ANALYSIS OF MECHANISMS OF THE CATALYTIC EFFECT OF HYDROGEN ON THE DECAY OF ALKYL MACRORADICALS IN POLYETHYLENE

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The suggested one-step and two-step mechanisms of decay of alkyl macroradicals in polyethylene are analyzed in detail at the activation energy level. For the one-step mechanism, the BEBO method is modified for reactions proceeding *via* a three-particle state. For the two-step mechanism, a three-process kinetic model is used; the contributions to the total energy barrier are calculated by the original BEBO method for two-particle transition states and by a molecular model for the diffusion of simple penetrants in polymers. The results indicate that the catalytic effect of hydrogen on the migration of the alkyls in the amorphous phase proceeds by the two-step mechanism.

A general reaction of macroradicals in polymers, generated by various destructive effects, is their decay[1,2]. This process is controlled by the transport of the radical centres in the matrix, which can occur either by physical migration with the participation of motions of various kind and/or by some chemical migration mechanisms such as hydrogen transfer, β-cleavage, combined depolymerization and polymerization. The way of macroradical generation (mechanical, radiolytic, chemical) at a given temperature determines the type of the macroradicals, which enter into various migration modes in dependence on the reaction conditions. For radiolysis at low temperatures or in closed reaction systems at high temperatures, an additional way of centre transport is conceivable, *viz.*, one in which the low molecular weight products, particularly molecular hydrogen, are involved[1]. This type of macroradical migration has been examined experimentally[3-10] for a series of morphological forms of polyethylene (PE). H_2 or D_2, which are soluble in the disordered regions of the semicrystalline matrix only[11-13], have been found to have a significant catalytic effect upon the decay of alkyl macroradicals $(\sim CH_2\dot{C}HCH_2\sim)$ either by their combination[3-10] or by their transformation to more stable allyl macroradicals[5,6]. The allyl decay, on the other hand, is unaffected by the presence of hydrogen or its isotopes[6]. The different reactivity of alkyls in the absence and in the presence of H_2 is due to the decay rate constant increasing in the latter case as a result of the lowered activation energy of the migration stage of the decay reaction. For instance, for 1st order kinetic models, the activation energy in the $0-60°C$ range decreases from

71.5 kJ mol^{-1} in the noncatalyzed state to 54.5 kJ mol^{-1} in the catalyzed state[6,7]. The following mechanisms of alkyl migration in amorphous zones of PE have been suggested to account for these facts. In the absence of hydrogen, the hydrogen transfer

$$\dot{R} + HR \rightarrow RH + \dot{R} \qquad (A)$$

is the dominant process at higher temperatures. A detailed analysis of this transport mode has been made and a preference of the intermolecular mechanism in conjunction with the segment-conformational mobility of the chains in the amorphous zones has been suggested[14,15]. For the catalyzed situation, on the other hand, two different mechanisms involving hydrogen transfer have been postulated. That one, so-called two-step process, can be written as[3,4]

$$\dot{R}(r) + H_2 \rightarrow RH + \dot{H} \qquad (B)$$

$$\dot{H} + HR \rightarrow H_2 + \dot{R}(r'), \qquad (C)$$
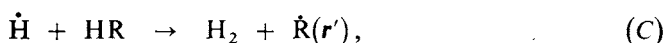
where $\dot{R}(r)$ and $\dot{R}(r')$ are alkyl centres with position vectors r and r'. Here the alkyl detaches hydrogen from a H_2 molecule, and the atomic hydrogen regenerates to H_2 giving rise to an alkyl radical in a different site of the matrix. The other, so-called one-step mechanism, has been suggested[5] to proceed *via* a three-particle complex as
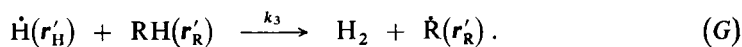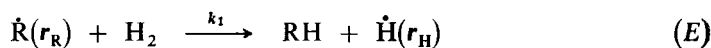
$$\dot{R}(r) + H_2 + HR(r') \rightarrow [R \cdots H \cdots H \cdots H \cdots R] \rightarrow$$
$$\rightarrow RH(r) + H_2 + \dot{R}(r'); \qquad (D)$$
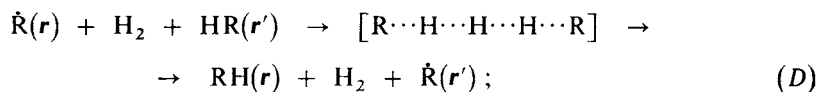
here hydrogen does not occur in the free atomic state.

The two-step mechanism is contradicted by the following experimental facts[5,6,10]: *1*) atomic hydrogen in the matrix is not detected by ESR; *2*) the amount (pressure) of the gas in the reaction system is not reduced due to the competitive quenching reaction $\dot{H} + \dot{R} \rightarrow HR$; and *3*) the amount of the insoluble gel, formed by combination of the alkyl radicals, is not reduced due to its reaction with hydrogen atoms. Hence, the one-step mechanism should rather be valid. On the other hand, the two--step process may be favoured by the very short life of $\dot{H}$ radicals at relatively higher temperatures and by the relatively low concentration of $\sim\dot{C}H\sim$ and $\dot{H}$ radicals with respect to $\sim CH_2\sim$.

In the present work, the postulated mechanisms of hydrogen catalysis of the alkyl centre migration in PE are analyzed in detail at the activation energy level, with the purpose to obtain theoretical evidence in favour of one of them.

THEORETICAL

The kinetic model for the two-step transfer mechanism of the hydrogen-catalyzed alkyl centre migration in polyethylene can be written in detail as

$$\dot{R}(r_R) + H_2 \xrightarrow{k_1} RH + \dot{H}(r_H) \tag{E}$$

$$\dot{H}(r_H) \xrightarrow{D_2} \dot{H}(r'_H) \tag{F}$$

$$\dot{H}(r'_H) + RH(r'_R) \xrightarrow{k_3} H_2 + \dot{R}(r'_R). \tag{G}$$

The three processes are characterized by the rate constants of abstraction of hydrogen from H_2 by the macroradical $\dot{R}$ (k_1), diffusion coefficient of atomic hydrogen (D_2), and the rate constant of abstraction of hydrogen from the macromolecule RH by the radical $\dot{H}$ (k_3). According to the theory of diffusion-limited reactions, the effective rate constant of the decay is[16,17]

$$k_{eff} = k_m = 4\pi r D, \tag{1}$$

where r is the contact distance for the centre decay by combination or transformation and D is the overall diffusion coefficient of the radical centre migration $(D = 2D_1)$; the statistical theory of diffusion of a particle in the threedimensional space gives

$$D_1 = (1/6)\, l^2 v, \tag{2}$$

where v is the frequency of the transfer reaction (E) given by $k_1[H]$ and l is the mean distance of the free valency displacement due to the occurrence of processes (F) and (G), given by the relation $l = (6D_2\tau)^{1/2}$, where τ is the average lifetime of $\dot{H}$, $\tau = (k_3[RH])^{-1}$. Then

$$k_m = 8\pi r D_2(k_1/k_3)\,([H_2]/[RH]). \tag{3}$$

In terms of Arrhenius' relations for the rate constants and the diffusion coefficient, the activation energy of the two-step catalyzed migration obeys the relation

$$E_m = E_1 + E_2 - E_3. \tag{4}$$

The contributions E_1 and E_3 can be calculated by the BEBO method, E_2, by means of the statistico-mechanical model of diffusion of simple penetrants in polymers.

For a transfer reaction of hydrogen proceeding *via* a two-particle two-bond complex

$$X\text{---}H + \dot{R} \rightarrow [X \overset{n_1}{\cdots} H \overset{n_2}{\cdots} R] \rightarrow \dot{X} + HR, \tag{H}$$
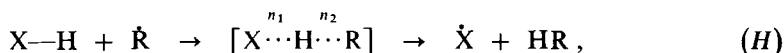
where $\dot{R}$ is either $\sim CH_2\dot{C}HCH_2 \sim$ or $\dot{H}$ and X—H is either H_2 or $\sim CH_2CH_2CH_2 \sim$, the total potential energy of the reaction region is calculated by the BEBO method[18,19] as

$$E = D_1 - D_1 n_1^p - D_2 n_2^q + D_3 B(n_1 n_2)^{0.28\beta} \left[1 + B(n_1 n_2)^{0.28\beta}\right], \qquad (5)$$

where D_1 and D_2 are the chemical dissociation energies of the decaying and the forming bonds, respectively, D_3 is the dissociation energy of the R—X bond, n_1 and n_2 are the respective bond orders $(n_1 + n_2 = 1)$, p and q are the so-called BEBO parameters, β is the spectral parameter of the R—X bond and B is a coefficient determined by the geometrical and spectral parameters of the reactants and products of the particular reaction[18,19]. In agreement with the transition state concept, the energy barrier of the reaction is given by the maximum value of E with respect to the bond order n after including corrections for the zero point energy of the reactant and the transition state[19]. By this approach the experimental activation energies of diverse transfer reactions of hydrogen are obtained with an average error[19] of ± 5.4 kJ mol^{-1}.

According to the molecular theory of diffusion of simple penetrants in the amorphous phase of polymers[20,21], the diffusant can move within the locally quasi-arranged matrix in two ways: *1*) by gliding inside interchain channels or in regions of low local density of the disordered zones; and *2*) by jumping across chains after their sufficient separation by bending, caused by small rotations of bonds of the chain segments. The two penetrant motion modes occur in series, so that the activation energy of diffusion is given by the energy demands for the minimal separation of chains, allowing for diffusant penetration into the neighbouring channel. The apparent activation energy of diffusion $E_d = E_2$ for a temperature range from T_1 to T_2 with activation energies $E(T_1)$ and $E(T_2)$, respectively, is

$$E_d = \left[E(T_1)/T_1 - E(T_2)/T_2\right]/\left[1/T_1 - 1/T_2\right] \qquad (6)$$

for which

$$E(T) = 5.23\gamma^{1/4}(\varepsilon^*\varrho^*/\lambda^2)^{3/4} (d')^{-1/4} \{0.077[(\varrho^*/\varrho)^{11} (\varrho - 10d') -$$
$$- \varrho^*(\varrho^*/(\varrho^* + d))^{10}] - 0.58 \left[(\varrho^*/\varrho)^5 (\varrho - 4d) - \varrho^*(\varrho^*/(\varrho^* + d))^4\right]\}^{3/4}, \qquad (7)$$

where γ is the average bending modulus of a chain per unit length, ε^* and ϱ^* are the energy and length parameters, respectively, of the Lennard–Jones potential for a structure element, *i.e.*, a $\sim CH_2 \sim$ group of the chain, λ is the average distance of the elements along the chain, d is the diameter of the rigid sphere of penetrant, ϱ is the equilibrium distance of the chains, and $d' = d + \varrho^* - \varrho$. It is clear that E is a function of temperature *via* $\varrho(T)$, which can be expressed by means of the thermal ex-

pansion coefficient as $d(\varrho^*/\varrho)/dT = (1/2)\,\alpha_V$. This approach was used with success for establishing the relationship between the activation energy of penetrant diffusion E_d and its size d over a series of diffusant–polymer systems, particularly in polyethylene.

RESULTS AND DISCUSSION

One-Step Mechanism

According to this concept, the catalysis should proceed by pathway (D) by a simultaneous occurrence of two hydrogen transfer reactions *via* a common central hydrogen atom. The energy barrier of this process can be calculated by means of the BEBO method, which was modified by us with respect to the different nature of the transition state,

$$\overset{n_1 \quad n_2 \quad n_3 \quad n_4}{\left[R \cdots H \cdots H \cdots H \cdots R \right]}.$$
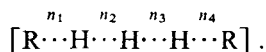
Our modified BEBO method for reactions *via* three-particle four-bond systems (M-BEBO) includes (1) the presumption of linearity of the transition state; (2) the concept of conservation of the total bond order $(n_1 + n_2 + n_3 + n_4 = 2)$; and (3) neglect of the weak intreactions between the side atoms of the complex because of their long mutual distance. The transition state can be characterized as
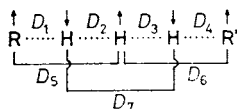
where the D's are the chemical dissociation energies of the respective bonds; it is clear that for symmetry reasons, $D_3 = D_7 = D_2$, $D_5 = D_1$, and $D_6 = D_4$.

The total potential energy of this complex can be written in a compact form as

$$E = D_1 - D_1 n_1^p - D_2 n_2^q + D_5 X + D_3 - D_3 n_3^r - D_4 n_4^s + D_6 Y + D_7 Z, \quad (8)$$

where the n's are the bond orders of the four-bond complex and p, q, r, and s are the respective BEBO parameters. The 2nd, 3rd, 6th and 7th right-hand terms are the contributions from the bonding interactions between atoms with antiparallel spins; the 4th, 8th, and 9th terms express the repulsive triplet interaction of atoms with parallel spins. These repulsion terms are formally identical in form, but they differ in the input parameters which depend on the atom quality:

$$X = B_X(n_1 n_2)^{0.28\beta} \text{ RH} \left[1 + B_X(n_1 n_2)^{0.28\beta} \text{ RH}\right] \qquad (9)$$

$$Y = B_Y(n_3 n_4)^{0.28\beta} \text{ R'H} \left[1 + B_Y(n_3 n_4)^{0.28\beta} \text{ R'H}\right] \qquad (10)$$

$$Z = B_Z(n_2 n_3)^{0.28\beta} \text{ HH} \left[1 + B_Z(n_2 n_3)^{0.28\beta} \text{ HH}\right], \qquad (11)$$

where the B's have the same meaning as in the original BEBO method[18,19].

In our case, $\dot{R}' = \dot{R}$, *viz.* $\sim CH_2\dot{C}HCH_2\sim$, so that the situation is totally symmetric, including the side parts of the complex; the calculation is thereby simplified appreciably. We have $r = q$, $s = p$, and $D_4 = D_6 = D_1$. With the simultaneous course of the two transfer reactions *via* a common H atom, the weakening of the 1st bond in the first reaction is accompanied by a strengthening of the 2nd bond and at the same time, in the second reaction, weakening of the 3rd bond occurs, accompanied by an adequate strengthening of the 4th bond. It follows from the symmetry that $n_1 + n_2 = 1$ and $n_3 + n_4 = 1$, so that $n_2 + n_3 = 1$ and also $n_1 + n_4 = 1$. In the symmetric transition state, then, the bond orders of the found bonds are identical, equal to $n = 0.5$. The chemical energy barrier, obtained from Eqs (8) and (9)−(11) is 122·3 kJ mol^{-1} (the values of the parameters, taken from refs[18,19,22], were $D_{C-H} = 412.7$ kJ mol^{-1}, $D_{H-H} = 462.2$ kJ mol^{-1}, $\beta_{C-H} = 0.178$ nm, $\beta_{H-H} = 0.194$ nm, $p_{C-H} = 1.0768$, $q_{H-H} = 1.0768$, $B_X = B_Y = 0.1201$, $B_Z = 0.1067$). After correcting for the zero point energy of the reactants (*i.e.*, C—H and H—H bonds) and of the transition state, calculated as in ref.[19], the energy barrier of the hydrogen-catalyzed one-step migration of alkyls in PE is 87·5 kJ mol^{-1}. This value is somewhat lower than the sum of energy barriers of the separate reactions, 103·9 kJ mol^{-1} (see below), because of the simultaneous participation of the central H atom in the two transfer reactions, bringing about changes in the contributions from the repulsive interactions and in the correction for the zero point energies. At any case, the calculated value is considerably higher than the observed effective activation energy of the catalyzed decay (54·4 kJ mol^{-1}). It is thus evident that this mechanism of the catalytic effect is rather improbable because of its high energy demands.

This BEBO modification is of more general validity and can be easily applied to nonsymmetric states as well.

Two-Step Mechanism

Within the concept of the two-step mechanism, the catalysis is assumed to proceed by pathway (E)−(G) with an effective activation energy given by Eq. (4). The energy barrier of the first abstraction reaction of the alkyl macroradical with molecular hydrogen, as calculated by the BEBO method[19] using parameters $p_{H-H} = q_{C-H} = 1.0768$, $B = 0.1201$, is $E_I = 72.0$ kJ mol^{-1}. The energy barrier of diffusion of atomic hydrogen in the elastic state of the amorphous PE phase for the temperature

range of kinetic measurements of $0-60°C$ was obtained as $E_2 = 21·6$ kJ mol^{-1} by using Eqs (6) and (7) with the input data for the penetrant and matrix from ref.[21], viz. $\varepsilon^* = 308$ J mol^{-1}, $\varrho^* = 0·463$ nm, $(\varrho^*/\varrho)_{\text{ref}} = 1·00$, $T_{\text{ref}} = 298$ K, $\alpha_V/2 = 4·1$. $. 10^{-4}$ K^{-1}, $\gamma = 12·0 . 10^3$ J nm mol^{-1}, $\lambda = 0·127$, $d = 0·2$ nm. This relatively low energy value, consistent with the experimental activation energies of diffusion of He and H$_2$ (ref.[21]), points to a very high mobility of the small hydrogen atom in the disordered regions of the PE matrix. Last, the energy barrier of the second abstraction reaction of atomic hydrogen with methylene groups of the polyethylene, calculated by the BEBO method with $p_{\text{C}-\text{H}} = p_{\text{H}-\text{H}} = 1·0867$, $B = 0·1201$, is $E_3 = 31·9$ kJ . . mol^{-1}, a relatively low value again indicating a considerable reactivity of the atomic hydrogen. The total effective energy barrier of the hydrogen-catalyzed migration of alkyls in PE then is $E_m = 61·7$ kJ mol^{-1}, approaching reasonably closely the experimental value of $54·4$ kJ mol^{-1}.

Thus, having evaluated the two mechanisms of transport of alkyls in polyethylene with the participation of H$_2$ and tested their fit to the experiment, we can conclude that the dominant process is the two-step migration, comprising both chemical migration which includes two hydrogen transfer reactions, and physical diffusion of a fragment of the catalytic agent.

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Translated by P. Adámek.