Reactivity of C—H Bonds of Polyethylene and Low-molecular Paraffins with Respect to Cumyloxy Radicals

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By means of the data referring to the relative reactivity of cumyloxy radicals determined from the products of cumyl peroxide decomposition in *n*-heptane, *n*-octane and in high-density polyethylene in dependence on temperature, C-H bonds reactivity of both the low- and the high-molecular paraffins in substitution radical reactions have been compared. The kinetic data obtained result in the conclusion that neither the activation energy nor the frequency factor of the reaction show any considerable difference in the media observed.

In crosslinking the saturated polymers by peroxides, apart from the initiator efficiency, also the reactivity of the radicals produced by the initiator plays quite an important role. This reactivity, along with the structure of the chain elements, affects largely the reaction mechanism and thus also the extent of the undesirable occurrence of parallel polymer degradation. Since for the given purpose cumyl peroxide is used with regard to the high efficiency in generation of macroradicals as well as to other technical advantages, we investigated in the previous paper [1] the relative reactivity of cumyloxy radicals in substitution reactions, which we determined from kinetic measurements made in low-molecular hydrocarbons of various structures.

In view of the existing data on radical transfer by polymer, the problem of direct application of the results obtained on high-molecular objects appears, however, to be quite a questionable one. Apart from the found agreement of the character of the substitution reaction of the radical with low- and high-molecular hydrocarbons [2], it was also reported that such a reaction with a polymer may proceed with higher [3, 4] and even with lower activation energy [5]. On this ground we decided to find out which one of the phenomena referred to is manifested in just the case investigated or to what extent any of them might prove to be significant. In the present paper we describe the temperature course of relative reactivity of cumyloxy radical determined by the method of concurrent reactions [1] in n-heptane, n-octane and in high-density polyethylene as well as the appropriate activation energies and frequency factors of the analyzed processes.

Experimental and Results

n-Heptane, *n*-octane and cumyl peroxide used in the present work were purified in just the same way as in [1]. Equally we proceeded also in the preparation of hydrocarbon samples with different cumyl peroxide concentration (0.5-3 weight %), their sealing in glass test tubes in nitrogen atmosphere, heating and chromatographic analysis of peroxide decomposition products (cumyl alcohol and acetophenone).

Table 1

Temperature [°C]	Reaction time [hrs]	[CA]/[APh]		
		<i>n</i> -heptane	n-octane	polystyrene
110	135	-		8.1 ± 0.9
136	10	1.39 ± 0.07	1.50 ± 0.10	$3.9~\pm~0.4$
145	4	0.98 ± 0.05	$1.16~\pm~0.09$	3.6 ± 0.2
155	2	$0.82~\pm~0.05$	$0.93~\pm~0.10$	2.6 ± 0.3
166	1	0.68 + 0.06	0.78 ± 0.09	2.0 + 0.1

Molar ratio of cumyl alcohol (CA) and acetophenone (APh) formed by cumyl peroxide decomposition in *n*-heptane, *n*-octane and polyethylene at various temperatures

The values show in n-heptane and n-octane the average of 10, in polyethylene of 7 measurements made at various peroxide concentrations to the extent previously described.

The polyethylene used in the experiment was the high-density commercial product (Hostalene GD 6250, Hoechst), specific gravity 0.95 g/cm³, CH₃ groups content less than 0.1 mole %, m.p. of crystallites from 127-131°C. We purified the polymer by three-fold precipitation of its 3% toluene solution (cooling down from b.p. to laboratory temperature) in nitrogen atmosphere. The precipitate thus obtained was sifted through a sieve, mesh size 0.3 mm and dried at 40°C to constant weight. Polyethylene samples containing cumyl peroxide were prepared by impregnation of polymer powder by methanol solution of peroxide of required concentration (0.5-2 weight % of peroxide per polymer weight), from which the solvent was removed by drying at laboratory temperature. The polymer samples thus prepared were charged (by 3 g) into glass test tubes sealed in nitrogen atmosphere by the technique previously used [6] and heated in a thermostated oil bath at various temperatures. After the peroxide decomposition the reaction products were extracted from the polymer by boiling chloroform. The chloroform extract was used for quantitative determination of both cumyl alcohol and acetophenone made by the method of gas-liquid chromatography at the temperature of 140°C. In this analysis a 150-cm column filled with 15% of neopentyl glycol sebacate on W AW Chromosorb was used.

The results obtained by the method described in all of the three analyzed hydrocarbons are summarized in Table 1.

Discussion

According to the analyzed kinetics of the process of cumyl peroxide decomposition in hydrocarbon medium [1] there may be determined from the ratio of cumyl alcohol and acetophenone formed in this reaction

$$Ph(CH_3)_2CO_{\bullet} + SH \xrightarrow{k_3} Ph(CH_3)_2COH + S_{\bullet}, \qquad (1)$$

$$Ph(CH_3)_2CO \longrightarrow PhCOCH_3 + CH_3,$$
 (2)

the relation of rate constants of the cumyloxy radical transfer (k_2) and its fragmentation (k_3) from the equation

$$\frac{k_2}{k_3} = \frac{[\text{CA}]}{[\text{APh}] [\text{SH}]} \tag{3}$$

where [SH] expresses the molar concentration of hydrocarbon. The temperature dependence of the k_2/k_3 constants ratio calculated from the relation (3) (Table 1) is shown in coordinates according to Arrhenius equation (Fig. 1). To make the frequency factors comparable we substituted [SH] in polyethylene with the equivalent *n*-octane value corresponding to 8 elementary units.



Fig. 1. Logarithm of k_2/k_3 rate constants ratio vs. reciprocal absolute temperature for *n*-heptane (1), *n*-octane (2) and polyethylene (3).

Using the solution shown in Fig. 1, the differences of activation energies of the substitution reaction of cumyloxy radical with the appropriate hydrocarbon and its fragmentation $(E_2 - E_3)$ as well as the ratios of frequency factors of corresponding reactions (A_2/A_3) may well be obtained. The values of the kinetic constants determined (numerically by the method of least squares) in the media investigated are shown in Table 2.

It may be derived from the results stated that the values of activation energies as well as those of frequency factors do not exhibit within the exactness of the results any considerable difference either as regards the low-molecular paraffin or polyethylene. Alike, there is observed no deviation of the polyethylene course over the m.p. of crystallites.

Table 2

Differences of activation energies of the substitution reaction of cumyloxy radical and its fragmentation $(E_2 - E_3)$ and logarithms of the ratios of frequency factors of corresponding reactions (A_2/A_3) for the three hydrocarbons under investigation

Hydrocarbon	${E_2-E_3}$ [kcal/mole]	$\log A_2/A_3$ [kg/mole]
<i>n</i> -heptane	-8.3 ± 1.1	-5.3 ± 0.6
<i>n</i> -octane	-7.8 ± 0.6	-5.0 ± 0.3
polyethylene	-8.2 ± 0.5	$-4.7~\pm~0.2$

Hence, the $E_2 - E_3$ value amounts to about -8 kcal/mole in all of the three media thus being in quite a good agreement with the data referred to as the difference between the activation energy of cumyloxy radical fragmentation and its transfer by hydrocarbons (7 kcal/mole) [7]. It might, however, appear that owing to the different contents of both the methyl and the methylene hydrogens the activation energy of transfer and the corresponding absolute $E_2 - E_3$ value should decrease in the sequence n-heptane-n-octane-polyethylene. These differences, however, are found to be so small (between n-heptane and n-octane attaining a few cals only and between n-heptane and polyethylene a few hundreds cals maximum) that they cannot be manifested experimentally. Neither the expected increase of the activation energy of the reaction considered which, in polymer chain is assumed to be due to steric hindrances occurring in adjusting the electron structure from the saturated tetrahedral to the planar radical [3, 4] plays, in the case under discussion at least, a role not suggesting any marked manifestation of the mentioned influence. To the same conclusion lead also the results of other authors [2] who in studying the substitution reaction of stable nitroxy radical with n-heptane, cetane and polyethylene, respectively, found practically equal values of its activation energy. On the other hand, the observed relative decrease of the activation energy of the considered reaction in polymer, when compared with its analogous gaseous components [5], will then result from the specificity of the physical state of the investigated object (the reaction was studied in polyethylene below the temperature of its glassy transition) and not only from its high-molecular character.

The determined A_2/A_3 ratio of all of the three hydrocarbons finds itself within the limits of one order (roughly 10^{-5} kg/mole) and the possible sequence of these values pursuing the mentioned order of media (Table 2) might then logically be caused by the corresponding increase of the effective collision diameter of the molecule or polymer segment. Under a well-founded assumption of the unchangeability of the rate constant of unimolecular fragmentation of cumyloxy radical (k_2) in the hydrocarbon media under investigation, this fact may also account for the sequence of the rate increase of the analyzed substitution reaction over the investigated temperature range (Fig. 1). This is then not due to the different reactivity of C—H bonds of the high- and the low-molecular paraffins but to various collision frequencies of the reacting particles.

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