# Relationships between the kinetic parameters of radical reactions and the state parameters, macro-characteristics and molecular mobility of polymers and solids

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Relationships between the kinetic parameters for free-radical recombination in polymers and low-molecular weight crystals and the pressure, volume and temperature have been studied. Experimental values for the activation volumes and energies of chemical reactions in solids have been shown to coincide with the corresponding $V^*$ and $E$ values in small-scale molecular dynamics. A relationship is established between the activation recombination parameters and the compound's coefficients of compressibility and thermal expansion. Equations are obtained relating the state parameters, reaction activation parameters and macro-characteristics of condensed media.

(Keywords: radical reactions; polymers; molecular dynamics; high pressure; activation volumes)

## INTRODUCTION

The dependence of the rate of reaction occurring in the kinetic regime on the structure and physical properties of a solid is a specific feature of solid-phase reactions. This actually means that the solid's reactivity is determined not as much by the electron structure of the reacting species as by their molecular mobility. Experimental implications of this feature are considered elsewhere[1] for the example of radical reactions in polymer ageing. One of the most important problems in the chemical physics of solids is that of establishing the mechanism that relates molecular dynamics to chemical kinetics. This will open the way to predicting the properties of materials and their changes under the service conditions.

Research in this area mainly concentrates on finding out common relationships in molecular dynamics and chemical reaction kinetics, on establishing the type of molecular motion governing the chemical reaction and the size of the kinetic elements, and on analysing correlations between parameters characterizing reaction rates and macro-properties of a solid body.

To solve all these problems one can successfully use uniform compression, which changes the free volume, molecular mobility and reactivity of condensed media[2-8]. The amount of information obtained through this technique has been substantially increased due to the establishment of basic relationships in molecular dynamics at high pressure[9].

The present work examines the effect of temperature, volume and pressure on radical decay rate constants and activation parameters in amorphous and crystalline polymers and crystals of low-molecular-weight carboxylic acids.

## EXPERIMENTAL

Free radicals were generated through $\gamma$-irradiation of compounds under study by a $^{60}Co$ source at 77 K in the absence of oxygen. The total irradiation dose was 5–10 Mrad for amorphous polymers and 10–25 Mrad for crystalline systems. The concentration of paramagnetic species ranged from $10^{18}$ to $10^{19}$ spins/cm$^3$. The e.p.r. spectra were registered using an X-band spectrometer. The number of lines in the e.p.r. spectra and the structure of free radicals identified on the basis of literature data[10] are listed in *Table 1*.

The kinetics of radical decay upon annealing was registered in the absence of oxygen. The treatment of kinetic data was done using the second-order equation, which satisfactorily describes experimental kinetic curves up to degrees of conversion of 50–60%.

Uniform compression experiments were carried out in a special hydrostatic pressure chamber. Transformer oil served as the pressure-transmitting liquid. A more detailed description of the high-pressure technique is given in ref. 8. The samples were placed into the chamber in sealed polyethylene ampoules.

The effect of high pressures on radical decay rate was studied on samples whose radicals are stable at room temperature. Since radicals were annealed outside the e.p.r. spectrometer resonator and the annealing kinetics was registered by determining the radical concentration at different annealing stages, investigations were carried out on samples whose radicals are stable at room temperature. The following procedure was adopted in order to minimize radical losses upon heating and cooling. The samples were placed into the chamber and the pressure was raised up to the maximal values

**Table 1** E.p.r. and literature data

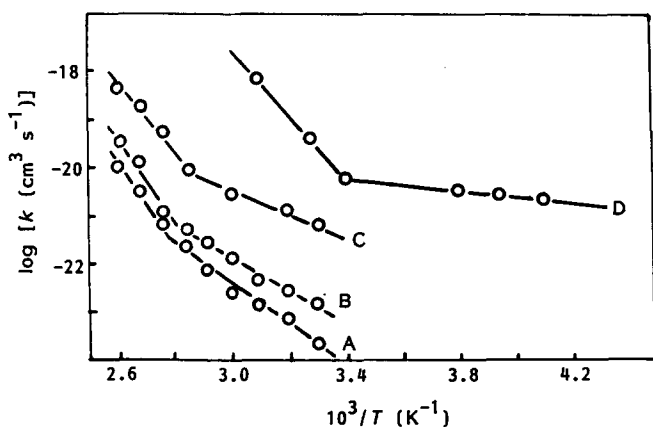| Compound | Number of lines in spectrum | Radical |
|---|---|---|
| Poly(methyl methacrylate) (PMMA) | 9 | $CH_2(COOCH)_3(CH_3)\dot{C}$ |
| Polystyrene (PS) | 3 | $CH_2\dot{C}H(C_6H_6)CH_2$ |
| Poly(vinyl acetate) (PVA) | 3 | $CH_2\dot{C}(OCOCH_3)CH_2$ |
| Poly(vinyl chloride) (PVC) | 7 | $CHClCH_2\dot{C}HCH{=}(CH)_3Cl$ |
| Polyethylene (PE) (SCC) | 6–10 depending on sample orientation in magnetic field | $CH_2\dot{C}HCH_2$ |
| Malonic acid | 2 | $HOOC\dot{C}HCCOH$ |
| Succinic acid | 6–8 | $COOH\dot{C}HCH_2COOH$ |



**Figure 1** Temperature dependences of macroradical recombination rate constants in PMMA (A), PVC (B), PS (C) and PVA (D)

(250 MPa). Then the temperature was increased to the desired value and the pressure was immediately reduced to the given level. When sampling was done the pressure was again increased (the reaction was thus stopped), the temperature lowered and the pressure reduced. In this manner it was possible to stop the reaction sharply at various stages.

In discussing the experimental results use was also made of the data obtained in Szöcs[7].

Single crystals of malonic and succinic acids were grown from acetone solution. Samples of polyethylene with a high degree of crystallinity (>97%) were obtained through annealing at high temperature (538 K) and pressure (700 MPa)[11]. The crystallites of such samples are formed by straightened chains (straightened chain crystallites, SCC).

The technique we used in this work to determine $\beta$-relaxation processes in polymers by thermally stimulated depolarization currents (t.s.d.) currents is described in Kovarskii et al.[12].

The data on volume variation with pressure, coefficients of thermal expansion and compressibility are taken from Ainbinder et al.[13].

## RADICAL DECAY IN AMORPHOUS POLYMERS

### The decay rates and molecular motion frequencies

A common feature exhibited by all temperature dependences of macroradical decay rate constants in amorphous polymers is an inflection (*Figure 1*) near the glass transition temperature (*Table 2*).

Such inflections near $T_g$ are typical of the temperature dependences of all processes in polymers governed by

molecular dynamics: rotational and translational diffusion of low-molecular-weight additives[14,15], ionic electro-conductivity and $\beta$-relaxation[16,17]. Therefore, the pattern of temperature dependences for macroradical decay rate constants suggests that this process is closely related to polymer molecular dynamics.

Let us compare the rate constants and molecular motion frequencies in amorphous polymers. To this end we shall use relaxation frequencies obtained by the thermally stimulated depolarization technique. It follows from *Figure 2* that there is a correlation between the rate constants and molecular motion frequencies.

Note that the general dependence $\log k = f(\log v)$ is fulfilled despite the differences in the structure of macro-radicals (terminal, middle, containing phenyl group, ordinary and double bonds). Thus, the specificity of the polymeric matrix as a relaxationally hindered system lies in the levelling off of the reactivity of species. The molecular dynamics of macroradicals acquires paramount importance as a parameter characterizing the reactivity.

What is important is that recombination of macro-radicals is a reaction occurring in the kinetic regime, since the limiting stage of these processes, at least below $T_g$, is the relay transfer of hydrogen atom:

$$\dot{R} + R'H \rightarrow RH + \dot{R}'$$
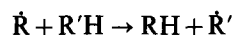
This mechanism leading to recombination of radicals does not require diffusional transitions of species over large distances and, consequently, molecular dynamics can 'interfere' with the process only at the stage of forming an activated complex in an elementary relay transfer act.

### Activation volume

The baric dependences of macroradical decay rate constants in amorphous polymers exhibit two specific features[7,8]. First, the rate constants fall sharply with pressure, i.e. the activation volumes $V^*$ calculated by:

$$V^* = -RT\left(\frac{\partial \ln k}{\partial p}\right)_T$$

are within 10–80 cm$^3$ mol$^{-1}$ and increase with temperature (*Table 3*). Secondly, the baric dependences are nonlinear—as the pressure is increased, they become weaker. Let us look into the reason for this.

The $V^*$ values show the lack of agreement with the existing ideas according to which an activated complex in a bimolecular reaction occupies a smaller volume than the total volume of the reacting molecules. Therefore $V^*$ values must be negative, i.e. pressure must accelerate the reaction. This follows from the theory and is corroborated

**Table 2** Effective activation energies for macroradical decay and relaxation processes in polymers

| Polymer | $T_g$ (K) | $T_L{}^a$ (K) | $E_1(T<T_g)$ (kJ mol$^{-1}$) | $\log[k_1^0$ (cm$^3$ s$^{-1}$)] | $E_2(T>T_g)$ (kJ mol$^{-1}$) | $\log[k_2^0$ (cm$^3$ s$^{-1}$)] | $E_\beta$ (kJ mol$^{-1}$) | $E_\alpha$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | | | Reaction | | | | Dynamics[b] | |
| PVA | 303 | 293 | 15 | −18.0 | 121 | 3.4 | 17 | 182 |
| PVC | 356 | 355 | 62 | −13.2 | 169 | 2.4 | 63 | 422 |
| PS | 360 | 353 | 48 | −14.0 | 145 | −0.3 | – | 352 |
| PMMA | 396 | 362 | 78 | −12.2 | 168 | 1.9 | 67 | 355 |

[a] The inflection temperature for Arrhenius dependences
[b] According to (9)
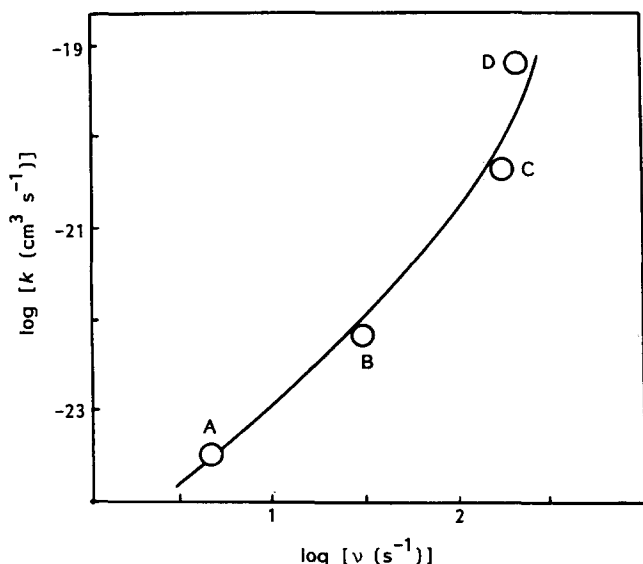


**Figure 2** The dependence of macroradical recombination rate constant on $\beta$-relaxation frequency in PMMA (A), PVC (B), PS (C) and PVA (D)
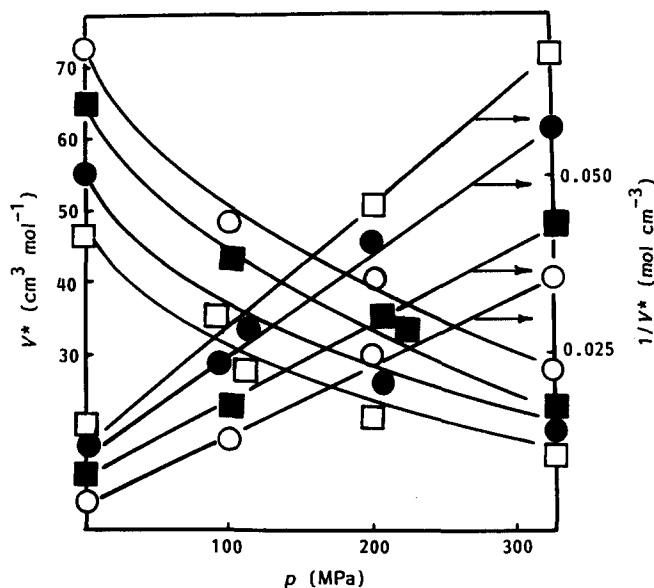


**Figure 3** The baric dependence of activation volume for macroradical recombination in PMMA at various temperatures: (O) 353 K, (■) 343 K, (●) 333 K and (□) 323 K

**Table 3** Activation volume for macroradical decay in polymers at $p \to 0$

| Polymer | $T$ (K) | $V^*$ (cm$^3$ mol$^{-1}$) |
|---|---|---|
| PMMA | 323 | 45 |
| | 333 | 52 |
| | 343 | 65 |
| | 353 | 77 |
| PS[a] | 353–473 | 21–66 |
| PVC[a] | 350–400 | 9–26 |

[a] According to (7)

by numerous studies into the kinetics of bimolecular reactions in the liquid phase[4-6].

So what are the reasons for high positive $V^*$ values in radical recombination in polymers? Unlike liquid media, the polymeric matrix has considerably higher relaxation times of molecular motion. Molecular mobility governs the kinetics of chemical reactions, limiting the number of encounters between active species. The observed fall in the recombination rates is most probably due to a decreased intensity of molecular motions brought about by an increased hydrostatic pressure. Let us compare the $V^*$ value for macroradical decay with the activation volumes of the main types of molecular motions. The $V^*$ values for $\alpha$-relaxation (vitrification) lie in the range 150–500 cm$^3$ mol$^{-1}$, for $\beta$-relaxation (small-scale dynamics) in the range 20–40 cm$^3$ mol$^{-1}$ (ref. 9).

This means that the activation volumes of radical recombination are close to the $V^*$ values for $\beta$-relaxation. Therefore, the activation volumes obtained in the high-pressure experiments characterize the magnitude of the fluctuation free volume required for small-scale molecular motion.

Another manifestation of the relation between the reaction kinetics and polymer molecular dynamics and macro-properties is the non-linearity of baric dependences of $\log k$, i.e. the decrease of the activation volume with pressure (*Figure 3*). Such deviations from linearity are typical of the baric dependences of molecular motion frequencies and are covered in detail by Kovarskii and Aliev[9,18]. The reason for this is a decrease with pressure of the polymer compressibility $\beta$ (or an increase of the bulk modulus $K = 1/\beta$).

The bulk modulus is known to increase linearly with pressure, whereas the compressibility coefficient decreases with pressure according to the hyperbolic law[13]. The baric dependence of the activation volume is also hyperbolic and becomes linear in $1/V^*$ *versus* $p$ coordinates (*Figure 3*). A clear relation between activation volume and polymer compressibility is suggested by the existence of a nearly linear relationship between the two quantities (*Figure 4*). The $V^*/\beta$ ratio is $(1.5 \pm 0.2) \times 10^5$ cm$^3$ MPa mol$^{-1}$. The $\beta$-relaxation processes in polymers are also characterized by similar $V^*/\beta$
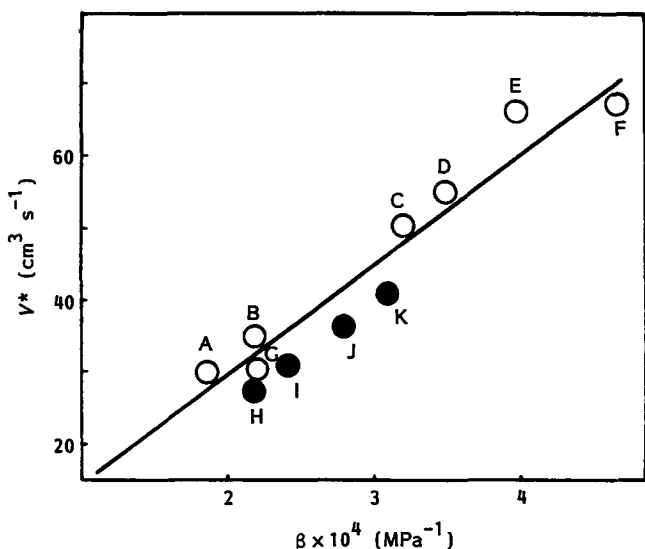
**Figure 4** The dependence of activation volumes for macroradical decay (open circles A–G) and $\beta$-relaxation (full circles H–K) on polymer compressibility: (A) PMMA, 333 K, 200 MPa; (B) PMMA, 333 K, 100 MPa; (C) PMMA, 323 K, 0.1 MPa; (D) PMMA, 333 K, 0.1 MPa; (E) PMMA, 343 K, 0.1 MPa; (F) PS, 373 K, 0.1 MPa; (G) PVC, 350 K, 0.1 MPa; (H) PVC, 295 K, 0.1 MPa; (I) PMMA, 294 K, 0.1 MPa; (J) polychlorotrifluoroethylene, 304 K, 0.1 MPa; (K) polyethyleneterephthalate, 295 K, 0.1 MPa. The activation volumes for $\beta$-processes were taken from (9)

values (*Figure 4*). The relation of $V^*$ with $\beta$ and $K$ allows one to write:

$$V_p^* = V_0^* K_0 / K_p \qquad (1)$$

where $p$ and $0$ correspond to pressures $p$ and $p \to 0$.

For rate constants we have[8,18]:

$$\log k_p = \log k_0 - \frac{p V_0^* K_0 / K_p}{2.3RT} \qquad (2)$$

or

$$\log k_p = \log k_0 - \frac{V_0^* K_0 \, \Delta V / V_0}{2.3RT} \qquad (3)$$

The equations indicate that there is a linear relationship between $\log k$ and $p/K$, which is corroborated by experimental data on macroradical decay in PMMA[8]. It should be noted that these coordinates also linearize the basic dependences of molecular motion relaxation times[19], i.e. the chemical and physical kinetics in polymers are governed by common relationships.

Since the compressibility coefficient characterizes the volume variation in the given pressure range, the relationship between $k$ and $V$ indicates that the main parameter determining the change of reaction rate upon isothermal compression is the system volume. Experimental data support this conclusion (*Figure 5*).

*Reaction energetics*

The technique of uniform compression makes it possible to determine the activation energy not only at constant pressure ($E_p$) but also at constant volume ($E_V$). Let us examine the values of the parameters, their physical meaning and their relation to the matrix macro-properties.

The activation energies at constant pressure ($p = 0.1$ MPa) for macroradical decay reactions vary over a wide range of values and depend upon the physical state of the polymer. Below $T_g$, $E_p$ is $15$–$70$ kJ mol$^{-1}$; at $T > T_g$,

it increases to $120$–$170$ kJ mol$^{-1}$ (*Table 2*). These $E_p$ values are close to the activation energies of $\beta$-relaxation processes in polymers. It was shown[17] that the activation energy of the $\beta$-process increases in the vicinity of $T_g$. Thus, in PMMA, $E_p$ varies from $77$ kJ mol$^{-1}$ below $T_g$ to $180$ kJ mol$^{-1}$ at $T > T_g$. The $E_p$ values for macroradical decay reactions in this polymer also vary.

Note that the macroradical decay rate does not seem to be directly related to the large-scale $\alpha$-relaxation process, since its effective activation energies (and volumes) are considerably higher ($200$–$400$ kJ mol$^{-1}$).

Let us now compare the experimental values of the activation energy obtained at constant pressure and constant volume (*Figure 6, Table 4*). In PMMA, $E_p$ is $78$ kJ mol$^{-1}$. Pre-exponential factors at constant pressure
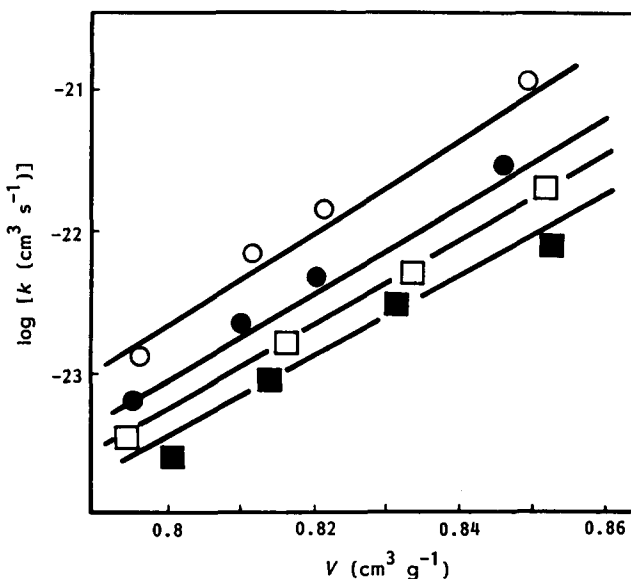


**Figure 5** The dependence of $\log k$ on the specific volume of PMMA at 323 (■), 333 (□), 343 (●) and 353 K (○)
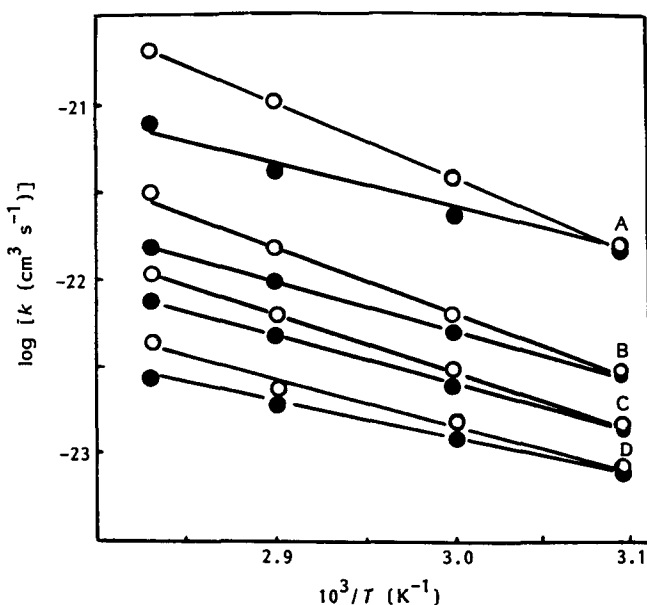


**Figure 6** The Arrhenius dependences of radical recombination rate constants in PMMA at constant pressure (open circles) and constant volume (full circles): (A) 0.1 MPa; (B) 100 MPa; (C) 200 MPa; (D) 300 MPa. The volumes are listed in *Table 3*

**Table 4** Parameters of equations (5) and (14)-(16) for macroradical decay reaction in PMMA $(T < T_g)$

| $p$ (MPa) | $E_p$ (kJ mol$^{-1}$) | $E_V{}^a$ (kJ mol$^{-1}$) | $E_p - E_V$ (kJ mol$^{-1}$) | $V^{*b}$ (cm$^3$ mol$^{-1}$) | $pV^*$ (kJ mol$^{-1}$) | $cT\alpha V_0 = T\alpha KV^{*c}$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|---|
| 0.1 | 78 | 45 (0.86) | 33 | 77 | 0 | 27.5 |
| 100 | 71 | 47 (0.84) | 24 | 48 | 4.8 | 16.9 |
| 200 | 64 | 50 (0.82) | 14 | 31 | 6.2 | 10.9 |
| 300 | 56 | 52 (0.8) | 4 | 22 | 6.6 | 7.8 |

$^a$ Specific volume (cm$^3$ g$^{-1}$) is indicated in parentheses
$^b$ At $T = 353$ K
$^c$ Calculations at $V_0 = 85.6$ cm$^3$ mol$^{-1}$; the values of $\alpha$ and $\beta$ at different pressures are taken from (13)

are 2–4 orders of magnitude higher than $k_0$ values measured at constant volume.

As the external pressure increases, $E_p$ falls and comes closer to $E_V$. Pre-exponential factors also decrease, tending to 'normal' values.

Differences in $E_p$ and $E_V$ values can be explained in terms of the transition-state theory and the Frenkel kinetic theory of liquids. Analysing the first of them we can write[2]:

$$E_p = \Delta H^* \quad \text{and} \quad E_V = \Delta H^* - p_t V^* \qquad (4)$$

where $H$ is the activation enthalpy and $p_t$ is the thermal pressure, representing the increase in pressure with rising temperature at constant volume:

$$p_t = T\left(\frac{\partial p}{\partial T}\right)_V$$

Thermodynamic analysis leads to the correlation:

$$\left(\frac{\partial p}{\partial T}\right)_V = \alpha K$$

Equation (4) assumes the form:

$$E_p - E_V = T\alpha KV^* \qquad (5)$$

Thus, the difference in activation energies at constant pressure and volume depends on the activation volume, compressibility and coefficient of thermal expansion.

The Frenkel theory[20] allows one to get a more profound understanding of the molecular mechanism accounting for the difference in the activation energies. According to this theory, molecular mobility depends on the energy of formation of a fluctuation hole with volume $V^*$ in agreement with:

$$\tau = \tau_0 \exp\left(\frac{E + pV^*}{RT}\right) \qquad (6)$$

where $E$ is the energy of hole formation at $p \to 0$ and $\tau_0$ is the period of molecular oscillations in the equilibrium state.

The value of $E$ depends on the state parameters. The dependence upon the external pressure is taken into account in equation (6). The dependence on volume and temperature is determined by the following relations:

$$E = E_0 - c \, \Delta V = E_0 - c\alpha V_0 T \qquad (7)$$

$$\tau = \tau_0 \exp\left(\frac{E_0 - c\alpha V_0 T}{RT}\right) \qquad (8)$$

where $c$ is a constant, $E_0$ is the value of $E$ at $T = 0$, i.e. the maximal barrier of hole formation at $p \to 0$, and $V_0$ is the specific volume at $T = 0$.

The physical meaning of correlations (7) and (8) is as follows. An increase in temperature in an open system causes an increase in its volume and intermolecular distances, which facilitates formation of fluctuation holes. Evidently, the simplest way of determining the barrier experimentally is to heat the system under isochoric conditions $(\Delta V = 0)$, when only the kinetic energy of molecules undergoes changes.

Isobaric heating, traditionally used in experiments $(p = 0.1$ MPa), results, in accordance with (8), in changing both the kinetic energy of the molecules and the energy of hole formation, i.e. the numerator and denominator in the exponent of equation (6). The molecular motion frequencies will increase in a sharper manner than in isochoric conditions. Besides, $E$ measured at constant pressure is found to be temperature-dependent and it is, consequently, an effective value, that is devoid of physical meaning. $E_{eff}$ is shown[21] to be related to the activation barrier through:

$$E_{eff} = E - T\frac{\partial E}{\partial T} \qquad (9)$$

Combining (9) and (7) we obtain:

$$E_{eff} = E - T\frac{\partial(E_0 - c\alpha V_0 T)}{\partial T} = E + c\alpha V_0 T \qquad (10)$$

The equation obtained is totally identical to (5) at $c = V^*/V_0\beta$. As follows from *Figure 4*, $V^*/\beta = $ constant and, consequently, $c$ is a constant independent of the state parameters. Thus, the temperature coefficient of the rate constant (molecular motion frequencies) measured at constant volume is the activation energy under given conditions $(T, V)$, whereas at constant pressure one determines the effective value $(E_p = E_{eff})$. A similar expression is obtained for $k_0$:

$$\ln k_{0,eff} = \ln k_0 - cV_0\alpha/R \qquad (11)$$

Comparing (10) and (7) one sees that $E_{eff} = E_0$, i.e. effective $E$ (or $E_p$) are equal to the maximal activation energy (at $T = 0$). This equation, however, is valid only if $\alpha$ is independent of temperature. As a rule this condition is not fulfilled in condensed media. For $\alpha(T)$ equation (10) assumes the form:

$$E_{eff} = E + TcV_0\left(\alpha + T\frac{\partial\alpha}{\partial T}\right) \qquad (12)$$

It is known that near $T_g$ the $\alpha$ value jumps[13], which explains the marked variation of the temperature coefficients for radical reaction rate constants (*Figure 1*). Using (10) one can write:

$$E = E_{T>T_g} - E_{T<T_g} = cV_0 T_g \Delta\alpha \qquad (13)$$
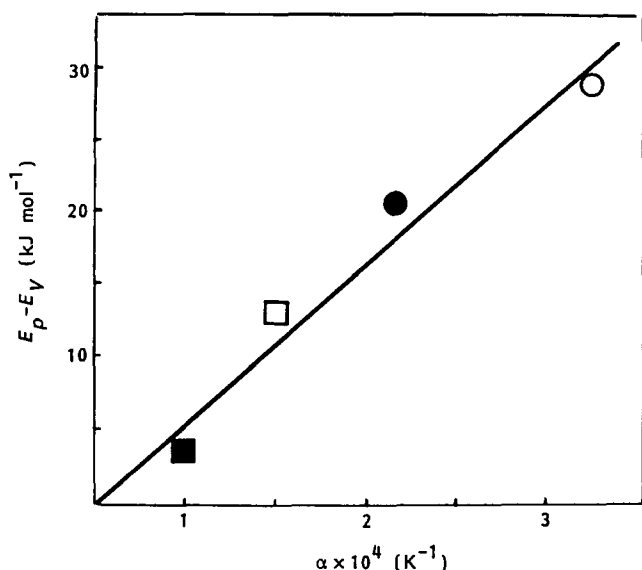
**Figure 7** The $E_p - E_V$ dependence for macroradical decay in PMMA on thermal expansion coefficient at various pressures $(T < T_g)$: 0.1 MPa (O); 100 MPa (●); 200 MPa (□); 300 MPa (■)

where

$$\Delta\alpha = \alpha_{T > T_g} - \alpha_{T < T_g}$$

Let us now consider the results obtained in compression (*Table 4*). As the pressure is increased, $E_p$ falls sharply whereas $E_V$ grows slowly. The reason for these activation energy changes is clear from the following correlations obtained on the basis of (6) and (10):

$$E_V = E_V(p=0) + pV^* \tag{14}$$

$$E_p(p) = E_V(p) + cT\alpha V_0 = E_V(p \to 0) + pV^* + cT\alpha V_0 \tag{15}$$

$$E_p(p \to 0) = E_p(p) + cTV_0 \Delta\alpha - pV^* \tag{16}$$

where

$$\Delta\alpha = \alpha(p \to 0) - \alpha(p)$$

and $V_0$ is weakly dependent on pressure.

It follows from (14) that $E_V$ must grow proportionally to pressure. This growth, however, is partly compensated by the decreased $V^*$. *Table 4* shows that, within the range of pressure from 100 to 300 MPa, $pV^*$ changes by $\sim 2 \text{ kJ mol}^{-1}$, which is less than the experimental error.

It follows from (16) that the decrease in $E_p$ with pressure is caused by a decrease in the thermal expansion coefficient. The correlation between the two parameters obtained experimentally (*Figure 7*) supports this conclusion. Coefficient $c$ can be determined from equations (13) (*Figure 1*) and (15) (*Figure 7*), and calculated on the basis of the above-mentioned equation $c = V^*/V_0\beta$. According to calculations $c$ equals $4 \pm 2 \text{ kJ cm}^{-3}$.

The value $cT\alpha V_0$ becomes comparable with the error in determining $E$ ($\sim 6 \text{ kJ mol}^{-1}$) at $p \geq 300 \text{ MPa}$ and, consequently, at these pressures $E_p \simeq E_V$.

## SPECIFIC FEATURES OF REACTIONS IN CRYSTALS

Chemical reactions occur in both amorphous and crystalline polymer regions. Crystalline regions are noted not only for regular molecular packings but for the absence of large-amplitude motions, and also for a difference in elastic constants. That is why it is useful to compare

the kinetic parameters and volume effects of chemical reactions in amorphous substances and in crystals. Such an analysis was carried out in the present work, which studied radical decay reactions in the annealing of polyethylene (PE) crystals with straightened chains (SCC) and low-molecular-weight dicarboxylic acids (*Table 5*). The e.p.r. spectra of these compounds exhibit marked variations depending on how the sample is oriented in the magnetic field. This indicates that radicals in the sample are arranged in a regular manner.

When crystals are annealed the concentration of radicals starts falling drastically at temperatures 80–90°C below $T_m$. This is also the beginning of unfreezing molecular motions in crystals. E.p.r. studies in PE demonstrated that molecular motions accelerate at 333 K, i.e. at 80°C below $T_m$ (ref. 23). The wide-line n.m.r. technique[24] also indicates that annealing of polymeric crystals results in a significant increase in the number of mobile segments.

The melting temperature seems to be one of the characteristic parameters determining the kinetic properties of crystals. The rate constants and activation energies of compounds under study are directly related to $T_m$. In crystals with similar $T_m$ (SCC, malonic acid) the values of $k$ and $E$ are also found to be similar (*Table 6*). The decay of radicals in succinic acid crystals, with higher $T_m$, exhibit lower $k$ and high activation energy values.

Unlike amorphous polymers, the baric dependences $\log k$ in crystals are linear (*Figure 8*). Crystal bulk modulus is much less dependent on pressure as compared to glasses. Apparently this can be explained by the fact

**Table 5** Activation volumes of radical decay in crystals

| Crystal | $V^* \pm 4$ (cm$^3$ mol$^{-1}$) | $V_w{}^a$ (cm$^3$ mol$^{-1}$) | $V^*/V_w$ |
|---|---|---|---|
| Malonic acid | 32 | 49.71 | 0.7 |
| Succinic acid | 35 | 59.94 | 0.5 |
| SCPE | 19 | 20.46$^b$ | |

$^a$ According to (22)
$^b$ The volume of a monomeric unit
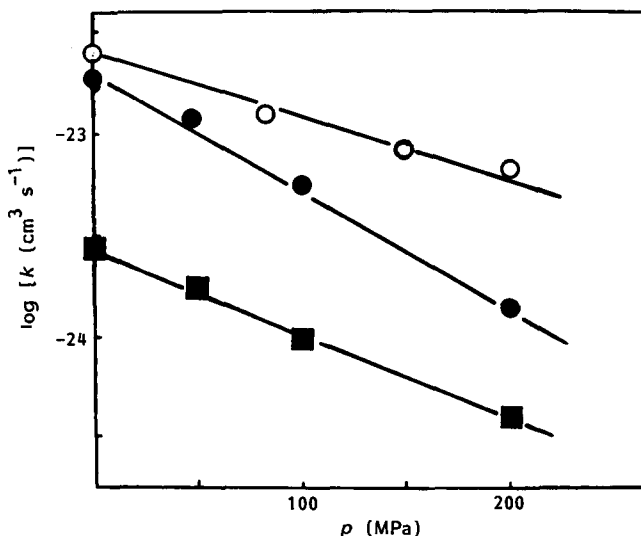


**Figure 8** The baric dependences of radical decay rate constants in crystals of succinic acid (378 K) (■), malonic acid (353 K) (●) and PE (353 K) (O)

**Table 6** Activation energies of radical decay in crystals

| Radical | Crystal | $T_m$ (K) | Range of temperatures (K) | $E_p \pm 5$ (kJ mol$^{-1}$) | $\log[k^0 \text{ (cm}^3\text{ s}^{-1})]$ |
|---------|---------|-----------|---------------------------|------------------------------|--------------------------------------------|
| $\dot{C}H(COOH)_2$ | Malonic acid | 409 | 313–343 | 74 | −11.72 |
| $\dot{C}HCH_2(COOH)_2$ | Succinic acid | 462 | 381–405 | 122 | −6.45 |
| $\sim CH_2-\dot{C}H-CH_2 \sim$ | PE (SCC) | 409 | 333–363 | 72 | −12.2 |

that glasses exhibit a wider distribution in the size of defects accepting compressive loads, which means that the distribution of compressibility coefficients is also wider. There is no significant difference between the activation volumes of radical decay in crystals and polymers (at $T \ll T_g$). Similar positive values of reaction activation parameters in crystals and glasses indicate that in both cases these reactions are governed by small-scale molecular dynamics. The ratio of activation volume to molecular volume can be used as a parameter characterizing the scale and the type of molecular motion[9,25]. Thus, with low-amplitude rotational–orientational dynamics in polymers ($\beta$-processes) the $V^*/V_w$ ratio ($V_w$ is the Van der Waals volume of a kinetic element) lies in the range 0.1–0.4; this range extends to 0.6–1.0 if account is taken of the translational component of molecular dynamics.

The ratio $V^*/V_w$ for malonic and succinic acids is $\sim 0.6$. Thus, the activation volume for radical decay reactions in dicarboxylic acid makes up about half of the proper molecular volume. Using the above value to calculate a kinetic element volume in PE crystals (SCC) we obtain $V_w = 33$, which slightly exceeds the volume of a monomeric unit.

So, limiting radical recombination to crystals of organic compounds, the hydrogen atom transfer reaction requires rather appreciable fluctuations of the free volume. These fluctuations are likely to be caused by low-amplitude shifts of kinetic elements, comparable to the size of the molecules (carboxylic acids) or monomeric units (PE).

## CONCLUSIONS

The analysis of temperature and baric dependences of the kinetic parameters for free-radical decay reactions in polymers and solids indicates that there is a close relationship between the rates of chemical reactions and the small-scale molecular mobility.

It should be noted that the limiting stage of radical recombination in polymeric glasses and crystals is *chemical relay transfer*, which is why molecular dynamics governs the reactions occurring in the kinetic regime, i.e. the reactions that do not require species transfer over large distances. Evidently, the main role here is played by reorientational motions, which 'interfere' with the chemical process at the stage of formation of the activated complex in hydrogen atom transfer reactions. Thus, in relaxationally hindered systems, which polymers are, the rate of species passage along the reaction coordinate is limited by the frequency of small-scale molecular motions required to rearrange the local surroundings. The activation energies and volumes are determined by the corresponding values $E$ and $V^*$ of segmental motion.

Earlier[26] the technique of uniform compression was used to clarify the mechanisms of $\alpha$- and $\beta$-processes in polymers. In particular it was shown that the $\beta$-process results from low-amplitude orientational movement of macromolecular segments involving from 2 to 10 monomeric units.

Note that the correlation between reaction rates and the average frequencies of $\beta$-processes is rather approximate and cannot be accurate in principle, since the motion frequencies of radical fragments that are chain defects may differ from the average values determined by relaxational techniques. The difference will depend on the specific structure of macroradicals. The reactivity, for instance, is known to decrease in the order peroxy, alkyl, allyl and polyenyl radicals. It is reasonable to place these radicals in the same sequence with respect to increasing internal rotation barriers. Radical reactions in polymeric crystals and low-molecular-weight organic compounds have common relationships and also depend on molecular mobility. The following features support this conclusion:

(1) positive activation volumes of bimolecular reaction; and

(2) similar values of activation parameters for reactions in crystals and rigid glasses in which the relationship between reaction rate and molecular dynamics has been established unambiguously.

The fluctuation volumes required for reactions and determining the scale of molecular motion in carboxylic acid crystals constitute $\sim 0.6$ of the molecular volume. With PE crystals the required fluctuations are provided by the movement of kinetic elements consisting of 1–2 units.

The experimental data obtained in this work and equations describing them point to a close relationship between chemical and physical kinetics and system macro-characteristics. The latter include thermal expansion and compressibility coefficients and the temperatures of relaxational and phase transitions.

Compressibility (bulk modulus) is one of the parameters determining the experimental value of the activation volume and, consequently, of the baric coefficient for reaction rate constants and molecular motion frequencies. The coefficient of thermal expansion affects the experimental value of the activation energy, i.e. the thermal coefficient of these processes. In their turn both parameters ($\alpha$ and $\beta$) depend on the physical state of a compound and temperatures of the corresponding physical transition (relaxational or phase). Jumps of compressibility and expansion coefficients at the transition points cause drastic variations in $E$ and $V^*$ values. The $\alpha/\beta$ ratio is known to be independent, in a first approximation, of pressure and temperature. On the basis of what has been said earlier one should expect the existence of a correlation between $E_p$ and $V^*$ (ref. 9).

From (5) it follows that $(E_p - E_V)/V^* = T\alpha K$. Since with polymers[13,22] $\alpha K = 1 \pm 0.2$ MPa K$^{-1}$, $(E_p - E_V)/V^* =$

0.3–0.4 kJ cm$^{-3}$. This expression satisfactorily describes the data on PMMA presented in *Table 3*.

A basic and clear understanding of the reason for the relationship of $E$ and $V^*$ with expansion and compressibility coefficients can be derived through analysing the state equation given in Frenkel[20]:

$$\frac{V_f}{V_0} = nV^* \exp\left(-\frac{E + pV^*}{RT}\right)$$

where $V_f = V - V_0$ is the free volume, and $n$ the number of molecules in unit volume. It follows from this equation that:

$$\alpha = \frac{V_f}{V_0}\frac{E}{RT^2} \quad \text{and} \quad \beta = \frac{V_f}{V_0}\frac{V^*}{RT}$$

It is seen that coefficients $\alpha$ and $\beta$ depend on the fluctuation hole activation parameters. The same parameters determine, in their turn, molecular motion frequencies and reaction rates.

The existence of the same mechanism governing reactivity and macro-characteristics of solids should be taken into account when developing techniques for predicting changes in physicochemical properties under the action of temperature and compressive loads.

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## REFERENCES

1   Emanuel, N. M. and Buchachenko, A. L. 'Chemical Physics of Degradation and Stabilization of Polymers', VNU, Amsterdam, 1988
2   Whalley, E. in 'Advances in Physical Organic Chemistry' (Ed. V. Gold), Academic Press, London, 1964, Vol. 2, p. 93
3   Kelm, H. (Ed.) 'High Pressure Chemistry', Reidel, Dordrecht, 1977
4   Asano, T. and Le Noble, W. *Chem. Rev.* 1978, **78**, 407
5   Isaaks, N. 'Liquid Phase High Pressure Chemistry', Wiley, Chichester, 1981
6   Zhulin, V. M. in 'Physical Chemistry, Modern Problems' (Ed. Y. M. Kolotyrkin), Khimiya, Moscow, 1984, p. 112
7   Szöcs, F. *High Temp.–High Pressures* 1977, **9**, 511
8   Kovarskii, A. L. and Aliev, I. I. *Chem. Phys. (USSR)* 1985, **4**, 966
9   Kovarskii, A. L. *Vysokomol. Soed. (A)* 1986, **28**, 1347
10  Ranby, B. and Rabek, J. F. 'ESR Spectroscopy in Polymer Research', Springer-Verlag, Berlin, 1977
11  Zubov, Yu. A., Selichova, V. I., Konstantinopolskaya, M. B. *et al. Vysokomol. Soed. (A)* 1972, **14**, 2090
12  Kovarskii, A. L., Mansimov, S. A. and Buchachenko, A. L. *Polymer* 1986, **27**, 1014
13  Ainbinder, S. B., Tyunina, E. L. and Tsirule, K. L. 'Properties of Polymers in Stressed States', Khimiya, Moscow, 1981
14  Vasserman, A. M. and Kovarskii, A. L. 'Spin Labels and Probes in Physical Chemistry of Polymers', Nauka, Moscow, 1986
15  Reitlinger, S. A. 'Permeability of Polymer Materials', Khimiya, Moscow, 1974
16  Saito, S., Sasabe, H., Nakajama, T. and Yada, K. *J. Polym. Sci. (A-2)* 1968, **6**, 1297
17  Sasabe, H. and Saito, S. *J. Polym. Sci. (A-2)* 1968, **6**, 1401
18  Kovarskii, A. L. and Aliev, I. I. *Vysokomol. Soed. (A)* 1983, **25**, 2293
19  Kovarskii, A. L. and Aliev, I. I. *Vysokomol. Soed.* 1985, **27**, 110
20  Frenkel, J. 'Kinetic Theory of Liquids', Dover, New York, 1955
21  Lebedev, Ya. S., Tzvetkov, Yu. D. and Voevodskii, V. V. *Kinet. Katal.* 1960, **1**, 496
22  Van Krevelen, D. W. 'Properties of Polymers. Correlations with Chemical Structures', Elsevier, Amsterdam, 1972
23  Shimada, S., Hory, Y. and Kashiwabara, H. *Polymer* 1978, **19**, 763
24  Geil, Ph. H. 'Polymer Single Crystals', Wiley, New York, 1963
25  Dadali, A. A., Vasserman, A. M., Buchachenko, A. L. and Irzhak, V. I. *Eur. Polym. J.* 1981, **17**, 525
26  Kovarskii, A. L., Mansimov, S. A. and Buchachenko, A. L. *Dokl. Akad. Nauk USSR* 1986, **291**, 1142