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Comparison of the Alfrey-Price Q-e Scheme and a Simple Molecular Orbital Treatment of Copolymerization

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SUMMARY

A simple Huckel treatment of the transition states for the monomer-radical reactions in free radical copolymerization is developed. The resulting equations for the reactivity ratios are compared with those from the Q-e treatment of Alfrey and Price. It is concluded that the Q-e scheme can be regarded as a version of a molecular orbital approach.

INTRODUCTION

Simple molecular orbital or Huckel theory has been widely used for correlating and predicting chemical reactivity semiquantitatively [1]. A number of authors have applied this theory to the transition state in free radical polymerization and have had some success in correlating monomer reactivities in copolymerization [2]. Despite this success and the fundamental basis of the approach, polymer chemists still prefer to use the semiempirical scheme of Alfrey and Price in which each monomer is characterized by two parameters–Q and e [3]. The parameter Q is assumed to represent the general reactivity of the monomer, while e is assumed to give its polar properties. On this basis the reactivity ratios for the copolymerization of monomers i and j are given by

$$\begin{aligned} r_i &= (Q_i/Q_j)\exp[-e_i(e_i - e_j)] \\ r_j &= (Q_j/Q_i)\exp[-e_j(e_j - e_i)] \end{aligned} \tag{1}$$

An important assumption in Eqs. (1) is that the effective charge on a monomer, as exemplified by e, is the same as that on its conjugate radical. In order to remove this assumption each monomer has to be characterized by three parameters [4].

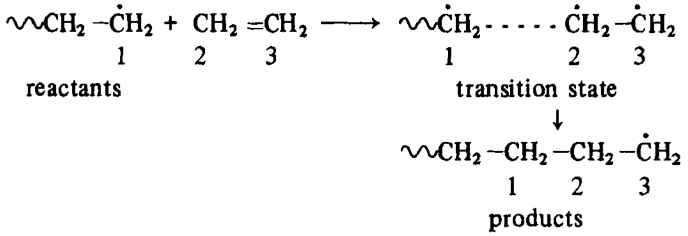
The Alfrey-Price scheme is usually regarded as a useful empirical relationship without a strong theoretical foundation. Nevertheless, comparisons between this scheme and the more rigorous MO calculations are often made and Levinson has shown, for example, that there is a relationship between Q and the localization energy of a monomer, and between e and the electron affinity [2]. Also Hayashi et al. [5] have deduced a scale of Q and e values from essentially MO considerations. The position of the MO treatment of copolymerization and of its relationship to the Q-e scheme has been summarized in an admirable review by O'Driscoll and Yonezawa [6].

In the present paper a simple Huckel treatment of the transition state in copolymerization is developed and its relationship to the Q-e scheme is discussed. The approach is essentially an adaptation of Wheland's theory [7]. It bears a formal resemblance to the treatment of Szwarc and Binks [8] for radical addition and abstraction reactions, and shows some similarities to the treatment of O'Driscoll et al. [9] in their considerations of synergistic effects in copolymerization.

THEORY AND DISCUSSION

Homopolymerization

The approach is most easily illustrated by reference to the propagation step in the polymerization of ethylene.



$$\underset{\text{reactants}}{\sim\!\sim CH_2-\underset{1}{\dot{C}H_2} + \underset{2}{CH_2}=\underset{3}{CH_2}} \longrightarrow \underset{\text{transition state}}{\sim\!\sim\underset{1}{\dot{C}H_2}\cdots\cdots\underset{2}{\dot{C}H_2}-\underset{3}{\dot{C}H_2}}$$

$$\downarrow$$

$$\underset{\text{products}}{\sim\!\sim CH_2-\underset{1}{CH_2}-\underset{2}{CH_2}-\underset{3}{\dot{C}H_2}}$$

In the transition state the macroradical electron is localized on C1 while the π-electrons of the monomer double bond are localized on C2 and C3. Interaction between the p-orbitals of C1 and C2 occurs, eventually leading to a σ-bond between C1 and C2 in the products.

The energy of the radical electron, E_r, is α and the energy of the monomer π-electrons, E_m, is $2\alpha + 2\beta$, where α and β have their usual significance. Thus the total ground state energy of these three electrons, E^0, is

$$E^0 = 3\alpha + 2\beta \tag{2}$$

When the electrons are localized in the monomer their energy, E_m^*, is 2α; the localization energy is -2β. The total energy of these three electrons in this excited state, E^*, is 3α. The excited state represents an upper limit to the energy of the transition state. Therefore the upper limit of the energy of activation for the reaction is -2β. The actual energy of the transition state is lower than the upper limit because of interaction between the p-orbitals on C1 and C2. Let the resonance integral between these centres be $h\beta$, where $0 < h < 1$. Then the secular determinant for this interaction is

$$\begin{vmatrix} x & h \\ h & x \end{vmatrix} = 0$$

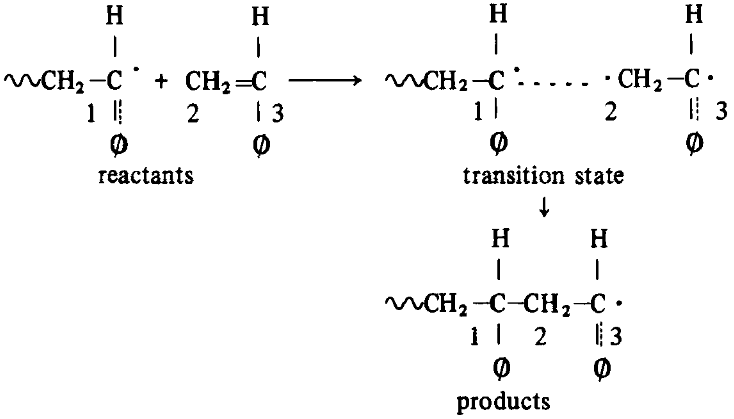
where $x = (\alpha - E)/\beta$, yielding two molecular orbitals of energy $\alpha + h\beta$ and $\alpha - h\beta$, respectively. Thus the total energy for the electrons associated with C1 and C2 is $2\alpha + 2h\beta$. When h is very small, i.e., there is virtually no interaction, the total energy is that of two isolated localized electrons, 2α. The total energy of the three electrons in the transition state is $3\alpha + 2h\beta$, and the activation energy for propagation, E_{act}, is given by

$$\begin{aligned} E_{act} &= 3\alpha + 2h\beta - E^0 \\ &= -2\beta(1 - h) \end{aligned} \tag{3}$$

Since β is negative this is lower than the upper limit, -2β.

As $h \rightarrow 1$, $E_{act} \rightarrow 0$, since $h = 1$ implies complete bond formation. Since h is determined to a large extent by the proximity of the p-orbitals of C1 and C2, E_{act} is determined to some extent by the polarity of the radical and monomer. The implications of this are developed later.

The case of ethylene homopolymerization is the simplest since the macroradical electron is localized and there are no substituents on the monomer to aid stabilization in the transition state. Styrene is a more typical monomer. The propagation step may be written as



The dotted line ⁞ implies delocalization to the benzene ring. It is assumed that in the transition state the macroradical electron is localized on C1, that one electron from the π-bond of the monomer is localized on C2, and that the third electron on C3 is delocalized within the benzene ring.

The energy of the radical electron, E_r, is equal to $\alpha - L_r'$, where L_r' is the energy required to localize the electron on C1. Also

$$E_m = \alpha - L_m + E_3$$

where L_m is the energy required to localize one electron on C2 and E_3 is the energy of the electron associated with C3. It follows that

$$E^0 = 2\alpha - (L_r' + L_m) + E_3 \qquad (4)$$

When the electrons are localized in the transition state on C1 and C3, the total energy E^* is equal to $2\alpha + E_3$. Thus the upper limit to the value of the activation energy is $L_r' + L_m$. Interaction of the p-orbitals on C1 and C2 reduces the energy of the electrons in the transition state to $2\alpha + 2h\beta + E_3$, and the energy of activation is given by

$$E_{act} = 2h\beta + (L_m + L_r') \qquad (5)$$

Figure 1 is a diagrammatic representation of these energies.

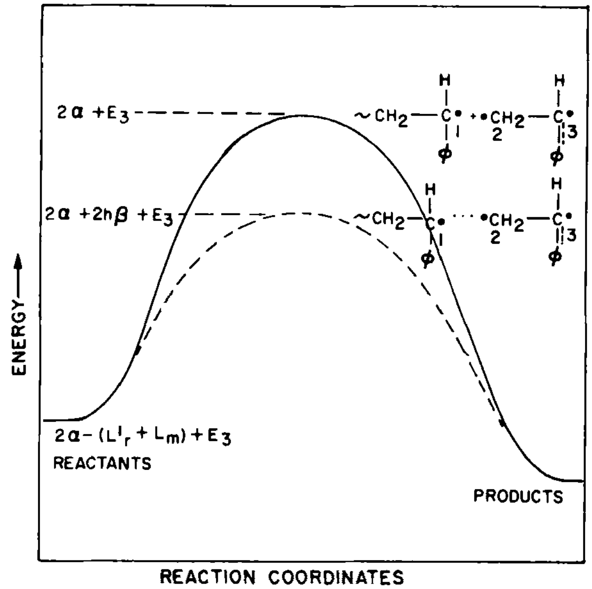


Fig. 1. Activation energies for addition of styrene monomer to styrene macroradical. Dotted curve shows energy profile for interaction of p-orbitals on C1 and C2.

It may be argued that there is no justification for assuming that the macroradical electron is localized in the transition state and therefore that the parameter L_r' need not appear in Eqs. (4) and (5). This may be a fair criticism but, as will be shown in the next section, the term L_r' disappears when the reactivity ratio in a copolymerization is deduced, so that assumptions concerning the precise energy of the macroradical electron in the transition state do not affect the final outcome of the present treatment.

Copolymerization

Applying this treatment to the propagation step in copolymerization between radical i and monomer j yields an activation energy E_{ij}:

$$E_{ij} = (L_i' + L_j) + 2h_{ij}\beta \qquad (6)$$

where L_i' is the localization energy for radical i. The corresponding rate coefficient k_{ij} is given by

$$k_{ij} = A_{ij} \exp(-E_{ij}/RT) \tag{7}$$

Also

$$r_i = \frac{k_{ii}}{k_{ij}} = \frac{A_{ii}}{A_{ij}} \exp\ [(E_{ij} - E_{ii})/RT] \tag{8}$$

Since the two reactions involved in the reactivity ratio r_i are very similar, the steric factors for the two steps should also be very similar; we can therefore equate the ratio of the frequency factors to unity and Eq. (8) becomes

$$r_i = \exp\ [(E_{ij} - E_{ii})/RT] \tag{9}$$

and

$$\ln r_i = (E_{ij} - E_{ii})/RT$$

Substituting for E_{ij} and E_{ii} from Eq. (5) yields

$$\ln r_i = \frac{1}{RT}\ [(L_j - L_i) + 2\beta(h_{ij} - h_{ii})] \tag{10}$$

Similarly

$$\ln r_j = \frac{1}{RT}\ [(L_i - L_j) + 2\beta(h_{ji} - h_{jj})] \tag{11}$$

The corresponding expressions from the Q-e scheme are

$$\ln r_i = (\ln Q_i - \ln Q_j) + (e_i e_j - e_i^2) \tag{12}$$

$$\ln r_j = (\ln Q_j - \ln Q_i) + (e_j e_i - e_j^2) \tag{13}$$

The forms of these two pairs of equations are similar. Furthermore, the polar e factors must determine the relative interactions of radical i and monomer j, compared with radical i and monomer i, so that the terms in h and e must be related. The Q factors must therefore in turn be related to the localization energies. By this reasoning pairs of terms between the equations can be identified. For the Q and L parameters identification leads to the relationship

$$\ln Q_i = -KL_i/RT \tag{14}$$

where K is a constant whose dimensions will depend on the units used for L and the arbitrary reference point chosen for the scale of Q values. Equation (14) shows that ln Q should be a linear function of L. Levinson predicted such a relationship intuitively and demonstrated its existence [2].

Since localization energies are always positive, Eq. (14) suggests that the Q scale should be chosen so that the Q values of all monomers are less than or equal to unity. Thus the reference value of unity for styrene would appear to be too high. In practice, however, the arbitrary reference point for the Q scale is unimportant, since r values are determined from Eqs. (1) by the ratio of Q values.

In the case of the e and h parameters no direct identification can be made, i.e., $h_{ij} \neq e_ie_j$. h_{ij} must be > 0 by definition, but e_i and e_j can be positive or negative. On the view of the transition state expressed in this paper the quantity $(h_{ij} - h_{ii})$ is the difference in the proximities of radical i-monomer j and radical i-monomer i. When $h_{ij} > h_{ii}$ the activation energy for i - j is less than that for i - i. The relative magnitudes of h_{ij} and h_{ii} therefore depend upon the polar characters of i and j. In other words, the e parameters merely represent a convenient figure for estimating the relative magnitudes of the resonance integrals for the radical-monomer interaction i-j and i-i in the transition state. This suggests that the relationship for the e and h parameters is

$$(h_{ij} - h_{ii}) \propto (e_ie_j - e_i^2) \qquad (15)$$

This relationship can be illustrated qualitatively by the following simple examples. In each case $Q_i = Q_j$ ($L_i = L_j$), which means that r_i is determined only by the polarity of the monomers.

(i) $e_i = +1$, $e_j = -0.5$

$(e_ie_j - e_i^2) = -1.5$. From Eq. (12) ln r_i is negative or $k_{ii}/k_{ij} < 1$.

With two monomers of these polarities there is a net attraction between radical i and monomer j, and a repulsion between radical i and monomer i. Hence $h_{ij} > h_{ii}$ and from Eq. (10) ln r_i is negative (since β is negative) or $k_{ii}/k_{ij} < 1$.

(ii) $e_i = +0.5$, $e_j = +1$

$(e_ie_j - e_i^2) = +0.25$, and ln r_i is positive or $k_{ii}/k_{ij} > 1$.

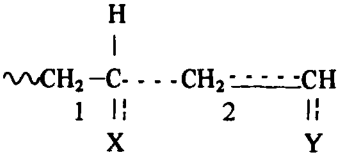
The repulsion between i and j is greater than between i and i, hence $h_{ij} < h_{ii}$ and ln r_i is positive.

This argument supports the view of Kawabata et al. [10] that the e parameters have no separate physical meaning and only acquire significance in Eqs. (12) and (13). We would propose, however, that the foregoing treatment strengthens the theoretical foundation of the Alfrey-Price scheme which can be viewed as a version of a MO treatment of the transition state for the propagation processes in free radical copolymerization.

Equations (10) and (11) bear a formal relationship to that of Fueno et al. [11]

$$\log r_1 = a(L_2 - L_1) + b(\Delta E_{11} - \Delta E_{12}) \tag{16}$$

where ΔE_{12} is the stabilization energy due to π-conjugation between radical 1 and monomer 2 in the transition state



$$\sim\!\!\sim CH_2-\underset{\substack{1\ \ \vdots\\ X}}{\overset{\substack{H\\ |}}{C}}\cdots CH_2\underset{2}{\overset{}{\cdots\cdots}}\underset{\substack{\vdots\\ Y}}{CH}$$

Equation (16) was derived by assuming a relationship like that in Eq. (14) between Q and L, and the relationship

$$e_1e_2 = \text{const} - 2.3b\Delta E_{12}$$

In the present treatment the relationships between Q and L, and h and e follow from the transition state model and the analogy between Eqs. (10) and (12).

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