

## Volume Effects in the Decay of Free Radicals in Organic Crystals

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The decay kinetics of the free radicals produced by  $\gamma$ -irradiation of single crystals of organic dicarboxylic acids is studied at hydrostatic pressures up to 200 MPa. Correlation is established between the reaction's activation parameters ( $V^*$  and  $E^*$ ) and the crystals macrocharacteristics—the compressibility and thermal expansion coefficients. A common equation is proposed to describe the variation of the radical decay rate constant with temperature and pressure in malonic, succinic, adipic, glutaric, suberic, and sebacic acids. © 1991 Academic Press, Inc.

### Introduction

Studies of the kinetics of chemical reactions under conditions of uniform compression allow one to obtain a number of important additional parameters which specify the mechanism of the process (1-5). Among them is the activation volume  $V^* = -RT(\partial \ln k / \partial P)_T$ , i.e., the baric coefficient of the rate constant. This is one of the few parameters that permit the determination of the reaction regime and the role of the molecular dynamics of the species involved in the reaction. The physical meaning of the value and the sign of this parameter depend on the mechanism of the process. The molecular motion activation volume is always positive (the process is slowed down by pressure) and represents the smallest size of the free volume fluctuation required for the elementary act of motion (translation or reorientation). For a chemical reaction occurring in a purely kinetic regime  $V^*$  is determined by a change in the volume of molecules upon formation of the activation complex and can be both positive (dissocia-

tion) and negative (synthesis). Therefore on the basis of the magnitude and the sign of the volume effect one can form a judgment concerning the limiting stage of the reaction and its mechanism. This approach is especially valuable for the systems whose parameters, for the size of independent kinetic units and the type and the frequency of their motion, are difficult to establish. Thus, for example, the analysis of volume effects in polymer radical reactions has demonstrated that the latter are entirely controlled by small-scale  $\beta$ -relaxation processes (4, 5). The activation values also permit an assessment of the size of  $\beta$ -relaxors and the amplitude of their orientational motion (8, 9). Moreover, experiments under conditions of changing external factors enabled us to establish the relationship between the activation parameters of chemical reactions and state parameters and macrocharacteristics (the compressibility and thermal expansion coefficients) of polymers and organic glasses (4, 5). The present work presents an analysis of the volume effects in the radical reactions in crystals of dicarboxylic acids

TABLE I

THE DENSITY ( $\rho_0$ ), THE COMPRESSIBILITY PARAMETERS ( $K_{T_0}$ ,  $\mu$ ,  $\beta$ ) AND THE THERMAL EXPANSION CONSTANT ( $\alpha$ ) OF DICARBOXYLIC ACID CRYSTALS AT 297 K

Substance	$\rho_0$ (g/cm <sup>3</sup> )	$K_{T_0}$ (GPa)	$\mu$	$\beta \times 10^4$ (MPa <sup>-1</sup> )	$\alpha \times 10^4$ (K <sup>-1</sup> )
Malonic acid	1.90	7.9	9.2	1.27	2.55
Succinic acid	1.57	8.0	10.4	1.18	3.62
Glutaric acid	1.42	6.1	10.2	1.63	4.80
Adipic acid	1.36	6.6	8.4	1.47	3.16
Suberic acid	1.27	6.65	9.9	1.53	3.92
Sebacic acid	1.20	5.55	10.4	1.82	2.10
NaCl	2.164	2.33	6.3	—	—
Al	2.706	73.2	6.0	—	—

with the example of the free radical decay reaction. This type of reaction was chosen because it is widely observed in organic systems and because the kinetics and the mechanism of the radical reactions' individual stages are sufficiently well studied (10). They reveal that the free valency migration is the limiting factor in recombination. The most likely migration mechanism is the relay transfer of a hydrogen atom:  $P + PH \rightarrow PH + \dot{P}$ . This process does not require the species to travel over great distances and occurs in the kinetic regime. The main arguments in support of this migration mechanism are high rate constants which exceed the  $k$  values calculated on the basis of the diffusion coefficients (1-10), the isotope effect (11), and the fact that the recombination is speeded up by oxygen, hydrogen, and by photolysis. Another convincing piece of evidence is the fast exchange of places of the isotopes in selectively deuterated substances (12).

## Experimental

The study was conducted on the monocrystals of dicarboxylic acids whose characteristics are listed in Table I. The crystals were grown from solution by slowly evaporating the solvent (water and ethanol) at

room temperature. Free radicals were obtained by  $\gamma$ -irradiation of the substances under study in a Co<sup>60</sup> source at room temperature. The overall radiation dose was 5-10 Mrad. The concentration of paramagnetic species in the samples was  $10^{19}$ - $10^{20}$  spin/cm<sup>3</sup>. The samples were annealed in a hydrostatic pressure chamber. Transformer oil served as the pressure-transmitting liquid. The samples were removed from the chamber at different stages of annealing and the radical concentration was determined by the ESR method. The following procedure was used to minimize the losses of radicals upon heating and cooling the chamber. The samples were placed in the chamber and the pressure was raised up to the highest values (250 MPa). The temperature was then raised to a required level and the pressure was quickly reduced to a particular value. While taking samples the pressure was again sharply increased (the reaction was stopped), then the temperature lowered and the pressure reduced. In this manner the reaction was suddenly stopped at different stages. It should be noted that with crystals there was no need for isolating the samples, since in a separate experiment transformer oil was found not to affect the radical decay kinetics.

Thermal expansion coefficients were mainly measured by the method of hydrostatic weighing at different temperatures with the accuracy of two significant figures.

The coefficient of isothermic compressibility  $\beta = -(\partial V/\partial P)_T/V_0$  was determined by the "displacing piston" method (17). The powder of a substance under study was placed in a cylindrical chamber equipped with two pistons. An obvious shortcoming of this method is that an appreciable friction force arises between the sample and the high-pressure chamber's walls in the process of loading, and the loading conditions are not hydrostatic. Besides, there is an avoidable problem of the porosity of organic samples. To eliminate these faults the pow-

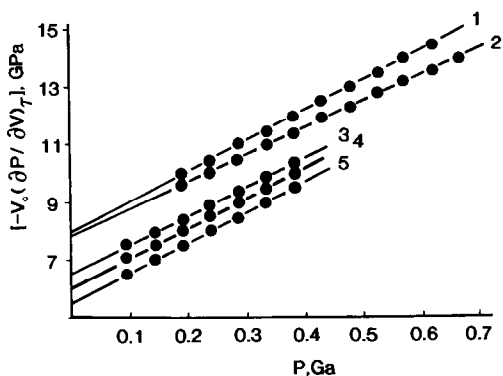


FIG. 1. The  $-V_0(\partial P/\partial V)_T$  dependence on  $P$  for some dicarboxylic acids: 1, succinic acid; 2, malonic acid; 3, suberic acid; 4, glutaric acid; 5, sebacic acid.

ders under study were immersed in paraffin. The latter was introduced into the original powder in benzene solution and the solvent subsequently evaporated. The paraffin content in the samples was 30% by volume. This enabled us to get rid of the porosity of the samples, to create hydrostatic loading conditions, and virtually eliminate friction on the high-pressure chamber's walls. The inner diameter of the chamber was 10 mm and the load was developed up to 0.5 GPa by means of a hydraulic press. The sample volume was  $\sim 0.8 \text{ cm}^3$ . The samples were kept under the pressure to obtain the highest density. The pressure was increased stepwise with increments of 0.05 GPa. The pressure was recorded after each step by means of an outside pressure gauge and the piston displacement indicator. Deformation was determined on the basis of five experiments with the results being averaged. The piston displacement in this method is determined by the deformation of all the compounds of the loading system: the substance under study, paraffin, punches, the high-pressure chamber, and the press parts. To determine the deformation of the elements of the apparatus, substances with well known compressibility (Al, NaCl) were used.

Figure 1 shows the experimental depen-

dences obtained by differentiation of compressibility curves. These dependences are described by a linear relationship of the type

$$-V_0(\partial P/\partial V)_T = K_{T_0} + \mu P, \quad (1)$$

which enables one to determine two compressibility parameters:  $K_{T_0}$ , the isothermal compressibility modulus at normal pressure and  $\mu$ , the slope of the first derivative dependence on pressure. Table I lists the values for all the studied compounds, calculated using the least squares method. By integrating Eq. (1) we obtain the compressibility isotherm equation:

$$P(V, T_0) = K_{T_0}/\mu[\exp \mu(1 - V/V_0) - 1]. \quad (2)$$

This equation was used to estimate the deformation of the reference substances with parameters  $K_{T_0}$  and  $\mu$  from Table I obtained on the basis of experimental data available in the literature.

### The ESR Spectra and the Radical Decay Kinetics

The structures of the free radicals formed upon radiolysis of dicarboxylic acid single crystals have been sufficiently reliably identified with the help of ESR spectra (18–21) and are given in Table II. An interesting feature of the ESR spectra is a sharp dependence of their form on the position of monocrystals in the magnetic field. This indicates that radicals are located in the crystalline lattice, rather than defects. A notable decrease in the intensity of the ESR spectrum is observed when samples are heated to temperatures 60–80°C lower than  $T_m$ . Figures 2, 3, and 4 show the temperature dependences of the intensity of ESR spectra obtained after 10 min exposure at each temperature. The annealing curves for all systems have the same form. The difference lies only in the correspondence of temperatures of

TABLE II  
 PARAMETERS OF THE ACIDS UNDER INVESTIGATION

Substance	Radical	$T_m$ (K)	$T_{tr}$ (K)	Temperature range of radical decay (K)	Type of lattice
Malonic acid	$\text{COOH}-\dot{\text{C}}\text{H}-\text{COOH}$	409	358 <sup>a</sup>	313–343	Triclinic
Succinic acid	$\text{COOH}-\dot{\text{C}}\text{H}-\text{CH}_2-\text{COOH}$	460	410 <sup>b</sup>	363–405	Monoclinic
Glutaric acid	$\text{COOH}-\dot{\text{C}}\text{H}-(\text{CH}_2)_2-\text{COOH}$	371	347 <sup>b</sup>	323–339	Monoclinic
Adipic acid	$\text{COOH}-\dot{\text{C}}\text{H}-(\text{CH}_2)_3-\text{COOH}$	426	—	333–363	Monoclinic
Suberic acid	$\text{COOH}-\dot{\text{C}}\text{H}-(\text{CH}_2)_5-\text{COOH}$	417	363 <sup>c</sup>	373–395	Monoclinic
Sebacic acid	$\text{COOH}-\dot{\text{C}}\text{H}-(\text{CH}_2)_7-\text{COOH}$	407	—	333–368	Monoclinic

<sup>a</sup> Triclinic—rhombohedral transition (13).

<sup>b</sup> Monoclinic—triclinic transition (14, 15).

<sup>c</sup> Transition with no change in the crystalline lattice (16).

the start of intensive radical decay to the phase transition temperatures. On this basis the dicarboxylic acids can be divided into three groups:

1. The total radical decay occurs near the melting point (suberic acid, Fig. 2).

2. The total radical decay occurs near the point of polymorphous transition (malonic, succinic, and glutaric acids, Fig. 3).

3. The total radical decay occurs far from the melting point at temperatures  $T/T_m = 0.8$  (adipic and sebacic acids, Fig. 4).

The differences in the temperature ranges

of radical decay in organic crystals was first discovered in (22). The polymorphous transitions in the second group of crystals are accompanied by a jump in enthalpy and heat capacity which is typical for the first-order phase transitions. Since melting is also a first-order phase transition, the two first groups can be united into one where the phase transition leads to total radical decay regardless of whether the process is accompanied by amorphization (melting) or by restructuring of the crystalline lattice (polymorphous transitions). Radicals in the

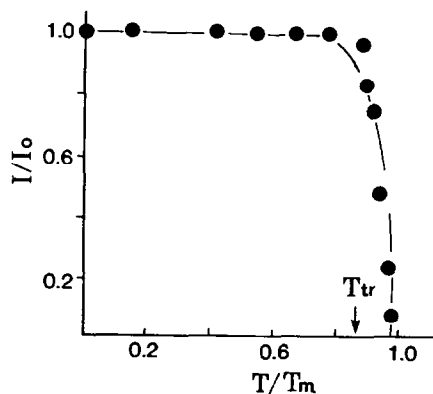


FIG. 2. The annealing curve of radical decay in monocystals of suberic acid.

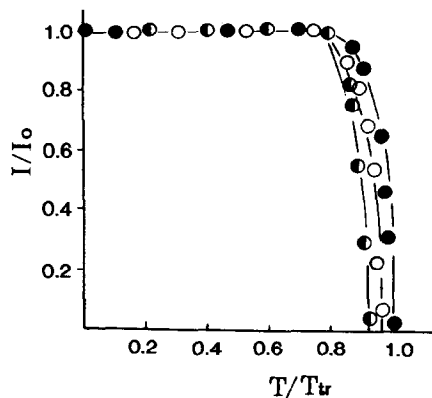


FIG. 3. Annealing curves of radical decay in monocystals of malonic (○), succinic (●), and glutaric (●) acids.

crystals of adipic or sebacic acid decay at temperatures below the melting point. Polymorphous transitions in these systems have not been observed. The reason for the observed phenomena lies, in our view, in the following. The kinetics of radical decay in solids is connected with molecular mobility. This has been repeatedly supported by experimental data. Thus the macroradical recombination rates in polymeric glasses were found to be determined by the intensity of small-scale  $\beta$ -relaxational processes (5). It was also shown (22) that a drop in the radical decay annealing curve in hexamethylbenzene, observed in the 150- to 220-K range, coincides with the temperatures of the NMR line narrowing. The frequencies of the molecular motions, required to ensure high recombination rates, can be realized in various temperature ranges depending on the structure and the nature of interactions in crystals. The scales of molecular motions (amplitudes and sizes of kinetic elements) which lead to radical decay and which are involved in the crystalline lattice rearrangement can coincide or differ. Apparently, in the first two groups of crystals they do coincide, while in the restructuring process of the third group larger scale motions are likely to be involved, the reactions occurring at lower temperatures and with small-

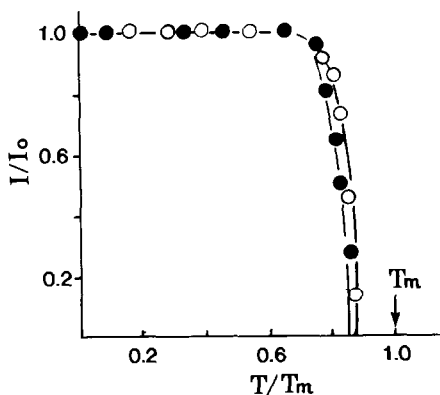


FIG. 4. Annealing curves of radical decay in monocrystals of adipic (○) and sebacic (●) acids.

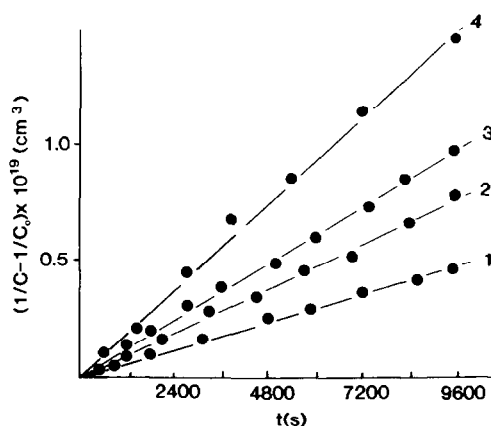


FIG. 5. Radical decay kinetics in  $\gamma$ -irradiated monocrystals of dicarboxylic acids: 1, glutaric acid, 328 K; 2, adipic acid, 347 K; 3, sebacic acid, 360 K; 4, suberic acid, 385 K.

scale dynamics. The transition in suberic acid, observed at 363 K (16), does not lead to radical decay, but the range of a drastic decrease in their concentration starts right after this point. The nature of this transition is not entirely clear, but the authors point out that the transition is accompanied by an increase in the amplitude of the rotational molecular motion, which is manifested in the kinetics of radical decay.

No change in the ESR spectra pattern was observed when annealing the crystals. The kinetic curves of radical decay, shown in Fig. (5), demonstrate that up to 80–90% conversion they can be satisfactorily described by the second-order rate equation  $1/C - 1/C_0 = kt$ . This is what makes crystals differ from organic glasses whose radical decay kinetics are often polychronous and do not obey the second-order rate equation.

#### Baric Dependences and Activation Volumes

The baric dependences of the logarithm of the radical decay rate constant are linear in all systems (Fig. 6). The activation volumes calculated from the slope angle of

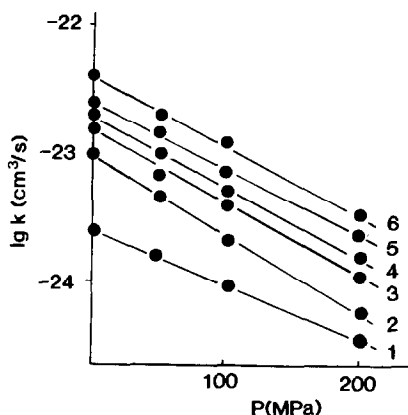


FIG. 6. Baric dependences of radical decay rate constants in monocystals of dicarboxylic acids: 1, succinic acid, 378 K; 2, sebacic acid, 360 K; 3, suberic acid, 385 K; 4, glutaric acid, 339 K; 5, malonic acid, 343 K; 6, adipic acid, 373 K.

these dependences are positive (the reaction is slowed down by pressure) and range from 30 to 50 cm<sup>3</sup>/mole (Table III). These data are in contradiction with the results obtained for radical reactions in liquids. As it was pointed out in the Introduction the limiting stage in radical recombination is the hydrogen atom relay transfer. Hydrogen atom abstraction by free radicals in the liquid phase is characterized by negative activation volumes (the reaction is accelerated by pressure) ranging from  $-8$  to  $-15$  cm<sup>3</sup>/mole (1). The process of radical recombination

in organic liquids, not being controlled by diffusion, is characterized also by negative  $V^*$  ( $-15$  to  $-20$  cm<sup>3</sup>/mole). The results of the reaction studies in liquids are in good agreement with the prediction of the activated complex theory according to which bimolecular reactions are accelerated by pressure (23). With solid state reactions this condition is not fulfilled. The data obtained for many polymeric glasses indicate that radical reactions are slowed down by pressure (2, 4, 5). The activation volumes for macroradical decay (20–70 cm<sup>3</sup>/mol) coincide with the  $V^*$  for small-scale orientational dynamics of the kinetic elements ( $\beta$ -process). Table III shows that the radical decay in dicarboxylic acid crystals is characterized by the  $V^*$  values of the same order as in organic glasses. Thus, the activation volumes of radical reactions in crystals, as in glasses, reflect the scales of molecular motions which govern the rate of reactions. According to the Frenkel theory (6) and the free volume model (7)  $V^*$  is determined by the size of a fluctuation "hole." This is valid in both liquids and crystals.

The next important parameter which ought to be considered is the ratio of the activation volume to the proper volume of the molecules. This parameter enables us to estimate the excess free volume that is required to realize the molecular motions of a certain type. Studies of the rota-

TABLE III  
ACTIVATION PARAMETERS OF FREE RADICAL DECAY ( $E^*$  AND  $V^*$ ), PREEXPONENTIAL FACTORS ( $k_0$ ), AND THERMAL PRESSURE ( $P_T$ ).

Substance	$V_w^a$ (cm <sup>3</sup> /mole)	$V^* + 3$ (cm <sup>3</sup> /mole)	$V^*/V_w$	$E_p^* \pm 4$ (kJ/mole)	$\log k_p^0$ (cm <sup>3</sup> /sec)	$E^* \pm 4$ (kJ/mole)	$\log k_p^0$ (cm <sup>3</sup> /sec)	$P_T$ (MPa)	$P_T V^*$ (kJ/mole)
Malonic acid	50.7	35	0.69	74	-11.2	61.3	-13.6	646	22.6
Succinic acid	60.4	32	0.53	122	-6.4	90.0	-10.8	1000	32.0
Glutaric acid	71.4	45	0.63	168	0.8	125.9	-3.6	949	42.7
Adipic acid	81.2	39	0.48	100	-8.1	72.9	-12.2	704	27.5
Suberic acid	102.3	43	0.42	130	-4.5	93.0	-10.3	955	41.1
Sebacic acid	121.9	50	0.41	60	-14.2	42.3	-16.9	442	22.1
Plexiglas	56.1	45	0.8	78	-9.7	50.0	-13.6	622	28.0

<sup>a</sup> The volumes of molecules are calculated by the method of group contributions (24).

tional–translational dynamics of low-molecular-weight species (spin probes) have demonstrated that  $V^*/V$  is determined by the type of molecular motions, the nature of intermolecular interactions, and the compressibility of the matrix. For rotation in glasses the typical values  $V^*/V_w$  ( $V_w$  Van der Waals volume of a molecule) is 0.1–0.3 (8). In the crystals studied this value is higher. The volume effects of radical reactions in crystals are also characterized by the absence of a relationship between the molecular size and the activation volumes, which is typical of the molecular mobility of the species (8). Both specificities are apparently caused by the nature of intermolecular interactions in the dicarboxylic acids, which differ in density and length of hydrogen bonds. Thus in succinic acid the number of intermolecular hydrogen bonds is 12 while the shortest length of a transversal hydrogen bond is 3.1 Å. For glutaric acid these parameters are 6 and 3.0 Å, respectively. The same reason accounts for the absence of a simple relationship between the size of the molecules and the coefficients of compressibility and expansion. These dependences will be analyzed by us elsewhere.

One steadily reproducible result, both for molecular dynamics and for radical decay in glasses and crystals, is a clear relationship between the activation volumes and the matrix compressibility (Fig. 7). The dependence is likely to be caused by the relation between both parameters  $V^*$  and  $\beta$  and the amplitude of a molecular motion, the free volume, and their baric dependences. The state equation derived by Frenkel provides the physical meaning of this dependence. It has the form

$$V = V_0[1 + nV^* \exp(-U/RT)], \quad (4)$$

where

$$U = U_0 + PV^*$$

$n$ , number of molecules per a volume unit;

$V_0$ , specific volume at 0 K;

$U$ , energy for “hole” formation.

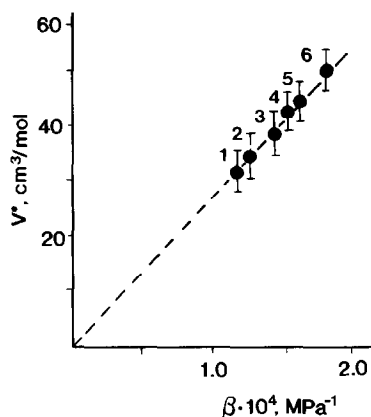


FIG. 7. The radical decay activation volume in crystals of dicarboxylic acids versus volumetric expansion coefficient: 1, succinic acid; 2, malonic acid; 3, adipic acid; 4, suberic acid; 5, glutaric acid; 6, sebacic acid.

From Eq. (4) it is easy to get

$$\beta = V_f/V_0V^*/RT, \quad (5)$$

where

$V_f$ , specific free volume of the sample.

Typically at  $\beta \Rightarrow 0$ ,  $V^*$  also tends to 0, i.e., in an incompressible system the baric dependence of the rate constant is absent. The dependence shown in Fig. (7) is described by  $V^* = A\beta$  with  $A = 2.7 \cdot 10^5$  cm $^3$  MPa/mole. Note that for radical decay in nonpolar organic glasses the  $A$  value is nearly twice as low ( $1.5 \cdot 10^5$  cm $^3$  MPa/mole) (8).

### The Energetics of Reactions

The hydrostatic pressure technique makes it possible to determine two values for the reaction activation energy—at constant pressure and constant volume ( $E_p^*$  and  $E_v^*$ ). Both quantities are related through a thermodynamic equation:

$$E_p^* - E_v^* = P_T V^*, \quad (6)$$

where  $P_T = T\alpha/\beta$  — thermal pressure.

The member on the right side of Eq. (6)

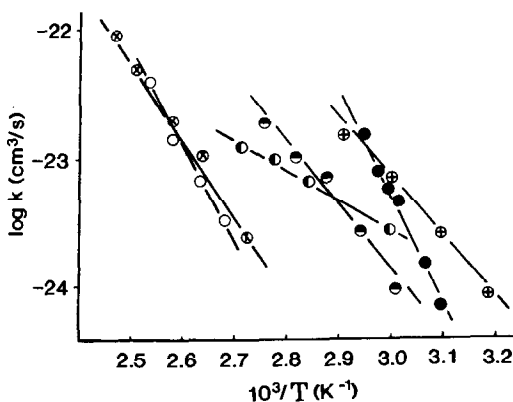


FIG. 8. Log  $k$  versus  $1/T$  for radical decay in monocrytals of dicarboxylic acids: (●) glutaric acid; (⊕) malonic acid; (⊙) adipic acid; (⊛) sebacic acid; (⊗) succinic acid; (○) suberic acid.

determines the work of internal (thermal) pressure which arises upon heating an isochoric system. The activation energy at constant volume can be higher or lower than  $E_p^*$ , depending on the sign of  $V^*$ . The log  $k$  temperature dependences in the temperature range studied are linear (Fig. 8), i.e., they obey the Arrhenius equation

$$\log k = \log k_0 - E^*/2.3RT. \quad (7)$$

The equation parameters (Eqs. (6) and (7)) for radical decay in our crystals are given in Table III. For suberic acid  $E_v^*$  was obtained experimentally while for other acids it was calculated via Eq. (6) using experimentally measured values. Data on suberic acid show that the experimental  $E_v^*$  values are in agreement with the theoretical. Thus  $E_v^*$  was found to be 93 kJ/mole while the theoretical  $E_v^*$  value (based on Eq. (6)) is 89 kJ/mole. Data in Table III show that in all cases the internal pressure work  $P_T V^*$  constitutes a smaller part ( $\sim 25\%$ ) of the activation enthalpy at constant pressure. The  $E_v^*/E_p^*$  ratio is equal to  $\sim 0.75$ . The data on macroradical decay in organic glass (Table III) indicate that there is no substantial difference in the reaction parameters for the two states of the

substance. In turn, as is shown in (4) the values of the activation parameters of radical reactions in glasses are determined by the energetics of the small-scale rotational dynamics ( $\beta$ -process).

An important part of the kinetic analysis is the definition of the physical meaning of the experimental value of the activation energy and its correspondence to the model concepts about the barrier of the process. It is known that the activation energies of the chemical reactions and molecular motions in the condensed phase, calculated using the Arrhenius equation (in our case  $-E_p^*$ ), are effective. The analysis of data, obtained in this paper, support this conclusion. The pre-exponential factors of the Arrhenius equation, measured at constant pressure ( $p = 0.1$  MPa), exceed in most cases the normal  $k_0$  values ( $10^{-10}$  cm<sup>3</sup>/sec).

Conducting the experiment under isochoric conditions enables one to avoid additional contributions to  $E^*$ . The experimental  $E_v^*$  and  $k_v^0$  are lower than  $E_p^*$  and  $k_p^0$  and are likely to be closer to real values. Figure 9 shows the dependence of  $E_p^*$  on the coefficient of thermal expansion for crys-

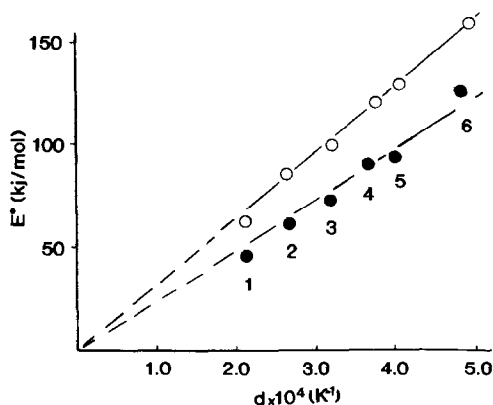


FIG. 9. Dependence of  $E_p^*$  (open circles) and  $E_v^*$  (solid circles) of radical decay in monocrytals of dicarboxylic acids on the thermal expansion coefficient ( $\alpha$ ): 1, sebacic acid; 2, malonic acid; 3, adipic acid; 4, succinic acid; 5, suberic acid; 6, glutaric acid.



tals. It is seen that for all dicarboxylic acids there is a common dependence which tends to zero and has the slope angle of  $3.2 \cdot 10^5$  kJ K/mole. The existence of this relationship is very important, since it makes it possible to replace a complex parameter devoid of a clear physical sense,  $E_p^*$ , by an objective characteristic of the substance. According to Eq. (6) the  $E^*(\alpha)$  dependence should cut off the coordinate axis  $\alpha$  section equal to  $E_v^*$ . However, it follows from Fig. 9 that  $E_v^*$  also depends on  $\alpha$ . The relation between activation energy and  $\alpha$  is predicted by the Frenkel theory. From Eq. (4) we have

$$\alpha = V_f/V_0 U/RT^2. \quad (8)$$

This equation shows that the thermal expansion coefficient is determined by the activation energy  $U$  which presents according to the Frenkel theory the energy of "hole" formation. That is why it is natural that  $\alpha \Rightarrow 0$  at  $E^* = 0$ . Calculations of  $V_f/V_0$  on the basis of this equation permit defining more exactly the meaning of  $E^*$  and relating it to the parameters of Eq. (6). It turns out that the substitution into (8) of both  $E_p^*$  and  $E_v^*$  results in fairly understated, as compared to the theoretical values,  $V_f/V_0$  values. By combining Eqs. (8) and (5) one can obtain  $U = TV^*\alpha/\beta$ . Comparing this relationship with Eq. (6) allows one to realize very clearly that the activation energy in the Frenkel equation  $U$  is  $E_p^* - E_v^*$ . One more feature of the solid phase radical reactions is the relationship between the values of the activation energy  $E_p^*$  and the preexponential factor, i.e., the "compensation effect" (Table III). The most valid reason accounting for this effect seems to be the change of the reaction barrier upon raising the temperature, caused by variation of intermolecular distances. This issue is dealt with in detail in (4) on the example of the radical reactions in organic glasses. The main parameter which determines the effective values  $E^*$  and  $k_0$  is shown to be the thermal expansion coefficient  $\alpha$ . The relation between  $E^*$  and

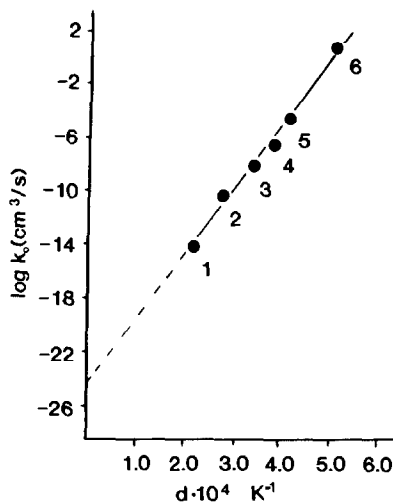


FIG. 10.  $\log k_0$  of radical decay in monocrystals of dicarboxylic acids versus the thermal expansion coefficient ( $\alpha$ ): 1, sebacic acid; 2, malonic acid; 3, adipic acid; 4, succinic acid; 5, suberic acid; 6, glutaric acid.

$\alpha$  for radical decay, as was shown above, is observed for radical reactions in molecular crystals. The existence of a linear relationship between  $\log k_0$  and  $\alpha$  follows from Fig. 10. It is described by

$$\log k_0 = C + D\alpha, \quad (9)$$

where  $C$  and  $D$  are constants. Despite the fact that this relationship is predicted in (4, 6) the physical meaning of  $\log k_0$  at  $\alpha \Rightarrow 0$  so far remains obscure.

## Conclusion

The results of the present work allow one to establish the following features of the radical decay reactions in organic crystals. The reactivity of crystals is controlled by the molecular mobility. The main characteristics of the volume effects of molecular dynamic processes in condensed media are reproduced in the process of studying the reactions. Among them are: the positive  $V^*$  values of radical recombination, which coincide in magnitude with the activation vol-

umes of small-scale rotational mobility of molecules in glasses: the same value of the  $E_v^*/E_p^*$  ratio for reactions and molecular mobility, and the link between the activation parameters of reactions with the physical properties of a solid. It is evident that the fast decay of radicals near phase transitions is caused by jumplike movements of molecules, which ensure the structural rearrangement in the solid. In terms of chemical reactions the phase transition of the first order produces the effect of a "microagitator" which instantly changes the position of the weight center and the orientation of the molecules. Below the phase transition point the decay of radicals is slowed down exponentially as the temperature is decreased, i.e., it formally obeys the Arrhenius equation. One has all the reasons to believe that the rate of the hydrogen atom transfer reaction which leads to recombination is controlled in crystals as in glasses by the rotational dynamics of molecules.

The question of what the frequencies of molecular motion should be to obtain the observed values for the radical decay rate constants arises. When migration of radicals, which controls their recombination, occurs via the mechanism of chemical relay transfer, the rate constant is described by the equation (10)

$$k = \frac{4}{3}\pi r_0 \lambda^2 \gamma = v_c \nu, \quad (3)$$

where

- $r_0$ , radius of the reaction cell ( $\sim 5$  Å);
- $\nu$ , frequency of the relay transfer steps;
- $\lambda$ , average distance by which a free valency moves at one relay transfer "step" (3–5 Å);
- $v_c$ , volume of the cell.

Using the experimental values for the rate constants  $10^{-23}$ – $10^{-24}$  cm<sup>3</sup>/sec and Eq. (3) we obtain  $\nu = 10^{-1}$ – $10^{-2}$  Hz. The quantity  $\nu$  characterizes the bottom values for the molecular rotational motion frequencies, which govern the recombination rates, i.e.,

provided that each reorientation act of a reaction species results in a hydrogen atom transfer.

An important consideration for describing the kinetics of solid phase reactions follows from the relationships obtained in this paper between the reaction activation parameters and the solid's macrocharacteristics—the compressibility and thermal expansion coefficients. The data make us believe that in the activation theory equations the model parameters  $E^*$  and  $V^*$  which are analyzed with difficulty, can be substituted by the objective, well-known, and tabulated parameters. Thus by substituting the relationships  $E^* = B\alpha$ ,  $V^* = A\beta$ ,  $\log k_0 = C + D\alpha$  into the known equation

$$k = k_0 \exp[-(E^* + PV^*)/RT] \quad (11)$$

we obtain

$$\log k = C + D\alpha - (B\alpha + A\beta P)/RT \quad (12)$$

At  $P = 0$  Eq. (12) simplifies to

$$\log k = C + \alpha(D - B/2.3RT). \quad (13)$$

The radical decay in the crystals of dicarboxylic acids is rigorously described by Eq. (12) with the parameters

$$\begin{aligned} A &= 2.7 \cdot 10^5 \text{ cm}^3 \text{ MPa/mole} \\ B &= 3.2 \cdot 10^5 \text{ kJ K/mole} \\ C &= -25 \text{ cm}^3/\text{sec} \\ D &= 5.5 \cdot 10^4 \text{ cm}^3 \text{ K/sec.} \end{aligned}$$

The aim of further studies into this area is to establish the dependence of the coefficients of Eq. (12) on the chemical properties and the structure of solids.

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