

Physical factors determining the activation energy of alkyl radical addition to unsaturated compounds

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A parabolic model of the transition state is used for the analysis of experimental data (rate constants and activation energies) for reactions of addition of alkyl and phenyl radicals to multiple bonds of unsaturated compounds. The parameters describing the activation energy as a function of the enthalpy of the reactions were calculated from the experimental data. The activation energy depends also on the strength of the forming C—C bond, the presence of π -bonds in the α -position near the attacked C=C bond, and the presence of polar groups in the monomer and radical. The empirical dependence of the activation energy of a thermoneutral addition reaction $E_{\text{e}0}$ on the dissociation energy D_{e} of the forming C—C bond was obtained: $E_{\text{e}0} = (5.95 \pm 0.06) \cdot 10^{-4} D_{\text{e}}^2 \text{ kJ mol}^{-1}$, indicating the important role of triplet repulsion in the formation of the transition state of radical addition. The contribution of the polar interaction to the activation energy of addition of polar radicals to polar monomers was calculated.

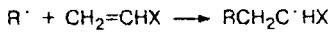
Key words: olefins, alkyl radicals, phenyl radicals, addition, parabolic model, polar interaction, triplet repulsion, activation energy, enthalpy of reaction.

Reactions of addition of alkyl radicals to unsaturated compounds are widely used in modern technologies of manufacture and modification of polymer materials and in fine chemical synthesis. They occur under the action of light and radiation on organic compounds. The problem of the reactivity of radicals and monomers in addition reactions has repeatedly been discussed previously.^{1–7} The important role of the reaction enthalpy and polar interaction in these processes was established. However, these two factors do not explain the variability observed for the reactivity of reactants in processes of radical addition.⁶

The parabolic model of the transition state is an efficient tool for analysis of the reactivity of compounds in radical reactions.⁸ As applied to reactions of radical abstraction, this model made it possible to determine 10 factors affecting the activation energy.⁹ It has been proved previously¹⁰ that the parabolic model can be used for the analysis of addition reactions. In this work, the model was used for the analysis of the reactivity of reactants in the addition of carbon-centered radicals to double C=C and triple C≡C bonds of unsaturated compounds.

Calculation procedure

In the radical addition reaction



the double C=C bond is broken to form a new σ -C—C bond. The parabolic model of the transition state considers this reaction as the result of intersection of two potential curves,¹⁰

one of which describes the vibration of the double C=C bond (vibration frequency v_i), and the other curve describes the vibration of the forming C—R bond (vibration frequency v_f). The vibrations are considered as harmonic, so that their potential energies are the following: $U_i = b_i^2 r_i^2$ and $U_f = b_f^2 r_f^2$, where r_i and r_f are the amplitudes of vibrations of the corresponding bonds, and $2b_i^2$ and $2b_f^2$ are their force constants. In terms of the parabolic model, the addition reaction is characterized by the following parameters.

1. Enthalpy (ΔH_{e}) that is related to the enthalpy of the reaction (ΔH) by the correlation⁹

$$\Delta H_{\text{e}} = \Delta H + 0.5hL(v_i - v_f) \quad (1)$$

where h is Planck's constant, and L is Avogadro's number.

2. Activation energy (E_{e}) related to the Arrhenius activation energy ($E = RT\ln(nA/k)$, where A is the pre-exponential factor, n is the number of reactive C atoms, k is the reaction rate constant, R is the universal gas constant, and T is the absolute temperature), by the correlation⁹

$$E_{\text{e}} = E + 0.5hLv_i - 0.5RT \quad (2)$$

3. Coefficients b and α ($b = b_i = \pi v_i (2\mu_i)^{1/2}$, where v_i and μ_i are the vibration frequency and the reduced mass of the C=C bond, respectively, and $\alpha = b_i/b_f$).

4. Distance (r_{e}) separating the minima of two intersecting parabolas.

These parameters are related by the following correlation⁹:

$$br_{\text{e}} = \alpha(E_{\text{e}} - \Delta H_{\text{e}})^{1/2} + E_{\text{e}}^{1/2} \quad (3)$$

The br_{e} parameter characterizes the activation energy of the thermoneutral reaction $E_{\text{e}0}$ for the group of reactions with $r_{\text{e}} = \text{const}$ and $b = b_i = \text{const}$ ¹⁰:

$$E_{\text{e}0} = (br_{\text{e}})^2 (1 + \alpha)^{-2} \quad (4)$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 445–450, March, 1999.

For the calculation of the activation energy E from the value of the reaction rate constant k , we used the value of the pre-exponential factor $A_g = 1.2 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for the reaction of the radical in the gas phase with one $\text{CH}_2=$ or $\text{RCH}=$ group (the average value for the series of measurements of the rate constant of the reaction of the methyl radical with olefins¹¹) and $A_{\text{liq}} = 5 \cdot 10^8 \text{ L mol}^{-1} \text{ s}^{-1}$ for the reactions in the liquid phase ($A_{\text{liq}} > A_g$ because of a higher frequency of collisions of particles in the liquid¹²). The A_{liq}/A_g ratio was calculated as the average value of the ratio of rate constants for the reactions of the methyl radical with ethylene in the liquid and gas phases. For the calculation of the br_e parameter from Eqs. (1)–(3), we used the following values of coefficients characterizing the reactions of alkyl radicals with $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds.¹⁰

Bond	α	$0.5hLv$ kJ mol ⁻¹	$0.5hL(v_i - v_f)$ kJ mol ⁻¹
$\text{C}=\text{C}$	1.202	9.9	1.7
$\text{C}\equiv\text{C}$	1.542	12.7	4.5

The $\Delta H(\text{R}')$ values used for the calculation of the enthalpy of the addition reaction (in the gas phase) were taken from Ref. 13,

Table 1. Dissociation energies of the $\text{C}-\text{H}$ bond ($D(\text{C}-\text{H})/\text{kJ mol}^{-1}$), enthalpies ($\Delta H_e/\text{kJ mol}^{-1}$), activation energies ($E_e/\text{kJ mol}^{-1}$), and parameters $br_e/(\text{kJ mol}^{-1})^{1/2}$ of the addition of methyl radicals to olefins in the liquid phase

Olefin	$D(\text{C}-\text{H})$	$-\Delta H_e$	E_e	br_e	Reference
$\text{CH}_2=\text{CH}_2^*$	422.0	98.5	40.2	20.50	11
$\text{CH}_2=\text{CH}_2$	422.0	98.5	37.9	20.19	16, 17
$\text{CH}_2=\text{CHMe}^*$	412.0	96.1	37.0	19.95	11
$\text{CH}_2=\text{CHMe}$	412.0	96.1	36.8	19.93	6
$\text{CH}_2=\text{CHEt}$	413.0	96.6	36.0	19.84	6
$\text{CH}_2=\text{CMe}_2$	400.0	98.3	35.7	19.88	6
<i>trans</i> - $\text{MeCH}=\text{CHMe}$	413.0	95.6	44.3	20.87	16, 18–20
<i>cis</i> - $\text{MeCH}=\text{CHMe}$	413.0	99.0	42.0	20.75	16, 18–20
<i>cyclo</i> - C_5H_8	405.4	99.8	42.9	20.91	18
<i>cyclo</i> - C_8H_{14}	402.0	87.3	42.4	20.20	18
$\text{CH}_2=\text{CHCl}$	410.9	104.3	33.6	19.91	6
$\text{CH}_2=\text{CClMe}$	401.9	94.3	32.2	19.19	6
$\text{CH}_2=\text{CCl}_2$	401.7	117.3	27.6	19.72	6
$\text{CH}_2=\text{CHF}$	410.0	100.3	32.2	19.51	21
$\text{CH}_2=\text{CHOAc}$	399.5	104.8	35.3	20.17	6
$\text{CH}_2=\text{CHOEt}$	396.5	96.5	34.5	19.63	6
$\text{CH}_2=\text{C(Me)OMe}$	378.2	109.0	34.9	20.33	6
$\text{CH}_2=\text{C(Me)OAc}$	392.3	117.0	34.9	20.72	6
$\text{CH}_2=\text{CHCOOMe}$	398.8	102.0	26.6	19.53	6
$\text{CH}_2=\text{C(Me)COOMe}$	389.0	128.3	25.7	19.99	6
<i>trans</i> - $\text{MeCH}=\text{CHCOOH}$	398.8	127.6	25.3	19.89	22
<i>cis</i> - $\text{MeCH}=\text{CHCOOH}$	398.8	131.8	22.3	19.64	22
$\text{CH}_2=\text{CHCH}_2\text{OAc}$	399.5	102.3	34.9	19.99	20
$\text{CH}_2=\text{CHOC(O)CH}_2\text{Ph}$	399.5	104.8	29.8	19.40	20
$\text{CH}_2=\text{CHCN}$	388.4	129.7	25.1	19.97	18, 23
$\text{CH}_2=\text{C(Me)CN}$	384.5	127.0	25.0	19.82	18, 23, 6
$\text{CH}_2=\text{CHCH}=\text{CH}_2$	349.4	145.2	26.4	20.88	24
$\text{MeCH}=\text{CHCH}=\text{CHMe}$	345.4	136.7	31.1	21.15	24
$\text{CH}_2=\text{C(Me)C(Me)}=\text{CH}_2$	339.3	149.2	26.1	21.03	24
<i>cyclo</i> - $[(\text{CH}=\text{CH})_2\text{CH}_2]$	312.0	158.9	32.1	22.27	18
<i>cyclo</i> - $[(\text{CH}=\text{CH})_2\text{CH}_2\text{CH}_2]$	305.4	165.8	29.5	22.23	18
$\text{CH}_2=\text{CHPh}$	364.1	143.0	26.9	20.82	6
$\text{CH}_2=\text{CMePh}$	354.7	139.0	26.9	20.67	6
$\text{HC}\equiv\text{CH}$	464.0	104.4	40.5	24.93	16
$\text{MeC}\equiv\text{CH}$	454.0	105.2	41.9	25.18	16
$\text{Pr}^n\text{C}\equiv\text{CH}$	454.0	104.2	41.3	25.03	16
$\text{MeC}\equiv\text{CMe}$	454.0	94.0	48.6	25.39	16

* In the gas phase.

and $\Delta H(\text{CH}_2=\text{CXY})$ were taken from the data base.¹⁴ For several polyatomic radicals $\text{RCH}_2\text{C}^{\cdot}\text{XY}$, the enthalpy of formation was calculated from $\Delta H(\text{RCH}_2\text{CHXY})$ by the equation

$$\Delta H(\text{RCH}_2\text{C}^{\cdot}\text{XY}) = \Delta H(\text{RCH}_2\text{CHXY}) + D(\text{C}-\text{H}) - \Delta H(\text{H}^{\cdot}), \quad (5)$$

where $D(\text{C}-\text{H})$ is the dissociation energy of the $\text{C}-\text{H}$ bond in the CHXY group (published data¹⁵).

The results of the calculation of the br_e parameters of the reactions of methyl, alkyl, and phenyl radicals with olefins are presented in Tables 1 and 2.

Results and Discussion

Triplet repulsion in the transition state of the addition reaction

The data in Table 1 show that all reactions of addition of methyl radicals to olefins are characterized by almost the same br_e parameter with the average value

Table 2. Enthalpy (ΔH_e kJ mol⁻¹), activation energy (E_e kJ mol⁻¹), and parameters br_e (kJ mol⁻¹)^{1/2} of the addition of phenyl and alkyl radicals to olefins in the liquid phase

Reaction	$-\Delta H_e$	E_e	br_e	Reference
$\text{Et}^\cdot + \text{CH}_2=\text{CH}_2^a$	91.4	40.7	20.20	11
$\text{Et}^\cdot + \text{CH}_2=\text{CHOAc}$	97.9	34.6	19.68	25
$\text{Me}_2\text{C}^\cdot \text{H} + \text{CH}_2=\text{CH}_2^a$	89.7	40.6	20.09	11
$\text{Bu}^{\text{H}\cdot} + \text{CH}_2=\text{CH}_2^a$	91.4	41.6	20.31	11
$\text{Me}_3\text{C}^\cdot + \text{CH}_2=\text{CH}_2^a$	78.5	43.6	19.89	11
$\text{Me}_3\text{C}^\cdot + \text{CH}_2=\text{CH}_2$	78.5	42.5	19.74	26
$\text{Me}_3\text{C}^\cdot + \text{CH}_2=\text{CMe}_2$	78.3	42.1	19.68	26
$\text{Me}_2\text{C}^\cdot \text{H} + \text{CH}_2=\text{CHOAc}$	84.8	37.7	19.45	26
$\text{Me}_3\text{C}^\cdot + \text{CH}_2=\text{CHPh}$	121.3	29.1	20.14	26
$\text{Me}_3\text{C}^\cdot + \text{CH}_2=\text{CHSiMe}_3$	80.3	35.7	18.92	26
$\text{Ph}^\cdot + \text{CH}_2=\text{CHMe}$	154.2	26.6	21.32	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHEt}$	146.9	26.1	20.92	28
$\text{Ph}^\cdot + \text{cis-MeCH}=\text{CHMe}$	151.6	30.0	21.68	28
$\text{Ph}^\cdot + \text{trans-MeCH}=\text{CHMe}$	147.4	29.8	21.46	28
$\text{Ph}^\cdot + \text{CH}_2=\text{CHPr}^{\text{H}\cdot}$	146.9	25.8	20.87	28
$\text{Ph}^\cdot + \text{CH}_2=\text{CHCH}_2\text{Ph}$	174.1	18.5	20.98	28
$\text{Ph}^\cdot + \text{CH}_2=\text{CMe}_2$	149.9	22.9	20.59	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CCl}_2$	168.9	19.3	20.89	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHPh}$	195.7	18.9	21.96	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHOAc}$	156.4	24.4	21.10	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHCl}$	155.9	23.6	20.96	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHCH}_2\text{Pr}^{\text{H}\cdot}$	146.9	24.8	20.73	27
$\text{Ph}^\cdot + \text{CH}_2=\text{C}(\text{Me})\text{COOMe}^b$	179.9	18.5	21.23	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHCOOH}$	169.7	18.9	20.86	27
$\text{Ph}^\cdot + \text{CH}_2=\text{C}(\text{Me})\text{COOMe}^b$	179.9	19.8	21.43	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHCH}=\text{CH}_2$	209.0	19.6	22.60	27
$\text{Ph}^\cdot + \text{CH}_2=\text{CHPh}$	154.3	24.5	25.57	27

^a In the gas phase.

^b The results of different measurements.

equal to 20.01 ± 0.43 (kJ mol⁻¹)^{1/2}. The activation energy of the thermoneutral addition reaction (see Eq. (4)) $E_{e0} = 82.6 \pm 3.6$ kJ mol⁻¹ corresponds to this parameter. The addition of other alkyl radicals (Et[·], Me₂C[·]H, and Me₃C[·]) and the phenyl radical to the C=C bond of an olefin is characterized for each radical by a different br_e parameter (see Table 2). What is the reason for this difference?

The strong effect of the triplet repulsion on the E value was established in the analysis of activation energies of reactions of radical abstraction.^{8,9} The effect appears in the fact that for reactions of the X[·] + HY type, the stronger the X—Y bond along which the hydrogen atom is transferred, the higher the value of the br_e parameter.⁸ In the addition of R[·] to CH₂=CXY, the labile three-electron R[·]...C[·]H₂...C[·]XY bond is formed in the transition state, and since three electrons cannot be localized on one σ -orbital of the C=C bond, both bonding and antibonding orbitals of the C=C bond participate in the rearrangement of the orbitals. Therefore, this effect and the influence of the strength of the R—C bond on the value of the activation energy should be expected for addition reactions. This phenomenon

has previously been observed for the addition of atoms at the double C=C bond.²⁹ For the R[·] + CH₂=CXY reactions, the br_e and E_{e0} parameters (see Eq. (4)) were compared to the D_e value of the forming R—CH₂ bond.

R [·]	D_e /kJ mol ⁻¹	br_e /(kJ mol ⁻¹) ^{1/2}	E_{e0} /kJ mol ⁻¹
Ph [·]	436	22.60	105.3
Me [·]	378	20.01	82.6
Me ₂ C [·] H	372	19.49	78.3
Me ₃ C [·]	360	18.20	68.3

A distinct correlation between the br_e and D_e values of the C—C bond is observed: the stronger the forming bond, the higher br_e and E_{e0} . A similar conclusion follows from comparison of the parameters of the reactions of addition of the methyl radical to CH₂=CXY and HC≡CY (see Table 1). For the addition of Me[·] to acetylenes, the average br_e value is 25.23 ± 0.17 (kJ mol⁻¹)^{1/2}. The parameters for these two classes of reactions are compared below.

Compound	D_e /kJ mol ⁻¹	br_e /(kJ mol ⁻¹) ^{1/2}	E_{e0} /kJ mol ⁻¹
CH ₂ =CXY	378	20.01	82.6
HC≡CY	434	25.23	97.7

The dependence of the r_e value on the strength of the forming bond D_e is linear (Fig. 1) and is expressed by the empirical equation

$$r_e \cdot 10^{11}/\text{m} = (0.97 \pm 0.04) \cdot (D_e/\text{kJ mol}^{-1}). \quad (6)$$

It is very close to a similar dependence established for the addition of atoms (H, D, Cl, and Br) to the double

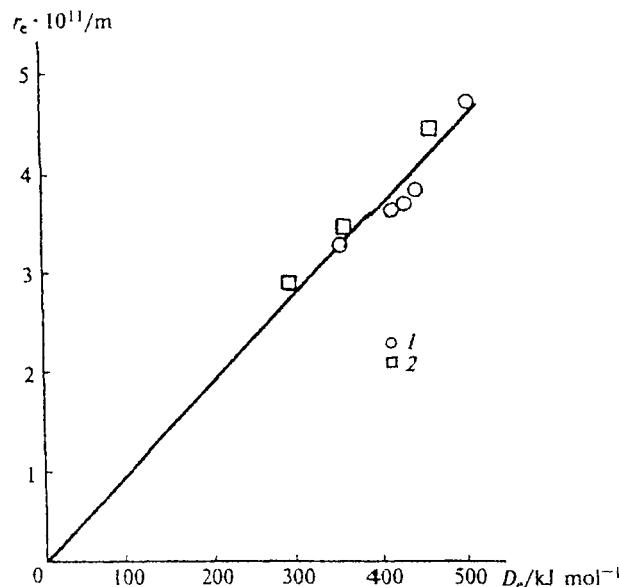


Fig. 1. Dependences of the parameter $r_e = b^{-1}(1 + \alpha)E_{e0}^{1/2}$ on the strength of the forming bond (D_e) for the addition of phenyl and alkyl radicals R[·] to olefins and acetylenes (1) and for the addition of atoms (H, D, Cl, and Br) to the double

Table 3. Effect of α - π -bonds (ΔE_π) on the activation energy of radical addition

Olefin	br_e^a	E_{e0}^b	ΔE_π^b
$\text{CH}_2=\text{CXY}$	20.01	82.6	0
$\text{CH}_2=\text{CHCH}=\text{CH}_2$	20.88	89.9	7.3
$\text{MeCH}=\text{CHCH}=\text{CHMe}$	21.15	92.2	9.6
$\text{CH}_2=\text{CMeCMe}=\text{CH}_2$	21.03	91.2	8.6
<i>cyclo</i> -[($\text{CH}=\text{CH}_2$) ₂ CH_2]	22.27	102.3	19.7
<i>cyclo</i> -[($\text{CH}=\text{CH}_2$) ₂ (CH_2) ₂]	22.23	101.9	19.3

^a In (kJ mol⁻¹)^{1/2}.^b In kJ mol⁻¹.

bond: $r_e \cdot 10^{13}/\text{m} = 1.03 \cdot [D(\text{C}-\text{X})/\text{kJ mol}^{-1}]$.²⁹ The data obtained should be considered as the empirical proof of the important role of the nonbonding orbital of the forming bond (so-called triplet repulsion) in the formation of the activation barrier of radical addition reactions.

The π -bonds adjacent to the attacked $\text{C}=\text{C}$ bond have a substantial effect on the activation energy and the br_e parameter (as well as E_{e0}). This is illustrated by the data (see Table 1) on the addition of the methyl radical to olefins and dienes with conjugated $\text{C}=\text{C}$ bonds (Table 3, for the method of calculation of ΔE_π , see Ref. 9).

The difference in the E_{e0} values of the reactions of the radicals with the double bond of an olefin, which has an adjacent π - $\text{C}-\text{O}$ bond, and with the double $\text{CH}_2=\text{CXY}$ bond can be considered as the contribution of conjugation of two π -bonds (ΔE_π) to the triplet repulsion in the transition state. For linear diolefins, it is equal, on the average, to 8.5 ± 0.9 kJ mol⁻¹. For cyclopenta- and cyclohexadienes, this contribution is substantially higher and equal to 19.5 ± 0.2 kJ mol⁻¹.

Similar regularities are also observed in the case of the addition of R^\cdot to styrene and its analogs (see Table 1). The br_e and E_{e0} values for the reactions of the methyl radical addition to α -phenylethylenes $\text{CH}_2=\text{CXY}$ are presented below.

X, Y	br_e	E_{e0}	ΔE_π
	$/(k\text{J mol}^{-1})^{1/2}$	kJ mol^{-1}	
H, R	20.01	82.6	0
H, Ph	20.82	90.0	7.4
Me, Ph	20.07	88.7	6.1
Ph, Ph	21.33	94.4	11.8

It is seen that one phenyl substituent in the α -position to the attacked $\text{C}=\text{C}$ bond increases the E_{e0} value by 6.7 ± 0.6 kJ mol⁻¹, whereas two Ph groups increase it by 12 kJ mol⁻¹. The linear dependence of the r_e value on the strength of the forming $\text{C}-\text{C}$ bond obtained above for the addition reaction (see Eq. (6)) makes it possible to estimate the degree of strengthening of the forming $\text{C}-\text{C}$ bond in the transition state due to the interaction of electrons of this bond with neighboring π -electrons: $\Delta D_\pi/\text{kJ mol}^{-1} = \Delta br_e/(5.37 \cdot 10^{-2})$.

Olefin	ΔE_π	ΔD_π
	kJ mol^{-1}	kJ mol^{-1}
$\text{CH}_2=\text{CHCH}=\text{CHR}$	8.5	18.8
$\text{CH}_2=\text{CHPh}$	6.7	14.9
$\text{CH}_2=\text{CPh}_2$	11.8	24.6

Thus, the results obtained prove unequivocally the important role of the triplet repulsion in radical addition reactions. The parameters calculated in this work and the correlations derived make it possible to estimate the activation energies of addition of various alkyl radicals to unsaturated compounds with $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds.

Polar interaction in addition reactions

The polar interaction appears in the transition state when an alkyl radical with a polar group reacts with a polar monomer. This effect was revealed in the studies on radical polymerization.^{3,4} The parabolic model allows one to estimate the contribution of this interaction (ΔE_μ) to the activation energy by the comparison of the br_e parameters for the addition reactions of the nonpolar (methyl) and polar (R_μ^\cdot) radicals using the equation⁹

$$\Delta E_\mu = [(br_e)^2 - (br_e)_{\text{Me}}^2](1 + \alpha)^{-2}. \quad (7)$$

The results of the calculations of the ΔE_μ values for the reactions of addition of hydroxyisopropyl, cyanoisopropyl, and *tert*-butoxyoxymethyl radicals to a series of polar monomers are presented in Table 4. It is seen that the polar interaction decreases the activation energy of the addition in the reactions of the $\text{Me}_2(\text{OH})\text{C}^\cdot$ and $\text{Me}_2(\text{CN})\text{C}^\cdot$ radicals, but increases it in the reactions of the $\text{Bu}^\cdot\text{OC(O)C}_2\text{H}_2$ radical. The ΔE_μ values vary from -23 kJ mol⁻¹ for the reaction of $\text{Me}_2(\text{OH})\text{C}^\cdot$ with $\text{CH}_2=\text{CHCN}$ to $+19.5$ kJ mol⁻¹ for the reaction of $\text{Bu}^\cdot\text{OC(O)C}_2\text{H}_2$ with $\text{CH}_2=\text{CMeOAc}$. Thus, the polar interaction can contribute substantially to the activation energy of addition.

The polar interaction between the attacking radical and the monomer also takes place in the reaction of chain propagation during radical polymerization.^{3,4} The initial data (rate constants from Ref. 4) and the calculated ΔE_μ values (see Eq. (7)) for the chain propagation during polymerization of several monomers are presented in Table 5. It is seen that for the monomers presented in Table 5, the effect of polar interaction is low, and the ΔE_μ values fall in the range of the measurement error (± 2 kJ mol⁻¹).

Comparison of parameters characterizing reactions of addition and abstraction of alkyl radicals

In terms of the parabolic model, the same parameters (ΔH_c , b , r_e and α) characterize reactions of abstraction and addition of radicals. This makes it possible to compare correctly two classes of the radical reactions indicated. Let us compare two individual reactions of

Table 4. Contribution of the polar interaction (ΔE_μ) to the activation energy of addition of polar alkyl radicals to polar monomers (calculated from Eqs. (1)–(3) and (7) according to Refs. 6, 30–32)

X, Y	Me [·] ,	Me ₂ (OH)C [·]		Me ₂ (CN)C [·]		Bu ¹ OCOC [·] H ₂	
	br _e ^a	br _e ^a	ΔE_μ ^b	br _e ^a	ΔE_μ ^b	br _e ^a	ΔE_μ ^b
H, OEt	19.63	19.87	-1.9	19.01	-4.9	21.20	13.2
Me, OMe	20.33	19.54	-6.5	19.17	-9.4	21.50	10.1
Me, OAc	20.33	18.27	-16.4	19.81	-4.3	22.54	19.5
H, OAc	20.17	18.27	-15.1	18.78	-11.2	22.17	17.5
Me, Cl	19.19	18.12	-8.2	18.62	-4.4	20.51	10.8
Cl, Cl	19.72	18.42	-10.2	19.24	-3.8	21.31	13.4
H, COOMe	19.53	16.85	-20.1	19.35	-1.4	21.09	13.1
H, CN	19.97	16.92	-23.2	19.86	-0.9	21.58	13.8
Me, COOMe	19.99			19.57	-3.4		
H, CHO	18.67			18.94	2.1		
Me, CN	19.82			19.27	-4.4		

^a In (kJ mol⁻¹)^{1/2}.

^b In kJ mol⁻¹.

Table 5. Contribution of the polar interaction (ΔE_μ) to the activation energy of radical addition

Compound	ΔH_e ^a	E_e ^a	ΔE_μ ^a	k (300 K) ^b	br_e ^c
CH ₂ =CMeCOOMe	76.5	44.4	-1.1	290	19.88
CH ₂ =CHCOOMe	87.3	41.5	-0.6	950	20.08
CH ₂ =CHOAc	86.2	42.0	-0.7	770	20.09

^a In kJ mol⁻¹.

^b In L mol⁻¹ s⁻¹.

^c In (kJ mol⁻¹)^{1/2}.

the methyl radical, namely the abstraction of the H atom from the ethane molecule and its addition to ethylene.

Reactant	ΔH_e	E_e	E (300 K)	A	k (300 K)
	kJ mol ⁻¹			L mol ⁻¹ s ⁻¹	
Ethane	-18.0	65.5	49.3	$6 \cdot 10^9$	15.6
Ethylene	-98.5	37.9	32.9	$1 \cdot 10^9$	$1.87 \cdot 10^3$

It is seen that the addition of the H atom to ethylene is a strongly exothermic reaction. Therefore, it occurs with a lower activation energy and more rapidly than the abstraction of the H atom from the ethane molecule.

The comparison of the parameters of these two classes of reactions (b/m^{-1} (kJ mol⁻¹)^{1/2}, r_e/m , $E_0/kJ mol^{-1} = E_{e0}/kJ mol^{-1} - 0.5hLv$) is presented below.

Reaction	α	$b \cdot 10^{11}$	$r_e \cdot 10^{11}$	E_{e0}	E_0	r^*/r_e
Abstraction	1.00	3.743	4.595	74.0	56.6	0.500
Addition	1.20	5.389	3.713	82.6	72.7	0.454

It follows from the comparison of the α values and the position of the transition state r^* at the segment r_e (r^*/r_e) that the transition state at $\Delta H_e = 0$ in the ab-

straction reaction is exactly in the middle of the r_e segment, whereas in the addition reaction, it is shifted toward the C=C bond. This results from the fact that in the abstraction reaction the parabolas of the breaking and forming C–H bonds are symmetrical because they are characterized by the same force constant, whereas in addition reactions, the breaking (C=C) and forming (C–C) bonds are characterized by different force constants. It is seen from the comparison of the r_e values that in the addition reaction, the transition state is more compact than that in the abstraction reaction. The force constants of the C–H and C=C bonds (coefficients b) differ significantly (see above); however, the E_{e0} and br_e values are sufficiently close. This is explained by the fact that for the reactions compared, the b and r_e values in the br_e product compensate each other.

The dependence of the activation energy on the reaction enthalpy is an important characteristic of each class of reactions. This dependence can be characterized by the derivative $dE_e/d(\Delta H_e)$ at $\Delta H_e = 0$. Transforming Eq. (3) for the case of low ΔH_e values, we can write⁹

$$E_e^{1/2} = br_e(1 + \alpha)^{-1} + \alpha \Delta H_e / (2br_e), \quad (8)$$

from which after differentiation at $\Delta H_e \rightarrow 0$ we obtain $dE_e/d(\Delta H_e) = \alpha(1 + \alpha)^{-1}$. The α and $dE_e/d(\Delta H_e)$ values for the classes of the reactions considered are presented below.

Reaction	α	$dE_e/d(\Delta H_e)$
Abstraction	1.00	0.50
Addition	1.20	0.54

These data indicate that the addition reaction is more "sensitive" to a change in the enthalpy than the reaction of hydrogen atom abstraction from the C–H bond.

As the ΔH_e value diminishes, the activation energy decreases and $E = 0.5RT$ at $\Delta H_e < \Delta H_{e,\min}$ (see Ref. 8).

The threshold value $\Delta H_{e,\min}$ depends on br_e , α , and $0.5hLv$ as follows⁸:

$$\Delta H_{e,\min} = -(br_e/\alpha)^2 + 2br_e\alpha^{-2}(0.5hLv)^{1/2} + 0.5(1 - \alpha^2)hLv. \quad (9)$$

For the addition reaction, $\Delta H_{e,\min} = -194.4 \text{ kJ mol}^{-1}$. This value differs substantially from $\Delta H_{e,\min} = -153.1 \text{ kJ mol}^{-1}$ for the abstraction reaction.

As shown above, the presence of π -electrons near the reaction center increases the E_e value of the addition reaction. A similar effect is also observed for abstraction reactions.⁸ The magnitudes of these effects in the abstraction and addition reactions are close, which is seen from the comparison of the ΔE_{π} values.

Reaction	$\Delta E_{\pi}(\text{Ar})$ kJ mol ⁻¹	$\Delta E_{\pi}(\text{C}=\text{C})$ kJ mol ⁻¹
Abstraction	7.8	14.7
Addition	8.5	19.5

In both addition and abstraction reactions, the triplet repulsion affects strongly the activation barrier and the interaction of polar groups of the radical and monomer.

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Received May 12, 1998