

Low-temperature, solid-phase transformations initiated by mechanical breakdown

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Low-temperature, solid-phase transformation in a vitreous chlorine-methyl cyclohexane system activated by irradiation is investigated. It is shown that the formation of cracks in a monolithic sample at low temperatures (4.2 K–77 K) initiates a transformation that is developed subsequently. New cracks, which accelerate the transformation that accounts for its explosive nature, appear during the process.

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The problems associated with the effect of defects in a solid, mechanical stress in a sample and macroscopic destruction of its structure on the dynamics of low-temperature transformations have been discussed frequently in recent years. We investigate in this paper the possibility of artificially initiating chemical transformations by destroying solid samples at low temperatures.

The observation of a photochlorination reaction, which occurs spontaneously as the temperature of a vitreous solid solution decreases, was reported in Ref. 1. The authors¹ interpreted this effect as a thermal explosion produced as a result of buildup of the energy of internal stress. We show below that the necessary condition for such transformation is the breakdown of integrity of the sample—appearance of cracks. A formation of cracks produces a positive feedback, which is necessary for the spontaneous explosive transformation to occur.

To break the integrity of the sample, we selected a method of inducing thermal stress by changing the rate of variation of the sample's temperature, which produced the cracks. We used in the experiments a chlorine-methyl cyclohexane (MCH) system¹ prepared as a solution with a molar ratio 1:3 at 175 K, which was cooled subsequently (going over to a vitreous state at $T_g = 90\text{--}95$ K) to 4.2 K in a cryostat that was adapted for calorimetric measurements. The heating rate of the sample was varied by using an electric heater that was built into the calorimeter. To record the variation rate of the temperature, which accounts for the cracks in the sample, and to record the cracks, we have selected a differential scanning calorimeter: the sample's temperature and the thermal effects of the processes occurring in it (i.e., appearance of a branched network of cracks or a chemical transformation) were recorded simultaneously during the heating or cooling of the sample; see Ref. 3 for a detailed description of the method.

There is no cracking when the samples are heated slowly from 4.2 K to 77 K and the calorimeter does not record any thermal effects (solid curves *A* and *B* in Fig. 1). A fast heating causes the sample to crack and the accompanying thermal effect is

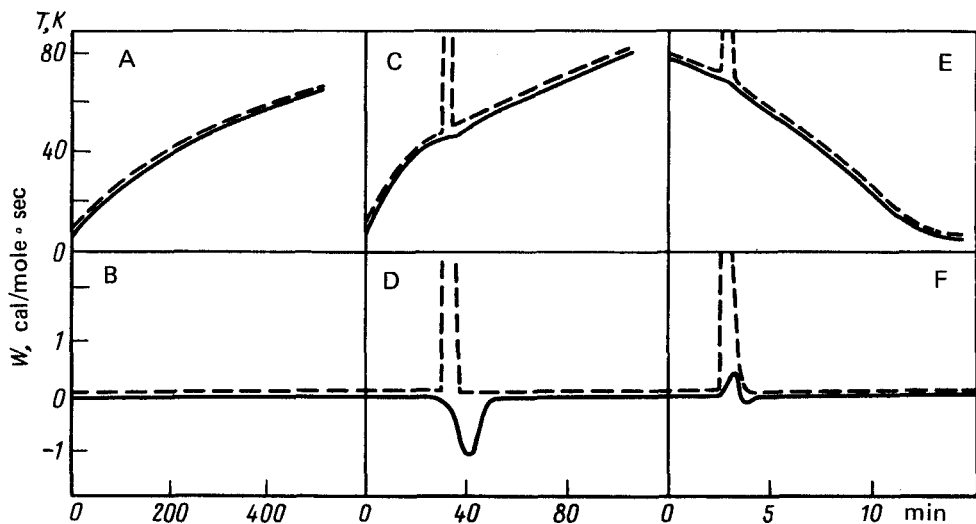


FIG. 1. Curves A, C, and E represent the time variation of the sample temperature (the molar ratio of $\text{Cl}_2 + \text{MCH}$ is 1:3) and curves B, D, and F represent the time variation of the accompanying reaction energy of the sample. The solid curves represent the nonirradiated samples and the dashed curves represent the samples irradiated by 2.7-Mrad-dose ^{60}Co γ rays at 77 K.

recorded by the calorimeter (solid curves C and D in Fig. 1).²⁾ After establishing the rate of variation of the temperature, which produces cracks in the sample, we conducted analogous experiments in which we used samples that were irradiated in advance by ^{60}Co γ rays (2.7-Mrad dose) in order to produce radicals R whose concentration was $\sim 5 \times 10^{18} \text{ cm}^{-3}$. The heating of the sample due to chemical reaction was not recorded when the sample was heated slowly, which did not produce its collapse (dashed curves A and B in Fig. 1). A fast heating of the sample produces a transformation during its cracking, which continues spontaneously in an explosive manner (dashed curves C and D in Fig. 1). The density of molecules undergoing transformation exceeded the initial density of radicals R by at least two orders of magnitude.

If this effect is indeed produced by the formation of cracks, then it is not important to know the mode in which the sample loses its integrity: fast heating or cooling. The curves E and F represent the data for the sample which was cooled sufficiently rapidly to produce cracking. As expected, the destruction of a γ -irradiated sample containing radicals R was accompanied by a fast transformation; a transformation did not occur in a nonirradiated sample.

To prove that the cracks play a key role in the transformation, we have conducted an experiment in which the sample was destroyed mechanically. The cracking of the sample, which contained the radicals R (3-Mrad-dose γ irradiation), was accomplished at a constant temperature of the thermostat (4.2 K) by rotating a thin metal rod that was embedded in the sample. The explosive transformation occurred at the moment this perturbation was introduced. Not that transformations analogous to those described above have also been observed in other systems, for example, chlorine-butyl

chloride and ethylene-hydrogen bromide.

The described experiments showed, therefore, that the buildup of stress alone is not enough to produce a spontaneous transformation in the system in question and that the cracks play a key role in it.

It must be noted that the process producing the cracks and possibly even their condition during formation are important. If the sample is crushed before the radicals are produced in it, then none of the selected heating rates will produce an explosion. The crack formation, therefore, plays the role of a trigger mechanism which puts into action a feedback mechanism giving rise to the explosive nature of the process. Only two mechanisms of this kind are known: thermal explosion and branching chain explosion. A more detailed experimental investigation, which includes the study of the initiation process, the induction stages, the effect of the sample size and of the characteristics of propagation of the reaction front as a result of its local initiation, must be conducted in order to determine unambiguously the mechanism involved in our case.

An analysis of the available results shows, however, that the positive-feedback mechanism in the system has the following form: the transformation occurring on the newly formed surfaces of the cracks generates new structural imperfections (for example, because of the difference in densities of the original and final products or because of the sharp temperature gradients produced during the transformation, which produce a thermoelectromotive force) and the increased density of macro-defects increases the reaction rate, which accounts for the progressive increase in density of the defects until the explosion occurs.

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¹) An exothermic reaction of the type $Cl_2 + RH \rightarrow HCl$ with the reaction energy $Q \approx 1.35$ eV and activation energy $E \approx 0.13$ eV, which were measured for the liquid phase² (R is the MCH radical), can occur in this system.

²) The formation of cracks in the sample can be recorded from the sound accompanying this process and also visually.

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