

A STUDY OF DECAY MECHANISM OF ALKYL MACRORADICALS IN POLYISOBUTYLENE

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The macroradicals generated in polyisobutylene by γ -radiolysis at 77 K have been studied from the point of view of their structure and reactivity with the use of the ESR method and various kinetic models. In the region of 223–243 K a single type of macroradicals is only present, $\sim \text{C}(\text{CH}_3)_2\dot{\text{C}}\text{HC}(\text{CH}_2)_2\sim$, these radicals being decayed according to the second order kinetics with effective activation energy of 77.5 kJ mol^{-1} . This result was interpreted within the model of diffusion-controlled reactions using the activation energy approach. Various potential mechanisms of transport of the centres have been tested on the molecular level. Approach of the reactants is controlled by intermolecular hydrogen transfer connected with quasi-crankshaft motions of the chain segments, and at suitable conditions, especially at early stages of the decay, it is possible also to consider a physical mechanism of approach of near-standing reactants with participation of crankshaft motions of the chain segments.

In a series of communications^{1–3} we dealt with molecular aspects of reactivity of macroradicals in solid polymers from the point of view of chemical reactions and physical processes, especially the chain dynamics. In the framework of the model of diffusion-controlled reactions at the activation energy level, acceptable mechanisms were suggested for the transport stages of decay of alkyl macroradicals in polyethylene and isotactic polypropylene at relatively low temperatures. It was found that a significant role is played by the conformational mobility during approaching of the reactants with or without connection with intermolecular hydrogen migration depending on the temperature.

The aim of the present communication was to carry out a detailed structural and kinetic study of macroradicals in polyisobutylene (current trivial name for 2-methylpropene polymer) and then to apply the above-mentioned approach to interpretation of the molecular mechanism of the transport stage of decay of the macroradicals.

EXPERIMENTAL

Polyisobutylene Oppanol (PASF), $\overline{M}_w 2 \cdot 10^6 \text{ g mol}^{-1}$, was dissolved in hot toluene and precipit-

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ated by addition of methanol after cooling. The precipitate was vacuum-dried and kept in glass ampoules at $1.33 \cdot 10^{-2}$ Pa for 30 h. The macroradicals were generated by γ -radiolysis using the ^{60}Co source with the dose rate of 5.86 kGy h^{-1} at 77 K. The spectral measurements were carried out with an ESR spectrometer Varian E-4 with additional temperature device E-257 with nitrogen gas as the carrier medium. Total number of the macroradicals was determined by a reference method using the Varian Strong-pitch standard.

RESULTS AND DISCUSSION

Structure of the Macroradicals

Figure 1 gives typical ESR spectra of the macroradicals generated at 77 K and recorded at various temperatures. The doublet represents the basic shape of the spectra within the whole temperature range from the lowest attainable temperature (113 K) up to total decay at about 273 K. With temperature this doublet is changed from a broad doublet with the hyperfine interaction constant a_{H} 2.8 mT to a narrow doublet with a_{H} 2.4 mT. According to ref.⁴ presenting a detailed analysis of the spectra from the point of view of chemical structure it is possible to obtain information on composition of the macroradicals by means of the spectral parameter B/A

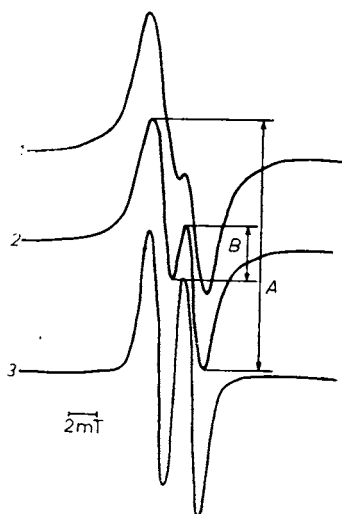


FIG. 1

The ESR spectra of the radical centres generated in polyisobutylene by γ radiation (23.4 kGy dose) at 77 K; the spectra were recorded after thermic treatment for 10 min; T (K): 1 113, 2 163, 3 213

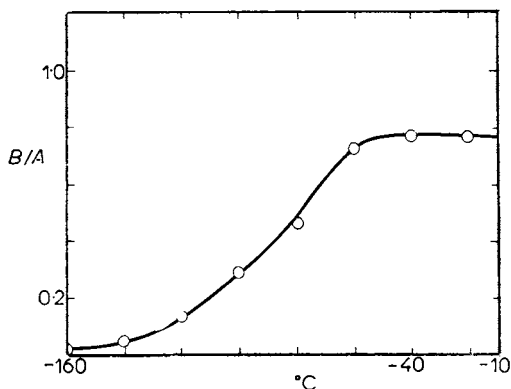
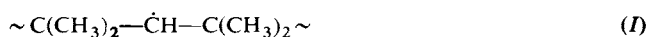


FIG. 2

Temperature dependence of the spectral parameter B/A of radical centres in γ -irradiated polyisobutylene

and the technique of subtraction of spectra. Our dependence $B/A = f(T)$ is represented in Fig. 2. Therefrom it follows that in the low-temperature range (113 to 218 K) the ratio is increased, which is accompanied by decreasing line width, but above 218 K the ratio assumes a constant value. Moreover, in this high-temperature region the shape of spectrum remains unchanged. These facts agree with the results of ref.⁴.

In this work⁴ it was also possible to identify the individual components by means of the subtraction technique. It was found that the dominant component in the spectra within the whole temperature range from 77 K up to total decay is represented by a narrow doublet due to the most stable alkyl macroradicals:



This is the only macroradical present in the matrix above 213 K. In the temperature region below 213 K this dominant component is accompanied by smaller amounts of less stable components, mainly that from the triplet of the methyl alkyl macroradical:



Reactivity of the Most Stable Alkyl Macroradicals

Figure 3 gives the decay curve of the macroradicals in polyisobutylene, $N/N_0 = f(T)$, for the reaction time of 10 min at the temperatures given. The picture shows two reactivity regions corresponding, in principle, to the regions of existence of the broad and the narrow doublets. According to the ref.⁴ the milder decrease of the

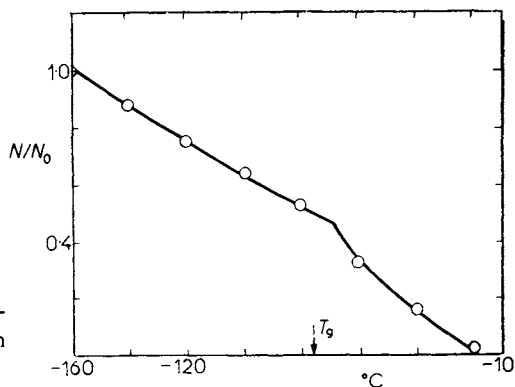


FIG. 3
The decay curve of radical centres in radio-lysed polyisobutylene (time of heating 10 min at each temperature)

total number of macroradicals in the low-temperature region is not only connected with mutual reactions between close macroradicals *I* and *II* (when the number of centres is lowered) but it is also connected with the transformation $II \rightarrow I$ (when the number is not lowered). On the other hand, the more distinct decrease of the number of the *I* centres in high-temperature region can be connected with α -molecular motions which cause a transition of the amorphous matrix from glassy to elastic state⁵.

The detailed kinetic investigation was focused on the high-temperature region from 223 to 243 K because of the defined character of the reaction system, *i.e.* the presence of the most stable macroradicals *I*. It is known^{6,7} that validity of individual kinetic models gives information not only on the reaction order and hence reaction mechanism but also – in the case of solid phase – on spatial distribution of the reactants. Therefore, the time-concentration course of the alkyl centres at 233 K was tested by means of various kinetic models. The results are given in Figs 4–6. If the macroradicals were present in the form of isolated radical pairs with identical geometry parameters (the interspin distance and mutual orientation), their decay should be of the geminal type describable by the I. order kinetic model in time⁶. The test of this model is presented in Fig. 4. The non-linear course of the time-concentration dependence in the coordinates of the I. order kinetics excludes this type of location of the radical centres. If the centres were present in the form of the radical pairs with different geometry parameters, the I. order kinetics should apply in dose⁷. From Fig. 5 it is seen that the relative concentration courses at two doses are not

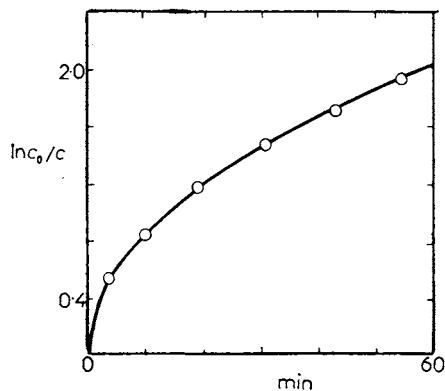


FIG. 4

Test of the I. order kinetic model in time for the decay of the alkyl centres *I* at 233 K

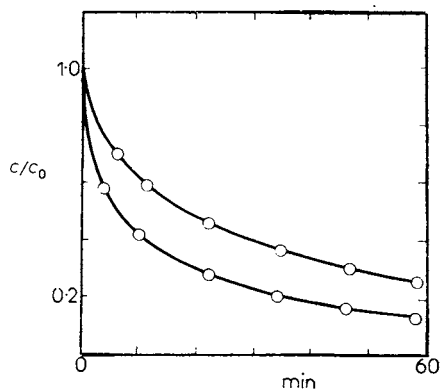


FIG. 5

Test of the I. order kinetic model in dose for the decay of the alkyl macroradicals *I* at 233 K: the upper curve 12.4 kGy, the lower curve 23.4 kGy

overlapped, wherefrom it follows that increasing of the radiation dose is connected with an increase of the number of the decayed centres due to the possibility of reaction of a given centre with another adjacent macroradical. Finally, if the reactants were distributed uniformly in a homogeneous matrix, the ordinary kinetics of the II. order should apply. The test of this model in relative coordinates, $c_0/c = f(t)$, provides a linear dependence, which indicates a bimolecular mechanism of the decay process (Fig. 6). Figure 7 shows the kinetic curves $1/c = f(t)$ after normalization to $1/c_0 = \text{const.}$ for all the temperatures of the interval 223 to 243 K. Their slopes were used for calculation of the rate constants $k_{\text{eff}}(T)$. The normalization of the kinetic curves was carried out for the sake of a synoptic representation in a single graph, and it is justified with respect to the time independence of the rate constants, i.e. independence of the initial concentration of the reactants. The temperature dependence of the rate constants obeys the Arrhenius equation in the form $k_{\text{eff}}(T) = k_0 \exp(-E_{\text{eff}}/RT)$, where k_0 means the pre-exponential factor ($3.98 \cdot 10^{-5} \text{ cm}^3 \cdot \text{spin}^{-1} \text{ s}^{-1}$), and E_{eff} is the effective activation energy ($77.5 \pm 5.4 \text{ kJ mol}^{-1}$) (Fig. 8).

Only a kinetic study is described in literature for decay of macroradicals in polyisobutylene: it was carried out in the temperature interval from 203 to 223 K and gave the activation energy of 75.4 kJ mol^{-1} . In spite of the coexistence of the macroradicals *I* and *II* in this region, similarity of this value to that found by us could indicate the dominant role of the *I* macroradical in the decay in accordance with the

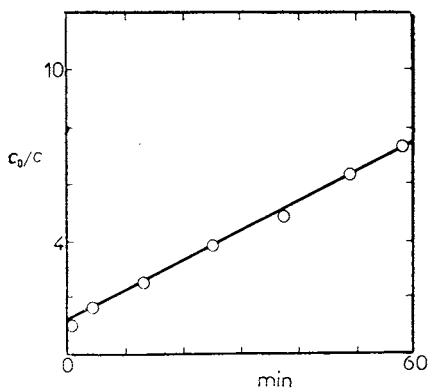


FIG. 6

Test of the II. order kinetic model for the decay of the alkyl macroradicals *I* at 233 K

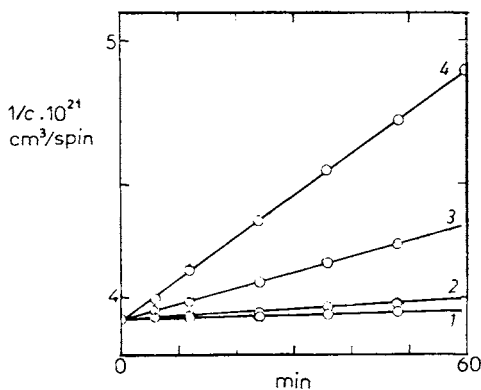


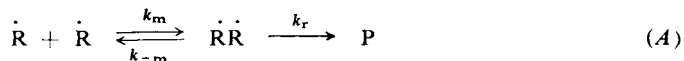
FIG. 7

Kinetic curves, $1/c = f(t)$, for the decay of the alkyl macroradicals; T (K): 1 223, 2 230, 3 237, 4 243

spectral analysis and/or the similarity of the transport mechanisms irrespective of the macroradical type in the temperature range investigated (203 to 223 K).

Interpretation of the Decay Mechanism

The kinetic data on decay of macroradicals in polymeric matrices can be interpreted by means of a model of diffusion-controlled reactions:



which – within the approximation of the diffusion-limited reactions – leads to the expression of the effective rate constant of decay of the radicals \dot{R} , $k_{\text{eff}} \doteq k_m$, presuming that $k_r \gg k_m, k_{-m}$. The symbols k_m and k_{-m} stand for rate constants of migration of the reactants to and from their contact, respectively, and k_r means the rate constant of the proper reaction in the optimum configuration of the reactants at the contact stage. Generally, if the free valence transport involves both the approach of the reactants due to physical migration with participation of molecular motions and the chemical interaction in the chemical migration phase, it can be written^{1,2}:

$$E_{\text{eff}} \doteq E_m = \bar{E}_{\text{phm}} + E_{\text{chm}}, \quad (1)$$

where $E_m, \bar{E}_{\text{phm}}, E_{\text{chm}}$ mean the energy barriers to the migration and its contributions, and E_{eff} stands for effective activation energy of decay of the centres.

Application of this model to our data on decay of the most stable alkyl centres in polyisobutylene necessitates verification of the presumption of low energy demands

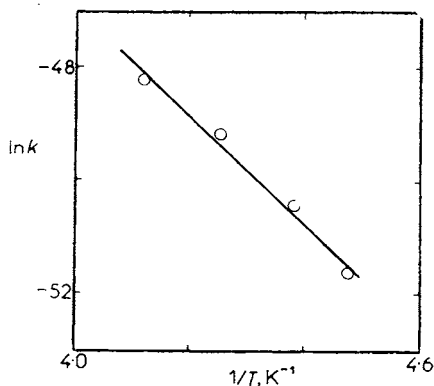
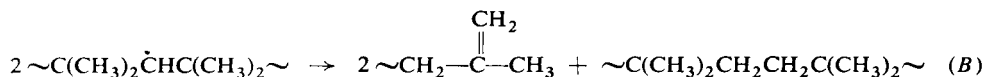


FIG. 8
The Arrhenius plot for the rate constant of the decay of the alkyl macroradicals I

of the final decay process. From the radiation chemistry of polymers it is known that polyisobutylene belongs to the group of radiation-degraded polymers, the chain scission proceeding by the radical mechanism^{8,9}. On the basis of a detailed analysis of the radiation yields of non-radical and radical products of the radiolysis the following scheme was suggested for the degradation decay of the alkyl centres *I* in the whole temperature range from 77 to 300 K (ref.⁴):



This chemism of the degradation decay is strongly supported by the findings based on material balance and changes in microstructure of the macromolecules⁴. The activation energy estimate for the degradation¹⁰ is 3.4 kJ mol⁻¹, which agrees with its course at low temperatures. The said facts justify the application of the diffusion-limited model.

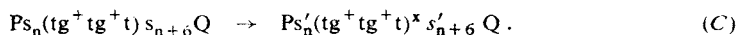
Hypothesis of Physical Migration

According to this hypothesis, the approach of the macroradicals is achieved by motions of macromolecules in the matrix. Therefrom we come to the special case when $E_{\text{eff}} \doteq E_{\text{m}} = \bar{E}_{\text{phm}}$, where \bar{E}_{phm} means the averaged energy barrier to the molecular motions.

Figure 3 shows the temperature correlation between the reactivity of the alkyl centres and α -molecular mobility in the elastic state of the amorphous matrix, which suggests a certain connection between the both phenomena. Character of this connection¹, *i.e.* if this is a direct relation (when the α -molecular motions realized in the given temperature region are also directly responsible for the transport of the reactants in their decay) or an indirect one (when the α -mobility only enables the course of other transport mechanisms), cannot be determined by comparison of activation energies of the both processes. The reason lies in that the decay obeys the Arrhenius-type relation, whereas the α -mobility obeys the WLF dependence¹¹. In the case of the α -molecular motions it is accepted that they are caused by the so-called micro-Brownian motion of the chains without any detailed specification of the motion mechanism. Another suggestion is presented in ref.¹²: anomalous elasticity of polyisobutylene — as compared with cognate polymers polypropylene and polyethylene — should be connected with the existence of very low barriers to low-amplitude conformational transitions in the rotational energy diagram for the rotation around the bonds in the model chain.

Within the concept of conformational mobility of segments, and considering the set of criteria defined in our previous papers^{1,2}, it is possible to determine a suitable motion type. The radical criterion says that a chain segment which moves in a local

free volume of the matrix contains the respective macroradical, *i.e.* it must involve $N > 2$ bonds. The alkyl macroradicals I do not contain any β -protons, so their geometry conformational structure cannot be determined directly from EPR spectrum. From several cases it is known, however, that the presence of \dot{C}_{sp^2} leads to a small effect on the conformational state of the both $\dot{C}_\alpha-C_\beta$ bonds in the macroradical as compared with chemically undisturbed bonds^{2,3}. Therefore, it can be admitted that the conformation of $\dot{C}_\alpha-C_\beta$ bonds is close to that of the non-radical chain. Several conformational analyses¹²⁻¹⁴ of model compounds of polyisobutylene show that the most stable conformation of an isolated chain is a helix of 8/3 type characterized by the presence of distorted bond pairs $\sim tg^+ \sim$ and $\sim g^- t \sim$, the most stable pairs being the combinations $\sim t_- g_+^+ \sim$ and $\sim t_+ g_-^- \sim$. Moreover, studies of relations between conformation of chains in elastic polyisobutylene and relaxation behaviour in the α -region by means of the modified Adam-Gibbs model for glass transition showed that conformation of the macromolecules in amorphous phase is decisively determined by intramolecular interactions enabling the existence of relatively long segments of right- and left-hand helices. From these data on conformational microstructure of polyisobutylene in elastic state of the amorphous phase we can arrive — after considering the mobility criterion, *i.e.* the demand of the minimum motions of the chain residues — at the conclusion of possible participation of the crankshaft motion type of the minimum seven-bond segment. This motion mechanism is characterized by simultaneous crossing of two barriers by the S_n and S_{n+6} -th bond, whereby the mobile part of segment (tg^+tg^+t) moves in local free volume of the matrix:



Calculations of kinetic energetics of the individual motions of this type involve the above-mentioned aspect of distortion of the rotational states, *i.e.* the existence of the local minima $\sim t_- g_+^+ \sim$, $\sim t_+ g_-^- \sim$, $\sim t_-^+ g_-^+ \sim$, $\sim t_+^+ t_+^+ \sim$, $\sim t_- g_-^- \sim$, $\sim t_+ g_+^+ \sim$ (refs¹²⁻¹⁴). Hence, there exist 21 physically different combinations of the starting rotational states of the end (s_n, s_{n+6}) bonds of the segment which give — in accordance with the simple jump concept² — 42 modes of the crankshaft motion; they are given in Table I. Their energy barriers, $E_{phm}^{(a)}$, were estimated according to the described procedure^{1,2}. The intramolecular contributions, $E_{intra}^{(a)}$, were calculated with the use of the energy barriers from the rotational energy diagram of the model compound 2,2,4,4,6,6-hexamethylheptane^{1,2}. The intermolecular contribution, $E_{inter}(\bar{T})$, is given by the cohesion energy of two structural units in a mobile part of the segment at 234 K. This energy was obtained by means of a relation between molar cohesion energy and molar volume and by means of the expansion model of polymers². The energy barriers to the individual modes of motion were averaged through the probabilities of occurrence of combinations of rotational states of the segment end groups, $p_i^{(a)}$,

using the conformational energies from the rotational energy diagram¹² and the value of total barriers. Then the average energy barrier \bar{E}_{phm} to the crankshaft motion is 82.1 kJ mol⁻¹. This value approaches the experimental activation energy of decay of the alkyl centres. On the basis of this relatively good agreement the decay process can be represented in terms of the hypothesis of physical migration as a sequence of two phases: *a*) approach of the radical centres as a result of the crankshaft motions of inner segments of the chains, *b*) the degradation interactions of the alkyl centres. From inspection of Table I it follows that contributions of the individual modes of the crankshaft motion are comparable, which is connected with their close energy barriers. On the other hand, if the presumption is accepted that macromolecules of the amorphous phase of polyisobutylene are formed exclusively by right- and left-hand helices in the most stable conformations, then the corresponding modes realized from these states (the 23rd, 24th, 41st, and 42nd modes) possess the highest probabilities of occurrence of their rotational states, but their contribution to the overall process is lowered because of the highest barriers. Therefrom it can be concluded that the crankshaft motions preferentially take place in the regions of bend of the chain helices. In this respect the situation of polyisobutylene is similar to that found in isotactic polypropylene³.

Two published facts can be given in favour of the presented suggestion of the migration process. The first one concerns the existence of radical pairs in the temperature region investigated. From our proposal of the motion mechanism it follows that the approach should involve relatively near centres. In fact, the presence of the radical pairs was proved at least in the lower temperature range of the investigated temperature interval of the kinetic measurements¹⁵. The second fact concerns the magnitude of the minimum segment which is rearranged into another configuration independently of its environment. This quantity appears as a parameter in the modified Adam-Gibbs model of the α -mobility in amorphous polymers¹⁴. A fitting procedure showed¹⁴ that the minimum segment contained four monomeric units, which agrees fully with our proposal of the seven-bond segment. Hence it can be concluded that the chemical interaction of at least a part of the alkyl macroradicals (at least at the beginning of the decay process) can proceed *via* reaction of close reactants brought into contact by relatively large-amplitude crankshaft motions of the inner chain segments.

Finally, the observed temperature correlation between the decay, controlled crankshaft motions, and α -molecular mobility can be explained by the following way. For the suggested motions of the inner segments to take place it is necessary that a sufficient local free volume may be present near them to enable the displacement of the mobile part of the segment. This condition can be fulfilled in the region of α -mobility connected probably with low-amplitude conformational motions¹² causing density fluctuations and, hence, fluctuations of free cavities within small regions of the polymeric matrix.

TABLE I

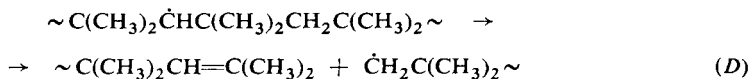
Kinetic energetics of the segmental-conformational motions of the crankshaft type for the minimum seven-bond segment in polyisobutylene (in kJ mol^{-1})

a	Conformational transition		$E_{\text{intra}}^{(a)}$	$E_{\text{inter}}(\mathcal{T})$	$E_{\text{pbm}}^{(a)}$	$P_i^{(a)}(\mathcal{T})$ %	$c_a(\mathcal{T})$ %
	initial state	final state					
1	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{t}_+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{g}^- \text{t}_+ \text{Q}$	37.7	37.9	75.6	0.053	2.218
2	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{t}_+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_- \text{Q}$	37.7		75.6	0.053	2.218
3	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{g}^- \text{t}_+ \text{Q}$	37.7		75.6	0.053	2.218
4	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_- \text{Q}$	37.7		75.6	0.053	2.218
5	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{g}^- \text{t}_+ \text{Q}$	37.7		75.6	0.053	2.218
6	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_- \text{Q}$	37.7		75.6	0.053	2.218
7	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_+) \text{t}_- \text{t}_- \text{Q}$	43.3		81.2	0.983	2.217
8	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	42.5		80.4	0.983	3.416
9	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_+) \text{t}_- \text{t}_- \text{Q}$	43.3		81.2	0.983	2.217
10	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	42.5		80.4	0.984	3.416
11	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	41.7		79.6	0.433	2.217
12	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	42.5		80.4	0.433	1.503
13	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{t}_- \text{t}_- \text{Q}$	41.7		79.6	0.433	2.217
14	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_- \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	42.5		80.4	0.433	1.503
15	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{g}^- \text{t}_- \text{Q}$	42.5		80.4	0.983	3.416
16	$\text{Pt}_+ \text{t}_+ (\text{t}_+ \dots \text{t}_+) \text{g}^+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{t}_+ \text{t}_+ \text{Q}$	43.3		81.2	0.983	2.217
17	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_+ \text{g}^+ (\text{t}_- \dots \text{t}_-) \text{g}^- \text{t}_- \text{Q}$	42.5		80.4	0.983	3.416
18	$\text{Pt}_- \text{t}_- (\text{t}_- \dots \text{t}_-) \text{g}^+ \text{t}_+ \text{Q}$	$\nearrow \searrow$ $\text{Pt}_- \text{g}^- (\text{t}_+ \dots \text{t}_+) \text{t}_+ \text{t}_+ \text{Q}$	43.3		81.2	0.983	2.217

Hypothesis of Chemical Migration

In terms of this hypothesis, chemical interaction takes part in the migration process. Potential mechanisms for the alkyl macroradicals involve β -scission and transport mechanisms proceeding by abstraction of hydrogen with or without participation of low-molecular radiolysis products.

First of all let us examine a possible course of β -scission of a chain radical according to the following scheme:

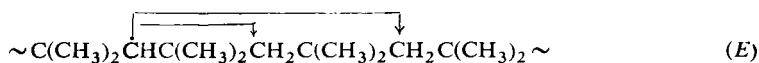


This scission of β -bond (with respect to the free valence) produces a transient terminal macroradical which, being highly reactive, undergoes a transformation with regeneration of the macroradical *I* at another place of the matrix. The overall kinetics of these subsequent reactions is determined by the slowest process – the β -scission. The activation energy (E_{chm}) was estimated by the Vojevodský method² to be 128.0 kJ mol⁻¹. This value is substantially greater than the measured activation energy of decay, so this process will not significantly contribute to the free valence transport.

A large group of the migration mechanisms involves chemical transports with hydrogen abstraction. It can be divided into two subgroups: *a*) the hydrogen abstraction with participation of low-molecular compounds formed during radiolysis of the matrix, *b*) the intra- and intermolecular pathways without participation of low-molecular radiolysis products.

From the radiation chemistry of polyisobutylene it is known that the radiolytic destruction gives molecular hydrogen and methane as the main low-molecular products⁹. In principle, these molecules, having relatively high mobility in the matrix, can participate in the free valence migration. However, analysis of this migration way of free valence gives negative results as far as its dominant participation in the centres is concerned. The method, calculation procedure and other details will be given in another communication¹⁶.

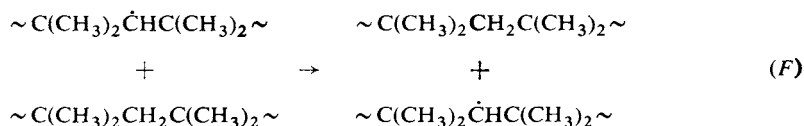
From the second group let us – first of all – analyze the intramolecular mechanisms. With respect to the fact that – in the decay course – a doublet signal from *I* can only be detected, it can be expected that possible intramolecular transfers will be of odd type: 1.3 and 1.5 H-transfer:



Energy barrier to the 1.3-transfer was estimated by means of the E-BEBO method¹⁷: $E_{\text{chm}}^{1.3}$ is 149.5 kJ mol⁻¹, which is substantially more than $E_{\text{eff}} = 77.5$ kJ mol⁻¹.

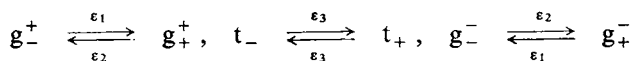
Hence, this way of approaching of the centres can be excluded. Analysis of the 1.5 H-transfer can only be qualitative, because neither the calculation by means of an adequate theoretical method nor the activation energy of an analogous low-molecular reaction are available. In spite of that, however, we can give a fairly convincing argument based on conformational energetics of chains and on application of the geometry-energy criterion which indicates a low probability of participation of this mode of intramolecular migration. Considering the geometry-energy criterion in looking for the optimum conformational sequence of skeletal bonds of the cycle (which leads to the maximum approach of the \dot{C}_1 atom and H, H' at the C_{1+4} atom) we can find the sequence $\sim tg^\pm tg^\pm \sim$. However, conformational energy calculations¹² show that this sequence is characterized by a high content of intramolecular energy, which makes the probability of its occurrence negligibly low. Therefrom it can be deduced that the 1.5 isomerization will not contribute significantly to the transport of the centres either.

Finally, the last possibility within the terms of the hypothesis of chemical migration consists in potential operation of the intermolecular mechanism according to the following scheme:



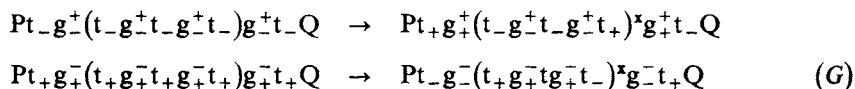
The energy barrier calculated by the ZAV/3 method² provides the $E_{\text{chm}}^{\text{inter}}$ value of 57.7 kJ mol⁻¹. This value is lower than the experimental activation energy of the decay, hence this transport way of free valence cannot be excluded.

In the terms of the activation energy approach^{1,2} this result means that a certain part of the total energy barrier is due to some motion of a chain part which enables the contact situation for the transfer reaction. Attempts at finding of a possible mechanism also make use of the rotational energy diagram of the model compound of polyisobutylene¹². Therefrom it follows that there exist not only relatively high barriers between the t , g^+ , and g^- rotational states but also relatively low barriers separating the distorted rotational states:



with the values ε_1 2.6 kJ mol⁻¹, ε_2 1.1 kJ mol⁻¹, and ε_3 4.2 kJ mol⁻¹. The conformational state of polyisobutylene chains being known¹²⁻¹⁴, it is possible — after considering the mobility criterion — to postulate a low-amplitude analogy of the crankshaft motion, the so-called quasi-crankshaft motion. This motion is character-

ized by a correlated transition of two end bonds ($S_n, S_{n+\epsilon}$) of a seven-bond segment from one local minimum to another. In principle, the expressions from ref.¹ can be used for estimation of the kinetic energetics of individual modes of the quasicrankshaft motion. The intramolecular contribution is given by the additive scheme. The intermolecular term can be expressed by the general relation (5) from ref.¹, but, with respect to the low-amplitude character of the motion (which is whole realized in the force field of the adjacent chains), it is impossible to use the approximation $\Delta\epsilon_m = \epsilon_m^0$, where ϵ_m^0 means the cohesion energy of the m -th structural unit in the mobile part of the segment. In any case it is $\Delta\epsilon_m < \epsilon_m^0$, *i.e.* the intermolecular contribution represents a part of the maximum value ϵ_m^0 which is justified for high-amplitude segmental-conformational motions requiring the presence of a sufficient local free volume near the mobile part of the segment. A recent experimental work¹⁸ correlated a large series of polymers and showed that the activation energy of motion of kinetic units of the chain is composed of an intra- and an intermolecular components, the former being connected with rotational barriers of the bonds and the latter term being equal to $1/3\epsilon_m^0 n_s$, where n_s means number of structural units in a statistical segment of the chain. Comparison of these results¹⁸ with the above-given conclusions which follow from our model of the conformational dynamics¹ reveals a noteworthy consistency. As the motion mechanism consisting in crossing of low energy barriers¹² is very likely for the α -molecular motion in polyisobutylene, and a statistical segment of polyisobutylene includes 6 bonds¹⁹, *i.e.* 3 units, it is possible to put $\Delta\epsilon_m \doteq 1/3\epsilon_m^0$. Hence, the estimate of energy barrier to the quasicrankshaft motions with the most stable chain conformations



gives $E_{\text{phm}} = 12.6 \text{ kJ mol}^{-1}$, so that $E_m = 70.3 \text{ kJ mol}^{-1}$. This value is close to the experimental one (77.5 kJ mol^{-1}). On the basis of this relatively good agreement and with regard to the fact that this physico-chemical migration mechanism enables the approach of more distant radical centres we can conclude by stating that the intermolecular transfer of free valence connected with the quasicrankshaft motions can represent the dominant mechanism for the transport of both close and distant reactants in the initial and especially in the later phases of the decay processes of alkyl centres in polyisobutylene.

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