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High speed autowave reaction regimes in low-temperature solid state chemistry

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ABSTRACT. The results of studies on new phenomena of the travelling wave type in low-temperature solid state chemistry, observed in a wide variety of solid-state chemical reactions at the temperatures of liquid nitrogen or helium, are surveyed. The processes investigated are characterised by anomalously high rates of reaction for the temperature range indicated, comparable to the rates of the fastest high-temperature combustion reactions in classical chemistry. A mechanism is proposed with an autocatalytic mechanochemical step which permits a qualitative explanation of all the characteristic features observed in the phenomenon. It is suggested that the mechanism indicated occurs widely in space chemistry and in the processes involved in the chemical evolution of the universe.

The bibliography includes 67 references.

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I. Introduction

Quite recently, at the beginning of the 1970s, the very possibility of a chemical reaction in the solid state near the absolute zero of temperature appeared doubtful (electron transfer reactions[1] in the solid state at low temperatures are not considered in this review). An event which made it necessary to revise the existing ideas was the discovery of the phenomenon of the low-temperature limit of the rate of a chemical reaction in relation to the radiation-initiated polymerisation of formaldehyde;[2] the existence of this phenomenon was subsequently established in a number of other chain and non-chain reactions (see Gol'danskii et al.[3] and the references therein). It was discovered that there exist systems in which a reaction occurs even at the temperature of liquid helium at a low but entirely measurable rate, which is independent of temperature. In order to account for the phenomenon of the low-temperature limit in cryochemical reactions, the concept of molecular tunnelling was put forward. It was subsequently developed taking into account low-temperature intermolecular interactions (see Gol'danskii and co-workers[3–7] and the references therein).

A fundamentally new factor in the introduction of the concept of the tunnel mechanism into the kinetics of low-temperature radiation-initiated chain reactions in the solid state was the assumption of the energy equilibrium in the reacting solid-phase system. However, the universality of the proposed kinetic models for the processes indicated, wholly based on the classical ideas of equilibrium Arrhenius kinetics, was never regarded as axiomatic, particularly since the subject under consideration consisted of various chemical reactions stimulated by ionising radiation supplied from the outside, i.e. under conditions where temperature ceases to be the only parameter characterising the energy state of the system.

The appearance of alternative mechanisms, according to which the leading role in low-temperature solid-phase reactions was attributed to non-equilibrium states, was entirely natural. As early as 1960, Semenov[8] proposed a mechanism involving energy chains in order to describe the radiation-stimulated solid-phase polymerisation. According to this mechanism, the energy evolved in each elementary step during the growth of the polymer chain ensures the overcoming of the activation barrier in the next step of this kind. The polymer chain can grow via this mechanism at the rate of propagation of the exciton ($\sim 10^6$ mm s^{-1}). This exciton chain model has been examined theoretically in detail.[9] The important conclusion was reached that very high rates of a solid-phase reaction really occur even at very low temperatures as a result of the chain transfer of energy via the frozen matrix.

A combined mechanism, assuming the operation of the tunnel mechanism in the reaction initiation stage, postulating the subsequent very rapid development of a chain process as a result of the recovery of the energy of the reaction steps, has been described.[10]

Together with this chain-tunnel mechanism, mention should be made of yet another combined mechanism. This is the chain-thermal mechanism proposed and developed[11–13] in order to interpret the limiting phenomena in the accumulation of radicals during the irradiation of frozen specimens of different organic substances.

Here however we should like to draw attention not to the difference between the equilibrium tunnel mechanism and the mechanisms of the non-equilibrium type but to the simplifying assumption, from which all these approaches have originated, and which must be abandoned in many instances. This topic will be dealt with later in the review.

The point is that in the models investigated the solid matrix itself was regarded in essence from a single standpoint, namely as a kind of ideal defect-free system in mechanical equilibrium. In other

words, in the analysis of the phenomena the fact that the systems investigated are characterised by a significant mechanoenergetic disequilibrium was rejected. This quality of the specimens actually studied was a consequence of both the conditions in their preparation and of the effect of fluxed of ionising radiation. It is known that the initial spatial disposition of the molecules is significantly distorted in the irradiated solid, the phase state of the solid is modified, homogeneity is affected, the internal stresses field is greatly altered, and the strength characteristics are appreciably reduced. The transition in the experiments to the post-effect conditions does not eliminate the problem of the role of the mechanical disequilibrium of the specimen in the solid-phase reaction because the specimen remains a significantly non-equilibrium object even after the γ-ray energy flux has been switched off because of the retardation at low temperatures of all kinds of relaxation processes. Apart from the factors quoted, the chemical reaction itself, which has been initiated in the solid matrix, must be a source of intensification of distortions in the lattice i.e. of further accumulation in the latter of mechanical potential energy

The considerations described above served as a starting point in the formulation of tasks in a series of studies[14–24] The factor which stimulated the consideration of the mechanochemical aspect of the radiation cryochemistry of the solid state was the observation[14] of initiation of the reaction by a local break in irradiated specimens stabilised by a low temperature.

The principal questions can be briefly formulated in the following way. Can one liberate the potential energy accumulated in the mechanically non-equilibrium matrix of the frozen specimen of the reactants by its brittle breakdown. Will the stored mechanical energy be transformed into chemical energy and will a chemical reaction occur under these conditions?

The possibility of a positive answer to these questions was supported by the general postulates of the theory of the strength of a solid, from which it followed that the mechanical energy of the elastic deformation at the instant when the break occurs is concentrated in the region directly adjoining the surface being formed. It is known[25] that this energy transformation process is accompanied by a significant change in the physicochemical properties of the substances on the freshly formed surface compared with the bulk-phase properties: the brittle breakdown is coupled with phenomena such as electron and ion emission, luminescence, the formation of radicals, and a sharp acceleration of transport processes on the cleavage planes. In other words, it appeared likely that the transition of the process from the homogeneous regime to a significantly heterogeneous regime via the brittle breakdown of the specimen involves a non-equilibrium mechanism of energy transfer to active centres previously "frozen" in the three-dimensional matrix and induces thereby a chemical reaction at low temperatures. To the foregoing, one should add that in the traditional mechanochemical processes, a notable role was always attributed to brittle breakdown (although it did occur under the conditions of forced dispersion of the specimen) (see Lyakhov and Boldyrev[26] and the references therein).

We may note yet another factor which has stimulated a revision of the existing ideas. In previous studies, both the kinetic models themselves, describing the solid-phase radiation-chemical reactions, and the experimental methods were based on the assumption that the system is uniform and that the chemical reaction is homogeneous. This stage was entirely natural because, with the aid of calorimetric and spectroscopic methods using an integrated signal, it was difficult to discover and investigate the characteristic features of non-uniform chemical reaction regimes. We may note that doubts about the admissibility of the application of zero-dimensional kinetic models in the radiation chemistry of the solid state have always existed, because it is well known that an irradiated specimen is never homogeneous (highly active regions, tracks and spurs, arise during radiolysis and the stabilising radicals and ions are distributed non-uniformly throughout the space within the body). Apart from the neglect of the inhomogeneity factor in the development of the process throughout the specimen, the homogeneous approach was also restricted by the fact that it did not make it possible to go outside the framework or linear (or almost linear) kinetic models and hindered the discovery of the features of significantly non-linear mechanisms—mechanisms with feedback. Nevertheless, their existence in complex chemical systems such as a reactive solid had to be regarded as extremely likely. In particular, the existence of feedback between the mechanical state of the system and its chemical activity is extremely probable. These considerations also stimulated the study of the role in the solid-phase processes investigated of all kinds of artificially introduced or spontaneously arising local perturbations.

The selected approach justified itself, the initial postulates proved to be legitimate, and the investigations led to the discovery of highly intense autowave regimes in low-temperature solid-phase reactions. The principal results of this first stage of these studies have been surveyed in a previous review.[27] In order to maintain a logical consistency, certain fundamental conclusions arising from previous studies were introduced into the present review, which is devoted to the analysis of the state of the problem of autowaves in cryochemistry of the solid state at a new stage of its investigation.

II. Objects of study

The objects of study[27] were systems in which a spontaneous development of reaction chains is impossible in the solid state at radiolysis temperatures of 77 and 4.2 K. In the course of the γ-irradiation of these solid-phase systems at the nitrogen and helium temperatures, non-chain radiation-chemical reactions take place and lead to the formation of energy-rich active centres which are chemically stable in the temperature range indicated. Various classes of reactions have been investigated: chlorination of hydrocarbons, chlorination and hydrobromination of alkenes, polymerisation, etc. The characteristic features of solid-phase reactions were investigated in the first stage in the following systems: (1) a vitreous solution of chlorine in butyl chloride (molar ratio 1 : 3, glass point $T_g \simeq 100$ K);[28] (2) a vitreous solution of chlorine in methylcyclohexane (ratio 1 : 3, $T_g \simeq 93$ K);[14] (3) the crystalline complex $C_2H_4.HBr$ (T_m† = 110 K);[29,30] (4) a vitreous solution of SO_2 in 2-methylbuta-1,3-diene (ratio 1 : 1, $T_g \simeq 110$ K).[17]

III. Activating role of brittle breakdown in the reaction excitation stage

In order to achieve the brittle breakdown of the specimen, the method involving the induction of thermoelastic stresses by selecting a rate of change of the specimen temperature sufficient to induce cracking was applied initially. The rate of change of temperature was recorded and the thermal signals accompanying the breakdown

† Melting point (Ed. of translation).

were observed with the aid of a differential scanning calorimeter (for a more detailed description of the method, see Barkalov et al.[31]).

When the specimens are heated slowly from 4.2 to 77 K, which does not lead to cracking, the calorimeter does not reveal any thermal effects (Figs. 1*a* and 1*b*, continuous lines). Rapid heating induces the cracking of the specimen and the accompanying thermal effect is recorded by the calorimeter (Figs. 1*c* and 1*d*, continuous lines). After selecting a rate of change of temperature such that the specimen cracks, similar experiments were carried out but this time with specimens treated with a definite dose of ^{60}Co radiation (in order to create stabilised active centres in the system). During slow heating of the irradiated specimen, unaccompanied by its cracking, the system remained chemically inert, i.e. thermal effects were not recorded (Figs. 1*a* and 1*b*, dashed lines). At a high heating rate, a chemical reaction was initiated at the instant of the brittle breakdown of the specimen (Figs. 1*c* and 1*d*, dashed lines).

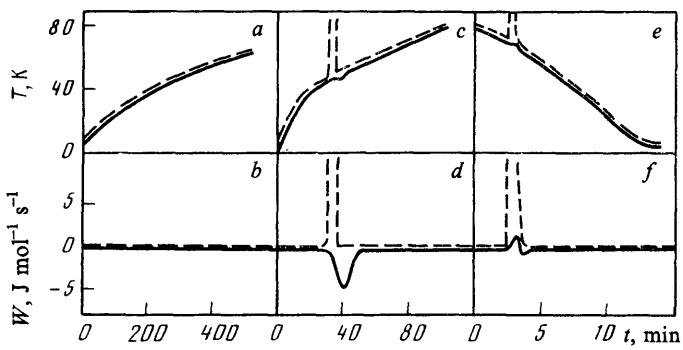


Figure 1. Time variation of the temperature of a vitreous solution of chlorine in methylcyclohexane (*a*, *c*, *d*) and of the accompanying thermal effects (*b*, *d*, *f*): continuous—non-irradiated specimen; dashed lines—specimens irradiated with ^{60}Co γ-rays at 77 K at a dose of 27 kGy.

The brittle breakdown of the specimen and the accompanying chemical reaction were achieved also on rapid cooling. Figs. 1*e* and 1*f* present data obtained on fairly rapid cooling of the specimen inducing the cracking of the solid matrix. Evidently the cracking of the irradiated specimen was accompanied by a chemical reaction (there was no reaction in the non-irradiated specimen).

In order to demonstrate the decisive role of the formation of cracks as a factor initiating the chemical reaction, a direct experiment was formulated involving a non-thermal disruption of the solid mixture of reactants. The cracking was achieved at a constant thermostat temperature of 4.2 K by rotating a thin metallic rod frozen into the specimen. At the instant of the introduction of such perturbation into the matrix containing the stabilised active centres, a rapid, one might say "explosive", chemical reaction occurred. Despite the local initiating, the reaction spread throughout the cell—the dark colour induced by the γ-radiolysis vanished.

The results described above permitted two fundamentally important conclusions: (1) in the systems investigated, brittle breakdown induces an abrupt solid-phase chemical reaction and (2) the development of the process initiated by the cracking of the specimen is self-accelerating and involves the entire specimen. Consequently the formation of the primary crack plays the role of an initiating device incorporating a positive feedback mechanism, which ensures a self-maintaining process regime. In order to elucidate this mechanism, experiments were formulated in order to investigate the dynamics of the reactions developing in this system in response to the perturbation introduced.

The observed features of the dynamics of the development of an abrupt reaction demonstrated convincingly that the classical thermal feedback mechanism is not decisive in the given instance. The establishment of the leading role of the surface formed on disruption of the matrix made it possible to formulate the following hypothetical non-thermal mechanism of the self-activation of the system investigated: the chemical reaction arising on the cleavage planes and in the adjoining regions generates in its turn breaks in continuity in the regions of the solid matrix not involved in the reaction (for example, as a consequence of the appearance during the reaction of temperature or density gradients, which create stresses disrupting the specimen). This model, which can be classified as of the branched-chain type, describes qualitatively a number of experimentally observed facts, namely: (1) the critical phenomena involving the appearance and spontaneous self-accelerating development of a reaction accompanied by intense dispersion of the solid matrix comprising the reactants; (2) the initiation of a similar explosive process by creating in the initial instant an initiating network of cracks by the mechanical or thermal disruption of the specimen (in the absence of such perturbations, the rate of reaction is immeasurably small); (3) the degeneracy of critical phenomena (see the bibliography in the paper of Barelko et al.[27]).

IV. Autowave reaction regimes

It is known that a fundamental feature of the systems described by non-linear branched-chain models is autowave phenomena characteristic of such systems. The autowave reaction regimes should arise in sufficiently large specimens in response to a locally introduced perturbation.

On the other hand, in the first experiments[16] it proved possible to initiate the spontaneous propagation of the reaction wave by means of a local perturbation (by creating a local cleavage plane in the specimen as a result of mechanical action or by supplying a thermal pulse disrupting a limited region in the solid matrix). The characteristic results obtained in experiments with a cylindrical specimen of a frozen mixture of reactants 0.5–1.0 cm in diameter and 5–20 cm long are presented below. Since the reaction was accompanied by a change in the colour of the specimen, the velocity of the fronts was measured successfully using the possibilities of cine-techniques. The cinegrams show clearly how the front, propagated parallel to itself along the axis of the cell at a constant rate of 1–2 cm s^{-2}, is formed on local mechanical breakdown.

In order to investigate the structure of the wave front (its temperature profile), a series of thermographic experiments on the autowave process were carried out. The rate was determined from the time taken by the waves to traverse the distance between two thermocouples frozen into the specimen.[16–18]

Fig. 2 presents the characteristic profiles of the travelling temperature waves (in terms of time and spatial scans) for initial temperatures of 77 K (*a*) and 4.2 K (*b*). The form of the profile does not undergo qualitative changes when the thermostat

temperature is altered. The process consists of the following stages: *AB*—inert heating (at 77 K, this stage was not recorded, i.e. was almost isothermal); *BC*—abrupt start and explosive course of reaction (characteristic break at point *B*); *CD*—cooling stage. The *BC* stage is rapid. The oscillograph scan of this zone of the running wave front shows that at 77 K (Fig. 2*a*) the duration of the given stage is ~0.1 s, i.e. at a wave velocity $U \simeq 20$ mm s^{-1} the zone width is $\delta \simeq 0.2$ cm, while at 4.2 K (Fig. 2*b*) the duration of the stage is ~0.3 s and the width is $\delta \simeq 0.3$ cm (wave velocity $U \simeq 10$ mm s^{-1}).

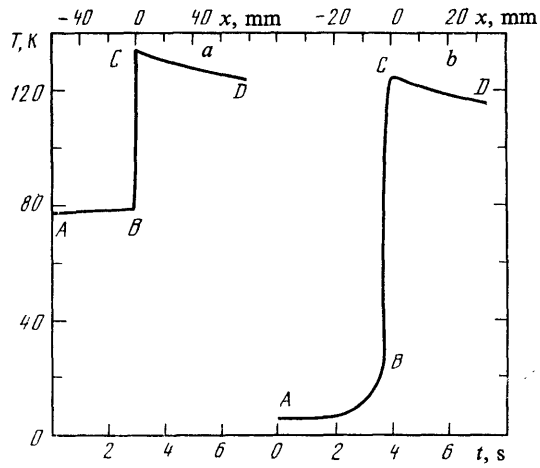


Figure 2. Time and spatial scans of the characteristic temperature profiles of the $C_4H_9Cl + Cl_2$ reaction propagation waves at 77 K (*a*) and 4.2 K (*b*): *a*, $U = 20$ mm s^{-1}; *b*, $U = 10$ mm s^{-1}. Preliminary irradiation dose 27 kGy.

In the structure of the travelling front of a low-temperature reaction presented, it is possible to see clearly features which are completely atypical for classical thermal self-propagation processes: (1) the stage of the inert pre-explosion heating is weakly expressed or is altogether absent; (2) the reaction starts and stops abruptly (characteristic breaks at points *B* and *C*), the reaction at point *B* starting at temperatures significantly lower than the temperature of the onset of the thermally activated reaction ($T_g \simeq 100$ K); (3) the dynamic picture of the development of the process in the spontaneous layer-by-layer initiation of the reaction by the travelling wave is identical with the picture of the forced initiation of the reaction by impact heating; (4) the rate of propagation of the wave changes only slightly on reducing the temperature from 77 to 4.2 K despite the marked alteration of the heat evolution.

The next important step in the elucidation of the role of the thermal factor in the mechanism of the phenomena investigated involved the study of the influence of the size of the specimen on the characteristics of the autowave process.[20] Can the self-maintaining wave regime of the reaction be precluded by intensifying the heat evolution as a result of the reduction of the diameter of the cylindrical tube with the frozen mixture of reactants?

When the experiments with travelling waves were carried out in capillaries 0.5–1.0 mm in diameter (which corresponds to an increase in the parameter characterising the intensity of heat evolution by more than an order of magnitude), it was established[20–22] that there is no degeneracy of the autowave process under these conditions in any of the systems considered. Furthermore, it was discovered that the characteristic rates of autopropagation of the reaction do not undergo any appreciable changes under these conditions.

In the course of development of the relevant research, a series of experiments were performed with thin film specimens of the reactants.[22,27] The experiments were carried out with films frozen onto a flat support and immersed in liquid nitrogen, i.e. under conditions where there was no shield between the surface of the film and the bath of the cooling agent. When the films were punctured or scratched, an autowave process was excited. The use of such objects made it possible to achieve quasi-isothermal process conditions and to promote thereby the manifestation of the isothermal mechanism mentioned above, consisting of the layer-by-layer self-dispersion of the specimen as a result of the difference between the densities of the initial reactants and the final reaction products. Under these conditions, the autowave was not only not suppressed but actually became even more pronounced.

V. Theory of autowave processes in solid-phase cryochemical reactions

The experimental results made it possible to formulate in greater detail the hypothesis concerning the mechanochemical nature of the self-activation of the solid-phase reaction and to construct a tentative qualitative picture of the development of the autoclave process in a chemical interaction in the systems under consideration. The occurrence of the process can be represented as the movement in the solid specimen of a narrow zone extensively intersected by a dense network of freshly formed cracks. The chemical reaction arises in precisely this zone on the surface of the cracks (or near them) and creates in its turn conditions for the continuation of the breakdown in the neighbouring layer of the solid matrix. Such layer-by-layer dispersion of the specimen is induced by the propagating field of the stress, which can be generated, as already stated, either by the difference between the densities of the initial reactants and of the final products (isothermal mechanism) or by the appearance in the specimen of steep temperature gradients as a result of the exothermicity of the reaction (a non-isothermal mechanism). Naturally, these two factors can also operate simultaneously. The non-isothermal mechanism has been analysed[18] in relation to massive cylindrical specimens in which, as shown above, significant heating can take place due to the reaction and the role of thermal stresses in the dispersion steps should be very notable.

The model considered[18] was constructed on the basis of the following assumptions. It is assumed that the specimen is infinite in size and no account is taken of the heat exchange with the surrounding medium, i.e. it is assumed that the characteristic time for the evolution of the heat of reaction is much shorter than the characteristic time for the removal of heat. These conditions constitute the basis for the analysis within the framework of a one-dimensional model. According to the hypothesis, the initiation of the reaction in the given section of the specimen occurs when a stress exceeding the tensile strength of the solid matrix is generated. Since one is dealing with thermal stresses and the region of elastic deformation and brittle breakdown is considered, it follows that, in relation to the given physical model, the stresses can be replaced by temperature gradients assuming that there is an unambiguous

correspondence between them (Fig. 3). Such change of variables greatly simplifies the model and makes it possible to exclude from consideration mechanical equations and to reduce the analysis to only one heat balance equation in which, instead of the limiting brittle breakdown stress, a critical value of the temperature gradient is introduced as the parameter.

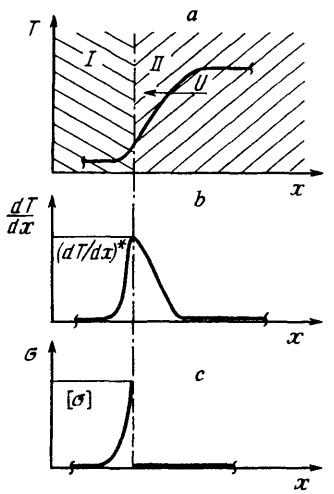


Figure 3. Characteristic form of the temperature profile (*a*), the temperature gradient (*b*) and the stresses field (*c*) in the running wave front: (I) zone of the specimen not involved in the reaction; (II) zone of the specimens dispersed as a result of the reaction.

Taking into account the assumptions made, the equation describing the autowave process assumes at first sight a form analogous to the fundamental equation of the theory of combustion:[32]

$$\lambda \frac{d^2T}{dx^2} - Uc\rho \frac{dT}{dx} + Q = 0, \qquad (1)$$

where T is the temperature, x the coordinate, λ the thermal conductivity, c and ρ are respectively the heat capacity and density of the solid mixture of reactants, Q is the rate of evolution of the heat of reaction, and U is the rate of propagation of the thermal wave front.

However, there are fundamental differences between the process under consideration and combustion, which are reflected in the character of the dependence of Q on the variable: Q is a function not of temperature but of its derivative with respect to the coordinate. We express Q as a function varying abruptly from 0 to Q^* at $dT/dx = (dT/dx)^*$, this value remaining unaltered throughout a specific time interval τ. Physically, this implies that the heat evolution in the reaction starts only in response to the brittle breakdown of the specimen under the influence of thermal stresses attaining the ultimate strength of the material. The use of the quantity τ as the parameter of the reaction time reflects both features of the hypothesis being developed, according to which the period when the chemical reactivity is maintained in the course of the formation of a crack is limited by the operation of a deactivation process (for example, as a consequence of the recombination of active species on the surface of the break). When applied to the stationary model considered here, described by Eqn. (1), the parameter τ contains information about the reaction zone (the dispersion zone) in the running front whose size is $U\tau$. At each point within this zone, the reaction takes place at a rate Q^*, while outside its limits its rate is $Q = 0$.

The boundary conditions are formulated in the following form:

$$T|_{x=-\infty} = T_0, \; T|_{x=+\infty} = T_0 + Q\tau/c\rho \equiv T_{max},$$

where T_0 is the initial temperature of the specimen and T_{max} the maximum temperature of the adiabatic heating of the specimen. The model is assumed to be quasi-homogeneous, i.e. it is postulated that the characteristic size of the grain formed in the dispersion zone is much smaller than the width of the temperature wave front.

Eqn. (1), where the heat source is represented by a function of the type indicated, can be integrated in an analytical form when account is taken of the boundary conditions presented above and has a solution in the form of a running wave. We shall concentrate attention on the analysis of the dependence of the rate of propagation of the reaction wave on the parameters. This dependence assumes the following form:

$$g(u) \equiv \{1 - \exp(-u^2)\}u^{-1} = G, \qquad (2)$$

where $u = U(\tau/a)^{0.5}$ is the dimensionless velocity of the travelling wave (the parameter to be determined), $G = (dT/dx)^*(a\tau)^{0.5}/(T_{max} - T_0)$ is the specified dimensionless critical temperature gradient, and $a = \lambda/c\rho$ is the thermal diffusivity.

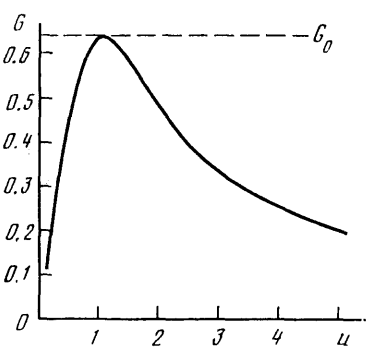


Figure 4. Dependence of the critical temperature gradient on the rate of propagation of the reaction wave.

Fig. 4 shows that an autowave solution of Eqn. (2) exists only for $G < G_0 \simeq 0.64$. Physically, this implies that, in the system described by the given model, the autowave regime in the propagation of the reaction in the solid mixture of reactants becomes impossible when the material of the specimen is strengthened to a definite extent, when the heat and rate of reaction are reduced, and also when the thermal diffusivity of the system is increased.

An important feature of Eqn. (1) is the non-unique nature of its solution. In the region $G < G_0$, two values of the stationary velocity of the running wave correspond to one value of the parameter g. We shall compare the characteristics of both regimes of the wave process. To simplify the treatment, we shall go over to the region $G \ll G_0$ in which Eqn. (2) is soluble for u. The expression for u, corresponding to the regime with a low velocity (the "slow" wave regime), has the form

$$u = a\,(dT/dx)^*/(T_{max} - T_0) \text{ or}$$
$$u = a\,(dT/dx)^*/(Q^*\tau/c\rho), \quad (3)$$

while the expression corresponding to a high velocity (the "fast" wave regime) is

$$u = (T_{max} - T_0)/(dT/dx)^*\,\tau \text{ or}$$
$$u = (Q^*/c\rho)/(dT/dx)^* \quad (4)$$

When the process takes place in the "slow" wave regime, it is possible to see features which reflect the similarity of this process, despite the differences in its physical nature, to the classical combustion process: the velocity of the wave depends on the thermal diffusivity in the same way as in the propagation of a flame; the position of the reaction zone in the wave front is the same as in combustion, i.e. it is located near the point of the maximum temperature T_{max} [the critical gradient $(dT/dx)^*$, for which the reaction is initiated, is in fact located near T_{max}]; most of the temperature profile of the front corresponds to the inert heating of the specimen (the zone referred to as the "Michelson" zone in the theory of combustion).

The characteristics of the process in the "fast" wave regime are significantly different. The most striking feature is the absence from Eqn. (4) of the dependence of the rate on the thermal diffusivity. The physical explanation of this result, which is unexpected for a problem with conductive heat transfer, is associated with the characteristic features of the structure of the "fast" wave front. In this case, the temperature profile of the wave front is much steeper than in the low velocity regime and the coordinate of the onset of reaction is located in the leading part of the front near T_0. This in fact explains the disappearance of the influence of the parameter a on the wave process, because the temperature gradients are high and close to the critical value even in the unheated part of the front. In terms of qualitative features, the "fast" wave regime is close to that observed experimentally.

In order to test the agreement between the experimentally observed phenomenon and the phenomenon considered in theoretical terms, it is of fundamental importance to attempt to realise experimentally the "slow" wave regime.

It was initiated (in conformity with theory) not by pulsed heating but by slow heating of the initiation zone. In special experiments,[18,22] the specimen was placed in a cryostat in boiling nitrogen vapour. Under these conditions, it was possible to observe, together with the "fast" wave (whose velocity did not differ from that described previously), also a "slow" wave (Fig. 5). Evidently the velocity of the "slow" wave is approximately an order of magnitude less than that of the "fast" wave, which agrees with data calculated by Eqns. (3) and (4).

It is noteworthy that the practical achievement of the "slow" wave involved certain difficulties. Initiation by slow local heating did not induce the appearance of a slowly propagated wave in each experiment. The "fast" wave was frequently initiated. Cases were observed where the "slow" wave generated was converted into the "fast" wave during its movement. This result is a consequence of the instability of the "slow" wave regime.

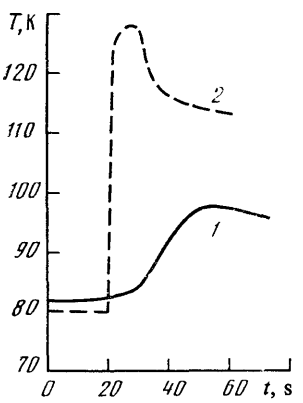


Figure 5. Time scan of the temperature profiles of the $C_4H_9Cl + Cl_2$ reaction propagation waves on slow (curve *1*) and rapid (curve *2*) heating; *1*, $U = 1$ mm s^{-1}; *2*, $U = 12$ mm s^{-1}.[18]

VI. Autowave reactions under the conditions of uniform compression and the role of mechanical stress dynamics

It follows from the above analysis that the effect of various factors on the strength characteristics of a solid mixture of reactants can serve as an instrument for testing the ideas being developed. For this purpose, studies were made of the influence of high pressures on the dynamic characteristics of autowave reactions[19] and also of the role of the rate of application of a stress and of the regimes in the cracking of the specimen on the excitation of reaction by a mechanical influence.[33]

In conformity with the theoretical prediction,[18] an increase in the pressure applied to the specimen reduced the velocity of the reaction wave front. The decrease in velocity at a pressure of 6×10^8 Pa proved to be very considerable—approximately by a factor of 2.5–3 compared with the rate of the process in the non-compressed specimen. Thus the increase in the homogeneity and structural order in the matrix under the influence of pressure, leading to its strengthening and hindering the formation of cracks, slows down the dispersion-reaction travelling wave, which is associated, according to Eqn. (4), with the increase in the critical value of the temperature gradient $(dT/dx)^*$ leading to the brittle breakdown of the specimen.

Experiments undertaken to investigate the role of the dynamics of the application of a mechanical stress, which determine the brittle or plastic character of the breakdown, were performed with film specimens 50–100 μm thick prepared from a chlorine–butyl chloride mixture. Impact by a striker (regime involving the rapid application of a stress, pressure $\sim 10^8$ Pa, duration of impact ~ 0.1 s) leads to the appearance of a network of cracks. Such treatment of

an irradiated film, inducing brittle breakdown, also induces an autowave.

On local impact by a striker in the regime involving a slow application of a stress to a film subjected to the same dose of γ-radiation, a chemical reaction is not initiated although an appreciable trace remains on the film in the form of a plastically deformed imprint having the shape of the cross-section of the striker.

Thus neither a significant plastic deformation (both on uniform compression and on local shearing) of the solid reaction systems investigated nor their transition to a highly stressed state under the influence of a static load are factors responsible for the critical phenomena and autowave processes observed in the reactions of these systems. A series of experiments[19,33] provided new important evidence for the decisive role of brittle breakdown in the mechanism of the phenomena under consideration (for further details, see Barelko et al.[27]).

VII. Expansion of the range of systems investigated (new types of autowave process)

Studies have demonstrated the wide occurrence of autowave phenomena in cryochemical reactions of solids and the identity of their physical mechanisms in a wide range of chemical systems. This justified the hypothesis that autowave reaction regimes can prove useful for the creation of new non-traditional chemical technologies. In the autowave processes described above, the principal technological problems (activation of the chemical system, supply of energy, and mixing of the reactants) are solved by combined procedures involving the use of the energy of the chemical reaction. The high rates of the chemical reaction occurring at low temperatures in the autowave regime are also extremely attractive. All this has stimulated the search for new objects of study.

1. Waves in acetaldehyde

In the light of the foregoing, the study of the post-polymerisation of γ-radiolysed solid acetaldehyde was extremely interesting. The kinetics of this reaction had been studied previously by an integral calorimetric method.[34] However, the development of ideas about autowave processes made it necessary to return to the analysis of the characteristics of the given reaction at a new qualitative level. This system is of special interest in connection with two factors. Firstly, the observation of the autowave regime in the polymerisation of acetaldehyde would provide the first example of a cryochemical wave in a one-component system. Secondly, the above reaction is characterised by a heat change smaller almost by an order of magnitude than in the systems studied previously. This created a basis for a more detailed specification of ideas concerning the role of the isothermal and non-isothermal mechanisms and about their interaction in an autowave process.

The propagation of the polymerisation front in solid radiolysed acetaldehyde at the relatively high temperatures 117–147 K (close to the melting point of the monomer which is 150 K) had been observed long before our investigations and had been recorded by thermographic measurements and cinefilming.[35]

This phenomenon was interpreted[35] within the framework of the classical thermal mechanism of combustion. Having restricted their treatment to one thermal conductivity equation and having made a number of assumptions, the authors obtained an extremely short time for the addition of one monomer unit to the polymer chain ($\sim 10^{-8}$ s). Subsequently, the kinetics of this reaction were studied in detail by the calorimetric method in the slow scanning regime with respect to temperature and directly in the field of the specimen.[34] The time required for the addition of one monomer was only $10^{-1}-10^{-2}$ s. The problem of the legitimacy of the application by Psheshezhetskii and Tupikov of the theory of combustion to the description of the layer-by-layer propagation of the polymerisation front naturally arose in this connection.

The principal ideas concerning the mechanochemical feedback in an autowave process were confirmed in the study of this system. An autowave polymerisation regime occurred in polycrystalline acetaldehyde already at 4.2–77 K and its principal characteristics were investigated.[36] The polymerisation wave in crystalline acetaldehyde was observed in massive (cylindrical) and thin-film specimens in both nitrogen (77 K) and helium (4.2 K) baths. The wave was excited in response to the local brittle breakdown of frozen aldehyde.

When the autowave passed through the specimen in the helium bath, the maximum temperature in the front did not exceed ~130 K, i.e. was significantly lower than the melting point of the monomer (150 K). Consequently this system provides an example of an autowave process occurring exclusively in the solid phase. This is in fact why conditions were created for the analysis of the changes in the structure and phase state of the polycrystalline specimen induced by the passage of the mechanochemical cryowave through it. According to the ideas being developed, the chemical reaction front consists of a mechanical dispersion zone moving in the solid reactant. Examination of the cinegrams recording the passage of the wave established that behind the front the initially opaque polycrystalline specimen is fully clarified. It could be assumed that this clarification is associated with the amorphisation of the specimen.

This hypothesis was tested by calorimetric analysis which made it possible to determine the ratio of the amorphous and vitreous phases in the solid matrix from the change in the heat of fusion. In order to carry out such analysis, the acetaldehyde specimen was transferred to a bath of liquid nitrogen after an autowave had passed through it in liquid helium and was then sliced into several parts along the height of the cylinder. Each part was placed in a calorimeter at 77 K and the calorimetric heating curve was recorded for it. It was found that, after the passage of the wave, the specimen contained no crystalline phase along its height (only a heat capacity jump accompanying devitrification was detected in the calorimetric experiments and a signal corresponding to the heat of fusion was absent). On the other hand, when the process was carried out not in the autowave regime but in the regime involving the slow heating of the entire specimen in the calorimeter (without the brittle breakdown initiating the autowave), the unreacted monomer retained its crystallinity. Thus the passage of the mechanochemical wave through the polycrystalline specimen results in its amorphisation, for which two factors are responsible: the formation as a result of the reaction of an amorphous polymer and the mechanical dispersion of the specimen in the front.

The rate of propagation of the autowave depends on the dose of the preliminary γ-irradiation. As in the system studied previously,[27] there is a critical dose necessary for the attainment of the autowave regime. The size of this dose increases with decrease in the thermostat temperature (Fig. 6). It could be postulated that the increase in the rate of propagation of the wave with increasing dose is caused by the increase in the concentration of stabilised active centres accumulated in the system during the preliminary radiolysis. However, the increase in the concentration of paramagnetic centres

(radical-ions and radicals) during the radiolysis at 77 K of polycrystalline acetaldehyde takes place linearly only up to a dose of ~50 kGy and then slows down. After the attainment of ~700 kGy, the accumulation of centres ceases altogether. On the other hand, the rate of propagation of the wave in this range continues to increase in proportion to the dose.

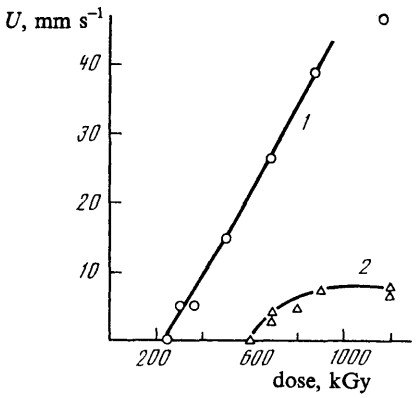


Figure 6. Dependence of the rate of propagation of the polymerisation wave front in polycrystalline acetaldehyde on the preliminary irradiation dose at 77 K (curve *1*) and 4.2 K (curve *2*).[36]

It is known that, in the low-temperature radiolysis of acetaldehyde in a matrix, its decomposition products appear—methane and carbon monoxide, which are in the condensed state at 77 K. When the polymerisation wave passes through the system, these radiolysis products are gasified (the boiling points of CH_4 and CO are respectively 111 and 81 K), which can facilitate the brittle breakdown of the specimen and can accelerate the movement of the running reaction front.

The problem of achieving the wave process in the vitreous acetaldehyde matrix is of great interest. Even on rapid cooling, pure acetaldehyde cannot be converted into the vitreous state[34] and its polymerisation in the vitreous state had not therefore been studied previously. Kichigina et al.[37] investigated a vitreous solid solution of acetaldehyde in butyl chloride (BC), in which local brittle breakdown induced an autowave polymerisation regime. It was found that the critical dose of the preliminary γ-irradiation, above which the autowave propagation of the process in the vitreous solution can be attained, is only 60 kGy, while in crystalline acetaldehyde it exceeds 300 kGy.

Convincing evidence has also been obtained for the occurrence of polymerisation in this system via a cationic mechanism. On the other hand, in previous studies,[27] autowave regimes had been observed only in systems in which characteristic reactions are radical processes.

2. Autowaves of the detonation type

Experimental data indicating the explosive character of the reaction occurring in condensates of atomic magnesium with halogenohydrocarbons (the formation of organomagnesium compounds) and the polymerisation of cyclopentadiene with $TiCl_4$, initiated a 77 K by the impact of a metallic needle, have been published.[38,39] The authors of the above studies did not, however, investigate the dynamics of these processes and the characteristics of their development in time and space. The idea arose naturally that the above studies[38,39] were concerned with yet another type of autowave cryochemical reactions occurring under qualitatively new conditions and not requiring a preliminary activation of the solid matrix by γ-radiation. Furthermore, Kabanov et al.[39] drew attention to the wave character of the polymerisation process in a film and even estimated the velocity of the front (~200 mm s^{-1}).

We observed similar phenomena in experiments with non-irradiated thin-film ethylene + chlorine, propene + chlorine, and vinyl chloride + chlorine cocondensates.[23] It was possible to establish that the chlorination of these hydrocarbons at 77 K takes place not in the form of a homogeneous explosion but in an autowave regime and the film is pricked or scratched and is characterised by extremely intense dispersion in the front of the self-propagating reaction, which is indicated, in particular, by the "recoil" of finely dispersed fragments of the reacting matrix accompanying the wave. The second of the above factors as well as the high velocity of the front (tens of centimetres and even metres per second) give grounds for agreement with the authors,[39] who believe that yet another variety of a low-temperature wave, mechanochemical in nature and close in its essential physical features to detonation phenomena (admittedly with features of degeneracy—presonic velocities), may exist in a solid.

This problem is complex and requires the development of fundamentally new theoretical and experimental approaches to the elucidation of the mechanisms of the chemical reaction energy transfer in low-temperature detonation processes in solid systems.

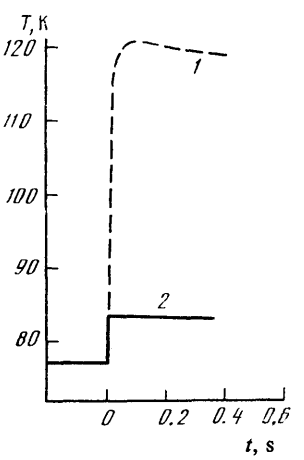


Figure 7. Temperature profiles of the reaction wave in radiolysed (curve *1*) and photolysed (curve *2*) $C_4H_9Cl + Cl_2$ specimens. The initial concentration of radicals was in both cases 2×10^{18} g^{-1}:[40] *1*, $U = 10$ mm s^{-1}; *2*, $U = 400$ mm s^{-1}.

Here one is dealing not with the usual mechanism of the excitation of the detonation wave, known in the classical theory of explosion, but with an unusual type of detonation which may be called gas-free detonation.

3. Autowaves in photoactivated systems

There exists yet another and apparently very wide and varied, as regards manifestations, class of solid systems which react at low temperatures in accordance with the travelling wave laws. Here we have in mind experiments on the local mechanical initiation of a reaction in photoactivated solid matrices.[40] It has been found that preliminary treatment of previously investigated solid systems, for example $C_4H_9Cl + Cl_2$, at 77 K not by γ-radiation but by light also leads to the accumulation in the matrix of potential energy, which can be used for the subsequent initiation of a specific chemical reaction with the aid of local mechanical breakdown. Under these conditions, the process occurs, as in the case of γ-irradiation, in the form of a layer-by-layer dispersion running wave accompanied by a chemical reaction. Furthermore, in the first experiments designed to investigate autowave reaction regimes in photolysed matrices, new features were discovered in addition to the usual features characteristic of the self-propagation of reactions in a solid at low temperatures.

We shall compare the principal characteristics of reaction autowaves in radiolysed and photolysed $C_4H_9Cl + Cl_2$ systems at 77 K (Fig. 7). In the front of a wave propagated in a photolysed specimen, there is no pre-explosive heat exchange, as in the radiolysed system. However, the remaining characteristics of the wave processes differ appreciably. Indeed the rate of propagation of the front in the photolysed system is significantly higher ($\sim$400 mm s^{-1}) than in a radiolysed system ($\sim$10 mm s^{-1}) for identical concentrations of the stabilised alkyl radicals.

The temperature profiles of the front also differ greatly: the maximum temperature in the radiolysed system is 121 K, while in the photolysed system it is only 83 K, i.e. in the latter case the superheating in the reaction zone relative to the thermostat reaches only $\sim$6 K. These differences are probably associated with the difference between the mechanisms of the chemical reactions occurring on mechanical breakdown. For the same initial concentrations of the alkyl radicals, the initial rate of reaction in the radiolysed system is slower than in the photolysed system, because some of the chlorine atoms propagating the chain are captured by Cl^- ions, which are not formed on photolysis.[41]

The problem of the vibrational instability of the movement of the cryoreaction front, demonstrated in relation to the pulsating character of the cryowave in the methylcyclohexane + chlorine system, has been formulated.[20] The hypothetical mechanism of this phenomenon was based on the fact that in the radiolysed system the zone corresponding to dispersion induced by the chemical reaction moves ahead abruptly (at rates of the order of the velocity of sound) to a depth comparable to the characteristic fragmentation grain size. The chemical reaction begins in this disrupted layer and a new jump of the reaction zone in space occurs only after the attainment of a critical density or temperature gradient. Since the rate of the chemical reaction in the breakdown zone of the photolysed system is higher, the necessary conditions for the next jump of the reaction zone are attained faster than in the radiolysed system, which in fact increases the average velocity of the wave.

One can also postulate that photolysis results in a more significant decrease than in the radiolysis by γ-rays, in the strength of the system and in the accumulation of metastable states in the latter, as a result of which the characteristic front velocities increase. One cannot rule out the possibility that the higher rates of the process in photolysed systems are also caused by the involvement of mechanisms of the detonation type.

4. The role of radicals and ions in solid-phase processes

We shall deal with yet another apparently very important aspect of the problem under consideration, which was considered by Barelko et al.[42] It is known that significant changes occurring in the lattice of the solid under the influence of the flux of radiation are not associated solely with the formation of stabilised radicals and ions. Appreciable energy changes occur in the matrix also as a result of its deformation and loosening. The deformation energy retained within the bulk of the solid can reach high values comparable to the solid–liquid and sometimes also solid–gas phase transition energies. One can apparently assume that in the irradiated solid there is a continuous spectrum of states whose energy band extends from the zero value (equilibrium state corresponding to an ideal crystal) to the energy corresponding to a free atom or fragment all the bonds of which with the lattice have been ruptured.

Thus one cannot rule out the possible activating role of this accumulated energy in the chemical process. Indeed, in the autowave reaction regimes described above, a pronounced non-linear relation was observed between the potential chemical reactivity (velocity of the wave) and the concentration of the stabilised active centres of the radical type. The most striking result of this kind was obtained in a study of the dependence of the rates of the layer-by-layer propagation of the polymerisation wave in solid acetaldehyde on the concentration of the radicals stabilised on radiolysis.[37] For doses in excess of the critical value ($\sim$300 kGy), local excitation initiates the reaction wave, whose velocity depends linearly on the dose throughout the experimental range (Fig. 8*a*). On the other hand, measurement of the EPR signal of the specimen indicates a significant deviation of the concentration of the radicals from the linear law even for doses of $\sim$50 kGy (this can be seen particularly convincingly in Fig. 8*b*). Consequently the potential chemical reactivity of the irradiated solid matrix, whose quantitative measure is the velocity of the autowave, is not determined solely by the concentration of the stabilised radicals.

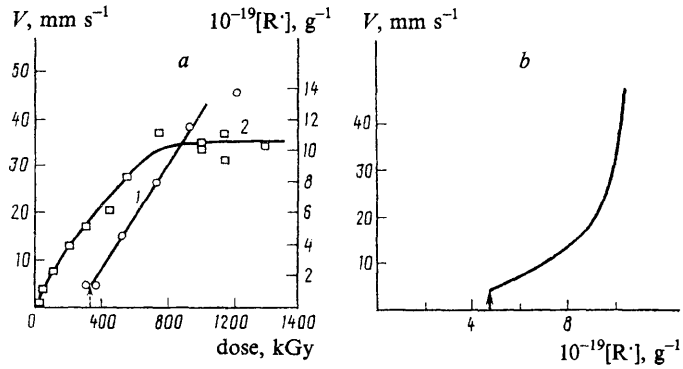


Figure 8. Dependence of the velocity of the polymerisation wave front (curve *1*) and of the rate of accumulation of radicals (curve *2*) in crystalline acetaldehyde on the γ-irradiation dose at 77 K (*a*) and the dependence of the velocity of the wave on the radical concentration (*b*) obtained from curves *1* and *2*.[37]

Direct experimental evidence has been obtained[43] for the amorphisation of crystalline methanol during its radiolysis. Direct calorimetric measurements during the heating of the specimen radiolysed at 77 K made it possible to detect heat evolution

associated with the crystallisation of the amorphised methanol. Calculation showed that the energy stored on irradiation, whose carrier is the metastable amorphous phase formed, exceeds appreciably the part of the energy accumulated in the radical and ionic states.

VIII. Conclusion

In conclusion of the description of the relevant data, it is important to define the place occupied by the phenomena considered here in the general series of different self-propagating chemical processes. For this purpose, we shall attempt to classify the chemical systems characterised by autowave phenomena. Without going into details, we shall differentiate in terms of phenomenological features two large groups to which virtually any of the systems of this kind known at present can be assigned: (1) processes of the type of combustion (the factor determining the existence of the running wave regime in this case is thermal non-linearity) and (2) processes of the branched-chain type (the so-called "chain combustion" associated with kinetic non-linearity of an autocatalytic character). Evidently the mechanism of the self-activation of a frozen reactive system, which determines the characteristic features of the wave processes investigated, is in essence close to the branched-chain mechanism.

The concept of the branched-chain mechanism in solid state chemistry is itself by no means new and has been discussed in the literature for many decades.[44,45] It is constructed on the basis of the claim that the active centres ("nuclei") of the reaction are all kinds of defects distributed in the solid matrix of the reactants and progressively multiplying in it when acted upon by the influences induced in the solid by the reaction itself. The operation of this mechanism has been examined in greatest detail and most convincingly in a large series of investigations[46–50] of the thermal decomposition of ammonium perchlorate at temperatures of about 500 K.

The authors of these studies, who observed the changes in the structure of a decomposing crystalline specimen, established that (1) the reaction of the solid reactant takes place within the framework of the strong influence on the process by the mechanical stresses induced by the decomposition reaction and consists of stages involving the formation and growth of the reaction "nuclei", their multiplication, the increase in their density, and their coalescence and (2) that, on coalescence of the separately developing reaction zones, a single reaction front may be formed and can move within the specimen in the form of a cloud of multiplying nuclei at low but quite definite velocities (of the order of 10^{-4} mm s^{-1}).

Critical phenomena, which are known to constitute a necessary feature of branched-chain and autowave processes, were not observed in the above studies.[46–50] This is most probably due to the retention in the perchlorate decomposition reaction of the leading role by the thermal mechanism. This is in fact indicated by the pronounced exponential dependence of the overall rate of decomposition of the salt (as well as of the velocity of the front) on temperature: on cooling, the reaction rapidly slows down and ceases almost completely already at 460–470 K. One should add that the perchlorate decomposition reaction is not strictly a solid-phase reaction, because it is accompanied by a change in the phase state. The authors[46–50] in fact see in this feature (in the formation of gaseous decomposition products) the cause of the mechanical deformation of the solid reactant matrix and of the development in the latter of defects activating the reaction.

Several years ago, the concept examined above was extended to low-temperature solid state chemistry.[51] The authors[51] used the idea of the self-activation of the matrix due to the feedback between the chemical reaction and the stressed state of the frozen specimen comprising the reactants to explain and describe the so-called "explosion on cooling" which they observed in the photolysed $CH_3C_6H_{11} + Cl_2$ system. The model proposed[51–53] is unfortunately not entirely concrete, because it operates with an abstract quantity called by the author the "excess free energy of internal stresses". No methods were proposed in the above studies for its measurement or for the estimation of its numerical values. Nor is the relation between this characteristic and the defectiveness of the solid matrix discussed. Furthermore, in order to achieve the feedback, the authors had to introduce into the model the feed balance equation, although their claims are based on non-thermal ideas about the mechanism of the self-activation of the reactants at low temperatures. Nevertheless, the essential features of their ideas[51–53] can be formulated by the following phenomenological postulate: the mechanical energy accumulating in the matrix promotes directly the acceleration of the chemical solid-phase reaction by the corresponding reduction of its activation barrier. In other words, in contrast to the molecular tunnelling mechanism,[4] the proposed model of low-temperature reactions in a solid is constructed wholly within the framework of the classical Arrhenius kinetics supplemented merely by certain elements of the kinetic theory of mechanical strength.[54]

We shall attempt to estimate the reality of this model. For this purpose, we turn to the results of our studies of cryochemical solid-phase reactions carried out under the conditions of the artificial transition of the specimen to a highly stressed state (see Section VI). To make the system concrete, we shall deal with the same hydrocarbon chlorination reaction which was investigated in the above studies[51–53] but with preliminary activation by γ-irradiation and not by light. It has been established experimentally that application of a mechanical stress to the specimen under the conditions of uniform compression up to pressures $P = 6 - 10^8$ Pa not only does not promote the reaction but actually hinders it: the reaction does not occur in a matrix in a highly stressed state, while the rate of the autowave process in the compressed specimen is appreciably reduced. Estimation of the specific energy introduced into the specimen yields $\Delta U = P^2/E \simeq 6-12$ kJ mol^{-1}, where E is the modulus of elasticity amounting to $(3-6) \times 10^9$ Pa, according to Benderskii et al.,[55] at low temperatures for this vitreous systems investigated. This value of $\Delta\mu$ is fully comparable to the activation energies for the test reactions measured previously[28] ($\sim$20 kJ mol^{-1}) and it should seemingly reduce significantly the activation barrier and accelerate and not inhibit the reaction. Naturally, the above considerations are far from sufficient to reject the concept developed by Benderskii and co-workers.[51–53] However, they throw doubt on the very idea that the mechanical energy of the deformed solid matrix can participate directly in its chemical activation.

Having concentrated in their investigations on the study of critical effects, Benderskii and co-workers[51–53] confined themselves to considering uniform quasi-homogeneous models in the zero-dimensional approximation. Problems concerning the extent to which the onset of the reaction in the specimen is synchronous and the mechanisms of the transfer of the excitation of the chemical reactivity within the bulk of the reacting solid, which are of fundamental importance, were only touched upon in the above

studies,[51-53] while the question of the existence of autowave regimes remained almost fully outside the framework of these investigations.‡

The ideas which we have developed concerning the nature of autowave highly intense regimes in a cryochemical reaction are constructed on the basis of a mechanism, which can be called, by analogy with the mechanism already mentioned,[8] an "energy chain". It follows from the data presented in this review that this analogy is entirely justified because the proposed mechanism involves a chain of stages, closed by negative feedback and accompanied by the transformation of the energy of the chemical reaction in time and space. Indeed, it is suggested that during the reaction part of the energy evolved accumulates in the solid matrix in the form of an elastic deformation, i.e. the unreacted part of the specimen passes in this stage to a mechanically non-equilibrium and in a certain sense "excited" state; the potential energy of this metastable state is then transformed into chemical energy. However, the transformation is not direct but occurs only through the brittle breakdown stage in which conditions are created for the chemical reaction, occurring on freshly cleaved surfaces or near them where the energy has been concentrated. This mechanism in fact determines the self-maintaining regime in the reaction of a solid specimen excited by layer-by-layer autodispersion. Ideas postulating the branched-chain character of the process are reflected by the pattern of the continually branching and migrating network of cracks in the reacting matrix.

The operation of this mechanism of the recovery of the energy of the chemical reaction, leading to the self-activation of the solid matrix, is especially favoured by low and ultra-low temperatures. Under these conditions, where the dissipation of the energy stored in the mechanically non-equilibrium matrix is retarded (as a consequence of the limiting constraint on the molecular mobility and the virtually complete loss of plasticity), there is in fact the possibility of an extremely large accumulation of energy in the lattice. The liberation of this energy on mechanical breakdown ensures the subsequent development of the self-maintaining reaction of the reactants.

In the study of solid-phase chemical reactions under the conditions of high pressures combined with shear forces, an "ultrahigh" molecular mobility was observed.[56] In order to interpret such chemical processes, the authors[56] had to postulate the existence of diffusion coefficients exceeding by 10–15 orders of magnitude the usual values. It is to be expected that the autowave ideas, based on allowance for the self-dispersion of the reacting matrix, will prove useful for the explanation of these surprising phenomena.

The postulates being developed must be resorted to also in order to account for the processes involving the "cold" evolution of matter in the universe. In particular, one can imagine a process in which compounds such as ammonia and methane are formed from a frozen mixture of the elements. Such compounds have been detected in appreciable amounts in the solid state on the cold planets of the solar system. The diurnal changes in temperature and the thermal stresses arising under these conditions in the solid coating of the planet might have served as the instrument for continuous mechanism breakdown leading to the chemical bonding of the components which were additionally activated by solar radiation. The next stage of evolution, in which solid ammonia and hydrocarbons, dispersed in the "solar mill", are converted into the simplest amines, also appears likely. It is to be expected that a direct experimental test of the chain of cryosyntheses described here will be an important step in the understanding of many secrets of space chemistry.

The importance of the results of studies on autowave phenomena examined in this review may go beyond the framework of the low-temperature field alone. It may be that the exceptionally high rates of reaction frequently observed experimentally in systems of different chemical nature are in fact associated with the autodispersion of a solid reactant matrix—a process which transfers the chemical reaction from the bulk phase to the highly reactive cleavage surface. These rates may be comparable to or exceed greatly the rates of the corresponding processes in liquid media and special attention should therefore be devoted to the non-thermal, non-equilibrium mechanisms of the activation of a solid matrix due to the inclusion in the chemical process of the energy accumulated by the lattice. A specific example illustrating this general consideration is provided by a study[57] in which the self-activating role of the dispersion of the particles of a refractory component was considered in the formation of intermetallic compounds from powders in a completely different temperature range. In this system, the dispersion of the solid component is referred to as the wetting of the particles by the liquid reaction products (a kind of mechanochemical autocatalysis).

The problem of the legitimacy of the quasi-uniform ideas, very widely used in solid-phase cryochemical kinetics, which rule out from consideration matter and energy transfer processes within the bulk of a solid matrix, was touched upon in the Introduction. The ideas described in this review concerning the autowave dynamics of reactions of solid reactants, the sensitivity of the process to local perturbations, and the non-uniformity of the development of the reaction in the specimen intensify doubts about the applicability of the above classical approach to the kinetics of solid-phase reactions. Under conditions where non-linear mechanisms operate, which are particularly characteristic of solid state chemistry, a spatially uniform course of the process is extremely unlikely. As a result of this, the integral signal due to the chemical reaction (and this signal has in fact been recorded in the vast majority of studies on the kinetics of solid-phase reactions) represents a superposition of signals arising from different points within the specimens and differing both as regards rate and phase. Evidently such a signal cannot carry reliable information about the true process kinetics and the attempt to correlate it with theoretical kinetic models described by a system of ordinary different equations would be simply erroneous.

‡ In addition to the above considerations, we should like to draw attention to an important methodological factor which might have escaped the attention of Benderskii and co-workers.[51-53] This concerns the influence of the material of the cells on the conditions in the initiation of the photochemical reaction. When experiments are carried out in γ-irradiated or photolysed systems, cooling of the specimen can, as already stated above, induce a rapid reaction. However, a decisive factor was not cooling as such but the rate of decrease of temperature. By reducing the rate of cooling, it was easy to maintain the specimen in a fully inert state down to 4.2 K. However, this is characteristic only of Pyrex bulbs. Another picture is observed when quartz bulbs are used. The strict reproducibility of "explosion on cooling"[51-53] might have been associated with the exclusive use of quartz cells in the experiments. The coefficients of the thermal deformation of this material differs greatly (in contrast to that of ordinary glass) from that of the reactants, as a result of which the inevitable peeling of the substance from the walls of the bulb on cooling (i.e. fracture) induced the "explosion" described by Benderskii and co-workers.[51-53]

We shall now turn, as an example, to the case of "polychronic" kinetics well known in solid-phase radiation chemistry.[58] In order to explain the phenomenon of the "kinetic arrest of the reaction", actually recorded with the aid of integral methods, a spectrum of kinetic constants is introduced. Its presence is attributed to the non-uniformity with respect to energy states of the active centres distributed in the matrix. The autowave approach makes it possible to explain the experimental phenomenon without resorting to a polychronic kinetic scheme: it is easy to image that separate reaction waves arise on local perturbations during the process and are propagated frontally throughout the specimen, being arrested at some kind of non-uniformities of the matrix or its macrodefects. Another situation, where the chemical process simply cannot develop uniformly because of spatial instability and the reaction is accompanied by the formation of the so-called "dissipative domain structures",[59] is also entirely realistic.§ Thus in each specific case, quasi-uniform models and in particular "polychronic" kinetic models require special experimental justification, which rules out the influence of autowave phenomena on the dynamics of the development of the reaction.

The ideas about the activating role of self-disruption may prove useful in a number of related fields of study dealing with solids.

This may in fact be a clue to the high sensitivity of many explosive substances to friction and impact. Hitherto the general theory of the sensitivity of explosive substances to mechanical influences has been constructed solely on the basis of thermal ideas, according to which the mechanical energy introduced into the specimen must be transformed initially into thermal energy to create a hot spot, and only then can it excite explosion via a "centre of origin" mechanism. It appears likely that the initiation of an explosive reaction is caused not by the conversion of mechanical energy into thermal energy but by the appearance in the specimen of chemically high reactive cleavage planes arising on friction or impact.¶

The processes involving the transition of a solid from a metastable, amorphous state to a polycrystalline state, which have been vigorously investigated (especially in recent years) (see Shklovskii[64] and the references therein) are autowave in character and outwardly resemble the solid-phase cryochemical reactions considered in this review. In this class of processes, one cannot rule out the operation of the same autodispersion mechanism, facilitating the phase transformation as a result of its transfer from the bulk phase to the fracture surface. Indeed, both classes of processes resemble one another as regards their essential physical features and are associated with the rearrangement of the solid matrix. Both are exothermic and differ only in the magnitude of the thermal effect. Furthermore, one should add that the cracking and dispersion of the specimens, which can be observed even with the naked eye, are extremely typical for wave processes involving the decomposition of amorphous states.†

Yet another field, seemingly very remote from solid state chemistry, is that concerned with the puncturing of transparent media by a flux of radiant energy with a high power (radiant breakdown).[66] As regards their character, these processes can also be classified as autowave processes. The current theory describing these processes, is close in its essential features to the theory of combustion. The difference consists solely in the transition from the exponential temperature variation of the intensity of the chemical heat evolution in the case of combustion to the exponential absorption of radiant energy by the solid medium in the optical breakdown. Analysis of the literature on the optical strength of glasses suggested the idea that the mechanism of the autoacceleration which we have developed in relation to chemical reactions in a solid can be resorted to also in order to describe the dynamics of the radiant disruption of glasses. Using these ideas, the picture illustrating the disruption of the specimen by a light flux can be represented as follows. The light-absorbing submicron impurities, always present in glasses, are heated by the radiant flux. The temperature attained under these conditions presents no risk to the material because of the intense conductive removal of heat from a given small centre and the heated zone, around the impurity particle, is just as small as the absorbing centre itself. However, owing to the high curvature of the spherical centre of such size, the temperature gradients generated are very high. This factor in fact influences the strength of the material and leads to cleavage and the peeling of the particles from the matrix. The non-equilibrium states on the cleavage plane arising at the instant of fracture begin to absorb energy vigorously, which leads to the heating of a fresh surface and then to the cracking of the next layer of the irradiated transparent medium. The cracking at the impurity can be initiated in this way with subsequent wave propagation of the disruption under the conditions of the layer-by-layer dispersion of the specimen. This process can be described theoretically with the aid of a phenomenological model completely identical with the model examined in the present review. The information published[66] about two regimes in the cracking of glasses, occurring as a function of the initial excitation conditions, is qualitatively predicted by the model indicated. The considerations described here concerning the mechanism of the optical breakdown of transparent media are apparently convincing, as shown, in particular, by their use of specialists in the given field.[67]

In conclusion of the review of studies on the phenomena involving the running waves of cryochemical reactions in a solid and of the analysis of the mechanisms controlling these processes, we may note that the studies which have been carried out are mainly phenomenological in character. Naturally, the next task is the solution of a whole series of fundamentally important problems associated with the elementary stages of the process. The main ones are the elucidation of the nature of the active states arising on the cleavage planes, their lifetimes, the establishment of the mechanism of the intensification of transport processes on fresh fracture

§ Similar phenomenon have been observed in heterogeneous catalysis,[60-62] in the field close to solid state chemistry.

¶ V V Boldyrev drew our attention to the fact that similar ideas concerning the nature of the sensitivity of explosives to friction and impact were put forward more than 30 years ago by Ubbelohde.[63] However, owing to the lack at that time of adequate physical justification, this concept was not developed further and was in essence forgotten.

† Yet another possible application of the ideas about self-maintaining phase transitions in a solid, formulated in a brief communication by American geophysicists, is extremely interesting.[65] They put forward a hypothesis according to which the phase transformations in terrestrial rocks as a result of the operation in them of an autocatalytic self-disruption mechanism are the main cause of earthquakes and other catastrophic geotectonic processes.

surfaces, the search for electrical signals associated with the emission of charged particles during the cracking process, and also the search for signals of the type of triboluminescence arising from the front of the dispersion (chemical reaction) running wave.

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