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Some Problems of the Kinetics of Radical Reactions in Solid Polymers

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The kinetics of radical reactions in solid polymers have a number of features which are examined in the present review in relation to the destruction of macroradicals, the reactions of macroradicals with macromolecules, and also the reactions involving low-molecular-weight substances. The mechanism and kinetics of the migration of the free valence in solid polymeric matrices are discussed in detail. Attention is concentrated on the relation between molecular mobility and the kinetics of radical reactions in solid polymers.
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I. INTRODUCTION

Interest in theoretical problems of the kinetics of radical reactions in solid polymeric matrices arose in the period between the 1950's and 1960's in connection with the development of the radiation chemistry of polymers and later in connection with roblems of the stabilisation and modification of polymers and the micromechanics of their decomposition.

The first studies already showed that the kinetics of radical reactions in solid polymers are distinguished by a number of features: they depend to a greater extent than in the liquid phase on the physical properties of the medium, primarily on the molecular mobility; the main ideas about chemical kinetics, developed for reactions in the gas and liquid phases, namely the Law of Mass Action and the Arrhenius equation, in many instances do not hold formally, etc. This makes it necessary to regard the kinetics of radical reactions in solid polymers as an independent branch of chemical kinetics. The problems of the kinetics of radical processes in solid organic low-molecular-weight matrices are related to this field. The results of these studies have been surveyed in a series of reviews and monographs[1-11].

Unusual phenomena have been recently observed in this field, which entailed the creation of new theoretical models; the amount of quantitative kinetic information has increased. The aim of this review is to analyse the present state of the experimental and theoretical studies (primarily those of recent years) on the kinetics of radical reactions in solid polymers, to discover the main characteristics of these processes, and to formulate the main ideas and key problems. At the same time the review does not claim to cover fully the extensive experimental and theoretical data available.

II. KINETICS OF RADICAL REACTIONS IN SOLID POLYMERS

The kinetics of radical reactions in solid polymers are distinguished by a number of phenomenological features.

1. The transition from the liquid phase to solid polymers is frequently accompanied by the replacement of simple kinetic laws by complex laws specific to the solid phase. The most striking example is provided by the so-called stepwise kinetics—the decrease of the reaction rate long before the complete consumption of the reactants ("kinetic arrest"). It is observed in the recombination of radicals and radical pairs, in the addition of oxygen to macroradicals, in radical substitution, etc. The theory of stepwise kinetics has been described[2,10-13]. It is assumed that the observation of stepwise kinetics shows that the reacting species have a range of rate constants†. Therefore, in contrast to the usual kinetics, describing the reaction with the aid of a single "monchromatic" constant, the stepwise kinetics are frequently also referred to as "polychromatic".

2. In most cases the experimental Arrhenius parameters of the rate constants for bimolecular reactions in solid polymers (the effective activation energies and pre-exponential factors) are much higher than the "normal" values characteristic of gas-phase and liquid-phase reactions; they are frequently linked by the compensation relation [the compensation effect (CEF)]:

$$\lg (k_0)_{\text{eff}} = a + bE_{\text{eff}} \quad . \qquad (1)$$

The CEF is common in both chemical kinetics and in the kinetics of certain physical processes (diffusion, viscous flow, molecular mobility, etc.) and has been discussed in a number of studies[1,7,14-18]. In the vast majority of cases the CEF does not have a real physical significance and is merely a consequence of the incorrect application of the Arrhenius equation. The most general idea concerning the origin of the CEF has been put forward by Lebedev et al.[15] If the true activation energy varies with temperature for any reason, then the Arrhenius equation is strictly speaking inapplicable to the analysis of experimental results. However, if the temperature variation of the activation energy ($\partial E/\partial T$) is not too great, then the experimental data can be described formally by the Arrhenius equation within a comparatively narrow temperature range, but the effective values of E_{eff} and $(k_0)_{\text{eff}}$ then obtained differ from the true values:

$$E_{\text{eff}} = E - T(\partial E/\partial T) \quad ,$$
$$(k_0)_{\text{eff}} = k_0 \exp\left(-\frac{1}{R}\frac{\partial E}{\partial T}\right) \quad ,$$

and are linked by the compensation relation (1). If, for example, E = 10 kcal mol^{-1} and $\partial E/\partial T = -0.05$ kcal mol^{-1} K^{-1}, then at 300 K we obtain E_{eff} = 25 kcal mol^{-1}, i.e. 2.5 times greater than the true value. This is compensated by the apparent increase of the pre-exponential factor by a factor of 10^{11}.

†A recent study of the kinetics of the reaction $\dot{C}_2H_5 + O_2 \rightarrow C_2H_5\dot{O}_2$ in solid methanol[14] has shown that this conclusion is not ambiguous. If the stepwise kinetics are due to a range of rate constants, then the decrease of the concentration of $\dot{C}_2H_5$ can be described by the expression

$$[\dot{C}_2H_5] = [\dot{C}_2H_5]_0 \sum g_i \exp(-k_i[O_2]t) \quad ,$$

where g_i is the statistical weight of the rate constant k_i. The $\lg\{[\dot{C}_2H_5]/[C_2H_5]_0\} - [O_2]_t$ kinetic curves obtained for different values of $[O_2]\{[O_2] \gg [C_2H_5]_0\}$ should merge, which is not observed.

Another cause of the appearance of the CEF may be associated with the "polychromaticity" of the reaction kinetics in the solid phase. If the presence of a range of rate constants for the reacting species is caused by the presence of the corresponding range of activation energies, then the compensation effect automatically arises[16,17]. One must note that the CEF can obtain also for a fairly narrow range of rate constants when the "stepwise nature" of the kinetics is not yet observed directly.

3. The absolute values of the rate constants for reactions in solid polymers are in most cases much lower than the rate constants for the analogous reactions in the gas and liquid phases. This applies not only to rapid reactions, whose rates are limited in polymeric matrices by the rate of encounters of the reactants (this is quite natural), but also to the comparatively slow processes occurring under kinetic conditions.

4. As shown below, the kinetics of reactions in solid polymers are associated with the kinetics of molecular movement. In principle, there are two "channels" via which the molecular dynamics of the polymer can influence the kinetics of chemical reactions: (1) the change in the rate constant for the encounters as a result of a change in the coefficients of the translational diffusion of low-molecular-weight reactants as well as macroradicals and macromolecules (in the latter case as a consequence of the change in the frequencies and amplitudes of segmental movements); (2) the influence on the interaction of reacting species in the vapour and in the cage, i.e. on the chemical step proper. The first "channel", transmitting the influence of molecular mobility on the kinetics, is fairly trivial. On the other hand, the direct influence of molecular mobility on the chemical step is of great interest—it is specific to reactions in solid polymers and so far has no analogy in the liquid phase.

Apart from the fundamental characteristics of the kinetics of reactions in solid polymers indicated above, one may also mention a series of other less significant features—the clear kinetic non-equivalence of different regions of the polymer and the non-uniformity of the distribution of the reactants in the specimen (particularly in amorphous-crystalline polymers), which is frequently encountered. These anomalies are associated mainly with the structural-physical inhomogeneity (microheterophase nature) of many polymers and a fairly extensive "freezing" of the diffusion of the reacting species.

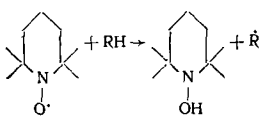
With increase of temperature, the intensity of molecular movement in the polymer increases, while at the same time the typical "solid-phase" stepwise kinetics approach increasingly closely the usual "liquid phase" kinetics. The glass point T_g constitutes the boundary, although the latter is not always sharp. On transition through T_g, a change in the kinetic laws governing the destruction of macroradicals[10], the isomerisation of low-molecular-weight substances in polymeric matrices[19-21], and complex processes such as oxidation[22] and graft polymerisation[23], is observed; there is also a change in the nature of the influence of the external pressure on the kinetics of the recombination of macroradicals[22-25]. At the temperature T_g a break is sometimes observed in the curves for the temperature variation of the rate of decomposition of radical initiators[26] and for the destruction of macroradicals[27,28], as well as for the diffusion coefficients of gases and vapours[29].

The stepwise solid-phase kinetics, which obtain under the conditions where molecular movements are extensively frozen below T_g, have been frequently discussed[1-4,10-13]. On the other hand, the kinetics of reactions in "softer" polymeric matrices, which are of great practical interest, have begun

to be studied extensively only in recent years. In the present review attention will be concentrated on the latter case.

Before considering the kinetics of specific radical reactions in solid polymers, it is necessary to answer the question whether the above kinetic anomalies are due to the high molecular weight of the reacting species or whether they are associated with the phase state of the polymer as a solid. Many factors support the second hypothesis.

1. The rate constants for the reactions of a stable nitroxy-radical, i.e.



with fused polyethylene and its low-temperature analogues (n-heptane and n-hexadecane) are identical at 175–220 °C.[30]

2. The rate constants for the reactions of the t-butoxy-radical with polypropylene, polystyrene, and their low-molecular-weight analogues in solution at 125 °C also hardly differ[31]. At a low temperature (45 °C) certain differences do appear, but they are probably caused by the presence under these conditions of a specific conformation of the macromolecules (coil) which decreases the accessibility of many sections of the macromolecules and is equivalent to a decrease of the effective concentration of the polymer.

3. The rate constants for the destruction of peroxy-macroradicals of polystyrene in solution at 25 °C (1.6×10^5 litre mol^{-1} s^{-1} [32]) and their low-molecular-weight analogues—the peroxy-radicals derived from isopropyl-benzene (10^4–10^5 litre mol^{-1} s^{-1} [33,34])—are very similar.

On the other hand, many kinetic features of the radical reactions in solid polymers are observed also in those cases where both reactants are low-molecular-weight substances (see Section III below) and also for reactions in solid low-molecular-weight matrices[1–3,8]. Thus the main cause of the kinetic anomalies of reactions in solid polymeric matrices is associated with the characteristics of the phase state of the above systems, mainly with the restriction of the molecular movement.

III. REACTIONS INVOLVING LOW-MOLECULAR-WEIGHT SUBSTANCES

The characteristic features of these reactions consist in the fact that at least one of the reactants migrates comparatively readily in the polymer via physical diffusion and the rate of the process is limited by the encounters of the reactants only for fairly rapid reactions. However, since the diffusion coefficients of low-molecular-weight substances in solid polymers are nevertheless lower than in liquids, the boundary at which the kinetics change to the diffusion-dependent type shifts to the region of slower reactions. For the majority of processes involving low-molecular-weight substances, the problem of their chemical nature does not arise and the kinetic information obtained can be referred to a specific elementary reaction.

The theory of diffusion-controlled reactions in solid matrices (including polymeric matrices) has been considered in a number of studies[2,7,10,35,36] and in the most general form by Whaite[37]. For a bimolecular reaction between A and B, where B is a low-molecular-weight substance, it is possible to distinguish three stages:

(1) the macrodiffusional stage in which the reactants are non-uniformly distributed in the given volume and B diffuses as a consequence of its concentration gradient;

(2) the microdiffusional stage—there is no concentration gradient and the rate of the process is determined by the rate of encounters of A and B, the encounters resulting in the formation of the pair [A...B];

(3) the kinetic stage—chemical interaction in the pair.

The case where there is no concentration gradient is of greater interest. According to the simplest model[35], chemical interaction takes place when A and B enter a single cage with a volume v^* (of the order of magnitude of the molecular volume). In the quasi-stationary approximation, we obtain the following expression for the concentration of the pairs [A...B]:

$$-d[A]/dt = -d[B]/dt = k_{eff}[A][B] \quad ,$$

$$k_{eff} = \frac{k_d k_x}{k_d + k_x} v^* \quad , \qquad (2)$$

where k_d and k_x are the rate constants for the microdiffusional and chemical stages. If $k_d \ll k_x$, then $k_{eff} \cong k_d v^*$ (stage 2 is rate-limiting); on the other hand, if $k_d \gg k_x$, then $k_{eff} \cong k_x v^*$ (stage 3 is rate-limiting). In the general case k_d and k_x are combined in accordance with the law of kinetic resistances [Eqn.(2)].

Although there are extensive experimental data on reactions with participation of low-molecular-weight substances, a large proportion of these are either qualitative or the kinetics have been studied under specific conditions (mechanodegradation, low temperature#), which preclude a sufficiently rigorous comparison of the rate constants obtained with the corresponding parameters of the liquid-phase reactions.

Fairly numerous studies have been made on the addition of oxygen to macroradicals. This process is of interest for the kinetics of the oxidation of polymers. The rate constants for the interaction of O_3 with alkyl radicals in the liquid phase are large ($\sim 10^8$ litre mol^{-1} s^{-1} [33]) and therefore in solid polymers, where the diffusion coefficients of O_2 are significantly lower than in a liquid, this reaction usually proceeds under diffusion-dependent conditions[36,40–42]. Thus in polystyrene the rate of addition of O_2 is independent of the nature of the radicals[40]. The diffusion coefficients of O_2, obtained on the basis of the kinetics of the reaction $\dot{R} + O_2 \rightarrow R\dot{O}_2$, are close to the values found by independent methods. For example, D_{O_2}, obtained on the basis of the kinetics of the oxidation of allyl macroradicals in the amorphous phase of γ-irradiated polyethylene, is 1×10^{-10} cm^2 s^{-1} at 190 K,[41] while direct measurements of D_{O_2} [43] yielded 5×10^{-11} cm^{-2} s^{-1} (extrapolation to 190 K). The stepwise kinetics of the oxidation of macroradicals are observed at low temperatures[40,42], which agrees with the "stepwise" nature of the diffusion of oxygen itself[44]. However, according to Bresler and Kazbekov's data[3], the interaction of O_2 with the macroradicals of poly(methyl methacrylate), polystyrene, and poly(vinylacetate), obtained in the mechanodegradation of polymers, takes place under kinetic conditions and the observed rate constants are clearly lower than the diffusion-dependent values.

#At low temperatures tunnel effects can be significant[38,39].

Table 1. The rate constants for the reactions of low-molecular-weight substances in solid polymers and in the liquid phase (at 25 °C).

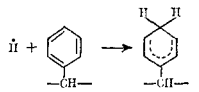
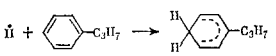
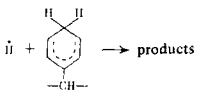
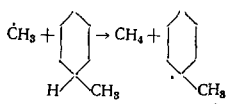
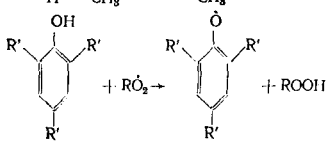
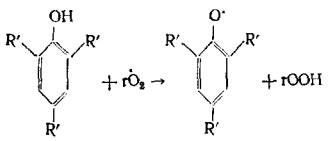
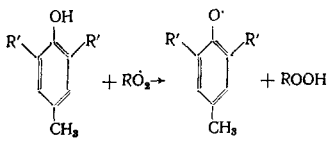
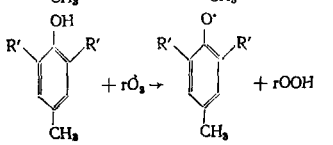
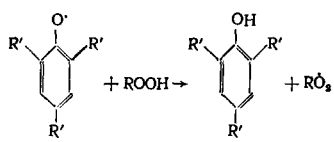
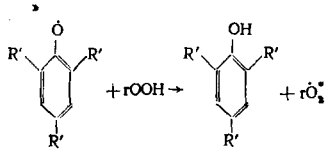
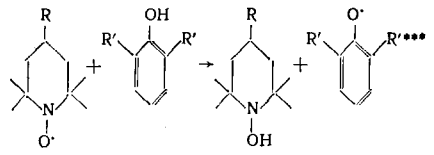
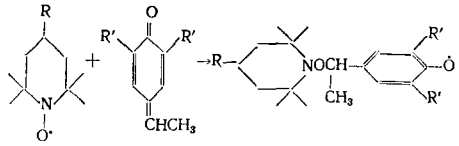
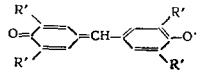
Reaction	Polymer or solvent	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1} s^{-1}	References
	polystyrene	$0.4\cdot10^4$	1,3	$1\cdot10^4$	[48]
	n-heptane	—	—	$3.3\cdot10^8$(23°)	[33]
	polystyrene	$1.2\cdot10^6$	0.8	$3.2\cdot10^5$	[48]
$\dot{H}$ + radicals → products	liquid phase	—	—	$>10^8$	[33]
$\dot{C}H_3+RH\rightarrow CH_4+\dot{R}$	polypropylene	$2.7\cdot10^{11}$	20 6	0.2(100°)	[49]
	n-heptane	$7\,3\cdot10^9$	10.7	$3.8\cdot10^3$(100°)	[33]
	polypropylene	$6.3\cdot10^{15}$	19.8	$3.2\cdot10^3$(80°)	[46]
	ethylbenzene	$8\,8\cdot10^6$	4.1	$2.5\cdot10^4$(80°)	[50]
	polypropylene	—	—	$8.1\cdot10^3$(115°)	[51]
	ethylbenzene	$3.7\cdot10^7$	4.9	$6.5\cdot10^4$(115°)	[50]
	polypropylene	$2,5\cdot10^9$	16,0	$4,5\cdot10^{-3}$	[52]
ditto	polypropylene	$9,7\cdot10^{15}$	26,6	$3,1\cdot10^{-4}$	[46]
»	polyethylene	$2,5\cdot10^{10}$	16,5	$2\cdot10^{-2}$	[52]
	benzene	$3,3\cdot10^6$	9,6	0,30	[45]

Table 1 (cont'd).

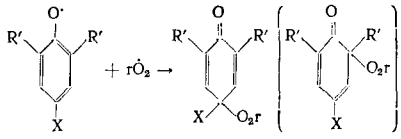
Reaction	Polymer or solvent	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1} s^{-1}	References
$\dot{G} + ROOH \rightarrow RO_2^{\cdot} + GH$ **	polypropylene	$1{,}7 \cdot 10^{11}$	23,5	$1{,}1 \cdot 10^{-4}$	[53]
ditto	solution of polypropylene hydroperoxide in benzene	$1{,}6 \cdot 10^{5}$	10,0	$6{,}8 \cdot 10^{-3}$	[54]
	polypropylene	$5 \cdot 10^{8}$	18,0	$3 \cdot 10^{-5}$	[55]
ditto	benzene	$1{,}3 \cdot 10^{4}$	10.0	$5.6 \cdot 10^{-4}$	[55]
	polypropylene	$1.6 \cdot 10^{4}$	11.0	$1.4 \cdot 10^{-4}$	[56]
	benzene	$1.6 \cdot 10^{2}$	7.0	$1.2 \cdot 10^{-3}$	[56]

*Reaction with t-butyl hydroperoxide.

**$\dot{G}$ = galvinoxyl 

***R = $-COC_6H_5$.

Under diffusional conditions, the phenoxy-radicals apparently recombine with the macroradicals. In the liquid phase the rate constants for the reaction



(here and henceforth R′ = t-Bu in structural formulae) are close to 10^8 litre mol^{-1} s^{-1};[45] in solid polypropylene this quantity is significantly reduced: $k = 6 \times 10^6$ litre mol^{-1} s^{-1} for X = $C(CH_3)_3$ at 80 °C.[46] The diffusion coefficient of the 2,4,6-tri-t-butylphenoxy-radical estimated from these data (2.5×10^{-8} cm^2 s^{-1} at 80 °C) agrees with the diffusion coefficient of ionol, which has a similar molecular weight, measured directly in this polymer[47].

The reactions occurring under kinetic conditions are of much greater interest for the theory of radical reactions in solid polymers (Table 1). The data presented in Table 1 must be treated with extremely great caution. One of the reasons for this is that one cannot always eliminate from the polymer the residual amount of the solvents usually employed for the introduction of low-molecular-weight substances into the polymer. As will be shown below, sometimes even traces of the solvent are capable of greatly increasing the rates of reaction in solid polymers. For this reason, the measured rate constants[52,53,55,56] must be regarded as merely the upper limits of the true rate constants in solid polymeric matrices.

The first feature to which attention is drawn in the analysis of the data in Table 1 is a significant decrease (by a factor up to ~10^4) of the rate constants for reactions in solid polymers compared with the liquid phase. In most cases this is caused by the increase of the activation energy (the CEF is then usually observed); on the other hand, for reactions of hydrogen atoms, this is caused by the decrease of the pre-exponential factor§. We emphasise yet again that the decrease of the rate constants on transition to solid polymers, noted above, is in no way associated with diffusion-dependent obstacles—in certain cases (for example, in reactions of the methyl radical with polymers, of phenoxy-radicals with polymeric hydroperoxides, and of nitroxy-radicals with phenols) the rate constants for the encounters of the reactants, estimated from the diffusion coefficients of the corresponding low-molecular-weight substances exceed the experimental constants by 5–10 orders of magnitude.

Another characteristic feature of reactions involving low-molecular-weight substances, which was first observed by Karpukhin et al.[57], is some levelling of the reactivities of reactants having similar structures. Thus the rate constants for the reactions of peroxy-macroradicals with oxidation inhibitors (phenols, aromatic amines) in the solid polymers differ much less than in the liquid phase[46,50,57,59]. This phenomenon can hardly be explained by the fact that the above reactions proceed under diffusional conditions. This is particularly evident for reactions in the comparatively "soft" polypropylene at high temperatures, where the calculated rate constants for the encounters of the inhibitors with peroxy-radicals exceed the experimental reaction rate constants by a factor of 10^2–10^3.

§We may note that the rate constants for the reactions of hydrogen atoms have been measured at a low temperature where the tunnel mechanism frequently operates[38,39] and low pre-exponential factors are in fact characteristic of the tunnel mechanism.

The influence of molecular mobility on the rates of reactions involving low-molecular-weight radicals is extremely interesting. The rate constants for the reactions of phenoxy-radicals with polyolefin hydroperoxides[52,53] and of the nitroxy-radical with phenolic compounds[55] and methylenequinone[56] increase appreciably (the pre-exponential factors and activation energies diminish) after the addition of small amounts of chemically inert aromatic solvents and gradually approach the "liquid-phase" values (Table 2). The role of solvents, plasticising the polymer, evidently reduces to increasing the molecular mobility. Indeed the increase of the rate constants is correlated with the increase of the rotational frequency of the paramagnetic probe[52,55,56], characterising the intensity of the segmental movements in the polymer (Fig. 1). Since the above reactions are known to occur under kinetic conditions, one must consider the influence of molecular mobility directly on the chemical step. Presumably the decrease of the rate constants for the other reactions in Table 1, on passing from the liquid phase to the solid polymer, is also associated mainly with the decrease of molecular mobility.

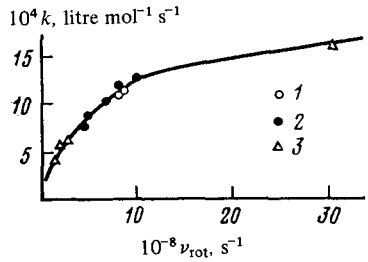


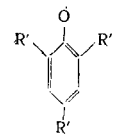
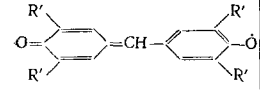
Figure 1. Dependence of the rate constant for the reaction of the 4-benzoyl-2,2,6,6-tetramethylpiperidinyloxy-radical with 2,4-di-t-butylphenol at 60 °C in polymer matrices [*1*) polyethylene; 2) polypropylene; 3) polystyrene] on the rotation frequency of the nitroxy-radical ν_{rot} (according to the data of Griva et al.[55]).

IV. DESTRUCTION OF MACRORADICALS

Although the number of studies devoted to the kinetics of the destruction of radicals in solid polymers is very large (they have been surveyed in a number of reviews[4,6-8,10-12]), only comparatively few of them define sufficiently clearly the experimental conditions: the nature of the radicals, their location and spatial distribution (the latter is particularly significant when the radicals are generated by ionising radiation), the concentration of low-molecular-weight substances, which can significantly influence the kinetics of the destruction process, as will be shown below, etc. We were therefore forced to approach very cautiously the discussion of the extensive experimental data, preference being given to studies in which the experimental conditions have been defined sufficiently unambiguously.

At temperatures below T_g the rate of destruction of radicals is usually low and is frequently described by stepwise kinetics. Above T_g, the usual bimolecular kinetics are as a rule observed¶, but the rate constants for the destruction of microradicals (k_t) are almost always lower than the corresponding constants in the liquid phase†, the effective activation energies are high, sometimes reaching 30–40 kcal mol^{-1}, and the CEF is usually observed. The kinetics of the destruction process are strongly influenced by factors which alter the intensity of the molecular movements in the polymer–orientation, mechanical deformation, external pressure, plasticisation, etc. (for further details, see below).

Table 2. The influence of benzene on the rate constants for the reactions of phenoxy-radicals with polypropylene hydroperoxide at 25 °C.

Phenoxy-radical	$[C_6H_6]$, %	k_0, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k, litre mol^{-1}	References
	0	$9.7\cdot10^{15}$	26.6	$3.1\cdot10^{-4}$	[46]
	≤0.4	$2.5\cdot10^{9}$	16.0	$3.5\cdot10^{-3}$	[52]
	8	$6.3\cdot10^{7}$	12.5	$3.8\cdot10^{-2}$	[52]
	100	$3.3\cdot10^{6}$	9.6	0.30	[45]*
	0	$1.7\cdot10^{11}$	23.5	$1.1\cdot10^{-4}$	[53]
	10	$5.2\cdot10^{4}$	9.5	$5.5\cdot10^{-3}$	[53]
	100	$1.6\cdot10^{5}$	10.0	$6.8\cdot10^{-3}$	[54]

*For the reaction with t-butyl hydroperoxide.

In solid polymers the rate of destruction of macroradicals is usually limited by the rate of their encounters and the problem of the kinetics of the destruction process thus reduces to the problem of the mechanism and kinetics of the processes leading to the encounters. For this reason, the study of the destruction of macroradicals yields information about the physical and chemical processes resulting in the migration of the free valence in the solid polymer rather than about the nature of the elementary step. One can imagine two fundamental mechanisms of such migration—physical diffusion of macroradicals and chemical migration of the free valence (relay process, "chemical" diffusion), which takes place as a result of the alternation of chemical reactions.

The rate constant k_e for the encounter of the radicals $\dot{R}_A$ and $\dot{R}_B$ is related to their diffusion coefficients (physical or "chemical" diffusion) D_A and D_B (cm^2 s^{-1}) by the

¶Faster initial sections are frequently noted, which is characteristic of diffusion-controlled processes[10,37].

†In the liquid phase the recombination (disproportionation) rate constants are usually 10^8–10^9 litre mol^{-1} s^{-1}, while the activation energies are close to zero. Peroxy-radicals are an exception; the rate constants for their destruction are significantly lower, particularly for tertiary peroxy-radicals (10^3–10^5 litre mol^{-1} s^{-1}, activation energies up to 8–10 kcal mol^{-1}).[33,59].

Smoluchowski equation:

$$k_e = 4\pi a(D_A + D_B)6\cdot 10^{20} \quad \text{(litre mol}^{-1}\text{ s}^{-1}\text{)},$$

where a is the effective distance (cm) over which the radicals interact chemically. If $D_A = D_B = D$, then

$$k_e \simeq 1.5\cdot 10^{22} aD \quad \text{(litre mol}^{-1}\text{ s}^{-1}\text{)}.$$

In the chemical migration the physical significance of the quantity D depends on the specific migration mechanism (see below), but in any case D is an effective parameter characterising the rate of migration of the free valence. As in the liquid phase, the quantity a is close to the kinetic diameter of small molecules (3–5 Å)#. The possible mechanisms of the encounters are examined below.

1. Physical Diffusion

At temperatures above T_g the intensity of small-scale molecular movements in polymers is fairly high and does not differ in principle from that in viscous liquids. For example, the rotation of stable nitroxy-radicals (the paramagnetic probe), controlled by the low-amplitude movements of elements of the macromolecules, takes place at a frequency in excess of 10^9 s^{-1} in polypropylene and polyethylene at temperatures in excess of 60 °C.[71–73]. According to high-resolution neutron spectroscopic data[74], the hydrogen atoms in the C–H bonds in the amorphous phase of polyethylene execute random movements about the equilibrium position with an amplitude of 2.5 Å and a frequency of $5 \times 10^{12} \exp(-4500/RT)$ ($\sim 5 \times 10^9$ s^{-1} at 60 °C), which is close to the rotation frequency of the paramagnetic probe. However, with the exception of radical pairs, the average distance between the radicals almost always significantly exceeds 3–5 Å and movements with this amplitude cannot therefore by themselves ensure the encounter of the radicals.

The movements of segments of the macromolecules are characterised by a much greater amplitude (up to 30 Å), but the diffusion coefficients corresponding to this type of molecular mobility are usually fairly low even at temperatures above T_g. Thus $D \cong 10^{-21}$ cm^2 s^{-1} near T_g in polystyrene[65]. In the comparatively "soft" polyethylene at 60 °C (higher by 60–80 °C than T_g) we have $D \cong 10^{-18}$ cm^2 s^{-1},[60] which corresponds to a rate constant for the encounters (for $a = 5$ Å) $k_e \cong 10^{-3}$ litre mol^{-1} s^{-1}; on the other hand, the experimental value of k_t for the destruction of peroxy-radicals under the same conditions is greater by 7 orders of magnitude[61]. This constitutes a further reason why there is no point in considering the diffusional mechanism of the encounters of macroradicals in the crystalline phase or in the amorphous phase at temperatures T_g, because the intensity of the segmental movements is then negligible. One must note that in many instances of practical importance (for example, in the oxidation of polyolefins[75]) the average distance between the radicals amounts to hundreds of angstroms and their encounters cannot be ensured by physical diffusion alone even in principle.

The absence of a dependence of the rate of destruction of macroradicals on their nature is a virtually unambiguous criterion of the diffusional mechanism of the encounters. This case apparently obtains above T_g in isobutylene and in the ethylene–propene copolymer, where the rate constants for the destruction of alkyl and peroxy-radicals are similar and the frequencies of the diffusional jumps calculated from the kinetic data for the destruction process are of the same order of magnitude as the frequencies of the segmental movements determined by independent methods[10]. On the other hand, the rate constants for the destruction of macroradicals usually depend greatly on their nature (Table 3) and this phenomenon cannot be accounted for by a change in the probability of reaction on encounter, because the peroxy-radicals, for which the destruction rate constants in the liquid phase are significantly lower than for other active radicals, are in fact destroyed at the highest rate[33]. A diffusional mechanism of the encounters can be postulated for radicals with a low reactivity (for example, the allyl radicals in polyethylene[60]), whose chemical migration is unlikely.

Table 3. The rate constants for the destruction of certain macroradicals (at 60 °C).

Polymer	Radical	t, °C	$(k_t)_0$, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k_t, litre mol^{-1} s^{-1}	Refs.
PE**	allyl	60÷100	$1.6\cdot 10^{21}$	35.0***	$1.6\cdot 10^{-2}$	
PE**	$RO_2^{\cdot}$	−5÷+24	$1.4\cdot 10^{16}$	18.5	$1\cdot 10^4$	[61]
i-PP**	$RO_2^{\cdot}$	25÷102	$3.2\cdot 10^{21}$	28.5	$6\cdot 10^2$	[62]
i-PP****	$RO_2^{\cdot}$	50÷90	$5\cdot 10^{15}$	24.7	$4.5\cdot 10^{-3}$	[63]
a-PP	$RO_2^{\cdot}$	45÷63	$1.3\cdot 10^{11}$	13.0	$3.6\cdot 10^2$	[64]
PS	alkyl	40÷100	$1\cdot 10^{15}$	24.0	0.18	[65]
PS	$RO_2^{\cdot}$	−25÷+14	$1.4\cdot 10^{10}$	13.0*****	40	—
PS	$RO_2^{\cdot}$	−8÷+10	$1\cdot 10^{14}$	17.6	$2.5\cdot 10^2$	[66]
PMMA	$\sim CH_2\dot{C}(CH_3)COOCH_3$	−40÷100	$1.5\cdot 10^{17}$	29.0	$1.5\cdot 10^{-2}$	[65]
PMMA	$RO_2^{\cdot}$	5÷37	$2\cdot 10^{13}$	19.2*****	5	—
PMMA	$RO_2^{\cdot}$	−22÷15	$2.5\cdot 10^{12}$	17.0	18	[67]
Nylon-6	alkyl	−3÷47	$1.3\cdot 10^9$	12.0	16	[68]
Nylon-6	$RO_2^{\cdot}$	−40÷+25	$1.6\cdot 10^{14}$	14.6******	$3\cdot 10^3$	—
PVA	alkyl	20÷61	$1\cdot 10^{15}$	23.0	0.8	[65]
PVA	$RO_2^{\cdot}$	−17÷37	$2\cdot 10^{10}$	13.5*****	28	—
PIB	alkyl and $RO_2^{\cdot}$	−63÷−23	$1.9\cdot 10^{17}$	18.0	11(−30°)	[10]
EPC	alkyl and $RO_2^{\cdot}$	−63÷−23	$3\cdot 10^{21}$	22.0	46(−30°)	[10]

*PE = polyethylene; *i*-PP = isotactic polypropylene; *a*-PP = atactic polypropylene; PS = polystyrene; PMMA = poly(methyl methacrylate); PVA = poly(vinyl acetate); PIB = polyisobutylene; EPC = ethylene–propene copolymer.
**In the amorphous phase.
***Calculated from data of Wenn et al.[60]
****In the crystalline phase.
*****Calculated from data of Bresler et al.[65]
******Calculated from data of Davydov et al.[69]

Analysis of experimental data suggests that the diffusional mechanism of the destruction of macroradicals in solid polymers is more an exception than the rule, and that in most cases neither the amplitude nor the intensity of the molecular movements can ensure the encounter of the radicals. From the standpoint of the diffusional mechanism of the migration of the free valence, the acceleration of the destruction of macroradicals in the presence of low

#According to Butyagin[70], the quantity a reaches 75 Å in polymers. Such high values of a, which evidently have no physical significance, are apparently obtained as a result of the not entirely correct application of Waite's diffusional model[37] to the analysis of experimental data for the kinetics of the destruction of macroradicals.

concentrations of chemically active low-molecular-weight substances (H_2, O_2, Cl_2, cumenyl hydroperoxide, monomers, etc.) is completely inexplicable. There is no doubt that the main mechanism ensuring the encounter of macroradicals in solid polymers at not unduly high temperatures is "chemical" diffusion.

2. The Relay Migration of the Free Valence with Participation of Macroradicals Alone

This version of "chemical" diffusion has been most widely discussed in the literature. The migration of free valence can be achieved as a result of a sequence of identical-transfer reactions, for example, for alkyl radicals in polyethylene:

$$\sim CH_2\dot{C}HCH_2 \sim + \sim CH_2CH_2CH_2 \sim \rightarrow \sim CH_2CH_2\dot{C}H_2 \sim + \sim CH_2\dot{C}HCH_2 \sim \quad (3)$$

or the repetition of a cycle of reactions, for example for the destruction of peroxy-radicals:

$$R\dot{O}_2 + RH \rightarrow \dot{R} + ROOH \quad , \quad (4)$$

$$\dot{R} + O_2 \xrightarrow{\text{fast}} R\dot{O}_2 \quad . \quad (5)$$

We shall refer to this type of migration mechanism as trivial relay; it has been proposed by Dole et al.[76] and Koritskii et al.[77] and subsequently developed[7,65,78]. The effective diffusion coefficient, characterising the trivial relay, is defined by the expression

$$D_r = \frac{\lambda_r^2 k_p [RH]}{6} \quad ,$$

where λ_r is the average distance over which the free valence migrates during a single "step" (of the order of magnitude of the length of a chemical bond), k_p is the rate constant for the rate-limiting reaction in the relay process [for example, reaction (3) or (4)] and [RH] is the concentration of the monomeric unit; the product k_p[RH] has the significance of the jump frequency. The rate constant for encounters is given by the following expression:

$$k_e = \frac{8\pi a \lambda_r^3 k_p [RH]}{6} 6 \cdot 10^{20} \simeq 2.5 \cdot 10^{21} a \lambda_r^3 k_p [RH] \text{ (litre mol}^{-1}\text{ s}^{-1}\text{)}. \quad (6)$$

The principal argument in support of the trivial relay is the sharp increase of the constant k_t in the series of radicals allyl < alkyl < peroxy,[8] in qualitative agreement with the variation of k_p in the same sequence[33].

The most significant experimental confirmation of this mechanism of the migration of the free valence is available for peroxy-radicals. The destruction of peroxy-macroradicals is accompanied by the chain process involving the absorption of O_2 and the formation of a hydroperoxide[7,79,80]. In fact the chain oxidation of polymers is itself a process involving the relay migration of the free valence.

Oxygen in many instances accelerates the destruction of alkyl macroradicals even when the concentration of peroxy-radicals is too low to be detected by EPR.[81-83]. This is possible if the rate of reaction (5) is comparatively low and the chain propagation reaction (4) is in fact very effective. Analysis of this situation shows[81,82] that the kinetics of the destruction of alkyl radicals should obey a bimolecular law and the effective rate constant should be proportional to the oxygen concentration, which agrees with experiments[81].

Comparison of the experimental values of k_t and k_e, calculated by Eqn.(6), is possible only in rare instances, since accurate values of the rate constant k_p in solid polymers, necessary for the calculation of k_e, are usually unknown.

Sufficiently reliable values of k_t and k_p are available for peroxy-radicals in amorphous atactic polypropylene[64] and in the amorphous phase of isotactic polypropylene[62,80,84]. It has been shown[62,85] that at 60 °C $k_t = 6 \times 10^2$ litre mol^{-1} s^{-1} and $k_p = 1.5 \times 10^{-2}$ litre mol^{-1} s^{-1}. Assuming that $\lambda_r = 3 \times 10^{-8}$ cm, $a = 5 \times 10^{-8}$ cm, and [RH] = 22 M, we find $k_e = 3.7 \times 10^{-2}$ litre mol^{-1} s^{-1} from Eqn.(6), i.e. lower by 4 orders of magnitude than the experimental value of k_t. A similar result has been obtained also for atactic polypropylene. In order to achieve agreement between k_e and k_t, it is necessary to assume that, under the given conditions, the "step" of the relay is $\lambda_r \cong 400$ Å, which is naturally unrealistic within the framework of the trivial relay.

An unusual version of the relay mechanism of the migration of the free valence obtains under the conditions of graft polymerisation. When the monomer M is brought into contact with a polymer containing stabilised macroradicals $\dot{R}_p$, a chain polymerisation process develops:

$$\dot{R}_p + M \rightarrow [\dot{R}_M]_1$$
$$\cdots\cdots\cdots$$
$$[R_M]_i + M \xrightarrow{k_{po}} [\dot{R}_M]_{i+1} \quad .$$

This process is accompanied by an appreciable acceleration of the destruction of macroradicals.

One chain propagation step leads to the migration of the free valence over a distance λ_{po}, equal to two chemical bond lengths (~2–3 Å); the jump frequency is evidently k_{po}[M]. Then the effective diffusion coefficient for the migration of the free valence is $D_{po} = \lambda_{po}^2 k_{po}$[M]/6 while the bimolecular rate constant for the encounters of the radicals is

$$k_e = 2.5 \cdot 10^{21} a \lambda_{po}^3 k_p [M] \quad .$$

This mechanism of the migration of the free valence is in essence similar to that of migration with participation of macroradicals alone. The difference is that the slow stage of the relay

$$\dot{R}\,(R\dot{O}_2) + RH \xrightarrow{k_p} RH\,(ROOH) + \dot{R}$$

is replaced by the much faster polymerisation chain propagation reaction. The ratio of the rate constants for the encounters determined by chain polymerisation and the trivial relay mechanism, which amounts to k_{po}[M]/k_p[RH], can be fairly large even for [M] ≪ [RH], because the ratio k_{po}/k_p for vinyl monomers reaches 10^3–10^5.[33]

The results of the study of the kinetics of the destruction of macroradicals in the postpolymerisation of tetrafluoroethylene on γ-irradiated Teflon[87] agree satisfactorily with the analysis presented above.

3. The Relay-Diffusion Mechanism of the Migration of the Free Valence

As shown in the preceding section, the simplest variant of "chemical" diffusion—the trivial relay—is usually unsatisfactory. Firstly, the trivial relay does not explain the fairly large "step" in the relay, reaching sometimes hundreds of angstroms, and the high absolute rates of migration of the free valence observed in many cases. Secondly, in this variant of "chemical" diffusion, purely physical stages of the migration of the free valence are in essence ignored, which, as a rule, prevents a quantitative explanation of the clear relation between the kinetics of the destruction of radicals and molecular mobility. The idea that mobility influences the chemical step proper in the valence transfer reaction does not always help. The calculation of the rate constants for encounters by Eqn.(6), even

when "liquid-phase" rate constants for the transfer of valence k_p (which is apparently the upper limit of this quantity in solid polymers[88]) are used, leads to values of k_e which are in many instances lower by several orders of magnitude than the experimental k_t.

We shall consider the relay-diffusion model of the migration of the free valence in which the chemical relay is combined with the diffusional migration of segments (Fig.2). As an example, we shall consider reaction (3). As a result of the thermal movement of the segments, both the radical centre $-\dot{C}H-$ (black circle) and the $-CH_2-$reaction group (open circle) are capable of migrating within a sphere having a radius λ_s of the order of magnitude of the size of the segment. This single reaction step can result in the transfer of the free valence over a distance up to $2\lambda_s$. Depending on the ratio of the frequencies of segmental movements (ν_s) and relay transfer steps $\{k_p[RH]\}$, the followng extreme situations are possible. If $\lambda_s \ll k_p[RH]$ (molecular mobility is greatly reduced), then the segmental movements should not contribute much to the migration process and this case will not differ from the trivial relay considered in the previous section. If the segmental mobility is high $\{\nu_s \gg k_p[RH]\}$, then during a period $1/k_p[RH]$ between two elementary steps in the transfer of the free valence, the reaction centres have sufficient time to move around the entire sphere with a radius λ_s and during a single "step" of the relay the free valence migrates not over a distance λ_r but over a much larger distance in the range $\lambda_r < \overline{\lambda}_s \leq 2\lambda_s$. Thus the chemical relay takes place with a step close to the characteristic amplitude of the segmental movements. The analytical expression for the rate constant for encounters is analogous to the Eqn.(6), it being only necessary to replace λ_r by $\overline{\lambda}_s$. If the frequencies of the segmental movements and of the relay are comparable, then k_e has an intermediate value.

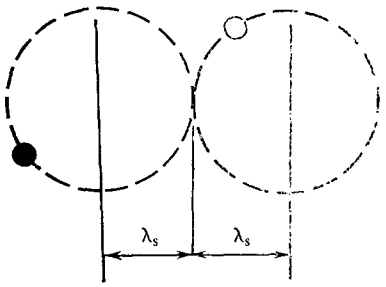


Figure 2. Illustration of the relay-diffusional model of the destruction of macroradicals in solid polymers.

It must be emphasised that in the mechanism of the transfer of the free valence considered here the decisive factor remains the chemical relay, the segmental mobility ensuring only a much larger step in the relay. The relay-diffusion mechanism agrees with the idea that diffusion-controlled stages are present in this process—the stages comprising the movements of the segments are of this kind. In very "rigid" polymers, where even a limited segmental mobility is virtually absent, the step of the relay is $\lambda \cong 1.5$–3 Å and the migration of valence is ensured solely by the chemical reaction (trivial relay). In "soft" polymers the amplitude of segmental movements is large ($\overline{\lambda}_s$ up to 60 Å), which, in principle, can ensure fairly high rates of migration.

Since the effective diffusion coefficient of the free valence is proportional to λ^2, even a comparatively small increase of the parameter λ leads to an appreciable increase in the rate of migration of the free valence compared with the trivial relay—in the limit by a factor $(2\lambda_s/\lambda_r)^2$. This can evidently still prove to be inadequate to explain the very rapid macroradical destruction processes. For example, in the case of the destruction of peroxy-radicals in polypropylene at 60 °C considered in the previous section {$k_p = 1.5 \times 10^{-2}$ litre mol^{-1} s^{-1}, [RH] = 22 M, $a = 5 \times 10^{-8}$ cm}, k_e is only 15 litre mol^{-1} s^{-1} even for $\lambda_r = 2\lambda_s = 60$ Å, which is lower by a factor of 40 than the experimental value $k_t = 6 \times 10^2$ litre mol^{-1} s^{-1}.

4. Migration of the Free Valence with Participation of Low-Molecular-Weight Radicals (Kinetic Analysis)

The constant k_e can increase sharply if low-molecular-weight radicals, with a much greater mobility than macroradicals and therefore capable of migrating over comparatively long distances in the solid polymer, participate in the migration processes. The analytical expressions for D_r and k_e depend on the mechanism of the formation of light radicals. We shall consider three versions: chain transfer to the low-molecular-weight admixture, the dissociation of macroradicals, and the formation of light radicals in the decomposition of the initiator.

The case of the transfer of the free valence to a low-molecular-weight admixture rH as a result of the reaction

$$\dot{R} + rH \xrightarrow{k_1} RH + \dot{r} \qquad (7)$$

has already been considered[89]. If $\dot{r}$ disappears mainly in the reverse free valence transfer reaction

$$\dot{r} + RH \xrightarrow{k_2} rH + \dot{R} \quad , \qquad (8)$$

then its lifetime between elementary steps of reactions (7) and (8) is $\tau = 1/k_2[RH]$. During the time τ, the radical $\dot{r}$ (its diffusion coefficient is D_0) makes a jump over a distance

$$\lambda = \sqrt{6D_0\tau} = \sqrt{6D_0/k_2[RH]}$$

and the frequency of these jumps is evidently $\nu = k_1[RH]$. For the effective diffusion coefficient of the free valence, one can write

$$D_r = \lambda^2\nu/6 = k_1D_0[rH]/k_2[RH] \quad .$$

The corresponding expression for the rate constant for encounters is

$$k_e = \frac{4\pi a 2D_0k_1[rH]}{k_2[RH]} 6 \cdot 10^{20} \simeq 1.5 \cdot 10^{22} \frac{aD_0k_1[rH]}{k_2[RH]} \quad . \qquad (9)$$

The derivation of Eqn.(9) can be approached in a different way. Since usually $[\dot{r}] \ll [\dot{R}]$, the reaction

$$\dot{r} + \dot{R} \xrightarrow{k_3} \text{products} \qquad (10)$$

can be regarded as virtually the only one in which the total number of radicals diminishes. The kinetic mechanism incorporating reactions (7), (8), and (10) is described by the system of differential equations

$$d[\dot{r}]/dt = k_1[\dot{R}][rH] - k_2[\dot{r}][RH] - k_3[\dot{r}][\dot{R}] \quad ,$$

$$d[\dot{R}]/dt = -k_1[\dot{R}][rH] + k_2[\dot{r}][RH] - k_3[\dot{r}][\dot{R}] \quad .$$

When the concentration of $\dot{R}$ is high and $k_3[\dot{R}] \gg k_2[RH]$, we obtain for the rate of destruction of macroradicals

$$-d[\dot{R}]/dt \simeq 2k_1[rH][\dot{R}] \ .$$

On the other hand, usually $k_3[\dot{R}] \ll k_2[RH]$, which implies that the encounter of the free valences is preceded by several cycles of reactions (7) and (8) or, in other words, the distance over which $\dot{r}$ migrates during its lifetime is significantly shorter than the overall migration path of the free valence before destruction. Then

$$-d[\dot{R}]/dt \simeq \frac{2k_1k_3[rH]}{k_2[RH]}[\dot{R}]^2 \ ,$$

i.e. the destruction of macroradicals is described by a second-order equation with respect to the radical with the effective constant

$$k_{eff} = 2k_1k_3[rH]/k_2[RH] \ . \qquad (11)$$

We shall assume that reaction (10) is controlled by diffusion with D_0, whereupon we obtain

$$k_3 = 4\pi aD_0 \times 6 \times 10^{20} \ . \qquad (12)$$

On substituting Eqn.(12) in Eqn.(11), we obtain Eqn.(9). If the low-molecular-weight radicals are formed in the dissociation of macroradicals or in the decomposition of the initiator Y, reaction (7) must be replaced by reactions (13) and (14) respectively:

$$R \xrightarrow{k_4} \dot{r} + \text{products} \quad ; \qquad (13)$$

$$Y \xrightarrow{w_0} \dot{r} \ . \qquad (14)$$

Table 4. Kinetics of the destruction of macroradicals as a result of the migration of the free valence with participation of light radicals.

No. of radical r formation reaction	Rate of destruction of macroradicals		k_e for $k_3[\dot{R}] \ll k_2[RH]$
	for $k_3[\dot{R}] \gg k_2[RH]$	for $k_3[\dot{R}] \ll k_2[RH]$	
(7)	$2k_1[rH][\dot{R}]$	$\frac{2k_1k_3[rH][\dot{R}]^2}{k_2[RH]}$	$1.5 \cdot 10^{20}\frac{aD_0k_1[rH]}{k_2[RH]}$ (9)
(13)	$2k_4[\dot{R}]$	$\frac{2k_3k_4[\dot{R}]^2}{k_2[RH]}$	$1.5 \cdot 10^{20}\frac{aD_0k_4}{k_2[RH]}$ (9a)
(14)	w_0	$-w_0$	—

The expressions for the rate of destruction of macroradicals and the rate constant for the encounter of the free valences, obtained in terms of an approximation analogous to that used in the previous case, are presented in Table 4.

The above analysis shows that the bimolecular law governing the destruction of macroradicals with participation of light radicals, which is most frequently observed experimentally, can be realised if the source of light radicals is reaction (7) or (13), while $k_3[\dot{R}] \ll k_2[RH]$. If, on the other hand, the low-molecular-weight radicals are formed in the decomposition of the initiator, then the bimolecular law governing the destruction of macroradicals should not be observed for any values of $[\dot{R}]$.

We shall compare the bimolecular rate constants for encounters in the migration of the free valence with participation of light radicals (k_{e_1}) and as a result of the trivial relay (k_{e_2}), having assumed that the distance a over which the radicals react chemically is in both cases the same. When $\dot{r}$ is formed via reactions (7), the ratio k_{e_1}/k_{e_2} can be obtained on dividing Eqn.(9) by Eqn.(6):

$$k_{e1}/k_{e2} = 6D_0k_1[rH]/\lambda_r^2k_2k_p[RH]^2 \ .$$

Assuming that $\lambda_r = 3 \times 10^{-8}$ cm, $k_2 = k_p = 10^{-1}$ litre mol^{-1} s^{-1}, [RH] = 10 M, and $D_0 = 10^{-10}$ cm^2 s^{-1}, we find $k_{e_1}/k_{e_2} \cong 7 \times 10^5k_1[rH]$. The ratio $k_{e_1}/k_{e_2} \gg 1$ holds subject to the condition that $k_1[rH] \gg 1.5 \times 10^{-6}$ s^{-1}, which obtains readily even for comparatively low values of [rH]. If $\dot{r}$ is formed in the dissociation of macroradicals, the ratio k_{e_1}/k_{e_2} is obtained on dividing Eqn.(9a) by Eqn.(6):

$$k_{e1}/k_{e2} = 6D_0k_4/\lambda_r^2k_2k_p[RH]^2 \ .$$

Using the same values of λ_r, k_2, $k_p[RH]$, and D_0 as in the previous case, we find that $k_{e_1}/k_{e_2} \gg 1$, provided that $k_4 \gg 1.5 \times 10^{-6}$ s^{-1}, which is frequently also readily obtainable.

Thus the involvement of light radicals can ensure a more effective migration of the free valence than the trivial relay and the relay-diffusional mechanism of migration. It is then possible to attain fairly high absolute values of k_e. For example, an estimate[89] for the destruction of peroxy-radicals in polypropylene undergoing oxidation at 130 °C, based on the assumption that the free valence is transferred to low-molecular-weight products of thermo-oxidative degradation, leads to $k_e \cong 10^5$–10^6 litre mol^{-1} s^{-1}, which is fairly close to the experimental values of k_t.[62,90]. The mechanism of migration with participation of light radicals also agrees well with the idea that diffusion-controlled stages are present in the migration process; in the present instance the diffusion of light radicals is such a stage.

Table 4 shows that the two mechanisms of the formation of low-molecular-weight radicals [reaction (7) and (13)] cannot be distinguished solely on the basis of data for the kinetics of the destruction of macroradicals. The low-molecular-weight chain transferring agents rH in reaction (7) can be both specially introduced additives and random admixtures as well as polymer degradation products (in particular a high yield of low-molecular-weight products is observed in thermo-oxidative degradation). The latter case has been discussed[89].

We shall now consider a more universal mechanism of the formation of light radicals—the dissociation of macroradicals. Radicals tend to dissociate to a greater extent than the corresponding molecules, and the commonest dissociation mechanism involves the dissociation of the β-bond (the so-called β-decomposition). Radical recombination and disproportionation processes compete with the dissociation reaction. Since the lifetime τ_l of active radicals in the liquid and gas phases is usually short and rarely exceeds 1 s, it is possible to observe only comparatively rapid dissociation processes under these conditions§. The situation changes in solid polymers where τ_l is significantly greater and sometimes reaches many hours.

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§In the bimolecular mechanism of the destruction of radicals $\tau_l = 1/\sqrt{w_0k_t}$; the usual value of k_t for active radicals in the liquid phase is 10^9 litre mol^{-1} s^{-1},[33] while the rate of initiation w_0 in kinetic experiments is rarely below 10^{-9} mol litre^{-1} s^{-1}. Hence $\tau_l \leq 1$ s. The probability of the dissociation of the radical is 10% subject to the condition that $k_4 = 0.1/\tau_l \geq 0.1$ s^{-1}; thus in the liquid phase it is virtually impossible to detect dissociation processes with $k_4 < 0.1$ s^{-1}.

One can therefore expect that macroradical dissociation processes play a considerably greater role than the analogous reactions of low-molecular-weight radicals in the liquid and gas phases¶.

5. Migration of the Free Valence with Participation of Low-Molecular-Weight Radicals (Experimental Data)

We shall now consider experimental facts indicating the involvement of light radicals in free valence migration processes in solid polymers.

1. When chlorine is brought into contact with γ-irradiated polyethylene containing stable alkyl radicals, the polymer undergoes chain chlorination, which is accompanied by a decrease of the concentration of macroradicals at a rate several orders of magnitude greater than in the absence of molecular chlorine[96]. The high rate of destruction of alkyl radicals is ensured by the participation in the migration process of $\dot{C}l$ atoms formed by the reaction

$$\dot{R} + Cl_2 \rightarrow RCl + \dot{C}l$$

and capable of traversing comparatively long distances before recombining with $\dot{R}$ or before the reverse chain transfer reaction step:

$$RH + \dot{C}l \rightarrow \dot{R} + HCl \quad .$$

In this case chlorine plays the role of a kind of catalyst of the destruction of macroradicals.

2. Catalysis of the migration of the free valence by hydrogen is observed in γ-irradiated polyethylene[97-100]. The rate of migration can be inferred from the kinetics of not only the destruction of alkyl radicals ($\dot{R}_{alk}$) but also of the conversion of $\dot{R}_{alk}$ into allyl radicals ($\dot{R}_{all}$) (the rate of the latter process is apparently limited by the rate of encounters of the free valence with a double bond). Both processes are significantly accelerated by hydrogen (by a factor of ~15 for p_{H_2} = 400 mmHg at 24 °C in the transition $\dot{R}_{alk} \rightarrow \dot{R}_{all}$) and to a lesser extent by deuterium, the magnitude of the effect being proportional to the H_2 of D_2 pressure.

In the absence of hydrogen, the migration of the free valence in the polymer apparently takes place as a result of the reaction

$$\dot{R}_{alk} + RH \xrightarrow{k_6} RH + \dot{R}_{alk} \quad . \qquad (15)$$

In a hydrogen atmosphere migration can take place as a consequence of the repetition of the reaction cycle:

$$\begin{aligned} &\dot{R}_{alk} + H_2 \xrightarrow{k_7} \dot{H} + RH \quad , \\ &\dot{H} + RH \rightarrow H_2 + \dot{R}_{alk.} \end{aligned} \qquad (16)$$

The occurrence of deuterium isotope exchange in such a system[97] confirms the above mechanism. Reaction (16) can be more effective than reaction (15) from the standpoint of the migration of the free valence in the polymer, although $k_7 \ll k_6$. This is associated with the exceptionally high mobility of H atoms†.

3. The rate of the chain oxidation of polyolefins decreases in the presence of the low-molecular-weight hydroperoxide $C_6H_5C(CH_3)_2OOH$.[102] The effect is evidently also caused by the increase of the effective termination rate constant as a result of the involvement in this process of light radicals arising in the reaction

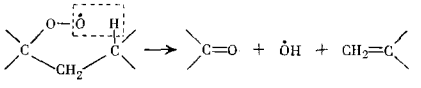
$$R\dot{O}_2 + C_6H_5C(CH_3)_2\dot{O}OH \rightarrow ROOH + C_6H_5C(CH_3)_2O\dot{O} .$$

This mechanism has been confirmed directly in a study[75] where the increase of the rate of destruction of peroxy-radicals in polypropylene in the presence of a low-molecular-weight hydroperoxide {by a factor of ~7 for $[C_6H_5C(CH_3)_2.OOH] = 0.12$ M at 25 °C} was observed directly by EPR. However, the effect is comparatively small, which implies that an extremely effective migration mechanism, possibly involving low-molecular-weight radicals (see below), obtains in solid polypropylene even without the addition of a low-molecular-weight hydroperoxide.

4. In poly(methyl methacrylate), polystyrene, and poly(vinyl acetate) at temperatures below T_g, i.e. under the conditions of highly limited mobility of the polymer molecules, the destruction of macroradicals proceeds at a measurable rate (Table 3) and is accompanied by the formation of considerable amounts of low-molecular-weight products[67,103]. The authors[67,103] concluded that the high rates of destruction of radicals are ensured by the involvement in the free valence migration processes of low-molecular-weight radicals arising on dissociation of the macroradicals. A new confirmation of this migration mechanism in polystyrene has been recently obtained[104]. The destruction of the peroxy-macroradicals in the presence of an alkyl radical acceptor—a stable nitroxy-radical $R_2\dot{N}O$—is accompanied by the formation of the ether R_2NOr, which is not "attached" to the polymer. This evidently implies that low-molecular-weight alkyl radicals arise in some way in processes leading to the destruction of macroradicals.

5. Light radicals apparently play a significant role also in processes involving the destruction of peroxy-macroradicals in polypropylene and polyethylene. The thermal oxidation of polyolefins is accompanied by the formation of volatile products[7] and of low-molecular-weight as well as polymeric hydroperoxides[105]. These data indicate an intense decomposition of the macroradicals, in which the decomposition products can include low-molecular-weight radicals. The latter have been detected directly by EPR in the thermal decomposition of solid polypropylene hydroperoxides[106]. It was assumed earlier that the dissociation is undergone mainly by alkoxy- and terminal alkyl radicals. However, recent studies have shown that one of the main processes responsible for the degradation of polyethylene[107] and polypropylene[108,109] is the decomposition of peroxy-macroradicals#.

A specific mechanism of the decomposition of RO_2 has been proposed[112,113]:

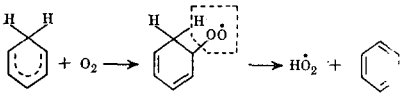


¶This also applies to low-molecular-weight sterically hindered radicals, which cannot compete or disproportionate with one another even in the liquid phase owing to steric hindrance. The range of such radicals has greatly expanded in recent years[91-95]. Many of these are destroyed at a low rate as a result of the β-decomposition followed by the recombination of the fragment radical with the initial radical.

†In solid polymers hydrogen atoms diffuse over distances up to ~10^{-6} cm without reacting with macroradicals[101].

#Data indicating the dissociation of peroxy-radicals in polytetrafluoroethylene have been published[22,110,111].

However, the ȮH radicals formed in this process are very reactive and for this reason can hardly traverse long distances in the polymer. Another mechanism of the decomposition of $\dot{R}O_2$ can be associated with the ejection of the considerably less active $H\dot{O}_2$ radical. Processes of this kind are known in the liquid phase close to room temperature for peroxy-radicals derived from hydroxy-compounds[114,115] and certain unsaturated hydrocarbons[116], for example, in the oxidation of cyclohexa-1,4-diene:



This mechanism has been invoked to account for the sharp increase of the rate of destruction of macroradicals of the cyclohexadienyl type in polycarbonate in the presence of O_2.[117] One cannot rule out the possibility that the decomposition of $R\dot{O}_2$ with ejection of $H\dot{O}_2$ takes place also in polyolefins and other polymers.

The bimolecular rate constant for the destruction of peroxy-radicals in polypropylene subjected to preliminary oxidation decreases with increase of the concentration of the polymeric hydroperoxide in accordance with the law[75,80]

$$k_t = \frac{a}{b + c[\mathrm{ROOH}]} \quad , \qquad (17)$$

where a, b, and c are constants. This dependence of k_t on [ROOH] can be accounted for most naturally within the framework of the mechanism of migration with participation of low-molecular-weight radicals. The polymeric hydroperoxide plays in this case the role of a trap for light radicals. As a result of the reaction

$$\dot{r} + \mathrm{ROOH} \xrightarrow{k_1} rH + R\dot{O}_2 \quad ,$$

the latter are replaced by polymeric peroxy-radicals, which reduces the effective rate of migration. The expression for the rate constants for the encounters of the free valences will differ from those quoted in Table 4 by the fact that the term k_1[ROOH] appears in the denominator. For example, if the light radicals arise in the dissociation of the macroradical $R\dot{O}_2$, the following expression is obtained:

$$k_e = 1{,}5 \cdot 10^{23} \frac{aD_0 k_t}{k_2[\mathrm{RH}] + k_1[\mathrm{ROOH}]} \quad ,$$

the form of which does not differ from that of Eqn.(17). Of the two possible mechanisms of the formation of light radicals participating in the migration of the free valence—chain transfer to a low-molecular-weight impurity and the dissociation of the macroradical—the second mechanism is more probable in the given instance[75].

6. The Influence of Molecular Mobility on the Kinetics of the Destruction of Macroradicals

Many facts are known indicating a relation between the kinetics of the destruction of macroradicals in solid polymers and molecular mobility—the decrease of the rate of destruction on passing from an amorphous to a crystalline phase[8,15,63,118–119], a lower value of k_t in oriented specimens compared with non-oriented specimens[65,120], the increase under these conditions of the effective activation energy for the destruction process[68], the increase of the stability of macroradicals when the polymer is cross-linked[121,122], the identity in many instances of the activation energy for the destruction of macroradicals and the activation energy for the segmental movements in the polymer measured by NMR (see the references in the review of Pudov and Buchachenko[7])§, the increase in the rate of destruction of macroradicals in three-dimensional polymers with increase of the length of the oligomer block[123], etc.

Two methodological procedures, whereby the mobility can be subjected to a controlled variation within wide limits, based on the change of the external pressure and the plasticisation of the polymer by chemically inert solvents, have been used recently in the study of the influence of molecular mobility on the kinetics of the destruction of macroradicals.

In amorphous polymers—polystyrene[24], poly(vinyl acetate),[124] poly(methyl methacrylate),[125] polyamides[126], and polycarbonate[127]—the constant k_t decreases with increasing pressure at temperatures in excess of T_g (in some cases by a factor of 10^2–10^3 at $p \cong 10^4$ atm). Below T_g, the influence of p on k_t is comparatively small. The nature of the dependence of k_t on p is such (Fig.3) that the greatest effect is observed at comparatively low pressures p; at each temperature above T_g there is a critical pressure p_{cr}, above which k_t depends only slightly on p. At $p < p_{cr}$ the dependence of k_t on p is described by the relation[129]

$$k_t = A_0 \exp[-(E + pV^*)/RT] \quad , \qquad (18)$$

where V^* is the activation volume and E sometimes changes as the pressure is altered[25,129].

Although the specific cause of the influence of p on k_t in each case is not known exactly, a common factor is apparently the fact that the pressure affects the kinetics of the destruction of macroradicals via molecular mobility. With increase of pressure, the density of the polymer also increases, which lowers the intensity of molecular movements, this being manifested particularly by an increase of T_g [for example, in poly(methyl methacrylate) $dT_g/dp = 2 \times 10^{-2}$ K atm^{-1} [129]], a decrease of the free volume, a decrease of the rotation frequency of a paramagnetic probe[133], etc. Eqn.(18) shows that an increase of p affects k_t in the same way as a decrease of temperature. Presumably the glass point is attained at $p = p_{cr}$.

The variation of the external pressure constitutes an extremely promising instrument for investigating the mechanisms of processes involving the destruction of macroradicals (and apparently also other radical reactions in solid polymers), particularly in a simultaneous study of molecular mobility. For example, in the basis of the data of Szocs and Plack[25], Szocz and Rostasova[129] concluded that there are two mechanisms of the destruction of terminal radicals in poly(methyl methacrylate). In the region of low pressures and high temperatures (high mobility) the destruction process is characterised by $E = 29$ kcal mol^{-1} and $V^* = 70$ Å^3 and the destruction apparently takes place as a result of physical diffusion; in the region of high pressures and low temperatures (low mobility) $E = 17$ kcal mol^{-1}, $V^* = 7.5$ Å^3, and the free valence most probably migrates with participation of the light radicals formed on dissociation of the macroradicals. The study of the influence of pressure on the kinetics of the destruction of the radicals can also yield information about the localisation of the radicals in amorphous-crystalline polymers. Since pressure alters the molecular mobility virtually only in the

§This agreement between the activation energies should, incidentally, be treated with much caution, because radicals are sometimes localised in the crystalline phase of the polymer, while data for the mobility refer to the amorphous phase.

amorphous phase, the weak dependence of k_t on p at temperatures above T_g indicates the localisation of the radicals in the crystallites[129].

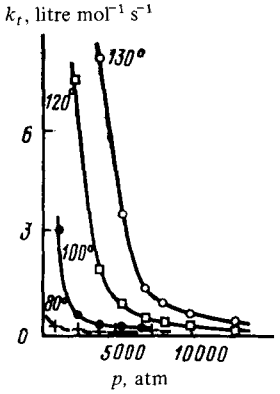


Figure 3. Dependence of k_t for terminal macroradicals in poly(methyl methacrylate) on pressure at different temperatures[125].

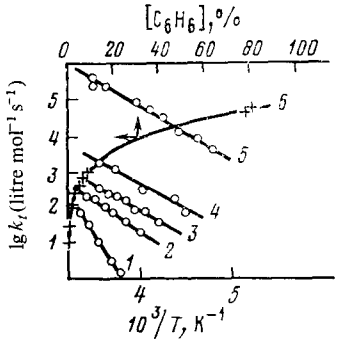


Figure 4. Temperature dependence of k_t for peroxy-radicals in polystyrene for different contents of benzene (%): *1*) 0; *2*) 2; *3*) 5; *4*) 12; *5*) 90; *6*) dependence of k_t on the benzene content at 270 K.[66]

The plasticisation of the polymers exerts a significant influence on the kinetics of the destruction of macroradicals. Thus the destruction of peroxy-radicals in polystyrene[66] (Fig. 4) and polypropylene[62,132] is greatly accelerated by the addition of comparatively small amounts of aromatic solvents, while the destruction of macroradicals in cellulose is accelerated by the addition of water[133]. The accelerating effect can be explained solely by an increase of molecular mobility. The variation of k_t in solid polypropylene in the presence of *o*-dichlorobenzene is correlated with the rotation frequency of the paramagnetic probe[132]. Table 5 shows that the increase of k_t is accompanied by a decrease of the activation energy and the pre-exponential factor; at fairly high concentrations of the additive these quantities approach the liquid-phase values.

The results of the consideration of the kinetics of the destruction of macroradicals are presented in Table 6. The operation of one of the mechanisms for the migration of the free valence in a specific system, discussed above, depends on the ratio of two factors: the intensity of the molecular movements in the polymer and the reactivity of the macroradicals. If the reactivity of the macroradicals is low and the intensity of the segmental movements is very great, the free valence will migrate mainly as a result of physical diffusion. This situation apparently obtains in elastomers above T_g and in highly plasticised polymers. In other cases physical diffusion leads to a very slow migration and cannot as a rule compete with "chemical" diffusion. When the free valence transfer reaction is fairly effective (high values of k_p), one may expect that the migration will take place via a relay-diffusional mechanism or, in the specific instance where the mobility is frozen to a large extent, via the trivial relay mechanism. If, finally, the macroradicals tend to dissociate or low-molecular-weight chain transferring agents are present in the system, the dominant mechanism of the migration will involve processes with participation of light radicals. Such migration mechanism ensures, in principle, the highest absolute rates of destruction of macroradicals.

Table 5. The influence of added aromatic solvents on the kinetics of the destruction of peroxy-macroradicals in solid polyolefins.

Low-molecular-weight additive	$(k_t)_0$, litre mol^{-1} s^{-1}	E, kcal mol^{-1}	k_t^*, litre mol^{-1} s^{-1}	Refs.
	Polypropylene			
—	$3.2\cdot10^{21}$	28.5	4	[62]
~2.5 M benzene	$5.6\cdot10^{13}$	14.5	$1.2\cdot10^3$	[62]
0.8 M *o*-dichlorobenzene	—	—	45	[132]
	Polystyrene			
—	10^{14}	17.6	12.5	[66]
0.6 M benzene	$3.2\cdot10^7$	6.3	$8\cdot10^2$	[66]

*The values of k_t at 25 °C are quoted.

Table 6. Characteristics of the valence migration processes in a solid polymer.

Migration mechanisms	Factors determining migration mechanism				Parameter determining rate of migration	Factor influenced by molecular mobility
	segmental mobility (D, λ_r)	k_p	presence of low-molecular-weight chain transferring agents (k_1[rH])	tendency of macroradical to dissociate (k_s)		
Physical diffusion	high	low	absent	low	D_2	D
Trivial relay	low	high	absent	low	$k_p\lambda_s^2$	k_p
Relay-diffusion mechanism	high	high	absent	low	$k_p\lambda_c^2$	k_p, $\bar{\lambda}_c$
With participation of light radicals:						
(a) chain transfer to low-molecular-weight admixture	comparatively low	low	present	low	k_1[rH] D_0	k_1, D_0
(b) dissociation of macroradicals	comparatively low	low	absent	high	$k_s D_0$	D_0

It is clear from the foregoing that the mechanism of the migration of the free valence is actually determined not only by the nature of the polymer and temperature but also by the type of macroradical, the localisation of the radicals in the amorphous or crystalline phases of the polymer, the presence of low-molecular-weight admixtures (plasticisers or chain transferring agents), etc.

The last column of Table 6 shows the parameters through which molecular mobility influences the kinetics of the destruction of macroradicals as a function of the migration mechanism. Furthermore, in each specific instance it is as a rule impossible to specify the "channel" for the exertion of the influence, because, as we have seen, it is fairly difficult to establish reliably the migration mechanism.

V. REACTIONS OF MACRORADICALS WITH MACROMOLECULES: $\dot{R}_1 + R_2H \rightarrow R_1H + \dot{R}_2$

Since both reactants are in a single "cage", the reactions of this type always proceed under kinetic conditions. At low temperatures (as a rule below T_g), where the destruction of radicals is still inappreciable, the reactions of macroradicals with macromolecules can be investigated directly, by following the concentrations of $\dot{R}_1$ and $\dot{R}_2$ by EPR. The reactions of terminal radicals in polyethylene[134]

$$\sim CH_2\dot{C}H_2 + \sim CH_2CH_2CH_2 \sim \rightarrow \sim CH_3CH_3 + \sim CH_2\dot{C}HCH_2 \sim$$

and the reactions of peroxy-radicals (chain propagation in oxidation)

$$R\dot{O}_2 + RH \rightarrow \dot{R} + ROOH \qquad (19)$$

in polyethylene, polypropylene[135], polyethylene–urea complexes[136], polystyrene[67,88], poly(methyl methacrylate)[10,67], polycaproamide, and polyacrylonitrile[67] have been investigated in this way. The $R\dot{O}_2 \rightarrow \dot{R}$ transition at low temperatures is as a rule described in terms of stepwise kinetics.

The quantity k_p for $R\dot{O}_2$ can also be obtained from the kinetics of the chain oxidation. The rate of oxidation w_{O_2} is given by the following expression on the assumption of fairly long chains:

$$w_{O_2} = \frac{k_p}{\sqrt{k_t}}[RH]\sqrt{w_0} \quad . \qquad (20)$$

If the rate of initiation w_0 is known, then it is possible to find the parameter $k_p/\sqrt{k_t}$ with the aid of Eqn.(20). Independent measurements of the termination rate constant k_t are necessary for the determination of k_p. The relevant data are presented in Table 7.

The most detailed information has been obtained for polypropylene. The quantities $k_p/\sqrt{k_t}$, measured at different temperatures and using different initiators, are fairly similar. The discrepancies between the k_p are very significant owing to the considerable discrepancies between the k_t in different studies.

In principle, k_p can be calculated from k_t for the destruction of macroradicals subject to the condition that the migration of the free valence is caused by "chemical" diffusion. However, even if the migration mechanism has been established reliably (which can be done, as already stated above, in comparatively rare instances), the calculation of k_p involves large errors, because the necessary parameters [for example, the elementary jump $\bar{\lambda}_s$ for the relay-diffusional mechanism of the migration of the free valence—see Eqn.(6)] are usually estimated very approximately.

Thus the information about the rate constants for reactions of macroradicals with macromolecules is so far fairly limited and refers virtually only to the reactions of peroxy-radicals.

We shall consider the influence of molecular mobility on the kinetics of reaction (19). Since both reactants are always in direct contact, one may consider here the influence of mobility solely on their interaction in the cage.

In the crystalline regions of isotactic polypropylene the radicals $R\dot{O}_2$ are destroyed ~10^4 times more slowly than in the amorphous regions and the transition $R\dot{O}_2 \rightarrow \dot{R}$ hardly occurs[53], although the rate constant for reaction (19) in the amorphous phase is extremely large[84]. Thus at 80 °C $k_p = 1.5 \times 10^{-1}$ litre mol^{-1} s^{-1}, which corresponds to an average reaction time $1/k_p[RH] \cong 0.3$ s. Apparently the only cause of the enormous difference between the reactivities of $R\dot{O}_2$ in the crystalline and amorphous phases is the difference between the intensities of the molecular movements.

It has been shown[143,144] that the rate of oxidation of polypropylene diminishes and the relative decrease of stability after oxidation in the presence of the same amount of absorbed oxygen is smaller when the system is oriented. This apparently implies that the chain propagation rate constant k_p for strained polymer chains with a limited mobility is significantly lower than for the unstrained chains.

The results of the study of reaction (19) in amorphous polystyrene in an inert atmosphere below T_g are even clearer[88]. At 210–293 K the process is described in terms of stepwise kinetics with a hyperbolic initial distribution of peroxy-radicals with respect to rate constants. Thus peroxy-radicals of identical chemical nature differ greatly in their reactivities. Analysis of the stepwise kinetics makes it possible to find the limits of the distribution of $(k_p)_{max}$ and $(k_p)_{min}$ and of the corresponding activation energies (Table 7). It is of interest that the quantity $(k_p)_{max}$ is fairly close to the rate constant for the reaction of a low-molecular-weight analogue of polystyrene (cumene) with its peroxy-radical in the liquid phase[33].

The physical significance of the stepwise kinetics in the given instance is that at a given temperature the more active radicals are "burnt off" more rapidly with k_p close to $(k_p)_{max}$; as a result, the distribution curve shifts towards radicals with $(k_p)_{min}$ (Fig.5) and the overall rate of the process is sharply retarded. An analogous phenomenon is observed in poly(methyl methacrylate).[10] Evidently any influences on the polymer promoting the restoration of the initial distribution will "restore" the initial rate of reaction. This has been achieved[88] by a brief dispersion of the specimen, in which the active radicals have been "burnt off", at 77 K¶.[12] The dispersion results in relative migrations of macroradicals and macromolecules and in a change of the local environment of the radical and of molecular mobility in the vicinity of the radical; in other words, the distribution functions with respect to k_p are mixed, which results in the restoration of favourable relative orientations of the radical and the surrounding macromolecules from the standpoint of reaction (19). When reaction (19) is carried out in an atmosphere of O_2, "chemical" mixing of the distribution function takes place[10,88] as a result of the generation of new peroxy-radicals in the

¶At 77 K reaction (19) does not proceed even under dispersion conditions owing to the presence of a large activation barrier.

Table 7. The values of $k_p/\sqrt{k_t}$ (litre$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$) and of the rate constants k_p (litre mol^{-1} s^{-1}) for the reaction $R\dot{O}_2$ + RH → $\dot{R}$ + ROOH in solid polymers (at 80 °C).

Polymer*	Oxidation conditions (initiator, t, °C)	$(k_p/\sqrt{k_t})$	E, kcal mol^{-1}	$(k_p/\sqrt{k_t})$	References	$(k_p)_0$	E, kcal mol^{-1}	k_p	References
PE	dicumenyl peroxide 110÷130	$5.6\cdot10^{3}$	21.2	$4\cdot10^{-5}$	[138]	$6.5\cdot10^{16}$	30.5	$7.7\cdot10^{-3}$	**
PE	in urea clathrate compounds, 70–108	—	—	—	—	—	24.6	—	[136]
a-PP	di-t-butyl peroxy-oxalate, 45–63	$3.1\cdot10^{2}$	8.5	$1.8\cdot10^{-3}$	[64]	$1.1\cdot10^{8}$	15.0	$5.5\cdot10^{-2}$	[64]
a-PP	benzoyl peroxide, 76–105	4.8	6.2	$6.9\cdot10^{-4}$	[139]	$1.6\cdot10^{7}$	12.1	0.54	[139]
i-PP	autoxidation,	$1.7\cdot10^{2}$	9.0	$4.5\cdot10^{-4}$	[140]	$3.4\cdot10^{6}$	9.0	0.89	[140]
i-PP	110–140 autoxidation, 120–140***	$6.2\cdot10^{4}$	12.8	$7.5\cdot10^{-4}$	[141]	—	—	—	—
i-PP	photo-oxidation, 20–140***	$1.4\cdot10^{2}$	8.5	$4\cdot10^{-4}$	[142]	—	—	—	—
i-PP	PP hydroperoxide, azobisisobutyro-nitrile, 44–92****	17	6.6	$8.1\cdot10^{-4}$	[84]	$9.6\cdot10^{11}$	21.0	0.1	[82]
PB-1	benzoyl peroxide, 76–119	$9.1\cdot10^{5}$	18.0	$6.5\cdot10^{-4}$	[139]	$1.3\cdot10^{11}$	18.0	0.89	[139]
P-4-MP-1	benzoyl peroxide, 85–95	10^{7}	20	$4\cdot10^{-4}$	[139]	—	—	—	—
PEO	radiation oxidation, 25	—	—	$3.3\cdot10^{-4}$(25′)	[137]	—	—	—	—
PS(max)	−63÷+20					$3.7\cdot10^{7}$	10.3	0.7(20°)	[88]
PS(min)****	—					$1.4\cdot10^{12}$	21.0	$3\cdot10^{-4}$(20°)	[88]
PMMA(max)*****	0÷−20					$8\cdot10^{6}$	12.0	$8\cdot10^{-3}$(20°)	[10]
PMMA(min)*****						$1.4\cdot10^{14}$	25.8	$8\cdot10^{-6}$(20°)	[10]

*PB-1 = polybut-1-ene, P-4-MP-1 = poly-4-methylpent-1-ene, and PEO = poly(ethylene oxide); for the significance of the remaining abbreviations for the polymers, see Table 3.

**The constant $k_t = 1.4 \times 10^{16} \exp(-18500/RT)$ (litre mol^{-1} s^{-1}) taken from Davis et al.[61] was used.

***Recalculated for the amorphous phase on the assumption that the degree of crystallinity is 0.6.

****The constant $k_t = 3.2 \times 10^{21} \exp(-28500/RT)$ (litre mol^{-1} s^{-1}) taken from Roginskii and Miller[62] was used.

*****On the basis of the "stepwise" kinetics of the transition $R\dot{O}_2$ → $\dot{R}$ in an inert atmosphere.

reaction

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

"Thermal" mixing of the distribution functions is also possible.

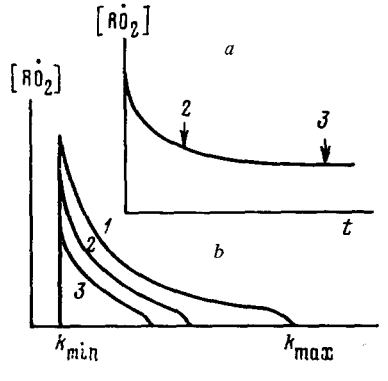


Figure 5. *a*) Kinetics of the reaction $R\dot{O}_2$ → $\dot{R}$ in polystyrene; *b*) changes in the curve illustrating the range of rate constants for $R\dot{O}_2$ reactions in the course of the kinetic experiment (according to Radtsig's data[10]).

Molecular mobility influences the rate of reaction (19) also in "softer" polymer matrices where the stepwise kinetics are not as yet observed. Thus k_p increases significantly in the oxidation of solid polypropylene at 25 °C in the presence of the chemically inert *o*-dichlorobenzene, the growth of k_p being correlated with the increase of the rotation frequency of the paramagnetic probe characterising molecular mobility[132].

VI. PHYSICAL MECHANISMS OF THE INFLUENCE OF MOLECULAR MOBILITY ON REACTIVITY

As shown in the previous sections, one of the characteristic features of radical reactions in solid polymers is that their rate is frequently related to the kinetics of molecular movements even under kinetic conditions. This is manifested both in reactions of macroradicals and macromolecules and in processes involving low-molecular-weight substances. If the treatment is confined to processes whose rates are not limited by the encounters of the reactants, it is possible in principle to set up two physical models relating the kinetics of chemical reactions in polymers to molecular mobility.

In the first model, which can be called the *delayed rehybridisation model*[146], it is assumed that the macrorelaxation time in polymers is long compared with the duration of the chemical step. For example, in the abstraction of a hydrogen atom from an sp^3-carbon atom in the polymer chain the hybridisation should change to sp^2, this being accompanied by a change in valence angles (from 109° to

120°) and bond lengths; the latter requires structural relaxation. In the liquid and gas phases both steps—the abstraction of a hydrogen atom and rehybridisation—take place sychronously, while in a polymer matrix they are separated in time. As a result of the low rate of structural relaxation in polymers, the energetically most favourable activated complex cannot be formed during the reaction step. The process therefore follows a higher profile of the potential energy surface compared with the liquid (gas) phase, which leads in its turn to an increase of the activation energy and a decrease of the reaction rate constants. With increase of mobility, structural relaxation is facilitated and the delay of rehybridisation is correspondingly diminished; as a result, the activation energy falls and the rate constant increases, approaching the liquid-phase values.

There is no direct evidence for the reality of the delayed rehybridisation model, which remains hypothetical. Although many kinetic features of radical reactions in solid polymers can be accounted for in the framework of this model, some of its consequences are not fulfilled. In particular the model predicts a significant decrease in the rate constants for radical substitution reactions only in processes involving the atoms in the main chain of the macromolecule, whereas it has been observed, as shown above, that the rate constants for reactions involving the side groups of macromolecules as well as low-molecular-weight substances are lower than in the liquid phase.

We shall now consider the second model. For the chemical reaction to occur, a rigorously defined orientation of the reacting species and their elements (for example, the unpaired electron orbital and the chemical bond) is necessary. Thus the abstraction of a hydrogen atom by a free radical requires that the bond undergoing association should be arranged coaxially with the unpaired electron at a distance of 1.5–2.0 Å. In other words, it is necessary that the state preceding the reaction (the prestart state) should be located on the reaction coordinate. To attain this state, a reorientation of the reacting species, as a result of translational and rotational diffusion, is necessary. This model (we shall call it the *structural-orientational correspondence model*) can in principle explain also the marked dependence of the reaction rate on the molecular dynamics of the polymer and its microstructure.

Many characteristic features of the kinetics of radical reactions in solid polymers can be naturally explained within the framework of this model: the sensitivity of the kinetics to the structure and morphology of the polymers, the decrease of the rate constants and the increase of the activation energies compared with the liquid phase, and the relation between the kinetics and molecular mobility. Solid polymers are structurally inhomogeneous systems with a broad distribution with respect to the frequencies and amplitudes of molecular movements. Such frequency-amplitude "polychromaticity" leads to a kinetic "polychromaticity"—a wide range of rate constants and activation energies for the reactants.

With increase of temperature, the molecular movements are gradually "unfrozen"; as the temperature increases, movements on a larger scale are "unfrozen". As a result of this, the effective activation energy (or the range of activation energies) depends on the temperature. A kinetic consequence of this change is the compensation effect and the anomalously high activation energies and pre-exponential factors, which lack physical significance. This also applies to the rotational[131] and translational[147] diffusion of low-molecular-weight substances, which are likewise controlled by the molecular dynamics of the polymer. It is striking that, if the Arrhenius parameters of the chemical reaction[65] or the rotational diffusion of the paramagnetic probe[131] in solid polymers have been obtained under the conditions of a constant intensity of the molecular movements of the polymer, then the activation energies and pre-exponential factors approach the "normal" liquid-phase values.

However, when specific versions of the structural-orientational correspondence model are considered, considerable difficulties are encountered.

(1) In the model of "black spot" spheres[56,148–151] it is assumed that the reacting species exhibit a marked anisotropy in their reactivity. In other words the reaction centre occupies only a small proportion (the "black spot") of the surface of the species. In order that contact between the species in the cage should be accompanied by reaction, their mutual orientation involving the coincidence of the "black spots" is necessary. Analysis of the results of studies[148,150] in which the above model has been considered most rigorously shows that the dependence of the effective rate constant for a bimolecular reaction on the rotation frequency of the reactants can be observed in those cases where the rate of reaction is limited by the encounters of the reactants, i.e. occurs under diffusional conditions. However, as already stated, such dependence is observed experimentally also for reactions which clearly take place under kinetic conditions.

A similar dependence is to be expected also when the required orientation (contact between the "black spots") cannot be realised, in principle, during the existence of the pair†. This situation is in its turn possible if the rotation frequency of the reacting species in the pair is significantly lower than the frequency of their translational migrations (the latter determines the frequency of the decomposition of the pair) or if the fraction of the required orientations is low (this is equivalent to a low pre-exponential factor).

Comparison of the rotation frequencies of stable nitroxy-radicals with the frequencies of their translational jumps in solid polymers[152] shows that the first case apparently does not occur. The second case can occur, according to the data of Griva et al.[56] for the reaction involving the addition of a nitroxy-radical to methylenequinone in the matrices of solid polyolefins: the pre-exponential factor in the expression for the rate constant for this reaction in the liquid phase is only ~10^2 litre mol^{-1} s^{-1}; however, it must be admitted that the reactions with such low pre-exponential factors are nevertheless encountered fairly rarely.

Thus the versions of the "black spot" model considered cannot as a rule explain the experimental relation between the rate constants for bimolecular reactions in solid polymers and the molecular mobility.

(2) The *stepwise orientation model* can be represented by the following scheme:

$$A + B \xrightarrow{\nu_t} [A \ldots B]_1 \xrightarrow{\nu_r} [A \ldots B]_2 \xrightarrow{\nu_r} [A \ldots B]_n \xrightarrow{k} \text{products}.$$
$$\uparrow \qquad\qquad |\nu_t \qquad\qquad |\nu_t \qquad\qquad |\nu_t$$

The pair $[A \ldots B]_1$ formed can either dissociate as a result of the translational jump of one of the reactants at a frequency ν_t or can be converted into another pair $[A \ldots B]_2$ with a different orientation of the reactants, etc. The rotational movement of the partners in the pair at a frequency ν_r "sorts through" the orientational states of the pair until the latter is in the "starting" state $[A \ldots B]_n$ with the orientation of the reactants favourable for reaction. The

†Otherwise the pair of reacting species is able to pass through all the possible orientational states and the rate of chemical reaction no longer depends on the rotation frequencies.

effective rate constant for a bimolecular reaction is

$$k_{\text{eff}} = \frac{k\nu_t}{k+\nu_t}\left(\frac{\nu_r}{\nu_r+\nu_t}\right)^n ,$$

where n is the average number of orientational states preceding the "starting" state $[A...B]_n$. The dependence of k_{eff} on the intensity of molecular movements involves mainly the numerator $[\nu_r/(\nu_r + \nu_t)]^n$.

(3) The "*rigid cage*" model[151,153] postulates that the orientation of the partners in the cage favourable for reaction has a statistically low probability, since it requires that a potential barrier be overcome. In fact one assumes here that the species in the cage are in thermodynamically favourable orientations, but the reaction takes place in other thermodynamically unfavourable states. It is postulated that, when molecular movements are "unfrozen", the statistical weight of the favourable orientations increases. This model is in essence similar to the previous one, the difference consisting in the fact that it involves a statistical thermodynamic and not a kinetic treatment.

The "rigid cage" and "stepwise orientation" models, as well as the "black spot" model discussed above, can operate under conditions where the rate-limiting stage of the process is the attainment of a favourable relative orientation of the reacting species in the cage as a result of their rotational diffusion. As already stated, this is apparently improbable.

The situation might be saved by the fact that the rotation of the species in the polymer matrix is in general anisotropic, i.e. the rotation frequencies relative to different molecular axes are different. One might assume that the rotation about an axis which requires the overcoming of a comparatively large potential barrier and is therefore slow is important for the attainment of a favourable orientation of the reactants in the cage and not rotation in general (which, as already stated, takes place at a higher frequency in solid polymers than translation). In other words, it is necessary to assume that the activation energies for rotation about different axes are different, i.e. that the anisotropy of the rotation depends on temperature.

An experimental test[154] did not confirm the latter hypothesis. It was found that the rotation of the nitroxy-radicals in polymer matrices is indeed anisotropic (incidentally the rotation frequencies about different axes differ by not more than an order of magnitude even for non-spherical radicals), but the anisotropy is independent of temperature and hence the activation energies for rotation about different axes are the same. Thus even allowance for the anisotropy of the rotation in the structural-orientational correspondence model does not eliminate its difficulties.

(4) Finally mention must be made of the *free volume model*[155]. It postulates that the reaction takes place only in certain local microregions of the polymer in which the free volume fluctuates and for this reason the local molecular movements are "unfrozen". This model is partly phenomenological; it does not deal in detail with the kinetics of the elementary reaction step, but relates the effective rate constants to physical parameters of the polymer such as compressibility, coefficient of thermal expansion, etc. An impression is created that the free volume model can explain the dependence of the rate of reaction on mobility only under the conditions of a low intensity of the molecular movements at temperatures below T_g, while the greatest difficulty arises in explaining this dependence in "soft" polymer matrices at temperatures significantly above T_g.

Thus the problem of the physical causes of the relation between the chemical kinetics and the molecular dynamics in solid polymers for reactions under kinetic conditions in essence remains open.

* * *

The problems considered in the review, namely the relation between the kinetics of radical reactions and the molecular dynamics of the polymer, the kinetics and mechanisms of the migration of the free valence, and the physical models of radical reactions, are fundamental key problems, on the solution of which further development of the given field of chemical kinetics, i.e. the kinetics of radical reactions in solid polymers, largely depends.

In assessing the general state of this field, one must recognise that, despite extremely extensive experimental data, the majority of the problems can be discussed at the present time mainly at the phenomenological level. The most important tasks are a detailed investigation of molecular dynamics in polymers and its relations with chemical kinetics, the elucidation of the true mechanism of radical processes, and an increase of the accuracy and reliability of kinetic information. All these require much effort and in particular the development of new research techniques and new experimental approaches.

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