Kinetics of Benzoyloxy Radical Transfer by Polyethylene

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By quantitative determination of the products of thermal decomposition of benzoyl peroxide over the temperature range 70—90°C, using the method of competition reactions, temperature dependences of rate constants ratio of benzoyloxy radical transfer and its fragmentation in high density polyethylene and in its low-molecular model (*n*-heptane) have been determined. The results obtained suggest that the radical transfer reaction proceeds within the overall temperature range at a higher rate in polyethylene than in *n*-heptane. On the basis of the determined values of activation energies as well as of the preexponential terms of the corresponding Arrhenius equations the character of the influence of polymer hydrocarbon medium on the kinetics of its substitution reaction with oxyradicals is evaluated.

In our previous papers [1, 2], the relative reactivity of cumyloxy radical in its transfer by hydrocarbons has been determined and the kinetics of this process in both the analogous low and high molecular alkanes compared. The results obtained suggest that despite the practically identical activation energy the transfer reaction proceeds over the temperature range 135—165°C at a threefold rate in polyethylene melt when compared, *e.g.* with *n*-heptane. This difference, which is most likely due to the change of the frequency factor, does not then result from different reactivity of C—H bonds but from different physical character of both hydrocarbon media.

To evaluate this polymer influence more completely we checked the transfer reaction kinetics also over the temperature range in which polyethylene still contains the crystalline phase. For experimental reasons we used as the source of oxyradicals benzoyl peroxide, decomposing at an optimum rate over the required temperature range (70—100°C). We followed the kinetics of the reaction discussed by the same method as previously [2] in polyethylene and in *n*-heptane. From the products of benzoyl peroxide decomposition quantitatively corresponding to the relative transfer ability of benzoyloxy radicals, benzoic acid and benzene were determined.

Experimental and Results

The purification of benzoyl peroxide used for these experiments was performed by threefold precipitation from its chloroform solution with methanol.

In purifying the high density polyethylene (Hostalen GD 6250) and *n*-heptane as well as in preparing samples of hydrocarbons containing benzoyl peroxide and in their heating we proceeded in just the same way as in the investigation of the cumyloxy radical transfer kinetics [2].

Whereas the decomposition products of benzoyl peroxide in *n*-heptane were directly determined from polyethylene, they have primarily been isolated by extraction of

the polymer with chloroform, the extract thus obtained being used for the analysis. Benzoic acid formed in the reaction was determined by titration of samples diluted by benzene—methanol mixture (in the ratio 2 : 3) by 0.1 N alcoholic solution of potassium hydroxide using alkaline blue as indicator. For quantitative determination of benzene the method of gas—liquid chromatography was used. The analysis was performed at 50°C on a 200-cm column containing as anchored phase 10% of Carbowax 400 on Chromosorb W AW of granularity 60—80 mesh.

Out of the determined quantities of benzoic acid (BA) and benzene (Bz) formed in the decomposition of benzoyl peroxide of different concentration (0.5—3%) in both polyethylene and n-heptane the kinetic characteristics of the transfer reaction of benzoyloxy radical with hydrocarbons (CH) was calculated from the relation

$$\frac{k_2}{k_3} = \frac{[BA]}{[Bz][CH]} , \qquad (1)$$

where k_2 denotes the rate constant of the elementary transfer reaction and k_3 that of the competing benzoyloxy radical decarboxylation. The equation (1) was deduced on the same principle as for the analogous case of cumyloxy [1] or tert-butoxy radical [5], based on the fact that the ratio of products of transfer (BA) and fragmentation (Bz) determines the extent of the radical ability to decay by a substitution reaction with the medium. (Though carbon dioxide is the immediate product of benzoyloxy radical fragmentation we have, in view of the fact that it arises even in induced peroxide decomposition, substituted its amount equivalent to oxyradicals decarboxylation by the concentration of benzene formed by decay of the other product of the reaction considered, i.e. of phenyl radicals, by transfer with the medium. The decay of phenyl radicals by another mechanism is unimportant with respect to the found character of the induced benzoyl peroxide decomposition in hydrocarbons [3, 4].)

In conformity with equation (1), the validity of which has already been verified in the case of a few oxyradicals [1, 2, 5—7] the ratio of the formation of their reaction product of both the transfer and the fragmentation over a narrower concentration range is independent of peroxide concentration as seen from Fig. 1. The determined average values of the ratio of benzoyl peroxide decomposition products in polyethylene and n-heptane at various temperatures are shown in Table 1.

The temperature dependences of the ratios of constants k_2/k_3 calculated from the results referred to according to relation (1) are shown in coordinates according to Arrhenius equation in Fig. 2. (To make the frequency factors comparable the values corresponding
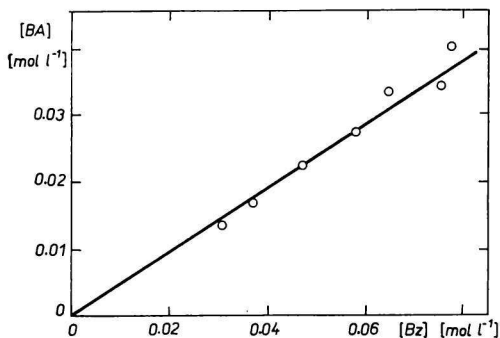

Fig. 1. Dependence of concentration of benzoic acid on benzene concentration determined after 135 hours of benzoyl peroxide decomposition over its concentration range 0.5—3% in n-heptane at 70°C.

Table 1

Molar ratios of benzoic acid (BA) and benzene (Bz) determined in benzoyl peroxide decomposition in polyethylene and *n*-heptane at various temperatures

Reaction time [hrs]	Polyethylene		*n*-Heptane	
	temperature [°C]	$\dfrac{[BA]}{[Bz]}$	temperature [°C]	$\dfrac{[BA]}{[Bz]}$
135	70	3.9 ± 0.3	70	0.48 ± 0.03
45	80	3.6 ± 0.4	79	0.44 ± 0.04
15	90	3.4 ± 0.2	90	0.36 ± 0.02
5	100	3.1 ± 0.3	101	0.32 ± 0.02

Chosen reaction times corresponded according to the determined kinetics of benzoyl peroxide decomposition in polyethylene [8] to 10 half-life of peroxide decomposition at the appropriate temperature.
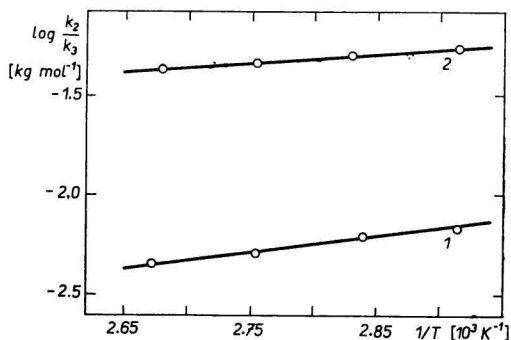

Fig. 2. Logarithm of the ratio of rate constants k_2/k_3 in dependence of the reciprocal absolute temperature in benzoyl peroxide decomposition in *n*-heptane (*1*) and polyethylene (*2*).

to one elementary CH_2 link were substituted in both hydrocarbons for [CH].) The numerical data of the differences of activation energy of the substitution reaction of benzoyloxy radical and its fragmentation $E_2 - E_3$ as well as of the ratios of frequency factors of the corresponding reactions (A_2/A_3) obtained by this solution are expressed by mathematical formulations of the appropriate relations, *viz.*

$$\frac{k_2}{k_3} = 10^{-4.4\pm0.2} \exp\left(\frac{3500 \pm 300}{RT}\right) \text{ [kg mol}^{-1}\text{]}, \qquad (2)$$

for *n*-heptane and

$$\frac{k_2}{k_3} = 10^{-2.6\pm0.1} \exp\left(\frac{2100 \pm 100}{RT}\right) \text{ [kg mol}^{-1}\text{]}, \qquad (3)$$

for polyethylene.

Discussion

From the given results it may be deduced that, similarly as in the previous case of cumyloxy radical [2], the ratio of frequency factors (A_2/A_3) in polyethylene exceeds that in *n*-heptane. It is, however, not very probable that the increase of this fraction is caused by the decrease of A_3 because in this case it concerns the frequency factor of an unimolecular reaction, the change of which in condensed phase might be under-standable in the contrary sense, but only in the processes accompanied by a reversible reaction in the cage. It would apparently be more justified to attribute the cause of this phenomenon to the increase of the bimolecular reaction of oxyradical transfer by hydro-carbon chain. Here, the physical sense of A_2 increase might well be due to the increase of collisions frequency of reacting particles as seen from the expression of the frequency factor of a general bimolecular reaction in condensed phase [9]

$$A = 10^{-3} N_A 4\pi r_{AB}^2 \Delta r \frac{2}{C\tau} \quad [\text{l mol}^{-1} \text{ s}^{-1}]. \tag{4}$$

(N_A denotes the Avogadro's number, r_{AB} the collision diameter of particles of the reacting pair, Δr the thickness of cage walls, C its coordination number and τ the vibration period.) The relative increase of the matrix density and the effective dimensions of the reacting segments of the hydrocarbon component may cause in polymer the decrease of both the vibration period and the coordination number of the cage as well as the increase of the thickness of its walls and, consequently (4), also the increase of the frequency factor.

Unlike the preceding case of cumyloxy radical [2] a reduction of the difference of acti-vation energies $(E_2 - E_3)$ of the reactions investigated in polymer, namely an apparent increase of the activation energy of the elementary transfer reaction by 1.5 ± 0.4 kcal mol^{-1} takes place here. We might well try to look for the cause of this fact in the differen-ces between the both systems compared, consisting in the difference partly of the reacting oxyradical, partly of the physical structure of the polymer medium.

When evaluating the influence of different reactivity of the two concrete oxyradicals let us admit that in either case the activation energy of the transfer by polymer exceeds that by its low-molecular analogue, whereas, in the cumyloxy radical, its small increase overlapped by the dispersion of experimental values could not have become evident. If this, however, were the cause of the fact discussed, such an increase of activation energy of transfer would have to be manifested more markedly in the more selective cumyloxy radical and not in the more reactive benzoyloxy radical.

The cause looked for might then rather be due to the difference of the physical structure of polyethylene which in one case (cumyl peroxide) occurred over the whole tempera-ture range of the experiment as an amorphous one, whereas in the second case (benzoyl peroxide) the amorphous phase represented only one part of the polymer matrix tending to increase with increasing temperature. If starting from the well-founded presumption that the reaction discussed is practically confined to amorphous polymer segments, the temperature change of the ratio [BA]/[Bz] will, apart from the direct influence of the temperature on the change of the rate constants ratio of the appropriate reactions, include also its indirect influence, *i.e.* the change of [CH] in equation (1), thus expressing the concentration of CH$_2$ elements only of the amorphous phase at a given temperature. Since the amorphous fraction of polyethylene of this type increases over the temperature range investigated monotonously from about 50% at 70°C to 65% at 100°C [10], this approximately 1.3-fold increase of the amorphous phase may, in the used manner of k_2/k_3 calculation (when [CH] was considered as a constant) become evident by an apparent decrease of the $E_2 - E_3$ difference by about 2 kcal mol^{-1}. With respect to this fact the corrected numerical data k_2/k_3 may be expressed by the following Arrhenius equation

$$\frac{k_2}{k_3} = 3 \times 10^{-4} \exp\left(\frac{4000}{RT}\right) \quad [\text{kg mol}^{-1}], \tag{5}$$

where the value of the activation energy already roughly corresponds to the data measured in n-heptane, as is the case with cumyl peroxide as well.

In view of the preceding analysis the $E_2 - E_3$ value for benzoyloxy radical is -3.5 kcal mol^{-1} approx. and for cumyloxy radical -8 kcal mol^{-1} [2]. By means of Polányi's rule [11], according to which

$$E_2 = (11.5 \pm 1.3) - 0.25 \, \Delta H \quad [\text{kcal mol}^{-1}], \tag{6}$$

the activation energy of the elementary transfer reaction may be estimated, for which, after substituting ΔH by the strength difference of the O—H bond of alcohols (103—-105 kcal mol^{-1} [12]) and C—H bond of methylene hydrogens (94 kcal mol^{-1} [12]), the value of $E_2 \cong 9$ kcal mol^{-1} is obtained. For the activation energy of splitting off $\dot{\text{C}}\text{H}_3$ from cumyloxy radical, the value of about 17 kcal mol^{-1} is then the result. Though there is no reference available of these direct data, it can, however, well compare with the activation energy of fragmentation of the structurally very similar *tert*-butoxy radical, the found value of which is 17 ± 3 kcal mol^{-1} [13]. For the activation energy of benzoyloxy radical decarboxylation we thus obtain, from the measured difference of $E_2 - E_3 =$ $= -3.5$ kcal mol^{-1}, the value $E_3 \cong 12.5$ kcal mol^{-1}. Its value, estimated analogically, but from the experimentally determined difference of activation energies of benzoyloxy radical addition on styrene and its fragmentations is, according to other authors, 14 kcal mol^{-1} [14].

Although in both cases it is the question of only an approximative estimation, there may, nevertheless, be inferred from the difference $4-5$ kcal mol^{-1} found from the measured $E_2 - E_3$ values in both peroxides that the tendency to fragmentation in benzoyloxy radical exceeds that in cumyloxy radical. The probable higher reactivity of benzoyloxy radical to transfer reactions with hydrocarbons, when compared with cumyloxy radical cannot, namely, bring about, according to relation (6), such a change of activation energy of this process that it would result in such considerably different $E_2 - E_3$ values in the two radicals compared.

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