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Kinetics and Nature of Mechanochemical Reactions

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Certain general characteristics of the kinetics, mechanism, and nature of the primary step in chemical reactions initiated by mechanical action in various low- and high-molecular-weight substances have been examined. The formal kinetics of mechanochemical reactions occurring in constant and variable mechanical fields have been analysed in Section II. In constant fields the rate of the process is determined by the rate of the primary chemical stage and in variable fields the rate-limiting stage may be the supply and absorption of elastic energy. Section III deals with the mechanisms of the conversion of elastic into chemical energy. The chemical changes in a substance are associated either with the elastic deformation of the electron shells of the reacting species or with the generation of non-equilibrium vibrationally excited states in the process of dissipation of elastic energy as heat. Under certain conditions, local short-lived regions of intense absorption of elastic energy may play a major role. Data concerning the nature of the primary active species in mechanochemical reactions —free radicals in various charged states—are discussed in the last section.
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I. INTRODUCTION

The studies in various fields of mechanochemistry are widely scattered. The mechanochemistry of polymers [1-9] is separated from studies on mechanochemical reactions in solids (the German term is tribochemical reactions)[10-16]; reactions initiated by ultrasonic waves [17-22], chemical reactions in solids at high pressures with shear stress[23-27], reactions in shock waves [28,29], the phenomenon of detonation on impact [30,31], corrosion under stress [32-34], cryogenic processes [35-37], etc. occupy a special place. All these fields have not been combined into a single discipline and one can only hope that ten years hence mechanochemistry, the science of the initiation and acceleration of chemical reactions in gases, liquids, and solids under the action of elastic energy, will be treated uniformly as part of the field of non-thermal chemical reactions together with radiation chemistry, photochemistry, and other processes.

One may suppose that, despite the historic separation of individual branches of mechanochemistry and despite the differences in the methods used to create mechanical fields and the differences in physicomechanical properties of low- and high-molecular-weight substances in various phase states, there exist common characteristics in the thermodynamics, kinetics, and the nature of the primary step in many classes of mechanochemical reactions. In this review an attempt has been made to isolate, using the simplest and most thoroughly investigated reactions, certain characteristic features of the kinetics and mechanisms of mechanochemical reactions. The main examples have been taken from the mechanochemistry of polymers: in linear macromolecular systems it is simpler to analyse the specific features of the phenomenon; extension to three-dimensional systems probably does not involve fundamental changes in the mechanism of the processes.

II. FORMAL KINETICS OF MECHANOCHEMICAL REACTIONS

Usually the primary data on the mechanisms of chemical reactions are obtained in kinetic studies, for example, in measurement of the variation of the reaction rate constant with temperature, concentration, and other parameters. In radiation chemistry the rate of reaction is not understood as the change of concentration per unit time but as the change of concentration as the result of the absorption of a specified energy dose (the energy yield G is the number of species which have reacted after absorption of 100 eV of energy) and the principal parameters are the dose and the dose rate of the radiation. Similarly in photochemistry the quantum yield of the reaction is primarily determined.

Unfortunately in mechanochemistry an equally clear-cut energy approach has not been developed and energy estimates are encountered extremely rarely. This is associated in the first place with methodological difficulties in measuring the amount of mechanical energy absorbed and also with the indeterminacy of the stresses which actually operate and in the second place with the lack of clear concepts concerning the nature of mechanochemical reactions. As a rule, the appearance of hypotheses about the mechanism of a particular process is accompanied by the simultaneous development of an energy approach in the analysis of its kinetics (a good example of this is ultrasonic chemistry) [38-40].

Mechanochemical reactions constitute a complex multistage process, which include stages involving mechanical deformation of a substance (the supply and absorption of mechanical energy), the primary chemical reaction proper, and various secondary processes. In the kinetics of mechanochemical reactions it is possible to isolate two limiting cases: the first corresponds to conditions under which the rate of the entire process is determined by the rate of the primary mechanochemical stage and in the second the rate-limiting stage is the supply or absorption of mechanical energy. Thus the ratio of the rates of absorption of elastic energy and of the mechanochemical reaction proper constitutes a criterion for the subdivision of mechanochemical processes into two types (based on their kinetics).

1. Kinetics in Constant Mechanical Fields

The first case may obtain under conditions where the substance is in a constant field of mechanical stresses.

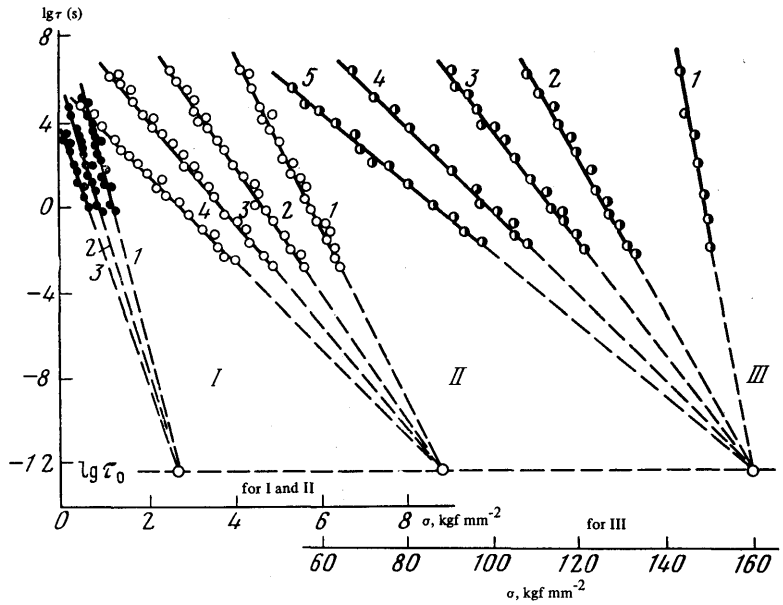


Figure 1. Temperature and time variation of tensile strength: I) rock salt [1) 400°C; 2) 500°C; 3) 600°C]; II) polycrystalline aluminium [1) 18°C; 2) 100°C; 3) 200°C; 4) 300°C]; III) Kapron fibre [1) −180°C; 2) −120°C; 3) −75°C; 4) +20°C; 5) +80°C].

When a constant load is applied, elastic energy is absorbed rapidly and the stage involving elastic deformation may be resolved in time from subsequent slower chemical reactions. Under such conditions, the rate of the mechanochemical process should be determined by the rate of the primary chemical reaction initiated by elastic stresses and the variation of the rate constant with external parameters should reflect the characteristics of this primary reaction.

An example of a process of this type may be degradation of macromolecules on monoaxial extension of polymeric films or fibres by the application of a constant stress. According to the kinetic concept of strength[8], the breakdown of the specimen occurs as a result of the dissociation of mechanically strained macromolecules.

In the idealised case of a uniform distribution of stresses throughout the specimen (under the condition σ = const.), the number of chains bearing the load will decrease with time according to the law

$$N \simeq N_0 \exp(-k_{\text{mech}}\tau). \qquad (1)$$

Here it is assumed that the rate of dissociation of the strained bonds is described by an equation for first-order kinetics (see, for example, Tobolsky and Eyring[41]) and k_{mech} is the rate constant for the mechanical dissociation of polymeric chains. Catastrophic breakdown of the specimen begins when $k_{\text{mech}}\tau = 1$, i.e. the time up to the rupture or, what amounts to the same thing, the lifetime of the specimen τ_{life} is inversely proportional to the rate constant k_{mech}. In other words, the time up to the rupture of the specimen coincides with the characteristic time of the reaction involving the breakdown of the strained polymeric chains and measurements of the lifetime under various stress conditions (medium, temperature, the stress itself, etc.) should in principle throw light on the nature of the primary mechanochemical step.

The formulation of Eqn. (1) only reveals the possibility of a relation between the lifetime and the rate constant for the mechanical dissociation of bonds. A rigorous kinetic theory, which is now being developed, should take into account many aspects of the phenomenon: the structural inhomogeneity of the material and the form of the distribution functions for the stresses throughout its bulk, the variation of the rate constant with the degree of polymerisation and with the magnitude of the effective stresses, secondary free-radical reactions, and the probability of a chain propagation of degradation, etc.

Fig. 1 presents[8] the results of measurements of the variation of the lifetime ($\tau_{\text{life}} \propto 1/k_{\text{mech}}$) of three materials—rock salt, polycrystalline aluminium, and Kapron† fibre with stress (monoaxial extension at σ = const.) at different temperatures. For each material, the $\tau_{\text{life}} = f(T, \sigma)$ relation obeys the Zhurkov equation[42] over a fairly wide range of temperatures T and stresses σ:

$$\tau_{\text{life}} = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{RT}\right). \qquad (2)$$

where R is the gas constant and τ_0, U_0, and γ are constants for the given material; γ depends on the nature and history of the specimen and is called the structural factor. The constant τ_0 is always close to magnitude to the vibration period of the atoms in the crystals (about 10^{-13} s). Table 1 presents[8] the results of the calculation of the constant U_0 from measurements of the lifetime at σ = const. and includes for comparison the corresponding values of E—the heats of sublimation of metals or the

†A type of nylon produced in the USSR (Ed. of Translation).

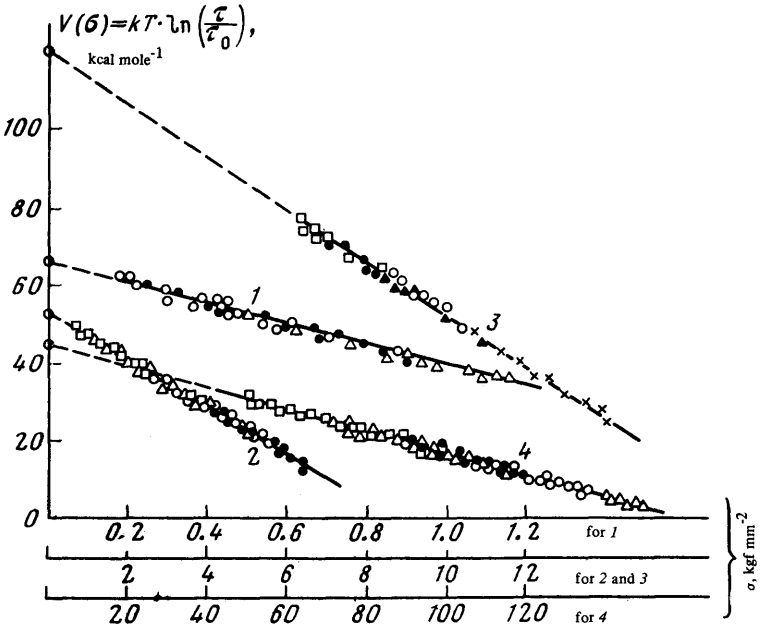


Figure 2. Variation of the effective energy barrier $U = RT\ln(\tau_{life}/\tau_0)$ with tensile stress σ: 1) rock salt; 2) polycrystalline aluminium; 3) polycrystalline platinum; 4) Kapron fibre.

activation energies for the thermal degradation of polymers. A graphical determination of the constant U_0 is illustrated by the data in Fig. 2. [8] To a first approximation, U_0 does not differ markedly from the energy of interatomic bonds.

Table 1. Comparison of the constants U_0 with the heats of sublimation of metals and the activation energies for the thermal degradation of polymers [8].

Substance	U_0, kcal mole^{-1}	E, kcal mole^{-1}
Platinum	120	127
Iron	100	97
Copper	81	80
Aluminium	53	55
Zinc	30	31
Rock salt	68	–
Polytetrafluoroethylene	75	76
Polypropylene	56	58
Kapron	45	43
Poly(vinyl chloride)	35	32

The agreement of τ_0 and U_0 with molecular constants confirms the hypothesis that the kinetic behaviour of mechanochemical processes in constant mechanical fields are indeed determined by the characteristics of the primary chemical reaction stage.

Reactions in constant mechanical fields include also the electrochemical dissolution of metals under the simultaneous influence of mechanical stresses (corrosion under stress) [32-34,43-45]. In this case measurements are made of the so called polarisation diagrams: the variation of the anodic (or cathodic) current i with the electrical potential φ. [43] In the absence of mechanical stresses, these values are related as follows:

$$i = K_{el}\exp\left(\frac{\alpha\varphi - \varphi^0}{b}\right), \qquad (3)$$

where K_{el} is a constant, φ^0 the standard electrode potential of the metal, $b = RT/zF$, z is the valency of the ion, and F the Faraday.

Line *1* in Fig. 3*a* illustrates [43] this relation in terms of a plot of φ against $\lg i$. In a mechanically deformed metal the linear relation between φ and $\lg i$ persists, but, over a certain range of stresses, the corresponding straight lines are displaced upwards to an extent which is greater for increasing relative deformation. The data in Fig. 3*b* illustrate [44] the relation between the mechanochemical effect (the variation of the corrosion current—curve *2*) with increase in strength on deformation. Evidently, in the stage involving an intense increase in strength on deformation (region *E*), the effect increases and in the concluding stage, when the planar accumulations of dislocations break down, the effect diminishes [34].

Thus, in the stage involving an increase in strength (region *E*), the metal "becomes less noble" under the influence of mechanical stresses—the standard potential φ^0 diminishes by an amount $\Delta\varphi^0$, which depends on the degree of increase in strength $\Delta\sigma$ due to deformation ($\Delta\sigma$ is the amount by which the stress applied to the material exceeds the microscopic yield point). According to the literature [34,35],

$$\Delta\varphi^0 = -\frac{nR}{\bar{\alpha}R'ZF}\Delta\sigma,$$

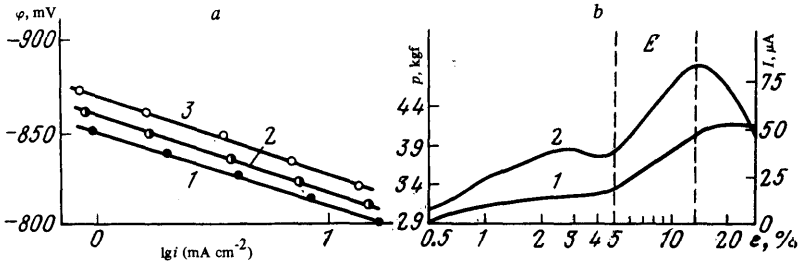


Figure 3. Kinetics of corrosion under stress: *a*) variation of the anodic current with electrical potential for steel 20 in 1.1 *N* sulphuric acid at 20 (°C ?) [degree of deformation (%): 1) 0; 2) 10; 3) 30]; *b*) variation of the corrosion current (curve *2*) and the extending force (curve *1*) with the degree of deformation; 08SV steel in 7 *N* sulphuric acid solution; rate of extension 34% per minute.

where n is the number of coplanar dislocations in planar accumulations, $\bar{\alpha}$ the coefficient in the equation relating the density of dislocations to the degree of deformation of the metal, $R' = kN_{max}$, k is the Boltzmann constant, and N_{max} the maximum possible density of dislocations (in metals $N_{max} \simeq 10^{12}$ cm^{-2}). The general equation for the kinetics of electrochemical or chemical dissolution of a metal under the simultaneous influence of mechanical stresses is of the form

$$i = K_{\text{electrochem}} \exp\left(\frac{A}{RT} + \frac{n\Delta\sigma}{\bar{\alpha}R'T}\right), \qquad (4)$$

where A is chemical or electrochemical affinity. The second term in the exponent reflects the effect of mechanical stresses on the chemical potential of the metal, which determines the rate of the process in a constant mechanical field.

2. Reactions in Variable Mechanical Fields

The second limiting case of the kinetics of mechanochemical processes [9,46] corresponds to conditions under which the rate of supply or absorption of elastic energy is much less than the rate of reaction initiated as a result of the absorption of this energy. Such conditions may obtain, for example, under the influence of periodic stress application at frequencies in the range of the intrinsic mechanical losses of the material. This may occur in various types of fatigue tests, under the influence of ultrasonic waves on polymer solutions, in the comminution of solids in mills, in the breakdown of the surface layer of materials on friction, etc.

When the material is acted upon in cyclic processes under steady-state conditions, the time-average mechanical power supplied to the specimen remains constant. In each single stress-application cycle part of the mechanical energy is absorbed by the material and after a certain number of cycles an average steady-state degree of deformation of the material and a corresponding average level of absorbed energy ΔE_{def} are established. The rate of absorption of energy is directly proportional to the power supplied W and the rate of dissipation is equal to the average level ΔE_{def}. Under steady-state conditions,

$$\alpha W = \frac{1}{\tau_r}\Delta E_{def} \quad \text{or} \quad \Delta E_{def} = \alpha\tau_r W \qquad (5)$$

where α is a coefficient the value of which is close to the mechanochemical efficiency of the process (efficiency $< \alpha < 1$) and τ_r is the relaxation time of the stresses.

Real materials are inhomogeneous and the deformation energy is non-uniformly distributed among the system of bonds: the form of the distribution function is in general unknown. To make the treatment concrete, one may suppose that the distribution is fairly steep and is described by an exponential law, i.e. the fraction of bonds characterised by a deformation energy E_{def} and above is proportional to $\exp(-E_{def}/\Delta E_{def})$. Moreover, since the stresses operate periodically, there is a constant redistribution of energy in the system with a characteristic time $1/A$, which depends both on the frequency of application of mechanical action and on the intrinsic relaxation time of the material.

When the rate of the mechanochemical process is limited by the redistribution of mechanical energy in the system, the rate constant should be proportional to the rate of redistribution of deformation energy among the bonds (A, s^{-1}) and the probability of the accumulation at a given bond of a certain critical deformation energy E^*_{def} sufficient to initiate the mechanical reaction. Therefore, considering Eqn. (5), [46] we then have

$$k_{\text{mech}} \simeq A \exp\left(-\frac{E^*_{def}}{\alpha\tau_r W}\right), \qquad (6)$$

Outwardly Eqn. (6) resembles the Arrhenius equation for the variation of the unimolecular decomposition rate constant with temperature, but the significance of the constants is in this case quite different. The pre-exponential factor in Eqn. (6) should be close in magnitude to the rates of relaxation of stresses and not to the vibration frequencies of atoms (10^{12}–10^{13} s^{-1}). The temperature in the exponent in Eqn. (6) is replaced by the rate of supply of mechanical energy. One must stipulate that the distribution function of stresses may also have a different form with a corresponding change in the form of Eqn. (6).

The variation of the rate constant for a mechanochemical reaction with the rate of supply of mechanical energy in variable fields has been measured (Fig. 4) [40,46] in several cases: in ultrasonic degradation of polystyrene in dilute solutions [40], in the comminution of poly(methyl methacrylate) in a vibration mill [46], and in dynamic tests on vulcanised rubbers [47]. In the first two cases the range of rates is very wide (W changes by a factor of 20,

which is much more than usually happens in measurements of the activation energies for thermal reactions where the temperature changes at most by a factor of 2–3).

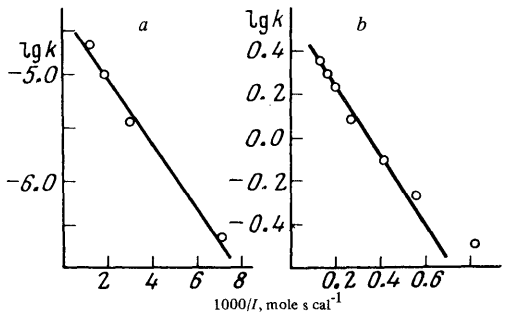


Figure 4. Variation of the rate constant for mechanical degradation with the rate of supply of mechanical energy (lg k plotted against $1000/I$): *a*) comminution of poly(methyl methacrylate) in a vibration mill; *b*) ultrasonic degradation of polystyrene.

Very low values of the pre-exponential factor (10^1–10^{-4} s^{-1}) were obtained throughout (Table 2). This confirms the hypothesis that the rate of the process is indeed limited by the rate of redistribution of elastic energy in the system, i.e. by the physicomechanical properties of the material. Unfortunately the constants α and τ_r are unknown and therefore E^*_{def}, i.e. the minimum deformation energy necessary to initiate the reaction, cannot be determined. To estimate the order of magnitude of the constant τ_r, one may suppose that $\alpha \simeq 10^{-2}$ (this is confirmed by the energy yields for degradation) and $10^4 < E^*_{def} < 10^5$ cal mole^{-1}. Then we have for poly(methyl methacrylate):

$$\frac{E^*_{def}}{\alpha\tau_r} = 700 \text{ or } \tau_r = \frac{10^4 - 10^5}{700 \cdot 10^{-2}} \simeq 10^3 - 10^4 \text{ s}^{-1}.$$

As was to be expected, the relaxation time τ_r and the constant $1/A$ are of a similar order of magnitude.

Table 2. The constants A and $E^*_{def}/\alpha\tau_r$ in Eqn. (6) for various materials.

Material	Conditions of measurements	A, s^{-1}	$E^*_{def}/\alpha\tau_r$	Refs.
Poly(methyl methacrylate)	Dispersion in vibration mill	10^{-4}	70	46
Polystyrene	Ultrasonic degradation in solution	3÷5	3700	40
Vulcanised rubber	Dynamic tests	10^{-2}	—	48

Eqn. (6) has several important consequences. Firstly, in variable mechanical fields the efficiency of the mechanochemical process should increase sharply with the intensity of mechanical action, the conditions of maximum concentration of mechanical energy per unit volume of the substance and per unit time being the most favourable. When the intensity is low, the characteristic effects associated with the contribution by non-relaxed stresses (the ΔE_{def} level) may not appear at all.

Secondly, in mechanochemical processes in variable fields, the frequency of application of mechanical action plays a major role. Thus in the mechanical degradation of poly(methyl methacrylate) in a vibration mill, $\tau_r \simeq 10^3$ to 10^4 s. Consequently, when the process is interrupted for a period of this duration, the rate of the mechanochemical reaction should fall appreciably. Fig. 5 presents [46] results of the measurements of the rate of degradation of poly(methyl methacrylate) under two types of conditions: continuous and periodic (duration of interruption 300 s). In degradation with interruptions the rate of bond dissociation fell almost by a factor of 2.

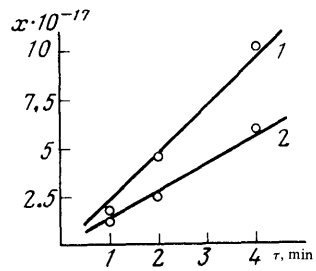


Figure 5. Mechanical degradation of poly(methyl methacrylate) in a vibration mill (x = number of bonds dissociated; temperature 100°K): 1) continuous conditions; 2) periodic conditions (5 min interruptions).

In solids the frequency of application of mechanical action should probably fall within the limits of the frequency spectrum of mechanical losses, including the low-frequency region (see, for example, Fitzgerald [49]). For mechanochemical reactions in gases, it is important that the frequency should correspond to the relaxation time for the transmission of energy from translational to vibrational degrees of freedom of molecules (the phenomenon of the dispersion of sound in gases [17]).

The temperature variation of the rate of a mechanochemical reaction is not explicitly included in Eqn. (6), but the constants of this equation, related to the relaxation times of the stresses, depend on temperature. For example, in polymers they should change sharply in the region of structural transitions, primarily near the glass temperature T_g. Therefore one may expect that, for degradation in variable mechanical fields, the form of the temperature variation of the rate of degradation will alter as T_g is approached. We may note for comparison that under static conditions (constant mechanical fields), when the rate constant for degradation is determined by the molecular constants τ_0 and U_0, the temperature variation of the rate of degradation of polymers does not change near T_g (see, for example, Fig. 1).

Polukhina and Baramboim [51] measured simultaneously the rate of mechanical degradation (comminution of polymers in a vibration mill) and the modulus of elasticity (the rate of propagation of longitudinal sonic waves C_e).

The relation between k_{mech} and C_e for polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) in the temperature range 223–303°K is presented in Fig. 6.[51] Below T_g ($10^{-6}C_e$ cm $s^{-1} > 15$), the points corresponding to the three different polymers fit satisfactorily on a common section of line A. Above the glass temperature ($10^{-6}C_e$ cm^{-1} $s^{-1} < 10$) the nature of this relation changes sharply (straight line *B*). These data confirm yet again the hypothesis that in variable mechanical fields the rate of a mechanochemical reaction and the temperature variation of k_{mech} are closely related to the physicomechanical properties of the substance, i.e. the rate-limiting stage is the redistribution of elastic energy.

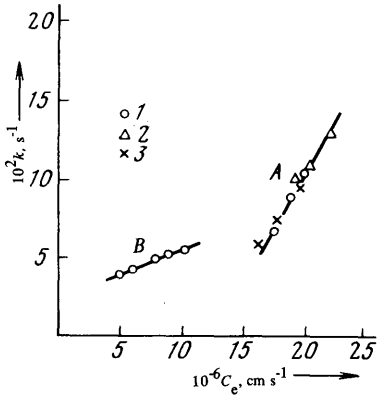


Figure 6. Relation between the rate constant for the mechanical degradation of polymers and the rate of propagation of longitudinal sonic waves C_e in the temperature range 223–303°K; polymer: 1) poly(vinyl acetate); 2) polystyrene; 3) poly(methyl methacrylate).

3. Characteristics of the Kinetics of Reactions in Polydisperse Systems

The conclusions concerning the rate-limiting stages in the kinetics of mechanochemical reactions are probably valid for a wide range of processes in both low- and high-molecular-weight systems. Eqns. (2), (4), and (6) explain the nature of the rate constant. However, frequently the rate constant for a mechanochemical reaction does not remain constant during the mechanical treatment of the substance. Its variation may be due to changes in the properties of the material: in the type of distribution of stresses and structural defects, degree of dispersion, etc. Below we consider the characteristics of the kinetics of mechanochemical reactions which are typical for polydisperse systems. Examples of such reactions are those in polymers (distribution with respect to chain length) and comminution of solids (distribution with respect to particle size). The kinetics of reactions in polydisperse systems have been analysed in greater detail for the mechanical degradation of macromolecules [52].

The absorption of mechanical energy by macromolecules and at the same time the rate of the mechanochemical reaction depend on the length of the macromolecule—the degree of polymerisation. As a result of the dissociation of bonds, the degree of polymerisation falls and therefore, under steady-state conditions of mechanical treatment, the rate of bond dissociation will not be constant: its variation will be caused by changes in the molecular weight distribution of the polymeric substance during the reaction. Other conditions being equal, the kinetic equation for the degradation is determined by the form of the variation of the elementary rate constant with the length of the polymer chain. The formal kinetics of such reactions have been developed by Palov [52] and the subsequent treatment has been taken from his paper.

We shall denote the rate constant for the decomposition of molecules with a length equivalent to z units by $k(z)$. Then the following relation holds for the rate of increase of the number of molecules in the system:

$$\frac{dn}{d\tau} = \sum_1^\infty k(z) n_z, \qquad (7)$$

where n is the total concentration of molecules and n_z the concentration of molecules with a length z. After dividing both parts of Eqn. (7) by $n = \sum_1^\infty n_z$, we obtain

$$\frac{d\ln n}{d\tau} = \frac{d\ln n/n_0}{d\tau} = \frac{\sum_1^\infty k(z) n_z}{\sum_1^\infty n_z} = \overline{[k(z)]}, \qquad (8)$$

where n_0 is the initial concentration of the species and $\overline{[k(z)]}$ is by definition the number average of $k(z)$. Bearing in mind that $n/n_0 = P_0/P$, where P_0 and P are the initial and actual number-average degrees of polymerisation, we finally obtain

$$\frac{d\ln(P_0/P)}{d\tau} = \overline{[k(z)]}. \qquad (9)$$

This equation describes the rate of degradation as characterised by the left-hand side in terms of the average rate constant for the decomposition of the macromolecules. Since it is impossible to predict beforehand the type of variation of $k(z)$, in the general case Eqn. (9) cannot be given a concrete form. If it is assumed that the degradation rate constant is independent of the length of the macromolecule [$k(z) = k$], then

$$\frac{d\ln(P_0/P)}{d\tau} = k \text{ and } P = P_0 \exp(-k\tau). \qquad (10)$$

When the rate constant is directly proportional to the length of the polymeric molecule $k(z) = k_1 z$, the kinetic equation $d\ln(P_0/P)/d\tau = k_1 P$ assumes the following form after solution:

$$\frac{1}{P} - \frac{1}{P_0} = k_1\tau \qquad (11)$$

which is characteristic of the so called random degradation.

Random degradation occurs on ultrasonic treatment of polymers in cavitation fields when chains are actually ruptured by active radicals formed when the cavities are flooded and not as a result of the direct action of shear stresses. The characteristic changes in the molecular weight distribution have been examined by Jellinek and White [53].

Using Eqn. (9), it is also possible to solve the converse problem, the determination of the form of the variation of the elementary rate constant with chain length from data on the decrease of the degree of polymerisation in the degradation process. We shall postulate that $k(z) = \delta k(P)$, where δ is a coefficient which depends on the variance in

the distribution of molecules with respect to length; then the variation of $d\ln(P_0/P)/d\tau$ with P is the same as the variation of $k(z)$ to within the coefficient δ. Figs. 7*a* and 7*b* show [52] the variation of $k(z)$ plotted by graphical differentiation for the ultrasonic degradation of polystyrene in solution. The kinetic curves analysed were taken from different studies [40,50] with markedly differing conditions (concentration, frequency, and ultrasonic power). Although the form of the $k(z)$ curves is different, they both show clearly the existence of the so called degradation limit—the minimum chain length on reaching which the degradation rate constant falls almost to zero. Thus under the specified conditions mechanical degradation is possible only for macromolecules with lengths above a specific limit.

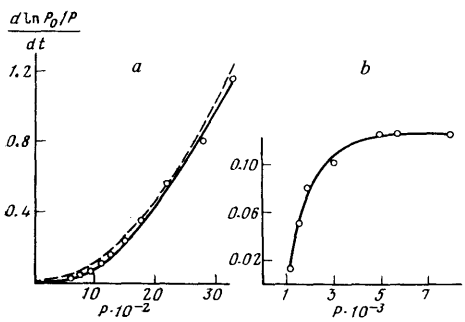


Figure 7. Variation of the rate constant with the degree of polymerisation in the ultrasonic treatment of polystyrene solutions: *a*) Schmid's data [54]; *b*) data of Berlin and El'tsefon [40].

The existence of the limit, associated with a sharp decrease of the rate of the mechanochemical process when the particle size diminishes, is the most characteristic feature of reactions in polydisperse systems. The limiting particle size enters into almost all the kinetic equations: the empirical Schmid equation [54], the Baramboim equation [1] corresponding to the degradation of macromolecules at "weak" bonds, the Schrader equation for the comminution of solids, and others. With increase in particle size, the rate constant rises sharply. Under these conditions, the quadratic relation $k(z) = k_2z^2$ is comparatively common. In the kinetics of the mechanical degradation of macromolecules, the Schmid equation [52] corresponds to the quadratic law. A relation of the type $k(z) = k_2z^3$ was observed also in the comminution of solids in surface-active media [55].

Rigorous analysis of kinetic data combined with the derivation of a relation for $k(z)$ is apparently possible only for mechanochemical processes in liquid media (degradation of polymers in solution, dispersion of solids in an aqueous medium, etc.) when the individual species are fairly well stabilised.

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The above very brief discussion of the formal kinetics of mechanochemical reactions shows that the rate of the process may be related to various parameters which depend on external conditions: to the inhomogeneity of the distribution of mechanical stresses throughout the bulk of the substance, the relaxation times of the stresses, and the characteristics for the absorption of mechanical energy by species of different size; finally, when the rate-limiting stage is the primary chemical step, the bond strength and vibration frequency enter into the kinetic equation.

Other factors with a marked influence on the rate of mechanochemical reactions undoubtedly exist. These include primarily the effect of mechanical stresses on the rate of diffusion of species in the condensed phase. This problem is not considered in the present review.

III. POSSIBLE MECHANISMS OF MECHANOCHEMICAL REACTIONS

Mechanochemical reactions differ from other chemical reactions initiated by physical methods in that they can develop with a comparatively low average level of elastic energy per unit volume of the substance. In photochemistry the energy quanta are comparable to the excitation energies for the electronic levels of the molecules. In radiation chemistry the energy of the particles acting upon the substance greatly exceeds the energies of the chemical bonds and one of the tasks in investigations of this kind is to follow the pathways in the dissipation of the excess energy. In the analysis of a mechanochemical process an attempt is made in the first place to deduce the mechanisms of the concentration of energy at individual bonds or in small local volumes in the substance.

Apparently there exist two direct mechanisms for the conversion of elastic into chemical energy which are specific to mechanochemistry: the first of these is associated with the deformation of the electron clouds of the reacting species (a change in the interatomic distances, valence angles, etc.) and the second with the vibrational excitation of the bonds during the dissipation of elastic energy as heat. The first mechanism may be referred to as the equilibrium mechanism, since the equilibrium Maxwell–Boltzmann distribution of energy among the degrees of freedom persists in the system, while the second is a non-equilibrium mechanism.

1. The Equilibrium Process

When a chemical bond is extended, its energy diminishes. At equilibrium, the deformation energy is

$$U_{\text{def}} = \int_{r_0}^{r} f_U dr \quad \text{or} \quad U_{\text{def}} = \int_{V_0^*}^{V^*} \sigma_U dV^*, \tag{12}$$

where f_U and σ_U are the force and the stress acting on the bond, r_0 and r are the length of the initial and the deformed bond, and V_0^* and V^* are the corresponding activation volumes; $V^* = rs^*$ and s^* is the effective cross-section of the molecule (bond) is relation to the applied stress.

In calculations of the deformation energy and the activation energy for bond dissociation when a force f_U operates, one usually employs the Morse potential function. The variation of the activation energy for decomposition with the force f_U is [56]

$$\frac{U}{U_0} = \sqrt{1-\frac{f_U}{F_0}} - \frac{f_U}{2F_0}\ln\frac{1+\sqrt{1-\frac{f_U}{F_0}}}{1-\sqrt{1-\frac{f_U}{F_0}}}, \tag{13}$$

where F_0 is the ultimate strength of the bond. A plot of the function $L(f_U)$ is presented in Fig. 8 (curve *1*). Under real conditions, a specific group of bonds are deformed; the characteristic features of the energy relations of the process in this case have been analysed [57]. The functions $U(f_U)$ corresponding to the extension of sections of the macromolecule with lengths equivalent to 10, 20, 50, and 100 bonds are compared in Fig. 8 (curves *2–5*) [57].

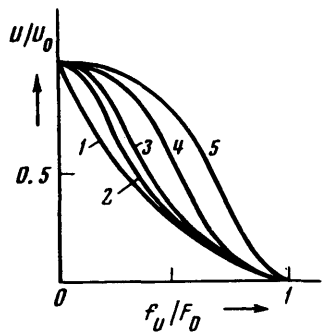


Figure 8. Plot of the function $U(f_U)$; number of bonds in deformed section of chain: 1) ∞; 2) 100; 3) 50; 4) 20; 5) 10.

Eqn. (13) in fact describes the simplest case of the conversion of mechanical into chemical energy and is used to account for the dissociation of mechanically strained bonds. Eqn. (13) is approximate: in complex molecules account must be taken of the deformation of valence angles, angles of internal rotation, and the interaction between atoms not linked by valence bonds [58].

The activation energy for thermal decomposition reactions in the Arrhenius equation is the same as the bond energy U_0:

$$k = k_0 \exp\left(-\frac{U_0}{RT}\right), \qquad (14)$$

where k is the decomposition rate constant (s^{-1}) and k_0 the pre-exponential factor, close to 10^{12}–10^{13} s^{-1} in order of magnitude. When the bonds are mechanically strained, U_0 may be replaced by the expression for the strength of an elastically deformed bond [$U(f_U)$, see Fig. 8]:

$$k_M = k_{0,M} \exp\left(-\frac{U(f_U)}{RT}\right). \qquad (15)$$

An analogous approach based on estimates of the decrease of the energy barrier to purely thermal transitions under the influence of "weak" factors is frequently employed in the analysis of the kinetics or thermodynamics of various processes (diffusion processes, migration of dislocations, effect of the medium on the equilibrium position, etc.). Thus in an equilibrium process the role of mechanical stresses reduces to a decrease of the energy barrier in the thermal reaction. A direct purely mechanical dissociation of bonds without the involvement of thermal fluctuations is possible only when stresses exceeding the bond strength F_0 are applied during a time less than the vibration period (10^{-12}–10^{-13} s). This implies that, for a bond length of the order of 10^{-10} m the rate of propagation of stresses

$$w \simeq \frac{10^{-10}}{10^{-12}-10^{-13}} \simeq 10^{2}-10^{3}\ \text{m s}^{-1},$$

must be comparable to the velocity of sound. Probably this limiting case of a purely mechanical rupture occurs under the conditions of a severe stress, for example under the action of shock waves.

The most striking example of a mechanochemical process with an equilibrium mechanism is the degradation of molecules on deformation (monoaxial extension) of polymeric films or fibres. Here all the consecutive stages of the process have been investigated experimentally.

The existence of strained bonds in the main valence chain in polymeric materials subjected to mechanical deformation has been recently demonstrated by infrared spectroscopy [59–61]. Fig. 9*a* shows [61] the variation of the form of the 975 cm^{-1} band corresponding to the skeletal vibrations in oriented polypropylene on monoaxial extension of the specimen. Under load, the position of the maximum shifts insignificantly but the line contour becomes greatly extended towards longer wavelengths, which reflects the existence of a continuous distribution of bonds overstrained to different extents. The frequency $\nu \simeq 940$–950 cm^{-1} corresponds to the bonds deformed to the maximum extent. The distribution function of external stresses with respect to the chemical bonds of the specimen, obtained by analysing the form of the line contour for $\sigma = 84$ kgf mm^{-2}, is plotted in Fig. 9*b*. [61] The distribution is extremely inhomogeneous and extends far into the region of high stresses. According to the first estimates, the maximum stresses reach $\sigma_{max} \simeq 1000$ kgf mm^{-2}; since the decomposition rate constant increases exponentially with increase of the true stress [Eqn. (15)], the degradation process should be virtually confined to bonds subjected to maximum stress.

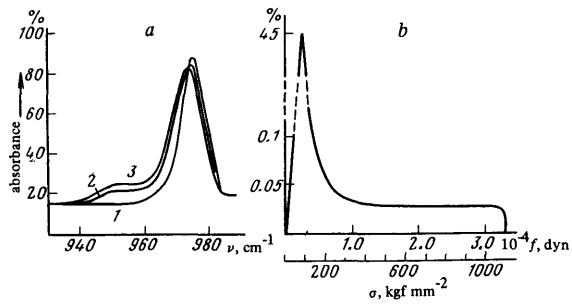


Figure 9. *a*) Variation of the absorption band contour at 975 cm^{-1} in oriented polypropylene under load [applied load (σ, kgf mm^{-2}): 1) 0; 2) 65; 3) 80]; *b*) distribution of stresses with respect to bonds.

The decomposition of the strained parts of the chains is confirmed by the formation of free radicals as a result of the dissociation of chemical bonds. Free radicals have been detected in monoaxial extension processes in various polymers directly in the resonator of an ESR spectrometer and also in cold-drawn specimens [62–71].

Under the conditions where σ = const., the rate of formation of radicals, which is proportional to the rate of dissociation of overstrained bonds, depends on the stress according to the law [64]

$$\frac{d[R^{\cdot}]}{d\tau} = B\exp(\beta\sigma),$$

where B and β are constants.

Over a wide range of variation of external parameters (σ and T), $d[R^{\cdot}]/d\tau$ agrees well with the rate of decomposition of the specimens. The logarithms of the rates of formation of radicals (corresponding to the steady-state sections of the kinetic curves) are plotted in Fig. 10 against the lifetimes of the specimens [64]; all the points are located on a single straight line with a slope of unity. The kinetics of the accumulation of radicals and the formation of submicrocracks—the primary breaks in the continuity of the material—likewise proved to be similar in polymers [71].

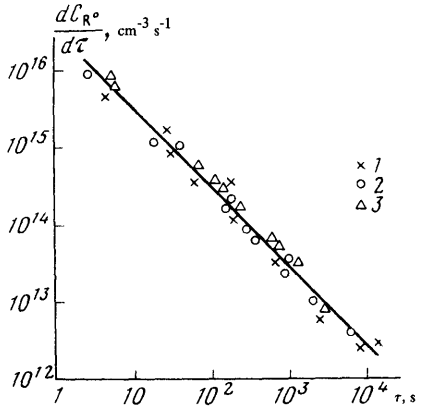


Figure 10. Relation between the rate of formation of radicals and their lifetime in oriented Kapron: 1) −50°C; 2) +18°C; 3) +50°C.

All these data and also the results of many other investigations (see, for example, Pozdnyakov and Regel' [72]) convincingly confirm the reality of the equilibrium mechanism of dissociation of deformed bonds and also the thermal-fluctuation concept of the strength of solids based on this mechanism [8].

The equilibrium processes include the corrosion of metals under stress. A theory has been developed which takes into account the effect of the perturbations of the electronic levels in metals, associated with the generation of dislocations, on the standard electrode potential [73].

2. The Non-equilibrium Process

Mechanochemical reactions can develop not only under stress but also during the removal of stresses or during their redistribution in the substance when elastic energy is transformed into thermal energy [9,46]. In a material subjected to elastic stress, the bonds of the framework of the substance which withstand the mechanical stress are mainly deformed and when the stresses are removed, thermal (vibrational) energy is liberated at these bonds. For example, at the instant of contraction of the macromolecule one may expect vibrational excitation of the bonds in the main chain. Subsequently the vibrational excitation energy is redistributed among all the degrees of freedom of the system. In other words, since the entire flux of elastic energy dissipated as heat passes through the bonds of the main chain, it follows that, for a certain definite period τ^*, these bonds are in a vibrationally excited state.

The conversion of the elastic energy of the deformed bonds (U_{def}) into thermal energy (Q_{therm}) can be represented schematically as follows:

$$U_{def} \rightarrow \Delta U_{vibr} \rightarrow Q_{therm}$$

where ΔU_{vibr} is the vibrational excitational energy of the deformed bonds.

Under steady-state conditions the concentration of the vibrationally excited bonds $[A^*]$ is defined by the relation

$$[A^*] \simeq \tau^* \frac{dU_{def}}{d\tau} . \qquad (16)$$

The lifetime of the vibrationally excited states in solids is short and hardly exceeds 10^{-10} s (i.e. corresponds to 10^2–10^3 vibration periods). During the time τ^*, the excitation energy can either pass to other degrees of freedom of the system or can give rise to a mechanochemical reaction; if τ_{chem} is the characteristic reaction time, the ratio τ^*/τ_{chem} defines the probability of reaction during the lifetime of the vibrationally excited state. When $\tau^*/\tau_{chem} \geq 1$, excitation always leads to reaction.

In order to estimate qualitatively τ_{chem}, one may postulate that, during the dissipation of elastic energy, excitation extends over a region sufficiently large to employ the concept of the vibrational temperature T^*. To a very rough approximation, $RT^* \simeq \Delta U^*_{vibr}$; then, for example for the bond dissociation energy [46] (with $\Delta U_{vibr} \gg RT$),

$$\tau_{chem} \simeq \tau_0 \exp\left(\frac{U_0}{\Delta U_{vibr}}\right) \qquad (17)$$

or in the general case

$$\tau_{chem} \simeq \tau_0 \exp\left\{\frac{U(f_U)}{\Delta U_{vibr}}\right\} .$$

For the inequality $\tau^*/\tau_{chem} \geq 1$ to hold, it is necessary that

$$\Delta U^*_{vibr} \geqslant \frac{U(f_U)}{\ln\frac{\tau^*}{\tau_0}} , \qquad (18)$$

i.e. the dissipation of energy greater than ΔU^*_{vibr} will always lead to bond dissociation. The critical energy ΔU^*_{vibr}, necessary for the dissociation of the bond during the period τ^*, is appreciably less than the bond energy U_0; when $\tau^* = 10^2\tau_0$, $\Delta U^*_{vibr} \simeq 0.2U$.

The rate of the mechanochemical reaction is proportional to the concentration of the vibrationally excited bonds $[A^*]$ and consequently [16] the rate of dissipation of elastic energy as heat is

$$\frac{dC}{d\tau} \simeq \tau^* \frac{dU_{def}}{d\tau} , \qquad (19)$$

Thus the principal feature of the non-equilibrium mechanism is that the rate of the mechanochemical reaction is determined by the rate of relaxation of the elastic energy in the system.

The non-equilibrium mechanism of mechanochemical reactions can be confirmed either by direct spectroscopic measurements or on the basis of a series of indirect chemical characteristics. There are so far no spectroscopic data in the literature, but the first chemical measurements have already been made [46]. In polymers the dissociations of the vibrationally excited sections of the chains should lead to the formation of hot macroradicals capable of further chemical reactions at low temperatures where the usual thermal reactions are retarded. The most probable reaction of hot radicals is decomposition with formation of low-molecular-weight compounds. Fig. 11 presents the results of measurements of the amount of low-molecular-weight products formed on mechanical breakdown of polyisobutylene and polyformaldehyde powders in a mill at −78°C. [46] At the same time measurements were made of the concentration of radicals by ESR. In all the experiments the amount of low-molecular-weight decomposition products (mainly monomeric compounds—isobutene and formaldehyde) exceeds by severalfold the concentration of the radicals formed, i.e. the excess vibrational energy is sufficient for the ejection of several monomeric units.

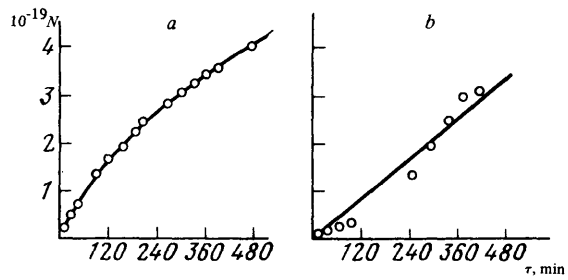


Figure 11. Formation of low-molecular-weight products in the mechanochemical disintegration of polyisobutylene (*a*) and polyformaldehyde (*b*) powders at −78°C.

The data in Fig. 11 and also the measurements of the amount and composition of volatile products evolved during the extension and after the rupture of polymeric films [72, 74,75] at higher temperatures confirm the occurrence of chemical decomposition reactions during the dissipation of elastic energy.

The possibility of the dissipation of energy after the dissociation of macromolecules [76] or after "ejection" of energy on breakdown of a solid subjected to an elastic stress [77] are usually discussed in an examination of the correspnding processes. As already pointed out, elastic deformation and non-equilibrium excitation are consecutive stages of the same process. The essential feature of the non-equilibrium mechanism [46] consists in the fact that the dissipation of an amount of the elastic energy stored by the system less than is required for its breakdown leads to the generation of non-equilibrium excited states, resulting in chemical reactions including bond dissociations and degradation of the macromolecules.

The generation of non-equilibrium vibrationally excited states was recently postulated in connection with the explanation of the kinetics of the photochemical degradation of mechanically strained macromolecules [78].

3. Local Regions of the Absorption of Elastic Energy

The direct pathways for the conversion of elastic into chemical energy discussed above do not cover all the hypotheses which have been put forward concerning the nature of mechanochemical reactions. In ultrasonic chemistry [19,79,80,81], in tribochemistry [10,82], in the theory of impact detonation of explosives [30,31], and in the chemistry of shock-waves [28], models explaining the occurrence of mechanochemical reactions as a result of the generation of local regions where elastic energy is concentrated and absorbed in the bulk or in the surface layer of the substance are widely used. The duration of the existence of such local regions is short and in various hypotheses is estimated as 10^{-3}–10^{-6} s and less, their radius being 10^{-3}–10^{-7} cm. The high pressures and the intense heating in the local regions initiate chemical reactions.

Among the existing theories of the conversion of elastic energy in small volumes within the substance, only the theories of the propagation of shock waves and cavitation have been comparatively thoroughly developed.

In ultrasonic fields and in turbulent flow, the local absorption of elastic energy is associated with the phenomenon of cavitation. Cavitation—local, point disruption of the liquid with the appearance of cavities filled by the dissolved gas and the saturated vapour of the liquid—constitutes an unusually effective mechanism of the absorption of the energy of elastic vibrations in liquids. Chemical reactions begin when the cavities collapse during the contraction phase of the sonic wave. The high pressures (10^4 atm) and temperatures (thousands of degrees) developed in the stage of the adiabatic compression of the bubble [19] lead to the excitation and dissociation of the molecules filling it; after collapse, the active species [83] (in aqueous solutions H atoms, OH radicals, hydrated electrons [84,85], etc.) pass into solution where they can initiate various oxidation reactions, polymerisation, and many other processes. Adiabatic compression of gas bubbles is among the processes involved in the initiation of the detonation of explosives by impact [86].

The brief existence of local regions with high pressures and temperatures (the shock wave front, the "hot spots" in the friction of solids, the magma–plasma model, etc.) has been confirmed by various model experiments. However, the specific features of mechanochemical reactions, the direction of the process, its rate, etc. cannot always be accounted for by purely thermal effects or the simultaneous action of heat and pressure.

The chemical and physicochemical reactions in shock waves are unusually rapid ($\tau \ll 10^{-6}$ s) [88], much more rapid than would be expected on the basis of the existing hypotheses concerning the growth of the nuclei of a new phase or the mechanisms of diffusion in a condensed phase [28]. For such ultrafast processes, the term "diffusion-free" reactions has been proposed. It has been suggested [87] that, at the pressures developed in the shock-wave front, the substance passes into the state of a single activated complex, close to the metallic state characteristic of high degrees of compression. On releasing the pressure after the passage of the shock wave, the form of matter stable when the degree of expansion corresponds to the instant of decomposition of the single activated complex becomes stabilised (this is because electronic transitions are much faster than the rearrangement of atoms). This hypothesis has been put forward to account for the polymorphic transformations of the graphite–diamond type in powerful shock waves. Outwardly similar hypotheses concerning the rapid "quenching" of different

forms of a substance, corresponding to the instant when "hot spots" exist, have been used in the mechanochemistry of solids.

The specific features of mechanochemical processes are also associated with plastic deformation and the nature of the strained state of the substance. Pressure and temperature can supply sufficient energy for the reaction to occur (they can create a "thermodynamic background" [28]), but it is also necessary that mechanical stresses should act in the same direction as the reaction. Thus, in the mechanical degradation of macromolecules, sheer or tensile stresses not only dissociate the bonds in the main chain but they also liberate from the "cages" the radicals formed and prevent their recombination. In polymerisation it is not sufficient to set up a pressure at which the density of the monomer becomes comparable to that of the polymer; it is also necessary to consider the possibility of chain propagation, which is achieved by plastic deformation of the material with simultaneous application of pressure and sheer deformation [26,27].

IV. PRIMARY ACTIVE CENTRES IN MECHANOCHEMICAL REACTIONS

In the analysis of the elementary mechanisms of various mechanochemical reactions, it is important to know the nature of the primary active species or surface centres formed as a result of the transformations of elastic energy. Information about the nature of the primary centres has been obtained mainly in studies on the mechanical degradation of macromolecules, certain organic reactions, chemical reactions in ultrasonic fields, and, to a lesser extent, in processes involving the disruption of solids.

According to the most general considerations, in the ideal case of the dissociation in vacuo of chemical bonds of different types (ranging from homopolar to purely ionic), the formation of electrically neutral decomposition products is more favourable on energy grounds. In principle, two cases are possible:

$$\sim A-B\sim \begin{cases} \rightarrow \sim A^{\cdot} + {}^{\cdot}B\sim \text{ (I)} & U_{A-B} \\ \rightarrow \sim A^{+} + {}^{-}B\sim \text{ (II)} & U_{A-B}+(I_A-A_B). \end{cases}$$

In the first case the energy expenditure is equal to the strength of the A–B bond, while in the second case it is necessary to supply additional energy equal to the difference between the ionisation potential of the fragment $\sim A(I_A)$ and the electron affinity of the species $B\sim(A_B)$. In the dissociation of bonds in compounds of the alkane series this difference approaches

$$I_{C_2H_7^{\cdot}} - A_{C_2H_7^{\cdot}} = 8.7-1.0 = 7.7 \text{ eV} \simeq 170 \text{ kcal mole}^{-1}.$$

In the majority of organic reactions, the difference $I - A$ in the dissociation of bonds is somewhat less, but nevertheless remains considerable; thus the electron affinities of certain radicals may reach 1.5–2.0 eV, but the ionisation potentials of molecules or their fragments are rarely less than 6 eV; therefore the difference $I - A$ can hardly be less than 4–5 eV.

In exactly the same way, when the typically ionic compound NaCl decomposes in a vacuum,

$$I_{Na} - A_{Cl} = 5.14-3.81 = 1.33 \text{ eV} \simeq 30 \text{ kcal mole}^{-1},$$

i.e. even in this limiting case of an ionic bond the formation of electrically neutral Na and Cl atoms remains more favourable than the formation of Na^+ and Cl^- ions. Recently it was established that, in the mechanical disruption of NaCl crystals, sodium (it was referred to as the amalgam) and gaseous chlorine are evolved in considerable amounts [89].

In polar media, where there is a possibility of an energy gain owing to the solvation or polarisation of the species formed, the situation may alter significantly. One may expect that in the majority of organic substances the main pathway for bond dissociation in mechanical disruption (and also in thermal degradation) is radical or molecular but not ionic. All the experimental data accumulated hitherto are consistent with these general considerations: in the mechanical disruption of carbon chain and heterochain organic polymers, free radicals are formed. Initially they were detected by the acceptor method [1–5], but in the last decade vigorous investigations of the free-radical products of the mechanical degradation of polymers by ESR began [90,91].

The dissociation of linear macromolecules with formation of radicals has been observed in solutions under the influence of sheer and ultrasonic gradients and in polymeric substances in the rubber-elastic, vitreous, and crystalline states.

Table 3. The structure of the primary free radicals formed in the mechanical rupture of polymer chains.

Substance	Structure of radicals	References
Polyethylene	$\sim CH_2\dot{C}H_2 + \dot{C}H_2CH_2\sim$	92,93
Polytetrafluoroethylene	$\sim CF_2\dot{C}F_2 + \dot{C}F_2CF_2\sim$	94
Polystyrene	$\sim CH(C_6H_5)\dot{C}H_2 + \dot{C}H(C_6H_5)CH_2\sim$	95
Polyamides	$\sim CH_2\dot{C}H_2 + \dot{C}H_2(NHCO)\sim$	93
Poly(ethylene oxide), poly(ethylene sulphide) (X = O or S)	$\sim X\dot{C}H_2 + \dot{C}H_2X\sim$	96,97

The structure of the primary radicals has been elucidated by ESR, i.e. the sites of the preferential mechanical rupture of polymer chains have been established (Table 3), quantitative measurements of the rates of bond dissociation under various conditions of disruption of polymeric materials have been begun (monoaxial extension [62–64,69], comminution [46], etc.), and the direction and kinetics of secondary free-radical reactions are being investigated, i.e. the further fate of radicals is being traced [92,98–103].

Active species capable of initiating various chemical reactions, including chain processes have been detected also when low-molecular-weight substances are subjected to mechanical action.

In ultrasonic fields (cavitation conditions) chemical reactions are initiated by the free-radical decomposition products of water [83]. The decomposition of H_2O can occur either as a result of a sharp adiabatic compression of the cavity [19,79] or under the influence of microdischarges (electrical breakdown of the cavity) in the stage of its formation [80] or its collapse [81]. None of these mechanisms can so far be rejected. Hydrated electrons were recently detected [84] in water decomposition products:

$$H_2O \xrightarrow{u.s.} OH^{\cdot}, H^{\cdot}, H_2O_2, e^-_{aq.} \text{ etc.}$$

The probabilities of various elementary processes leading to the formation of excited species, radicals, and ions in the cavity have been compared in a review [85]. The chemical effect of ultrasonic cavitation resembles in broadest outline the indirect effect of radiation on aqueous solutions.

One of the most sensitive methods for demonstrating the existence of active species in various systems is the

initiation of chemical chain reactions. Chain polymerisation was observed in ultrasonic cavitation fields [104,105] (in the absence of traces of water there is no polymerisation [106]), in shock waves [107-109], under the influence of high pressures with shear [26,27,110], and finally in the mechanical dispersion of solids [111-114]. In the last two systems the reaction mechanism was established by measuring the copolymerisation rate constants: when high pressures with shear operate, the reaction is propagated by free radicals [110] and in the comminution of the monomer together with various solids, polymerisation is caused by the effect of charged species [114,115] and possibly of emission electrons [115].

The problem of the analysis of the nature of the primary centres is much more complex in the mechanochemistry of solids where it is necessary to take into account not only the dissociation of various bonds but also the behaviour of the entire crystal and its surface. The primary active states in solids are investigated by adsorption, low-temperature electron emission, luminescence, ESR methods, etc. The results of studies on the nature of paramagnetic centres detected by ESR in solids of different types are compiled in Table 4. Analysis and interpretation of the ESR spectra in polycrystalline solids constitutes a fairly complex problem and as a rule the nature of the centres has been established indirectly by the analysis of their physical and chemical properties.

As already mentioned, in complex organic reactions free radicals are formed. When the two-dimensional networks of graphite are broken, free radical centres are formed on the basal planes, their concentration reaching 10^{14} cm^{-2}. There is at present no unanimous view concerning the nature of the paramagnetic centres in silicon. Judging from chemical characteristics, a considerable proportion of the centres detected in SiO_2 are of a free-radical type, but this has not been demonstrated convincingly.

Table 4. The nature of the paramagnetic centres detected in the mechanical disintegration of certain materials.

Polymer	Free radicals	Charged states	References
Cellulose	+	—	116, 117
DNA	+	—	118
Horns and hooves	+	—	119
Graphite	+	—	120, 121
Silicon	?	—	122—130
Silicon carbide	+	—	131
Quartz	?	—	90, 125, 132—138
Germanium dioxide	—	+	139
Barium sulphate	—	+	90, 139

Charged states (electrons in shallow traps) stable only at a low temperature have been detected in both GeO_2 and $BaSO_4$. One may suppose that the formation of charged centres is part of the range of mechano-emission phenomena accompanying the mechanical disruption of solids and reflected in static electrification [140], luminescence [10], electron emission [141,142], etc. There is so far no general theory of emission phenomena. In the electrical theory of adhesion [143,144] the emission of high-energy electrons is explained by the formation of an electrical double layer at the surfaces in contact. When the adhesion contact is broken, a powerful electric field abstracts electrons from the surface and disperses them. Electrical excitation of matter can occur as a result of the interaction of elastic waves with current carriers (the electroacoustic effect) [145-147]; the polarisation of substances in shock waves is apparently associated with this mechanism [148,149]. The emission and luminesence on friction and on impact by solids has also been explained within the framework of the magma–plasma model [10].

Electro-emission phenomena are of great importance for mechanochemistry, since an electrical discharge between solid surfaces or a planar surface discharge [150] can lead to the formation of active species, including electrons, which initiate various chemical reactions [115].

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Mechanochemical phenomena occur widely in nature and are of considerable importance for many branches of science and engineering; these are the problems of the strength of solids and of the physicochemical mechanics of materials, certain branches of colloidal chemistry, the physics and physical chemistry of polymers, geochemistry, biophysics, the technology of inorganic substances, and chemical kinetics, the theories of the reactivity of molecules and molecular acoustics, and problems of friction and wear, heterogeneous catalysis and adsorption, detonation and propagation of shock waves, metal corrosion, etc. Mechanochemical reactions are of a wide variety of types and at first sight it is difficult to compare processes involving the absorption of sound in gases with chemical changes in the friction of solids or reactions in shock waves with corrosion of a mechanically strained metal. However, the chemical reactions are throughout induced by the absorption of elastic energy and these widely differing processes have common features reflected in the nature of the primary steps and their kinetics. In the present review particular attention has been devoted to these problems in the analysis and classification of published data. Many no less important aspects of mechanochemical reactions have not been mentioned or only touched upon: the process energetics and thermodynamics, the relation between mechanochemistry on the one hand and physicochemical mechanics and processes involving the disruption of materials on the other [77], mechano-emission phenomena, processes in which a substance is subjected to the simultaneous action of various types of energy [78,151] (for example elastic and emission energies), the characteristics of reactions in inorganic substances [152], the generation of luminescence and the occurrence of gas-discharge processes [153], etc.

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