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Radical Degradation and Stabilisation Reactions of Solid Polymers

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The thermal and oxidative thermal degradation of the majority of polymers occurs by radical mechanisms. Therefore the stabilisation of such polymers consists in the inhibition of the radical degradation processes. The aim of this review is to consider and analyse the kinetics and mechanisms of elementary radical degradation and stabilisation reactions in the solid phase, i.e. to examine the set of reactions which constitute the basis of the degradation and stabilisation processes.
Before analysing and interpreting the experimental data, it is necessary, firstly, to note the characteristic features of solid-phase radical reactions which distinguish them from reactions in gases and liquids and, secondly, to consider the general theoretical postulates concerning the kinetics of solid-phase reactions.
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I. KINETIC CHARACTERISTICS OF SOLID-PHASE RADICAL REACTIONS

The specific physical features of the solid state give rise to the definite kinetic characteristics of solid-phase reactions. The principal features of this type are as follows.

1. For reactions to occur, the reacting species must approach one another; however, in contrast to gas-phase reactions, the duration of contact, i.e. the lifetime of the pair of reacting species, is long, so that a static equilibrium involving all the degrees of freedom is established in the pair. This implies that such pairs must be regarded as kinetically independent species, which has a significant effect on the kinetics and frequently modifies the kinetic equations.

2. Since the pairs are comparatively long-lived, it is also necessary to consider the physical elementary steps involved in the motion of the reacting species (rotation, translation, orientation, etc.). It is then found that the kinetics of chemical reactions are related to the kinetics of molecular motion, i.e. the physical properties and the structure of the polymer.

3. The same chemical elementary steps in the solid phase can occur with a higher activation energy than in the gaseous or liquid phases. Indeed, in a gas or liquid the intrinsic chemical step (for example, the transfer of a hydrogen atom from the molecule to a radical) and steps involving a change in the structure of the reactants (for example, those occurring when the bond hybridisation is altered) take place simultaneously. In the solid phase these steps frequently occur at different times, since the rearrangement of the structure of the reactants after the reaction occurs much more slowly than the chemical reaction itself (during a period of the order of magnitude of the structural relaxation time). This applies to reactants in both the initial and the final states. In practice it implies that the potential surfaces of the elementary reactions in the solid phase may lie higher than for gas-phase or liquid-phase reactions.

The general theory of the kinetics of solid-phase reactions must reflect these features. In the most general case of a reaction between two reaction centres A and B, three kinetic stages may be distinguished: (a) the macrodiffusion stage when the reacting species A (or B) fill the specimen non-uniformly and diffuse as a result of an average concentration gradient; (b) the microdiffusion stage when there is no concentration gradient and the rate of reaction is determined by the frequency with which the species A and B, which are uniformly distributed throughout the specimen, approach one another (the mechanism involved in their mutual approach is unimportant at this stage); this stage results in the formation of the pair (A + B); (c) the intrinsic kinetic stage when the rate of the process is determined by the rate of the chemical interaction in the pair (A + B).

Here A and B may be understood as reaction centres in a group of macromolecules and macroradicals, molecules of reacting gases, low-molecular substances, inhibitors, etc.

We shall consider initially the case where there are only two stages—the microdiffusion and kinetic stages—i.e. where the reaction centres are uniformly distributed in the specimen. For this case, Lebedev proposed a simple cell reaction model and derived formal kinetic rate equations [1]. It is suggested that the chemical interactions of A and B begins only when A and B form a pair, i.e. enter a single "cage" with a volume v^* (of the order of $\frac{4}{3}\pi\lambda^3$, where λ is the effective length of the "monomer" unit). As a result of thermal or any other type of activation from outside, A and B can migrate in the specimen with a migration rate constant k_t and in the vapour phase they can also react with a rate constant k_p. In the steady-state case (with the rates of formation and destruction of the pairs are equal), it is easy to obtain a kinetic rate equation:

$$-\frac{d(A)}{dt} = -\frac{d(B)}{dt} = k_{eff}(A)(B), \quad (1)$$

where

$$k_{eff} = \frac{k_t k_p}{k_t + k_p} v^*; \quad (k_t = k_t^A + k_t^B) \quad (2)$$

Thus the law of the additivity of the kinetic resistance in each component stage holds for the effective rate constant for the overall process:

$$1/k_{eff} = 1/k_t v^* + 1/k_p v^* \quad (3)$$

When $k_t \gg k_p$, the kinetic stage is rate-limiting and $k_{eff} = k_p v^*$; when $k_t \ll k_p$, the rate is limited by the microdiffusion stage and $k_{eff} = k_t v^*$.

In the above equations k_t is the rate constant for physical or chemical diffusion of the species and k_p is the unimolecular rate constant for the destruction of the pair, which may be determined either by the frequency of rotation and steric factors for the species in the vapour phase or by the rate of the intrinsic chemical interaction. Since a wide variety of species may be involved in the reactions, the physical significance of k_t and k_p may be various; they can assume any relative values and therefore either of two types of kinetic regimes may be realised.

The cell model for bimolecular solid-phase reactions is confirmed also by non-steady-state kinetics, i.e. kinetics under conditions such that the steady-state concentration of the pairs has not yet been attained (an example is provided by the kinetics of the recombination of the radicals corresponding to the initial sections of the curves relating the rate of degradation of the radicals to time, which were analysed by Lebedev [1]).

The rates of bimolecular reactions in the solid phase were calculated by Waite [2] even earlier and more rigorously using the macroscopic diffusion equation (for the microdiffusion stage); the results of this calculation are virtually identical with those obtained on the basis of the cell model, but the latter has the advantage of simplicity of the interpretation of the experimental data and clear physical significance of the kinetic constants.

II. KINETICS OF RADICAL DEGRADATION AND STABILISATION REACTIONS OF POLYMERS

We shall now consider the experimental data on the mechanism and kinetics of radical degradation and stabilisation reactions of polymers taking into account the general kinetic considerations described in the preceding section. It will be more convenient to examine the individual reactions of macroradicals and low-molecular-weight radicals, which will henceforth be conventionally referred to as microradicals.

1. Oxidation of Macroradicals

The addition of oxygen to macroradicals is one of the fundamental kinetic chain propagation reactions in the oxidation of polymers. All the experimental data on the kinetics of this reaction were obtained in studies of the conversion of alkyl allyl macroradicals $\dot{R}$ in irradiated polymers into peroxy-macroradicals $R\dot{O}_2$. Such conversion takes place under the action of gaseous oxygen and therefore its rate may be determined by any of the three stages—macrodiffusion, microdiffusion, and kinetic.

The "recognition" of the rate-determining step in a complex multistage process of this kind is difficult. The system of kinetic equations for this case is of the form

$$-\frac{\partial n}{\partial t} = k_{\text{eff}} nc, \tag{4}$$

$$\frac{\partial c}{\partial t} = -k_{\text{eff}} nc + D\nabla^2 c, \tag{5}$$

where n is the concentration of radicals in the polymer (it is postulated that these are stationary) and c the concentration of oxygen. At zero time ($t = 0$) we have $n = n_0$ and $c = 0$ in the bulk phase and $c = c_0 = K_S p$ on the surface of the polymer [K_S is the solubility (Henry's law) constant and p the pressure of oxygen]. The first of these equations corresponds in form to Eqn. (1); the constant k_{eff} is defined by Eqn. (2). Eqn. (5) describes the kinetics of the reaction and of the macrodiffusion of the gas into the polymer.

A rigorous analytical solution of Eqns. (4) and (5) is impossible. A solution was obtained numerically by Lebedev [3] using a computer and the results of the rigorous calculation were compared with approximate analytical solutions. Approximate solutions were obtained for limiting cases in which it was possible to neglect certain kinetic stages and to simplify Eqns. (4) and (5). In both cases (exact and approximate) the effective reaction time t_Σ, i.e. the time during which the initial concentration of the radicals $\dot{R}$ diminishes by the factor e, was calculated. Here t_Σ is used instead of $k_\Sigma = 1/t_\Sigma$, where k_Σ is the effective rate constant for the overall diffusion-kinetic reaction $\dot{R} \rightarrow R\dot{O}_2$, which is described, as before, by the bimolecular equation $dn/dt = k_\Sigma nc$.

Comparison of the results of the exact and approximate calculations showed that it is possible to formulate several limiting regimes which are realised under various experimental conditions. The principal data are presented in Table 1. The fact that they were obtained for the case where the specimen is in an infinitely long cylinder of radius l does not diminish the generality of the results; for specimens of other shapes (spherical grains, films, etc.), the kinetic expressions remain unchanged except for constant coefficients [only the form of the diffusion term $D\nabla^2 c$ in Eqn. (5) depends on the shape of the specimen].

We shall now consider briefly each regime—the conditions under which it occurs and the kinetic parameters. The quasi-steady-state regime is observed when the rate of reaction is high and the solubility of oxygen is low. Table 1 shows that the law of the additivity of the kinetic

Table 1. Kinetic regimes in the diffusion-kinetic process $\dot{R} + O_2 \rightarrow R\dot{O}_2$.

Regime	Experimental conditions	Criteria	Effective duration of reactions t_Σ	Characteristic kinetic features of the regime
Steady-state	high radical concns., low oxygen pressures	$\frac{n_0}{K_p p} > 10$	$\frac{1}{k_{s\phi} K_p p} + \frac{0.63 l^2 n_0}{aDK_p p}$	t_Σ decreases in proportion to p and depends on the dimensions of the specimen and the initial radical concn. n_0
Membrane	large specimen, n_0 large, p small	$\frac{k_{s\phi} n_0 l^2}{D} > 100$ $n_0/K_p p > 10$	$\frac{0{,}63 l^2 n_0}{aDK_p p}$	t_Σ decreases in proportion to p and increases in proportion to n_0 and l^2
Kinetic	small size (l small), n_0 and p small	$\frac{k_{s\phi} K_p p l^2}{D} < 0{,}1$ $k_{s\phi} n_0 l^2/D < 1$	$\frac{1}{k_{s\phi} K_p p}$	t_Σ independent of the dimensions of the specimen and the initial radical concentration n_0
Quasi-diffusional	l large, p large, n_0 small	$\frac{k_{s\phi} K_p p l^2}{D} > 10$ $n_0/K_p p < 0{,}1$	$l\sqrt{\frac{4}{aDK_p p k_{s\phi}}}$ $a \simeq 8$	t_Σ independent of n_0, decreases in proportion to p and increases with l

resistances of all three stages holds for k_Σ; the effect of the diffusion constant is then given not by the term aD/l^2 (obtained from the usual Smoluchowski equation $l^2 = aDt$) but by the term $(aD/l^2)(c_0/n_0)$ (as already mentioned, $c_0 = K_S p$).

If the rate of reaction is very high compared with the rate of macrodiffusion, the conditions may be referred to as a membrane regime, since the rate of the process is limited by the rate of leakage of gas through the layer of the specimen (membrane) in which the reaction has already occurred. When the diffusion is rapid, a purely kinetic regime may be realised.

In an experimental study of the variation of t_Σ with oxygen pressure, the concentration of radicals, and the dimensions of the specimen, it is possible, using Table 1, to identify the regime and the rate-determining step of the reaction; by varying the experimental conditions, it is possible to pass from one regime to another.

In the limiting cases it is possible to calculate the following combinations of constants and their temperature variation:

$$\text{kinetic regime} - k_{\text{eff}}K_s = k^0_{\text{eff}}K^0_s \exp\left(-\frac{\epsilon_{\text{eff}} - \Delta H_s}{RT}\right)$$

$$\text{membrane regime} - DK_s = D^0K^0_s \exp\left(-\frac{\epsilon_D - \Delta H_s}{RT}\right)$$

$$\text{quasi-diffusion regime} - k_{\text{eff}}DK_s = k^0_{\text{eff}}D^0K^0_s \exp\left(-\frac{\epsilon_{\text{eff}} + \epsilon_D - \Delta H_s}{RT}\right),$$

and then it is easy to determine the complete set of kinetic constants, the activation energies, and the heats of solution.

On the other hand, if all the constants are already known, it is possible to calculate the rate of the diffusion-kinetic process and to predict the rate-limiting stage. An example of the use of the above theory for the determination of the rate constants for the reaction $\dot{R} + O_2 \rightarrow R\dot{O}_2$ is a study by Lebedev [3]. For alkyl radicals in Teflon,

$$k_{\text{eff}} = 5 \times 10^{-15} \exp(-10000/RT) \text{ cm}^3 \text{ s}^{-1}$$
$$K_s = 2 \times 10^{12} \exp(10000/RT) \text{ (cm}^3 \text{ mmHg)}^{-1},$$
$$D_{O_2} = 2 \times 10^{-3} \exp(-9000/RT) \text{ cm}^2 \text{ s}^{-1}.$$

From these relations, it is easy to find that $k_t \gg k_p$, i.e. $k_{\text{eff}} = k_p v^*$. If it is assumed that $v^* = 4 \times 10^{-21}$ cm^3 (for $\lambda = 10$ Å), it is easy to estimate $k^0_p \simeq 10^7$ s^{-1}. On the other hand, $k^0_p = f_p \nu$ where ν is the normal pre-exponential factor for the vapour-phase reaction of $\dot{R}$ and O_2 (of the order of magnitude of the vibration frequency $\nu \simeq 10^{12}$ s^{-1}), whence the steric factor for the vapour-phase reaction between $\dot{R}$ and O_2 is $f_p \simeq 10^{-5}$.

Most of the kinetic data on the reactions between $\dot{R}$ and O_2 were obtained in studies on the mechanochemistry of polymers. Although the oxidation conditions (regimes) were not investigated, it may be assumed, since radicals are formed on the surface, that diffusion-dependent stages are absent and the constants determined are equal to $k_p v^*$, as for fluoroalkyl radicals. Table 2 summarises these results.

In the liquid and gaseous phases the reactions $\dot{R} + O_2 \rightarrow R\dot{O}_2$ usually have activation energies close to zero and pre-exponential factors in the range 10^{-11}–10^{-13} cm^3 s^{-1}.

The activation energies for solid-phase reactions are much higher and the pre-exponential factors are much lower. This very interesting feature of solid-phase reactions is probably due to the considerations related to potential surfaces of solid-phase reactions discussed above (see Section I). However, the stage reached in research on quantitative solid-phase reaction kinetics is not yet advanced enough for a serious discussion of any theoretical problems concerning the elementary reaction step.

In concluding our discussion of the kinetics of reactions between $\dot{R}$ and O_2, we may mention that Loy [7] has quoted 6 kcal mole^{-1} as the activation energy for this reaction in irradiated poly(vinyl chloride). However, the rate of reaction depended on the surface area of the powder, i.e. on the dimensions of the polymer grains; this implies that the above activation energy does not refer to the kinetic stage. However, Loy does not quote any other data which would make it possible to identify the regime governing the reaction and find the rate-determining step.

Table 2. Pre-exponential factors and activation energies for the reactions between $\dot{R}$ and O_2 in polymers.

Polymer	$k_p\nu^*$, cm^3 s^{-1}	ϵ_p, cal mole^{-1}	References
Poly(methyl methacrylate)	$6 \cdot 10^{-15}$	7900	4
Ditto	—	~3800	5
Poly(vinyl acetate)	$1.6 \cdot 10^{-15}$	5900	4
Polystyrene	$4 \cdot 10^{-17}$	5300	4

Although the results presented in Table 1 refer to a particular reaction between gases and stationary radicals in the solid phase, their value is much wider and more fundamental. In particular, in the oxidation of solid polymers (where n should be replaced by the steady-state concentration of radicals, which depends on the rates of their initiation and destruction) these relations permit the determination of the limits of diffusion-dependent kinetics. For example, by studying the rate of sensitised oxidation of polymer film or powder under different experimental conditions (different film thickness, oxygen pressure, rate of initiation, etc.) and using the kinetic results for various regimes, it is possible to determine, in principle, all the constants for the elementary radical oxidation reactions. So far no experimental studies have been carried out on these lines.

The importance of kinetic regimes is not restricted to oxidation reactions. The kinetics of many degradation and stabilisation reactions may be modelled by Eqns. (4) and (5) and the regimes listed in Table 1. Among them, we may include the chain-termination reaction under conditions such that the inhibitor is non-uniformly distributed in the polymer and diffuses to the radical generation centres or reactions where the stabiliser, which inhibits degenerate branching, diffuses in the polymer towards the hydroperoxy-groups responsible for the branching.

2. Reactions with Low-Molecular Substances

The addition of macroradicals $\dot{R}$ to monomeric molecules M was investigated by Butyagin and coworkers in studies of the mechanical dispersion of polymer solutions in various monomers [8,9]. It was found for various combinations $\dot{R}_i + M_j$ that the activation energies (4–6 kcal mole^{-1}) and the pre-exponential factors (10^5–10^7 litre mole^{-1} s^{-1}) are close to the values of ϵ and k^0 in the liquid phase.

The same method was used to determine the rate constants for reactions with low-molecular hydrocarbons: $\dot{R} + rH \rightarrow RH + \dot{r}$. Since the macroradicals formed in the dispersion process are surrounded by solvent molecules, the reaction with them is determined by the true rate constants $k = k_p v^*$; it can be found from the rate of destruction of macroradicals and the rate of accumulation of low-molecular radicals $\dot{r}$ using the equation

$$\frac{(\dot{R})}{(\dot{R}) + (\dot{r})} = \frac{1}{k\,(rH)\,t}\{1 - \exp[-k\,(rH)\,t]\}$$

The rate constants for the reactions of polystyrene radicals with toluene, ethylbenzene, and cumene (10^{-14}–10^{-15} $cm^3\ s^{-1}$) determined in this way at 77°K proved to be anomalously high compared with the "liquid phase" constants extrapolated to this temperature; it was suggested that these reactions take place under non-equilibrium conditions in the course of the dispersion of the polymer [8,9].

Activation energies of 38 and 36 kcal $mole^{-1}$ have been quoted [4] for the reaction with cumene of the macroradicals of poly(methyl methacrylate) and poly(vinyl acetate) (obtained mechanochemically) respectively (it should be noted that the maximum activation energy observed for reactions of similar type is only 15 kcal $mole^{-1}$–for the reaction $\dot{C}H_3 + CH_4 \rightarrow CH_4 + \dot{C}H_3$). [10] Since in the study quoted the formation of low-molecular radicals $\dot{r}$ was not observed, the validity of these data and their physical significance remain obscure.

Qualitative evidence for reactions of macroradicals $\dot{R}$ and $R\dot{O}_2$ with aldehydes, phenols, mercaptans, and thiophenols has been quoted in a number of studies [8,11,12], but quantitative data on the kinetics of such reactions are not available.

The above brief analysis shows that there are virtually no quantitative kinetic data for the reactions of macroradicals with low-molecular substances (including inhibitors) although these reactions are important in degradation and stabilisation processes. Firstly, low-molecular substances can serve as transfer-agents for oxidation chains, secondly, they take part in chain-termination reactions, and, thirdly, they function as catalysts for the recombination of macroradicals. In particular, the effectiveness of inhibitors is determined, apart from other conditions, by the relative efficiencies of the inhibitors in chain transfer and chain termination or their ability to catalyse the recombination of the macroradicals. The quantitative kinetic criteria governing such relative efficiencies are essential for practical purposes.

The extensive data on the rate constants for the reaction of radicals $R\dot{O}_2$ with inhibitors in the liquid phase can be hardly used for solid-phase reactions; this follows from general theoretical concepts (see Section I) and is confirmed by the reaction between $\dot{R}$ and O_2 considered above. We may note that, in order to determine the effectiveness of inhibitors in chain termination, it is necessary to know not only the rate constant for the interaction of $R\dot{O}_2$ with the inhibitor (which characterises the kinetic stage) but also the diffusion coefficient of the inhibitor in the polymer (the microdiffusion stage).

3. Reactions of Macroradicals with Macromolecules

These reactions play an important role in the transfer ($\dot{R} + R'H \rightarrow RH + \dot{R}'$) and propagation ($R\dot{O}_2 + RH \rightarrow RO_2H + \dot{R}$) of kinetic chains in polymer degradation. So far there have been no experimental studies designed to determine directly the rate constants for these reactions; here the only source of information is the kinetics of the recombination of alkyl and peroxy-macroradicals in irradiated polymers. Before discussing the kinetics, we shall first consider the recombination mechanism.

The destruction of macroradicals in irradiated polymers follows a bimolecular law. It is reasonable to suppose (as was in fact done in the early studies) that the recombination involves the mutual approach of macroradicals by diffusion. However, later it was found that many important facts are inconsistent with these hypotheses.

Firstly, data on the diffusion mobility of polymeric segments show that the idea of recombination via molecular collision is unsound. Thus even in low-molecular rubbers the diffusion coefficient is $D \simeq 10^{-14}$ $cm^2\ s^{-1}$; it has been estimated [13] that in polystyrene at temperatures close to the glass point $D \simeq 10^{-21}$ $cm^2\ s^{-1}$ and at 20°C $D \simeq 10^{-27}$ $cm^2\ s^{-1}$. This means that the recombination of radicals in such matrices would require an infinitely long period if it involved a diffusion mechanism; in fact the recombination is quite fast even in crystalline polymers, where physical diffusion of macromolecules is altogether without significance.

Secondly, in the same polymers, even in the same specimens, radicals of different chemical structures (alkyl, allyl, and peroxyradicals) recombine at different rates under the same conditions; the temperature ranges in which different radicals recombine are also markedly different. Thus peroxy-radicals usually recombine 10^2–10^3 times faster than alkyl radicals. If the rate of recombination of radicals were determined by the physical diffusion of macromolecules or their segments, the chemical structure of the radicals would have no effect on the rate of recombination.

Table 3. Number of oxygen molecules n for each recombined macroradical.

Polymer	T, °C	p_{O_2}, mmHg	n	References
Isotactic polypropylene	60	150	8±1	15,19
	75	150	4.5±1	15
Poly(vinyl chloride)	22	150	6±1	15
	35	150	5±1	15
			3	7
Polyethylene			5	16
Poly(methyl methacrylate)	25	~6; 525	1.5–2	17
Polyepoxyethylene	25		5–10	18

Thirdly, from the standpoint of the diffusion mechanism one cannot explain the finding that in a number of polymers [poly(vinyl chloride), polyformaldehyde] the interaction between oxygen and alkyl radicals does not result in the appearance of peroxy-radicals, although the destruction of alkyl radicals is greatly accelerated; the kinetics of their destruction remain bimolecular as before, and its rate is proportional to the pressure of oxygen [14] (for a more detailed discussion of the kinetics of such catalysis, see below).

Fourthly, the recombination of peroxy-radicals is accompanied by the formation of polymeric hydroperoxide and the absorption of oxygen. Table 3 presents data which show how many oxygen molecules are absorbed for each radical recombined.

Thus, as noted by Loy[7], a peroxy-radical migrating in the polymer leaves behind a trail—a chain of hydroperoxides—until it encounters another radical with which it recombines. It should be noted that the values of n in Table 3 are in fact too low, since no account was taken of the amount of oxygen involved in the $R\dot{O}_2$ recombination step; furthermore, during radiolysis radicals are frequently distributed non-uniformly in the specimen, forming groups, and therefore the path traversed by the radicals prior to their recombination is smaller than the path which would be traversed in the case of a uniform distribution. The low value of n for poly(methyl methacrylate) is due to the fact that the radicals were obtained by the mechanical degradation of the polymer and are probably localised on the surface.

Table 4. Activation energies and pre-exponential factors for the recombination of the radicals $\dot{R}$ in polymers.

Polymer	Temp., °C	Method of formation of radicals	k^0, $cm^{-3}\,s^{-1}$	ϵ, kcal $mole^{-1}$	References
Poly(methyl methacrylate	30—55	mechanical degradation	10^{-8}	29	13
	30—60	radiolysis	10^{-8}	28	26
		mechanical degradation	2	26	9
		mechanical degradation	—	37	5
Polyformaldehyde	45—86	radiolysis	10^{-7}	19	14
		destruction in the presence of O_2	10^{-9}	17	14
Poly(vinyl chloride)	70—100	radiolysis	0.7	38	27
		ditto	—	44	28
Acrylate polyesters		radiolysis	$2\cdot10^{-3}$	26.5	29
			$2\cdot10^{-12}$	12.1	29
			$2\cdot10^{-11}$	17.1	29
Polyethylene	40—100	radiolysis	10^{3}	38	24
	—158—123	ditto	$7\cdot10^{-17}$	0.7	30
	—103—73	»	$3\cdot10^{-5}$	23.1	30
	—53—23	»	$5\cdot10^{-3}$	24.8	30
High-pressure polyethylene	40—100	»	1	32	24
Polypropylene	20—80	»	10^{-6}	23	24
	—123—23	»	—	11	31
	—23—25	»	—	48	31
Crystalline Teflon	220—270	»	10^{6}	63	24
Amorphous Teflon	180—220	»	10^{-7}	30	24
Polybutadiene		»	$2\cdot10^{-15}$	1.0	20
		»	$3\cdot10^{-14}$	4.0	20

All these features of the recombination can be explained by a "chemical" mechanism for the diffusion of radicals, i.e. the migration of free valence (relay mechanism) via the consecutive reactions $\dot{R} + RH \rightarrow RH + \dot{R}$ or $R\dot{O}_2 + RH \rightarrow RO_2H + \dot{R}$. This mechanism probably obtains in the majority of solid polymers; rubbers and amorphous polymers above the glass point probably constitute an exception. Thus in polybutadiene the activation energies for the recombination of allyl radicals are 1–4 kcal $mole^{-1}$,[20] which is close to the values observed for the recombination of radicals in liquids; the recombination rate constants in polybutadiene and amorphous polycapramide diminish markedly with increase in the number of cross-links, i.e. with the increase in the rigidity of the matrix[21,22]. The latter property constitutes a form of criterion for the recombination mechanism.

Eqn. (1) remains valid also for recombination; however, in contrast to the reaction between $\dot{R}$ and O_2 where $k_t \gg k_p$, here the rate-limiting stage is the relay process and not recombination in the vapour phase, i.e. $k_t \ll k_p$. Then $k_{rec} = k_t v^*$. This equation can also be obtained in another way. We introduce the valence diffusion coefficient $D = \frac{1}{6}\lambda^2 k_t$, where k_t is the frequency of "jumps", i.e. the frequency of the elementary steps in physical or chemical diffusion and λ the length of the diffusion path (of the order of dimensions of a monomer unit or the lattice constant). The recombination rate constant $k_{rec} = 8\pi\lambda D$; on substituting D in this expression, we have $k_{rec} = \frac{4}{3}\pi\lambda^3 k_t$ or $k_{rec} = k_t v^*$. Thus the recombination kinetics are determined by the kinetics of the valence transfer reactions and the recombination rate constants are the bimolecular rate constants for the relay process. This hypothesis was tested in a recent study[23]; the calculation of k_{rec} for the radicals $\dot{R}$ in polyethylene using the above equation for D and k_t for the reaction between $\dot{C}_2H_5$ and heptane in the liquid phase gave good agreement between the calculated and experimental values of k_{rec}. Tables 4 and 5 list the experimental results on the kinetics of the recombination of $\dot{R}$ and $R\dot{O}_2$ radicals in solid polymers.

Table 5. Activation energies and pre-exponential factors for the recombination of the radicals $R\dot{O}_2$ in polymers.

Polymer	Temp °C	Method of formation of radicals	k^0 $cm^{-3}\,s^{-1}$	ϵ, kcal $mole^{-1}$,	Refs.
Poly(methyl methacrylate)	5–37	mechanical degradation	$5\cdot10^{-9}$	17	32
		ditto	$1\cdot10^{-9}$	18	13*
Crystalline Teflon		radiolysis	10^{-10}	26	24
Amorphous Teflon		ditto	10^{-16}	10	24
Poly(vinyl acetate)	−17–(+37)	mechanical degradation	10^{-8}	18	13*
Ditto		ditto	—	14.5	4
Polystyrene	−25–(+40)	»	10^{-7}	18	13*
		»	—	12	4.33

*Recalculated by Butyagin[17].

It is striking that the activation energies for recombination reach enormous values; in most cases the pre-exponential factors are anomalously high and are without physical significance; furthermore, there is a linear relation between the logarithm of the pre-exponential factor and the activation energy—the compensation effect (CEF)[24] (the nature of the compensation effect in these reactions is discussed below).

Clearly these results give no information about the kinetics of the valence transfer reactions. The reason for this is probable that the kinetics of reactions in polymers are related to the kinetics of molecular motion and in this sense the measured constants are not elementary. One can only suppose that the activation energies are about 13–17 kcal $mole^{-1}$ for reactions between $\dot{R}$ and RH and 10–15 kcal $mole^{-1}$ for reactions between $R\dot{O}_2$ and RH. In particular, the activation energy of the reaction between $R\dot{O}_2$ and RH in poly(methyl methacrylate), determined by a chemiluminescence method, is 11 kcal $mole^{-1}$.[17]

In certain polymers [polyformaldehyde, poly(vinyl chloride), polyamides] alkyl radicals are not fully converted into peroxy-radicals under the action of oxygen, as is usually the case, but the rate of their destruction is greatly increased. The rate of such catalytic recombination was calculated by Lebedev[25], who showed that catalysis is possible under conditions such that the diffusion of oxygen is hindered and the relay process $R\dot{O}_2 + RH \rightarrow RO_2H + \dot{R}$ is much faster than the reaction between $\dot{R}$ and RH. The rate of recombination is then $w_{rec} = k_{rec}(\dot{R})^2(O_2)$, where k_{rec}^{-1} may be calculated as the sum of the kinetic resistances in all the stages: macrodiffusion, microdiffusion, and kinetic; a linear relation between

w_{rec} and oxygen pressure has been observed experimentally [14].

The above analysis shows that at present there are no reliable data for the chain-propagation constants in solid polymers. Even the few studies available on the solid-phase oxidation of polymers, carried out in recent years, are open to a number of serious objections.

Recently an interesting study was carried out on the oxidation of polypropylene (degree of crystallinity 50%) at 110-140°C. [34]. The steady-state concentrations of the hydroperoxide and peroxy-radicals and the rate of absorption of oxygen were measured; these data are insufficient for the calculation of all the elementary constants. It was shown that the oxidation mechanism is almost the same as the mechanism of the oxidation of liquid hydrocarbons: the initiation takes place on decomposition of the hydroperoxide and the rate of reaction is proportional to $(ROOH)^{1/2}$, i.e. the chain termination is quadratic (recombination of $R\dot{O}_2$).

The chain propagation constant for reaction between $R\dot{O}_2$ and RH is of the form

$$k_{prop} = 5 \times 10^{-16} \exp(-9000/RT) \text{ cm}^3 \text{ s}^{-1}.$$

The chain termination constant is $k_{ter} = 7.5 \times 10^{-15}$ cm^3 s^{-1} and the activation energy for chain termination is zero. From the standpoint of the above hypotheses concerning the migration of free valence by a relay mechanism, ϵ_{form} should be close to ϵ_{prop}. Even if one assumes that chain termination takes place via the physical diffusion of segments, the high chain termination rate constant and the zero activation energy are still quite incomprehensible (k_{ter} is higher almost by a power of ten than k_{ter} for 2,4,6-trimethylheptane, which may be regarded as a model of polypropylene [35]).

The results obtained by Chien and Boss [34] can be understood and can be seen to have physical significance if it is assumed that chain termination is effected by a product which readily reacts with the macroradicals $\dot{R}$ (with an activation energy close to zero) and readily diffuses in the polymer (also with an almost zero activation energy); this product then plays the role of a catalyst for the recombination reaction. This hypothesis has not of course been proved (although a method for experimental tests may be suggested), but, if found to be valid, it may be of fundamental importance. One cannot exclude the possibility that in the oxidation of solid polymers this mechanism of the termination of kinetic chains plays a leading role.

Denisov et al. [83] found for the sensitised oxidation of solid polyethylene (temperature range 13 deg)

$$k_{prop}/\sqrt{k_{ter}} = 7 \times 10^{7} \exp(-21250/RT) \text{ mole}^{-1/2} \text{ kg}^{1/2} \text{ s}^{-1/2}.$$

4. Decomposition of Hydroperoxides and Degenerate Branching in Polymers

Hydroperoxides are responsible for the degenerate branching in oxidative thermal degradation of polymers. Degenerate branching constitutes the principal stage in the oxidation process. Therefore the study of the kinetics of the decomposition of the hydroperoxides of polymers and of the probability of forming free radicals in the decomposition process constitutes a serious and important problem.

We shall consider initially the results obtained for the mechanism and kinetics of the decomposition of hydroperoxides in polymers and then the data on the formation of radicals and the probability of degenerate branching in polymers.

Decomposition of hydroperoxides. The following principal mechanisms for the decomposition of hydroperoxides (HP) have been considered in the literature;

$$ROOH \rightarrow R\dot{O} + \dot{O}H \quad (I)$$

$$ROOH + RH \rightarrow R\dot{O} + H_2O + \dot{R} \quad (II)$$

$$ROOH + ROOH \rightarrow R\dot{O} + H_2O + R\dot{O}_2 \quad (III)$$

The unimolecular decomposition [reaction (I)] takes place with a high activation energy of about 35-40 kcal mole^{-1}. [36] It occurs only at low hydroperoxide concentrations in solvents without weakly bound hydrogen atoms. Reactions (III) and (II) are more probable; the heat of reaction (III) is approximately 9 kcal and that of reaction (II) varies within wide limits, depending on the R-H bond energy [37]. Reaction (III) predominates at high hydroperoxide concentrations, while at low concentrations and for enthalpy changes comparable with the heat of reaction (III) reaction (II) predominates. In solid polymers reaction (III), in the form in which it occurs in liquids, is even less probable. However, one cannot exclude another kinetic variant of this reaction, which is described by a first-order equation, while the stoichiometry of the reaction corresponds to Eqn. (III). The point is that, as already mentioned, hydroperoxides are obtained in the oxidation of polymers as a result of a sequence of two elementary reactions $R + O_2 \rightarrow R\dot{O}_2$ and $R\dot{O}_2 + RH \rightarrow RO_2H + \dot{R}$. Owing to the relay mechanism of the oxidation process, hydroperoxides are distributed in chains, each of which is in contact only with the nearest adjacent hydroperoxy-groups and the interaction with other peroxy-groups is unlikely. Then the decomposition of the hydroperoxide can occur in pairs and the decomposition kinetics are described by a first-order kinetic law.

In polymers containing weakly bound hydrogen atoms mechanism (II) will predominate; since usually [ROOH] $\ll$ [RH], it will also be described by a first-order kinetic equation. The only polymer for which the decomposition of hydroperoxides was studied in detail is polypropylene. However, even in this case there are contradictory views. A number of investigators [38,39] believe that the decomposition of the hydroperoxide is described by a second-order kinetic equation, in accordance with mechanism (III). This conclusion is based on the finding that the time variation of the concentration of the hydroperoxide derived from polypropylene is satisfactorily described by the equation

$$\frac{1}{[ROOH]} - \frac{1}{[ROOH]_0} = kt \quad . \quad (6)$$

The activation energy (27 kcal mole^{-1}) obtained by these investigators, which is typical for a process of this type, is also consistent with mechanism (II).

However, this is inconsistent with another observation by Dudorov et al. [38], who established that the degree of conversion of the initial peroxide is independent of the initial concentration of the hydroperoxide. Such a relation is typical for a first-order reaction. As a result, the rate constant for the decomposition of the hydroperoxide calculated from Eqn. (6) does not remain invariant when the initial hydroperoxide concentration is changed. Evidently the decomposition of hydroperoxides in atactic polypropylene cannot be described by mechanism (III). In fact recalculation of the results of Dudorov et al. [38] in terms of kinetic equations which are first-order in to the hydroperoxide concentration shows that, over a wide concentration range (7.4×10^{-3}-0.5 mole kg^{-1}), the constant remains satisfactorily invariant.

The above example confirms yet again the rule that, in order to determine the true order of the reaction, it is

insufficient to investigate time dependences alone; a comprehensive kinetic study of the reaction is necessary. This is even more valid for polymers, since the hydroperoxide cannot be isolated from the latter in a pure form. For this reason the reaction is studied in a medium consisting of the oxidised polymer where the peroxide ROOH is present in addition to the hydroperoxide (incidentally, one usually obtains a set of different hydroperoxides, which may decompose at different rates); the peroxides are as a rule more stable than the hydroperoxides. When the mixture contains peroxides which decompose at different rates, the variation with time of their overall concentration is described by an equation which has nothing in common with the true reaction mechanism. Fig. 1 shows as an example the calculation of the time variation of the overall concentration of hydroperoxides in a 4 : 1 mixture assuming that the rate constants for their monomolecular breakdown are 4.6×10^{-2} min^{-1} and 4.6×10^{-3} min^{-1}.

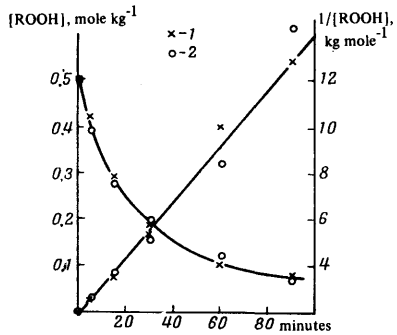


Figure 1. Decomposition of polypropylene hydroperoxide: 1) calculated points; 2) experimental values taken from Dudorov et al. [38]

Fig. 1 shows that the change in overall concentration up to 90% conversion is satisfactorily described by a second-order kinetic equation even though the hydroperoxides decompose [by a known unimolecular mechanism].

In a study [40] dealing with the decomposition of the hydroperoxides derived from isotactic polypropylene it was shown that the time variation of the concentration of the hydroperoxide is satisfactorily described by a second-order equation and the calculated rate constant remains invariant as the initial concentration of the hydroperoxide is varied.

However, the activation energies obtained [38-40] (25 to 27 kcal mole^{-1}) are inconsistent with the hypothesis of a purely unimolecular decomposition of the hydroperoxide (I). Furthermore, it has been established that the rate constant for the decomposition of hydroperoxides from isotactic polypropylene increases on introduction into the polymer of substances with labile hydrogen atoms [40] and diminishes when the polymer is diluted with substances in which all the hydrogen atoms are strongly bound [41]. Fig. 2 presents the decrease of the first-order rate constant when polypropylene is diluted with naphthalene or cetane. On the basis of these data, it is suggested [40,41] that the decomposition of hydroperoxides from isotactic polypropylene takes place according to mechanism (II). The hydrogen atoms attached to the tertiary carbon atoms evidently participate in the reaction. The experimental yield of water [41] amounts to 85% of theoretical.

The above mechanism is confirmed by the results obtained in a study of the kinetics of the absorption of oxygen and the assimilation of hydroperoxides in the oxidation of isotactic polypropylene [42]. On the basis of the mechanism proposed for the process, the authors calculated from these data the rate constant for the decomposition of the hydroperoxides by two independent procedures. The calculated constant agreed satisfactorily with the value obtained in the study of the thermal decomposition of polypropylene hydroperoxides.

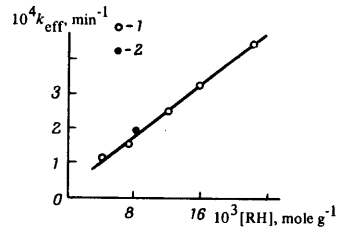
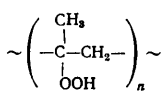


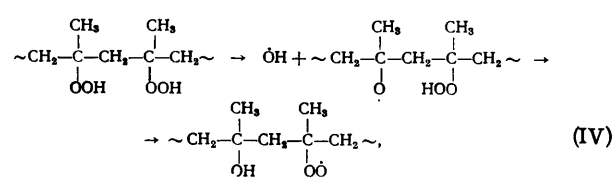
Figure 2. Variation of the effective rate constant for the decomposition of polypropylene hydroperoxide with polymer concentration: 1) dilution with naphthalene; 2) dilution with cetane.

The study of the decomposition of the polypropylene hydroperoxides obtained in the sensitised oxidation of the polymer in a dilute solution is of considerable interest [43]. In this procedure hydroperoxy-groups distributed along the macromolecule at adjacent tertiary carbon atoms should form:



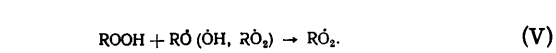
The authors demonstrated [44] that their hydroperoxides have precisely this structure; furthermore, they obtained the distribution of groups with respect to n, as shown in Fig. 3. It was found that 50% of the hydroperoxides are present in the form of pairs and only 7–9% in the form of single molecules.

The authors describe the breakdown of such hydroperoxides by the sum of two first-order kinetic equations with rate constants of 16×10^{-4} and 8×10^{-5} s^{-1} at 120°C. They suggest that the rapid reaction ($k = 16 \times 10^{-4}$ s^{-1}) is the chain decomposition of adjacent hydroperoxy-groups:



(IV)

and the slow reaction is the chain decomposition of isolated groups:



(V)

The authors believe that this mechanism is confirmed by the fact that the contribution of the slow reaction is

10–15%, i.e. is close to the fraction of isolated hydroperoxy-groups and that the introduction of large amounts of an inhibitor (ionol) diminishes the contribution of the fast reaction and lowers the rate of the slow reaction to a limiting value, which can also be obtained by reducing the initial concentration of the hydroperoxide.

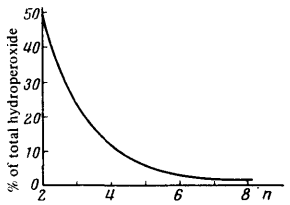


Figure 3. Distribution of adjacent hydroperoxy-groups with respect to n in polypropylene according to the data of Chien et al. [44]

However, the above study involves significant contradictions. In the first place the chain decomposition of the hydroperoxide cannot follow a first-order kinetic law. This is also shown by the variation of the rate constant for the slow reaction with the initial concentration of the hydroperoxide found by the authors themselves [43]. Furthermore, the contribution of the "slow" reaction must be much greater (30–40%). Indeed in the decomposition of two adjacent hydroperoxy-groups by mechanism (IV) two radicals, $\dot{O}H$ and $R\dot{O}_2$, are formed. Probably there is a high probability of the conversion of $R\dot{O}_2$ into the hydroperoxide, which will be formed as a separate molecule. Thus one half of the binary and one third of the ternary hydroperoxide sequences must ultimately decompose at the rate of the "slow" reaction.

Furthermore, in the chain decomposition of the hydroperoxide the yield of radicals per decomposition step should be much less than two, while Chien and Jabloner [43] found it to be 1.8. These findings show that the mechanism proposed [43] for the decomposition of the hydroperoxide derived from polypropylene is open to serious objections. It is difficult at present to interpret these results unambiguously.

In the decomposition of hydroperoxides in other polymers (other than polypropylene) the situation is even less satisfactory; data for such processes are virtually lacking. The results of Chien and coworkers [45] and Denisov and coworkers [46] for the decomposition of the hydroperoxides derived from polyethylene constitute an exception. However, the two sets of data show considerable discrepancies.

While Denisov and coworkers concluded that in polyethylene the hydroperoxides undergo a chain decomposition (an inhibitor retards the reaction), Chien and coworkers suggest that there is no chain decomposition in the breakdown of the polyethylene hydroperoxides, since inhibitors do not affect the decomposition process. According to these authors' findings [45], two unimolecular reactions take place in polyethylene: fast and slow reactions with activation energies of 25 and 27 kcal mole^{-1} respectively. According to Denisov [46], the activation energy for the inhibited decomposition of the hydroperoxides is 35 kcal mole^{-1}; it is suggested that the decomposition process is unimolecular and has mechanism (I). The authors of both investigations found that the rates of decompositions of the polyethylene hydroperoxides are the same in solution and in the solid phase.

Probability of radical formation in the decomposition of hydroperoxides. The available literature data on the probability of radical formation in the decomposition of hydroperoxides derived from polymers can be divided into two groups. The first group includes results obtained for the decomposition of the hydroperoxides in a vacuum or in an inert atmosphere [47] and the second group includes data obtained in an atmosphere of oxygen [42,43,45,46].

The inhibitor method in one form or another is used for the quantitative determination of the number of radicals formed in the breakdown of the hydroperoxide. The following difficulties must be overcome. As a rule, it is possible to obtain hydroperoxides derived from the polymers at concentrations of 10^{-5}–10^{-4} mole g^{-1}. In order to ensure the complete removal of the radicals by the inhibitor, the concentration of the latter in the polymer must be about 10^{-4} mole g^{-1}. When the probability of the formation of radicals is 10^{-2}–10^{-3}, about 1% of the inhibitor is consumed. Such a change in concentration is outside the error limits of the measurements.

In order to calculate the number of radicals formed in the decomposition of polypropylene hydroperoxides in a vacuum [47,48], a new version of the inhibitor method was developed. Phenoxy-radicals with t-butyl group in the *ortho*-positions can split off isobutene [49]. The amount of isobutene serves as a measure of the number of phenoxy-radicals formed in the interaction between phenol and radicals.

The mechanism of the radical processes can be represented by the following series of reactions:

$$ROOH \rightarrow \delta\dot{R} \xrightarrow{PhOH} \delta\, Ph\dot{O} \rightarrow \sigma\gamma\ (iso\text{-}C_4H_8)\ .$$

In order to find δ, it is necessary to determine, in addition to the amount of isobutene, also γ—the yield of isobutene in the decomposition of a phenoxy-radical. It was found that at 130°C in polypropylene 10% of phenoxy-radicals derived from ionol broke down with formation of isobutene, i.e. $\gamma = 10 \times 10^{-2}$. [47] The calculations showed that 17 radicals are formed for each thousand polypropylene hydroperoxide molecules decomposed in a vacuum. Such a low yield of radicals in the absence of a chain process can be explained either by postulating that the main bulk of the hydroperoxides break down without the formation of radicals or that most of the radicals formed are destroyed by recombination within the cage:

$$ROOH + RH \rightarrow H_2O + (R\dot{O} + \dot{R}_{in}) \begin{cases} \nearrow \text{destruction} \\ \downarrow \\ \delta\dot{R} \leftarrow (\dot{R}_t + \dot{R}_{in}) \rightarrow \text{destruction} \end{cases}$$

A number of facts suggest that the latter explanation is correct. Thus, in a study dealing with the oxidation of isotactic polypropylene [42], it was shown, by comparing the rates of absorption of oxygen and of the decomposition of the hydroperoxide, that in the presence of O_2 the yield of radicals is much higher and approaches 2.

Table 6 shows the variation of δ with the pressure of O_2. The fact that in the presence of oxygen the mechanism of the decomposition of the hydroperoxide does not change is confirmed by the constancy of the rate of its decomposition both in a vacuum and in the presence of O_2.

Analogous calculation based on the data of Chien and Boss yields $\delta = 1.2$ for solid polypropylene at $p_{O_2} =$ 760 mmHg and 120°C. [34,43] For comparison, it should be

noted that, using the inhibitor method, Chien obtained $\delta = 1.8$ for the decomposition of polypropylene hydroperoxides in solution at an O_2 pressure of 760 mmHg [43] and $\delta = 0.2$ for polyethylene hydroperoxides under the same conditions [45]. Denisov and coworkers [46] showed that the probability of the formation of radicals in the decomposition of polyethylene hydroperoxides is the same in solution and in the solid phase and is lower than the probability reported by Chien and coworkers [45] by a factor of 100. It is difficult to account for such a discrepancy between the results.

Table 6. Dependence of the yield of radicals δ in the decomposition of polypropylene hydroperoxide on the pressure of O_2 ($T = 130°C$).

p_{O_2}, mmHg	δ
0	$17 \cdot 10^{-3}$
50	0.25
100	0.5
200	0.8
400	1.2
600	1.5

The data for the variation of δ with oxygen pressure can probably be explained only on the basis of the cage effect hypothesis. The decomposition of hydroperoxides derived from polymers entails the formation of a pair of radicals which, in the absence of powerful radical acceptors, recombine with a high degree of probability. By adding to the radicals, oxygen can participate in the cage reactions and can alter the value of δ. However, it must be admitted that the mechanism of such participation remains obscure.

The participation of oxygen in the cage reactions makes it possible to estimate the lifetime of the cage τ. Evidently the order of magnitude of this time must not be less than that of the time during which the oxygen molecule migrates over the distance separating two nearest oxygen molecules (or half this distance). Using the available data on the solubility and diffusion of O_2 in polypropylene [50], we obtain τ for the amorphous polymer at 130°C of the order of 10^{-6}–10^{-8} s; in the crystalline polymer this quantity is probably somewhat larger. The value of τ obtained here agrees well with τ estimated from the probability of the breakdown of RȮ radicals (see below).

Shlyapnikova and Yasina [51] secured direct evidence that the yield of radicals in the breakdown of the hydroperoxides derived from solid propylene increases under the influence of oxygen; δ then varies linearly with oxygen pressure: $\delta = \delta_0 + \delta_i p_{O_2}$, where $\delta_i/\delta_0 \simeq 2 \times 10^{-3}$ mmHg^{-1} for the liberation of methane from the cage and $\delta_i/\delta_0 \simeq 1.3 \times 10^{-2}$ mmHg^{-1} for the liberation of propene.

From the standpoint of the stabilisation of polymers, it is significant that the yield of radicals in the decomposition of polymer hydroperoxides can also be increased by certain inhibitors. Thus in a study of the effect of ionol on the yield of hydrocarbons in the breakdown of polypropylene hydroperoxide [48], the results presented in Fig. 4 were obtained. Volatile hydrocarbons (methane, ethane, propane, propene, and isobutene) are produced in the breakdown of alkyl macroradicals generated from the hydroperoxide and isobutene is formed in addition also from phenoxy-radicals—the product of the interaction of ionol with macroradicals. Fig. 4 shows that the yields of all the hydrocarbons, with the exception of isobutene, decrease with increase in the concentration of the inhibitor; however, the decrease is not to zero but only to a limiting value. At the same time the amount of isobutene increases continuously. These results can be readily explained if it is supposed that the inhibitor can participate in an additional radical generation process. Then, starting with a certain inhibitor concentration, the concentration of radicals in the polymer becomes constant and independent of the concentration of the inhibitor, because the rates of formation and destruction of radicals are both proportional to the latter. This is why the rate of formation of hydrocarbons and consequently their yield cease to depend on the inhibitor concentration. At the same time the total amount of radicals and hence also the yield of isobutene increase continuously with increasing ionol concentration. Thus the inhibitor participates both in the destruction of radicals and in their formation.

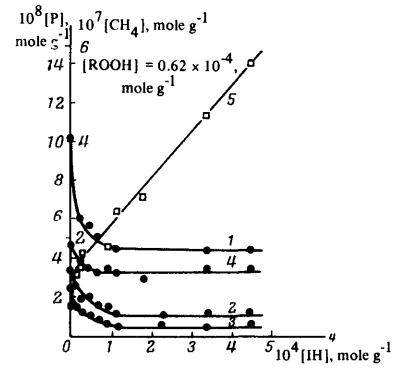


Figure 4. Dependence of the yield of polypropylene hydroperoxide decomposition products on the concentration of ionol: 1) methane; 2) ethane; 3) propane; 4) propene; 5) isobutene.

A kinetic analysis of the role of the inhibitor in the production of radicals and quantitative estimates of this participation have been made [48]. For example, in the breakdown of the polypropylene hydroperoxides in a vacuum at 130°C the yield of radicals in the presence of 5×10^{-4} M ionol increases by a factor of 5.

In principle, one can consider two mechanisms for the involvement of the inhibitor in radical generation. Firstly, the inhibitor may "enter" the cage (RȮ + Ṙ$_{in}$) destroying one of the radicals; the second radical is then capable of chain propagation. Secondly, the inhibitor can react with the polymer hydroperoxide; such a reaction is an additional source of radicals.

The branching function of the inhibitor can be shown only when the primary yield of radicals in the breakdown of the hydroperoxide (without the participation of the inhibitor) is very low.

In fact the inhibitor can successfully compete with the cage recombination of radicals only if the rate constant for its interaction with the radicals is not less than the rate constant for their recombination and the concentration of the inhibitor is also fairly high. At the usually employed

inhibitor concentration (0.01–0.01 mole kg^{-1}) the probability of the interaction of the inhibitor with the cage is low (10^{-2}–10^{-4}). For this reason, such interaction can be important only when the spontaneous liberation of radicals from the cage is also low. In the direct interaction of the inhibitor with the hydroperoxide the following factors are evident. If the probability of the formation of radicals in the breakdown of the hydroperoxide is low, then even a slight interaction between the inhibitor and the hydroperoxide can have a significant effect on the yield of radicals. Otherwise even a high rate of interaction of the inhibitor with the peroxide cannot affect appreciably the efficiency of radical formation.

The above analysis of the data shows that no unambiguous results are yet available on the yield of radicals in the breakdown of polymer hydroperoxides in the presence of oxygen. In some studies the yield of radicals in the presence of oxygen has been determined as about 10^{-2} to 10^{-3}, while in others it is of the order of unity.

Nevertheless this finding is fairly important. The point is that the idea of the involvement of the inhibitor in degenerate branching in the oxidation of polymers and the associated theory of the effect of inhibitors (critical concentrations, classification of inhibitors into "strong" and "weak", etc.) are based on the hypothesis of a low value of δ; these hypotheses were put forward by Shlyapnikov and Neiman [52,53] and confirmed in studies of the high-temperature (180–220°C) inhibited oxidation of polypropylene.

Thus there exists a definite contradiction concerning the value of δ. Possibly in solid polymers (at 100–130°C) δ is close to unity, while in melts at temperatures in the range 180–220°C δ is small (although from the physical point of view the opposite relation would be expected). Evidently the unambiguous solution to the problem of the probability of degenerate branching in the breakdown of hydroperoxides in polymers is very important for the theory of polymer stabilisation.

5. Decomposition of Macroradicals (Degradation of the Polymer Chain)

The kinetics of the decomposition of macroradicals of different types are of exceptional interest for the theory of degradation processes. Unfortunately there are virtually no quantitative data for the rates of decomposition in the solid phase. For this reason, only the qualitative aspects of this problem will be considered here.

In various forms of polymer degradation the following types of radicals play a leading role: alkyl macroradicals and peroxy- and alkoxy-macroradicals.

Decomposition of alkyl macroradicals. These reactions are usually investigated in thermal degradation processes of polymers at temperatures in excess of 300°C; this is because the rate of their decomposition is low. Thus it is known from the kinetics of gas-phase reactions [54] that low-molecular alkyl radicals break down with an activation energy exceeding 30 kcal $mole^{-1}$. Probably the activation energy for the decomposition of high-molecular radicals does not differ appreciably from this value. The breakdown of alkyl macroradicals leads to the rupture of the polymer chain and the formation of radicals with a free valence at the end of the macrochain (terminal macroradicals). These radicals give rise to volatile degradation products and in many cases alkyl macroradicals may isomerise, which leads to a wide range of degradation products. For example, in the thermal degradation of polypropylene the following reactions are postulated [55,56]:

$$\sim CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\dot{C}H_2 \rightarrow \sim \dot{C}H_2 + CH_2-CH=CH_2,$$

$$\sim CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\dot{C}H_2 \rightarrow \dot{C}H_3 + \sim CH_2-CH=CH_2 ,$$

etc.

Decomposition reactions of alkyl macroradicals have been observed in the inhibited oxidation of polypropylene at 200°C, [57] in the mechanical degradation of a number of polymers [58], and also in the breakdown of polypropylene hydroperoxide at 130°C. [59] In the last case a detailed study was made of the kinetics of the formation of volatile hydrocarbons—the degradation products of the terminal macroradicals. The yield was found to be extremely low. In the breakdown of 1.26×10^{-4} mole of hydroperoxide, at a concentration of 1.26×10^{-4} mole g^{-1} in the polymer, the amounts of products were 16.7×10^{-7} mole of methane, 0.85×10^{-7} mole of ethane, 0.89×10^{-7} mole of propane, 1.4×10^{-7} mole of propene, and 0.19×10^{-7} mole of isobutene. These data make it possible to estimate the probability of the decomposition of alkyl macroradicals at 130°C. In the same study it was shown that the terminal macroradicals are obtained mainly in the breakdown of alkoxy- and not alkyl radicals. For this reason, only half of the radicals liberated from the "cage" ($R\dot{O} + \dot{R}_{in}$) are terminal. Since the yield of radicals is in this case 1.7×10^{-2}, [47] it follows that 1.26×10^{-4} mole of hydroperoxide gives 10.7×10^{-7} mole of $\dot{R}_t$. Consequently only 8% of the $\dot{R}_t$ radicals decompose with formation of propene while the remaining 92% are converted into "inner" macroradicals by the reaction

$$\dot{R}_t + RH \rightarrow R_tH + \dot{R}_{in}$$

or isomerise and yield other hydrocarbons (propane, ethane, isobutene, etc.). Thus the rate of the chain-transfer reactions exceeds at least by a factor of ten the rate of decomposition of the terminal macroradicals.

In those cases where the activity of the alkyl macroradicals is low, the yield of the monomer is much higher; for example, in the degradation of poly(methyl methacrylate) (PMMA) almost pure monomer is found among the products. The rate constants for the depolymerisation of the terminal macroradicals have been measured in such processes: the rate constant for the breakdown of macroradicals in the photo-degradation of PMMA was measured by Cowley and Melville using the sector method at 167°C [60] and was found to be 5.8×10^{-2} s^{-1}. According to the same authors' estimate, the activation energy is 18.5 kcal $mole^{-1}$. These values agree well with data obtained in the measurements of the rate of decomposition of the radicals $\sim \dot{C}(CH_3)(COOCH_3)$ in PMMA at 20°C. [32] It was found that at a radical concentration of 10^{18} spins g^{-1} the rate of formation of methyl methacrylate is 0.56×10^{15} particles per cm^3 per second; hence the rate constant for the decomposition is 0.56×10^{-3} s^{-1}. According to the data of Cowley and Melville, it should be about 10^{-3} s^{-1} at 20°C. Thus depolymerisation in the solid phase takes place at the same rate as in the liquid phase [9].

Alkoxy-macroradicals. The activation energy for the decomposition of alkoxy-radicals in the gaseous and liquid phases does not exceed 10–12 kcal $mole^{-1}$, [61] i.e. they are much more stable than alkyl radicals.

In the mechanism of the thermal oxidative degradation it is thought that alkoxy-radicals play a leading role in

the dissociation of polymer chains. Thus Tobolsky, who studied the sensitised oxidation of polypropylene (in the absence of branching) at 80°C, established[62] that under these conditions at least one rupture of polymer chain occurs on the average for each oxidation chain. Hence it was concluded that the polymer chain ruptures in the recombination process of peroxy-radicals:

$$R\dot{O}_2 + R\dot{O}_2 \rightarrow 2R\dot{O} + O_2 .$$

The RȮ radicals formed break down with rupture of the polymer chain. Thus the probability of the decomposition of RȮ radicals is close to unity.

In oxidation processes with degenerate branching the principal source of RȮ radicals is the breakdown of hydroperoxide:

$$ROOH + RH \rightarrow (R\dot{O} + \dot{R}_c) + H_2O .$$

A quantitative study of the decomposition products of polypropylene hydroperoxides made it possible to estimate the probability of the breakdown of alkoxy-radicals[59]. It was established that in the decomposition of polypropylene hydroperoxide the amount of oxygen-containing products formed (formaldehyde, acetone, acetaldehyde, etc.), which may be obtained only from terminal hydroperoxides, is about 10–15% of the total amount hydroperoxides decomposed. Hence the yield of oxygen-containing products is equal to $\alpha\beta$, where α is the probability of the decomposition of RȮ radicals and β is the fraction of terminal hydroperoxides relative to the total amount of hydroperoxides; β may be determined as follows.

If it is assumed that in the breakdown of the hydroperoxide $\alpha\dot{R}_t$ and $(1 - \alpha)\,\dot{R}_{in}$ were formed, then these radicals would initiate new oxidation chains of length ν. Each chain, begun by the radical $\dot{R}_t$, contains one R_tOOH molecule and $(\nu - 1)R_{in}OOH$ molecules and the chain begun by $\dot{R}_{in}$ consists entirely of $R_{in}OOH$. Hence $\beta = \alpha/2\nu$ or $\alpha^2/2\nu = 0.10–0.15$. According to Pudov[63], ν at 130°C varies in the range 5–1.5; hence $0.5 \leq \alpha \leq 1$.

Thus the rate of dissociation of the polymer chain in the oxidation of polypropylene must not be less than the rate of decomposition of the hydroperoxides.

Bearing in mind that the probability of the breakdown of the radicals RȮ is high (about 1.0) and the yield of radicals liberated from the cage is low (about 1.7×10^{-2}), one must conclude that the decomposition of these radicals takes place during the lifetime of the cage. If 11 kcal mole^{-1} is adopted for the activation energy for the breakdown of RȮ radicals in polypropylene and about 10^{13} s^{-1} for the pre-exponential factor, it is possible to estimate the lower limit of the lifetime of the cage $(R\dot{O} + \dot{R}_{in})$; it proves to be 10^{-6}–10^{-7} s^{-1}.

A high probability of the dissociation of the chain in the breakdown of the peroxide was observed in the oxidation of polyoxymethylene copolymers at 160°C.[64] In the oxidative thermal degradation of rubbers it was also shown by a kinetic procedure that the probability of the breakdown of alkoxy-radicals is unity[65], i.e. even in rubbers the breakdown of RȮ at 100–130°C is much faster than the recombination in the vapour phase $(RO + \dot{R}_{in})$.

Thus alkoxy-radicals appear to be the principal species responsible for both the formation of volatile degradation products and the dissociation of polymer chains.

The kinetics of the decomposition of peroxy-radicals in Teflon according to the reaction

$$R\dot{O}_2 \rightarrow \dot{R} + O_2$$

were investigated by Voevodskii and coworkers[24]. The rate constant is $k = 10^8 \exp(-20\,000/RT)$ s^{-1}. The energy of the R–OȮ bond in this radical is about 10 kcal mole^{-1}.

We shall now consider the contribution of $R\dot{O}_2$ radicals to chain degradation. In 1959 Neiman and coworkers[66] compared the rates of decomposition of the hydroperoxide in the polymer and the rate of isomerisation of peroxy-radicals and concluded that they are of the same order of magnitude. Recently published data confirm this finding. Chien and Boss[34] showed that in the oxidation of polypropylene at 130°C the steady-state concentrations of the hydroperoxide and peroxy-radicals are 0.30×10^{-6} and 10.2×10^{-6} mole litre^{-1} respectively and the rate constant for the breakdown of the hydroperoxide is 16.5×10^{-4} s^{-1}. If it is assumed that the activation energy for the isomerisation of peroxy-radicals is about 20 kcal mole^{-1}†,[67] it is found that the rates of isomerisation of peroxy-radicals and of the decomposition of the hydroperoxide are comparable. This conclusion is confirmed by the data of Denisov and coworkers[68], according to which the contribution of the isomerisation of $R\dot{O}_2$ to the degradation of polymer chains is about 10%.

6. Cage Effects and Radical Pairs in Solid Polymers

Numerous studies on cage effects in the decomposition of initiators in the liquid phase showed that the probability of the liberation of radicals from the cage or from a radical pair is 0.3–0.7, i.e. 30–70% of the radicals avoid recombination in the cage. The principal mechanism of the liberation of radicals involves diffusion; this is confirmed by the finding that the yield of radicals depends on the viscosity, obeying the Debye–Stokes diffusion equation[69].

The data on the yields of radicals in highly viscous media (including polymers) are somewhat contradictory. In a number of studies yields of radicals close to those observed in the liquid phase are quoted. Haas[70] found that in the decomposition of benzoyl peroxide in polystyrene and poly(vinyl chloride) the probability of the liberation of radicals from the cell is 0.5–0.6. These data agree with the results of Denisov and coworkers[71], according to which about 70% of the radicals recombine in the cage in the breakdown of lauroyl peroxide in solid polystyrene (at 80°C) and about 95–96% in the breakdown of bisazoisobutyronitrile.

It may be expected that the yield of radicals liberated by the diffusion mechanism will be sharply reduced in solid polymers; this is clearly illustrated by the data in Table 7.

Evidently, the fraction of the products of recombination in the cage (t-butyl peroxide) increases with the viscosity of the medium and there is a parallel decrease of the fraction of the products derived from the radicals liberated from the cage (t-butyl alcohol).

In very viscous media relay mechanisms, including the interaction between an active species and the wall of the cage, play a significant role[70,73] supplementing to the diffusion mechanism of the liberation of radicals from the cage. It is useful to estimate the relative contributions of the mechanisms whereby radicals are released from the cage. The migration of low-molecular species by diffusion in polymers is characterised by diffusion coefficients in the range 10^{-7}–10^{-10} cm^2 s^{-1}. The liberation of radicals from the cage via interaction with the cage walls (for example, the abstraction of a hydrogen atom) can also be

†This value is fairly accurate. In fact for $R\dot{O}_2$ we have $\epsilon_{isomer} - \epsilon_{prod} \simeq 8.5$ kcal mole^{-1};[67] when $\epsilon_{prod} \simeq 12$ kcal/mole^{-1}, $\epsilon_{isomer} \simeq 20$ kcal mole^{-1}.

characterised by a "chemical" diffusion constant, which is related to the rate constant for the abstraction of a hydrogen atom by the expression $D = \frac{1}{6}\lambda^2 k'$, where λ is a quantity of the order of magnitude of the intermolecular distance and k' is the frequency of the step involving the abstraction of a hydrogen atom, equal to the product of the rate constant for this reaction k and the polymer concentration (RH).

Table 7. Products of the decomposition of di-t-butyl peroxyoxalate at 35°C.[72]

Medium	Viscosity, cP	Yield of products as t-butoxy-radicals, %		
		t-butyl-peroxide	t-butyl alcohol	acetone
n-Pentane	0.22	4	95	1
Liquid silicone	74	46	46	0.5
Liquid paraffin	80	78	16	0
Polychlorotrifluoroethylene	560	88	2	7
Polyisobutylene	>1000	93	4.6	0

On substituting in this equation the usual values $\lambda \simeq 5$ Å and (RH) $\simeq 10^{22}$ cm^{-3}, we obtain $D \simeq 4 \times 10^{-6} k$. Thus, for the liberation of radicals from the cage by the relay mechanism to be comparable with the liberation by the diffusion mechanism, k must be of the order of 2.5×10^{-14}–10^{-17} cm^3 s^{-1}. Hence it is clear that for mobile species ($D \geq 10^{-7}$ cm^2 s^{-1}) the diffusion mechanism predominates; only in the case of the most reactive radicals can interaction with the cage wall play an appreciable role.

The liberation from the cage of less mobile species probably takes place by both mechanisms, their relative contributions being determined by the reactivity and mobility of the species. This is illustrated by the data of Smirnov et al.[74], who measured the effectiveness of various initiators in liquid and solid acrylate oligo-esters. The effectiveness of bisazoisobutyronitrile diminishes from 0.5 to 0.035 on transition from the liquid to the solid acrylate oligo-ester, while the decrease of the effectiveness of acyl peroxides is only from 0.5 to 0.3. The authors suggest that, for the relatively unreactive radicals $(CH_3)_2\dot{C}CN$, the extent of liberation from the cage is wholly determined by the diffusion of the radical and therefore depends markedly on the viscosity of the medium. On the other hand, for the radicals RCO$\dot{O}$ a relay mechanism plays an important role in the separation of the radical pair and the effectiveness of the initiation depends much less on the viscosity of the medium. It is possible to account for the results of Haas[70] quoted above and other data in a similar manner.

It has recently been shown that radical pairs in the cages can be detected by ESR. In such pairs dipole and exchange interactions take place between the unpaired electrons of the radicals and are reflected in the ESR spectra. The ESR spectra have been reviewed in relation to the theory of biradical systems (including radical pairs)[75]. In radical pairs trapped in crystals the distances between the radicals are rigidly fixed and therefore the energy of the dipole interaction between unpaired electrons is rigorously determined; this dipole splitting is a characteristic feature of the ESR spectra of radical pairs. The average distance between the unpaired electrons is found from the magnitude of the splitting.

In most cases the distance is 4–6 Å.[76] The kinetics of the reaction in pairs of azobutyronitrile radicals were investigated by Lebedev[77]. The probability of the liberation of radicals from the pair at 77°K in azobutyronitrile is about 2×10^{-3}. The rate constant for the "quenching" of the pair, i.e. for the recombination of the radicals in the pair, is given by an expression of the form[76]

$$k = 10^8 \exp(-3500/RT)\ \text{s}^{-1}.$$

Thus in the solid phase even recombination in the pair requires an activation energy, i.e. the lifetime of the radical pair may be fairly long.

In glasses and polymers a fairly wide distribution of separations between radicals in each pair is to be expected. The ESR spectra in such cases are fairly broad and in general it is impossible to detect pairs in the region of the usual ESR transitions ($\Delta M_S = 1$). However, recently radical pairs have been detected in irradiated polymers (polyethylene, polyformaldehyde, polypropylene, etc.) by recording the "forbidden" $\Delta M_S = 2$ signal[78] (this signal corresponds to the simultaneous reorientation of both electron spins in the pair).

It is difficult to determine the concentrations of the pairs from such signals and to investigate the kinetics of their reactions, but the very fact of their detection in polymers is remarkable. The search for the broad signals due to radical pairs corresponding to $\Delta M_S = 1$ is more promising and these have also been observed[78,79].

III. RELATIONS BETWEEN THE KINETICS OF RADICAL REACTIONS AND THE KINETICS OF MOLECULAR MOTION IN POLYMERS

In the previous section convincing evidence was presented showing that in the majority of solid polymers radical recombination occurs by a relay mechanism. At first sight it would appear to follow from this that the kinetics of such reactions must be determined only by the chemical reactivity of the radicals and should not be sensitive to the physical state and the physical properties of the polymer matrix. However, a number of facts are inconsistent with this conclusion. Thus it is known that the temperature ranges in which molecular motion is "unfrozen" (for example, as measured by NMR) are the same as the temperature ranges in which radicals are destroyed. The kinetics of radical recombination in acrylate polyester glasses are qualitatively related to the rigidity of the matrix[29]. The rate of destruction of alkyl radicals in oriented polystyrene is much lower than in the non-oriented polymer[13]. The rate of recombination of PMMA peroxy-radicals in the stressed polymer is much higher than in the polymer subjected to preliminary annealing[5].

The relation between the reaction kinetics and the kinetics of molecular motion is not only qualitative but also quantitative. Thus in PMMA the effective activation energy for the destruction of alkyl radicals is 28 kcal mole^{-1},[26] while the activation energy for segmental motion, measured by NMR, is 27 ± 10 kcal mole^{-1}.[80] In polypropylene the destruction of the radicals in the low-temperature region takes place with an activation energy of 11 kcal mole^{-1}; the activation energy for molecular motion in the same temperature range is (100–250°K) is 13 kcal mole^{-1}. In the high-temperature region (> 250°K) the activation energies are respectively 48 and 58 kcal mole^{-1}.[30] The same behaviour is observed in polyethylene[31]. In the high-temperature region radicals with stereochemical conformations corresponding to a regular spiral are destroyed,

while radicals with a distorted structure, markedly differing from the spiral structure, recombine at low temperatures (they are apparently localised in amorphous regions or structural defects).

Frequently such quantitative correspondance is regarded as proof of a diffusion mechanism for the recombination of radicals and the high activation energies for recombination are usually explained by the co-operative nature of the diffusion, requiring the simultaneous rearrangement of the structure and of the packing of a large number of segments and units of the polymer chains.

However, it should be noted that in the vast majority of such cases pre-exponential factors for the rate constant are anomalously high and are without physical significance. Furthermore, there is a linear relation between the logarithm of the pre-exponential factor (or the entropy of activation) and the energy (enthalpy) of activation, i.e. the compensation effect. Therefore it is clear that the above purely qualitative explanation of the correspondence between the reaction kinetics and the kinetics of molecular motion is inadequate.

Lebedev et al. were the first to draw attention to the compensation effect in the radical recombination reactions in polymers [24]. They proposed an explanation for this effect on the hypothesis that, over the temperature range of the recombination reactions, the activation energy decreases with increasing temperature as a result of changes in the structure of the polymer. The effective activation energy and the pre-exponential factor are then given by the following expressions:

$$\varepsilon_{\text{eff}} = \varepsilon(T) - T\,\partial\varepsilon/\partial T\ , \tag{7}$$

$$k^0_{\text{eff}} = k^0 \exp\left(-\frac{1}{R}\frac{\partial\varepsilon}{\partial T}\right) \tag{8}$$

and are linked by the reciprocal relation $\lg k^0_{\text{eff}} = A + B\epsilon_{\text{eff}}$.

However, this explanation of the compensation effect and the kinetic characteristics of the recombination is valid only within the framework of the hypothesis of a diffusion mechanism for the recombination process. In fact it is necessary to seek kinetic models which would yield the compensation effect within the framework of the relay recombination mechanism, i.e. the compensation effect associated with the rate constants k_t for the relay processes (see Tables 5 and 6).

The following model is the most natural. The reaction of R and RH (or RO_2 and RH) requires that a definite orientation of the reactants—be achieved before the activated complex. Such a "preparatory" state i_p is attained via a series of thermodynamic equilibrium states $i_1, i_2, \ldots, i_{p-1}$, corresponding to different orientations of the reactants. The kinetic mechanism of the reaction can be represented as follows:

$$\dot{R} + RH \overset{K_1}{\rightleftarrows} i_1 \overset{K_2}{\rightleftarrows} \ldots \overset{K_p}{\rightleftarrows} i_p \overset{k_0}{\rightarrow} RH + \dot{R}\ , \tag{9}$$

where K_i are the constants governing the equilibria between the various states and k_0 is the rate constant for the reaction in the "preparatory" state.

It is easy to show that the measured effective rate constant is then $k_{\text{eff}} = k_0 \prod\limits_p K_p$, where $\prod\limits_p$ is the symbol representing the product of the constant K_p for all p states.

In the simplest case one may assume that all the states are of equal importance, i.e. for all the equilibrium constants one may write

$$K_p = e^{\Delta S_p/R} e^{-\Delta H_p/RT}.$$

Then

$$k_{\text{eff}} = k_0^0 \exp(p\,\Delta S_p/R) \exp\left(-\frac{\varepsilon + p\,\Delta H_p}{RT}\right) \tag{10}$$

where k_0^0 and ϵ are the pre-exponential factor and the activation energy for the reaction in state i_p.

Evidently the compensation effect is implied in this equation; furthermore, since the number of states p may depend upon temperature, this equation involves an additional cause of the compensation effect—by the mechanism of Lebedev et al. [24] It is noteworthy that an equation similar to Eqn. (10) can be obtained on the hypothesis that the "pre-start" state is attained by the "simultaneous" rearrangement of a large co-operative group, but within the framework of the model considered above this hypothesis is not essential.

Eqn. (10) also implies a relation between the reaction kinetics and the kinetics of molecular motion. In fact mechanism (9) is applicable to the motion of the polymer segment or a certain probe-species in the polymer matrix (for example a paramagnetic probe [81]) and all the considerations associated with this mechanism are valid. Then for the frequency of motion of the segment (or the probe), we have the equation $\nu_{\text{eff}} = \nu_0 \prod\limits_p K_p$ or

$$\nu_{\text{eff}} = \nu_0^0 \exp(p\,\Delta S/R) \exp\left(-\frac{\varepsilon_r + p\,\Delta H_p}{RT}\right)$$

This equation is analogous to Eqn. (10); here ν_0^0 and ϵ_r are the true pre-exponential factor and the activation energy for the intrinsic motion of the segment or the probe. In particular, if it is found that ϵ and $\epsilon_r \ll p\Delta H_p$, then the effective activation energies for the reaction and molecular motion will be equal; examples of such agreement were quoted at the beginning of this section.

Thus the kinetic model represented by mechanism (9) gives a qualitatively satisfactory description of both the compensation effect and the relation linking the reaction kinetics to the structure of the polymer and the kinetics of molecular motion. It may be supposed that these considerations are in principle applicable to all radical reactions in solid polymers, including reactions in radical pairs.

Finally, the problem of the relation between the reaction kinetics and the structure, properties, and the molecular mobility of the polymers remains one of the most important and fundamental; in this respect hardly anything has been done and almost nothing is known apart from certain general hypotheses. A similar situation is typical also for liquid-phase radical reactions [82]; in both cases the solution of the general kinetic problem is necessary.

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The above review has dealt with almost all the most important radical degradation and stabilisation reactions of polymers, their role in the overall process has been assessed, and their quantitative kinetic characteristics have been described. It is noteworthy that the level achieved in the quantitative kinetics of radical degradation and stabilisation reactions of polymers is fairly low. For the majority of elementary reactions, there are no quantitative data and one must be satisfied with only approximate estimates of the activation energies and rate constants. For many reactions, the available data are very contradictory; this frequently applies not only to the kinetic constants but even to the mechanisms. The most contradictory data concern the chain propagation and termination reactions, degenerate branching reactions, and the

participation of inhibitors in these processes, despite the fact that these reactions are in fact the most important in oxidative thermal degradation.

However, the principal differences between the mechanism of degradation and stabilisation of solid polymers and the mechanism of liquid-phase oxidation are already clear; a kinetic theory for solid-phase reactions has been developed to a degree quite sufficient for the solution of problems associated with the degradation and stabilisation of solid polymers; the physical significance of the solid-phase rate constants and its difference from the physical significance of the "liquid-phase" and "gas-phase" constants are largely clear. Experimental difficulties in the study of elementary radical reactions in solid polymers are also not of fundamental importance in most cases.

Essentially, first steps have now been taken in this field and the principal kinetic problems associated with the specific features of the solid phase have been formulated. The solution of these problems constitutes an important component in the creation of a scientific basis for the stabilisation of polymers.

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