action were studied by ESR on 3-cm Varian E-12A and SE/X-2547 radiospectrometers. The X-ray powder diffraction analysis was carried out on a DRON-3 diffractometer (Cu-Kα-radiation).

Results and Discussion

The diagram of the increase in the pressure (measured by a piezosensor) on the sample is presented in Fig. 2, *a*. It is seen that the plot consists of four regions caused by elastic properties of PP plates. The first region (stage I) corresponds to the nonsteady-state creep of PP, the second region (II) corresponds to the steady-state creep, the third region (III) corresponds to the accelerated creep and decomposition, and the fourth region (IV) corresponds to

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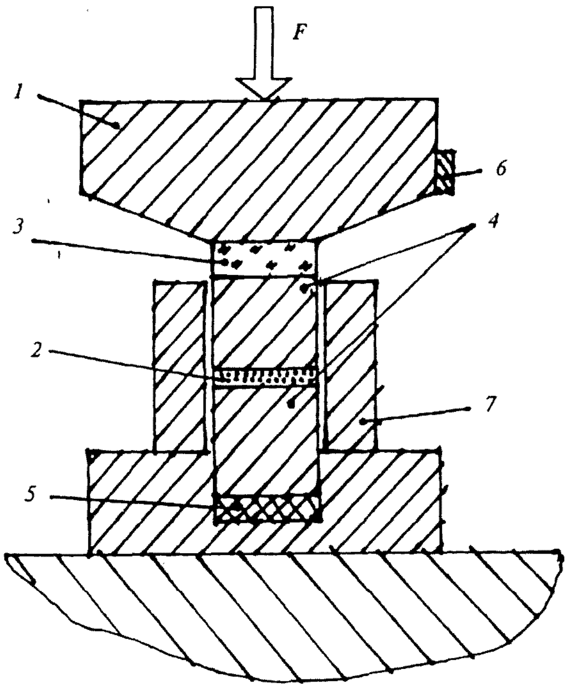

Fig. 1. Scheme of the experimental setup: *1*, Bridgeman anvil; *2*, sample; *3*, polypropylene plate; *4*, steel waveguides; *5*, piezosensor for measuring the pressure on the sample (V_{ew} ~ p_{ew}); *6*, piezosensor for starting up an S9-8 oscillograph for pulsed measurements; *7*, steel ring.

the explosion under pressure. The first three stages last about 4 s, while the fourth stage lasts for tens of microseconds. The duration of stage II shortens as the width of the PP plate decreases, *i.e.*, as though a thin sample is immediately clamped between the Bridgeman anvil and the waveguide. When the thickness of the sample is ~0.4 mm, stage IV (explosion) is absent, which testifies to the correct choice of the thickness of the samples studied (0.15—0.20 mm). During the first three stages, the sample undergoes only the compression in the closed volume, and during the fourth stage it undergoes the EW action as well. It follows from Fig. 2, *b* that the elastic wave is the discharge wave, *i.e.*, it corresponds to a sharp (during approximately 30 μs) pressure decrease. The higher the compression pressure, the greater the discharge depth. This is well reflected by the linear dependences (Fig. 3) between the press pressure before the explosion (p_{pr}, see Fig. 2, *a*) and the pulse intensity on the discharge wave (V_{ew}). The V_{ew} value was determined by a piezosensor connected to the S9-8 storage oscillograph (see Fig. 1). It is evident that V_{ew} characterizes a decrease in pressure in the elastic wave (p_{ew}), and it follows from Fig. 3 that $p_{pr} = kp_{ew}$. Therefore, in the further discussion we will consider the values $p = p_{pr}$ at which PP plates explode, and, hence, at which the EW action on the samples occurs.

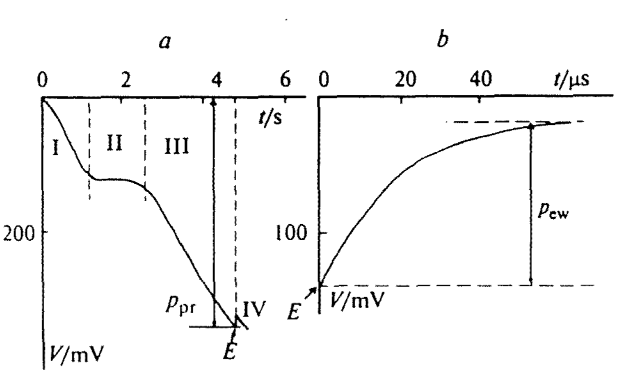

Fig. 2. Diagram of the growth (*a*) and decrease (*b*) in the pressure on the sample upon explosion. Point *E* corresponds to the moment of the explosion.

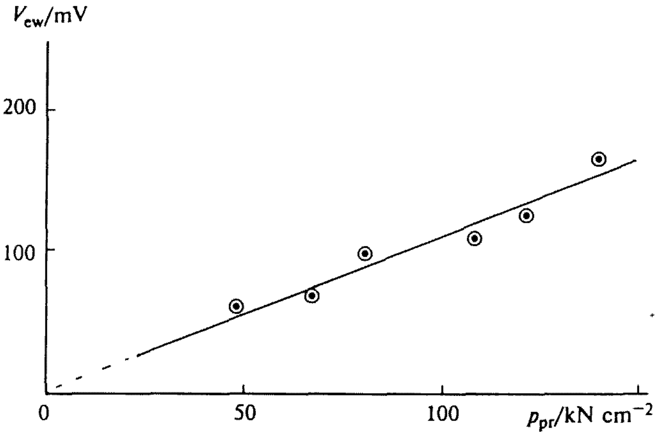

Fig. 3. Dependence of the intensity of the discharge pulse (V_{ew} ~ p_{ew}) on the press pressure before the explosion (p_{pr}).

The preliminary experiments show that the uniaxial compression of samples alone in the closed volume does not initiate chemical processes of radical and RP formation. However, the EW action on the sample compressed in the closed volume results in the appearance of the signals in the ESR spectra, which are similar to those observed previously[1] and are characteristic of 2-hydroxyphenoxyl radicals and radical pairs (DTBQH$^{\cdot}$...DTBQH$^{\cdot}$). The splitting parameter for RP in the zero field is independent of the EW power and is equal to 286 G. The EW power affects the concentration of paramagnetic products, and this dependence has a threshold character. It is established that the thresholds of the formation of 2-hydroxyphenoxyl radicals and RP in the DTBQ—DTBP—PS (45 : 45 : 10) mixture are equal to 80 and 120 kN cm^{-2}, and in the DTBQ—DTBP—S—PS (35 : 35 : 20 : 10) system they are 60 and 100 kN cm^{-2}, respectively. It is noteworthy that the addition of PS decreases the threshold values compared to those determined for the powder-like systems DTBQ—DTBP (50 : 50) and DTBQ—DTBP—S (25 : 25 : 50), which are equal[2] to 125, 175 and 75, 140 kN cm^{-2}, respectively.

In addition, both the initial samples (Fig. 4) and the samples subjected to the uniaxial compression or EW action at different pressures (Fig. 5) were analyzed by the X-ray powder diffraction method. The X-ray-gram of the DTBQ—DTBP—PS (45 : 45 : 10) sample, which was subjected to uniaxial compression up to p = 150 kN cm^{-2} exceeding all critical p_{pr} without the EW action, contains intense crystalline peaks at 2θ ≈ 8.2°, 12.2°, 16.8°, and 19.0° (see Fig. 5, *a*). It is seen from X-ray-grams *b* and *c* in Fig. 5 that the intensity decreases and the peaks broaden as the power of the EW action increases. For example, the EW action at p = 50 kN cm^{-2} decreases the intensity of the peaks at 2θ = 8.2° and 16.8°, and the intensity of the peaks at 12.2° and 19.0° even increases by 5 % compared to the initial one. It is most likely that DTBQ and DTBP crystals are preliminarily oriented under the EW action in this range, because no radical pairs are formed. Only the EW action at p ≈ 150 kN cm^{-2} results in a noticeable disappearance of the characteristic peaks and their broadening, which unambiguously indicates the deep dispersion of the initial substances (see Fig. 5, *c*). In this case, the concentrations of RP and 2-hydroxypenoxyl radicals reach almost the maximum values. When EW act on the DTBQ—DTBP—S—PS (35 : 35 : 20 : 10) system at p = 150 kN cm^{-2}, the dispersion is deeper, resulting in a nearly amorphous sample (only a very weak peak from elemental sulfur at 2θ = 23.2° is present in Fig. 5, *d*). In this case, the yields of all radical products are maximum.

Thus, the mechanochemical formation of both 2-hydroxyphenoxyl radicals and RP is associated with the deep dispersion of the initial compounds. It can be supposed that this is conjugated with the origination of microfractures (micropores), their growth and fusion, and separation of the material to form free surfaces at the stage of the pressure growth in the closed volume. These processes are accompanied by the formation of a free volume, "crystals of void."[3] Dislocations are formed along with these holes in the solid state. With a sharp pressure drop, the dislocations begin to move and "jump out" on the surface of the holes, adjacent atomic monolayers shift, and variable elastic strains appear (vibrational processes — acoustic emission[4]), which weaken chemical bonds and break the solid state lattice. All this results in the formation of electrons, charged and ultradisperse particles with the metastable surface that initiate chemical reactions. This explanation agrees with the experimental data considered above, but it requires refinement and specification.

The comparison of the X-ray powder diffraction analysis data for the mechanoactivated mixtures and the kinetics of the yields of free-radical and triplet paramagnetic centers testifies that the electron and hydrogen transfer reactions become possible only after the deep dispersion of the mixtures. However, the structure of the products remains unclear: whether the mixture obtained by the mechanoactivation is completely amorphous or it contains submicrocrystalline inclusions of the initial components and compounds formed.

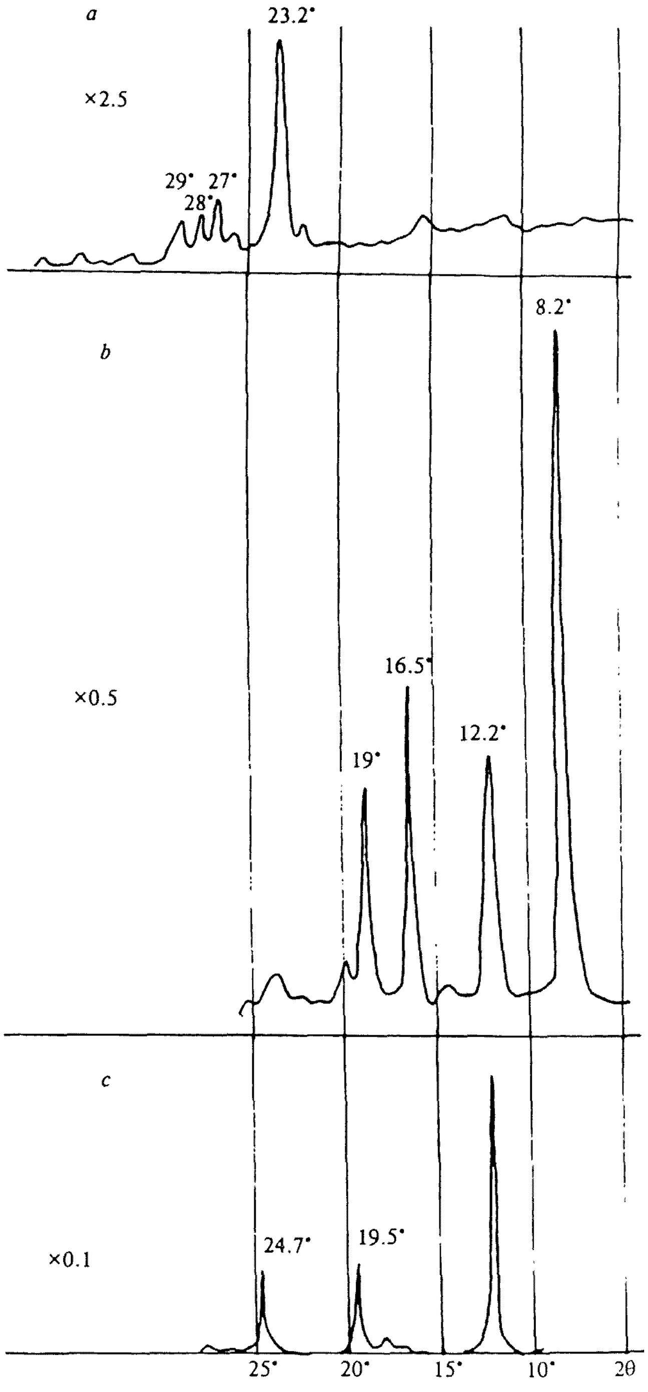

Fig. 4. X-ray-grams of the initial samples of different compositions: *a*, S : PS = 85 : 15; *b*, DTBP : PS = 85 : 15; *c*, DTBQ : PS = 85 : 15. The corresponding coefficients of amplification normed to unity are presented here and in Fig. 5.

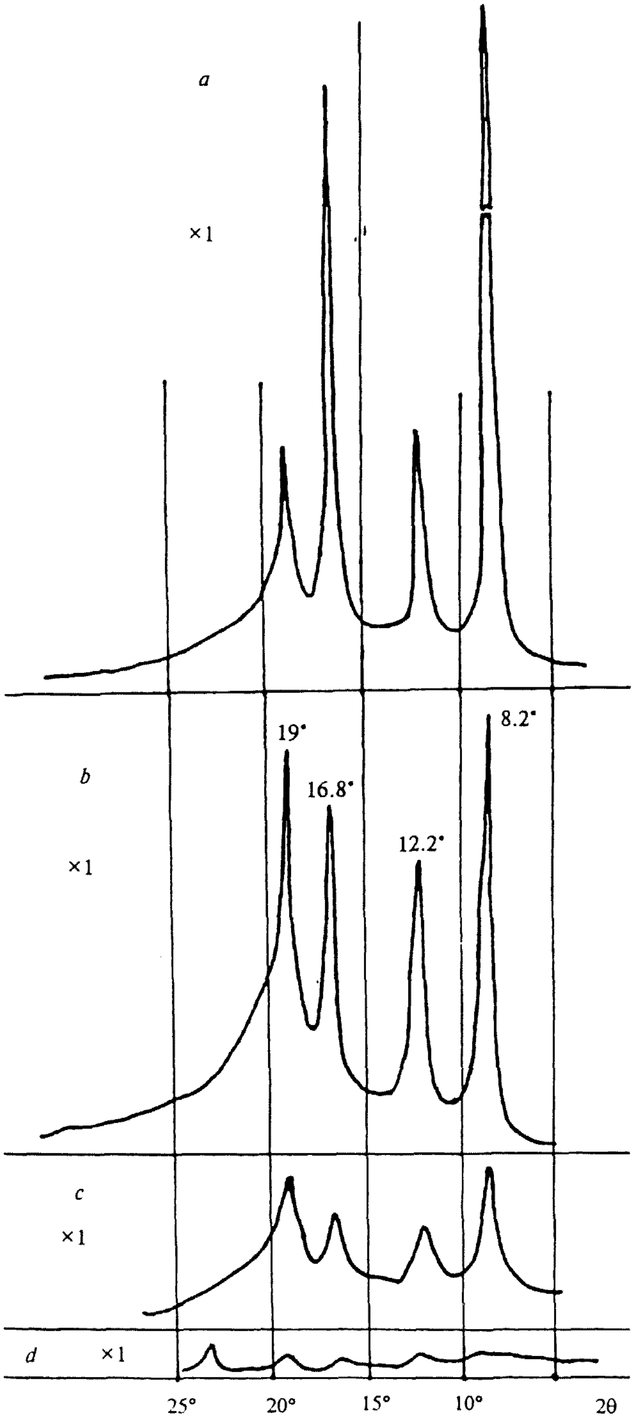

Fig. 5. X-ray-grams of the samples obtained by the uniaxial compression (*a*) and EW action at different explosion pressures (*b*—*d*): *a*, DTBQ : DTBP : PS = 45 : 45 : 10, p_{pr} = 150 kN cm^{-2}; *b*, DTBQ : DTBP : PS = 45 : 45 : 10, p_{ew} = 25 kN cm^{-2}; *c*, DTBQ : DTBP : PS = 45 : 45 : 10, p_{ew} = 100 kN cm^{-2}; *d*, DTBQ : DTBP : S : PS = 35 : 35 : 20 : 10, p_{ew} = 125 kN cm^{-2}.

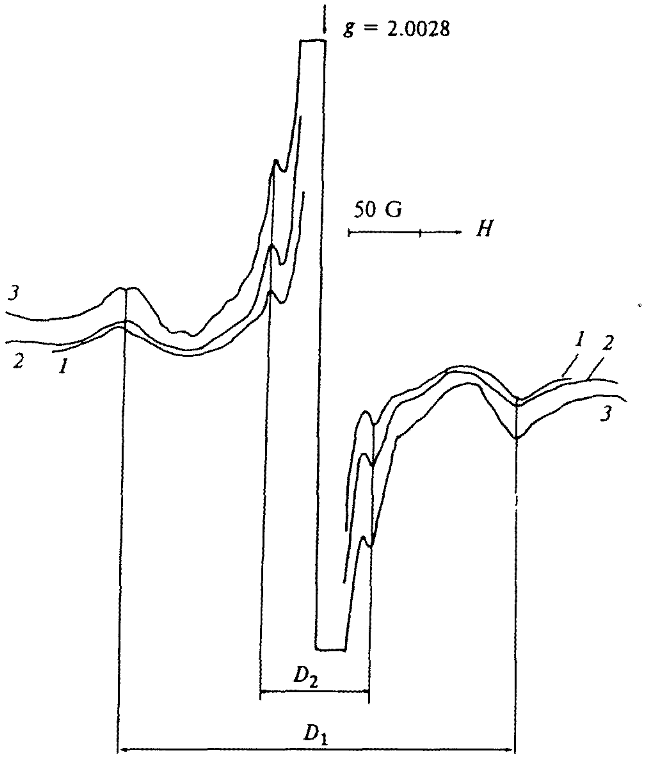

Fig. 6. ESR spectra of the samples after the EW action and UV irradiation for 1 (*1*), 2 (*2*), and 6 (*3*) min.

The latter question can be partially solved by the study of ESR spectra of photolysis products of mechanoactivated mixtures. It has been established previously[5] that the photolysis of pyrocatechol crystals doped with quinone results in the formation of RP of two types stable at 77 K. The ESR spectra of these pairs are characterized by the dipole-dipole coupling constants D = 286 and 75 G. The method for the approximate determination of D values from experimental ESR spectra of radical pairs (or any other paramagnetic centers in the triplet state) is illustrated in Fig. 6. The ESR spectra of radical pairs[6] with the constants D = 249 and 143 G are recorded upon the photolysis of vitrified solutions of the pyrocatechol—quinone mixtures in toluene. Thus, the mechanoactivation results in the formation of amorphous mixtures or doped microcrystals, while the appearance of some RP can be expected due to the photolysis.

The ESR spectra of the products obtained by the low-temperature (77 K) photolysis of the mixture after treatment with the EW pulse are presented in Fig. 6. It is seen that an increase in the intensity of the ESR signals of the radical pairs with $D_1 \approx 280$ G and the appearance of the pairs with $D_2 \approx 70$ G are observed during the photolysis. The ESR spectra of the pairs that appeared upon photolysis can be distinguished from those of RP generated by mechanical action only by the stability and the sign of the D constant. These differences manifest themselves in strong magnetic fields at very low temperatures.[7–9] Therefore, the formation of photolytic RP is indicated only by the increase in the intensity of the spectrum, which has been previously recorded for RP generated by the mechanoactivation (see Fig. 6), and the values of the parameter *D* are determined with great error. Nevertheless, the indicated values of *D* are apparently closer to the parameters of the spectra in crystalline structures. A more thorough comparison of the spectra presented in Fig. 6 with those obtained previously upon the photolysis[5,6] confirms that they are similar to those recorded during the photolysis of doped crystalline powders and differ substantially from the spectra of vitrified samples. This can be explained only by the formation of mixed crystals due to the mechanoactivation, because the photoinduced electron (proton) transfer between molecules incorporated into different crystals is impossible. Nevertheless, as has been already mentioned, the X-ray diffraction analysis data testify to the transition of the mixture into the amorphous state without the appearance of new crystalline structures. It is likely that mixed crystals are formed at the level of nanostructures that are not registered by X-ray diffraction method but substantial for the stabilization of free-radical states.

Thus, the results of the present work confirm the supposition that the formation of free-radical states in solid-state mechanochemical reactions is caused by the dynamic component (discharge pulse) rather than by the static deformation of the sample. The pulsed EW action results in the dispersion of the solid powder to submicrocrystalline particles, accompanied by the formation of particles of mixed composition.

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