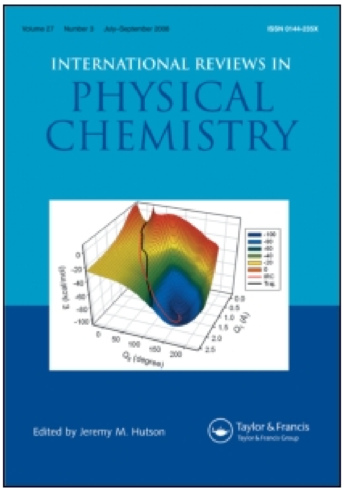

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THRESHOLD EFFECTS AND AUTOWAVE PROCESSES IN LOW-TEMPERATURE CHEMICAL REACTIONS IN IRRADIATED SOLIDS

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ABSTRACT

Fast self-propagating chain reactions (such as chlorination of hydrocarbons, hydrobromination of olefines, and polymerization) can be initiated at low temperatures (down to 4.2 K) by a local mechanical fracture of vitreous and polycrystalline samples which contain stabilized active centres (free radicals) accumulated during previous irradiation by ^{60}Co γ-rays. The dependence of the reaction rate on the strength of a triggering mechanical impact (as well as on the concentration of preaccumulated active centres) is found to be of the threshold type. A sharp isothermal rise in the rate of a chemical reaction synchronous with local brittle fracture, and observed regularities of the reaction zone propagation along an extended sample, distinguish the process from classical thermal self-propagation.

In all the systems studied the initial fracture produced autowave propagation of the reaction front along the sample with a rate much above that of heat transfer but much below the sound velocity. The jerky nature of the reaction front motion is established.

The suggested treatment of the new observed phenomena is based on the positive feedback between the mechanically triggered and accelerated (via various heterogeneous factors) chemical reaction in irradiated low-temperature solids and the further mechanical impact to the samples caused by this reaction.

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INTRODUCTION

Our studies (1970–1973) of the radiation-induced solid-state polymerization of formaldehyde at 4–140 K have led to the observation of the spontaneous growth of long polymer chains even in the vicinity of absolute zero (Kiryukhin *et al.*, 1972) and to the discovery of a quantum low-temperature limit of the chemical reaction rate (Goldanskii *et al.*, 1973).

A second example of such a limit observed in our laboratory dealt with the hydrobromination of ethylene at 30–90 K (Kiryukhin *et al.*, 1979; Barkalov *et al.*, 1980). The weakness of the kinetic isotope effect in this reaction allowed us to come to certain conclusions concerning the mechanism of this process, namely the decisive role played by the rapprochement of the reactants as whole molecules rather than by the transfer of hydrogen atoms, concerning the general high significance of low-frequency intermolecular motions in low-temperature chemical reactions in solids.

Many other examples of a low-temperature limit of chemical reaction rates have been observed since the publication of the papers by Kiryukhin *et al.* (1972) and Goldanskii *et al.* (1973) for various systems of solid reactants (*see* surveys by Goldanskii, 1979a, b); a general description of chemical reactions in solids as radiationless electron transitions was developed, where account should be taken both of quantized motion along the reaction coordinate and intermolecular vibrations (Klochikhin *et al.*, 1978; Goldanskii, 1979a, b; Ovchinnikova, 1979; Benderskii *et al.*, 1980, 1982; Trakhtenberg *et al.*, 1982). Thus, the aim of numerous experimental and theoretical studies of low-temperature chemical reactions in solids was the understanding of the nature of the elementary act of such reactions.

Meanwhile the continuation of our studies of post-conversions of irradiated solids at low temperatures resulted in the revelation of peculiar new macroscopic phenomena which are described below.

Briefly summarizing the subsequent presentation, we note that

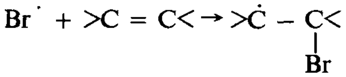
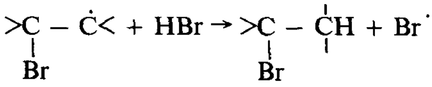
1. The chain chemical conversion of irradiated vitreous and polycrystalline mixtures of solid reactants can be triggered by mechanical impact like brittle fracture (while these mixtures do not interact at the temperatures under study without such mechanical initiation).
2. Such triggering is connected to various threshold effects, e.g., a threshold strength of the initiating mechanical impact (as well as a threshold dose of preceding radiation which means a threshold amount of preaccumulated active centres).
3. The positive feedback between the mechanical impact and chemical reaction leads to the auto-acceleration of the reaction (even under essentially isothermal conditions) and to the appearance of its autowave propagation with a velocity much above the rate of heat transfer but still much below the sound velocity.
4. The spatial and temporal development of chemical reaction has a pronounced stepped, pulsating structure.

This article is devoted mainly to the exposition of experimental facts and contains only a very short description of attempts at their mathematical treatment. We leave aside any approaches to the formulation of a unified theory of quantum low-temperature conversions in solids based on the modern theories of tunnelling phenomena in chemical reactions (Goldanskii *et al.*, 1973; Klochikhin *et al.*, 1978; Goldanskii, 1979a, b; Ouchinnikova, 1979; Bell, 1980; Benderskii *et al.*, 1980, 1982; Trakhtenberg *et al.*, 1982) and in elementary fracture processes (*see*, for example, Salganik, 1969, 1970; Gilman and Tong, 1971), although such approaches will present tempting problems for the future.

INVESTIGATED SYSTEMS

All our investigated systems contained as active centres the stabilized free radicals which were accumulated during the low-temperature radiolysis. These very radicals give rise to a chain of chemical conversions provided the required triggering conditions are established. In the absence of such conditions no reactions are observed—either in the course of γ-irradiation or after its completion. The following chain reactions were used:

1. *Chlorination of saturated hydrocarbons*
   (a) $\mathrm{RH} \overset{\gamma}{\rightsquigarrow} \mathrm{R}' + \mathrm{H}'$
   (b) $\mathrm{R}' + \mathrm{Cl}_2 \rightarrow \mathrm{RCl} + \mathrm{Cl}^{\cdot}$
   (c) $\mathrm{RH} + \mathrm{Cl}^{\cdot} \rightarrow \mathrm{HCl} + \mathrm{R}^{\cdot}$
   (d) $\left.\begin{matrix}\mathrm{Cl}^{\cdot} \rightarrow \\ \mathrm{R}^{\cdot} \rightarrow\end{matrix}\right\}$ termination

2. *Hydrobromination of olefines*
   (a) $\mathrm{RH} \overset{\gamma}{\rightsquigarrow} \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot}$
   (b) $\mathrm{R}^{\cdot} + \mathrm{HBr} \rightarrow \mathrm{RH} + \mathrm{Br}^{\cdot}$
   (c)

$\mathrm{Br}^{\cdot} + {>}\mathrm{C}{=}\mathrm{C}{<} \rightarrow {>}\dot{\mathrm{C}} - \underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}}{<}$
   (d)

${>}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}} - \dot{\mathrm{C}}{<} + \mathrm{HBr} \rightarrow {>}\underset{\mathrm{Br}}{\underset{|}{\mathrm{C}}} - \underset{|}{\overset{|}{\mathrm{C}}}\mathrm{H} + \mathrm{Br}^{\cdot}$
   (e) $\left.\begin{matrix}\mathrm{Br}^{\cdot} \rightarrow \\ \mathrm{R}^{\cdot} \rightarrow\end{matrix}\right\}$ termination

3. *Polymerization*
   (a) $\mathrm{M} \overset{\gamma}{\rightsquigarrow} \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot}$
   (b) $\mathrm{R}^{\cdot} + \mathrm{M} \rightarrow \mathrm{RM}^{\cdot}$
   (c) $\mathrm{RM}^{\cdot} \rightarrow$ termination

A brief characterization of the systems employed is given below.

Butyl chloride (BC) + Cl_2. On rapid freezing, a solution of Cl_2 in BC vitrifies (Kiryukhin *et al.*, 1977). Thawing this solution converts it into a super-cooled liquid at $T_g \approx 100$ K. The irradiation of the system by γ-rays from a $^{60}\mathrm{Co}$ source at $T \leqslant 77$ K results in the accumulation of stabilized active centres. The chain chlorination reaction typical of the whole class of post-radiation reactions proceeding in the course of devitrification of irradiated matrices (Barkalov, 1980) is initiated only on heating the system, starting from the devitrification region. The enthalpy change of this reaction is 33 ± 3 kcal/mole. At $T < 100$ K no chain chlorination was observed (Kiryukhin *et al.*, 1977; Barkalov, 1980).

Methylcyclohexane (MCH) + Cl_2. This system is similar to the BC + Cl_2 system. Its devitrification temperature $T_g \approx 90$ K.

Ethylene + HBr. This system represents an equimolar crystalline complex C_2H_4.HBr, whose melting point is 110 K. The phase transitions for this complex and the low-temperature chain hydrobromination kinetics at $T > 30$ K have been described by Kiryukhin *et al.* (1978, 1979) and Barkalov *et al.* (1980). Hydrobromination below 30 K was not observed.

2-methylbutadiene-1,3 (*MB*) + *SO_2*. On freezing, a solution of SO_2 in MB vitrifies. The thermoactivated copolymerization in this system containing active centres stabilized during the low-temperature radiolysis begins at $T \sim T_g \approx 100$ K.

ACTION OF ARTIFICIAL BRITTLE FRACTURE ON IRRADIATED FROZEN SYSTEMS

Samples were subjected to brittle fracture by producing thermo-elastic stresses, i.e., the rate of temperature change was chosen so that temperature gradients causing sample fracture should be provided. In the course of heating or cooling the sample, the temperature of its outer surface and integral thermal effects were measured (for details of the calorimetric technique, *see* Barkalov and Kiryukhin, 1980).

Experiments on non-irradiated samples of the vitrified MCH + CL_2 system (Zanin *et al.*, 1981c) showed that the slow heating of samples from 4.2 to 77 K caused no cracking and the calorimeter registered no thermal effects (*Fig. 1*: I and II, solid lines). On the contrary, fast heating resulted in the fracture of the sample, and the enthalpy change in this process was registered by the calorimeter (*Fig. 1*: III and IV, solid lines). The formation of cracks in the sample was also registered both visually and acoustically.

During slow heating of the sample containing stabilized radicals (^{60}Co γ-irradiation), when sample fracture does not occur, the reaction was not observed (*Fig. 1*: I and II, dashed lines). When brittle fracture occurs during rapid heating, the reaction takes place (*Fig. 1*: III and IV, dashed lines).

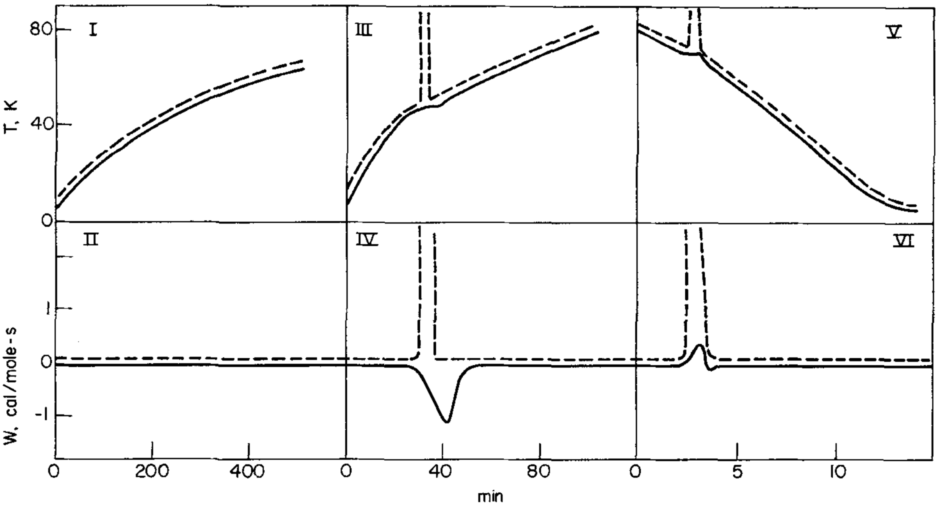


FIG. 1. Time dependence of the temperature of the sample (Cl_2 + MCH, molar ratio 1:3) (I, III, V) and thermal effects (II, IV, VI); solid lines: non-irradiated samples; dashed lines: samples irradiated by γ-rays from ^{60}Co at 77 K, dose 2.7 Mrad.

Brittle fracture of the sample was also effected during rapid cooling. *Figure 1* (V and VI) presents results for a sample which was cooled quickly enough to produce fracture. As expected, the fracture of the irradiated sample was accompanied by the initiation of the chemical conversion, the latter not being observed in the non-irradiated sample.

To prove the decisive role of the fracture of the sample in the initiation of chemical conversion in it, a direct experiment with mechanical fracture of the sample was performed at a fixed temperature of the thermostat. The brittle fracture of the sample containing stabilized radicals was accomplished at 4.2 K by turning a frozen-in thin metal rod. At the instant of local fracture of the sample, the chemical reaction was switched on and spread over the sample. Such an outburst of chemical conversion was observed in experiments both with vitreous (Zanin *et al.*, 1981a, c) and polycrystalline (Zanin *et al.*, 1981d) systems.

These first experiments showed that the brittle fracture of samples caused an abrupt rise in the rate of chemical conversion, the process having a self-accelerating nature and spreading throughout the sample. Thus it may be concluded that the fracture of the sample plays the role of a triggering device which switches on a certain mechanism of positive feedback. To ascertain the nature of this mechanism, investigations into the dynamics of the reaction outburst were carried out (Zanin *et al.*, 1981a).

DYNAMICS OF REACTION OUTBURST INITIATED BY LOCAL FRACTURE OF SAMPLES. THRESHOLD EFFECTS

The reaction was locally initiated by means of an electric microheater embedded into the sample during freezing. A capacitor could be discharged through the microheater, and the energy released during the pulse heating varied. With this technique it was possible to obtain the temperature gradients required for sample fracture in the region near the heater. The temperature in this region was registered with a thermocouple (copper–constantan) mounted on the heater surface.

Switching on the pulse heater did not give rise to the reaction burst in non-irradiated samples, i.e., when there were no active centres (free radicals) pre-accumulated in the samples. Increasing the dose of ionizing radiation (^{60}Co γ-rays) produced a rise in the concentration of active centres, and finally this enhancement of the pre-irradiation permitted certain threshold conditions to be reached, corresponding to the appearance of mechanical triggering of chemical conversion of pre-irradiated low-temperature solid samples.

In the case of such 'overcritically' pre-irradiated samples, the reaction broke out in step with the application of definite pulse energies to the heater. As seen from *Figure 2* (A and B), at the pulse energy $q < 2.5$ J the sample remained reactionless, and when $q > 2.5$ J, the reaction outburst took place. An oscillographic display of the process made it possible to measure the characteristic time of the reaction outburst at different pulse energies (*Fig. 2B*). The results obtained implied the following characteristic features of the process:

1. At $q < q_{cr}$ reaction is not observed (its rate is negligible).
2. The reaction outburst is synchronous with the application of the initiating pulse.
3. The outburst of the reaction proceeds quickly without any induction period, its characteristic time being about 0.05 s (for comparison, thermal lagging of the sample leads to times of tens of seconds) and does not depend on the pulse energy (*Fig. 2B*).

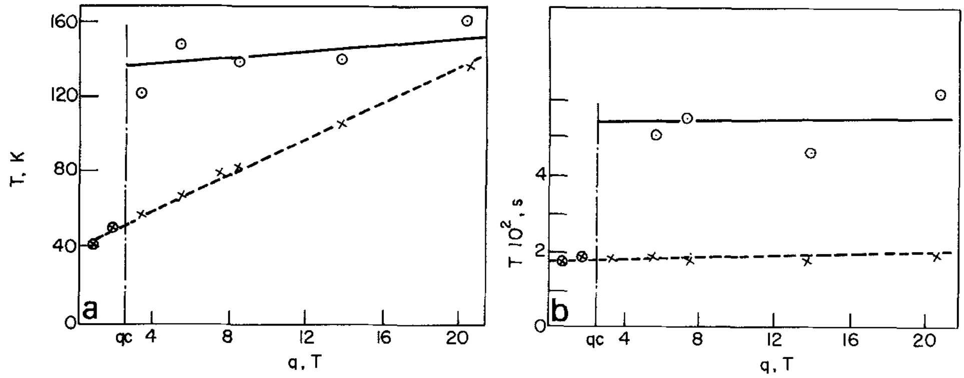


FIG. 2. Maximum temperature (a) and characteristic reaction time (that is required for reaching 0.5 T_{max}) for $Cl_2 + BC$, 1:3 (b) as functions of pulse energy, q; x: non-irradiated sample; ⊙ : sample irradiated by γ-rays from ^{60}Co, dose 2.7, Mrad.

These features of the dynamics of the outburst stage bear evidence of the fact that the classical thermal mechanism of feedback is not a determinant in this phenomenon. Thus in the subsequent treatment we assumed quite naturally that mechano-chemical effects were of crucial significance for all phenomena observed in our experiments and described in this paper. In principle, one can speak about two kinds of effects of mechano-chemical acceleration of chemical reactions:

1. *Homogeneous*, connected to the uniform thermoelastic stress of the reactant mixture and corresponding decrease of the activation energy.
2. *Heterogeneous*, connected to the formation of cracks of different sizes, various types of dislocations and defects, etc.

We have chosen the second of these variants and restrict ourselves here for simplicity to the treatment of effects of brittle fracture.

Indeed, as known from the mechanics of rigid bodies, the potential energy accumulated in a solid during its elastic deformation is concentrated in the region immediately adjacent to the surface which is formed when the fracture of the solid occurs (Regel *et al.*, 1974). This energy transformation is accompanied by considerable changes of physical and chemical properties of the substance at its surface (electron emission from fractured surfaces, a high concentration of radicals on them, a sharp increase of molecular mobility (Baramboim, 1978)). It is quite natural to hypothesize that such transformation of mechanical energy will contribute to chemical conversions in a solid at low temperatures when the ordinary mobility of reacting particles is insufficient to provide a reaction effectively. In other words, it can be assumed that the transition of the process from homogeneous to heterogeneous caused by the formation of fractured surfaces would considerably accelerate a low-temperature chemical conversion.

In accordance with the above-mentioned considerations, the rate of chemical reaction is a certain function of the specific surface area S (per unit volume) formed during the fracture. The feedback acting in the system manifests itself in that the active surface growth rate is proportional to the reaction rate. Then the equation describing the formation of a new surface may be represented in the form similar to a chain-branching process:

$$\frac{ds}{dt} = F(S) - G(S) \qquad (1)$$

where $F(S)$ is the generation rate of a new surface and $G(S)$ is the rate of its deactivation. As $G(S)$ must be a linear function (as in the case of a unimolecular process) and if $F(S)$ has an effective order higher than the first with respect to S, then the model will qualitatively describe the observed experimental facts:

1. Threshold effects of the origin and self-accelerating development of the reaction.
2. The possibility of initiating the reaction outburst by creating at the first instant some new surface by fracturing the sample either mechanically or thermally.

Evidently it is possible to suppress the onset of the process (i.e., to eliminate critical effects) by decreasing the generation rate $F(S)$, and since this rate is proportional to the initial concentration of radicals stabilized during the radiolysis, if this is reduced the parameter should be decreased. This was confirmed in experiments on the $C_2H_4 \cdot HBr$ system (Zanin *et al.*, 1981d).

AUTOWAVE PROPAGATION OF REACTION

It is important that systems described by a non-linear model—such as (1)—are characterized by autowave processes in samples of sufficient extent in response to a local disturbance. These processes are formally similar to the propagation of chain flames (Zeldovich, 1944) and catalytic activity waves (Barelko and Volodin, 1976).

Our earlier experiments (Zanin *et al.*, 1981b, 1982a) have demonstrated the initiation of the spontaneous propagation of reaction waves in all the systems in question by their local disturbance (mechanical fracture or thermal fracturing pulse). As the reaction is accompanied by a change in the colour of the sample, the propagation of the reaction front can be recorded by filming. It was detected in such a way that a flat front was quickly formed in samples immersed in liquid nitrogen or helium and then travelled parallel to itself along the reaction tube axis. The reaction front moved with practically constant speed of *c*. 1–2 cm s^{-1}.

If the initiating crack makes an acute angle with the tube axis (this can be achieved by application of a breaking force), an 'oblique' front is formed. Subsequent propagation of this front proceeds without change of its form or of its orientation with respect to the reaction tube axis (Zanin *et al.*, 1981b, 1982a). Thus the shape of the reaction front and the characteristics of its propagation are determined by the initiating fracture and its spreading rather than by the release and transfer of reaction heat, which would have led to the elimination of the oblique character of the reaction front and of its initial quaint shape.

To investigate the structure of the reaction wave front, a number of experiments for thermographing the autowave process have been concluded. The wave propagation velocity was calculated from the time required for the wave to travel a distance of 3–5 cm between two thermocouples. ***Figure 3*** presents typical profiles of the travelling temperature wave front swept in time and in the coordinate x direction at initial temperatures 77 K (*Fig. 3A*) and 4.2 K (*Fig. 3B*). From the oscillographic display ('*bc*') of the rapid onset of the reaction it was found that its duration was equal to *c*. 0.1 s, i.e., the width of this zone $\delta \approx 2$ mm at 77 K, and *c*. 0.3 s ($\delta \approx 3$ mm) at 4.2 K.

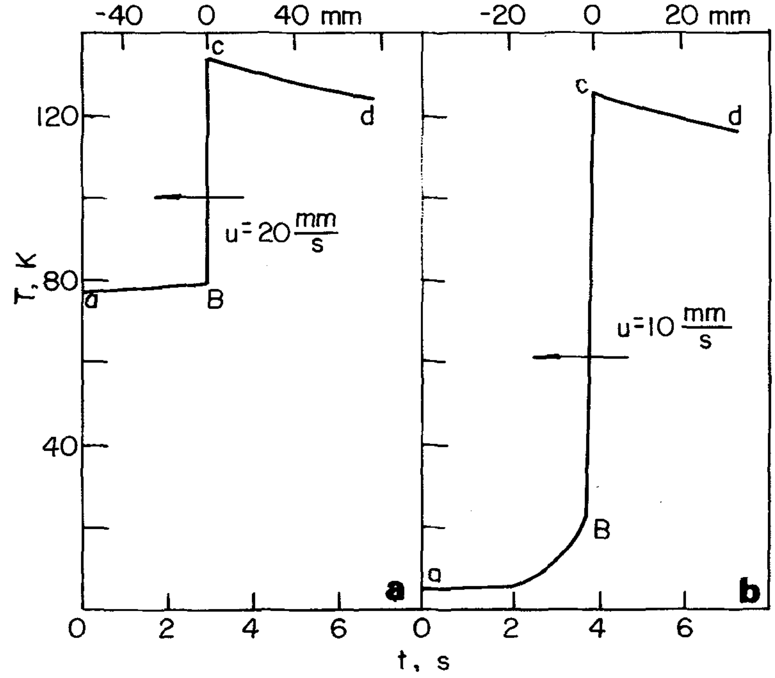


FIG. 3. Temporal and x-direction sweeping of typical temperature waves in the reaction $Cl_2 + C_4H_9Cl$ at 77 K (a) and 4.2 K (b); dose 2.7 Mrad.

The structural features of the reaction wave front that distinguish it from the customary form for classical thermal self-propagation are as follows:

1. The stage of the 'inert' (reactionless) pre-outburst heating is only weakly pronounced or is completely absent.
2. Switching the reaction on and off occurs spasmodically (*see* the lower and upper breaks on thermograms).
3. 'Switching-on' of the reaction occurs at temperatures far below the temperature for the outset of the thermoactivated reaction.
4. The velocity of wave propagation changes only slightly from 77 to 4.2 K—contrary to a corresponding significant change in convective heat transfer.

The influence of the diameter of cylindrical samples is also different from the case of classical thermal self-propagation. Decreasing the diameter from 10 to 0.5 mm failed to suppress the autowave process and the reaction wave velocity remained practically unchanged in this case. *Figure 4* shows a cinegram of the propagation of the reaction front in a capillary, *c.* 1 mm in diameter, immersed in liquid helium. The realization of the autowave process of the reaction propagation in such small samples testifies to the fact that the classical thermal mechanism is not determinant in the phenomenon in question.

Let us estimate the expected velocity of the wave propagation according to the classical thermal mechanism (the Arrhenius law of heat evolution) using the experimental width δ of the travelling wave front and the relationship $U = a/\delta$, where a is the thermal conductivity of the sample measured by the normal method,

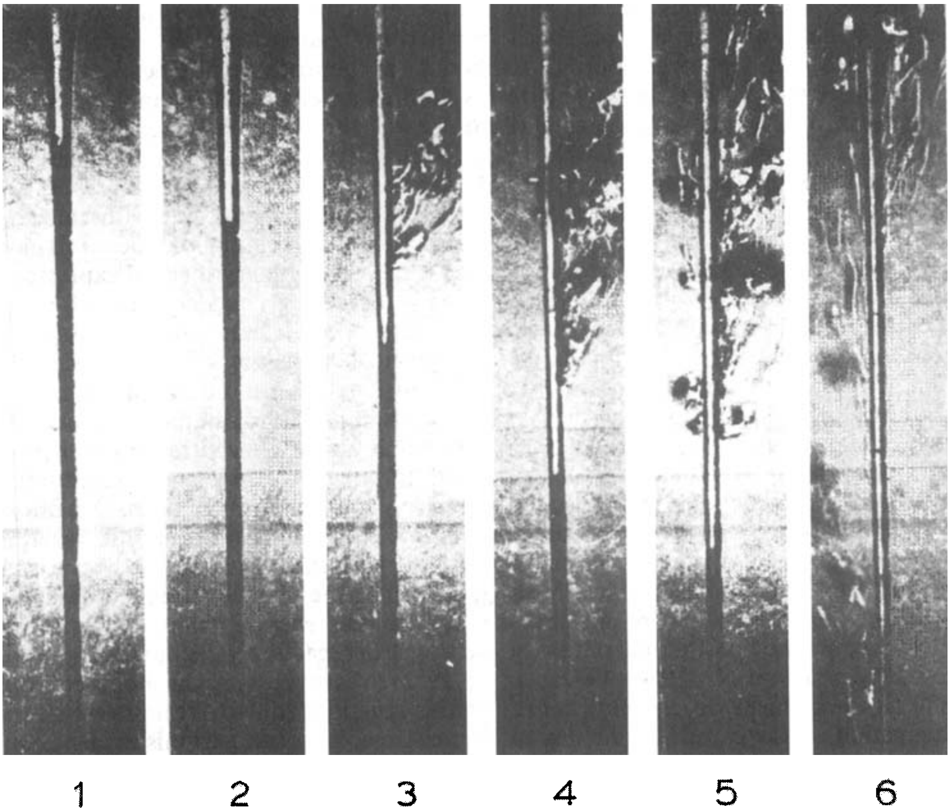


FIG. 4. Cinegram of reaction front propagation in a capillary, diameter *c.* 1 mm, at 4.2 K. Time intervals between frames 1 and 2: 0.14 s; 2 and 3: 0.06 s; 3 and 4: 0.14 s; 4 and 5: 0.14 s; 5 and 6: 0.72 s; dose 4.5 Mrad.

$a \approx 1 \times 10^{-2}$ cm^2 s^{-1}. This estimation gives 5×10^{-2} and 3×10^{-2} cm s^{-1} for 77 and 4.2 K, respectively, thus being a factor of 1.5–2 below the experimental velocity values.

A temperature difference in the wave front is connected with the degree of conversion of reactants. Since the heating of the system for *c.* 0.1 s may be considered adiabatic, it is possible to estimate the degree of conversion in the reaction front from the known temperature dependence of the heat capacity of the system and from the exothermicity of the reaction. For the Cl_2 + BuCl system (*Fig. 3*) it equals 10–15%, this being in good agreement with the experimental value. A small value of the degree of conversion is likely to be caused by the heating of the system above T_g which results in the partial decay of stabilized radicals.

Autowave propagation of the copolymerization process was observed in the system 2-methylbutadiene-1,3 + SO_2 immersed in liquid helium. In this case the propagation of a copolymerization wave in the sample converted it almost entirely into a copolymer (Zanin *et al.*, 1982b). The transition to a viscous super-cooled liquid at $T > T_g$ in the case of macroradicals did not result in their decay (Barkalov, 1980). Thus, a reduction in the temperature difference in the wave front to such an extent that the maximum temperature should not exceed T_g will lead to an increase of the conversion degree.

Studies of the kinetics and mechanism of elementary processes of photo-induced chain chlorination of hydrocarbons in vitreous matrices at low temperatures, performed jointly by two groups of researchers at the Institute of Chemical Physics (Misochko *et al.*, 1980), led to the observation of an additional example of a low-temperature plateau in the chemical reaction rate. The continuation of these studies by Benderskii *et al.* (1980, 1982a, b, c, 1983) was devoted to mechano-chemical explosions of pre-photolyzed mixtures of solid reactants at low temperatures. It was observed that the explosion of solid mixtures of methylcyclohexane with chlorine, after the photolysis of chlorine, was caused by the cooling of such mixtures (Benderskii *et al.*, 1980). Contrary to expectations for ordinary thermal explosions, the inflammation temperature rose here with increasing concentration of active centres. The above-mentioned practical absence of the 'inert' (reactionless) pre-outburst heating of reactant mixtures was confirmed by Benderskii *et al.* (1983). The acceleration of chain chlorination by one-dimensional laser-induced pulse compression, not accompanied by any mechanical destruction of the samples, was claimed by Benderskii *et al.* (1982a, b). It was shown that at low concentrations of hydrocarbon radicals ($\leqslant 2\times10^{17}$ cm^{-3}) the fraction of conversion does not exceed 0.02–0.03 and is not connected to the formation of any local regions (of linear size above *c.* 30 nm) with a high degree of conversion. Thus the explosion-type reaction proceeds during *c.* 1 ms with the chain length $\nu\sim100$, under the spatially-isothermal conditions. The absence of local heating, as well as the above-mentioned data (*see* §4) on the absence of pre-outburst heating at the reaction front, convincingly demonstrate the non-thermal nature of the triggering reaction. The model suggested by Benderskii *et al.* (1980, 1982a, b, c, 1983) was based on the homogeneous mechano-chemical acceleration of chemical reactions due to the decrease of activation energy caused by the thermoelastic stress. According to this explanation, part of the energy released in exothermic reaction is transformed into the excess energy of matrix deformation which, in its turn, accelerates the reaction. The shape of samples used by Benderskii *et al.* (1982a, b, 1983) was chosen from the point of view of studies of homogeneous explosion-type reactions and could not test the possibility of autowave processes of reaction propagation, whose observation shed additional light on the reaction mechanism. Thus, the uniformity of views expressed in Benderskii *et al.* (1980, 1982a, b, c, 1983) and numerous publications of our group quoted in this survey supports the main point—the formulation of mechanical, non-thermal initiation of chemical reactions in low-temperature radical-containing solids—while the differences are concentrated on questions of comparatively minor importance—whether the acceleration of reaction by mechanical impact and the positive feedback between this impact and the reaction rate is homogeneous (Benderskii *et al.*, 1980, 1982a, b, c, 1983) or heterogeneous (Zanin *et al.*, 1981a, b, c, d, 1982a, b) in origin.

SIMPLE MODEL TREATMENT OF AUTOWAVE PROCESSES IN LOW-TEMPERATURE REACTIONS

An illustrative approach to the description of the autowave process in question may be obtained from the approximation (1) by introducing into it a diffusion term which takes into account the spatial distribution of the reaction rate and other properties of the sample:

$$D\frac{d^2S}{dx^2} - U\frac{dS}{dx} + \left[F(S) - G(S)\right] = 0 \tag{2}$$

where S is the specific active area formed during fracturing, U is the velocity of the travelling fracture wave, x is the coordinate and D is a certain effective coefficient of crack migration which has the dimensions of a diffusion coefficient. This generalized model can be particularized provided the mechanism of the fracture front movement is accurately described. As mentioned above, this process can be realized as a result of density gradients in the reacting sample (an isothermal mechanism) or as a result of thermo-elastic stresses in it due to the exothermicity of the reaction. It is just this latter mechanism which is considered by Barelko *et al.* (1982), since it is closer to the experimental conditions characterized by non-isothermicity.

We consider that the brittle fracture which initiates the reaction occurs when the temperature gradient reaches its critical value $(dT/dx)^*$. This gradient produces a stress equal to the ultimate strength of the material. The reaction proceeds through a limited time interval τ during which fracture surfaces generated by reaction conserve their activity. The equation describing the wave process resembles in its form the fundamental combustion equation

$$\lambda\frac{d^2T}{dx^2} - C\varrho U\frac{dT}{dx} + Q = 0 \tag{3}$$

where T is the absolute temperature, λ is the thermal conductivity, C and ϱ are the heat capacity and density of the solid mixture of reactants, respectively.

The principal difference between the autowave and combustion processes is that in the former case Q is a function of the temperature gradient but not of the temperature itself. The value of Q is non-zero only within the reaction zone of width $\delta = U\tau$ and reaches its maximum value at $\frac{dT}{dx} \equiv \left(\frac{DT}{dx}\right)^*$.

Solving this problem (Barelko *et al.*, 1982) gives the equation for finding the wave velocity:

$$G(U) = U^{-1}\left[1 - \exp(-U^2)\right] = G \tag{4}$$

Here $G = \sqrt{a\tau}(\delta T/\delta x)^*/\Delta T$ is a given dimensionless critical gradient, $a = \lambda/C\varrho$ is the thermal conductivity, $u = U\sqrt{\tau/a}$ is the unknown dimensionless velocity of wave propagation, ΔT is an adiabatic temperature difference. The solution of this equation exists for $G < G_0 \approx 0.64$ and is not unique: two different values of u correspond to the same value of G. Consequently there are two types of stationary conditions of the reaction wave propagation differing in the velocity, structure and properties of the wave.

The slower reaction wave is similar to the usual combustion wave: the reaction zone is small compared to the heating zone, and the temperature in the reaction zone is close to a maximum. The velocity of the slower reaction wave is given by

$$U \approx a\left(\frac{\delta T}{\delta x}\right)^* \Big/ \Delta T \tag{5}$$

The faster reaction wave is entirely different in its nature: the temperature at the point of reaction switching does not differ practically from the initial temperature.

In this case the role of heat transfer consists only in ensuring continuity of the temperature and temperature gradient. Thus it is quite natural that at $u \gg 1$ the wave velocity is no longer dependent on the heat-transfer parameters. The velocity of the faster reaction wave is given by

$$U \approx \Delta T/\tau \left(\frac{\delta T}{\delta x}\right)^{*} \tag{6}$$

The faster-wave condition is less sensitive to perturbations (both mechanical and thermal) in comparison with the slower-wave condition. It is obvious that, in the case of slow movement, various inhomogeneities in the sample (for instance, local reduction in strength, i.e., a decrease of $(\delta T/\delta x)^{*}$) may lead to the displacement of the coordinate of the reaction onset towards the fore-part of the front and cause a

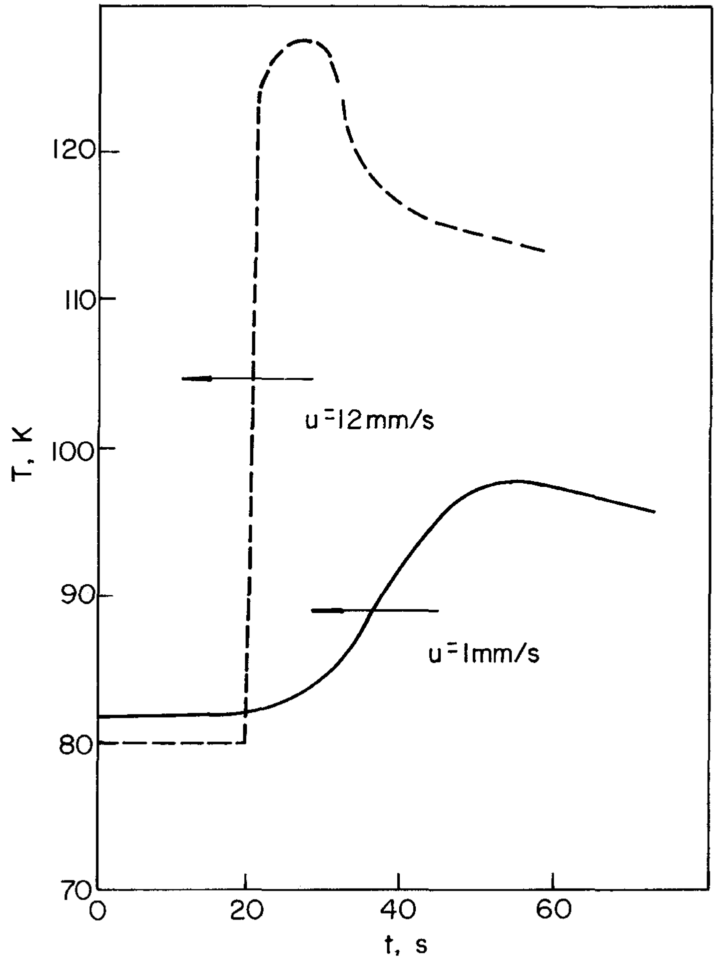


FIG. 5. Temporal scans of temperature profiles of $Cl_2 + C_4H_9Cl$ reaction waves. The system was placed in the vapour of liquid nitrogen. Initiation by slow (solid line) and quick (dashed line) heating (discharge of capacitor via heater).

spontaneous transformation of the slower wave into the faster one. In some qualitative aspects, a high-velocity condition of wave propagation resembles the autowave processes in question. Let us calculate the wave velocity from formula (6) using the parameter values obtained in the above experiments (*see Fig. 3A*): $\Delta T = 60$ K, $\tau \approx 0.1$ s, $(\delta T/\delta x)^* \approx 300$ K cm^{-1}. Then we have $U \approx 2$ cm s^{-1} which is close to the experimental value.

In special experiments when the sample was placed in the vapour of boiling liquid nitrogen, we succeeded in observing both the faster wave (initiated by a pulse heater or a local fracture) and the slower wave (initiated by slow local heating, as in *Fig. 5*). The velocity of the slower wave was approximately one order of magnitude smaller than that of the faster wave and equal to the value calculated from formula (5).

It should be noted that it is somewhat difficult to produce the slower wave. In some cases the generated slower wave transformed into the faster one in the course of its travel. This fact is in accordance with the above-mentioned considerations about the stability of slow and fast regimes of autowave processes.

COMPLICATED MODEL OF AUTOWAVE PROCESS. JERKY PROPAGATION OF WAVE

The model implies a simplifying assumption that the reaction front immediately follows the fracture front in which the temperature gradient reaches its critical value, i.e., both fronts coincide spatially. In fact, the fracture zone always has a finite size and the boundary of this zone jumps forward, with a velocity of the order of the velocity of sound, into the region of a smaller temperature gradient to a depth comparable with the characteristic size of a fracture grain. Only after such a jump does the heating-up before the fracture front start and when the temperature gradient reaches its critical value $\left(\frac{\delta T}{\delta x}\right)^*$, a second spatial jump of the reaction zone occurs. Thus, it may be expected that the propagation of the reaction along the sample is discrete rather than continuous.

Indeed, it has been ascertained (Zanin *et al.*, 1983) that the chemical reaction propagates jerkily both in time (analysis of acoustical effects, mentioned in Zanin *et al.*, 1981c, which accompany the sample fracture in the reaction front) and in space (investigation of the fine structure of the front by microfilming).

A phonogram of reaction wave propagation in irradiated samples of $Cl_2 + BC$ immersed in liquid nitrogen was recorded on magnetic tape. Analysis of the phonogram has shown that sound power is radiated as successive pulses—clicks. This may be evidence for the discreteness of the fracture process, i.e., the jerky propagation of the reaction wave front.

The average wave velocity calculated by using the total duration of sound pulses as the time required for the wave to propagate along the entire sample length is in good agreement with the earlier values obtained from thermographic and optical measurements. Further development of the acoustic method of observation of the wave process (spectral analysis of a signal, in particular) is expected to give additional information on the character of material fracture during reaction, dispersivity of a fractured layer, and on mechanical properties of the system.

Quartz reaction tubes with slits of width *c.* 1 mm were used for microfilming the spatial structure of the reaction front. The reaction was initiated, as usual, by a pulsed microheater positioned in the upper part of the tube. Thus the reaction wave

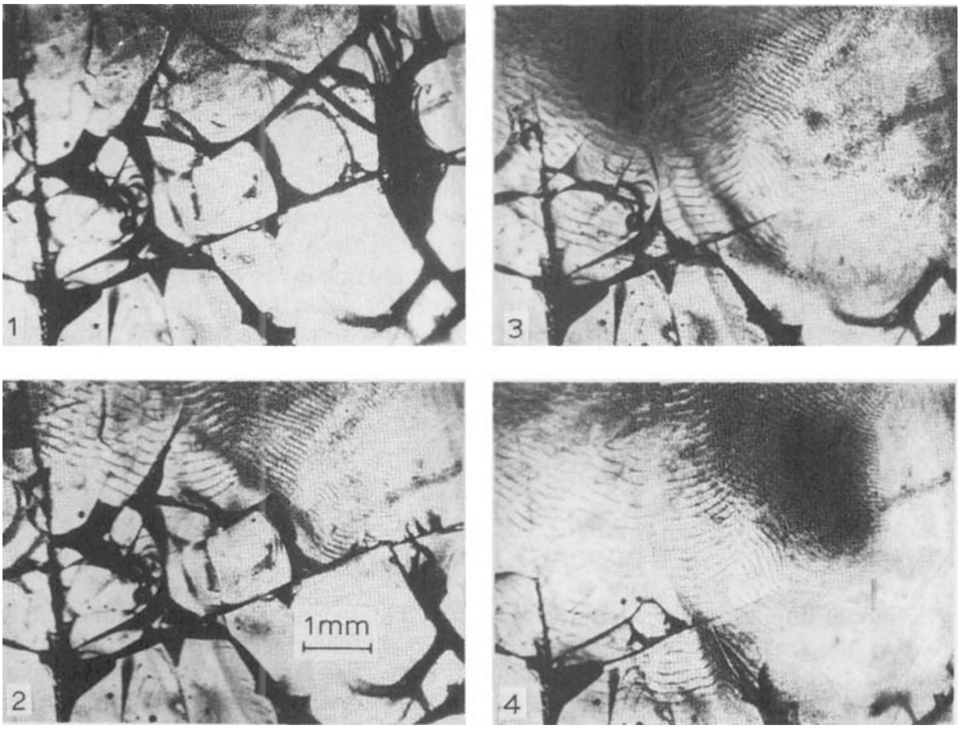


FIG. 6. Cinegram of the autowave process. Time intervals between frames 1 and 2: 0.11 s; 2 and 3: 0.06 s; 3 and 4: 0.03 s; dose 2.7 Mrad.

propagated downwards in the sample immersed in liquid nitrogen. Microfilming was performed in transmitted light with oblique illumination. *Figure 6* shows a cinegram of the autowave process. The initial sample (Frame 1) is characterized by a coarse-grained fracture (grain size 1–2 mm) produced during pre-irradiation freezing. The next frames illustrate the passage of the wave through the investigated fragment of the sample. As can be seen, the passing wave leaves a trace in the form of grooves parallel to the wave front and separated by 50–150 μm. Such a striped trace like a fingerprint testifies to the fact that the reaction front moves in a series of short jumps. This trace remains unchanged even on completion of the reaction, whereas the primary network of cracks loses its sharpness and even disappears in some places. The latter fact is likely to be connected with the fact that the passage of the reaction front causes transparency and the scattering power of the sample varies strongly owing to its finely dispersed break-up.

The form of the grooves points to the presence of some curvature of the reaction front, which appears flat in insufficiently magnified cinegrams (Zanin *et al.*, 1981b, 1982a). This is likely to be caused either by inhomogeneity of mechanical properties of the sample, and of its strength in particular, or by the loss of stability of the flat front and by the formation of spatial inhomogeneities of the type of dissipative structures (Glensdorf and Prigogine, 1971). It is for these reasons that zones of accelerated motion and delay zones (characteristic size of inhomogeneities *c.*

0.5 mm) appear on the originally flat front. As the front travels, the character of its curvature alters.

In the theory of the strength of materials there exist relationships which enable one to estimate the length of a single crack (the size of an elementary fracture grain) at a load of the order of the ultimate strength. According to Griffith's (1921) formula $\ell = \gamma E/\sigma^2$, where γ is the energy required for creating 1 cm^2 of a new surface, E is the modulus of elasticity, σ is the ultimate strength. At $\gamma \approx 10^5$ erg cm^{-2} (polymeric materials), $E \approx 3 \times 10^{10}$ dyne cm^{-2} and $\sigma + 7 \times 10^8$ dyne cm^{-2} (plexiglass), $\ell \approx$ 50 μm, and this value of ℓ coincides with the distance between the grooves of the striped structure. This is a telling argument in favour of the considerations presented here.

It is interesting to note that the striped 'imprints' of chemical conversions observed in our experiments resemble closely the pattern produced by the fatigue destruction of metals (Lair and Smith, 1962) and polymers (Döll, 1975). A deeper analogy may underlie this resemblance, namely, the pulsatory character of the fracture due to a chemical reaction is associated, as in the case of fatigue destruction, with the periodicity of loading.

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