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Kinetics of Radical Processes in Organic Crystals during High-Pressure Shearing

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The kinetic dependencies of radical generation and recombination during shearing under high pressure of an organic polycrystalline compound, arylindandione dimer, were investigated using modified EPR spectroscopy. The radicals were created as a result of dimer splitting at shear deformation. A statistical model of brittle crushing and a semiphenomenological theory of radical kinetics were proposed. The theory describes well the functional dependence of EPR spectral parameters on the shearing angle, shear rate, and pressure, as well as on shearing by impact. Comparison with experimental data enabled us to determine the parameters of the radical kinetics: grain dimensions, multiplicity of grains split during shearing, radical density on the grain surface, and the radical surface diffusion rate constant. The work reveals the broad capabilities of the EPR method in investigating microscopic parameters of destruction of solids by mechanical stresses. © 1993 Academic Press, Inc.

In our previous paper (*1*), experimental results from a study of the kinetic dependencies of radical generation and recombination during shearing of an organic polycrystalline compound, arylindandione dimer (*2*), were presented. Shearing was created under pressure directly in a modified spectrometer resonator; EPR spectra were registered along with shearing. The shapes of the kinetic curves of radical generation and recombination for various parameters of mechanical influence, pressure (P), shear angle (φ), and rate (ω), were described.

The present work gives a theoretical interpretation of the observed dependencies. As is evident from a previous investigation (*3*), a radical is formed during the splitting of a dimer. Our main assumption is that the splitting of the dimer takes place during the formation of a new surface in the process of brittle crushing of a molecular crystal. Radicals appear on different sides of newly formed crazes. Figure 1 (*4*) illustrates the structure of dimers. During shearing the C_α–C_α weak bond (splitting energy of 18 kcal/mole) (*3*) breaks. This energy is comparable with the van der Waals energy of molecular interactions in crystals (*5*). Thus, there are many directions of microscopic inner tension interactions, at which the probable displacement of molecules competes with the splitting of a dimer. Therefore, each newly formed surface is characterized by an initial density n_0 of newly appearing paramagnetic centers (PC), i.e., radicals. The n_0 value depends on the direction of the newly formed surface in relation to the crystalline axis.

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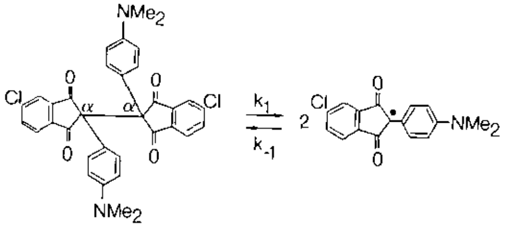

FIG. 1. Formula of the arylindandione dimer.

Model of Shearing

The disappearance of radicals is determined by their recombination. Since, as a rule, recombination is a nonactivational process, the limiting stage of the whole process becomes the delivery of radicals to each other. This takes place as the result of (a) their diffusion on the surface of a grain or (b) forced mixing. This mixing takes place during contacts between surfaces of adjoining grains, which are displaced by shearing. Thus, for a quantitative description of the kinetics of radical generation and recombination, it is necessary to determine the dependence of the formation of a new surface during brittle crystal crushing at the moment of action of shearing tensions.

Such a simple statistical mean model of brittle crushing during shearing under pressure on Bridgman's anvils is given in (5). Let us try to remember the main features of this model. A powder compressed with a sufficiently high force is a rigid system incapable of changing its shape. Motion of such a medium due to shearing tensions is feasible only by the system's grains being crushed. This statement is obvious for brittle destrictible (crushable) materials and is true for quite large grains, which always contain nucleation defects giving rise, at a certain tension, to major crazes that split the grain. Grains of smaller dimensions begin to slip.

At those grain dimensions at which sample deformation is linked to destruction, the order of shearing, when a single act of destruction of all grains takes place, can be conjectured for simple reasoning.

When a system consisting of parallel layers of grains is considered, the relative shift of one layer against another can take place only under the condition that all grains of the given layer are destroyed. Thus, the fragments will move and the entire layer will be displaced for the distance of

$$\Delta r \simeq \beta \times r, \qquad (1)$$

where r is the size of the grain and $\beta < 1$ is a smooth function of r. It is easy to notice that, during a single episode of destruction of all the particles in all the layers, the linear shear of the extreme layers is equal to $\beta \times h$ (Fig. 2), where h is the sample height and the tangent of the shear angle equals β.

$$tg\ \Delta\varphi \simeq \Delta\varphi. \qquad (2)$$

The rotation angle φ of Bridgman's anvil during a single act of destruction of all the grains is also approximately $\Delta\varphi \simeq \beta$.

It can be assumed, to some degree of approximation, that on the average a grain is split into two parts. The mean linear grain dimension depends on the ith index number of its destruction,

$$r_i = r_0 \times 2^{(-1/3 \times i)} \simeq r_0 \times \exp[-(0.23 \times i)], \qquad (3)$$

where r_0 is the initial grain radius.

Let us connect grain size with the rotational angle of the anvil. Note that by changing i by a unit we can write $\Delta i = \Delta\varphi/\beta$. Since the number of grains destroyed is $i \gg 1$, the discrete function $i(\Delta\varphi)$ can be replaced by a continuous one, and then we get

$$di = d\varphi/\beta(r, i). \qquad (4)$$

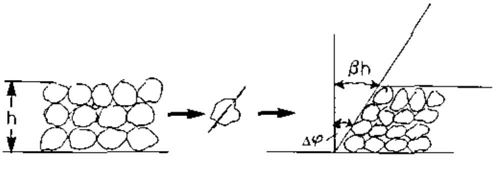

FIG. 2. Schematic representation of the action of shearing tensions.

Obviously, the β function increases with the reduction of r. Let us now write it in the form of a polynomial function,

$$\beta(r) = \beta_c \times (r_c/r)^{\alpha}, \tag{5}$$

where $\alpha \geq 0$ and must be determined from experiment, β_c is constant, and r_c is the radius of the grain, which cannot be destroyed at the given pressure. Substituting (3) and (5) in (4), we get

$$di/d\varphi = r_0/\beta_c \times r_c \times \exp[-(0.23 \times \alpha \times i)], \tag{6}$$

from which

$$i = 1/(0.23 \times \alpha) \times \ln(0.23 \times \alpha/\beta_c \times r_0/r_c \times \varphi). \tag{7}$$

After replacing (7) in (3), the equation

$$r(\varphi) \simeq r_0(0.23 \times \alpha/\beta_c \times r_0/r_c)^{-1/\alpha} \times \varphi^{-1/\alpha} \tag{8}$$

can be written.

Statistical Theory of Contact Destruction

Until now a strict statistical mathematical theory of contact destruction was absent. However, it is known that the major crack, which leads to destruction, is generated on certain types of defects in tension zones. The density of such defects (σ) on a newly formed splitting surface is a property of a material.

Let us establish that

$$r_c = (4\pi\sigma)^{-1/2} \tag{9}$$

is the radius of a grain which contains on the average only one defect.

The destruction of a single grain is stepwise. We define W_i as the probability that grains appearing in the ith splitting do not contain any defects on their surface:

$$W_i = \exp[-(4\pi r_{i-1}^2 \times \sigma)] = \exp[-(r_{i-1}/r_c)]^2. \tag{10}$$

Thus, our task is to find the total surface of grains, S_0, which have appeared by the ith splitting and, since i is linked to φ (see 7), then it is also necessary to find $S(\varphi)$.

The chain of events can be reconstructed as follows. We keep our attention fixed on the number of grains, assuming that each grain splits in half.

N_i is the number of grains after the ith splitting. Then

$$N_i = 2N_0(1 - W_1) + 2N_0W_1 = N_1' + 2N_0W_1$$

$$N_2 = 2N_1'(1 - W_2) + 2N_1'W_2 = N_2' + 2N_2'W_2$$

$$\ldots$$

$$N_i = 2N_{i-1}'(1 - W_i) + 2N_{i-1}'W_i,$$

where $N_k' = 2N_{k-1}'(1 - W_k)$.

The total number of grains after the ith splitting is

$$N_i = N_0\left[2^i \prod_{k=1}^{i}(1 - W_k) + \sum_{k=1}^{i} 2^k W_k \prod_{s=0}^{k-1}(1 - W_s)\right]. \tag{11}$$

Here the first addend in the square brackets gives the number of grains with r_i radius; the kth addend in the summation gives the number of grains remaining intact after the kth splitting.

The surface increment after the ith splitting is equal to

$$\Delta S = S_0 \times 2^{i/3} \times \prod_{k=1}^{i-1}(1 - W_k) \times (2^{1/3} - 1)/2^{1/3} \simeq 0.19 \times S_0 \times 2^{i/3} \times \prod_{k=1}^{i-1}(1 - W_k). \tag{12}$$

It is evident from relations (12) and (8) that unti $r \leq r_c$,

$$S(i) = S_0 \times \exp(0.23i). \tag{13}$$

Replacing (7) in (13) we find

$$S(\varphi) \simeq S_0 \times [1 + 0.23\alpha r_0/(\beta_c r_c)\varphi]^{1/\alpha}. \tag{14}$$

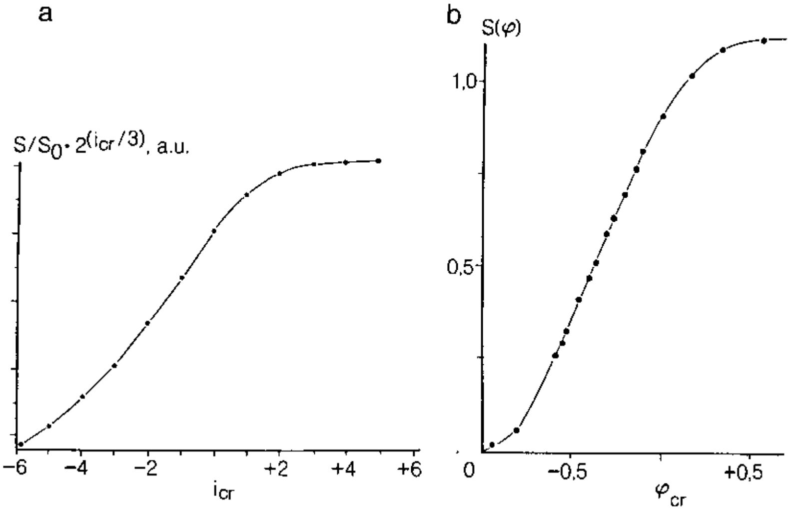

FIG. 3. Theoretical dependence of grain surface S on splitting number i (a) and shearing angle φ (b).

Figure 3 shows the dependence of $S(i)$ and $S(\varphi)$. In this illustration, the counting starts from i_c or φ_c, which corresponds to $r_i = r_c$. The combination of expressions (7), (10), and (12) enables us to obtain the increment rate of the developing surface with a rotation angle of $dS/d\varphi$.

Note that the σ parameter is the pressure function $\sigma(P)$ and is an increasing function of P, i.e.,

$$d\sigma/dP \geq 0. \tag{15}$$

This means that

$$dS(P, \varphi)/dP \geq 10. \tag{15a}$$

Since in experimental conditions the characteristic rates of macroscopic shear ($\omega \leq 3 \times 10^{-3}$ sec) are markedly lower than the velocity of sound in the sample, then the size of a newly appearing surface is only a function of the rotational angle $\varphi = \omega t$.

Kinetic Equation of Generation and Recombination of Radicals

As mentioned before, as a rule, on the newly formed splitting surface paramagnetic centers (PC) otherwise known as radical centers, appear. Their mean density can be denoted as n_0. The disappearance of a radical is the result of recombination. The delivery of radicals to each other becomes the limiting factor of this recombination, as well as for the majority of reactions in solids. According to the proposed model two mechanisms of delivery are feasible: (a) thermoactivated radical diffusion on the grain surface and (b) forced mixing, which is connected with the relative displacement of adjoining grain surfaces under external shearing forces.

The PC concentration is a function of two times, $n(t', t)$, where t' is the generation time and t is the time of observation. Thus, we are investigating the concentration of PC averaged over the ensemble of grains generated at the t' moment. The formal kinetic equation can be written in the following form:

$$\frac{\partial n(t', t)}{\partial t} = -K_D \times n^2(t', t) - K_m(t) \times n(t', t) \times \bar{n}(t) \tag{16}$$

$$\bar{n}(t) = \frac{\int_0^t n(t', t) \times dS/dt' \times dt'}{S(t)} \tag{17}$$

$$n(t', t') = n_0.$$

In these equations K_D is the recombination diffusion rate constant connected with the radical surface diffusion constant. In the case of two-dimensional diffusion (*6*),

$$K_D \simeq 4\pi D/[\ln(Dt/a^2)], \qquad (18)$$

where D is the diffusion coefficient, a is the characteristic reactive size of the radical (the recombination size), and K_m is the kinematic recombination constant due to mechanical mixing. This is the probability of radical interaction with another radical as the result of mixing or the surface sweep in seconds by the radical at forced grain movement due to shearing. It is estimated as

$$K_m = a \times V_{rel},$$

where V_{rel} is the relative rate of motion of two adjoining grains. For a grain located at R distance from the center of the anvil, we have

$$V_{rel} = \omega \times R \times r(\varphi)/h, \qquad (19)$$

where h is the height of the sample tablet. For the general case of arbitrary geometry of mixing,

$$K_m = a \times \nabla V \times r(\varphi) \equiv \omega \times S_0(\omega). \quad (19a)$$

Since one given grain comes into contact with grains of various generations (with generation times t'), then in the kinematic additive of the kinetic equation (16) the PC density averaged over generation time $\bar{n}(t)$ is included.

An experimentally registered value is

$$N(t) = \bar{n}(t) \times S(t) - \quad ,$$

the total number of PC at a given moment of time t. Because our primary task is the extraction of introduced model parameters from experimental data, it is necessary to find ways of resolving Eq. (16) in analytical form. Multiplying both parts of (16) by dS/dt' and integrating over t' between 0 and t, we get

$$\frac{d\bar{n}(t)}{dt} = \left\{[n_0 - \bar{n}(t)] \times \frac{d(\ln S)}{dt}\right\} - K_D\bar{n}^2(t) - K_m(t)\overline{n^2}(t). \quad (20)$$

The first term on the right-hand side is responsible for radical generation, while the two others are responsible for radical recombination. For quite small grains, during radical diffusion over different edges of surfaces from various generations, the probability of radical diffusional collision with another radical of the same generation might become lower than the probability of collisions with radicals of other, younger generations. Accordingly, the diffusional term of relation (16) most likely has the form of a kinematic expression, i.e., $K_D n(t', t)n(t)$. Therefore, in the last term of Eq. (20) with a fairly well developed splitting surface (large number of generations), $\overline{n^2}(t)$ can be replaced by $\bar{n}^2(t)$. Finally, we come up with the kinematic equation

$$d\bar{n}(t)/dt = \{[n_0 - \bar{n}(t)] \times d(\ln S)/dt\} - \bar{n}^2(t)[K_D - K_m(t)], \quad (20a)$$

where $S(t)$, K_D, and K_m are set by relations (14), (16), and (19).

Equation (20a) is related to a type of general Riccati equation and, unfortunately, cannot be resolved in analytical form. In the experiment (*1*), during shearing by impact, an "instant" sharp increase in the number of PC right after the blow is observed. Such a value of N is not seen during slow sample destruction. The rotation of the anvil by a final angle ($\approx 10°$) at impact load is a quick process ($\approx 10^{-1}$ sec). The newly generated PC did not have enough time for recombination, since characteristic times $(K_m \times n_0)^{-1}$ and $(K_D \times n_0)^{-1}$ are significantly greater. The observed peak on the kinetic curve indicates that n_0 is considerably greater than $n(t)$, which appears during slow destruction. This means that quadratic recombination of radicals (second term in Eq. (20a)) leads to a quasi-steady change of $n(t)$. For the quasi-steady solution of Eq. (20a) to be fairly accurate it is necessary that the characteristic time of radical diffusion recombination $(K_D \times n_0)^{-1}$ be noticeably smaller than the characteristic time of the development of a new surface,

$$(K_D \times n_0) \gg d(\ln S)/dt. \tag{21}$$

The lower limit for $K_D \times n_0$, estimated from impact experiments, is approximately 3×10^{-3} sec, and according to (14) at $\omega \approx 3 \times 10^{-5}$ sec^{-1} (0.1 deg/min), $d(\ln S)/dt \approx 10^{-4}$ sec^{-1}. Thus, the condition of a quasi-steady process (21) is achieved, which means that the PC concentration observed at these shear rates (ω),

$$n(t) \ll n_0. \tag{22}$$

Then from (20a) and taking into account (22) we get

$$n(t) = \frac{(n_0 \times d(\ln S)/dt)^{1/2}}{[K_D + K_m(t)]^{1/2}}. \tag{23}$$

This solution will be used for the interpretation of the experimental results. It should be noted, once again, that the smaller value of ω, the more accurate is this relation.

Statistical Picture of Shearing

From (23) and (19a) we can obtain

$$\bar{n}(\varphi) = \frac{[n_0 \times d(\ln S)/d\varphi \times \omega]^{1/2}}{[K_D + S_0(\varphi) \times \omega]^{1/2}}. \tag{24}$$

The value of the observed signal is $I(\varphi) = C \times N(\varphi)$, where C is a constant; i.e.,

$$I(\varphi) = C \times [n_0 \times S(\varphi) \times d(\ln S)/d\varphi \times \omega]^{1/2}/[K_D + S_0(\varphi) \times \omega]^{1/2} \tag{24a}$$

($S_0(\varphi)$, see (19a)). At small ω, when $K_D \gg \omega \times S_0(\varphi)$, we have

$$I(\varphi) \sim \omega^{1/2}. \tag{25}$$

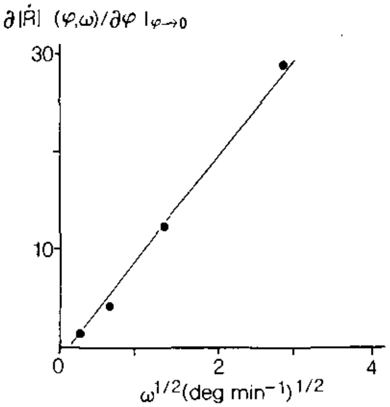

FIG. 4. Dependence of initial slope of radical concentration on shearing rate ω (1).

Figure 4 shows the plot for the dependence of initial slope of experimental $I(\omega)$-values on $\omega^{1/2}$ (1). Evidently, a good coincidence with the theoretical dependence (25) is achieved.

By comparing the experimentally registered linear dependence of $I(\varphi)$ at small φ ($\varphi \leq \varphi_c$) with relation (24a) it is easy to find that at $\varphi \leq \varphi_c$,

$$S(\varphi) \sim \varphi^{3/2}, \tag{26}$$

from which it can be established that $\alpha = \frac{2}{3}$ (by comparing (26) with (14)).

Introducing this value for α into (7) we get

$$\varphi \simeq 6.5 \times \nu^{-1} \times [\exp(0.15 \times i) - 1], \tag{27}$$

where the parameter

$$\nu \equiv r_0/(\beta_c \times r_c). \tag{28}$$

Using relation (27) and the plot of $S(i)$ from Fig. 3a, the plot of $S(\varphi)$ and $I(\varphi, \omega)$ dependence can be drawn, where φ is measured in units of critical angle φ_c,

$$\varphi_c \simeq 6.5 \times \nu^{-1} \times \exp(0.15 \times i_c),$$

in (24a). We assume that ω is small, hence $S_0(\varphi)\omega \ll K_D$. The plots of $S(\varphi)$ and $I(\varphi, \omega)$ are presented in Figs. 3b and 5, respectively. Comparing the angle at which the signal reaches a maximum, $\varphi_{\max} \simeq 0.9\varphi_c$, with the

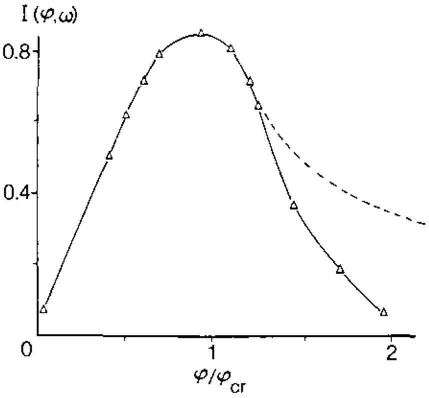

FIG. 5. Dependence of radical concentration on shearing angel φ (theoretical, solid line; experimental, dotted line).

experimental result, $\varphi_{max} \simeq 70°$ (at $\omega = 0.45$ deg/min), we get $\varphi \simeq 1.3$. The parameter ν can be obtained from the comparison of theoretical and experimental curves $I(\varphi)$ and $I(i)$ (Fig. 5):

$$\nu \simeq 10. \qquad (29)$$

Hence, according to (27) we find $i_c \simeq 10 \div 12$, i.e., 10 splittings of sample grains take place before destruction ceases. According to (3), $r_c/r_0 \simeq 10$, and from the definition of ν (formula (28)), we get $\beta_c \simeq 1$; i.e., the displacement of grains with r_c radius during destruction is of the order of grain size. Thus, we have determined all the parameters that define the statistical picture of fragile destruction.

Microscopic Parameters of Radical Processes at Shearing

Finally, we need to estimate the microscopic parameters characterizing radicals: n_0, K_D, r_0, r_c, the initial and final grain sizes, and the total surface of grains, S_0. Absolute values of $N(\varphi)$ must be used. Plots $S(i)$ and $S(\varphi)$ show the values

$$f(i) = S(i)/S_0 \times 2^{(i_c/3)} \simeq 1/10 \times S(i)/S_0,$$

$$f(\varphi) \simeq 1/10 \times S(\varphi)/S_0.$$

Hence, according to (24a),

$$\begin{aligned} N(\varphi) = {} & K_D^{-1/2} \times S_0/10 \\ & \times \{n_0 \times [f(\varphi) \times df/d\varphi \times \omega]/ \\ & [1 + s_0(\varphi) \times \omega/K_D]\}^{1/2}. \qquad (30) \end{aligned}$$

The $s_0(\varphi) = a \times R/h \times r(\varphi)$ value can be connected (linked) with $f(\varphi)$. Evidently, from the relation for sample volume the following equation can be written:

$$\begin{aligned} r(\varphi) & = 3V/S(\varphi) \\ & = 3V/[10 \times S_0(\varphi) \times f(\varphi)]. \qquad (31) \end{aligned}$$

Hence,

$$\begin{aligned} s_0(\varphi) = {} & 3 \times a \times R \\ & \times V/(10 \times h \times S_0) \times f^{-1}(\varphi) \end{aligned}$$

and (32)

$$\begin{aligned} N(\varphi) = {} & 10 \times S_0 \times \{[n_0 \times K_D \\ & \times \omega \times f(\varphi) \times (df/d\varphi)]/[1 + c/f(\varphi)]\}^{1/2}, \end{aligned}$$

where

$$\begin{aligned} c = {} & 3 \times a \times R \times \mathrm{V} \\ & \times \omega/(10 \times h \times S_0 \times K_D). \qquad (33) \end{aligned}$$

Now we see that the number of radicals observed depends on two parameters,

$$Y_1 = n_0 \times S_0^2/K_D \text{ and } Y_2 = S_0 \times K_D,$$

which can be determined from the comparison of $N(\varphi)$ (formula (32)) with experimental results. These two parameters contain three unknown values: n_0, S_0, and K_D. The experimental dependence $N(t)$ after shearing due to impact (1) can serve as the third condition. In this case, the characteristic diffusional time of radical annihilation will be

$$\tau_{dif} = (K_D \times n_0)^{-1}.$$

Thus, using the values for $N(t)$ at low ω and small angles, the dependence of φ_{max}

and ω, and the value of τ_{dif}, we get

$$\begin{aligned} Y_1 &= (n_0 \cdot S_0^2/K_D)^{1/2} \\ &= N(\varphi)/(10 \times \omega^{1/2}) \times [f(\varphi) \times f'(\varphi)]^{-1/2} \\ Y_2^{-1} &= (S_0 \times K_D)^{-1} \simeq h/(a \times R \times V \times \omega) \\ \tau_{\mathrm{dif}} &= (K_D \times n_0)^{-1}. \end{aligned} \tag{34}$$

The values of n_0, S_0, and K_D can be determined from Eq. (34). Substituting the experimental parameters, $N(\varphi) \simeq 10^{16}$, $h = 3 \times 10^{-3}$ cm, $R \simeq 3 \times 10$ cm^{-1}, $\omega \simeq 2 \times 10^{-3}$ sec^{-1}, $a \simeq 10^{-7}$ cm, $V \simeq 10^{-3}$ cm^{-3}, $\tau_{\mathrm{dif}} \simeq 10$ sec, $f(\varphi) \simeq 0.5$, $f' \simeq 1$ we come up with

$$(S_0 \times K_D)^{-1} \simeq 1.6 \times 10^{11} \text{and} K_D \simeq (10 \times n_0)^{-1}.$$

Consequently, $r_c \simeq 10^{-6}$ cm. Therefore, we have the following values of main microscopic parameters of radical processes at shearing: $n_0 \simeq 10^{13}$ cm^{-2}, $K_D \simeq 10^{-14}$ cm^3/sec, $S_0 \simeq 6 \times 10^2$, $r_0 \simeq 10^{-5}$ cm, $r_c \simeq 10^{-6}$ cm. All these values have reasonable physical meanings.

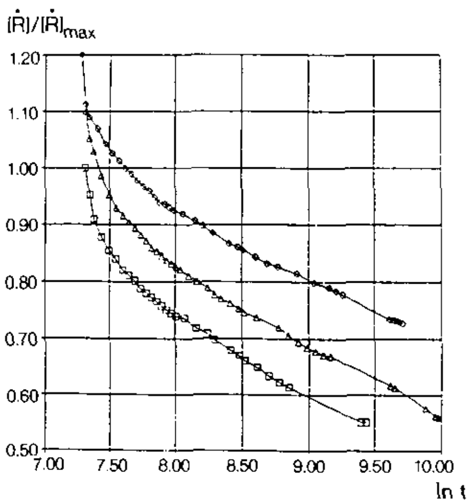

FIG. 6. Anamorphosae of radical recombination kinetic curves in coordinate $[\dot{R}]/[\dot{R}]_{\max}$ – ln t after shearing by one and the same angle $\varphi = 45°$ and at various pressures: ◇, 6 kbar; △, 8.7 kbar; □, 11.6 kbar. For convenience of illustration the curves are separated from each other on the ordinate axis by 0.1 (1).

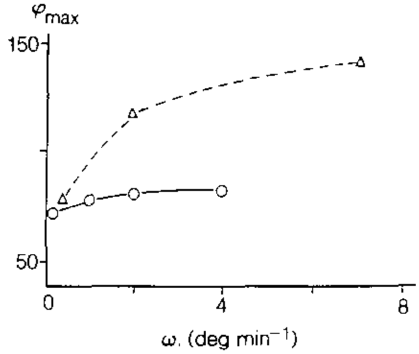

FIG. 7. Dependence of shear angle $\varphi_{\max}$, at which the kinetic curve passes through the maximum on shear rate ω: ○, theory; △, experiment (P = 8.7 kbar) (1).

Qualitative Interpretation of Experimental Kinetic Curves at Shearing

The K_D value, the radical surface diffusion rate constant, should not depend on pressure. This is confirmed by anamorphoses of radical recombination kinetic curves after shear by one and the same angle (45°) registered at various pressures (Fig. 6). Note that the anamorphoses are identical to each other. Consequently, the mechanism of surface diffusion does not change with a twofold increase in pressure from 6 to 11.6 kbar.

From relation (32) the dependence $\varphi_{\max}$ (ω) can be obtained. Hence $d\varphi_{\max}/d\omega > 0$. This coincides with experimental data at $C \geq 1$. However, the maximum theoretical value of $\Delta\varphi_{\max}$ is approximately 25%, which is markedly lower than the experimentally observed 100% increase (Fig. 7). A greatest error arising from the interpretation of experimental results is due to the fact that we deal with the mean values, disregarding the dispersion in the sizes of newly generated grains.

Moreover, at those stages of destruction where for each grain the number of radicals is close to a unit, the recombination due to diffusion is sharply reduced and cannot be described in terms of averaged diffusional

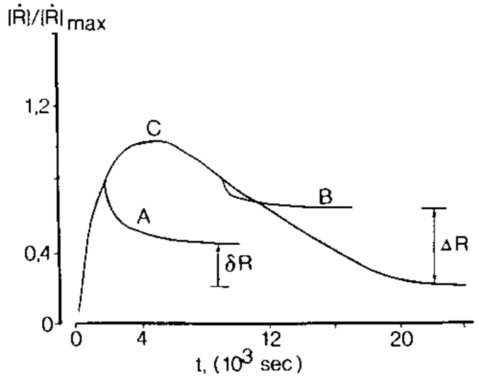

FIG. 8. Experimental dependence of relative radical concentration $[R]/[R]_{\max}$ on time of observation t (P = 8.7 kbar). Curve C was obtained without stopping the shearing, A and B were obtained after shearing had stopped. In all cases, ω = 1.8 deg/min.

investigation. Figure 8 shows the kinetic curves of A and B radicals shortly after the ending of shear due to pressure and with the starting point of recombination corresponding to $[R]/[R]_{\max} = 0.8$ on the common kinetic curve C. It is evident that after a quick initial recombination, these curves enter a plateau. In the beginning, the B curve "takes over" recombination that corresponds to the C curve, and finally slows down. The ΔR difference between the ordinates of slow changing parts of B and C curves corresponds to the amount of grains with a single radical. The absence of shearing at $\omega = 0$ excludes radical exchange between grains. Since diffusional input into recombination in limits of the grain becomes ineffective, this plateau can be seen at the very large t usually observed in experiments.

When the starting point is located on the initial part of the C curve, then a kinetic curve A with a significantly deeper recombination can be seen. Since the cracking number i of grains at small shear angles and times is also small, $i \ll i_c$, the mean size of the grain is still significantly greater than r_c. In the limit of such a large grain the kinetics of recombination, determined by radical surface diffusion, can be quite fast. This may account for the substantially "deeper" kinetic transformation of the A curve in comparison with the B curve. As a result, the plateau of curve A rises far less over the level of B, $\delta R < \Delta R$. Thus, a greater number of quite small grains (with one radical) corresponds more closely to curve B than to curve A. This seems reasonable, since the mean grain size in this case is far from r_c. For B the curve of grain size distribution r_c narrows, and its center of mass is displaced toward smaller r values. More accurate theoretical assumptions are in need of significantly more precise experimental data. Both will be developed in the future.

Conclusion

Thus: 1. Kinetic dependencies of radical generation and recombination are demonstrated on the example of an organic polycrystal. The radicals are formed in result of dimer splitting during shearing under high pressure. Experiments were conducted at various pressures, shear rates, and shear angles, as well as during shearing caused by impact.

2. A statistical model of brittle crushing and a semiphenomenological theory of radical kinetics are proposed. The theory explains well the functional dependencies of EPR signal parameters on rotational angle, angular velocity, and pressure. Comparison with experimental data enabled us to determine the value of the main statistical and microscopic parameters of crystalline brittle crushing and the kinetics of radical processes at shearing under pressure; $n_0 \simeq 10^{13}$ cm^{-2}, $K_D \simeq 10^{-14}$ cm^3/sec, $S_0 \simeq 6 \times 10^2$, $i_c \simeq 10$, $r_0 \simeq 10^{-5}$ cm, $r_c \simeq 10^{-6}$ cm.

This work demonstrates the wide range of capabilities of the EPR method for the investigation of microscopic destruction parameters.

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