

Energetics of Plastic Flow under High Pressure and Shear Deformation

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A polycrystalline organic compound was used to measure the total mechanical energy consumed in the process of shear deformation on Bridgman's anvils under pressure. We estimated quantitatively the energy consumed during shear deformation of a polycrystalline sample of arilinedandione dimer under pressure. It was established that 88% of the energy is converted to heat, while 11% is transferred in the form of anvil elastic deformation to the operating device. The share of total energy transformed into the chemical one—rupture of bonds—is low and does not exceed 1%. © 1992 Academic Press, Inc.

1. Introduction

In the process of shear deformation under pressure the mechanical energy imparted to a solid is converted into other forms: thermal energy, the work of new surface formation, the energy of integral friction, the elastic energy of lattices strain, the energy of various structural defects (vacancies, dislocations), and the rupture and formation of new chemical bonds. One of our aims is to evaluate the balance of energy consumed through each of these channels.

Quantitative data about the ratios of contributions by each energy type are very important for understanding the plastic deformation-induced microscopic trans-

formations. Besides, these ratios allow one to evaluate the efficiency of grinding machines used in practice and to optimize their operating mode. Our knowledge of the energetics of plastic deformation is yet scanty, mainly because of the experimental difficulties caused by a strong lack of equilibrium in the process of plastic flow of solids subjected to excessive mechanical loads. The available data are of indirect nature, calculated from parameters measured after the removal of the mechanical load. The energetics of structural and chemical defects, such as distorted and ruptured bonds, is of special interest for understanding the process of mechano-chemical activation. The energy yield of defect formation (vacan-

cies, dislocations, radicals, etc.) is determined as the number of moles the defects formed under mechanical energy consumption of 1 MJ in the process of milling at 80 K (1). The energy yield is very low for some linear polymers (2)—polyethylene, polystyrene, and cellulose, ranging from 1×10^{-3} to 3×10^{-2} mole/MJ—while with polyester methacrylate it increases up to 1.2×10^{-1} mole/MJ. In case of melted quartz the energy yield of radicals is 3×10^{-3} mole/MJ.

No more than 0.1% of the energy consumed by mills accounts for the free surface formation (3). No more than 10% of the consumed energy can be accumulated in a compound in the form of mechanically activated structural defects (3). Under plastic deformation of metals (4) 95% of mechanical energy can dissipate in heat.

The molecular dynamics technique was used to show that the energy yield of the primary ruptures of macromolecules is close to 0.1 mole/MJ (5). Within 10^{-10} sec after mechanical stress application one-third of the total energy is converted into the energy of phonons, another third into high-energy oscillation-excited states, and the last third is consumed to break macromolecules into high-energy chain fragments.

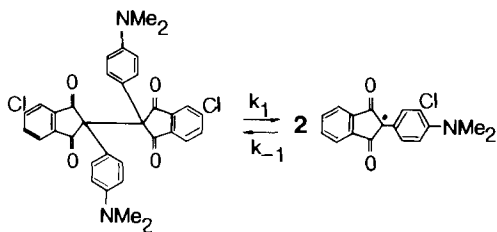
This short overview shows that the data on the energetics of mechano-chemical processes are mostly indirect and very scattered. No direct quantitative evaluation of the energy balance and the contributions by various types of energy consumption has been carried out. Bridgman's anvils are the most suitable tool for quantitative studies of the energy balance of plastic deformation under pressure.

The aim of the present paper is to estimate quantitatively the energy balance of shear deformation in an organic solid subjected to high pressure, to measure the amounts of energy consumed by various channels (scattering into heat, elastic deformation of anvils, and the total energy of chemical bond

rupture), and to evaluate their share in the total energy balance.

2. Experimental

The energy balance was measured using a model polycrystalline organic compound—arilinedandione dimer (6) (see



SCHEME 1

Scheme 1). The concentration kinetics of paramagnetic species induced by shear deformation under pressure was measured using a device which registered EPR spectra in the resonator of the spectrometer directly during the plastic deformation of a sample (7). The shear deformation was developed by means of the Bridgman's anvils, one of which served also as the SHF resonator of an EPR spectrometer. The device (8) was used to measure the total heat flow and the shift moment transferred from the rotating anvil via the sample under deformation to the other anvil. The device is designed in such a way that the shear deformation is developed through rotating one anvil, while the other one is firmly fixed to a thin-walled, deformation cylinder that is sensitive to twisting. The twisting moment of the cylinder is induced during shear deformation of the sample and recorded in the form of the shear-angle dependence. This procedure is more convenient than that of measuring the shift moment of the moving anvil. In the latter case one also has to take into account the energy losses due to mechanical friction of the device parts, which is a huge problem.

The total heat flow was measured using

a set of copper-constantan thermocouples whose junctions were located as near the anvils working zone as possible. The set of thermocouples was calibrated on the basis of the Joule heat release upon passing the electric current through a graphite sample placed between the anvils. A calibrated source of electric current was used and the device was thermostated. The experiments were performed under the same pressure of $P = 0.87$ GPa, the rate of shear deformation creation being 0.45 deg/min at $T = 293$ K.

To estimate the energy of mechano-induced ruptures of chemical bonds in arilinedandione dimer, the total amount of paramagnetic radicals formed during mechano-induced dissociation was determined by double integration of the EPR spectrum following shear deformation by 45° .

3. Results and Discussion

The total energy of the process is determined by the sum of contributions,

$$E = Q + A_m + E_R + U, \quad (1)$$

where Q is the total thermal flow, A_m is the anvil elastic deformation energy, and E_R is the energy of rupture of chemical bonds of all mechano-dissociated molecules.

Each of these contributions can be experimentally measured. The U member, however, cannot be measured experimentally, i.e., the energy of mechano-emission and the energy consumed to form extra surface and to distort the crystal's lattice.

Figure 1 shows the effect of the shear deformation angle on the amount of released heat. At small angles the heat flow grows, but at $\alpha > 15^\circ$ the process becomes steady-state with the curve reaching the plateau. In the steady-state mode the heat flow power is 7.8×10^{-3} W. The overall deformation time being 587 sec, the total amount of the released heat is (4.77 ± 0.35) J.

The dependence of the anvil elastic twist-

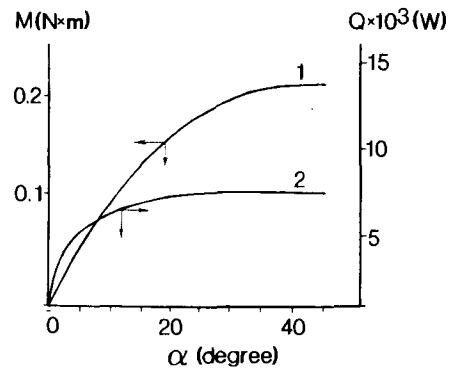


FIG. 1. Dependence of (1) the shifting moment (M , Newton \times meter) and (2) heat release (Q , Watt) on Bridgman's anvils at the largest shear deformation angle $\alpha = 45^\circ$.

ing moment on the shift angle has a similar form (Fig. 1). It slightly "lags behind" as compared to the heat release curve, reaching the plateau only at $\alpha = 35^\circ$ and keeping the constant value up to a maximum angle of 45° .

The overall work of the moment is determined by integration and is quantitatively equal to the area below the experimental curve. The work of the elastic deformation of the anvil is (0.55 ± 0.10) J up to $\alpha = 45^\circ$.

Figure 2 shows the kinetic concentration curve for mechano-induced radicals in the process of shear deformation up to $\alpha = 45^\circ$ under pressure. This dependence does not reach the plateau, but at large shear angles the rate of radical accumulation decreases noticeably.

The kinetics of change in radical concentration depending on the shear angle is determined by the competition of two processes: the generation and decay of radicals. The initial section of the curve (small shear angles) corresponds to the biggest rate of radical generation (ruptures of bonds) when the decay rate can be neglected. As the shear angle increases, the decay rate grows as the slope of the kinetic curve decreases. At $\alpha = 45^\circ$ the recombination effects are

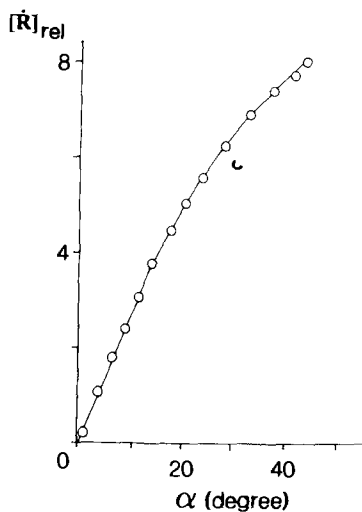


FIG. 2. Radical yield kinetics during shear deformation application. The largest shear deformation angle $\alpha = 45^\circ$.

very essential. The concentration of radicals is seen to increase by eight times at $\alpha = 45^\circ$ with the sample weight being (0.43 ± 0.05) mg. The concentration of radicals is $(2 \pm 1) \times 10^{19}$ spin/g. Consequently, only one out of 100–200 molecules of the sample dimer dissociates under shear mechanical stress. Knowing that the energy of breaking one $-C_\alpha-C_\alpha$ bond is 72 KJ/mole (6) (the bond is the weakest), we obtain that the energy in the channel of chemical dissociation of bonds is equal to $(4.25 \pm 2.00) \times 10^{-4}$ J (with no account taken of the recombination processes).

It is more difficult to determine the amount of energy consumed exclusively for breaking chemical bonds.

As the shear angle increases, the radical yield passes through a maximum at $\alpha \approx 250^\circ$ (Fig. 3), and the recombination process becomes prevalent. Let us assume that at all α values the rate of radical generation is constant and their recombination can be neglected.

Extrapolating the initial linear section of the kinetic curve to the region of the largest

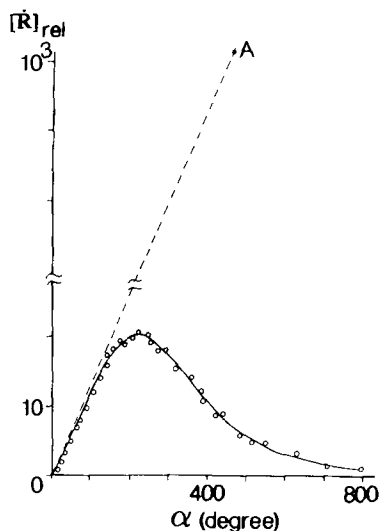


FIG. 3. Radical yield kinetics during shear deformation. The largest shear deformation angle $\alpha = 800^\circ$. See comments in the text.

shear angle $\alpha \approx 500^\circ$ (a dotted line, Fig. 3) we obtain the largest possible concentration of radicals (point A) of about 10^{21} spin/g. Therefore, with account taken of the recombination of radicals, the highest energy in the chemical dissociation channel (E_R) is $\approx (5.12 \pm 0.50) \times 10^{-2}$ J.

The resulting figures are listed in Table I, which presents the absolute values of all experimentally measured energy contribu-

TABLE I
ENERGY BALANCE OF SHEAR STRAIN
UNDER PRESSURE

	Energy (J)	K (%)
E	5.33 ± 0.40	100
Q	4.70 ± 0.35	88 ± 9
A_m	0.55 ± 0.10	11 ± 2
E_R	$(5.12 \pm 0.50) \times 10^{-2}$	0.9 ± 0.01

Note. E = total energy, Q = overall heat flow, A_m = energy of anvil elastic deformation, E_R = energy of rupture of chemical bonds of mechano-dissociated molecules, K = share of total energy.

tions (expression (1)) and their share in percent of the total energy (K). The member U is the sum of experimentally nonmeasurable contributions by mechano-emission, new surface formation, and crystalline lattice distortion. Naturally, this member is not included in the sum of the experimentally measured contributions (E), taken conventionally for 100%. The share of each contribution is taken at the highest value, their actual values in the overall energy balance being lower. The measured value of the overall energy consumed in the process of sample deformation is (5.33 ± 0.40) J.

The major part of the energy (Q), (4.70 ± 0.35) J or 88%, is converted into heat. The energy is stored in the form of anvil elastic deformation under shear (A_m) is (0.55 ± 0.10) J, which is 11% of the total energy. Let us call the shear in the total energy balance of the energy consumed to break chemical bonds the chemical efficiency of elastic deformation. Then, with no account taken of the recombination processes at the shear angle of 45° , the chemical efficiency does not exceed $10^{-2}\%$. For the process of chemical bond rupture exclusively and the largest shear angle $\alpha \approx 500^\circ$ the biggest value of the chemical efficiency does not exceed $(0.9 \pm 0.1)\%$. The value of this parameter will never exceed 1% even if we assume hypothetically that shear deformation leads to dissociation of all the dimer molecules in the sample.

The value of the chemical efficiency is determined by the microscopic mechanism of radical formation under shear strain. The radicals are localized at the structural defects—dislocations, microcracks, micrograins, etc. The biggest amount of energy stored in a solid (the energy of lattice deformation) does not exceed 10% (9). The fact that the energy differs from the chemical efficiency by 2–3 orders of magnitude indicates that the structural defects are mostly nonparamagnetic and are due to bond deformation rather than rupture.

The chemical efficiency is determined by the competition of two processes which accompany the shear deformation of a molecular crystal. These processes are the rupture of intermolecular Van der Waals bonds, on the one hand, and the rupture of chemical intermolecular bonds in dimer molecules, on the other hand.

The first process yield no radicals, the second one yields radicals. The low chemical efficiency is the result of the fact that “slipping” aggregates of molecules—micrograins with respect to each other in the process of plastic flow predominates over the rupture of internal bonds in some molecules. This feature is mostly typical for molecular crystals whose plastic flow is described by the microscopic mechanism of molecular friction. This problem will be discussed more thoroughly in the following articles on the subject.

Under shear deformation a solid acquires the properties of a specific viscous “quasiliquid.” Its “molecule” is a microcrystal—the solid grain which is the result of intensive milling accompanied by active surface development. With inorganic compounds (Si, Ge, diamond) the size of a grain is considerably larger than the lattice constant and is estimated to be $\sim 10^3 \text{ \AA}$ (10, 11).

The elastic deformation energy (A_m) of the anvil is adequate to the energy consumed to overcome the “viscosity” of such a “quasiliquid” under plastic flow. Its properties are determined by the size and the diffusion characteristics of grains, the intensity and energy of their mutual “engagement” (forced mass transfer), the external pressure, and the rate of shear deformation application.

As seen from Table I, the share of this energy is no more than 11%.

Thus, we estimated quantitatively the energy consumed during shear deformation of a polycrystalline sample of arilinedandione dimer under pressure. It was established that 88% of the energy is converted to heat,

while 11% is transferred in the form of anvil elastic deformation to the operating device. The biggest share of total energy transformed into the chemical one—rupture of bonds—is low and does not exceed 1%.

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