

Evaluation of Activation Energy for Addition Reactions of Radicals to Vinyl Compounds

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ABSTRACT: Evaluation of activation energy for the reactions of radical additions to vinyl compounds was studied as an extension of the theory employing two Morse functions for the initial and the final systems. The π -bond dissociation energies of vinyl compounds in the initial system were estimated by using the localization energy method. The difference between the $a'Dr^*$ values of the Morse functions of the initial and the final systems in the transition state was empirically determined as a function, $a_f'Dr_f^* - a_i'Dr_i^* = \omega\Delta H$, of the reaction heat ΔH . Based on the above finding, an empirical equation for evaluation of the activation energies of the radical addition reactions was derived, and its propriety was checked in comparison with the observed values. An approximate formula of the empirical equation was introduced in order to facilitate calculations of the activation energies. The Evans-Polanyi and Semenov rules, the Hammett-type rule and the $Q-e$ scheme in the radical copolymerizations were derived by using this approximate formula and are discussed in detail.

KEY WORDS Activation Energy / Evaluation / Radical / Addition / Vinyl Monomer / Morse Function / π -Bond Dissociation Energy / Heat / Polanyi Rule / $Q-e$ Scheme /

The theoretical studies which tried to evaluate quantitatively the activation energies of the reactions of radical addition to vinyl compounds were started by Evans *et al.*^{1,2} and followed by Bagdasaryan.^{3,4}

On the propagation reaction of radical copolymerization, which is one of the typical examples of radical addition reactions, Alfrey and Price^{5,6} made a study of the correlation between the reactivities of vinyl monomers and the structural factors in terms of the empirical values of Q and e . Since Furukawa *et al.*⁷ have discussed the $Q-e$ scheme in comparison with the Hammett-type rule, many researchers have made the considerations from various points of view.⁸⁻¹¹

Yonezawa-Fukui,¹²⁻¹⁴ Kawabata¹⁵ and Fueno,¹⁶ from the standpoint of the molecular orbital theory, have proposed useful addition-reactivity indexes as a measure of the monomer reactivity in radical polymerization and have considered them in relation to the experimental data.

This paper is a part of the series on the theoretical study of the activation energy evaluation employing the Morse potential energy function.^{17,18} The purpose of this report is to propose a method for evaluation of the activation energies of the

radical addition reactions to vinyl compounds as applied to the radical homopolymerization and copolymerization, and to discuss the relation between the method and the various empirical rules.

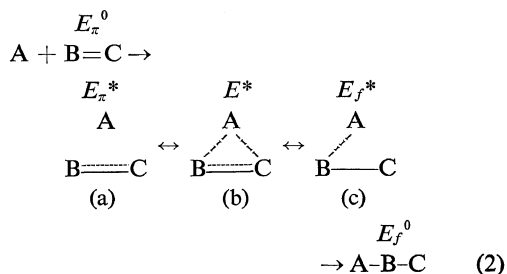
GENERAL CONSIDERATION

Model of the Transition State of the Radical Addition Reactions


The radical addition reactions in this paper are reactions of the three-center type such as



where A, B and C are reacting atoms or groups. Based on the considerations presented in the previous paper,¹⁷ the following picture is proposed



where (a), (b), and (c) are models of the transition state in which each potential energy is equivalent, $E_{\pi}^* = E^* = E_f^*$. The potential energy of the system along the reaction path is localized on the initial B=C bond in (a), E_{π}^* , and on the final A-B bond in (c), E_f^* , and delocalized on

the  in (b), E^* .

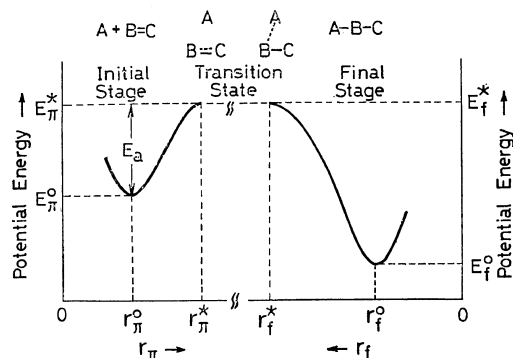


Figure 1. The potential energy curves of the initial and the final systems along the addition reaction path (1).

Using the above model of the transition state (Figure 1), the reaction can be explained from an energetic point of view by the following steps as in the case of the radical substitution reaction. (i) Until the transition state, the initial B=C molecule is continuously activated through energy transfer effected by collisions with the A radical. The energy transferred in this activation process is assumed to be accumulated only on the π -bond in B=C. In this process, the absorbed energy is assumed to be spent only on the dissociation of π -bond in the B=C double bond. (ii) In the transition state, the energy localized on the B=C bond migrates on the A-B bond. (iii) After the transition state, the energy is concentrated on the A-B bond, the reaction heat ΔH is released and the A-B-C radical is formed.

Function of the Potential Energy Curve along the Reaction Path

It has been assumed previously¹⁷ that the potential energy of the σ -bond is expressed by the Morse function. Then, for the final bond, we have

$$E_f = E_f^0 - E_f^0(1 - e^{-a_f'(r_f - r_f^0)})^2 \quad (3)$$

where E_f represents the potential energy of the final

A-B bond, E_f^0 the negative value of the bond dissociation energy of the final bond, D_f , r_f the distance between the reacting components (A and B), r_f^0 the equilibrium distance of the final bond, and a_f' the constant corresponding to the Morse one.

It can be considered that the difference between the potential energies of the double bond and σ -bond represents the potential energy, E_{π} , of the π -bond. On the speculation that the energy gained by activation is spent only on the dissociation of the π -bond in the B=C, we assume that the potential energy of the π -bond is also tentatively expressed by the Morse function

$$E_{\pi} = E_{\pi}^0 - E_{\pi}^0(1 - e^{-a_{\pi}'(r_{\pi} - r_{\pi}^0)})^2 \quad (4)$$

where E_{π}^0 is the negative value of the π -bond dissociation energy, D_{π} , r_{π}^0 the normal distance of the double bond, r_{π} the distance between B and C, and a_{π}' the Morse parameter.

Evaluation of the π - and σ -Bond Dissociation Energies

In order to evaluate the activation energies by using Eqs. 3 and 4, we have to know the values of the π - and σ -bond dissociation energies. Little information has, however, been reported on the π -bond dissociation energies of double bonds in complicated compounds. We have previously reported the rough D_{π} values of simple vinyl compounds calculated by means of the localization energy method.¹⁹ In the following scheme of the bond cleavage reaction of a vinyl compound



the double bond dissociation energy is in general represented as a sum of D_{π} and D_{σ} .

$$D_d = D_{\pi} + D_{\sigma} \quad (6)$$

It is assumed as a matter of convenience that the π -bond dissociation energy is related to the difference, ΔE^{π} , between the total π -electron energies of the biradical $\text{H}_2\text{C}-\dot{\text{C}}\text{HR}$ and the vinyl compound as follows*

* The π -bond dissociation energy for the polyatomic molecule is not always equal to the π -electronic bond energy which represents the difference between the total π -electron energies of the biradical and the vinyl compound, because of the complicated energy terms of the zero-point, the translation and the rotation. However, in the present paper, they are presumably expressed as the C constant independent of the structures of vinyl compounds.

Table I. The π - and σ -bond dissociation energies of vinyl monomer

Vinyl monomer	ΔE^π	ΔH	D_{π^a}	D_{σ^a} (kcal/mol)	D_{σ^b}	D_{π^b}	D_{σ^c}
1 Ethylene	114.8	22.5	61.5	84.0	145.5	71.0	84.0
2 Propylene	113.3	22.5	60.0	82.5	142.5	69.5	82.0
3 Isobutylene	113.0	12.8	59.7	72.5	132.2	69.2	74.0
4 Vinyl acetate	111.5	21.3	58.2	79.5	137.7	67.7	
5 Vinyl chloride	109.3	17.0	56.0	73.0	129.0	65.5	
6 Methyl acrylate	102.6	18.7	49.3	68.0	117.3	58.8	
7 Acrylonitrile	99.5	17.8	46.2	64.0	110.2	55.7	
8 Styrene	97.9	16.7	44.6	61.3	105.9	54.1	62.0
9 <i>p</i> -Methylstyrene	97.5	16.5	44.2	60.7	104.9		
10 <i>p</i> -Chlorostyrene	97.4	16.4	44.1	60.5	104.6		
11 <i>p</i> -Bromostyrene	97.3	16.3	44.0	60.3	104.3		
12 <i>p</i> -Iodostyrene	97.2	16.2	43.9	60.1	104.0		
13 α -Methylstyrene	95.5	8.4	42.2	50.6	92.8	51.7	58.0
14 <i>p</i> -Cyanostyrene	95.3	16.0	42.0	58.0	100.0		
15 <i>p</i> -Nitrostyrene	94.7	15.0	41.4	56.4	97.8		
16 Butadiene	94.7	17.3	41.1	58.4	99.5	50.6	
17 Methyl methacrylate	93.6	13.0	40.3	53.3	93.6	49.8	

^a Values calculated by using $C = 53.3$ kcal/mol.

^b Values calculated by using $C = 43.8$ kcal/mol. Data in ref. 19.

^c Bond dissociation energies of $\text{CH}_3\text{CH}_2\text{-CH}_3$ for ethylene, $(\text{CH}_3)_2\text{CH-CH}_3$ for propylene, $(\text{CH}_3)_3\text{C-CH}_3$ for isobutylene, $\phi(\text{CH}_3)\text{CH-CH}_3$ for styrene, and $\phi(\text{CH}_3)_2\text{C-CH}_3$ for α -methylstyrene.

energies on the right side of Eq. 15, we used the experimental data of the radical copolymerizations²²

$$E_{a(m,n)} = E_{a(m,m)} + RT \ln \bar{r}_m \quad (16)$$

where it was assumed that the entropy changes are little dependent on the kind of monomers, and $E_{a(m,n)}$ represents the activation energy of radical copolymerization of polymer-end radical $-C_m$ to vinyl monomer M_n , $E_{a(m,m)}$ that of radical

homopolymerization of $-C_m$ to M_m , and \bar{r}_m the average value of monomer reactivity ratio.

Using the experimental values of typical copolymerizations, we obtained an empirical function (Figure 2).

$$a_f' \Delta r_f^* - a_\pi' \Delta r_\pi^* = \omega \Delta H = 0.0280 \Delta H \quad (17)$$

Empirical Equation for Evaluation of the Activation Energies

Substituting Eq. 17 into Eq. 15, we have

$$E^* = \frac{4\kappa(1-\kappa)E_\pi^0 E_f^0 (E_f^0 - \kappa E_\pi^0)}{(E_f^0 - \kappa^2 E_\pi^0)^2} \quad (18)$$

hence

$$\begin{aligned} E_a &= E^* - E_\pi^0 = \frac{-E_\pi^0((1-2\kappa)E_f^0 + \kappa^2 E_\pi^0)^2}{(E_f^0 - \kappa^2 E_\pi^0)^2} \\ &= \frac{D_\pi((1-2\kappa)D_f + \kappa^2 D_\pi)^2}{(D_f - \kappa^2 D_\pi)^2} \quad (19) \end{aligned}$$

where κ is related to the reaction heat ΔH (in kcal/mol) by $\kappa = \exp(\omega \Delta H)$, and where ω is a constant equal to 0.0280. Eq. 19 shows that the activation energy can be calculated by using the π - and σ -bond dissociation energies (D_π , D_f) of the initial and the final compounds.

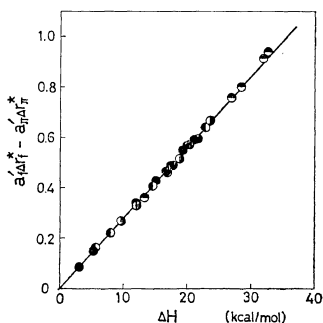


Figure 2. Plot of the $a_f' \Delta r_f^* - a_\pi' \Delta r_\pi^*$ values vs. the reaction heats, ΔH .

Polymer-end radical, ●: Styrene, ○: Acrylonitrile, ◐: Methyl acrylate, ⊙: Vinyl chloride.

Derivation of the Approximate Formula from the Empirical Equation

For the reaction heat ΔH ranging from 0 to 30 kcal/mol, κ and κ^2 in Eq. 18 are approximated as

$$\begin{aligned}\kappa &\simeq 1 + \omega\Delta H \\ \kappa^2 &\simeq 1 + 2\omega\Delta H\end{aligned}\quad (20)$$

Substituting Eq. 20 into Eq. 18 and using the relations, $\Delta H \simeq D_f - D_\pi$, and $\omega\Delta H \ll 1$, we have

$$E^* \simeq \frac{4\omega(\omega D_\pi - 1)D_\pi}{(2\omega D_\pi - 1)^2} \times D_f \quad (21)$$

where the first factor on the right side of Eq. 21, $4\omega(\omega D_\pi - 1)D_\pi/(2\omega D_\pi - 1)^2$, is a function only of the π -bond dissociation energy, D_π , of the initial double bond. For the π -bond dissociation energies of usual vinyl compounds ranging from 45 to 65 kcal/mol, as shown in Figure 3, the factor is expressed by a first-order function through the origin with respect to D_π , *i.e.*,*

$$\frac{4\omega(\omega D_\pi - 1)D_\pi}{(2\omega D_\pi - 1)^2} = \phi D_\pi = 0.0134D_\pi \quad (22)$$

Substituting Eq. 22 into Eq. 21, we have

$$E^* = \phi D_\pi D_f \quad (23)$$

* For the radical substitution reactions, the $4\omega'(\omega'D_i - 1)D_i/(2\omega'D_i - 1)^2$ factor in the range of D_i from 70 to 105 kcal/mol where $\omega' = 0.0190$, has been expressed by a first-order function with respect to D_i ,¹⁷ *i.e.*,

$$\frac{4\omega'(\omega'D_i - 1)D_i}{(2\omega'D_i - 1)^2} = \phi' + \phi'D_i = 0.0850 + 0.0080D_i \quad (i)$$

This difference in the approximate formulas (Eqs. 22 and i), *i.e.*, one-constant approximation and two-constant approximation, is considered to be due to both differences in the ranges of the bond dissociation energies of D_π and D_i and in the ω and ω' values. However, whether a straight line passes through the origin or not is not an essential problem in this paper. Eq. i is also roughly approximated by a one-constant formula as follows:

$$\frac{4\omega'(\omega'D_i - 1)D_i}{(2\omega'D_i - 1)^2} = \phi''D_i = 0.0091D_i \quad (ii)$$

The activation energies calculated from Eq. ii agree with a large number of experimental data to within ± 2.5 kcal/mol on the average, while those calculated from Eq. i to within ± 2.0 kcal/mol.

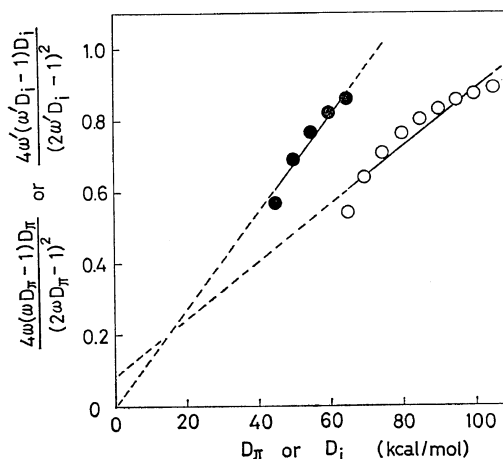


Figure 3. Plot of $4\omega(\omega D_\pi - 1)D_\pi/(2\omega D_\pi - 1)^2$ (or $4\omega'(\omega' D_i - 1)D_i/(2\omega' D_i - 1)^2$) vs. D_π (or D_i).

●: Radical addition reactions,

$$\frac{4\omega(\omega D_\pi - 1)D_\pi}{(2\omega D_\pi - 1)^2} = 0.0134D_\pi.$$

○: Radical substitution reactions,¹⁷

$$\frac{4\omega'(\omega' D_i - 1)D_i}{(2\omega' D_i - 1)^2} = 0.0850 + 0.0080D_i.$$

hence

$$E_a = D_\pi - \phi D_\pi D_f \quad (24)$$

RESULTS AND DISCUSSION

Prediction of the Monomer Reactivity

It is apparent from Eq. 24 that, in the addition reactions of the same radical with various vinyl compounds in which D_f is nearly constant, the activation energies increase with the increase in the π -bond dissociation energies, D_π , of compounds. This prediction is checked with the experimental data of the addition reactions of

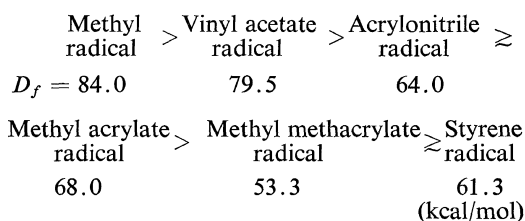
Table II. The relative reactivities of addition reactions of methyl radical to vinyl compounds

Vinyl compound	$\log k_a/k_{a(\text{ethylene})}^a$	D_π (kcal/mol)
Ethylene	0	61.5
Propylene	0.11	60.0
Isobutylene	0.32	59.7
Vinyl acetate	0.34	58.2
Vinyl chloride	—	56.0
Styrene	1.68	44.6
α -Methylstyrene	1.74	42.2
Methyl methacrylate	1.92	40.3

^a Data in ref. 23.

methyl radical to some vinyl monomers in liquid phase, as shown in Table II.²³

Similarly, in reactions of various radicals with the same vinyl compound in which D_π is constant, the activation energies increase with the decrease in the final bond dissociation energies, and the radical reactivities generally decrease in the following order



where D_f is assumed to be a constant depending only on the kind of radicals and independent of that of monomers.

The activation energies of the various types of radical propagation reactions are calculated by means of Eq. 19 and plotted against the reliable observed values in Figure 4. Using the approximate formula 24, we calculate the reactivity ratios of monomers in the radical copolymerizations, as shown in Table III.

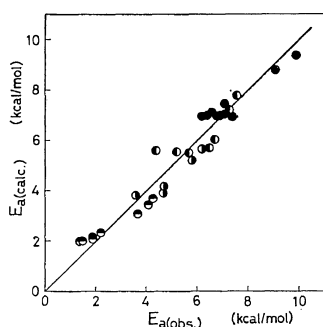


Figure 4. Comparison of the calculated activation energies of the radical copolymerization reactions with the observed ones.

Polymer-end radical, ●: Styrene, ○: Acrylonitrile, ◐: Methyl acrylate, ◑: Vinyl chloride.

The Evans—Polanyi and Semenov Rules

For the radical substitution reactions, Evans—Polanyi²⁴ and Semenov²⁵ have derived Eqs. 25 and 26, respectively

$$\Delta E_a = -x\Delta\Delta H \quad (25)$$

$$E_a = A - x\Delta H \quad (26)$$

where ΔE_a is the increase in the activation energy, $\Delta\Delta H$ the increase in the reaction heat, and x and A are the constants ranging from 0.2 to 0.4 and from 10 to 15 kcal/mol, respectively.

Rewriting Eq. 24 with use of the relation, $D_\pi \simeq D_f - \Delta H$, we have

$$E_a = (1 - \phi D_f)D_f - (1 - \phi D_f)\Delta H \quad (27)$$

and, for the analogous reactions in which D_f is nearly constant, we have

$$\Delta E_a = - (1 - \phi D_f)\Delta\Delta H \quad (28)$$

From Eqs. 27 and 28, we find that the calculated values of A and x are in the ranges of $6 < A < 11$ kcal/mol and $0.1 < x < 0.2$, respectively, provided that the values of D_f depending on the kind of the addition reactions are from 61 to 68 kcal/mol. The apparent values of A and x which are common to the various kinds of reactions are 11.2 kcal/mol and 0.35 respectively, as shown in Figure 5. This result shows that the simple parallelism between the activation energies and the reaction heats holds fairly well in the addition reactions as well as in the substitution reactions (Figure 5).

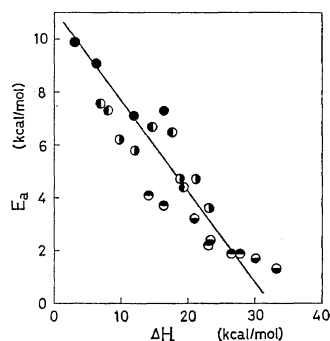


Figure 5. Semenov rule of E_a and ΔH of various radical copolymerization reactions.

$$E_a = 11.2 - 0.35\Delta H$$

Polymer-end radical, ●: Styrene, ○: Acrylonitrile, ◐: Methyl acrylate, ◑: Vinyl chloride, ◒: Vinyl acetate.

The Hammett-Type Rule

The Hammett-type rule for the radical copolymerizations has been reported by Walling *et al.*²⁶ Recently Otsu and Yamamoto *et al.*^{8,9} have made some extensions and corrections

Activation Energy Evaluation for Radical Addition Reactions

Table III. The reactivity ratios of vinyl monomers in the radical copolymerizations

Polymer-end radical Vinyl monomer	D_π (kcal/mol)	D_f (kcal/mol)	$E_{a(\text{calc})}^a$ (kcal/mol)	$r_{(\text{calc})}^b$ (kcal/mol)	$E_{a(\text{obs})}^c$ (kcal/mol)	$r_{(\text{obs})}^d$ (kcal/mol)
Styryl radical						
Vinyl acetate	58.2	61.3	10.4	38.7	9.9	55
Vinyl chloride	56.0	61.3	10.0	21.5	9.1	17
α -Methylstyrene	42.2	61.3	7.54	0.53	7.4	1.18
Styrene	44.6	61.3	7.96	1.00	7.25	1.00
<i>p</i> -Methylstyrene	44.2	61.3	7.89	0.90	7.1	0.83
Methyl acrylate	49.3	61.3	8.80	3.54	7.1	0.75
<i>p</i> -Chlorostyrene	44.1	61.3	7.88	0.89	7.1	0.74
<i>p</i> -Bromostyrene	44.0	61.3	7.86	0.86	7.0	0.70
<i>p</i> -Iodostyrene	43.9	61.3	7.84	0.83	6.9	0.62
Methyl methacrylate	40.3	61.3	7.20	0.32	6.8	0.52
Acrylonitrile	46.2	61.3	8.25	1.55	6.6	0.40
<i>p</i> -Cyanostyrene	42.0	61.3	7.50	0.50	6.4	0.28
Butadiene	41.1	61.3	7.34	0.39	6.3	0.23
<i>p</i> -Nitrostyrene	41.4	61.3	7.39	0.42	6.2	0.19
Acrylonitrile radical						
Vinyl acetate	58.2	64.0	8.29	13.1	7.6	4.05
Vinyl chloride	56.0	64.0	7.97	8.10	7.3	3.3
Methyl acrylate	49.3	64.0	7.02	1.94	6.7	1.3
Acrylonitrile	46.2	64.0	6.58	1.00	6.5	1.00
Butadiene	41.1	64.0	5.85	0.33	5.6	0.25
Methyl methacrylate	40.3	64.0	5.74	0.28	5.2	0.15
Styrene	44.6	64.0	6.35	0.71	4.4	0.04
Methyl acrylate radical						
Vinyl acetate	58.2	68.0	5.17	3.23	6.2	9
Vinyl chloride	56.0	68.0	4.97	2.43	5.8	5
Methyl acrylate	49.3	68.0	4.38	1.00	4.7	1.00
Acrylonitrile	46.2	68.0	4.10	0.66	4.7	0.95
Styrene	44.6	68.0	3.96	0.53	3.6	0.18
Vinyl chloride radical						
Isobutylene	59.7	73.0	1.30	1.13	4.33	2.05
Vinyl acetate	58.2	73.0	1.27	1.08	4.05	1.68
Vinyl chloride	56.0	73.0	1.22	1.00	3.70	1.00
Methyl acrylate	49.3	73.0	1.07	0.80	2.17	0.10
Acrylonitrile	46.2	73.0	1.01	0.73	1.93	0.07
Styrene	44.6	73.0	0.97	0.69	1.88	0.06
Butadiene	41.1	73.0	0.90	0.62	1.47	0.035
Methyl methacrylate	40.3	73.0	0.88	0.60	1.37	0.030

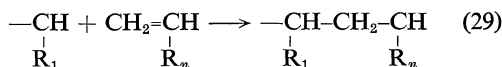
^a Values calculated from $E_a = D_\pi - \phi D_\pi D_f$.

^b Values calculated from Eq. 16 and $E_{a(\text{calc})}$.

^c Values obtained from Eq. 16 and $r_{(\text{obs})}$.

^d Data in ref. 6.

of this type of rule. They studied the following copolymerizations in which R_n in the monomer molecules indicates various substituents.



They paid attention to the small polar effect in the radical copolymerizations and presented the following Hammett-type equation

$$\log k_{1,n}/k_{1,1} = \log 1/r_1 = \rho\sigma + \gamma E_{R(n)} \quad (30)$$

where $k_{1,n}$ and $k_{1,1}$ are the rate constants of reactions of a polymer-end radical 1 with a monomer n and with a parent monomer 1, respectively, σ and ρ the Hammett substituent constant and the Hammett reaction constant, $E_{R(n)}$ the resonance substituent constant and γ the characteristic value indicating the degree of the resonance effect.

For the radical copolymerizations of a polystyryl radical with p - and m -substituted styrenes whose polar effects are very small, *i.e.*, $\rho \simeq 0$, we have

$$\log 1/r_1 = \gamma E_{R(n)} \quad (31)$$

Using Eq. 24, we have

$$\begin{aligned} \log 1/r_1 &= (1/2.3RT)(E_{a(1,1)} - E_{a(1,n)}) \\ &= (1/2.3RT)(1 - \phi D_{f(1)}) (D_{\pi(1)} - D_{\pi(n)}) \end{aligned} \quad (32)$$

where it is assumed that $D_{f(1,1)} = D_{f(1,n)} = D_{f(1)}$. It may be expected from Eqs. 31 and 32 that, if the polar effect on the reaction rate

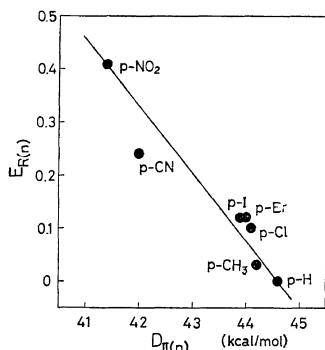


Figure 6. Relation between the resonance substituent constants of $E_{R(n)}$ and the π -bond dissociation energies of the double bonds in various vinyl compounds $\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-\text{R}_n$.

is very small, there should exist a linear relationship having a negative slope between $E_{R(n)}$ and $D_{\pi(n)}$. This is checked in Figure 6.

In the same manner, it was found that the $D_{\pi(n)}$ values are in some relation to the $R(n)$ values proposed by Kinoshita and Imoto,²⁷ which are the characteristic ones indicating the conjugation effect, and to the $\tau_{p(n)}$ values proposed by Migita and Shimamura,²⁸ which are the correction terms of the conjugation factors.

The Alfrey-Price $Q-e$ Scheme

The relation between the structure of monomers and their reactivity toward free radicals involves resonance, polar and steric factors. The $Q-e$ scheme proposed by Alfrey and Price^{5,6} is an attempt to combine the recognized effects of resonance stabilization and polarity on the relative reactivities of various monomers with various free radicals in a semi-quantitative fashion. The main assumption of the $Q-e$ scheme is that the rate constant, $k_{m,n}$, for the attack of radical m upon monomer n is given by

$$k_{m,n} = P_m Q_n \exp(-e_m e_n) \quad (33)$$

where P_m is characteristic of radical m , Q_n is the mean reactivity of monomer n , and e_m and e_n are measures of the polarity of the radical and monomer, respectively. The same polarity factor, e , is used for a monomer and its adduct radical. When Eq. 33 is applied to the relative rate constants for two monomers (m and n) with a given polymer-end radical (m), the radical reactivity factor, P_m , is canceled and the reactivity ratio, r_m , can be written as follows

$$r_m = \frac{k_{m,m}}{k_{m,n}} = \frac{Q_m}{Q_n} \exp(-e_m(e_m - e_n)) \quad (34)$$

hence

$$\ln 1/r_m = \ln Q_n - \ln Q_m - e_m e_n + e_m^2 \quad (35)$$

Using Eq. 24, we have

$$\begin{aligned} \ln 1/r_m &= (1/RT)(-D_{\pi(n)} + D_{\pi(m)}) \\ &\quad + \phi D_{f(m,n)} D_{\pi(n)} - \phi D_{f(m,m)} D_{\pi(m)} \end{aligned} \quad (36)$$

It is found from the comparison of Eq. 35 with Eq. 36 that the $\ln Q_m$ are in negatively linear relation with $D_{\pi(m)}$, and the squares, e_m^2 , of polarity factors are in linear relation having a

negative slope with the products, $D_{f(m,m)}D_{\pi(m)}$, of the bond dissociation energies of the initial and the final bonds. Figures 7 and 8 show the proprieties of the above considerations.

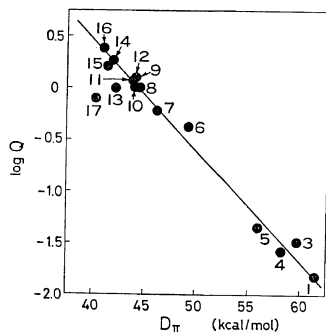


Figure 7. Relation between Alfrey—Price's Q values and the π -bond dissociation energies of various vinyl monomers. The number of a point represents the number in Table I.

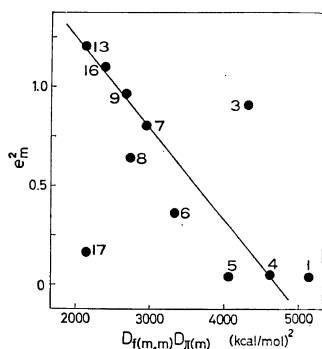


Figure 8. Relation between the squares, e_m^2 , of Alfrey—Price's polarity factors and the products, $D_{f(m,m)}D_{\pi(m)}$, of the bond dissociation energies. The number of a point represents the number in Table I.

If the rate constant, $k_{m,n}$, follows the Arrhenius equation and if its frequency factor, A , is a constant independent of the kind of monomer n and radical m , we then have

$$\begin{aligned} \ln k_{m,n} &= \ln A - E_{a(m,n)}/RT \\ &= \ln A - (D_{\pi(n)} - \phi D_{f(m,n)}D_{\pi(n)})/RT \quad (37) \end{aligned}$$

From Eq. 33, we have

$$\ln k_{m,n} = \ln P_m + \ln Q_n - e_m e_n \quad (38)$$

and, for the reactions having a small polar effect

on the rate constant

$$\ln k_{m,n} = \text{const.} + \ln Q_n + \ln P_m \quad (39)$$

In the case where the polymer-end radicals change and the monomer does not change, *i.e.*, $D_{\pi(n)} = \text{const.}$ and $Q_n = \text{const.}$, there should exist a linear relationship having a positive slope between $\ln P_m$ and $D_{f(m,n)}$. Since the reliable observed values of P_m have scarcely been reported, the localization energies, $L_{\alpha'(m)}$, in the propagation step, proposed by Fueno *et al.*,¹⁶ which are the characteristic values corresponding to the $\ln P_m$, have been plotted against the $D_{f(m,n)}$ (Figure 9).

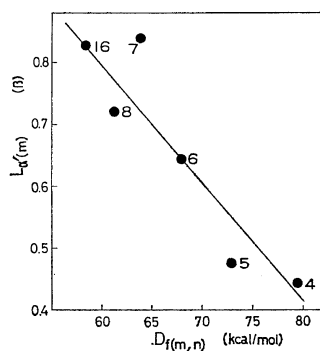


Figure 9. Relation between the localization energies and the bond dissociation energies of the final bonds. The number of a point represents the number in Table I.

It seems reasonable to conclude from these considerations that Eqs. 19 and 24 are not only useful for evaluation of the activation energies of radical addition reactions and the monomer reactivity ratios of radical copolymerizations, but also are in good relations with the empirical rules described above.

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