Kinetic calorimetry in the study of the mechanism of low-temperature chemical reactions

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Chemical reactions are always followed by a change in the reacting system enthalpy, hence, calorimetry as a method of enthalpy and heat capacity measuring is a universal and, sometimes, even the only possible way of studying chemical reaction kinetics. Throughout its long history, the calorimeter, having preserved the positions of the main method of thermodynamic studies, has conquered a new field of application: that of kinetic study of chemical reactions. The advantages and disadvantages of the kinetic calorimeter are now obvious. First, the advantages are:

(1) the possibility of measuring the rate of a chemical reaction without any special requirements being imposed on the reaction medium (solid, viscous, multicomponent systems);
(2) the high efficiency: a large volume of kinetic information in one experiment and a non-destructive character of changes;
(3) the possibility of measuring directly in the field of ionizing radiation (γ-radiation, accelerated electrons) and light; and
(4) recording of the chemical conversion directly at the time of its occurrence.

The disadvantages of this method are:

(1) the high inertia of standard calorimeter systems ($\tau_C \simeq 10^2$–10^3 s), which restricts the possibilities of studying fast processes; and
(2) the complexity of the correct organization of the calorimeter experiment when the parameters of the process are changed (overheating in the sample, conversion of the process to explosive and auto wave regimens).

One of the oldest and most universal methods of studying the mechanism of chemical reactions, calorimetry, is now passing through a period of turbulent development due to the advances in electronics and computerization. The wide variety of types of calorimeter set-ups and the large assortment of measurement schemes in the currently described methods complicate the experimental selection of the necessary instrument rather than facilitate it. The basic principles of the method, the types of calorimeters, and the measuring schemes are described [1–5]. However, despite the high working characteristics of modern calorimeters (Perkin–Elmer, Du Pont, LKB, etc.), all of them have one principal disadvantage: a cell with a sample is placed in them at room temperature. In cryochemical investigation, when the sample has metastable formations, the loading is made 'from nitrogen to nitrogen', i.e. the sample prepared at 77 K should be loaded into a calorimeter at 77 K. Besides, the existing installations do not allow measurements at the temperatures <110 K. For this reason, the Laboratory of Cryochemistry and Radiation Chemistry at the Institute of Chemical Physics in Chernogolovka has created original calorimetric techniques which allow:

(1) the carrying out phase analysis and the determination of the main thermodynamic characteristic of individual substances and complicated systems in the temperature range 5–300 K. Sample loading can be conducted at 77 K that allows us to study the systems containing: tetrafluoroethylene, hexafluoropropylene, ethylene, carbon monoxide, nitrogen, methane, hydrogen, oxygen, ozone, formaldehyde and many other gaseous substances;

(2) the study of the dynamics of chemical reactions and to measure the main kinetic parameters of the processes—the elementary rate constants and the activation energies. The experiment can be conducted both under direct action of radiation and UV light and in the post-effect mode [5,6].

1. Methodological peculiarities

Before examining the application of kinetic calorimetry to studies of the mechanism of cryochemical reactions we will discuss the specific feature of calorimetric measurements in obtaining kinetic information. The time dependence of the rate of the process studied in the calorimetric measurement required by the experimenter is obtained from the time dependence of the calorimeter signal. This transformation (deconvolution) should naturally be simple and correct. A number of additional conditions must be satisfied in the organization of the experiment for this. We will note two of them. First, organization of the relatively good thermal conductivity in both the reaction medium and in the calorimetric system is necessary to decrease the maximal temporal and spatial temperature gradients which arise during the reaction.

Second, for correct kinetic measurements, it is necessary to know (although only approximately) the inertia of the calorimetric system τ_C (it is easily determined in calibration experiments) and the characteristic time of the chemical process studied, τ_r. The case where $\tau_C \leqslant \tau_r$ is simplest. In this case, the kinetic information is obtained directly from the calorimetric measurements and does not require the introduction of any corrections. The more complex case is when $\tau_C \geqslant \tau_r$. Here, to obtain real kinetic information it is necessary to make corrections and to use special programmes to restore real parameters of the process [7–10].

Establishing thermal equilibrium in any body requires a finite time that is determined by thermophysical properties and sizes of a body: $\tau = l^2/ka$, where τ is the characteristic time of the body thermal inertia, l is the characteristic size of the body, a is the temperature conductivity coefficient, k is the coefficient involving the body shape (changes in 1–10).

The total inertia of such a system should be determined by the maximum of the characteristic inertia times of the given bodies. Not to distort the kinetics of the process by the calorimetric system inertia it is required to be less than the characteristic time of the process studied. This limitation becomes significant when studying fast reactions. In such cases, the calorimeter block reaction medium and thermometer are made in the form of thin films and the time levelling of the temperature may reach 10^{-5}–10^{-6} s [11]. Such characteristic times are obviously limiting for a calorimetric technique.

The solution of a heat balance equation for calorimeters with constant temperature in the case when the heat evolution rate is constant, has a simple analytic form:

$$\Delta T \sim T - T_0 = \frac{qVl}{\lambda S}\left[1 - \exp\left(-\frac{\lambda S}{Cl}\right)\right]\omega(t). \qquad (1)$$

where ΔT is the temperature difference between the calorimeter block and the shield (experimentally measured signal), λ is the thermal conductivity coefficient of the medium between the block and shield of the calorimeter, S is the surface area of the calorimeter block, C is the heat capacity, l is the distance between the block and shield, q is the thermal effect of the studied reaction, V is the sample volume and $\omega(t)$ is the studied reaction rate. Equation (1) shows that the characteristic time of the thermal inertia in the calorimeter measuring system is:

$$\tau_k = Cl/\lambda S.$$

An analysis of equation (1) shows that at the experiment times $t \ll \tau_k$ a calorimeter signal is:

$$\Delta T = \frac{qV}{C}\,\omega t,$$

i.e. it is proportional to the quantity of the reacted substance. In the other limiting case $(t \gg \tau_k)$, a calorimeter signal is:

$$\Delta T = \frac{qVl}{\lambda S}\,\omega(t),$$

i.e. it becomes proportional to the reaction rate. Ordinarily the calorimetric experiment is conducted so that one of these limiting cases—adiabatic or quasiisothermal regime—takes place.

There is one more methodological situation that should be taken into consideration: the characteristic time of switching on the initiating radiation should be $< \tau_C$. This is not always done in practice, especially when γ-radiation is used, where bringing the intensity from zero to the required value involves the use of mechanical systems.

2. Construction features

We shall not examine well-known classical calorimetric set-ups like differential scanning calorimeter (DSC) [2], diathermic [12–14] or adiabatic [15–18] calorimeters. We shall dwell only on the construction characteristics of the calorimeters made specially to study the mechanism of low-temperature chemical reactions in glassy and crystalline matrices.

2.1. Differential diathermic calorimeter

The calorimetric set-up of this type based on a Calve calorimeter [1] was devised in our laboratory. This set-up is made for serial measurements in a wide range of temperatures, both in and out of the γ-radiation field. The construction details and ways of their production are described elsewhere [19, 20]. A thermal contact of a studied sample with a calorimeter block is performed only through a diathermal shell. The shell is a thin-wall mica cylinder to which is attached a battery of 200 differential thermocouples copper–constantan. One junction of each thermocouple has a thermal contact with a calorimeter block, another—with a calorimeter cell containing a studied sample. The cylindrical cell itself (volume $\simeq 1$ cm^2) is made out of red copper.

A differential measuring scheme is used in this calorimeter: electric signals from two similar diathermal shells are switched on towards each other and are mutually subtracted. One of the cells is working, another—a standard. Such a scheme has some marked advantages. As the cells are identical any thermal fluctuations in the calorimeter block affects both the thermobatteries and is mutually subtracted. This peculiarity of the scheme is very useful when changing the regimes of heating and cooling. The differential scheme has its own advantages as well when measurements are conducted in the field of high-energy radiation (e.g. in the γ-field of ^{60}Co). Selecting an inert substance in the reference cell so that an accumulated dose is equal to that in the working cell it is possible to bring thermal fluctuations induced by radiation to a minimum.

Both the cells are placed in a copper calorimeter block (1) (figure 1). This block is provided with a constantan electric heater (2). Calorimeter cells (3) are inserted into cell on a slide fit. The calorimeter block is attached to a thin pipe of stainless steel (4) through which all the wires are let out. The absolute measurements of a sample are conducted with a thermocouple stuck to a working cell.
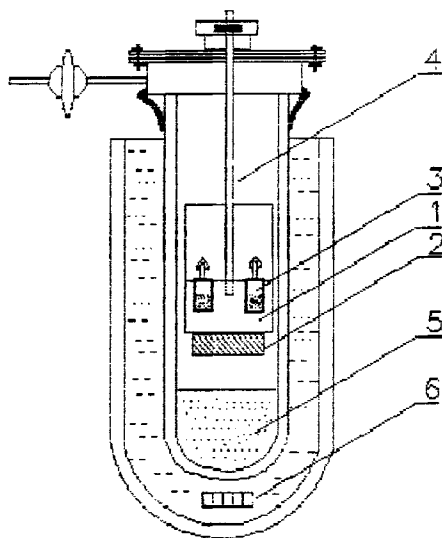
Figure 1.   Differential diathermic calorimeter set-up.

The calorimeter block is placed in a glass helium cryostat (5) so that it can be easy to regulate its height above liquid helium. On the bottom of the helium cryostat there is a heater–evaporator (6) that makes it possible to work in the cooling regime. Regulating the power of heaters 2 and 6 one can control the calorimeter temperature at any given point (within 2–3 h the necessary temperature is kept to an accuracy of ± 0.3 K). The working temperature interval of this set-up is 5–350 K.

The measuring scheme is controlled by a personal computer with a special program. Calorimeter calibration is made according to the Joule heat evolving in a calibration heater. In our experiments we could undoubtedly differentiate between the signals and the background noise at a heat evolution rate of $\simeq 10^{-6}$ cal s^{-1}. The calorimeter inertia at 80–300 K is 60–80 s, in the helium temperatures interval it is lower. This set-up proved to be convenient for studying the kinetics of chemical reactions in the field of ^{60}Co γ-radiation.

To measure the characteristic times of quite fast chemical reactions in the temperature range of 4–40 K the above calorimeter was modified, its differential scheme being unused. The body of such a low-inertia calorimeter is a thin-walled metal tube (1) (figure 2), into which the studied substance was placed. On the outer surface of this capillar there was a calibration heater (2) and a thermocouple Cu–Au–Fe (3) registering the temperature difference on the diathermal shell, i.e. between a calorimeter body (1) and a copper shield (6). The calorimeter is in a glass vacuum vessel (4) surrounded by a copper shield. The whole aggregate is placed into a helium bath of a glass cryostat (5). The specially constructed portable helium cryostat makes it possible to put the set-up easily in any point of the γ-radiation source chamber. The inertia of this calorimeter set-up was 1–3 s.

2.2. Quasi-adiabatic calorimeter

Even lower inertia was achieved using a film calorimeter working in the adiabatic regime (figure 3). The calorimeter is a thin aluminium disk (1) marked with a resistance thermometer (2) and a calibration heater (3). This disk is suspended by thin wires in a
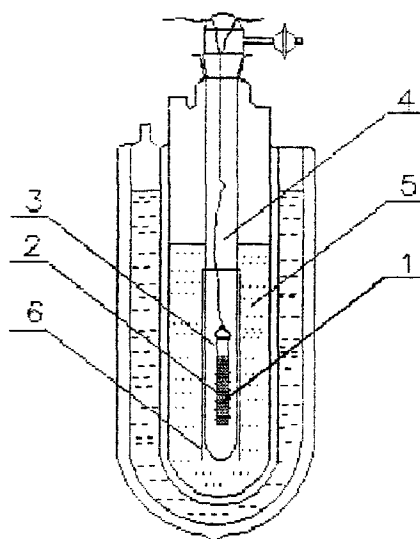
Figure 2. Scheme of a diathermic low-inertia calorimeter and helium cryostat.
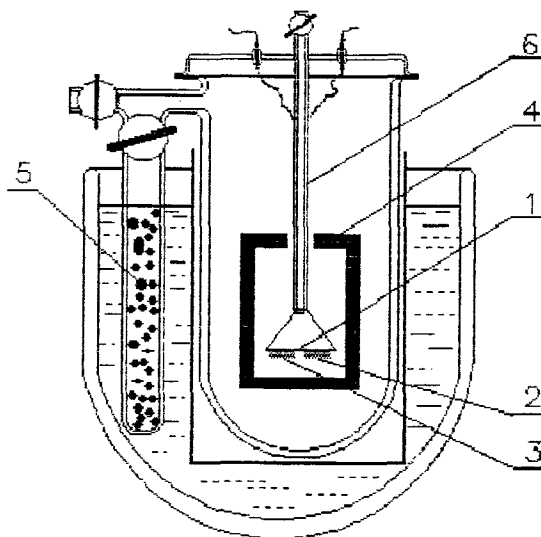
Figure 3. Scheme of a film adiabatic calorimeter.

copper thermal shield (4). All the assembly is placed into a vacuum glass vessel supplied with an adsorption pump (5). The studied substance (layer thickness 0·1–0·5 mm) from the gas phase is frozen on the calorimeter disk using a heated capillar (6).

To register a calorimeter signal in this low-inertia set-up an oscillograph was used, registering at the same time a calibration current impulse and a calorimeter response. Figure 4 gives a film calorimeter calibration oscillogram. The heat release rate in the calorimeter is seen to become constant only 0·4–0·5 s later. Therefore, the calorimeter characteristic time is $\tau \simeq 0\cdot 2$ s. Rather a low inertia of this set-up allows one to use it for the non-stationary kinetics study.

Figure 4.   Oscillogram of the film calorimeter calibration: (1) recording of a calorimeter signal; and (2) a character of current changing by a calibration heater.

An original calorimeter set-up working in the adiabatic regime is described in [21]. This set-up has a film calorimeter united constructively with a source of low-voltage electrons, which is used for initiating polymerization. The adiabatic calorimeters are also employed to study the low-temperature solid phase polymerization [22] and the polymerization in the absorbed state [23–26].
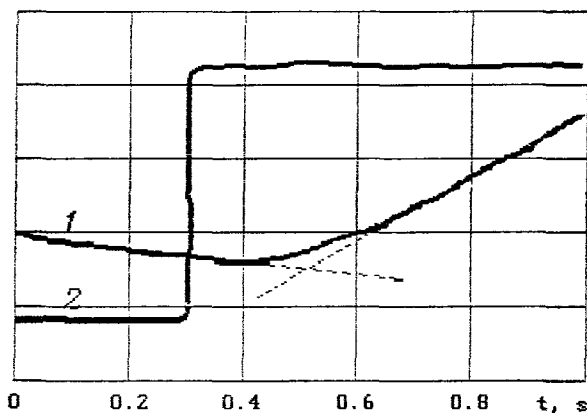
3.   Measurement types

Most of the organic compounds, among them different monomers, are known to undergo more or less complicated polymorphous transformations in the solid state. Polymorphous modifications of a substance are usually readily over cooled, i.e. pass to the temperature range where they are metastable. Just for that reason, the sample cooling rate is determining for the phase state of an investigated solid system. The interpretation of the chemical transformation kinetics against a background of complicated phase conversions naturally becomes very difficult. Actually, following different phase conventions in the solid matrix there may occur a significant change in the concentration of accumulated active centres. Moreover, the kinetic parameters of the processes in different polymorphous modifications are, as a rule, different in general production of a 'pure-phase' solid sample, i.e. containing only one polymorphous modification stable at a given temperature for kinetic studies in the solid phase is as important as purification from inhibitors and admixtures for liquid-phase studies. Thus any attempts at studying the mechanism of cryochemical reactions, especially in two-component systems, must be preceded by a detailed calorimetric analysis of the phase state and its dependence on the condition of preparation.

Application of a diathermal calorimeter allows one not only to analyse the whole picture of phase conversions (type of conversion, temperature ranges and transition heats) but also to optimize the regimens of preparing a required sample for a study. A good example of such a measurement is an analysis of polymorphous conversions in solid acrylonitrile [5,20]. The calorimetric phase analysis of solid monomers was carried out when studying solid-state polymerization of: metacrylonitrile [27], acrylic acid [28], formaldehyde [29], acetaldehyde [30], glyoxal [31], carbon suboxide [32], N-phenylmaliide [33], acetone [34], tetrafluorethylene [35], glycolide [18], organocyclosiloxane [36], etc.

Large information was obtained by a calorimetric analysis of inclusion compounds whose polymerization was intensively studied in order to produce stereo-regular polymers. The dynamics of complex formation and decomposition heats for channel complexes of acrylonitrile in urea [37, 38], 1,3-butadiene in urea [39], 2,3-dichlorobutadiene with deoxicholic acid [40], etc. were quantitatively characterized.

The calorimetric analysis was widely used to choose an optimum composition of two-component vitrifying (see §2) and crystallizing systems (see §1). However, the aim of the further report is an analysis of the fields of application of the kinetic calorimetry for the investigation of the mechanism and dynamics of radiation induced cryochemical reactions.

3.1. *Accumulation and quenching of active centres stabilized in radiolysis*

In the radiolysis of solids, some of the incident ionizing radiation energy accumulates in the solid matrix. It is believed that this energy basically accumulates in the form of active centres stabilized in conditions of low molecular mobility of ions and radicals. The possible storage of radiation energy in the form of the potential energy of structural defects is usually neglected in studying the kinetics of radiation induced reactions. With an increase in the absorbed dose, stabilized ions and radicals accumulate up to a certain limit (which usually does not exceed $\simeq 1\%$ of the low-molecular-weight matrix fragments). When such irradiated matrices are heated, quenching of active centres (recombination) takes place with a significant increase in the molecular mobility of the system, for example, in regions near phase transitions.

Electron spin resonance (ESR) has been widely used for studying the kinetics of the accumulation and decay of such centres. However, a significant limitation of this method is the possibility of only identifying paramagnetic particles. Calorimetry permits following the dynamics of accumulation of energy in an irradiated system (the endothermic effect: part of the incident energy flux is stored in the form of potential energy of stabilized radicals, ions and structural defects) and its release during heating of the irradiated system outside of the irradiation zone (exothermic effect). According to the estimation reported in [21], $\simeq 10\%$ of incident radiation energy accumulates in the irradiated matrix in the case of stabilization of radical and ions.

The experimental problem thus consists of measuring small heat effects against the background of larger exothermic effects of heating of the irradiated system. However, we only know of one study [21] in which an attempt was made to solve this problem. In the case of radiolysis of thin layers of heptane at 80 K an endothermic effect was identified and correlated with accumulation of stabilized radicals in the system $(G[R] \simeq 4-7)$ [21]. If all stored energy is attributed to stabilized radicals, then 10% of the absorbed energy should be stored. Measurements showed that $\simeq 15\%$ is stored. Radiolysis of heptane at 180 K, where radicals and ions are not stabilized due to the high molecular mobility, did not lead, as supposed, to identification of an endothermic effect. These measurements also permitted estimating the upper limit of the concentration of stabilized ions and ion pairs based on the sensitivity of the method used.

Recombination of ions and radicals and conversion of the potential energy of mechanical stresses in the region of defects into kinetic energy take place during heating of irradiated systems. These exothermic effects can be measured by differential scanning calorimeters. Measurements of this type can be conducted with a higher precision since they are performed outside of the radiation field. An example of this type of measurement is given in [41].

However, other channels of accumulation of energy in the system in low-temperature radiolysis are also possible [42, 43]. An experimental calorimetric study of the accumulation of different forms of energy (stabilized active centres and a metastable phase) during radiolysis of crystalline methanol at 77 K was conducted in these works. It was found that the crystalline methanol became almost totally amorphous with doses $\simeq 1$ MGy. The energy stored in the metastable amorphous phase is much higher than the recombination energy of radicals and ions.

3.2. *Kinetics of solid-phase polymerization*

In studying the kinetics of polymerization of solid monomers, calorimetry provides information on the rate of the process directly during its occurrence without perturbation of the matrix. The study of the non-stationary kinetics permits measuring the values of the constants of the elementary stages of polymer chain propagation and breaking as well as their temperature dependence. Measurements of this type, for example, were conducted in studying solid-phase polymerization of formaldehyde [44–49].

A low-inertia diathermic calorimeter was used for measurements of the characteristic time of generation of the polymer chain in solid formaldehyde (i.e. the effective termination constant) [44]. The detailed description of the results of these kinetic measurements was given in § 1, so here we shall consider only the characteristic features of the calorimetric measurement. The inertia of the calorimetric set-up in the temperature range 5–20 K was $\tau_C \simeq 1$–4 s. Polymerization was initiated by ^{60}Co γ-radiation. Since the sources of γ-radiation are mechanically raised to the working position and the dose-rate attains the maximum after 20–30 s, a special low-inertia device for switching on the γ-radiation was used for determining small time characteristics. A lead gate switched on the initiating radiation after $\simeq 0.05$ s.

After switching on the γ-radiation (dropping of the gate), the rate of heat release increases relatively rapidly from zero to some value. Only heating as a result of absorption of γ-radiation energy was identified in a similar experiment with polyformaldehyde where chain polymerization is absent. The characteristic time in this case was of the order of the time of inertia of the set-up: $\tau_C \simeq 1$–2 s. The difference of heat release rate in these two experiments produces the kinetics of the increase in the rate of polymerization (non-stationary kinetics). It is ease to show that in the case of monomolecular chain termination typical of solid-phase polymerization, the change in the rate of polymerization (heat release) W in time will be described by the equation

$$W = -\frac{d[M]}{dt} = GI(k_p[M]/k_t)[1 - \exp(-k_t t)], \qquad (2)$$

where G is the radiation yield of initiating sites, I is the γ-radiation dose rate, k_p and k_t are the polymer chain propagation and termination constants, and $[M]$ is the concentration of monomer. The experimental curve is satisfactory approximated with this equation, which allows determining the value of k_t at 5 K: $K_t \simeq 0.1$ s^{-1}. Using the dependence of the rate of the process W on time (2) reported above, it is easy to determine the product Gk_p. The value of k_p can be determined from this product only if it is possible to measure the radiation yield of initiating sites G in an independent experiment. For example, G can be determined by measuring the number of growing macro radicals by ESR [50], but unfortunately this cannot always be done.

Conducting a series of such experiments at different temperatures makes it possible to determine the activation energy of these elementary stages. For high enough degrees

of conversion, a decrease in the rate related to depletion of the monomer will be observed according to equation (2). The dependence of the rate on time will thus be extreme. The complete solution of equation (2) describes the kinetics of solid-phase polymerization of acetaldehyde relatively well; the values of k_p and k_t were also obtained [30]. In addition to the above monomers, the kinetic calorimetry was also used for studying solid-phase radiation polymerization of acrylonitrile [20], maleinic acid imide [51] and glyoxal [31].

3.3. *Liquid-phase polymerization*

The mean polymer chain propagation time is usually much less in polymerization of liquid monomers or polymerization in solution than in solid-phase polymerization. For this reason, it is not possible to study the non-stationary kinetics of this process with the usual calorimetric set-ups. The series of studies in [52–56] is a good example of the use of the calorimetric method for studying the initial stages of the kinetics of radiation polymerization of liquid monomers.

The method of kinetic calorimetry was valuable for studying the deep stages of liquid-phase radiation polymerization, especially in the study of the mechanism of the gel effect, where diffusion control of the process of breaking of propagating chain begins to play a role due to an increase in the viscosity of the medium during the process and the chain propagation time increases, exceeding the resolution of the usual calorimetric set-up.

The calorimetric curves of polymerization of heptyl methacrylate [57] and heptyl acrylate [58] obtained directly during γ-irradiation of liquid monomers at room temperature are shown in figure 5. When the ionizing radiation is switched on, the rate of polymerization of heptyl methacrylate with inertia of the calorimeter ($\tau_C \simeq 100\,\text{s}$) attains a value which remains constant for some time and then increases sharply. This acceleration is apparently due to crosslinking of the system and a decrease in the probability of breaking of the growing polymer chains. In contrast to heptyl methacrylate, the rate of polymerization of its acrylic analog increases rapidly after the γ-radiation is switched on, attains a maximum for $\simeq 40\%$ conversion of the monomer, and then monotonically decreases. This difference is due in large part to features in the

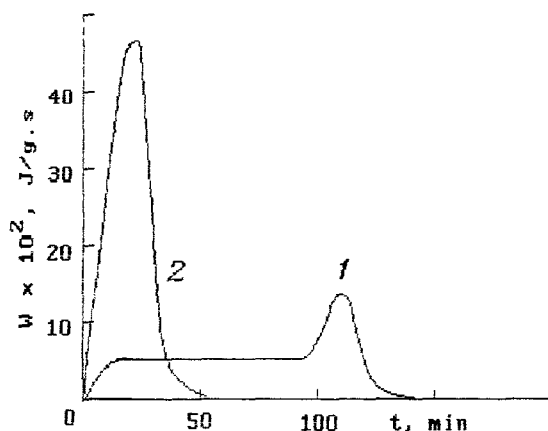

Figure 5. Dependence of the rate of polymerization of heptyl methacrylate (1) and heptyl acrylate (2) in the field of γ-radiation on the irradiation time ($T = 295\,\text{K}$, dose-rate–$5\,\text{kGy}\,\text{h}^{-1}$).
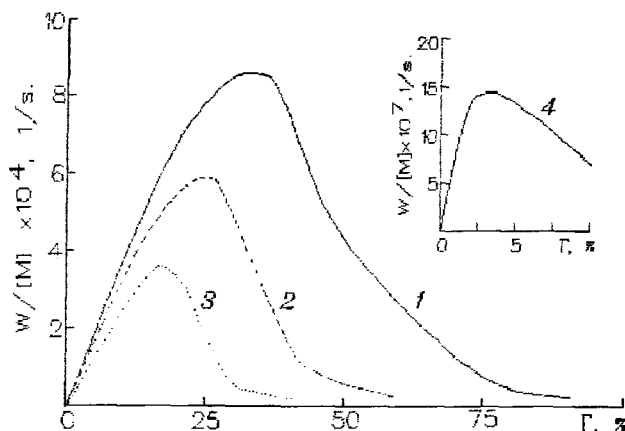
Figure 6.   Dependence of the reduced rate of polymerization of triethylene glycol dimethacrylate on the degree of polymerization at 293 (1), 273 (2), 238 (3), and 203 K (4), dose-rate–$1.2\,Gy\,s^{-1}$.

structure of the polymer product formed and the character of breaking of the polymer chains. Actually, polymerization of heptyl methacrylate results in the formation of a three-dimensional spatial network and a crosslinked insoluble product, in contrast to heptyl methacrylate.

3.4. Radiation curing

The use of radiation cured polymer–monomer mixtures and oligomers for creating coatings and composite materials is now one of the promising directions in applied radiation chemistry [59]. Unfortunately, most of the studies of the dynamics of radiation curing and the kinetics of the polymerization process were conducted with indirect methods or methods destructive to the system. We will demonstrate the potentialities of kinetic calorimetry in these studies on the example of low-temperature three-dimensional radiation polymerization of triethylene glycol dimethacrylate [60]. Its use in the field of γ-radiation provided extensive kinetic information on the polymerization process. The process initially develops according to an autocatalytic law and then as the maximum rate is attained, the stage of self-retardation begins (figure 6). This type of polymerization persists qualitatively in all the temperature range until the freezing point of the starting liquid oligomer, except that the self-retardation is much less pronounced at 203 K. A series of kinetic curves similar to those shown in figure 6 can be obtained for different dose rates. This makes it possible to follow the change in the character of chain termination with different degrees of conversion.

A more detailed kinetic analysis with the framework of a micro heterogeneous model of three-dimensional polymerization [61] showed that with a decrease in the temperature, Γ_{max}, the degree of conversion for which the rate attains the maximum, is regularly shifted toward lower degrees of conversion. This suggests that at lower temperatures, the first chains formed during polymerization cannot turn into globules by aggregating into formations with more or less unfolded chains. Since the formation significantly improves the physical–mechanical characteristics of the materials obtained, the practical importance of the results obtained becomes understandable. The processes of curing of methacrylhydroxyalkyl carbonates [62], their copolymerization with methyl methacrylate [63], polymerization in solution [64], curing of

polymer–monomer composites [57, 58], and three-dimensional polymerization triethylene glycol dimethacrylate in the presence of polymethyl methacrylate [65] have been studied in detail by kinetic calorimetry.

3.5. Graft polymerization

Radiation graft polymerization is an efficient method of modifying polymeric and inorganic materials. The reaction systems are usually a solid modified support and a liquid or gaseous monomer. Two processes simultaneously take place: graft polymerization, where the polymer chain propagates on the active sites which arise out of the solid support, and homo polymerization, when the polymer chains are formed on the active sites which arise in radiolysis of the monomer. Kinetic calorimetry has also been successfully used for studying the kinetics and mechanism of the process in such complex systems. As an example, we will examine the study of the non-stationary kinetics of liquid-phase graft polymerization of vinyl fluoride on to polytetrafluorethylene [66, 67]. The specific heat of polymerization of vinyl fluoride in presence of polymer powder was initially determined in separate experiments. It was equal to 100 ± 8 kJ mol^{-1} and did not differ from the heat of homopolymerization of monomer. This value was subsequently used for obtaining kinetic information from the calorimetric measurements. Typical calorimetric curves of polymerization of vinyl fluoride in γ-radiation field are shown in figure 7. The rate of the process at any time can easily be calculated from the rate of heat release recorded with the calorimeter using the specific heat of polymerization. The recorded heat release is due to the sum of two processes: homopolymerization and graft polymerization. By subtracting the rate of homopolymerization W_h from the total rate W_t, it is easy to determine the rate of graft polymerization: $W_g = W_t - W_h$. The calorimetric measurements at different temperatures allow determining the total activation energies of graft polymerization ($E = 12 \cdot 6$ kJ mol^{-1}) and homopolymerization ($E = 25 \cdot 2$ kJ mol^{-1}). Graft polymerization becomes dominant at low temperatures (190–200 K) due to the different temperature dependence of the total rates of grafting and homopolymerization. The mechanisms of termination of the growing polymer chains were also different for these two processes: the rate of homopolymerization of vinyl fluoride is proportional to the dose rate to a
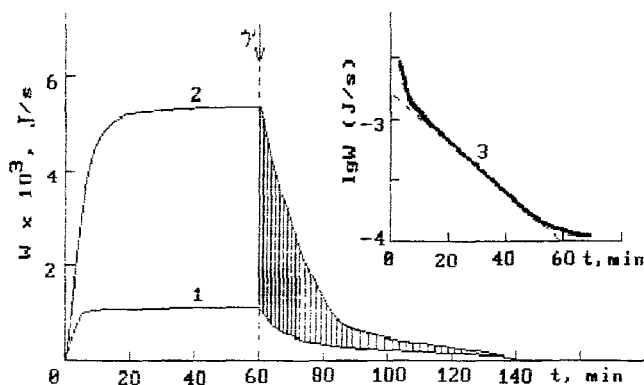

Figure 7. Change in the rate of polymerization of vinyl fluoride in time in the absence (1) and presence of polytetrafluoroethylene (2). The times of switching the γ-radiation on and off are indicated by the arrows. Top: decrease in the rate of graft polymerization (hatched part) after switching off the initiating radiation.

power of 0·5, and to the first power for graft polymerization. The use of the calorimetric method for studying the non-stationary kinetics of the process was possible since the characteristic time of grafting of vinyl fluoride was significantly higher than the characteristic calorimeter time ($\tau_C \simeq 50$ s). When the initiating radiation is switched off, the curve of the decrease in the rate is described by an exponent, and the experimental curve of the decrease in the rate is satisfactorily linearized in coordinates of $\ln(W_g) - t$. The constant of chain termination k_t was determined with the slope A series of experiments similar to those shown in figure 7 but at different temperatures allowed determining the temperature dependence of constants k_p and k_t. The following expressions were obtained for the 196–293 K interval:

$$k_p = 5 \times 10^{-16} \exp(-29000/RT) \, \text{cm}^3 \, \text{s}^{-1},$$
$$k_t = 0.7 \exp(-12600/RT) \, \text{s}^{-1}.$$

The low values of the pre-exponential factors are apparently a feature common to reaction of fluoroalkyl radicals in polymerization processes. The method of kinetic calorimetry has also been successfully used for determining the polymer chain propagation and termination constants, activation energy, heats of polymerization and adsorption for radiation polymerization of acrylonitrile, methylmethacrylate, and tetrafluoroethylene adsorbed on silica gel [68–71].

4. Kinetics of radiation-induced chain reactions

The great potential of kinetic calorimetry has recently been demonstrated in the study of the mechanism of radiation induced chain reactions of synthesis: chlorination of saturated hydrocarbons and hydrohalogenation of olefins. We will examine typical examples of such studies below.

4.1. *Low-temperature chlorination of hydrocarbons*

Chlorination of saturated hydrocarbons and their chlorinated derivatives in the gas and liquid phases in radiation and photo-initiation has been studied in some detail [72]. However, the feature of the mechanism of these processes in solid and viscous media have virtually not been investigated. The kinetic features of radiation chlorination in the solid phase and in a viscous super-cooled liquid were investigated in [73] on the example of a solution of molecular chlorine in butyl chloride vitrified in deep cooling.

As a result of the calorimetric analysis of the phase state of the system in a wide range of concentrations of molecular chlorine in butyl chloride, it was found that the solution with the molar ratio 1 : 3 passes into the glassy state on freezing ($T \simeq 96$ K) without phase separation. This observation is very important, since the interpretation of the kinetic data obtained is significantly simplified in the case of a homogeneous one-component system. A series of experiments with recording of the time dependence of the rate of heat release due to the chlorination reaction was conducted at different temperatures. The kinetic curves of the process were calculated using the measured heat effect of the reaction (140 ± 12 kJ mol^{-1} of chlorine). Radiation chlorination of butyl chloride takes place both in the solid phase below the region of devitrification of the system (figure 8) and in the super-cooled liquid state when the rate of the process increases. After γ-irradiation stops, the rate of the process slowly decreases in time. The time dependence of the rate is shown in semi-logarithmic coordinates in figure 8 (*c*). The termination constant $k_t = 1/\tau_t = 6.7 \times 10^{-4}$ s^{-1} was determined with the initial segments of a series of kinetic curves of chlorination of butyl chloride obtained at
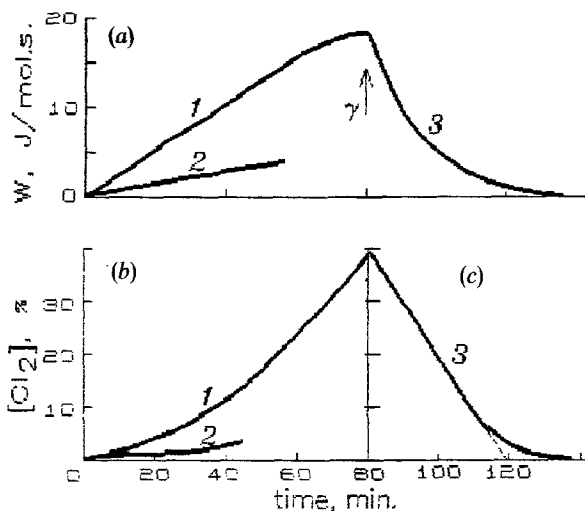
Figure 8. (*a*) Change in the rate of radiation chlorination of C_4H_9Cl in time at 107 (1) and 98 K (2); (3) after switching off γ-radiation (indicated by the arrow). (*b*) Time dependence of consumption of Cl_2, calculated from curves 1 and 2. (*c*) logarithmic anamorphosis of the rate drop (3), dose rate $0.3\,Gy\,s^{-1}$.

different temperatures: $k_p \simeq 10^4 \exp(-5600/RT)\,cm^3\,mol^{-1}\,s$. The temperature dependence of the termination constant, $k_t \simeq 10^{12} \exp(-7400/RT)\,s^{-1}$, was also obtained with the use of the proposed kinetic scheme. The overall rate of chlorination in the noted solid phase attains a maximum near the region of devitrification with an increase in the temperature, and it decreases with a further increase in the temperature and a decrease in the viscosity of the super-cooled liquid due to an increase in the rate of chain termination.

4.2. Solid-phase hydrobromation of ethylene

The reaction of solid-phase radiation hydrobromation of ethylene is the second example of long chains of chemical transformation at ultra low temperatures after polymerization of solid formaldehyde [74,75]. Since formation of the complex $HBr \cdot C_2H_4$ was established in [76], the calorimetric studies of radiation induced hydrobromation were conducted with this system. When the initiating γ-radiation was switched on, the rate of hydrobromation rapidly (with calorimeter inertia) reached the steady-state value. This meant that the kinetic chain propagation time $\tau_v \leqslant \tau_C \simeq 60\,s$ and it was consequently not possible to determine it with the given calorimeter. It was possible to determine the radiation yield of the hydrobromation of ethylene $G(-HBr)$ from the value of the heat release in the steady-state mode. The value of the heat effect of this reaction of $80 \pm 4\,kJ\,mol^{-1}$ established in special experiments was used and is in good agreement with the calculated value of $78.0\,kJ\,mol^{-1}$ reported in [77]. The temperature dependency of $G(-HBr)$, which is close to the kinetic chain length, was obtained from a series of kinetic experiments conducted in the 5–90 K range. Changing to a calorimeter with a low inertia permitted determining the characteristic kinetic chain propagation time τ_v based on the dynamics of the increase and decrease in the rate when the γ-radiation was switched on and off. On the assumption that the radiation yield of primary active centres was $g \simeq 1$, the time of propagation of one chain

unit $\tau_0 = \tau_v/G(-\mathrm{HBr})$ was calculated for the entire temperature range. It was found that pronounced weakening of the temperature dependence (emergence on to plateau) is characteristic of the τ_0 obtained in this way in going to ultra low temperature [75].

4.3. Telomerization

We will examine the study of the mechanism of radiation telomerization on the example of telomerization of tetrafluoroethylene in acetone [78]. This reaction takes place with a high radiation yield that indicates a long kinetic chain length. At the same time, the low molecular weight ($\simeq 50$) of the product formed indicates a very efficient process of chain transfer to the solvent. The specific heat of the telomerization process determined in separate experiments was $-\Delta H = 1430 \pm 80\,\mathrm{kJ\,kg^{-1}}$, which is in good agreement with the specific heat of polymerization of tetrafluoroethylene. A series of kinetic curves of radiation telomerization of tetrafluoroethylene with different dose rate was obtained. These curves, calculated from the calorimetric measurements, are S-shaped. However, the rate of the process relatively rapidly attains a constant value $W_{\max}$, which then decreases due to consumption of the monomer. The dependence of $W_{\max}$ on the dose rate J, $W_{\max} \simeq J^{0.5}$, obtained from these kinetic curves indicates bimoleculary chain termination in the system studied. The steady-state rate of telomerization is essentially dependent on the concentration of tetrafluoroethylene in acetone, which indicates that the order of the reaction is higher than first order. This is apparently due to the participation of the monomer in the chain initiation process.

In the 250–320 K range, the value of $W_{\max}$ decreases with an increase in temperature with $E_{ef} = -12 \cdot 6\,\mathrm{kJ\,mol^{-1}}$. Since a soluble product is obtained in telomerization, the number-average molecular weight of $M_n \simeq 550$ was determined by gel permeation chromatography. The kinetic chain length obtained from the calorimetric measurements was $v_k \simeq G(-M) = 1000$, and the material chain length was $v_m = 5–6$ monomer units. As a consequence, $v_k/v_m \simeq 200$ molecules of telomere is formed per primary radical appearing during radiolysis. The synthesized solutions of tetrafluoroethylene telomers can be used for application of thin protective coatings.

5. Kinetics of postradiation reaction

The study of the dynamics of the progress of the reaction after the initiation radiation is switched off provides rich information on the mechanism of the process. Two different variants in the study of the postradiation process are possible.

(1) The reaction studied develops relatively efficiently in the radiation field in the experimental conditions selected (for example, the temperature range). The study of the dynamics of the decrease in the rate of the process after the radiation is switched off is therefore in fact the study off the kinetics of a non-stationary process which provides information on the mechanism of kinetic chain termination and the value of its rate constant. As noted above, the inertia of the calorimetric set-up in these measurements does not allow studying the reaction with characteristic times less than $\simeq 10–20\,\mathrm{s}$. The initiating radiation should naturally be switched of after significantly shorter times in these experiments, which requires special switching devices when γ-radiation is used.

(2) The reaction studied virtually does not take place in the initiating radiation field. The active sites formed in radiolysis are stabilized in the matrix. In heating of this irradiated matrix, ejection of stabilized active centres form traps and initiation of a chain reaction takes place outside of the radiation field. It is possible to separate the stage of chain initiation and propagation in time in this case and use ESR for quantitative estimations and observations of the transformation of active centres.

5.1. *Non-stationary kinetic measurements*

The kinetics of the drop in the rate of polymerization of formaldehyde after switching off γ-radiation at 5 K was investigated with a low-inertia calorimeter in [79]. These experiments demonstrated the possibility of the occurrence of a chain reaction at such low temperatures in the absence of radiation, and different interpretations of the phenomenon were distinguished using the concepts on activation of the reaction in each new unit due to the radiation energy. The value of the polymer chain termination rate constant, determined from the drop in the rate after the γ-radiation was cut off, was the same as the termination rate constants calculated from the increase in the rate when the radiation was switched on, $k_t \simeq 0.1\ s^{-1}$.

Non-stationary kinetic measurements were also used in studying the mechanism of three-dimensional radiation polymerization of triethylene glycol dimethacrylate [60]. Not only a relatively wide temperature range, but also a wide range of degrees of polymerization were studied in detail. In all cases, the law of the decrease in the rate during the after-effect corresponded to quarternary quenching of growing radicals. The lifetime τ of the propagating radicals increased sharply both with an increase in the degree of polymerization and with a decrease in the temperature. This is understandable, since τ increases with a decrease in the mobility, which is frozen both with a decrease in the temperature and with an increase in the degree of conversion. The polymer chain propagation and termination constants were calculated and their activation energies were determined from the data on non-stationary and steady-state kinetics in the homogeneous approximation [60].

Non-stationary kinetic measurements after the initiating radiation was switched off were also conducted in studying reactions of solid-phase polymerization of carbonyl-containing compounds [31, 79], hydrobromation of ethylene [75], chlorination of saturated hydrocarbons [73], curing of polymer–monomer composites [57, 58], and radiation graft polymerization on inorganic supports [68–70].

5.2. *Heat-activated post effect*

As was noted above, the heat-activated post effect is the second variant. Radiolysis of the system studied is conducted at such low temperatures that the chain reaction is almost totally inhibited during irradiation. Only accumulation of active sites stabilized in the matrix takes place. Heating of the sample subsequently takes place outside of the irradiation zone in the calorimeter scanning mode. The exit of active centres from traps and initiation of the reaction studied takes place in a certain temperature range. The investigation of the mechanism of post polymerization in devitrification is a typical example of this type of study. In thawing of a glassy solution of acrylic acid radiolyzed at 77 K this glass softens at $T_g \simeq 100$ K. Intense heat release related to polymerization of the acrylic acid is observed immediately after the transition of the system to a super cooled liquid state. The total yield of polymer attains 80% [80].

In the devitrification region, transition of monomeric radicals and alcohol matrix radicals into radicals of the propagating polymer chain is recorded in the ESR spectra. However, in addition to chain generation, recombination of some of the monomeric radicals also takes place, and only half of them are converted into propagating polymer radicals. Concentration of propagating polymer radicals remains unchanged on subsequent heating of the system in the temperature region where acrylic acid is intensely polymerized. In the region of matrix devitrification, the polymerization process thus takes place virtually without chain termination. Their translational

mobility was estimated with the initial segment of the monomeric radical quenching curve [81]. It was equal to $v_t \simeq 2 \times 10^{-2} \, \mathrm{s}^{-1}$; the frequency of addition of monomer molecules to the active centre is $v_p \simeq 1 \cdot 3 \times 10^{-3} \, \mathrm{s}^{-1}$. The frequency of reorientations mobility in this system is $v_r \simeq 10^8 \mathrm{s}^{-1}$. Thus, $v_r \gg v_t > v_p$, i.e. these types of molecular mobility do not limit polymer chain propagation.

A combination of ESR and kinetic calorimetry in studying heat-activated post-radiation reaction was successfully used for explaining the causes of the difference in the polymerization efficiency of acrylic and methacrylic derivatives [81, 82], determining the feature of post-radiation curing of oligocarbonate acrylates [83, 84] and oligoester acrylates [85, 86], alternating copolymerization [87, 88], solid-phase polymerization of acetaldehyde [89] and carbon suboxide [90, 91], graft radical [92, 93] and ionic [94, 95] polymerization, chlorination of hydrocarbons [96], etc.

6. Study of autowave and auto-oscillating processes

The phenomena of autowave propagation of cryochemical reactions were detected and investigated in the cycle of studies in [97]. These peculiar mechanical-energetic chain reactions take place due to the creation of a positive inverse correlation between the brittle fracture of a solid sample and the chemical reaction caused by it. The chemical reaction is initiated at the time of brittle fracture and results in further autodispersion of the system due to the thermal or density gradients caused by it. Similar autowave modes of propagation of cryochemical reactions were demonstrated experimentally on the examples of chlorination of hydrocarbons, hydrobromation of olefins, and polymerization [97].

In the initial stage of this cycle of studies, the calorimetric method was used to demonstrate a correlation between brittle fracture and activation of the reaction. The method of induction of thermoelastic stresses by selecting the rate of change of the sample temperature was initially selected to cause brittle fracture of a glassy solution of chlorine in methylcyclohexane. A differential scanning calorimeter was used for recording the rate of the change in the temperature of the sample capable of causing failure and observing the signals that accompany this process: the temperature of its surface and the heat effects of the processes occurring in it (appearance of a branched network of cracks or a chemical transformation) were determined during heating or cooling of the sample.

As demonstrated in [98], slow heating of the glassy system from $4 \cdot 2$ to 77 K does not cause cracking of the sample, and the calorimeter does not detect any heat effects (figure 9(*a* and *d*, solid lines). Rapid heating causes cracking of the sample and the accompanying heat effect is recorded by the calorimeter (figure 9 *b* and *e*, solid lines). After selection of the heating rate which caused brittle fracture of the sample, analogous experiments were conducted, but with samples previously undergoing radiolysis with γ-rays to create stabilized active centres in the system. The heat release due to the chemical reaction could not be recorded during slow heating of the irradiated sample that did not cause cracking (figure 9(*a* and *d*), broken lines). The chemical transformation flares up at the time of brittle fracture in rapid heating (figure 9 *b* and *e*, broken lines).

Brittle fracture of the sample could also be induced with fast cooling. The data for a sample cooled relatively rapidly to cause cracking are shown in figure 9 *c* and *f*. As expected, fracture of the irradiated sample is also accompanied by a fast chemical conversion (the conversion did not occur in the unirradiated sample). The correlation
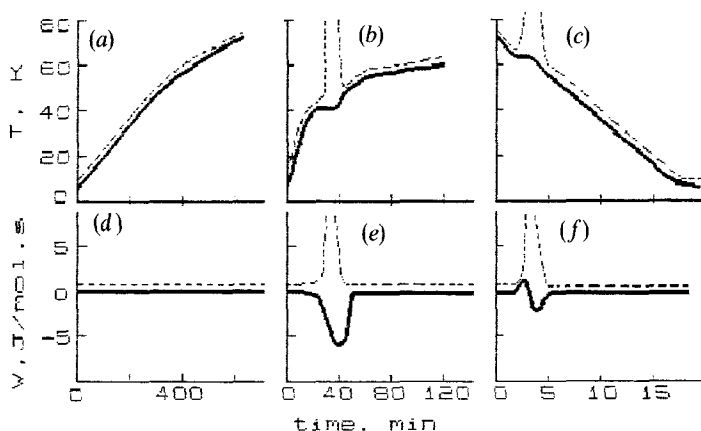
Figure 9.   Change in the temperature of the sample of methylcyclohexane + Cl_2 in time (a–c) and the accompanying heat effects (d–f); solid lines: unirradiated samples; broken lines: samples irradiated with ^{60}Co γ-rays at 77 K, dose of 27 kGy.
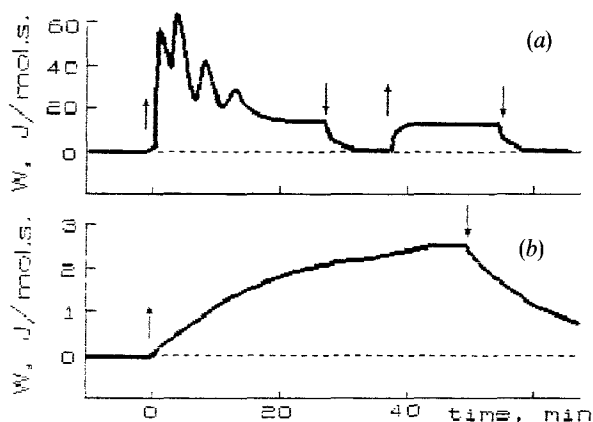

Figure 10.   Change in the rate of radiation hydrobromation of ethylene at a thermostat temperature of 85 K. Dose rate of 0·3 (a) and 4×10^{-4} Gy s^{-1} (b). The times of switching the γ-radiation on and off are indicated by the arrows.

established in this way between the brittle fracture of the system and its chemical activation permitted passing to the experimental organization of the autowave mode of the cryochemical transformation and the study of its feature.

Auto-oscillating modes of solid-phase chemical reactions were detected in studying solid-phase radiation hydrobromation of ethylene in [99]. At 85 K, the calorimeter detected oscillations in the rate of the chemical reaction (figure 10) after γ-radiation was switched on. The auto-oscillations of the rate were dumped in time during depletion of the reactions. The total degree of conversion was $\simeq 40\%$. When the γ-radiation was switched on again, no oscillations in the reaction rate were observed. There are several characteristic conditions required for the realization of such an oscillating mode of the occurrence of the reaction: (1) oscillations of the rate are only observed at thermostat temperatures above $\simeq 75$ K; (2) oscillations of the rate only

arise when dose rates above $0.2\,Gy\,s^{-1}$ are used (above the defined rate of heat release due to the reaction). An experiment conducted in the same conditions as the experiment in figure 10 *a* is figure 10 *b*, but the dose rate has been reduced to $4 \times 10^{-4}\,Gy\,s^{-1}$. Note that auto-oscillations of the rate of hydrobromation do not occur.

It was previously shown that the steady-state rate of radiation hydrobromation of ethylene is proportional to the dose rate to a power of 0.5 at 90 K and to a power of 1.0 at 50 K [75]. The first order of quenching of kinetic chains at low temperatures is not due to quenching of active centres, but to cessation of chain propagation because of the spatial isolation of the active site. Heating of a system irradiated at 50 K results in an increase in the molecular mobility, exit of active centres from spatial isolation, and the effective occurrence of a heat-activated post radiation reaction.

In the case of radiolysis of the system at 90 K, the active sites are not stabilized in the matrix, and bimolecular kinetic chain quenching is observed. In this case, the post-effect is naturally not observed. Mixed chain breaking takes place in the 70–80 K region. The appearance of slight heating of the sample relative to the thermostat is possible in the absence of sufficient heat transfer. The magnitude of heating increases with an increase in the reaction rate. However, when the temperature region where bimolecular termination becomes dominant is reached, the total concentration of active sites decreases. The rate of the process and, as a consequence, heating of the sample decrease correspondingly. The system again passes into the temperature region where the active sites can be stabilized. They accumulate, again causing an increase in the reaction rate.

Auto-oscillations of the rate have also been observed in the case of heat-activated post polymerization of crystalline heptyl acrylate [100] and a glassy solution of acetaldehyde in a butyl chloride matrix [101].

On cooling to 77 K, the solution of acetaldehyde in a butyl chloride (molar ratio of 1:4) passes into the glassy state. On heating the system in the calorimeter in the 94–97 K region, the glass becomes a super cooled liquid and subsequently crystallizes (112–115 K) and then melts ($T_m = 145\,K$). During heating of this system irradiated at 77 K, heat release caused by polymerization of acetaldehyde is observed in the region of devitrification. Different modes of occurrence of the process are possible as a function of the conditions of heat transfer from the calorimetric cell. The following parameters can be experimentally varied to steady-state conditions (absence of pronounced overheating of the substance in the calorimeter): (1) decreasing the temperature scanning rate; (2) improving the conditions of heat transfer by increasing the ratio of the surface area of the sample to its volume; (3) decreasing the dose of preliminary radiation (*decrease in the rate of initiation*). In this mode, the rate of post polymerization increases with an increase in the temperature (the initial segment of the calorimetric curve is satisfactorily linearized in Arrhenius coordinates, activation energy of $E \simeq 25\,kJ\,mol^{-1}$), attains a maximum, and subsequently smoothly decreases due to depletion of the monomer and active centres.

The thermal explosion mode is another limiting case. This mode occurs when the conditions of heat transfer from the cell worsen: an increase in the sample weight, heating rate, and dose of preliminary radiation. An oscillating mode of the process was recorded in conditions of heat transfer of intermediate intensity. Several cycles of an increase and a decrease in the reaction rate were observed in the experiment [101].

It is thus possible to assume that the experimentally determined oscillations in the rate are due to a thermokinetic mechanism. A mathematical model which qualitatively describes the three different regions of occurrence of the process observed is examined

in [100, 102]. We note that the oscillating mode in low-temperature chain reactions has a general character; it has been observed in crystalline [99, 100, 102] and glassy [101] states both in the γ-radiation field and in the after effect.

If the reader has become convinced of the rich potentialities of kinetic calorimetry in the study of the mechanism of radiation chemical reactions and has decided to use it in his own research after reading this review, we remind him that kinetic calorimetry is methodologically simpler than the standard set-ups for thermodynamic measurements. We are ready to offer methodological assistance.

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