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Radical Processes in Organic Crystals at Shear Deformation under Pressure (Experiment)

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The EPR technique has been used to study the kinetic regularities of radical generation and decay under shear deformation of organic polycrystalline compounds under high pressure (up to 1.2 GPa). The EPR spectra were registered simultaneously with developing deformation directly in the resonator of a modified spectrometer. Radicals were generated in the process of mechano-induced dissociation of arylindandione dimer molecules. It was show that the type of kinetic curves for radical decay and recombination is largely dependent on pressure, and the angle and the rate of shear deformation. Studies were also made of the radical processes under shear deformation developed in the shock regime. © 1992 Academic Press, Inc.

Shear deformation takes place in different circumstances when a solid body is exposed to mechanical treatment: grinding (*1*), striking and elastic flow (*2*), and shock waves (*3*, *4*). The common features of these phenomena are strong nonequilibrium and short time duration (10^{-6}–10^{-3} sec). This makes shear deformation stimulated physicochemical processes a difficult area for studies. This is especially true of the processes which involve chemically active species—short-lived radicals.

The kinetics of radical processes enables one to reconstruct the dynamics of complex transformations which occur in a solid by shear deformation. This can be done using model experiments (*5*) which should satisfy the following conditions: (a) relative uniformity of mechanical loads; (b) possibility of their qualitative control; (c) time duration long enough to register a spectrum; and (d) possibility of registering the microscopic characteristics of a substance under study while it is exposed to shear deformation.

We believe that the most acceptable, if not the only possible, procedure for such an experiment is the one which makes use of the Bridgman anvils (*6*) in combination with established spectroscopic techniques (*7*), such as the EPR method.

Toward this aim we have developed, manufactured, and used a device (*8*) which enabled us to register EPR spectra in the process of shear deformation of a solid exposed to high pressure. The device was used to study a model organic compound (*9*).

This paper presents experimental results on the generation and decay kinetics of paramagnetic species (PS)—radicals formed at shear deformation under pressure. We measured the following mechanical load parameters: pressure (P) and the angle (φ) and

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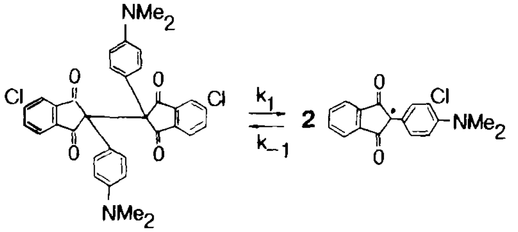
rate (ω) of shear deformation. The paper also presents the kinetic curves for radical yield at shear deformation in combination with shock loads.

Experimental

We used a setup (*8*) developed on the basis of an ordinary EPR spectrometer with reflecting HF-tract and $\lambda = 3$ cm. The central element was a cylindrical solid dielectric resonator with working mode H_{111}. The durable ceramic resonator (Al_2O_3) simultaneously served as one of the Bridgman anvils. Samples were placed in the center of the cylindrical resonator. The other anvil was movable and made of hardened beryllium bronze. The biggest load developed by a built-in screw press was 4 tons. The load was measured by a spring dynamometer. Shear deformation was created by turning around the metallic anvil's axis. The diameter of the working area is 3 mm. The deformation rate was varied by means of two in-line connected regulators, over a wide range from 1×10^{-3} deg/min to 20 deg/min. The setup was equipped with a device which developed shock loading in time $< 10^{-1}$ sec. The shock deformation was achieved when a load was dropped from a certain height.

The sample diameter is 3 mm and the thickness is $(3\text{–}4) \times 10^{-2}$ mm. Arylindandione dimer was used as a model compound (*3*). At shear deformation under high pressure the C_α–C_α bond in the dimer molecule is broken and radicals are formed as a result of mechano-stimulated dissociation (*2, 9*). The radicals are able to recombine thus restoring the dimer molecule (see Scheme 1).



SCHEME 1

The samples were all of the same weight, which was chosen so that a pressurized tablet would cover the entire working area of the anvil (∅ 3 mm) and so that there would be no extrusion of the substance. This "standardization" enables one to make valid quantitative comparisons for the kinetic curve parameters obtained for different tablets of the same substance under study. After a tablet has been replaced, the value of one of the experimental parameters (P, φ, ω) and the position of the starting point for recombination were changed. All the experiments were conducted at the same temperature, $T = 293$ K.

The shortest time for recording an EPR spectrum was ~20 sec. The spectrum of chromium ions, which occur in the resonator ceramics as a natural admixture, was used for reference purposes.

The radical concentration was determined by means of a secondary "point" reference—diphenylpicrylhydrazine.

Results and Discussion

The EPR spectrum of mechano-stimulated radicals in strained solid arylindandione dimer is a singlet with the distance between the sharpest slope points $\Delta H_{pp} = (14.5 \pm 0.1)$ G and $g = 2.002$. No dependence was observed for ΔH_{pp} on P, φ, and ω. An increase in radical concentration appears as an increased singlet intensity.

It can be said with confidence that radicals in this compound are generated through the action of the shear component of mechanical load only. Hydrostatic pressure without shear deformation does not lead to radical formation.

In a series of preliminary experiments we have studied the effect of hydrostatic (all round) pressure on paramagnetism of the arylindandione dimer samples. Use was made of a chamber designed to study EPR in conditions of high hydrostatic pressure (up to 0.7 GPa) (*10*). It was found that an increase in pressure up to the highest level does not affect either the width or the intensity of the EPR line. Hence, the conclusion was made that an increase in hydrostatic pressure does not stimulate the generation of radicals. The necessary condition for mechano-induced dissociation of the dimer is shear deformation. This conclusion is supported by the experimental results presented below.

Figures 1a and b show the kinetic dependencies of the radical concentration $[R]_{\text{relative}} = [R]/[R]_{\text{start}}$ on the shear deformation time (t) at constant pressure $P = 0.87$ GPa and various shear deformation rates ω: 7.2 deg/min, 1.8 deg/min, 0.45 deg/min, and 0.1125 deg/min. A common feature of all these dependencies is a sharp linear growth of radical concentration at low shear angles at the initial section of the curve. The process of radical generation prevails. An increase in φ leads to a decreased yield rate $[R]$, which indicates that an actively competing process of radical recombination is joining in. The ratio between the generation and decay rate constants determines the shape of the kinetic curve. At large shear angles recombination prevails, the total radical yield decreases, and the kinetic curve assumes an asymmetrical bell-shaped form. The narrowness and the position of the peak are controlled by the ratio between the rate constants of radical generation and decay. Figure 1 shows that the shape of the kinetic curve depends on shear deformation rate. Thus, with $\omega = 7.2$ deg/min a sharp maximum (peak) is observed at $t = 1.2 \times 10^3$ sec, and with $\omega = 1.8$ deg/min at $t = 3.8 \times 10^3$ sec. However, already with $\omega = 0.1125$ deg/min there is no maximum and the curve reaches a plateau. The plateau after $t \geq 8 \times 10^3$ sec points out that the radical decay and generation rates are leveled off.

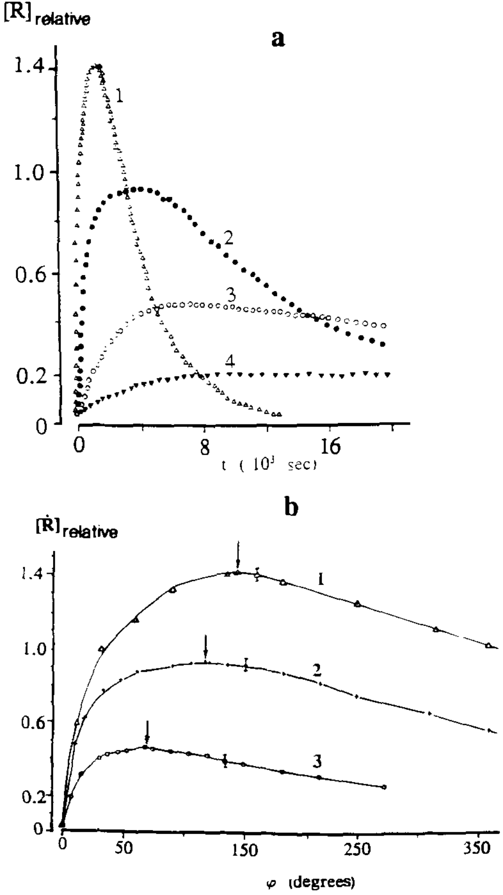


FIG. 1. The kinetic dependencies of radical yield (in relative units) on the exposure time (a) and angle (b) to shear deformation under pressure ($P = 0.87$ GPa) at different shear rates: 1, 7.2 deg/min; 2, 1.8 deg/min; 3, 0.45 deg/min; 4, 0.1125 deg/min.

The rate of the initial radical generation $D[R]/dt$ (the slope of the linear section at low t) is drastically decreased as ω is diminished. Since at these t values the recombination rate is negligibly low, the $d[R]/dt$ parameter characterizes unambiguously that the rate of the radical generation in conventional units is proportional to ω.

The highest radical yield (as seen in Fig. 1) is also proportional to the shear deformation rate: the highest yield is observed at $\omega = 7.2$ deg/min.

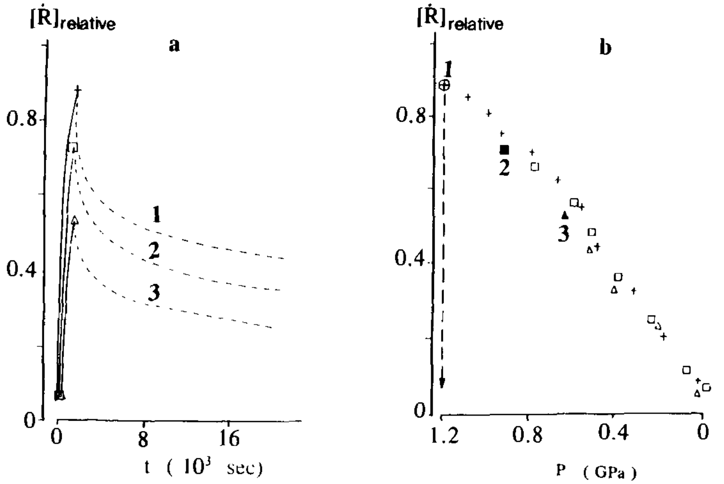


FIG. 2. Kinetics of radical recombination and yield (in relative units) on the exposure time to shear deformation at the same shear rate ($\omega = 1.8$ deg/min) and different pressure: 1, 1.20 GPa; 2, 0.87 GPa; 3, 0.63 GPa. (a) Full lines, radical yield during exposure to shear deformation and shear angle 45°; dashed lines, radical recombination under pressure after putting the shear to stop. (b) Radical concentration dependence at step-wise decrease of pressure and removal of shear deformation.

Figure 1b shows kinetic dependencies of $[R]_{\text{relative}}$ on the shear deformation angle φ at different ω. One can see that there is another dependence of their maximums positions on ω: $\varphi_{\max}$ decreases with increasing ω. That intriguing phenomenon will be explained in our future theoretical manuscript.

Figure 2a shows the type of kinetic curves at various pressures (full lines). The shear rate is constant—1.8 deg/min; the total shear deformation angle for each curve is 45°. It is seen that as the pressure grows from 0.63 GPa to 0.87 GPa to 1.2 GPa, $d[R]/dt$ increases monotonically. Unlike the previous experiments at various ω, however, in this case the increase in its value is less pronounced. Correspondingly the increase in the highest yield $[R]$ upon increasing pressure is also less considerable. Thus, as one can see, variation in one of the parameters (either P or ω) leads to qualitatively similar evolutions in the kinetic curves pattern. We should, however, bear in mind that the similarity is rather formal.

The given results describe the kinetics of radical yield only in the process of applied shear deformation. The contribution of competing generation and decay processes changes depending on the external experimental parameters—P, φ, and ω. Analysis of radical recombination curves enables us to estimate the contribution of each of the processes in the overall radical yield. The recombination regularities provides information about the dynamics of microscopic changes in a solid subjected to shear deformation before the shear was stopped and about the state of the solid in the actual moment of time. The conditions for such experiments were: P = const, φ = const, $\omega = 0$, $T = 293$ K.

A sharp drop in pressure down to the normal level immediately after stopping shear deformation leads to a virtually unregisterable drop in radical concentration (shown in Fig. 2 by an arrow). After this the radical concentration nearly reaches the initial equilibrium value $[R] \sim [R]_{\text{start}}$ minus the characteristic time of registering one spectrum (~ 20 sec). The recombination kinetics is not further observed.

When pressure is reduced in certain fixed steps one observes a smooth decrease in radical concentration (Fig. 2b). Curves 1, 2, and 3 correspond to pressures 1.17 GPa, 0.87 GPa, and 0.63 GPa, respectively. Each starts from a different $[R]$ value after the 45° shear. The rate of radical concentration decrease is independent of the initial pressure. Following the step-wise reduction of P down to the normal level, the curves meet at the same $[R]$ value, which is close to the initial $[R]_{\text{start}}$.

Thus, reducing the pressure down to the normal level (both fast and step-wise) leads to a blurred kinetic picture and to permanent loss of information about the radical processes.

From this point of view the kinetic curves of radical recombination after the stop of shear deformation under pressure are found to be more useful. Figure 2a (dashed lines) shows the kinetic recombination curves after putting a stop to shear deformation at various pressures. The corresponding radical yield curves (full lines) are discussed above. The recombination was observed at the same pressures as the radical yield: 1, 1.17 GPa; 2, 0.87 GPa; and 3, 0.67 GPa. Immediately after stopping the shear one observes a rapid radical recombination which is further noticeably lowered down. However, even when radical concentrations are observed over long periods of time, the concentration ever reaches (at no pressure value) the initial $[R]_{\text{start}}$ level. A drastic drop in pressure after observing recombination for a long time (using a similar procedure described above) causes only a minor drop in radical concentration which does not reach $[R]_{\text{start}}$.

Figure 3 shows the kinetic radical recombination curves in more complicated cases at the same pressure—0.87 GPa. The starting points for all the kinetic curves (full lines) are on the same kinetic curve (dashed line) of radical yield, obtained at $\omega = 7.2$ deg/min without stopping shear deformation. Each point on the curve corresponds to a different "kinetic" state of sheared solid body. In the starting points of the recombination curves the conditions of the solid body are different. Curves 1, 2, and 3 and 4, 5, and 6 of Fig. 3a have various prehistories. Thus, curves 1, 2, and 3 are at the section of fast initial radical accumulation, while curves 4, 5, and 6 are at the decrease section. On the other hand, curves 1 and 6 start from the $[R]/[R]_{\text{relative}} = 0.25$, 2 and 5 start from 0.50, while 3 and 4 start with 0.75. For the last three recombination curves (4, 5, and 6) the radical decay rate at the initial time moment is high and the curve runs below the dashed line. At long observation times the recombination rate decreases. At low values of the starting concentration 0.25 and 0.50 (curves 1 and 2 and 5 and 6) the initial recombination rate is lower than that at 0.75 values (curves 3 and 4). Note that the pattern of kinetic recombination curves depends on both the starting radical concentration and the position on the radical yield curve of the point corresponding to the stop of shear deformation (upward or downward sections).

Comparison of the recombination curves in Figs. 3a and 3b makes it possible to establish the impact of shear deformation rate. The dashed line in Fig. 3b shows the radical yield curve at $\omega = 0.45$ deg/min and $P = 0.87$ GPa without stopping shear deformation. The full lines show the recombination curves after putting the shear to stop at various values of relative starting concentrations—0.25, 0.50 and 0.75. Comparing the kinetic parameters of curves 3a (1, 2, 3, 4) and 3b (1, 2, 3, 4) allows one to answer the question of how the shear deformation rates affect the microscopic properties of a solid body. At all starting concentrations of radicals the degree of conversion is much more when $\omega = 0.45$ deg/min and less for cases

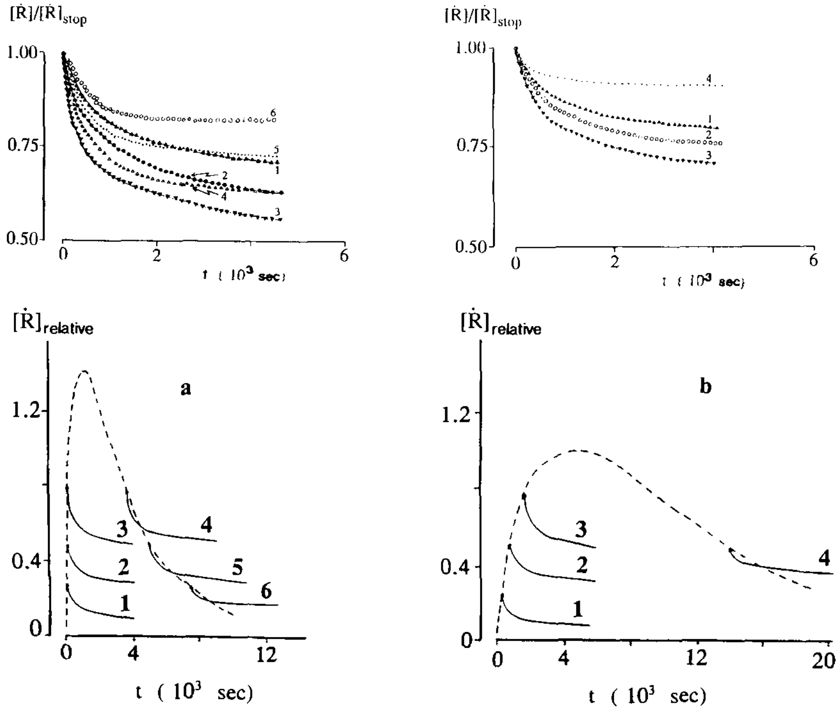


FIG. 3. Kinetics of radical recombination curves (full lines) under pressure (0.87 GPa) at different moments of stopping shear deformation and recombination starting at ω: (a) 7.2 deg/min (1 and 6, $[R]_{rel}$ = 0.25; 2 and 5, $[R]_{rel}$ = 0.50; 3 and 4, $[R]_{rel}$ = 0.75). (b) 1.8 deg/min (1, $[R]_{rel}$ = 0.25; 2 and 4, $[R]_{rel}$ = 0.50; 3, $[R]_{rel}$ = 0.75). Dashed lines stand for radical yield under pressure and continued shear.

when points of starting concentrations are placed on downward sections for both shearing rates. It should be noted that for each kinetic curve use was made of a new, previously unstrained sample of arylindandione dimer.

Figure 4 shows the kinetic curves obtained in the course of experiments which are substantially different from those described above. The experimental setup enabled us to study kinetic radical processes by EPR at shock shear deformation under pressure. Figure 4 (dots) shows the kinetic curve of radical yield under steady shear deformation (ω = 1.8 deg/min and P = 0.87 GPa). Curves 1, 2, and 3 correspond to radical yield in a sample subjected to shear shock. The pulses' magnitudes in all three cases were the same, but they were applied at different points of the radical yield curve obtained at steady shear deformation.

Thus, curve 1 corresponds to the initial section of radical accumulation, while curve 2 corresponds to the consumption section. Curve 3 starts at the same moment t as curve 1, but in this case the steady shear deformation was stopped at the instant of applying the shock.

One can easily see that the shock causes a sharp jump in radical concentration. The jump magnitude is larger for curve 1 than for curve 2, which is on the opposite slope of the kinetic curve. Despite the continued exposure to shear deformation, both curves show a rapid decrease in the "excessive" radical concentration right after the shock

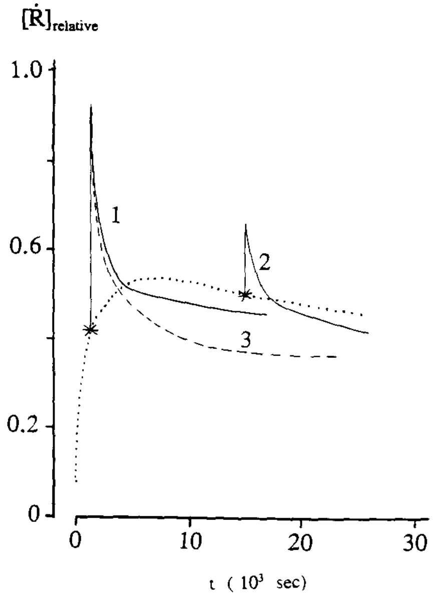


FIG. 4. Kinetic curves of radical yield and recombination (in relative units) on the shear exposure time (ω = 0.45 deg/min, P = 0.87 GPa) and shock shear deformation. The dots show the radical yield curve in the case of exposure to steady-state shear deformation only. Point (*) corresponds to shock shear deformation start; 1 and 2 are the radical yield curves after exposure to shock shear deformation simultaneously with the steady-state shear deformation; 3 (dashed line) stands for radical recombination after shock shear deformation combined with removal of steady-state shear deformation.

jump. The $[R]$ value tends to reach its value on the smooth kinetic curve with no stop of shear deformation.

When shear deformation (curve 3) is put to a stop simultaneously with shock treatment we obtain a recombination curve different from the curve 1 type.

Each of the shock shear deformation experiments, as well as the previous ones, was carried out with separate sample tablets.

Thus, we have presented the most typical experimental results obtained in the course of studying the kinetics of radical generation and decay during shear deformation under high pressure.

The next paper will present a theoretical interpretation of these experiments.

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