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Free radical addition: factors determining the activation energy

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Contents

I.	Introduction	153
II.	Enthalpy and entropy of radical addition	153
III.	Empirical correlation equations	154
IV.	Quantum-chemical calculations of the activation energy	155
V.	The parabolic model of radical addition	155
VI.	The contribution of enthalpy of an addition reaction to its activation energy	157
VII.	Force constants of reacting bonds	158
VIII.	Triplet repulsion in addition reactions	158
IX.	The influence of neighbouring π bonds on the activation energy of radical addition	159
X.	The role of the radius of the atom carrying the free valence	160
XI.	Interaction of two polar groups	160
XII.	Multidipole interaction in addition reactions	160
XIII.	Steric hindrance	161
XIV.	Competition between the addition of free radicals to the carbon and oxygen atoms of the carbonyl group	161
XV.	Comparison of radical addition and radical abstraction reactions	162
XVI.	Conclusion	163

Abstract. Empirical relations describing the reactivity of reagents in radical addition reactions and the results of quantum-chemical calculations of the activation energy of these processes are considered. The experimental data obtained for the addition of atoms and radicals to molecules with multiple bonds are analysed in terms of the parabolic model. The following characteristics and factors are shown to affect the activation energy of radical addition: the reaction enthalpy, the strength of the arising bond, the radius of the atom having a free valence, the presence of a π bond adjacent to the reaction centre, the interaction of two polar groups, the multidipole interaction, the steric factor, the non-linearity of the reaction centre, and the force constants of the reacting bonds. The bibliography includes 85 references.

I. Introduction

Radical addition to unsaturated compounds underlies the modern technology for production of polymers, copolymers and oligomers.[1–5] These reactions proceed during pyrolysis of hydrocarbons, halogenation of alkenes or oxidation of unsaturated compounds.[6–9] They are widely used in the synthesis of diverse medicines.[10–14] The addition of hydrogen atoms and hydroxyl radicals to unsaturated, aromatic and heterocyclic compounds is involved in the photolysis and radiolysis of organic materials and biological objects.[7] The problem of reactivity of compounds in the addition of atoms and radicals to double C=C bonds has been widely discussed and is still debated.[3, 6, 8, 15–24] Two factors which exert substantial influence on these processes have been noted, namely, heat (enthalpy) of the reaction and the interaction of polar groups of the reactants in the transition state (the so-called polar factor). Quantum-chemical calculations showed that the reaction centre in the transition state is non-linear.[16] When interpreting the results of these calculations, researchers restricted themselves to consideration of only three factors influencing the activation energy of addition, namely, the reaction enthalpy, the interaction of polar groups and the steric effect.[25–39]

Analysis of the experimental data (on activation energies) obtained in the studies of radical abstraction reactions in terms of the parabolic model showed that, apart from the factors mentioned above, there is a whole series of other factors that determine the activation energy of an elementary step.[40–42] The author of this review has analysed an extensive array of experimental data concerning radical addition reactions in terms of the parabolic model for this type of reaction.[43–53] The results of this analysis are presented in detail in this review.

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II. Enthalpy and entropy of radical addition

The radical addition reactions

$$X^{\bullet} + CH_2=CHY \longrightarrow XCH_2C^{\bullet}HY$$

involve the rupture of the C=C π bond and the formation of a C–X σ bond. A σ bond is normally stronger than a π bond; hence, radical addition is an exothermic reaction. This can be clearly seen when comparing the reaction enthalpies ΔH and the strengths of the bonds being formed D(Et–X) given in Table 1; the stronger the Et–X bond, the larger the $-\Delta H$ value. Yet another important factor influencing the reaction enthalpy is the energy of stabilisation of the radical $XCH_2C^{\bullet}HY$ formed: the higher this energy, the greater the heat of the addition of the $X^{\bullet}$ radical to an alkene. Stabilisation energy can be characterised as the difference between the strengths of the C–H bonds in Pr–H and EtYHC–H. Below we present the data characterising the contribution to the enthalpy of this reaction of the stabilisation

Table 1. Bond strength (kJ mol^{-1}), enthalpy (kJ mol^{-1}), entropy (J mol^{-1} K^{-1}) and Gibbs energy (kJ mol^{-1}) for the addition of atoms and X$^{\bullet}$ radicals to ethylene (T = 298 K).

X$^{\bullet}$	D(Et−X)	$-\Delta H$	$-\Delta S$	$-\Delta G$
H$^{\bullet}$	422	150	84	125
Cl$^{\bullet}$	352	82	88	56
C$^{\bullet}$H$_3$	370	100	122	64
Me$_2$C$^{\bullet}$H	364	92	134	52
PhC$^{\bullet}$H$_2$	318	63	122	27
N$^{\bullet}$H$_2$	353	81	109	49
HO$^{\bullet}$	343	122	100	93
CH$_3$O$^{\bullet}$	352	82	118	46
HO$_2^{\bullet}$	327	63	134	23

energy of the MeCH$_2$C$^{\bullet}$HY radical, resulting from the addition of a methyl radical to the monomer CH$_2$=CHY.

Y	H	C(O)OMe	Cl	CN	Ph
$D_{Pr-H} - D_{EtYHC-H}$ /kJ mol^{-1}	0.0	23.2	24.1	33.6	57.9
$-\Delta H$ /kJ mol^{-1}	95.8	102.0	104.3	129.7	143.0

It can be seen that the greater the energy of radical stabilisation, the smaller the reaction enthalpy.

All the addition reactions are accompanied by a decrease in entropy (two species are combined to give one species, see Table 1). Therefore, for addition reactions, $\Delta G < \Delta H$ (ΔG is the Gibbs energy) and, when the temperature is sufficiently high, exothermic addition is reversible because $\Delta G = \Delta H - T\Delta S$.

Free radical addition can be considered to be reversible if the equilibrium concentration of the X$^{\bullet}$ radicals is commensurate with the concentration of the XCH$_2$C$^{\bullet}$HY radicals formed, *i.e.* if the [X$^{\bullet}$]:[XCH$_2$C$^{\bullet}$HY] ratio in the equilibrium state is not smaller than 0.05. When [CH$_2$=CHY] = 10 mol litre^{-1} and T = 300 K, this condition results in the inequality $K \geqslant 200$ (K is the equilibrium constant). In turn, $-RT\ln K = \Delta G$; therefore, $\Delta G \leqslant -RT\ln 200 = -13$ kJ mol^{-1}. For addition reactions, $\Delta S \approx -100$ J mol^{-1} K^{-1}; therefore, the enthalpy of irreversible addition of X$^{\bullet}$ to an alkene

$$\Delta H = \Delta G + T\Delta S$$

should be smaller than -43 kJ mol^{-1} (at T = 300 K).

The ΔH values for radical addition reactions listed in Table 1 comply with this condition. Naturally, as the temperature rises, the boundary value of ΔH increases in absolute magnitude.

III. Empirical correlation equations

Activation energy and heat of reaction. A linear correlation between the change in the activation energy (ΔE) of the monomer addition to a macroradical and the change in the heat of the reaction (Δq) of the type

$$\Delta E = -\alpha' \Delta q, \quad (1)$$

where α' is an empirical factor of proportionality, was found by Evans *et al.*[54] Later, N N Semenov confirmed this correlation and extended it to a wider range of addition reactions.[15] However, even for a narrow series of reactions, for example, for the addition of methyl radical to CH$_2$=CHY, this correlation is nothing but a trend. Indeed, the correlation coefficient for the variation of $\Delta \log k$ as a function of Δq is 0.85 (k is the reaction rate constant).[55] Evidently, apart from the heat of reaction, other factors also influence the activation energy.

The Alfrey and Price $Q-e$ scheme[56] takes account of two factors affecting activation energy, namely, the energy of stabilisation of the radical formed in the reaction and the interaction between polar groups in the radical and the monomer. This scheme was based on the analysis of empirical rate constants for copolymerisation. The rate constant for the reaction of a radical with a monomer is postulated to have the following form:

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2), \quad (2)$$

where the factors P_1 and Q_2 reflect the reactivity and e_1 and e_2 are the charges of the radical and the monomer, respectively. The Q and e parameters are calculated from the corresponding rate constants for copolymerisation. When developing the $Q-e$ scheme, the researchers assumed that the charges on the molecule and on the radical are equal and constant (polarisation in the transition state was not taken into account) and that the copolymerisation rate constants do not depend on the dielectric constant of the medium. Subsequently, these assumptions have been critisised.[2] The $Q-e$ scheme made it possible to systematise the vast experimental information on radical copolymerisation of various monomers. It permits rough prediction of the rate constants for copolymerisation. The Q and e values for monomers in radical polymerisation are listed in Table 2.

Table 2. Correlation parameters for the reactivity of monomers towards radical polymerisation in terms of the Alfrey–Price (Q, e), Bamford–Jenkins (α, β) and Ito–Matsuda (K, P) schemes.[56–62]

Monomer	Q	e	α	β	K	P
CH$_2$=CHPh	1.00	−0.80	0.00	4.85	2.28	1.00
CH$_2$=CHSEt	0.27	−1.33	−0.50	4.21	1.30	2.78
CH$_2$=CHSO$_2$Et	0.07	1.29	−4.0	4.62	−1.40	−0.26
CH$_2$=CHCO$_2$Me	0.45	0.60	−3.0	5.20	0.00	0.58
CH$_2$=CHOCOMe	0.03	−0.88	0.0	3.00	−1.36	0.81
CH$_2$=CHCN	0.48	0.12	−3.0	5.30	0.89	−1.00
CH$_2$=CHOEt	0.02	−1.17	0.0	2.97	−0.59	1.63
CH$_2$=CMePh	0.98	−0.81	−1.0	4.72	1.30	1.69
CH$_2$=CMeCO$_2$Me	0.78	0.40	–	4.90	1.89	0.25
CH$_2$=CHCH=CH$_2$	1.70	−0.50	0.0	5.03	–	1.00
CH$_2$=CMeCH=CH$_2$	1.99	−0.55	0.0	4.92	–	1.09
CH$_2$=CClCH=CH$_2$	10.52	1.20	−1.5	5.82	–	0.10
CH≡CPh	0.45	0.5	0.5	4.41	–	1.00

The Bamford and Jenkins $\alpha-\beta$ scheme.[57] These researchers suggested that the reactivities of a radical and a monomer should be described by three parameters, namely, rate constant for the reaction of the macroradical (for example, R$^{1\bullet}$) with toluene (k_T)

$$R^{1\bullet} + PhMe \longrightarrow R^1H + PhCH_2^{\bullet};$$

the product of coefficient α with the Hammett constant σ, which takes into account the polar effect, and the coefficient β, reflecting the difference between the radical reactivities towards the monomer and towards toluene. Thus the equation for the rate constant for the addition of R$^{1\bullet}$ to the monomer M$_1$ is represented as follows:

$$\ln k_{11} = \ln k_T + \alpha_1\sigma_1 + \beta_1; \quad (3)$$

the coefficients σ_1 and β_1 are calculated from the dependence of $\ln(k_{11}/k_T)$ on σ, and the rate constant k_T is determined experimentally at T = 333 K. The values of α and β for a number of monomers are listed in Table 2.

The relationship between the parameters of the Alfrey–Price and Bamford–Jenkins schemes is expressed by the following equations:[58]

$$-e_1(e_1 - e_2) = \sigma_1(\alpha_1 - \alpha_2), \quad (4)$$
$$\ln Q_1 - \ln Q_2 = \beta_1 - \beta_2.$$

The Ito and Matsuda *K–P* scheme.[59–62] In terms of this scheme, the activation energy of an addition reaction is represented as the sum of two terms, E_1 and E_2. The first term E_1 is proportional to the change in the Gibbs energy in the reversible addition of the thiyl radical $XC_6H_5S^{\bullet}$ to the monomer, $E_1 \sim \log K$, where K is the equilibrium constant of the reaction

$$PhS^{\bullet} + CH_2=CHY \rightleftharpoons PhSCH_2C^{\bullet}HY.$$

The second term E_2 reflects the contribution of the polar interaction between the radical and the monomer to the activation energy. The contribution of the Gibbs energy to the activation energy is determined by the coefficient present in the linear dependence on $\log K$ of the logarithm of the rate constant (k_X) for the addition of the $XC_6H_4S^{\bullet}$ radical to the monomer $CH_2=CHY$

$$\Delta \log k_X = \alpha_Y \Delta \log K. \quad (5)$$

The α_Y value depends on the nature of the substituent Y in the monomer, this dependence being used to estimate the contribution of the polar effect to the activation energy. This contribution is characterised by the increment P

$$P = \alpha_Y + 2(\alpha_Y - \alpha_{styrene}). \quad (6)$$

The parameters K and P are listed in Table 2. Parameters of the Ito–Matsuda scheme are related to the parameters of the Alfrey–Price approach by simple relations:[62]

$$\log Q = 0.49\,K - 0.93, \quad (7)$$
$$e = 0.91\,P + 0.95.$$

All the above schemes include, in essence, different variants of empirical linear equations in which the rate constants for chain propagation in the free radical polymerisation are brought into correlation with thermodynamic [heat, Hammett constant (σ), the change in the Gibbs energy in the equilibrium reaction] and kinetic (logarithms of the rate constants of the reference reaction and the reaction under study) characteristics of the addition reaction.

IV. Quantum-chemical calculations of the activation energy

Quantum-chemical methods are widely used to study addition reactions.[26–39] The results obtained, in particular, the activation energies, depend significantly on the programme chosen for calculations. For example, Wong *et al.*[38] calculated the activation energy of the methyl radical addition to ethylene using the QCISD(T) programme package. The results of calculations by this programme are in good agreement with experimental data.

When atoms approach one another and a transition state is formed, the bond angles at the carbon atom attacked by an atom or radical substantially change. Figure 1 shows the configuration of atoms in the transition state for the addition of substituted methyl radicals $XC^{\bullet}H_2$ to substituted ethylenes $CH_2=CHY$.[38] The geometry of the transition state is characterised by the distance r(C–C), the angle of attack $\varphi_{at} = \varphi$(CCC) and the pyramidal angle $\varphi_{pyr} = \varphi$(HCC). The last-mentioned parameter

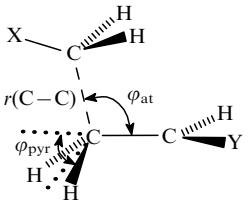


Figure 1. Geometry of the reaction centre in the transition state for the addition of substituted methyl radicals ($XC^{\bullet}H_2$) to substituted ethylenes ($CH_2=CHY$).[38]

Table 3. Interatomic distances and bond angles in the reaction centre and the activation energies for the addition of the $XC^{\bullet}H_2$ radicals to ethylene (quantum-chemical calculations).[38]

X	r (C–C) /Å	φ_{at}/ deg	φ_{pyr}/ deg	E/ kJ mol^{-1}
H	2.246	109.9	25.0	39.8
OH	2.226	108.2	25.9	35.0
CN	2.173	109.3	28.0	42.3

is the angle of deviation of the two C–H bonds of ethylene from the plane in which they have been located in the initial molecule (the four hydrogens and both carbons of ethylene lie in one plane). Table 3 presents the values of the three above parameters and the activation energies for the addition of methyl radicals and the $C^{\bullet}H_2OH$ and $C^{\bullet}H_2CN$ radicals to ethylene.[38]

The energy profile of the addition reaction is calculated using specific quantum-chemical programmes as a superposition of four different electron configurations of the reactants, namely,[38,39]

$$DA[XC^{\bullet}H_2(\uparrow)CH_2=CHY(\uparrow\downarrow)],$$

$$D^3A^*[XC^{\bullet}H_2(\downarrow)CH_2=CHY(\uparrow\uparrow)],$$

$$D^+A^-[XCH_2(+)CH_2=CHY(-)],$$

$$D^-A^+[XCH_2(-)CH_2=CHY(^+)],$$

where D is the radical, A is the molecule, the arrows mark the orientation of the electrons involved in the reorganisation, and (+) and (–) are the charges on the radical and on the molecule. The results (the activation energies) thus obtained are considered with allowance for the influence of two values, namely, the reaction enthalpy and the polar effect.

V. The parabolic model of radical addition

Within the framework of the parabolic model, radical addition

$$X^{\bullet} + CH_2=CHY \longrightarrow XCH_2C^{\bullet}HY$$

is represented [43] as a result of intersection of two potential curves, each of them describing the potential energy of the stretching vibrations of atoms as a parabolic function of the amplitudes of vibrations of atoms in the outgoing (i) and incoming (f) bonds. In terms of the parabolic model, radical addition can be characterised by the following parameters (Fig. 2).

1. Reaction enthalpy ΔH_e

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f) = \Delta H + 0.5hL(\nu_i - \nu_f), \quad (8)$$

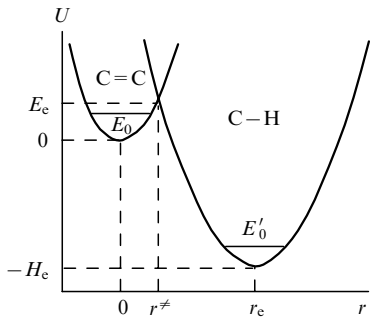


Figure 2. Diagram of the transition state for the hydrogen atom addition to ethylene in the coordinates of the amplitude of the stretching vibration of atoms in the reaction centre (r) and the potential energy of the stretching vibration (U) in terms of the parabolic model.[43]
E_0, E'_0 are the zero-point energies of the corresponding bonds.

Table 4. Parameters of various classes of addition of atoms and radicals to multiple bonds used in the parabolic model.[44–50]

Reaction	α	$10^{-11}b$ / $kJ^{1/2}\,mol^{-1/2}\,m^{-1}$	$0.5hLv$/ $kJ\,mol^{-1}$	$\Delta\Delta H_e$/ $kJ\,mol^{-1}$	$10^{-10}A$ / litre $mol^{-1}\,s^{-1}$
$H^{\bullet} + CH_2=CHR \longrightarrow CH_3C^{\bullet}HR$	1.440	5.389	9.9	−7.5	10
$H^{\bullet} + CH\equiv CR \longrightarrow CH_2=C^{\bullet}R$	1.847	6.912	12.7	−4.7	40
$D^{\bullet} + CH_2=CHR \longrightarrow DCH_2C^{\bullet}HR$	1.461	5.389	9.9	−2.7	10
$Cl^{\bullet} + CH_2=CHR \longrightarrow ClCH_2C^{\bullet}HR$	1.591	5.389	9.9	4.8	9
$Br^{\bullet} + CH_2=CHR \longrightarrow BrCH_2C^{\bullet}HR$	1.844	5.389	9.9	5.8	5
$R^{\bullet} + CH_2=CHR \longrightarrow RCH_2C^{\bullet}HR$	1.202	5.389	9.9	1.7	0.1
$R^{\bullet} + CH\equiv CR \longrightarrow RCH=C^{\bullet}R$	1.542	6.912	12.7	3.8	0.1
$N^{\bullet}H_2 + CH_2=CHR \longrightarrow NCH_2C^{\bullet}HR$	1.410	5.389	9.9	3.1	0.008
$RO^{\bullet} + CH_2=CHR \longrightarrow ROCH_2C^{\bullet}HR$	1.413	5.389	9.9	3.3	0.05
$RO_2^{\bullet} + CH_2=CHR \longrightarrow ROOCH_2C^{\bullet}HR$	1.737	5.389	9.9	4.6	0.1
$R^1_3Si^{\bullet} + CH_2=CHR^2 \longrightarrow R^1_3SiCH_2C^{\bullet}HR^2$	2.012	5.389	9.9	4.1	0.1
$PhS^{\bullet} + CH_2=CHR \longrightarrow PhSCH_2C^{\bullet}HR$	2.282	5.389	9.9	6.3	0.07
$H^{\bullet} + O=CR^1R^2 \longrightarrow HOC^{\bullet}R^1R^2$	1.600	5.991	10.3	−11.4	10
$R^{\bullet} + O=CR^1R^2 \longrightarrow ROC^{\bullet}R^1R^2$	1.570	5.991	10.3	3.7	0.05
$R_3Si^{\bullet} + O=CR^1R^2 \longrightarrow R_3SiOC^{\bullet}R^1R^2$	2.518	5.991	10.3	7.0	0.08

Table 5. Parameters ΔH_e, E_e, br_e and ΔE_H for the hydrogen atom addition to multiple bonds in the gas and liquid phases calculated from Eqns (8)–(10).[64–79]

Alkene	ΔH_e/ $kJ\,mol^{-1}$	Phase [a]	E_e/ $kJ\,mol^{-1}$	br_e/ $kJ^{1/2}\,mol^{-1/2}$	$-\Delta E_H$/ $kJ\,mol^{-1}$
$CH_2=CH_2$	162.1	gas (4)	22.5	24.26	79.1
$CH_2=CH_2$	162.1	liq (2)	22.6	24.32	79.0
$CH_2=CHMe$	165.3	gas (1)	21.6	24.34	80.0
$CH_2=CHMe$	165.3	liq (1)	20.3	24.08	81.3
$CH_2=CHEt$	166.2	gas (1)	20.2	24.15	81.4
$CH_2=CHEt$	166.2	liq (1)	19.6	24.01	82.0
$CH_2=CMe_2$	168.9	gas (1)	18.0	23.93	83.6
$CH_2=CHPr$	165.7	gas (1)	20.6	24.19	81.0
$CH_2=CHPr$	165.7	liq (1)	24.3	24.73	77.3
cis-$MeCH=CHEt$	158.5	gas (1)	23.9	24.34	77.7
trans-$MeCH=CHEt$	154.2	gas (1)	24.1	24.13	77.5
cis-$MeCH=CHEt$	158.5	liq (1)	26.9	24.34	74.7
$CH_2=CMeEt$	173.3	gas (1)	20.3	24.55	81.3
$CH_2=CMeEt$	173.3	liq (1)	23.5	25.00	78.1
$MeCH=CMe_2$	169.5	liq (1)	24.4	24.94	77.2
$CH_2=CMePr$	173.3	liq (1)	23.3	24.97	78.3
$CH_2=CEt_2$	168.9	liq (1)	23.3	24.75	78.3
$EtCH=CMe_2$	165.9	liq (1)	24.7	24.80	76.9
$MeCH=CHPr$	158.5	liq (1)	25.3	24.50	76.3
$Me_2C=CMe_2$	177.7	liq (1)	25.1	25.48	76.5
$MeCH=CHBu$	158.5	liq (1)	25.3	24.51	76.3
$MeCH=CEt_2$	163.1	liq (1)	24.5	24.63	77.1
$CH_2=CH(CH_2)_4Me$	165.7	liq (1)	24.2	24.71	77.4
$CH_2=CH(CH_2)_5Me$	165.7	liq (1)	24.3	24.74	77.3
$CH_2=CH(CH_2)_7Me$	165.7	liq (1)	24.2	24.72	77.4
cyclo-C_5H_8	158.3	liq (2)	25.2	24.48	76.4
cyclo-C_6H_{10}	161.7	gas (3)	23.6	24.47	78.0
cyclo-C_6H_{10}	161.7	liq (4)	22.9	24.34	78.7
cyclo-$C_6H_{11}CH=CH_2$	163.6	liq (1)	24.3	24.63	77.3
$CH_2=CHCH_2OH$	166.5	liq (1)	19.5	24.06	82.1
$CH_2=CHCOOH$	182.0	liq (2)	21.3	25.09	80.3
trans-$HO_2CCH=CHCO_2H$	184.3	liq (1)	18.8	24.82	82.8
trans-$MeO_2CCH=CHCO_2Me$	184.3	liq (1)	18.2	24.72	83.4
cyclo-$[C(CO_2H)=CH(CH_2)_3]$	189.1	liq (1)	20.9	25.39	80.7
cyclo-$[C(CO_2H)=CH(CH_2)_4]$	184.9	liq (1)	27.3	25.20	76.4
cyclo-$[CH=CHCH_2CH(CO_2H)(CH_2)_2]$	161.7	liq (1)	21.3	24.05	80.3
$CH_2=CHCl$	179.5	gas (1)	19.8	24.79	81.8
$CH_2=CHF$	174.3	gas (1)	19.7	24.50	81.9

[a] The value in parentheses is the number of determinations.

where D_i and D_f are dissociation energies, h is the Planck constant, L is the Avogadro number, and ν_i and ν_f are the stretching vibration frequencies of bonds i and f, respectively. The second term is the difference between the zero-point energies of the reacting bonds.

2. Activation energy E_e, which includes the zero-point energy of the bond being attacked ($0.5hL\nu_i$) and depends on the experimentally determined activation energy E

$$E_e = E + 0.5(hL\nu_i - RT). \quad (9)$$

3. Distance r_e, which is equal to the sum of the amplitudes of vibrations of the atoms of the reacting bonds in the transition state.

4. Parameters b_i and b_f, which are dynamic characteristics ($2b^2$ is the force constant) of the outgoing bond

$$b_i = \pi\nu_i(2\mu_i)^{1/2}$$

and the incoming bond

$$b_f = \pi\nu_f(2\mu_f)^{1/2},$$

where μ_i and μ_f are the reduced masses of atoms forming the bonds.

The above parameters are related to one another by the following expression:[42]

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (10)$$

By using the parameter br_e, one can calculate characteristics of a whole group of reactions with br_e = const, for example, the activation energy of the thermally neutral reaction E_{e0} for $\Delta H_e = 0$

$$(E_{e0})^{1/2} = br_e(1 + \alpha)^{-1} \quad (11)$$

and the position of the transition state $r^{\neq}$ in the segment r_e

$$\frac{r^{\neq}}{r_e} = \frac{1}{1+\alpha}. \quad (12)$$

As a rule, each reaction within one group is characterised by the same pre-exponential factor A (determined in relation to one reaction centre). This allows the activation energy to be expressed in terms of the rate constant k using the Arrhenius equation

$$E = RT\ln\frac{A}{k}. \quad (13)$$

Since for any elementary reaction, $E > 0$, relation (13) holds when $\Delta H_e > \Delta H_{e\,min}$, whereas for $\Delta H_e < \Delta H_{e\,min}$, the activation energy is very small and amounts to $0.5RT$. In accordance with the parabolic model, $\Delta H_{e\,min}$ is related to br_e and α by the expression [63]

$$\alpha^2\Delta H_{e\,min} = -(br_e)^2 + 2br_e(0.5hL\nu_i)^{1/2} + 0.5hL\nu_i(\alpha^2 - 1). \quad (14)$$

The physical, thermodynamic and kinetic parameters for 15 classes of reactions involving addition of atoms and radicals to carbon–carbon and carbon–oxygen multiple bonds are listed in Table 4.

The parabolic model makes it possible to develop an empirical hierarchy of addition reactions. All the known addition reactions are divided *a priori* into classes in accordance with the atomic structure of the reaction centre in the transition state. Each class is characterised by a pair of force constants of the outgoing and incoming bonds or by the parameters $b = b_i$ and $\alpha = b_i/b_f$ (see above). Subclasses are distinguished in each class. Each subclass is characterised by r_e = const or br_e = const, which is confirmed by analysis of a large array of experimental results. This fact is illustrated, for example, by the data on the addition of a hydrogen atom to alkenes with various structures (Table 5). For thirty two reactions, $br_e = 24.50 \pm 0.40$ kJ$^{1/2}$ mol$^{-1/2}$.

Each subclass of reactions can be described additionally by the energy of the thermally neutral reaction E_{e0} [see Eqn (11)] and by the threshold value $\Delta H_{e\,min}$, for which $E = 0.5\,RT$ provided that $\Delta H_e < \Delta H_{e\,min}$ [see Eqn (14)]. The kinetic parameters for various subclasses of addition reactions are listed in Table 6. It can be seen that each subclass is characterised by individual values of these parameters. For instance, E_{e0} varies from 31.4 kJ mol^{-1} for the addition of PhS$^{\bullet}$ to 105.3 kJ mol^{-1} for the addition of the phenyl radical to an alkene double bond.

Table 6. Kinetic parameters E_{e0} (kJ mol^{-1}), $b(1+\alpha)^{-1}\times10^{-11}$ (kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}), $r_e\times10^{11}$ (m), $(r^{\neq}/r_e)_0$ and $-\Delta H_{e\,min}$ (kJ mol^{-1}) calculated from Eqns (10)–(12) and (14) for addition reactions of various subclasses.[44–50]

X$^{\bullet}$	E_{e0}	$b(1+\alpha)^{-1}\times10^{-11}$	$r_e\times10^{11}$	$(r^{\neq}/r_e)_0$	$-\Delta H_{e\,min}$
Reaction X$^{\bullet}$ + CH_2=CHY ⟶ $XCH_2C^{\bullet}HY$					
H$^{\bullet}$	101.6	2.21	4.56	0.41	211.9
D$^{\bullet}$	99.6	2.19	4.56	0.41	204.9
Cl$^{\bullet}$	50.5	1.86	3.82	0.39	82.9
Br$^{\bullet}$	31.2	1.69	3.30	0.35	37.9
$C^{\bullet}H_3$	82.6	2.45	3.71	0.45	194.4
$C_6H_5^{\bullet}$	105.3	2.45	4.19	0.45	252.0
$N^{\bullet}H_2$	61.0	2.24	3.49	0.41	226.0
RO$^{\bullet}$	65.2	2.23	3.62	0.41	119.0
$RO_2^{\bullet}$	90.5	1.97	4.83	0.36	150.4
$R_3Si^{\bullet}$	76.6	1.78	4.92	0.33	117.5
PhS$^{\bullet}$	31.4	1.64	3.42	0.30	34.7
Reaction X$^{\bullet}$ + HC≡CY ⟶ XCH=C$^{\bullet}$Y					
H$^{\bullet}$	125.1	2.43	4.60	0.35	229.3
$C^{\bullet}H_3$	97.7	2.72	3.63	0.39	184.7
Reaction X$^{\bullet}$ + O=CR^1R^2 ⟶ $XOC^{\bullet}R^1R^2$					
H$^{\bullet}$	102.9	2.30	4.41	0.38	149.7
$C^{\bullet}H_3$	72.9	2.33	3.66	0.39	112.2
$R_3Si^{\bullet}$	114.5	1.70	6.29	0.28	176.8

VI. The contribution of enthalpy of an addition reaction to its activation energy

The parabolic model postulates a non-linear relationship between the activation energy and the enthalpy of a reaction [see Eqn (10)]. The contribution of enthalpy to the activation energy ΔE_H can be estimated as the difference $\Delta E_H = E_e - E_{e0}$.

Transformation of Eqn (10) gives the following equation for ΔE_H as a function of ΔH_e [42]

$$\Delta E_H = \frac{2\alpha(br_e)^2}{\alpha^2-1}\left\{\left[\frac{\Delta H_e(\alpha^2-1)}{(br_e)^2}-1\right]^{1/2}-1\right\}+\frac{\alpha^2\Delta H_e^2}{\alpha^2-1}. \quad (15)$$

When the range of variation of ΔH_e is narrow, this dependence is close to linear

$$\Delta E_H = \frac{\alpha}{1+\alpha}\Delta H_e + \frac{\alpha}{4(br_e)^2}\Delta H_e^2. \quad (16)$$

In a review,[42] the E_{e0} values calculated from experimental br_e parameters made it possible to evaluate correctly the contribution of the enthalpy of addition to its activation energy. As an example, Table 7 presents the results of this comparison for two groups of addition reactions.

It can be seen that these reactions are highly exothermic and the contribution of enthalpy to the activation energy is fairly high; it varies from −43.6 to −98.7 kJ mol^{-1}, *i.e.* amounts to 40%–50% of ΔH.

Table 7. Contribution of the reaction enthalpy ΔH to the activation energy ΔE_H.

R	Y	$-\Delta H$/ kJ mol^{-1}	E_e/ kJ mol^{-1}	$-\Delta E_H$/ kJ mol^{-1}
Reaction $H^{\bullet} + CH_2=CRY \longrightarrow CH_3C^{\bullet}RY$ (see Ref. 44)				
H	H	162.1	22.5	79.1
H	Me	165.3	21.0	80.6
Me	Me	173.3	18.0	83.6
H	Cl	179.5	19.8	81.8
H	Ph	204.1	19.2	93.0
Ph	Ph	213.3	19.0	98.7
Reaction $CH_3^{\bullet} + CH_2=CRY \longrightarrow C_2H_5C^{\bullet}RY$ (see Ref. 46)				
H	H	98.5	39.0	43.6
H	Me	96.1	36.9	45.7
Me	Me	98.3	35.7	46.9
H	Cl	104.3	33.6	49.0
H	Ph	143.3	26.6	63.4
Ph	Ph	154.0	24.5	69.3

VII. Force constants of reacting bonds

The activation energy of a thermally neutral reaction is determined by two parameters — the distance r_e and the force constants of the reacting bonds α and b. In some classes of radical abstraction reactions, namely in those presented below,

$$R^{\bullet} + R^1X \longrightarrow RX + R^{1\bullet} \quad \text{and} \quad H^{\bullet} + RX \longrightarrow HX + R^{\bullet},$$

only the force constants change on passing from one class to another; thus, only the parameters α and b determine the activation energy of a thermally neutral reaction.[80] There are no such examples among addition reactions; therefore, it is expedient to compare different classes of reactions assuming (conditionally) that r_e = const. The parameter r_e for each reaction was taken to be 3.713×10^{-11} m, as for the addition of the methyl radical to $CH_2=CRY$, while the parameters b_i and b_f were varied in conformity with the structure of the reaction centre. The calculations were carried out using Eqn (11).

Reaction	E_{e0} (calculated)/ kJ mol^{-1}	E_{e0} (exp)/ kJ mol^{-1}
$H^{\bullet} + C=C$	67.3	101.6
$H^{\bullet} + O=C$	73.2	102.9
$H^{\bullet} + C=C$	81.3	125.2
$Me^{\bullet} + C=C$	82.6	82.6
$Me^{\bullet} + O=C$	74.9	68.1
$Me^{\bullet} + C=C$	64.0	97.7

Comparison of the calculated and experimental E_{e0} values shows a substantial influence of, on the one hand, the force constants (the range of variation of E_{e0} is 64–83 kJ mol^{-1}) and, on the other hand, the parameter r_e [E_{e0} (calculated) $\neq E_{e0}$ (exp)].

VIII. Triplet repulsion in addition reactions

The activation energy of radical abstraction is influenced by the so-called triplet repulsion in the transition state.[40,42] This influence is manifested in the fact that the stronger the X–R bond towards which the hydrogen atom moves in the thermally neutral reaction $X^{\bullet} + RH$, the higher the activation energy of this reaction. The triplet repulsion is due to the fact that three electrons cannot be accommodated in the bonding orbital of X–C; therefore, one electron occupies the non-bonding X–C orbital. Meanwhile, the stronger the X–C bond, the higher the energy of the non-bonding orbital and the higher the activation energy of abstraction.

How do matters stand with radical addition? Comparison of E_{e0} and r_e with the energy of dissociation of the resulting bond D_e has shown that this influence certainly does exist.[44,46,48] The parameters E_{e0} and r_e are juxtaposed with the dissociation energy of the bond formed D_e(X–C) in Table 8 and in Fig. 3. For reactions of one class, namely, $X^{\bullet} + CH_2=CHY$, the linear correlation E_{e0} = const $[D_e(X-C)]^2$ holds; const = 5.95×10^4 mol kJ^{-1}. The following correlation was found to be fulfilled for reactions of all the thirteen classes considered:

$$r_e = a\, D_e(X-C), \tag{17}$$

where $a = (1.01 \pm 0.03) \times 10^{-13}$ for the addition of atoms and $a = (0.98 \pm 0.02) \times 10^{-13}$ m mol kJ^{-1} for the addition of radicals (see Fig. 3). This correlation should be regarded as an empirical proof of the fact that the non-bonding orbital of the bond being

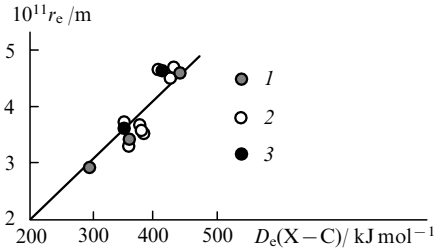


Figure 3. Correlation of the parameter r_e (parabolic model) with the strength D_e(X–C) of the bond formed upon atom and radical addition to the C=C and C=O multiple bonds;[47]
(*1*) atom + C=C, (*2*) $X^{\bullet}$ + C=C or C≡C, (*3*) $H^{\bullet}(R^{\bullet})$ + O=C.

Table 8. Parameters of various classes of radical addition and the strengths D_e(X–C) of the bonds formed.[44–50]

Reaction	E_{e0}/ kJ mol^{-1}	$r_e \times 10^{11}$ /m	D_e(X–C)/ kJ mol^{-1}	$\frac{r_e}{D_e(X-C)} \times 10^{13}$/m mol kJ^{-1}
$H^{\bullet} + CH_2=CHY \longrightarrow CH_3C^{\bullet}HY$	101.6	4.563	439	1.04
$D^{\bullet} + CH_2=CHY \longrightarrow DCH_2C^{\bullet}HY$	99.6	4.557	439	1.04
$Cl^{\bullet} + CH_2=CHY \longrightarrow ClCH_2C^{\bullet}HY$	50.5	3.427	357	0.96
$Br^{\bullet} + CH_2=CHY \longrightarrow BrCH_2C^{\bullet}HY$	31.2	2.949	299	0.99
$H^{\bullet} + CH\equiv CY \longrightarrow CH_2=C^{\bullet}Y$	125.2	4.608	462	1.00
$H^{\bullet} + O=CR^1R^2 \longrightarrow HOC^{\bullet}R^1R^2$	102.9	4.402	459	0.96
$C^{\bullet}H_3 + CH_2=CHY \longrightarrow C_2H_5C^{\bullet}HY$	82.6	3.713	378	0.98
$Me_2C^{\bullet}H + CH_2=CHY \longrightarrow Me_2CHCH_2C^{\bullet}HY$	78.3	3.617	372	0.97
$Me_3C^{\bullet} + CH_2=CHY \longrightarrow Me_3CCH_2C^{\bullet}HY$	68.3	3.377	360	0.94
$C_6H_5^{\bullet} + CH_2=CHY \longrightarrow C_6H_5CH_2C^{\bullet}HY$	105.3	4.194	436	0.96
$N^{\bullet}H_2 + CH_2=CHY \longrightarrow NH_2CH_2C^{\bullet}HY$	62.1	3.53	360	0.98
$RO^{\bullet} + CH_2=CHY \longrightarrow ROCH_2C^{\bullet}HY$	65.2	3.617	359	1.01
$R^{\bullet} + O=CR^1R^2 \longrightarrow ROC^{\bullet}R^1R^2$	68.1	3.540	365	0.97

formed actually does participate in the generation of the activation energy of addition. The stronger this bond, the higher the energy of the non-bonding orbital and the higher the activation energy. Empirical correlation (17) can be used to estimate roughly the activation energies of diverse addition reactions.

IX. The influence of neighbouring π bonds on the activation energy of radical addition

Radical abstraction reactions that involve molecules with π bonds in the vicinity of the reaction centre are characterised by higher E_{e0} values than the corresponding reactions involving similar hydrocarbons without these bonds. This is due to triplet repulsion.[41,42] In these reactions, the three electrons of the reaction centre interact with the neighbouring π electrons; as a consequence, the energy of the non-bonding orbital in the transition state increases and, hence, the activation energy also increases. Do neighbouring π bonds influence the E_{e0} values of radical addition? In order to answer this question, let us compare the br_e and E_{e0} parameters for the addition of H$^\bullet$, C$^\bullet$H$_3$, RO$^\bullet$, RO$_2^\bullet$, and R$_3$Si$^\bullet$ to the monomers CH$_2$=CHY and monomers with double bonds in the α-position relative to the double bond being attacked. If the monomer contains an aromatic ring or a double bond in the α-position, the activation energy of a thermally neutral reaction increases; if there are two aromatic rings in the α-position, E_{e0} increases to even a greater extent (Table 9). The difference between $E_{e0}(\pi)$ and E_{e0}(CH$_2$=CHY) can be used to estimate the contribution of this factor to the activation barrier[41]

$$\Delta E(\pi) = \Delta E_{e0}(\pi) - E_{e0}(CH_2{=}CHY). \quad (18)$$

Triplet repulsion also manifests itself in the reactions in question; for example, in the reaction

$$R^\bullet + CH_2{=}CHCH{=}CH_2 \longrightarrow RCH_2C^\bullet HCH{=}CH_2$$

Table 9. Influence of a π bond adjacent to the reaction centre on the activation energy of the radical addition to alkenes.[44–50]

Reaction	br_e [a]	E_{e0} [b]	ΔE_π [b]	$\Delta D_e(\pi)$ [c]
H$^\bullet$ + CH$_2$=CHY	24.59	101.6	0	0
H$^\bullet$ + CH$_2$=CHPh	25.85	112.2	10.6	24.1
H$^\bullet$ + CH$_2$=CPh$_2$	26.47	117.7	16.1	36.0
H$^\bullet$ + cyclo-Δ^{1,3}-C$_6$H$_8$	26.47	117.7	16.1	36.0
H$^\bullet$ + CH$_2$=CHCN	25.45	108.8	7.2	16.4
C$^\bullet$H$_3$ + CH$_2$=CHR	20.01	82.6	0	0
C$^\bullet$H$_3$ + CH$_2$=CHPh	20.82	89.4	6.8	15.5
C$^\bullet$H$_3$ + CH$_2$=CMePh	20.67	88.7	6.1	12.6
C$^\bullet$H$_3$ + CH$_2$=CPh$_2$	21.33	94.4	11.8	25.2
C$^\bullet$H$_3$ + CH$_2$=CHCH=CH$_2$	20.88	89.9	7.3	16.6
C$^\bullet$H$_3$ + MeCH=CHCH=CHMe	21.15	92.2	9.6	21.8
C$^\bullet$H$_3$ + CH$_2$=CMeCMe=CH$_2$	21.03	91.2	8.6	19.5
C$^\bullet$H$_3$ + cyclo-Δ^{1,3}-C$_6$H$_8$	22.27	102.3	19.7	43.2
C$^\bullet$H$_3$ + cyclo-Δ^{1,4}-C$_6$H$_8$	22.23	101.9	19.3	42.5
N$^\bullet$H$_2$ + CH$_2$=CHR	18.82	61.0	0	0
N$^\bullet$H$_2$ + (*E*)-CH$_2$=CHCH=CH$_2$	20.52	72.5	10.4	23.7
RO$^\bullet$ + CH$_2$=CHR	19.49	61.8	0	0
RO$^\bullet$ + CH$_2$=CHPh	21.09	76.4	14.6	30.6
RO$_2^\bullet$ + CH$_2$=CHR	26.04	90.5	0	0
RO$_2^\bullet$ + CH$_2$=CHPh	27.23	99.0	8.5	22.8
RO$_2^\bullet$ + CH$_2$=CPh$_2$	28.04	105.0	14.5	38.3
R$_3$Si$^\bullet$ + CH$_2$=CHR	26.46	76.6	0	0
R$_3$Si$^\bullet$ + CH$_2$=CHPh	28.52	89.0	12.4	27.9
R$_3$Si$^\bullet$ + O=CR^{1}R^2	37.62	114.5	0	0
R$_3$Si$^\bullet$ + O=CMePh	39.74	127.6	13.1	22.5
R$_3$Si$^\bullet$ + O=CPh$_2$	40.02	129.3	14.8	25.5

[a] Expressed in kJ$^{1/2}$ mol$^{-1/2}$; [b] expressed in kJ mol^{-1}; [c] $\Delta D_e(\pi)$ is the energy of triplet repulsion, kJ mol^{-1}.

a multicentre multielectron R···C···C···C···C bond arises in the transition state; this increases the strength of the bond, and, hence, enhances the triplet repulsion and its contribution to the activation energy. It can be seen from the data of Table 9 that this contribution can reach 20 kJ mol^{-1}. The increase in the dissociation energy D_e(X−C) caused by this electron delocalisation can be estimated using relation (18).

The same trend is observed for the addition of the benzyl radical to the monomers CH$_2$=CRY (see Table 10).[48] The average br_e and E_{e0} values for these reactions are 24.91 ± 0.49 kJ$^{1/2}$ mol$^{-1/2}$ and 128.0 kJ mol^{-1}, respectively; the values for the addition of methyl radical are 19.93 ± 0.4 kJ$^{1/2}$ mol$^{-1/2}$ and 82.6 kJ mol^{-1}. The greater E_{e0} value found in the case of the addition of benzyl radicals points to stronger triplet repulsion caused by electron delocalisation.

Table 10. Parameters br_e and E_{e0} for the addition of benzyl radicals to monomers CH$_2$=CRY.

R	Y	br_e/ kJ$^{1/2}$ mol$^{-1/2}$	E_{e0}/ kJ mol^{-1}
Me	OMe	24.98	128.7
H	OEt	24.85	127.4
H	Ph	24.88	127.7
Me	Ph	24.93	128.2

The substantial influence of the π bonds located near the reaction centre on the activation energy can also be followed for the addition of methyl radicals to the C=O group in *p*-benzoquinone. This can be clearly seen when comparing the corresponding parameters for the addition of a methyl radical to acetone and to *p*-benzoquinone.[49]

R^{1}COR^2	br_e/kJ$^{1/2}$ mol$^{-1/2}$	E_{e0}/kJ mol^{-1}	$10^{11} r_e$ /m
Me$_2$CO	21.95	68.1	3.54
OC$_6$H$_4$O	23.15	81.1	3.86

The observed difference in the parameters is due most likely to the electron delocalisation in the aromatic ring and, hence, to the increase in the triplet repulsion. The difference between the E_{e0} values for the reactions considered amounts to 13 kJ mol^{-1}. For the addition of polystyrene radical to *p*-benzoquinone, br_e = 25.03 kJ$^{1/2}$mol$^{-1/2}$ and E_{e0} = 94.8 kJ mol^{-1}. In this case, the E_{e0} value is 26.7 kJ mol^{-1} greater than that for the reaction of the methyl radical with acetone. The very large $\Delta E(\pi)$ value can be accounted for by the interaction of the π electrons of the two neigbouring benzene rings with the reaction centre.

The addition of peroxyl radicals to alkenes deserves special discussion. This class of reaction is characterised by the parameter br_e = 26.04 kJ$^{1/2}$mol$^{-1/2}$ (see Ref. 45). Estimation of this parameter from relation (17) gives br_e = 16.26 kJ$^{1/2}$mol$^{-1/2}$, which is much lower than the experimental value. One reason for this discrepancy, as in the case of reactions subject to the influence of π bonds, is as follows. In the RO···O···C···C transition state, the *p* electrons of the two oxygen atoms interact with the electrons of the atoms of the reaction centre; this increases the triplet repulsion and E_{e0}.

With allowance for the examples considered above, correlation (17) can be extended and written in the following form:

$$r_e = a[D_e + \Delta D_e(\pi)], \quad (19)$$

where $\Delta D_e(\pi)$ is the increase in the energy of the non-bonding orbital caused by delocalisation of the neighbouring π or *p* electrons. The $\Delta D_e(\pi)$ values are listed in Table 9.

X. The role of the radius of the atom carrying the free valence

The greater the radius of the atom carrying the free valence, the higher the E_{e0} for radical abstraction.[42] Does the radius of the atom which attacks the double bond influence the activation energy of addition reactions? This question was answered as a result of analysis of experimental data on the addition of triethylsilyl and phenylthiyl radicals to alkenes.[50]

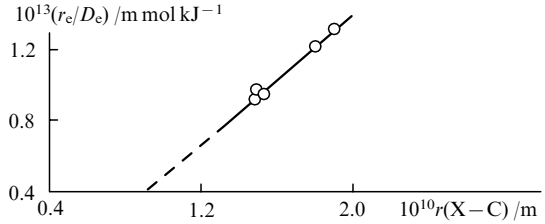


Figure 4. Correlation between the ratio of the parameters r_e/D_e (parabolic model) and the length r(X−C) of the incoming bond for the addition of the R$^{\bullet}$, N$^{\bullet}$H$_2$, RO$^{\bullet}$, RS$^{\bullet}$, and R$_3$Si$^{\bullet}$ radicals to alkenes (see also Table 11).[50]

Since the strength of the C−X (D_e) bond being formed influences the parameter r_e [see Eqn (17)], the characteristic to be compared for the addition of various radicals to alkenes is the r_e/D_e ratio (Table 11, Fig. 4). The lengths r(C−X) of the bonds formed upon the addition of radicals such as C$^{\bullet}$H$_3$, N$^{\bullet}$H$_2$ and RO$^{\bullet}$ to the C=C bond and upon the addition of C$^{\bullet}$H$_3$ to the C=O bond are close; therefore, the ratio r_e/D_e = const. However, in the case of addition of PhS$^{\bullet}$ and R$_3$Si$^{\bullet}$ to the C=C bond, the r_e/D_e ratio is much greater and a linear correlation is observed between r_e/D_e and r(C−X). The correlation has the following form [50]

$$r_e = \frac{(1+\alpha)}{b} E_{e0}^{1/2} = 8.81 \times 10^4 [r(\mathrm{C-X}) - 0.42 \times 10^{-10}] D_e. \quad (20)$$

Thus, the radius of the atom carrying the free valence has a substantial influence on the activation barrier to the addition reaction — the greater the radius of this atom, the higher the activation energy. Apparently, this effect is due to repulsion in the transition state, the repulsion being due to the interaction between the electron shells of the double bond being attacked and the atom which attacks this bond.

Table 11. Strengths (D_e/ kJ mol^{-1}) and lengths [r(C−X) or r(−X)/ m] of the bonds formed upon the addition of X$^{\bullet}$ radicals to C=C or C=O double bonds.[50]

X$^{\bullet}$	D_e	$10^{10}r$(C−X) or $10^{10}r$(O−X)	$10^{11}r_e$ /m	$10^{13}(r_e/D_e)$ / m mol kJ^{-1}
	X$^{\bullet}$ + CH$_2$=CHY ⟶ XCH$_2$C$^{\bullet}$HY			
C$^{\bullet}$H$_3$	378	1.52	3.71	0.98
N$^{\bullet}$H$_2$	360	1.47	3.53	0.98
RO$^{\bullet}$	359	1.43	3.62	1.01
RS$^{\bullet}$	284	1.79	3.41	1.20
R$_3$Si$^{\bullet}$	378	1.89	4.91	1.30
	X$^{\bullet}$ + O=CR^{1}R^2 ⟶ XOC$^{\bullet}$R^{1}R^2			
C$^{\bullet}$H$_3$	365	1.43	3.54	0.97
R$_3$Si$^{\bullet}$	487	1.64	6.28	1.29

XI. Interaction of two polar groups

The polar effect involved in radical addition has been repeatedly discussed in the scientific literature.[3, 6, 19–25] The parabolic model opens up new prospects for the correct estimation of the polar effect. It permits one to determine the contribution of this effect to the activation energy. This contribution (ΔE_μ) is estimated by choosing a reference reaction which involves the same reaction centre but in which one or both reactants are non-polar. The reference reaction is characterised by the parameter br_e and the reaction with two polar reactants is characterised by the parameter $(br_e)_\mu$. The component of the activation energy caused by polar interaction (ΔE_μ) is calculated from the equation [42]

$$\Delta E_\mu = [(br_e)_\mu^2 - (br_e)^2](1+\alpha)^{-2}. \quad (21)$$

Table 12 presents the results of calculation of ΔE_μ for the reactions of six polar radicals with a number of polar monomers.[45, 46, 81–83] It can be seen that the polar interaction in the transition states for the addition can either decrease ($\Delta E_\mu < 0$) or, in other cases, increase ($\Delta E_\mu > 0$) the activation energy. The ΔE_μ values vary from +19.5 to −23 kJ mol^{-1}, *i.e.* they can be rather large.

XII. Multidipole interaction in addition reactions

The multidipole interaction in a bimolecular reaction arises if one or both reactants contain several polar groups.[84] The multidipole effect shows itself as a deviation of the rate constant for the addition of a polar radical to a polyfunctional compound (calculated in relation to one reaction centre) from the rate constant for the addition to a monofunctional compound. The multidipole effect was discovered for radical abstraction of a hydrogen atom from polyfunctional esters induced by peroxyl radicals.[84] Later, this effect has also been found in the addition of peroxyl radicals to the double bonds of polyatomic unsaturated esters.[85] Table 13 summarises the results of calculations of the contribution of the multidipole effect to the activation energy performed using relation (21). A monofunctional ester of the corresponding structure served as the reference compound. It can be seen that the role of the multidipole interaction in these reactions is fairly low: the contribution of the interaction of several polar groups $\Delta\Delta E_\mu$ varies from 0.8 to 2.3 kJ mol^{-1}.

Table 12. Contribution of the polar effect (ΔE_μ/ kJ mol^{-1}) to the activation energy of the addition of polar radicals to polar monomers CH$_2$=CRY (calculated from the data of several studies [45, 46, 48, 81–83]).

CH$_2$=CRY	Me$_2$(HO)C$^{\bullet}$	Me$_2$(CN)C$^{\bullet}$	Me$_3$COC(O)C$^{\bullet}$H$_2$	*sec*-RO$_2^{\bullet}$	*tert*-RO$_2^{\bullet}$	HO$_2^{\bullet}$
CH$_2$=CHOEt	−1.9	−4.9	13.2	–	–	–
CH$_2$=CMeOMe	−6.5	−9.4	10.1	–	–	–
CH$_2$=CHOAc	−15.1	−11.2	17.5	9.5	7.3	11.5
CH$_2$=CMeOAc	−16.4	−4.3	19.5	–	–	–
CH$_2$=CClMe	−8.2	−4.4	10.8	–	–	–
CH$_2$=CCl$_2$	−10.2	−3.8	13.4	–	–	–
CH$_2$=CHCOOMe	−20.1	−1.4	13.1	−0.3	−2.0	–
CH$_2$=CMeCOOMe	–	−3.4	–	−5.2	−6.4	−4.7
CH$_2$=CHCN	−23.2	−0.9	13.8	−9.0	−10.8	−7.9

Table 13. Multidipole effect in the addition of cumeneperoxyl radicals to unsaturated polyatomic esters (n is the number of reacting double bonds in the ester molecule).[85]

Ester	k (323 K) [a]	k/n [a]	$\Delta\Delta E_\mu$ [b]
$CH_2=CHCO_2Me$	0.50	0.50	0
$(CH_2=CHCO_2CH_2)_2CMe_2$	0.76	0.38	0.8
$(CH_2=CHCO_2CH_2)_2CHOCOCH=CH_2$	1.05	0.35	1.0
$(CH_2=CHCO_2CH_2)_4C$	1.28	0.32	1.2
$CH_2=CMeCO_2Me$	1.79	1.79	0
$(CH_2=CMeCO_2CH_2)_2CHOCOMeC=CH_2$	3.93	1.31	0.9
$(CH_2=CMeCO_2CH_2)_4C$	3.08	0.77	2.3

[a] Expressed in litre $mol^{-1}\,s^{-1}$. [b] Expressed in kJ mol^{-1}.

The multidipole effect is also manifested in the addition of chlorine atoms to chloroalkenes. The scope of influence of this factor on the activation energy of these reactions can be judged from the data given in Table 14.

Table 14. Parameters br_e, ΔE_μ and $\Delta\Delta E_\mu$ for the addition of chloride to chloroalkenes.[44]

Alkene	br_e/ $kJ^{1/2}\,mol^{-1/2}$	ΔE_μ/ kJ mol^{-1}	$-\Delta\Delta E_\mu$/ kJ mol^{-1}
$CH_2=CHCl$	21.23	17.0	0.0
cis-$CHCl=CHCl$	20.43	11.4	5.6
$CH_2=CCl_2$	19.64	6.6	10.4
$CHCl=CCl_2$	20.50	11.8	5.2
$CCl_2=CCl_2$	19.46	5.6	11.4

The interaction of a polar reaction centre with one polar C−Cl group increases the activation energy by 17 kJ mol^{-1}, whereas the interaction with several polar C−Cl groups, conversely, results in a lower activation energy.

XIII. Steric hindrance

The addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is subject to a steric effect. This shows itself in the E_{e0} value for the $Et_3Si^\bullet$ addition to RCH=CHR being greater than that for the addition of the same radical to $CH_2=CHR$.[50] The contribution of steric repulsion to the activation energy can be characterised by the increment ΔE_s.

Alkene	br_e/ $kJ^{1/2}\,mol^{-1/2}$	E_{e0}/ kJ mol^{-1}	ΔE_s/ kJ mol^{-1}
$CH_2=CHR$	26.46	76.6	0.0
RCH=CHR	27.54	83.0	6.4 ± 0.7

No effect of this type is manifested for the addition of alkyl radicals to the same alkenes.[46] Evidently, the steric effect involved in the addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is due to the repulsion between the carbon and silicon atoms, caused by the large size of the silicon atom, in the reaction centre of the transition state.

The addition of tris(*tert*-butyl)phenoxyl radical to styrene can serve as an example of reaction subject to the steric effect. This reaction is characterised by $br_e = 23.89$ $kJ^{1/2}\,mol^{-1/2}$ (see Ref. 49), whereas the addition of the *tert*-butoxyl radical to styrene (a reaction with a similar structure of the reaction centre) has the parameter $br_e = 21.09$ $kJ^{1/2}\,mol^{-1/2}$ (see Ref. 49). The difference between these values is matched by the difference between the activation energies of the corresponding thermally neutral reactions, $\Delta E_{e0} = 21.6$ kJ mol^{-1}; this can be regarded as a rough estimate of the energy of additional repulsion in the transition state of the reacting system. This repulsion in the transition state is brought about by two *tert*-butyl groups of the phenoxyl radical.

XIV. Competition between the addition of free radicals to the carbon and oxygen atoms of the carbonyl group

The reaction enthalpy and the triplet repulsion are two factors influencing appreciably the activation energy of addition. The triplet repulsion in the addition of atoms and radicals to the C=C bonds attached to the CH_2 and CHY groups does not differ much because the D_e values for these processes are close (see Section VIII). The difference between the reactivities of the CH_2 and CHY groups is determined by the energy of stabilisation of the radicals formed and thus by the reaction enthalpy.

A different situation is observed for the addition of radicals to C=O bonds. In this case, triplet repulsion which accompanies the addition of the $X^\bullet$ radical to carbon differs substantially from that involved in the addition to oxygen because of the different strengths of the resulting bonds, C−X and X−O. For example, the dissociation energies in ethanol are $D_e(C-H) =$ 417 kJ mol^{-1} and $D_e(O-H) = 458$ kJ mol^{-1}. Therefore, the ratio of the activation energies E_{e0} of the corresponding thermally neutral addition reactions, which is proportional to the $D_e^2(C-H)/D_e^2(O-H)$ ratio, is equal to 0.83 [see Eqns (11)–(17)]. Thus, two factors compete in the addition of atoms and radicals to a carbonyl group, namely, the enthalpy of the reaction and the triplet repulsion, which both influence the activation energy. The problem of competition between the addition of atoms and radicals to either carbon or oxygen atom of the carbonyl group has been considered in the literature.[51] The thermodynamic and kinetic parameters of such addition are presented in Table 15. Analysis of the ΔH, E, and E_0 values leads to the following conclusions.

Table 15. Thermodynamic (ΔH, D_e in kJ mol^{-1}) and kinetic (α and E, E_{e0} in kJ mol^{-1}) parameters for the addition of radicals to the carbon and oxygen atoms of the carbonyl group.[51]

Reaction	α	ΔH	D_e	E	E_{e0}
$H^\bullet + Me_2CO \longrightarrow Me_2CHO^\bullet$	1.601	−53.3	406.5	39.8	82.5
$H^\bullet + Me_2CO \longrightarrow Me_2C^\bullet OH$	1.274	−102.2	459.7	41.8	138.0
$Me^\bullet + Me_2CO \longrightarrow Me_3CO^\bullet$	1.336	−34.0	366.4	56.5	83.1
$Me^\bullet + Me_2CO \longrightarrow Me_2C^\bullet OMe$	1.570	−21.3	353.1	44.2	63.7
$Me^\bullet + PhCOMe \longrightarrow PhMe_2CO^\bullet$	1.336	−14.2	333.8	64.3	69.0
$Me^\bullet + PhCOMe \longrightarrow PhMeC^\bullet OMe$	1.570	−44.2	348.6	41.2	62.1
$HO^\bullet + Me_2CO \longrightarrow Me_2C(OH)O^\bullet$	1.645	−81.2	424.0	35.7	88.8
$HO^\bullet + Me_2CO \longrightarrow Me_2C^\bullet O_2H$	1.850	165.0	171.1	171.4	12.2
$MeO^\bullet + Me_2CO \longrightarrow Me_2(MeO)CO^\bullet$	1.570	−37.2	379.6	46.6	75.2
$MeO^\bullet + Me_2CO \longrightarrow Me_2C^\bullet O_2Me$	1.850	157.6	164.1	164.0	11.2
$Me^\bullet + Me_2CO \longrightarrow Me_2(MeOO)CO^\bullet$	1.931	48.8	290.0	60.0	33.7

1. Hydrogen atoms add both to oxygen and to carbon, the corresponding rate constants being close (the difference between the activation energies is only 2 kJ mol^{-1}). This is due to the fact that the influence of the reaction enthalpy (see the ΔH values) is counterbalanced by the effect of triplet repulsion, which is higher for the hydrogen addition to oxygen: $\Delta H(O) - \Delta H(C) = -48.9$ kJ mol^{-1} but $E_{e0}(C) < E_{e0}(O)$ and $\Delta E_{e0} = 55.5$ kJ mol^{-1}. In this reaction, the thermodynamic (ΔE_H) and kinetic (E_{e0}) factors act in the opposite directions and cancel out each other.

2. When a methyl radical adds to the carbonyl group of acetone, the heat of the addition to carbon is greater than the heat of the addition to oxygen: $[\Delta H(C) - \Delta H(O)] = -12.7$ kJ mol^{-1}. However, due to the higher triplet repulsion [$E_{e0}(C) > E_{e0}(O)$], the activation energy for the addition of the methyl radical to carbon is higher than that for its addition to oxygen [the difference between the activation energies $E(C) - E(O) = +12.3$ kJ mol^{-1}]. In this case, triplet repulsion has the predominant influence on the energy. As a consequence, the more exothermic reaction has a higher activation energy.

3. In the addition of a methyl radical to the carbonyl group of acetophenone, both factors (thermodynamic and kinetic) act in the same direction (compare the ΔH and E_{e0}); therefore, the predominant pathway is the addition of the methyl radical to the oxygen atom, giving rise to a more stable benzyl radical: $\Delta E = E(C) - E(O) = 23$ kJ mol^{-1}.

4. Hydroxyl and alkoxyl radicals add only to the carbon atom because this addition is exothermic, whereas the addition to oxygen is endothermic.

5. The addition of a peroxyl radical to the carbonyl group is an endothermic reaction; the very high activation energy (60.0 kJ mol^{-1}) makes this process virtually impossible because the addition product would rapidly decompose to the starting compounds (see Section II).

XV. Comparison of radical addition and radical abstraction reactions

In a previous study,[41] diverse reactions of radical abstraction have been analysed in terms of the parabolic model and ten structural and thermodynamic factors determining the activation energy of these reactions have been established. In this study, we distinguish factors which influence the activation energy of radical addition. Since both addition and abstraction reactions are analysed in terms of the same (parabolic) model, it is possible to compare these two absolutely different types of reactions regarding the character and the degree of influence of each factor on the activation energy.

Table 16 lists the factors that influence the activation barriers to both radical abstraction and addition. It can be seen that the factors having a positive influence on the activation energy of abstraction and addition include the reaction enthalpy, the force constants of the reacting bonds, the strength of the bond being formed, the radius of the attacking atom, and π bonds or bulky substituents present in the vicinity of the reaction centre. Polar groups (one or several) in the reactant molecules either increase or decrease the activation energy.

Table 16. Factors influencing the activation energy of radical abstraction and addition.

Factor influencing the activation energy	Radical abstraction	Radical addition
Enthalpy	+	+
Force constants of the reacting bonds	+	+
Strength of the incoming bond	+	+
The presence of π-bonded groups	+	+
Different electronegativities of atoms in the reaction centre	−	no effect
Radius of the atom carrying a free valence	+	+
The presence of polar groups	±	±
Steric effect	+	+

Note. 'Plus' stands for an increase and 'minus' means a decrease in E due to the influence of this factor.

The difference between the abstraction and addition reactions is as follows. First, they differ in the geometry of the reaction centre. In the case of abstraction, the reaction centre is linear — all three atoms are aligned and this geometry ensures the minimum activation barrier. In the case of addition, since the molecular orbital of the π-C−C bond is arranged at an angle of 90° in relation to the line connecting the atoms, the reaction centre is a triangle (the three atoms X−C−C of the reaction centre are located at the vertices of a triangle with an X−C−C angle of 109°, see Fig. 1). Naturally, this distinction exerts an effect on the activation energy of addition. Second, the activation energy of abstraction is affected by the difference between the electronegativities of the atoms of the reaction centre, namely, the greater this difference, the lower the activation energy. No influence of this type has been noted in addition reactions.

It is pertinent to compare the activation parameters for various classes of addition reactions with the corresponding parameters of radical abstraction.[42] The results of this comparison for five parameters and six subclasses of abstraction and addition are summarised in Table. 17. The abstraction of a hydrogen atom in a thermally neutral reaction always proceeds more easily than the addition of a hydrogen atom to a double bond (see the E_{e0} values). This is due to the different geometries of the reaction centre in these reactions and to higher repulsion in the non-linear reaction centre. An important role is played by the

Table 17. Kinetic parameters of radical abstraction and addition.[42, 44, 46, 52, 53]

Reaction	E_{e0}/ kJ mol^{-1}	$10^{11} r_e$ /m	dE/dH	$(r^{\neq}/r_e)_0$	$\Delta H_{e\,min}$/ kJ mol^{-1}
$H^{\bullet} + RH \longrightarrow H_2 + R^{\bullet}$	54.6	3.762	0.48	0.48	94.5
$H^{\bullet} + CH_2{=}CHX \longrightarrow CH_3C^{\bullet}HX$	101.6	4.563	0.59	0.41	227.6
$R^{\bullet} + R^1H \longrightarrow RH + R^{1\bullet}$	74.0	4.595	0.50	0.50	153.1
$C^{\bullet}H_3 + CH_2{=}CHX \longrightarrow CH_3CH_2C^{\bullet}HX$	82.6	3.713	0.54	0.45	194.4
$RO^{\bullet} + RH \longrightarrow ROH + R^{\bullet}$	55.4	3.572	0.44	0.56	99.7
$RO^{\bullet} + CH_2{=}CHX \longrightarrow ROCH_2C^{\bullet}HX$	65.2	3.617	0.58	0.41	119.0
$RO_2^{\bullet} + R^1H \longrightarrow ROOH + R^{1\bullet}$	61.5	3.938	0.45	0.55	120.5
$RO_2^{\bullet} + CH_2{=}CHX \longrightarrow RO_2CH_2C^{\bullet}HX$	90.5	5.034	0.63	0.36	150.4
$R^{\bullet} + HOR^1 \longrightarrow RH + R^1O^{\bullet}$	55.4	3.572	0.56	0.44	99.7
$R^{\bullet} + O{=}CR^1R^2 \longrightarrow ROC^{\bullet}R^1R^2$	68.1	3.540	0.61	0.39	112.2
$H^{\bullet} + HOR \longrightarrow H_2 + RO^{\bullet}$	38.3	2.812	0.53	0.47	33.5
$H^{\bullet} + O{=}CR^1R^2 \longrightarrow HOC^{\bullet}R^1R^2$	102.9	4.401	0.61	0.38	149.7

force constant of the bond being attacked (the force constant of a multiple bond is always greater than that of a single bond).

It is expedient to describe the variation of the activation energy of a radical reaction as a function of the reaction enthalpy by the derivative dE/dH at $\Delta H_e = 0$. This value is determined by the parameter α: $(dE/dH) = \alpha(1 + \alpha)^{-1}$. For abstraction reactions, it can be greater than, smaller than, or equal to 0.5. For addition reactions, this ratio is always greater than 0.5 because the force constant of a multiple bond is always greater than that for a single bond. Thus, the activation energy of addition depends on ΔH to a greater extent than the activation energy of abstraction.

The ratio $(r^{\neq}/r_e)_0 = (1 + \alpha)^{-1}$ characterises the position of the transition state on the segment r_e for $\Delta He = 0$. Any of the possible cases can be found among abstraction reactions — the $(r^{\neq}/r_e)_0$ ratio can be equal to, greater than, or smaller than 0.5. In the case of addition, $(r^{\neq}/r_e)_0 < 0.5$, *i.e.,* an early transition state is always formed. As in the previous case, this is due to the fact that the force constant of a multiple bond is always higher than that of the σ bond arising and α is always > 1.

XVI. Conclusion

The use of the parabolic model as a tool for the analysis of addition reactions proved to be exceptionally fruitful. This method provides the possibility of elucidating a number of characteristics and factors influencing the activation energy of addition, based on experimental data. The following factors were found to be the most important.

1. Reaction enthalpy ΔH_e. The dependence of the activation energy E_e on ΔH_e obeys a parabolic law, $\Delta E_e^{1/2} \sim \Delta H_e$. When the ΔH_e value is rather low ($\Delta H_e \leqslant \Delta H_{e\,min}$), the activation energy does not depend on ΔH_e and is close to zero ($E = 0.5\,RT$). The parameters br_e calculated from experimental data make it possible to determine E_e for any reaction of the given subclass.

2. Force constants of the reacting bonds (the b_i and b_f coefficients). The activation energy of a thermally neutral reaction E_{e0} is proportional to $[b_i b_f (b_i + b_f)^{-1}]^2$. Depending on which bonds are reorganised during the reaction, the activation energy can change by a factor of 2 due to the difference in the force constants of the reacting bonds alone (the b_i and b_f coefficients).

3. A significant role is played by the arrangement of atoms of the reaction centre. In the case of addition, it is non-linear (triangular); naturally, this affects the activation energy.

4. A substantial contribution to the activation energy is made by the energy of the non-bonding orbital of the resulting bond due to the triplet repulsion in the transition state. The stronger the bond being formed (D_e), the higher the activation energy E_{e0}. For reactions of the same class (b = const and α = const), $E_{e0} \sim D_e^2$; for reactions of different classes, the empirical dependence (17) holds.

5. Yet another factor is also related to the triplet repulsion, namely, the dependence of E_{e0} on the π bonds present in the vicinity of the reaction centre. This proximity increases the activation energy by 6–15 kJ mol^{-1}. A π bond near the reaction centre increases the electron density on the reaction centre, which increases the energy of the non-bonding orbital and, correspondingly, its contribution to the formation of the activation barrier.

6. The radius of the atom carrying the free valence and attacking the double bond is also significant and influences the activation barrier. The dependence of E_{e0} on the length of the bond being formed r(C–X) is also non-linear [see Eqn (20)].

The activation energies of some subclasses of addition reactions also depend on several other factors, namely, the interaction of polar groups of two polar reactants (among the reactions studied, the contribution of the interaction of polar groups contained in the radical and in the molecule to the activation energy ranges from -25 to $+15$ kJ mol^{-1}); the multidipole interaction of several polar groups, and the steric factor.

Thus, in the case of both radical abstraction and radical addition, we come across a large variety of factors that influence the reactivity of the reactants. The parabolic model makes it possible to identify these factors and to characterise the contribution of each of them to the activation energy in terms of an appropriate increment.

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