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New empirical models of radical abstraction reactions

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Abstract. Two physical models of radical abstraction reactions are described: the model of intersecting parabolas and the model of intersecting Morse curves. A systematic account is given of the results of the analysis of a large set of experimental data (rate constants and activation energies) for a wide variety of radical reactions. It is shown that the activation energies for such reactions depend on their enthalpies, on the force constants of the reacting bonds, the strength, length, and polarity of the X – Y bond in the $X^{\bullet}$ + HY reaction, and also the presence in the **reactants of one or several polar groups,** π-bonds, and bulky **groups adjoining the reaction centre. Solvation plays an important role in processes involving polar reactants. Both methods are compared as instruments for the calculation of the activation energy and bond strengths. The limits of applicability of the methods are examined. The bibliography includes 93 references**.

I. Introduction

Bimolecular radical abstraction reactions are a component of the most varied chemical processes such as combustion, halogenation, the cracking and oxidation of hydrocarbons, polymerisation and degradation of polymers, photolysis and radiolysis of organic compounds, *etc*. They began to be investigated vigorously as early as the 1920s.

The comparison, analysis, and generalisation of data on the reactivities of molecules and radicals in various radical reactions occupy an important place in studies on bimolecular radical abstraction reactions. The first important step in this direction was taken almost 60 years ago when Evans and Polanyi [1] established empirically the linear relation between the changes in the activation energy ΔE and the heat of reaction Δq in a series of reactions of atomic sodium with alkyl halides. Later Semenov [2] demonstrated in relation to extensive experimental data that the linear relation

$$E = A' + \alpha' q \qquad (1)$$

holds also in other radical abstraction reactions. The Hammett [3] and Taft [4] linear correlation equations came to be widely employed in physical organic chemistry in the 1960 – 1970s and are also applicable to the kinetics of radical reactions.[5,6] It has been noted in Semenov's monograph [2] that these correlations may be reduced to the linear equation (1). Linear correlations of this kind assist to some extent in a systematic treatment of experimental data on activation energies and rate constants, but the possibility of using them for a deep analysis of the problem of reactivity is restricted to the range of isotypical reactions. Furthermore, the treatment of the physical sense of correlation coefficients is sometimes fairly arbitrary. Quantum-chemical methods, which constitute a theoretical alternative to experimental kinetic methods, also make it possible to calculate the rate constant for a particular individual reaction.[7–10] However, the problem of comparison and generalisation of kinetic data referring to different classes of chemical reactions as well as the problem of correlation between the reactivities of reactants and their structures and physical characteristics remain unsolved in this case too.

Several years ago, the author of the present review used a simplified model of an elementary bimolecular reaction — the intersecting parabolas model (the IP model) — in the analysis of the activation energies for a wide variety of radical abstraction reactions.[11–13] This model can be regarded as a further development of the empirical approach initiated in the studies of Polanyi [1] and Semenov.[2] As a result, it became possible to separate diverse radical abstraction reactions into classes and to differentiate in each class groups of isotypical reactions. Each reaction is

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described by two parameters referring to the entire given class of reactions: one parameter, characteristic of the group of reactions, and one individual parameter, namely the enthalpy of reaction, characteristic of the given reaction. The creation of a hierarchical system of reactions made it possible to identify at an empirical level the physical characteristics of the reactants determining the height of the activation barrier. Another model of such reactions, namely the model of two intersecting Morse potential curves (the MPC model) has been devised recently.[14] The present review is devoted to the description and comparison of the results obtained by these two methods in the analysis of a large set of experimental data referring to radical abstraction reactions in the gas [15–19] and liquid [5,20–26] phases.

II. The intersecting parabolas model

In the IP model,[11–13] the radical abstraction reaction

$$RH + X^{\bullet} \longrightarrow R^{\bullet} + XH,$$

in which a hydrogen atom is transferred from the initial (RH) to the final (XH) molecule, is regarded as the result of the intersection of two potential curves, one of which describes the potential energy $U_i(r)$ of the vibration of the H atom along the bond being dissociated in the initial molecule and the other describes the potential energy $U_f(r)$ of the vibration of the same atom along the bond being formed in the reaction product (U is the potential energy and r the amplitude of the atomic vibrations along the valence bond). The stretching vibrations of the H atom in RH and XH are regarded as harmonic and are described by the parabolic law

$$U(r)^{1/2} = br.$$

The following parameters are used to characterise the elementary step in the IP model (Fig. 1).

1. The enthalpy of reaction ΔH_e which includes the difference between the zero-point energies of the broken and generated bonds:

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f), \quad (2)$$

were D_i and D_f are the dissociation energies of the broken (i) and generated (f) bonds, ν_i and ν_f are the stretching vibration frequencies of these bonds, h is the Planck constant, and L is the Avogadro number.

2. The activation energy E_e, which is linked to the experimentally determined Arrhenius energy E by the relation

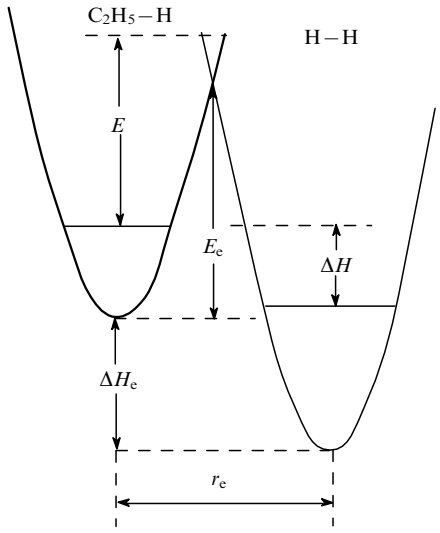


Figure 1. The energy profile of the $H^{\bullet} + C_2H_6$ reaction in the IP model.[12]

$$E_e = E + 0.5(hL\nu_i - RT). \quad (3)$$

3. The coefficients b_i and b_f, which describe the dependence of the potential energy on the atomic vibration amplitude along the initial (i) and final (f) valence bonds. There is a parabolic relation between the potential energy and the vibration amplitude:

$$U_i = b_i^2 r^2 \quad \text{and} \quad U_f = b_f^2 (r_e - r)^2$$

(Fig. 1). The quantity $2b^2$ is the force constant of the corresponding bond with $b = \pi\nu(2\mu)^{1/2}$, where μ is the reduced mass of the atoms forming the bond.

4. The distance r_e, which characterises the displacement of the abstracted atom in the elementary step.

In the IP model, these parameters are linked by the relation

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}, \quad (4)$$

where $b = b_i$, *i.e.* refers to the attacked bonds in the molecule, while the coefficient $\alpha = b_i/b_f$ represents the ratio of the force constants of the ruptured and generated bonds raised to the power 1/2.

In the case of structurally isotypical reactions (br_e = const), a thermally neutral reaction ($\Delta H_e = 0$) proceeds with an activation energy E_{e0}, which is determined by two parameters, namely α and br_e (or r_e, b_i, and b_f):

$$E_{e0} = \left(\frac{br_e}{1+\alpha}\right)^2 = \left(\frac{b_i b_f r_e}{b_i + b_f}\right)^2. \quad (5)$$

On substituting the parameter br_e in Eqn (4) by its value from Eqn (5), we obtain

$$(1+\alpha)E_{e0}^{1/2} = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (6)$$

Comparison of Eqns (5) and (6) makes it possible to understand the kinetic significance of the parameter br_e: it is directly proportional to the activation energy for a thermally neutral reaction raised to the power 1/2. The transition state in the IP model is characterised by the distance $r^{\neq}$, which is linked to the other parameters by the relation

$$\frac{r^{\neq}}{r_e} = \frac{E_e^{1/2}}{br_e} = \left[1 + \alpha\left(1 - \frac{\Delta H_e}{E_e}\right)^{1/2}\right]^{-1}. \quad (7)$$

In the case of a thermally neutral reaction with $\alpha = 1$, *i.e.* when the force constants of the attacked and generated bonds are equal, $r^{\neq}$ is equal to half the segment r_e. In the general case,

$$\left(\frac{r^{\neq}}{r_e}\right)_0 = \frac{1}{1+\alpha}.$$

The parabolic model is in essence empirical, since the parameter α is calculated from spectroscopic (ν_i and ν_f) and atomic (μ_i and μ_f) data, while the parameter br_e (or E_{e0}) is found from the experimental activation energies E [Eqns (3) and (4)] or *via* the rate constant k by means of the Arrhenius equation

$$E = RT\ln\frac{A}{k},$$

where A is the pre-exponential factor typical for such reactions. The enthalpy of such reaction is calculated by Eqn (2) from the experimental bond dissociation energies. The calculations[27] showed that br_e = const for structurally similar reactions. Thus $br_e = 14.74 \pm 0.21$ kJ$^{0.5}$ mol$^{-0.5}$ for 27 reactions of peroxyl radicals with the C–H bonds of aromatic alkyl-substituted hydrocarbons, which corresponds to $E_{e0} = 66.32 \pm 0.94$ kJ mol^{-1}.[28]

III. The intersecting Morse curves model

The model of the radical abstraction reaction based on the intersection of two Morse curves has been proposed[14] to test the reliability of the results obtained with the aid of the IP model. As

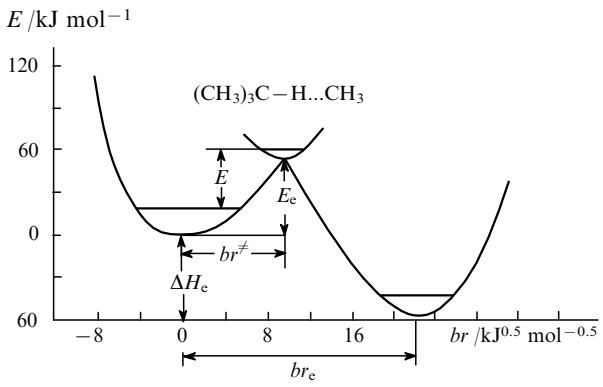


Figure 2. The energy profile of the $CH_3^{\bullet}$ + $(CH_3)_3CH$ reaction in the MPC model.[14]

in the intersecting parabolas model, the abstraction reaction reduces in this instance to the transition of a H atom from the initial to the final state (from RH to XH), the point of intersection of two unperturbed potential curves for R–H and X–H bonds corresponding to this process (Fig. 2). However, in contrast to the IP model, in this model the atomic vibrations along valence bonds are regarded as anharmonic and are described by the corresponding Morse formula [29]

$$U(r) = D_e[1 - \exp(-ar)]^2, \tag{8}$$

where $U(r)$ is the potential energy of the reacting bond as a function of the amplitude r of the atomic stretching vibrations along this bond, D_e is the bond dissociation energy including its zero-point vibration energy $0.5hLv$, and a is a coefficient calculated by the formula $a = bD_e^{-1/2}$, in which $b = \pi\nu(2\mu)^{1/2}$. The elementary step in the abstraction of an atom is described by the parameters D_{ei} and D_{ef} as well as the quantities E_e, b_i, b_f ($\alpha = b_i/b_f$), and r_e, as in the parabolic model [see Eqns (2) and (3)]. The parameter br_e ($b = b_i$) is linked to the other parameters by the relation

$$br_e = -D_{ei}^{1/2}\ln\left[1 - \left(\frac{E_e}{D_{ei}}\right)^{1/2}\right] - \tag{9}$$

$$-\alpha D_{ef}^{1/2}\ln\left[1 - \left(\frac{E_e}{D_{ef}} - \frac{\Delta H_e}{D_{ef}}\right)^{1/2}\right].$$

The activation energy for a thermally neutral reaction is described by the equation

$$E_{e0} = D_{ei}\left\{1 - \exp\left[-\frac{br_e}{D_{ei}^{1/2}(1+\alpha)}\right]\right\}^2. \tag{10}$$

Hence it is easy to obtain an expression which elucidates the physical significance of the parameter br_e:

$$br_e = -(1+\alpha)D_{ei}^{1/2}\ln\left[1 - \left(\frac{E_{e0}}{D_{ei}}\right)^{1/2}\right].$$

The position of the transition state, corresponding to the point of intersection of two curves (Fig. 2), is characterised by the relation

$$\frac{r_e}{r^{\neq}} = 1 + \alpha\left(\frac{D_{ei}}{D_{ef}}\right)^{1/2}\frac{\ln(1 - \Delta H_e/D_{ef})}{\ln(1 - E_e/D_{ei})}. \tag{11}$$

As in the parabolic model, the parameter br_e is calculated by Eqn (9) from experimental data (α, D_{ei}, D_{ef}, E). In the case of structurally isotypical reactions, br_e = const. Thus $br_e = 19.35 \pm 0.48$ kJ$^{0.5}$ mol$^{-0.5}$ for 10 RH + H$^{\bullet}$ reactions investigated in the gas phase.[14]

IV. Comparison of empirical and correlation equations

The IP model can be regarded as a special case of the MPC model if one is dealing with reactions having low activation energies whereupon $E_e/D_{ei} \ll 1$ and $E_e/D_{ef} \ll 1$. On expanding the logarithmic function in Eqn (9) in Maclaurin's series [$\ln(1-x) \approx x - 0.5x^2 + ...$] and retaining only one term, we pass in this case from Eqn (9) to Eqn (4).

In order to compare Eqn (4) for the parabolic model with the Polanyi–Semenov equation [Eqn (1)],[1,2] it is useful to transform Eqn (4) by expressing E_e explicitly as a function of ΔH_e, α, and br_e. For not unduly high values of ΔH_e, whereupon

$$\Delta H_e \ll \frac{(br_e)^2}{1-\alpha^2}, \tag{12}$$

we obtain the expression

$$E_e = \left(\frac{br_e}{1+\alpha} + \frac{\alpha\Delta H_e}{2br_e}\right)^2. \tag{13}$$

Since α' in the Polanyi–Semenov equation represents the ratio $\Delta E/\Delta\Delta H$, it follows that, after substituting Eqn (13) in Eqn (1), we obtain

$$\alpha' = \frac{\Delta E_e}{\Delta H_{e2} - \Delta H_{e1}} = \frac{\alpha}{(1+\alpha)} + \tag{14}$$

$$+ \frac{0.25\alpha^2}{(br_e)^2}(\Delta H_{e2} + \Delta H_{e1}),$$

where H_{e2} and H_{e1} are respectively the maximum and minimum enthalpies in the series of reactions considered. Analysis of the second term shows that the empirical coefficient α' depends not only on the force constants of the reacting bonds ($\alpha = b_i/b_f$) but also on the range of variation of the enthalpies in the given series of reactions. This is natural, since the dependence of E on ΔH is nonlinear. For a sufficiently wide range of variation of ΔH, whereupon condition (12) does not hold, the dependence of α' on the parameters α, br_e, and ΔH_e becomes more complex and is expressed by the following formula obtained from Eqn (4):

$$\alpha' = \frac{\alpha^2}{1-\alpha^2} + \frac{2\alpha}{(1-\alpha^2)^2}\mathrm{f}(br_e, \Delta H_e), \tag{15}$$

where

$$\mathrm{f}(br_e, \Delta H_e) = \frac{(br_e)^2}{\Delta H_{e2} - \Delta H_{e1}}\left\{\left[1 - \frac{\Delta H_{e1}(1-\alpha^2)}{(br_e)^2}\right]^{1/2} - \right.$$

$$\left. - \left[1 - \frac{\Delta H_{e2}(1-\alpha^2)}{(br_e)^2}\right]^{1/2}\right\}.$$

It is seen from Eqns (14) and (15) that the coefficient α' in Eqn (1) depends not only on the physical parameters (b_i, b_f, and r_e) but also on an incidental factor such as the range of variation of the enthalpies in the selected series of reactions. By virtue of this factor, the parameter α' in Eqn (1) can characterise only approximately the physical factors influencing the activation energy and this characterisation is less accurate the wider the range of variation of the enthalpies. This in fact explains, in particular, the experimentally observed parallel variation of α' and A' in the X$^{\bullet}$ + RH reactions [30] [see Eqns (14) and (15)]:

X$^{\bullet}$	HO$^{\bullet}$	H$^{\bullet}$	O$^{\bullet}$	$CH_3^{\bullet}$	$CCl_3^{\bullet}$
α'	0.25	0.38	0.52	0.52	0.94
A' /kJ mol^{-1}	31	46	64	62	67

The above considerations, concerning the Polanyi–Semenov method, refer also to the empirical procedure for the estimation of

activation energy proposed by Szabo.[31] According to the latter, the activation energy for a radical reaction can be determined from the following simple formula:

$$E = D_i - \alpha' D_f .$$

Since $\Delta H = D_i - D_f$ and the activation energy $E = E_0 = D_i(1-\alpha')$ when $\Delta H = 0$, it follows that $E = E_0 + \alpha'\Delta H$ and the coefficient α' is expressed by Eqn (14) within the framework of the parabolic model.

The correlations between the rate constants for a wide variety of reactions are widely used in the scientific literature:

$$\lg\frac{k}{k_1} = \rho\sigma , \qquad (16)$$

where σ is the Hammett,[3] Taft,[4] *etc*. function and ρ is an empirical coefficient. Together with Eqn (1), this equation is frequently applied to radical abstraction reactions.[6] Since the pre-exponential factor calculated per one reacting bond is constant for each series of radical reactions [28] and

$$\Delta E = -2.3RT\lg\frac{k}{k_1} ,$$

the following expression arises from Eqn (13):

$$\rho = \frac{\alpha T_0}{(1+\alpha)T}\frac{\Delta\Delta H_e}{\Delta\Delta G_0} + \frac{\alpha^2 T_0}{4(br_e)^2 T}\frac{\Delta\Delta H_e^2}{\Delta\Delta G_0} . \qquad (17)$$

Here the difference between the free energies $\Delta\Delta G_0$ concerns the reference reactions on which the comparison is based. It is linked to σ by the simple relation $\Delta\Delta G_0 = -2.3RT_0\sigma$. As can be seen from Eqn (17), the coefficient ρ depends not only on the parameters of the reactants (α, br_e) and temperature (T_0/T), but also on the range of variation of ΔG_0 and ΔH_e. This naturally hinders its use for the identification of the physical factors determining the reactivity of the reactants. The expression for ρ becomes still more cumbersome if the series includes reactions characterised by different coefficients br_e. However, despite this, a relation of type (17) frequently reduces to an equation of type (1) in the kinetics of radical reactions, which has been noted in Semenov's monograph.[2]

A fairly simple empirical equation, relating the activation energies for the forward (E) and reverse ($E + \Delta H$) bimolecular reactions, has been proposed:[32]

$$E(E + \Delta H) = \varepsilon^2 . \qquad (18)$$

By transforming Eqn (13), we obtain the following expression, within the framework of the parabolic model, for the activation energies for the forward (E_e) and reverse (E'_e) reactions (for the reverse reaction, $b' = b/\alpha$, $\alpha' = \alpha^{-1}$, and $\Delta H'_e = -\Delta H_e$):

$$(E_e E'_e)^{1/2} = \left(\frac{br_e}{1+\alpha}\right)^2 + \frac{\Delta H_e(\alpha-1)}{2(\alpha+1)} - \frac{\alpha\Delta H_e^2}{4(br_e)^2} . \qquad (19)$$

It is seen from the comparison of Eqns (18) and (19) that the product $E_e E'_e$ does indeed tend to a constant value with decrease in ΔH_e and $\varepsilon^{1/2} = br_e/(1+\alpha)$.

The parabolic model of radical reactions [12] is close to the Marcus model for the transfer of an electron and a proton,[33] but differs from it by two significant features. In the IP model, one considers the involvement in the elementary step of the individual R–H and X–H bonds, each of which is characterised by an intrinsic force constant (the coefficients b_i and b_f). Furthermore, account is taken of the zero-point vibration of the bond as its inherent characteristic.

The reduction of the reaction in the IP and MPC models to the migration of the attacked atom determined by the intersection of unperturbed potential curves is an evident simplification. In fact the orbitals are perturbed in the RH + H$^\bullet$ reactions and the electron densities of the orbitals of the R–H and X–H bonds overlap, which is a topic considered in quantum chemistry.[7–10] The question arises how the results of quantum-chemical calculations and the empirical parameter r_e, calculated with the aid of the IP and MPC models, are related. The most accurate quantum-chemical calculation of the energy profile of the abstraction reaction has been carried out for the H$^\bullet$ + H_2 reaction.[9] According to this calculation, the height of the potential barrier is 41 kJ mol^{-1}.[34] The following values of E_e and r_e correspond to this value of E in the IP and MPC models: E_e = 66.1 kJ mol^{-1} at T = 300 K [see Eqn (3)], $r_e = 3.67\times10^{-11}$ m (MPC model), and $r_e = 3.10\times10^{-11}$ m (IP model). The width of the potential barrier at the level of half its height is 9.6×10^{-11} m according to the quantum-chemical calculation.[34] Thus the distance r_e amounts to 32% of half the width of the potential barrier in the IP model and to 38% in the MPC model.

V. Classification of radical abstraction reactions

The two models of the radical abstraction reactions (IP and MPC) have an evident similarity: they take into account the relation between the activation energy and physical characteristics of the reacting bonds such as the dissociation energy and the force constant. The bond dissociation energy is an individual characteristic of the molecule entering into the reaction or formed. The force constants for the stretching vibration of bonds ($2\pi^2\nu^2\mu$) of each type (C–H, O–H, *etc*.) are virtually identical for the entire class of isotypical compounds. This important factor makes it possible to classify radical abstraction reactions in terms of the type of reacting bonds and the coefficients b characterising them. A pair of coefficients — b_i and b_f or $b = b_i$ and $\alpha = b_i/b_f$ — corresponds to each class of such reactions. In the calculation of the activation energy E_e from E and conversely, the zero-point vibration energy of the ruptured bond also becomes important [see Eqn (3)]. The quantities α, b, and $0.5hL\nu_i$ for the radical abstraction reactions of compounds in different classes are listed in Table 1.

Knowing these parameters, it is easy to find the analogous characteristics of the reverse reactions. For a reverse reaction, to which the index f corresponds, we have $\alpha_f = \alpha^{-1}$, $b_f = b/\alpha$, and $0.5hL\nu_f = 0.5hL\nu_i/\alpha$. For example, $\alpha_f = 0.796^{-1} = 1.256$, $b_f = (3.743\times10^{11})/\alpha = 4.702\times10^{11}$ kJ$^{-0.5}$ mol$^{0.5}$ m^{-1}, and $0.5hL\nu_f = 17.4/0.796 = 21.8$ kJ mol^{-1} for the R$^\bullet$ + HOR reaction.

The class of radical abstraction reactions may include a single reaction (for example, H$^\bullet$ + HCl), one group of reactions (for example, R$^\bullet$ + NH_3, where R$^\bullet$ is any alkyl radical), or several such groups (for example, the class of reactions $RO_2^\bullet$ + R′H, where R′H is a hydrocarbon, consists of three groups of reactions: $RO_2^\bullet$ + R^{1}H, $RO_2^\bullet$ + R^{2}H, and $RO_2^\bullet$ + R^{3}H, where R^{1}H, R^{2}H, and R^{3}H are any aliphatic, unsaturated, and aromatic alkyl-substituted hydrocarbons respectively). All the reactions belonging to one group are characterised by a single parameter r_e or br_e. Table 2 presents the results of the calculation of the parameters br_e by Eqns (4) (the IP model)[35] and (9) (the MPC model)[14] for reactions of the class H$^\bullet$ + RH. The quantities br_e calculated on the basis of one model for reactions involving hydrocarbons having different structures are very close; the average values of br_e are 15.30±0.59 kJ$^{0.5}$ mol$^{-0.5}$ in the IP model and 19.42 + 0.98 kJ$^{0.5}$ mol$^{-0.5}$ in the MPC model. The activation energies were calculated by the Arrhenius equation; the quantity A calculated per reacting C–H bond is 10^9 litre mol^{-1} s^{-1} for the liquid phase and 2×10^8 litre mol^{-1} s^{-1} for the gas phase. Knowing the parameter br_e, it is possible to calculate an important characteristic of the reactivity of each group of reactions such as the activation energy for a thermally neutral reaction E_{e0} [Eqns (5) and (10)]. The energies E_{e0} may differ significantly for reactions of different classes. Thus the following values have been obtained (kJ mol^{-1}) for reactions involving aliphatic hydrocarbons R^{1}H:

Reaction	H$^\bullet$ + R^{1}H	R$^\bullet$ + R^{1}H	$RO_2^\bullet$ + R^{1}H
E_{e0} (IP) [27, 36]	64.8	68.2	58.1
E_{e0} (MPC) [14]	66.1	71.3	61.8

Table 1. Kinetic parameters of radical abstraction reactions of different classes.[27]

Reaction	α	$10^{-11}b$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$0.5hLv_i$ /kJ mol^{-1}	$0.5hL(v_i-v_f)$ /kJ mol^{-1}	$(r^{\neq}/r_e)_0$
$H^{\bullet} + H_2$	1.000	4.133	26.3	0.0	0.500
$H^{\bullet} + HCl$	0.953	3.937	17.9	−8.4	0.488
$H^{\bullet} + HBr$	0.851	3.516	15.2	−11.1	0.460
$H^{\bullet} + HI$	0.743	3.072	13.8	−12.5	0.426
$H^{\bullet} + RH$	0.906	3.743	17.4	−8.9	0.475
$H^{\bullet} + NH_3$	1.042	4.306	20.0	−6.3	0.510
$H^{\bullet} + HOCH_3$	1.137	4.701	21.7	−4.6	0.532
$H^{\bullet} + HSiR_3$	0.668	2.756	12.6	−13.6	0.400
$H^{\bullet} + H_2S$	0.831	3.434	15.6	−10.7	0.454
$H^{\bullet}O + CH_4$	0.790	3.743	17.4	−4.4	0.441
$H^{\bullet}O + NH_3$	0.908	4.306	20.0	−1.8	0.472
$H^{\bullet}O + HOCH_3$	0.992	4.701	21.7	−0.1	0.498
$H^{\bullet}O + SiH_4$	0.591	2.861	13.1	−8.7	0.372
$H^{\bullet}O + HS_2$	0.724	3.434	15.6	−6.2	0.420
$R^{\bullet} + R'H$	1.00	3.743	17.4	0.0	0.500
$R^{\bullet} + H_2NR'$	1.207	4.517	20.9	3.5	0.547
$R^{\bullet} + HSiR'_3$	0.723	2.756	12.6	−4.8	0.420
$R^{\bullet} + HSR'$	0.808	3.026	13.8	−3.6	0.447
$RO^{\bullet} + R'H$	0.796	3.743	17.4	−4.3	0.443
$RO^{\bullet} + HSiR'_3$	0.581	2.756	12.6	−9.1	0.367
$RO_2^{\bullet} + R'H$	0.814	3.743	17.4	−3.8	0.449
$RO_2^{\bullet} + HOOR'$	1.000	4.600	21.2	0.0	0.500
$RO_2^{\bullet} + HOAr$	1.000	4.665	21.5	0.3	0.500
$RO_2^{\bullet} + HOAm$	1.000	4.665	21.5	0.3	0.500
$RO_2^{\bullet} + HAm$	0.940	4.324	20.0	−1.2	0.484
$RO_2^{\bullet} + HSAr$	0.658	3.026	13.8	−7.4	0.397
$ArO^{\bullet} + HR$	0.802	3.743	17.4	−4.1	0.445
$ArO^{\bullet} + HOAr'$	1.000	4.665	21.5	0.0	0.500
$ArO^{\bullet} + HOAm$	1.000	4.665	21.5	0.0	0.500
$ArO^{\bullet} + HAm$	0.927	4.324	20.0	−1.5	0.481
$Am^{\bullet} + HAm$	1.000	4.324	20.0	0.0	0.500
$Am^{\bullet} + HOAm$	1.079	4.665	21.5	1.5	0.519
$AmO^{\bullet} + HOAr$	1.000	4.665	21.5	0.0	0.500
$AmO^{\bullet} + HAm$	0.927	4.324	20.0	−1.5	0.481
$AmO^{\bullet} + HOAm$	1.000	4.665	21.5	0.0	0.500
$AmO^{\bullet} + HR$	0.802	3.743	17.4	−4.1	0.445
$AmO^{\bullet} + HSAr$	0.649	3.026	13.8	−7.7	0.394
$R_3Si^{\bullet} + HSiR'$	1.000	2.752	12.6	−8.9	0.500

[a] Here and henceforth AmH = amine, AmOH = hydroxylamine, $Am^{\bullet}$ = aminyl radical, and $AmO^{\bullet}$ = nitroxyl radical.

For reactions of one class, the values of E_{e0} found on the basis of both models are very close, the discrepancy not exceeding 3 kJ mol^{-1}.

The classification of radical reactions carried out in this way makes it possible to observe empirically (on the basis of the parameter br_e) structural differences between reactants within one class, to compare the classes and groups of reactions in terms of reactivity (in terms of the parameter br_e or E_{e0}), and to identify the physical factors determining the reactivities of groups of reactants. The parameters br_e for different groups of reactions are presented in Table 3.

The reactions of nitrogen- and oxygen-centred radicals with O–H and N–H bonds take place in solution in two stages *via* the preliminary formation of a hydrogen-bonded complex, for example:

$$Ar_2N^{\bullet} + HOAr = Ar_2N^{\bullet}...HOAr \longrightarrow Ar_2NH + ArO^{\bullet}.$$

The observed rate constant is the product of the equilibrium constant for the first stage and the rate constant for the second stage. However, in the gas phase such reactions apparently proceed as bimolecular processes. Therefore, in order to compare the parameters of these reactions in the gas and liquid phases and for their correct comparison with other bimolecular reactions, they were all regarded as bimolecular and the experimental pre-exponential factors were used in the calculations.

The activation energy for any individual reaction within the limits of the given group of reactions may be calculated correctly from the parameter br_e. Within the framework of the IP model, the quantity E_e was calculated by means of the following formulae:[27]
(1) for $\alpha = 1$,

$$E_e^{1/2} = 0.5br_e + \frac{\Delta H_e}{2br_e}; \tag{20}$$

(2) for $\alpha \neq 1$

$$E_e^{1/2} = \frac{br_e}{1-\alpha^2}\left\{1 - \alpha\left[1 - \frac{1-\alpha^2}{(br_e)^2}\Delta H_e\right]^{1/2}\right\}; \tag{21}$$

(3) for $\Delta H_e(1-\alpha^2) \ll (br_e)^2$

$$E_e^{1/2} = \frac{br_e}{1+\alpha} + \frac{\alpha\Delta H_e}{2br_e}\ . \tag{22}$$

Table 2. Kinetic characteristics of the $H^{\bullet}$ + RH reactions calculated with the aid of the IP [35] and MPC [14] models.

RH	Medium	T /K	k /litre mol^{-1} s^{-1}	$-\Delta H_e$ /kJ mol^{-1}	E_{ei} /kJ mol^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	
						IP	MPC
CH_4	Gas	298	2.24×10^2	6.5	64.9	15.71	19.83
CH_3CH_3	"	298	2.42×10^4	26.5	54.4	15.52	19.63
$CH_3CH_2CH_3$	"	298	5.84×10^3	27.3	55.1	15.65	19.84
$CH_3CH_2CH_3$	"	416	1.88×10^7	42.4	42.2	14.83	18.67
$CH_3(CH_2)_2CH_3$	"	512	2.60×10^6	27.3	49.4	14.96	18.74
$CH_3(CH_2)_2CH_3$	"	298	3.56×10^4	41.6	49.0	15.62	19.93
$CH_3(CH_2)_3CH_3$ [a]	"	763	1.02×10^8	41.6	47.8	15.48	19.68
$CH_3(CH_2)_3CH_3$ [a]	"	763	1.20×10^9	41.6	43.4	14.94	18.84
$CH_3(CH_2)_3CH_3$ [a]	"	763	1.37×10^8	41.6	52.8	15.37	19.40
$Pr^iCH_2CH_3$	"	673	6.76×10^7	41.6	50.3	15.78	18.92
$CH_3(CH_2)_4CH_3$	RH	313	6.10×10^4	41.6	47.7	15.47	19.67
$Bu^tCH_2CH_3$	RH	296	2.30×10^4	41.6	53.8	16.18	20.86
$Me_2CHCHMe_2$	RH	313	4.80×10^6	52.7	42.0	15.30	19.52
$CH_3CH(CH_2CH_3)_2$	RH	296	8.30×10^6	52.7	48.9	16.12	20.88
$Pr^i_2CH_2$	RH	296	2.60×10^5	52.7	47.9	16.00	20.68
$CH_3(CH_2)_{10}CH_3$	RH	313	5.00×10^6	41.6	47.9	15.49	19.71
cyclo-C_5H_{10}	H_2O	288	3.00×10^7	49.5	41.2	15.05	19.08
cyclo-C_6H_{12}	H_2O	288	3.00×10^7	45.3	41.6	14.90	18.80
cyclo-C_6H_{12}	RH	313	3.20×10^6	45.3	47.7	15.64	20.00
cyclo-$C_6H_{11}(CH_3)$	RH	396	1.40×10^5	56.4	47.6	16.14	20.94

[a] The quantities k, E_{ei} and br_e have been taken from different sources.

Table 3. The pre-exponential factors A (calculated for one reacting bond), the parameters br_e, and the quantities $\Delta H_{e,min}$ and $\Delta H_{e,max}$ for different groups of radical reactions in terms of the IP model.

Reaction	10^{-8} A /litre mol^{-1} s^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	$\Delta H_{e,min}$ /kJ mol^{-1}	$\Delta H_{e,max}$ /kJ mol^{-1}	Ref.
$R^{\bullet} + R^1H$	10	17.23	−153.1	153.1	27
$R^{\bullet} + R^2H$	1.0	18.86	−198.4	198.4	27
$R^{\bullet} + R^3H$	1.0	18.11	−176.9	176.9	27
$R^{\bullet} + R'_3SiH$	10	13.18	−147.3	100.0	37
$RO^{\bullet} + R^1H$	10	13.37	−99.7	83.6	27
$RO^{\bullet} + R^2H$	1.0	14.41	−131.6	105.6	27
$RO^{\bullet} + R^3H$	1.0	14.16	−123.6	100.1	27
$RO^{\bullet} + R'_3SiH$	10	10.13	−82.6	52.5	37
$RO_2^{\bullet} + R^1H$	0.1	14.23	−120.5	88.1	28
$RO_2^{\bullet} + R^2H$	0.1	15.68	−167.7	120.6	28
$RO_2^{\bullet} + R^3H$	0.1	14.74	−136.4	99.1	28
$RO_2^{\bullet} + ROOH$	10	13.13	−51.5	51.5	27
$RO_2^{\bullet} + Ar^1OH$	0.32	13.46	−56.3	56.3	38
$RO_2^{\bullet} + Ar^2OH$	0.32	14.40	−73.8	73.8	38
$RO_2^{\bullet} + AmH$	1.0	12.12	−41.2	42.7	39
$RO_2^{\bullet} + ArSH$	0.32	10.39	−70.4	45.7	40
$Ar^1O^{\bullet} + R^3H$	1.0	15.53	−167.3	131.1	41
$Ar^1O^{\bullet} + HOAr^1$	10	12.61	−42.1	42.1	41
$Ar^1O^{\bullet} + AmH$	1.0	10.13	−11.2	15.8	41
$AmO^{\bullet} + AmH$	1.0	11.63	−33.5	36.0	42
$Am^{\bullet} + R^3H$	1.0	16.87	−187.5	158.4	43
$AmO^{\bullet} + HOAr^1$	1.0	12.93	−47.3	47.3	42
$R_3Si^{\bullet} + R'_3SiH$	10	13.69	−90.2	90.2	37

In the MPC model, the activation energy E_e was found by the numerical solution of the equation [14]

$$F(E_e) = D_{ei}^{1/2}\ln\left[1-\left(\frac{E_e}{D_{ei}}\right)^{1/2}\right] + \alpha D_{ef}^{1/2}\ln\left[1-\left(\frac{E_e-\Delta H_e}{D_{ef}}\right)^{1/2}\right] + br_e = 0\,. \quad (23)$$

The Newton–Raphson method combined with a special computer program was used to solve Eqn (23) for fixed values of D_{ei}, D_{ef}, and α. Table 4 presents the results of the calculation of the activation energies for the $H^{\bullet}$ + RH reactions based on the IP and MPC models as well as experimental values of $E_{e,exp}$. The discrepancy between the calculated and experimental data for the IP and MPC models is 1.2±0.8 and 1.0±0.7 kJ mol^{-1} respectively, *i.e.* it does not exceed the scatter of experimental activation energies (±3 kJ mol^{-1}).

Table 4. Comparison of the experimental activation energies ($E_{e,exp}$)[18,21] and the activation energies calculated on the basis of the IP[35] and MPC[14] models for the $H^{\cdot}$ + RH reactions.

RH	Medium	T /K	$-\Delta H_e$ /kJ mol^{-1}	$E_{e,exp}$ /kJ mol^{-1}	E_e /kJ mol^{-1}	
					MPC	IP
CH_3OH	H_2O	300	49.1	44.2	43.5	42.7
CH_3OH	Gas	298	49.1	45.8	43.5	42.7
CH_3CH_2OH	H_2O	300	53.2	40.2	41.7	41.2
CH_3CH_2OH	Gas	298	53.2	40.8	41.7	41.2
$CH_3CH_2CH_2OH$	H_2O	298	56.7	38.3	40.1	39.9
CH_2OHCH_2OH	H_2O	300	54.6	41.8	41.1	40.7
$CH_2OHCHOHCH_2OH$	H_2O	300	60.6	36.8	38.5	38.5
$C_6H_5CH_2OH$	H_2O	300	81.8	30.3	29.9	31.5
$CH_2=CHCH_2OH$	H_2O	300	103.5	21.7	21.1	24.7
$(CH_3)_2CHOH$	H_2O	300	62.7	35.3	37.6	37.7
$(CH_3CH_2)_2O$	H_2O	288	61.2	37.9	38.2	38.3
$[(CH_3)_2CH]_2O$	H_2O	313	71.5	34.1	33.8	34.6
	H_2O	300	59.0	40.0	39.1	39.0
	RH	313	59.0	38.0	39.1	39.0
	H_2O	313	59.0	41.0	39.1	39.0
CH_3CH_2COOH	H_2O	288	55.9	41.0	40.5	40.2
HCOOH	H_2O	300	40.7	46.9	47.2	46.0
$CH_3(CH_2)_2COOH$	H_2O	298	55.9	41.5	40.5	40.2
$CH_3(CH_2)_2COOH$	H_2O	288	55.9	40.3	40.5	40.2
$(CH_3)_2CHCOOH$	H_2O	288	66.2	36.0	36.1	36.6

VI. Dissociation energies and force constants of the attacked and generated bonds

A clear-cut dependence of the activation energy on the heat (enthalpy) of reaction, which is equal in its turn to the difference between the dissociation energies of the ruptured (D_i) and generated (D_f) bonds, has been established for radical abstraction reactions.[2,30] In both models considered in the present review, the values of D_{ei} and D_{ef}, incorporating the zero-point energy of the bond vibrations, are examined. The enthalpy of reaction ΔH_e therefore also includes the difference between these energies [see Eqn (2)].

As noted above, all radical abstraction reactions can be divided into groups and the activation energy E_{e0} for a thermally neutral reaction can be calculated in each group. The possibility of calculating the activation energy for any reaction of the given series (group) from the value of E_{e0} (or br_e) and of estimating the contribution of the enthalpy to the activation energy follows from this important factor. The contribution of ΔE_H represents the difference between the activation energies for the given (ith) reaction and a thermally neutral reaction characterised by the quantity E_{e0}:[27]

$$\Delta E_H = E_{ei} - E_{e0} \,. \tag{24}$$

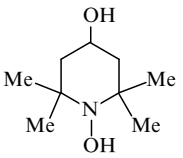
As an example, Table 5 presents the values of ΔE_H for the reactions of peroxyl radicals with antioxidants of different classes.[44] It follows from the table that the ratio $\Delta E_H/\Delta H$ for these groups of reactions is close to 1/2.

In terms of the parabolic model, it is possible to obtain simple and physically clear equations for the estimation of ΔE_H as a function of α, br_e, and ΔH_e. The following simple expressions follow from the combination of Eqns (5) and (2)–(22):[27]

(1) for $\alpha = 1$

$$\Delta E_H = 0.5\Delta H_e + \frac{0.25}{(br_e)^2}\Delta H_e^2 \,; \tag{25}$$

Table 5. The contributions of the enthalpy ΔE_H to the activation energy E for the reactions of a secondary peroxyl radical with various inhibitors (ΔH, E, and ΔE_H in kJ mol^{-1}).[44]

Inhibitor	ΔH	E	ΔE_H
PhOH	1.5	25.9	0.7
4-MeC_6H_4OH	−7.7	21.4	−3.8
4-$MeOC_6H_4OH$	−16.5	17.3	−7.9
4-$PhCH_2C_6H_4OH$	−18.0	16.6	−8.6
4-AcC_6H_4OH	4.0	27.2	2.0
2,3-$Me_2C_6H_3OH$	−12.0	19.4	−5.8
α-$HOC_{10}H_7$	−24.1	13.9	−11.3
2,6-$Bu^t_2C_6H_3OH$	−18.8	22.8	−8.9
2,6-Bu^t_2-4-MeC_6H_2OH	−26.5	19.3	−12.4
2,6-Bu^t_2-4-$MeOC_6H_2OH$	−34.8	15.8	−15.9
2,6-Bu^t_2-4-BnC_6H_2OH	−27.8	18.8	−12.9
2,6-Bu^t_2-4-$PhSC_6H_2OH$	−19.1	22.6	−9.1
Si[2,6-Bu^t_2-4-$CH_2CH_2OC_6H_2OH$]$_4$	−24.6	20.2	−11.5
Ph_2NH	−0.8	12.0	−0.4
(4-MeC_6H_4)$_2$NH	−14.9	5.7	−7.8
(4-$MeOC_6H_4$)$_2$NH	−24.3	1.8	−11.7
4-$MeOC_6H_4NHPh$	−18.3	4.2	−9.3
1-$C_{10}H_7NHPh$	−13.6	6.2	−7.3
4-$PhHNC_6H_4NHPh$	−18.6	4.1	−9.4
$Bu^t_2C=NOH$	−27.0	27.1	−12.7
$PhCH=CHC(O)N(OH)Bu^t$	−44.1	19.8	−20.0
	−63.3	12.4	−27.4
PhSH	−37.1	11.9	−15.0
4-MeC_6H_4SH	−30.7	13.7	−13.2

(2) for $\alpha \neq 1$,

$$(1-\alpha^2)\Delta E_H = 2\alpha(br_e)^2 - \alpha^2\Delta H_e - \\ -2\alpha(br_e)^2\left[1-\frac{(1-\alpha^2)}{(br_e)^2}\Delta H_e\right]^{1/2}; \quad (26)$$

(3) for $\Delta H_e\,(1-\alpha^2) \ll (br_e)^2$,

$$\Delta E_H = \frac{\alpha}{1+\alpha}\Delta H_e + \frac{0.25\alpha}{(br_e)^2}\Delta H_e^2\,. \quad (27)$$

It is seen from Eqns (25) and (27) that, for low values of the enthalpy of reaction, ΔE_H is directly proportional to ΔH_e which agrees with the Polanyi–Semenov equation.[2] The slope of the linear plot of ΔE_H as a function of ΔH_e depends on α, *i.e.* on the force constants of the bonds. The ratio $\Delta E_H/E_{e0} = \alpha(1+\alpha)^{-1}$, which includes the force constants of the reacting bonds, may serve as a parameter of the sensitivity of E_e to ΔH_e for low values of the latter. For reactions of different classes, the coefficient α varies in the range from 0.6 to 1.7 and the coefficient $\alpha(1+\alpha)^{-1}$ therefore varies from 0.38 to 0.63.

The activation energy increases with increase in ΔH_e and diminishes with increase in $|\Delta H_e|$ for $\Delta H_e < 0$. On the other hand, according to the law of conservation of energy, $E > 0$ for exothermic reactions and $E \geqslant \Delta H_e$ or endothermic reactions. It follows from the law of conservation of energy and Eqns (2)–(4) that the parameter br_e for one group of reactions is constant, while ΔH_e varies in the range $\Delta H_{e,min} \leqslant \Delta H_e \leqslant \Delta H_{e,max}$.[45] For highly endothermic reactions with $\Delta H_e > \Delta H_{e,max}$, the activation energy is $E = \Delta H + 0.5RT$, whilst for exothermic reactions with $\Delta H_e < \Delta H_{e,min}$ it is $0.5RT$. The limiting enthalpies of reaction $\Delta H_{e,max}$ and $\Delta H_{e,min}$ are related to the parameters br_e and α in the following way:[45]

$$\Delta H_{e,max} = (br_e)^2 + 2\alpha br_e(0.5hLv_f)^{1/2} + 0.5(\alpha^2-1)hLv_f\,, \quad (28)$$

$$\Delta H_{e,min} = -\left(\frac{br_e}{\alpha}\right)^2 + 2\alpha br_e(0.5hLv_i)^{1/2} + 0.5(1-\alpha^2)hLv_i. \quad (29)$$

As can be seen from Eqns (28) and (29), the range of variation of ΔH_e in which br_e = const is wider the greater the parameter br_e. For the reactions of alkyl radicals with aliphatic hydrocarbons ($\alpha = 1$, $br_e = 17.23$ kJ$^{0.5}$ mol$^{-0.5}$), we have $\Delta H_{e,max} = |\Delta H_{e,min}| = 153.1$ kJ mol^{-1}, *i.e.* the range of enthalpies ΔH_e where br_e = const is 306 kJ mol^{-1}. The enthalpies $\Delta H_{e,max}$ and $\Delta H_{e,min}$ for different groups of reactions are listed in Table 3.

Yet another important characteristic of radical abstraction reactions is the force constants of the ruptured and generated bonds. The dependence of the activation energy for reactions of the type $R^\bullet + RX \rightarrow RX + R^\bullet$, where X = H, Cl, Br, or I, on the coefficients b_i and b_f has been demonstrated experimentally.[46] It was found that r_e = const in these reactions, whilst the activation energy for a thermally neutral reaction is directly proportional to the force constant of the ruptured bond. It is seen from Fig. 3 that the smaller the force constant of the C–H bond, the lower E_{e0} and that this relation is linear. The same result has been obtained[46] also for reactions of the $H^\bullet$ + RCl, $H^\bullet$ + RBr, and $H^\bullet$ + RI classes. Analysis of the seven classes of reactions listed above within the framework of the MPC model[47] yielded a similar result (Fig. 3). The relation

$$E_{e0}^{1/2} = \gamma\frac{b}{1+\alpha}\,, \quad (30)$$

holds in this case and the proportionality coefficient γ for reactions of the $R^\bullet$ + RX and $H^\bullet$ + RX types is very close in both models: $\gamma = (4.80\pm0.15)\times10^{-11}$ m. This confirms the important role of the force constant of the reacting bonds in the formation of the activation barrier. The activation energies for the $R^\bullet$ + RX reactions can be easily estimated from the empirical formula

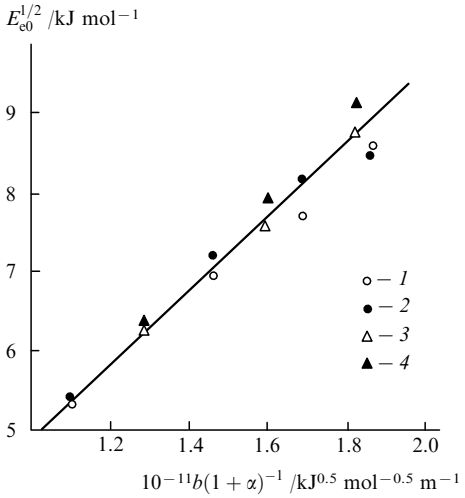


Figure 3. Dependence of E_{e0} on the coefficient $b(1+\alpha)^{-1}$ for the $R^\bullet$ + RX (X = H, Cl, Br, I) reactions on the basis of the IP (*1*)[46] and MPC (*2*)[47] models and the $H^\bullet$ + RX (X = Cl, Br, I) reactions on the basis of the IP (*3*)[46] and MPC (*4*)[47] models.

$$E_{e0}^{1/2} = 2.31\times10^{-11}b + 1.08\times10^{10}\frac{\Delta H_e}{b}\,, \quad (31)$$

while those for the $H^\bullet$ + RX (X = Cl, Br, I) reactions can be found from the formula

$$E_e^{1/2} = 4.81\times10^{-11}\frac{b}{1+\alpha} + 1.04\times10^{10}\alpha\frac{\Delta H_e}{b}\,. \quad (32)$$

VII. The role of the X–Y bond in the $X^\bullet$ + HY reaction

The hydrogen atom migrates from Y to X in the $X^\bullet$ + HY reaction. The transition state of this reaction can be regarded conventionally as a labile formation containing the X...H...Y pseudobond. The characteristics of this bond may influence the activation energy. This influence can be observed with the aid of the IP and MPC models, since each of them makes it possible to convert the activation energy for an individual reaction into the activation energy for a thermally neutral reaction [see Eqns (5) and (10)] and also to take into account the influence of the force constants of the X–H and Y–H bonds on E_{e0} [Eqn (5)]. When the hydrogen abstraction reactions are compared in relation to different classes of compounds, it is useful to employ the parameter r_e, in which the influence of ΔH_e, b_i, and b_f on the activation energy for the reaction has already been taken into account.

In the X...H...Y transition state, the X–Y pseudobond is formed by three electrons. According to the Pauli principle, one molecular orbital may be occupied by only two electrons with opposite spins.[29] Two molecular orbitals therefore participate in the transition state: the bonding orbital of the X–Y bond, in which two electrons are accommodated, and its nonbonding orbital containing the third electron. The energy of the nonbonding orbital D_T is higher the stronger the X–Y bond; it is described by the Sato formula[48]

$$D_T = D_e\{\exp(-bD_e^{-1/2}r) + 0.5\exp(-2bD_e^{-1/2}r)\}, \quad (33)$$

where D_e and D_T are the energies of the bonding and nonbonding X–Y orbitals respectively, $2b^2$ is the force constant, and r is the amplitude of the vibration of this bond. In the given instance, $r = r_{XH} + r_{YH} + r_e - r_{XY}$. The involvement of the nonbonding orbital of the X–Y bond in the formation of the activation barrier has come to be referred to as triplet repulsion.[49] This effect constitutes the basis of three semiempirical methods for the

calculation of the activation energies for radical substitution reactions: the 'bond energy–bond order' (BEBO) method,[49,50] the 'bond energy–bond length' (BEBL) method,[51] and the Zavitsas method.[52–54] In all these methods, the activation energy corresponds to the maxima on the 'potential energy–bond order' (BEBO) curves or the 'potential energy–bond length' (BEBL, Zavitsas method) curves while the potential energy curve represents a superposition of two Morse curves corresponding to the Y–H and X–H reacting bonds and the curve for the non bonding orbital of the X–Y bond [Eqn (33)].

The role of triplet repulsion in radical abstraction can be clearly traced on comparing reactions in which the energies of the X–Y bonds differ significantly.[55,56] The values of E_{e0} and r_e for a series of radical abstraction reactions found by the IP method [41,42] as well as the energies D_e of the X–Y bond are presented below.

X...H...Y	E_{e0} /kJ mol^{-1}	10^{11} r_e /m	D_e /kJ mol^{-1}
R...H...R	68.2	4.414	382
R...H...N	60.2	3.862	361
PhO...H...OAm	41.8	2.772	~ 0
RO_2...H...O_2R	43.1	2.854	88
RO_2...H...OAr	45.3	2.885	~ 0
RO_2...H...OAm	45.6	2.895	~ 0

The difference between the reactions with a high energy of the X–Y (C–C and C–N) bond, for which $E_{e0} \sim 60-70$ kJ mol^{-1}, and the reactions with a very low energy of this bond (O–O), for which $E_{e0} \sim 40-45$ kJ mol^{-1} can be clearly traced. Within the limits of the error of the measurement, the parameter r_e for the last four reactions is constant: $r_e = (2.85 \pm 0.05) \times 10^{-11}$ m. This value is characteristic of reactions with zero triplet repulsion in the transition state. On substituting this quantity in Eqn (5), we obtain the following equation for the estimation of the contribution of triplet repulsion ΔE_T to the activation energy E_{e0}:

$$\Delta E_T = \frac{(b_i b_f)^2}{(b_i + b_f)^2}(r_e^2 - 2.85^2 \times 10^{-22}). \quad (34)$$

For reactions of the R$^\bullet$ + RH class, this contribution is 40.0 kJ mol^{-1}, *i.e.* a considerable proportion of the activation energy E_{e0} = 68 kJ mol^{-1} is due precisely to the triplet repulsion in the transition state.

Another important characteristic of the X–Y bond is its polarity induced by the different electron affinities of the atoms or radicals X and Y.[27,55,56] The greater the difference, the greater the polarity of the bond, its strength and its dipole moment. According to Pauling, the polarity of the X–Y bond may be characterised by the extent to which its strength differs from half the sum of the bond dissociation energies of the XX and YY molecules by virtue of the different electronegativities of the atoms X and Y:

$$\Delta EA(XY) = D_{XY} - 0.5(D_{XX} + D_{YY}). \quad (35)$$

The question arises whether the polarity of the X–Y bond affects the X$^\bullet$ + YH radical abstraction reactions. We shall compare two reactions:[35] H$^\bullet$ + H_2 and Cl$^\bullet$ + H_2.

Reaction	E_{e0} /kJ mol^{-1}	10^{11} r_e /m	D_{XY} /kJ mol^{-1}
H$^\bullet$ + H_2	58.2	3.69	436.0
Cl$^\bullet$ + H_2	36.7	3.04	431.6

Evidently the dissociation energies of the H–H and Cl–H bonds are very close and the triplet repulsion in the transition states of these reactions is therefore almost identical. Nevertheless the quantities E_{e0} and r_e in these two reactions differ very considerably. The reason for this is that the H–H bond is nonpolar, while the Cl–H bond is polarised and ΔEA = 92.3 kJ mol^{-1} [Eqn (35)] for the latter. As in the HCl molecule, in the transition state there is evidently a strong attraction between Cl and H, which in fact induces a decrease in r_e and E_{e0}. If the H$^\bullet$ + HCl reactions were characterised by the same parameter $r_e = 3.69 \times 10^{-11}$ m as the H$^\bullet$ + H_2 reaction, the energy E_{e0} = 56.5 kJ mol^{-1} [Eqn (5)] would have been obtained for it. The difference between the expected and observed activation energies ($\Delta E_{EA} = 36.7 - 56.5 = -19.8$ kJ mol^{-1}) must be attributed to the influence of the unequal electronegativities of the hydrogen and chlorine atoms on E_{e0} in the H$^\bullet$ + HCl reaction.

The R$^\bullet$ + RH and RO$^\bullet$ + RH reactions may serve as another example.[55,56]

Reaction	E_{e0} /kJ mol^{-1}	10^{11} r_e /m	D_{XY} /kJ mol^{-1}
R$^\bullet$ + RH	68.2	4.414	376
RO$^\bullet$ + RH	54.8	3.553	361

In this case, the similarity of the R–R and RO–R bond dissociation energies also leads to the similarity of the triplet repulsion energies in the R...H...R and RO...H...R transition states. However, in these reactions too the quantities E_{e0} and r_e differ appreciably. The polarity of the O–C bond in the RO$^\bullet$ + RH reaction is manifested here. On substituting the dissociation energies $D(CH_3-CH_3)$, $D(CH_3O-OCH_3)$, and $D(CH_3-OCH_3)$ in Eqn (35), we obtain ΔEA = 80 kJ mol^{-1}. Calculation of the contribution of the electronegativities of the O and C atoms to the activation energy for the RO$^\bullet$ + RH reaction yields $\Delta E_{EA} = -26.1$ kJ mol^{-1}, which should be regarded as very considerable bearing in mind that E_{e0} = 54.8 kJ mol^{-1}.

When the fragments X and Y approach one another in the X...H...Y transition state, their outer electron shells begin to repel one another. It is to be expected that the repulsion will be stronger, the larger the radii of the atoms X and Y. The examples presented below confirm this conclusion. We shall compare the R$^\bullet$ + RH, R$^\bullet$ + $HSiR'_3$, and $R_3Si^\bullet$ + $HSiR'_3$ reactions.[37]

Reaction	10^{11} r_e /m	10^{11} r_{XY} /m	D_{XY} /kJ mol^{-1}	ΔEA /kJ mol^{-1}
R$^\bullet$ + RH	4.414	15.13	376	0.0
R$^\bullet$ + $HSiR'_3$	4.782	18.70	376	11.0
$R_3Si^\bullet$ + $HSiR'_3$	4.967	23.59	354	0.0

An evident parallel variation of the increment in r_e and in the bond length r_{XY} is observed. On the other hand, the strengths of the X–Y bonds in this series are similar, so that the increase in r_e is not caused by a change in the triplet repulsion. The electronegativities of the C and Si atoms are also similar and in the first and third reactions ΔEA = 0.

The empirical dependence of the parameter r_e (in m) on D_{XY}, ΔEA, and r_{XY} in the interaction of radicals carrying a free valence on the C and O atoms with the C–H, O–H, Si–H, and S–H bonds has the following form:[37]

$$10^{22} r_e^2 = 18\left[\left(\frac{r_{XY}}{r_{HH}}\right)^{1/2} - 1\right] + 13.7\left(\frac{D_{XY}}{D_{HH}}\right) - 22.4\left(\frac{\Delta EA}{D_{HH}}\right). \quad (36)$$

A similar formula has been proposed [37] for reactions with participation of H$^\bullet$:

$$10^{22} r_e^2 = 12.8\left[\left(\frac{r_{XY}}{r_{HH}}\right)^{1/2} - 1\right] + 13.7\left(\frac{D_{XY}}{D_{HH}}\right) - 22.4\left(\frac{\Delta EA}{D_{HH}}\right). \quad (37)$$

These formulae make it possible to estimate the contribution of each factor — triplet repulsion ΔE_T, electronegativity, ΔE_{EA}, and repulsion ΔE_R of the electron shells of the X and Y atoms in the transition state — to the activation barrier E_{e0} for each class of radical abstraction reactions. Since $E_{e0} = b r_e (1 + \alpha)^{-1}$, it follows that, by employing the corresponding increment from Eqns (36) and (37), it is possible to calculate the contribution of a particular factor. Table 6 presents the results of such calculation for 21 classes of radical abstraction reactions.

The influence of the radius of the atom Y on the X$^\bullet$ + HY reactions is indicated by the data obtained by the present author.[46]

Table 6. The contributions of triplet repulsion (ΔE_T), the electron affinity of the fragments X and Y (ΔE_{EA}), and the repulsion of the atoms forming the X–Y bond (ΔE_R) to the activation energy E_{e0} for the $X^{\bullet}$ + HY reaction.

Reaction	$10^{-11}\,b(1+\alpha)^{-1}$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$10^{11}r_e$ /m	ΔE_T /kJ mol^{-1}	ΔE_{EA} /kJ mol^{-1}	ΔE_R /kJ mol^{-1}
$R^{\bullet}$ + HR	1.87	4.41	41	0	25
$R^{\bullet}$ + H_2NR	2.05	3.84	45	−8	32
$R^{\bullet}$ + HOOR	2.06	3.80	37	−7	29
$R^{\bullet}$ + HOAr	2.08	3.80	35	−19	26
$R^{\bullet}$ + $HSiR'_3$	1.60	4.78	30	−3	27
$R^{\bullet}$ + HSR	2.13	4.09	44	0	46
$HO^{\bullet}$ + HR	2.09	3.67	53	−22	30
$HO^{\bullet}$ + SiH_4	1.79	3.30	55	−45	28
$RO^{\bullet}$ + HR	2.08	3.55	49	−20	30
$RO^{\bullet}$ + $HSiR'_3$	1.74	3.68	45	−34	26
$RO_2^{\bullet}$ + HR	2.06	3.80	37	−7	29
$RO_2^{\bullet}$ + HOOR	2.30	2.85	15	0	28
$RO_2^{\bullet}$ + HOAr	2.33	2.88	0	0	45
$AmO^{\bullet}$ + HR	2.08	3.66	28	−23	26
$AmO^{\bullet}$ + HOAr	2.33	2.77	0	0	42
$R^3Si^{\bullet}$ + $HSiR'_3$	1.38	4.97	18	0	27
$H^{\bullet}$ + HR	1.96	3.76	53	−8	10
$H^{\bullet}$ + NH_3	2.11	3.45	63	−21	9
$H^{\bullet}$ + H_2O	2.20	3.91	76	−43	8
$H^{\bullet}$ + SiH_4	1.69	4.09	34	−2	15
$H^{\bullet}$ + H_2S	1.88	3.60	42	−5	16

Thus linear dependences of the distance r_e on the radius of the halogen atom (Y) have been observed in the $O^{\bullet}$ + HY and $HO^{\bullet}$ + HY (Y = Cl, Br, I) reactions: $r_e = 0.29\,r_Y$ and $r_e = 0.32\,r_Y$ (IP model). These relations reflect the real contribution of the repulsion of the molecular orbitals of the atoms approaching one another to the formation of the activation barrier.

It is seen from the data presented in Table 6 that the triplet repulsion ΔE_T makes an additional contribution to the activation energy E_{e0}. The reactions in which the X–Y bond is not formed (for example in the $RO_2^{\bullet}$ + HOAr reaction) are an exception.

The difference between the electronegativities of the fragments X and Y lowers the activation energy. When the discrepancy between the electron affinities is large, this decrease may be very considerable. For example, $\Delta E_{EA} = -45$ kJ mol^{-1} for the $HO^{\bullet}$ + SiH_4 reaction and $\Delta E_{EA} = -43$ kJ mol^{-1} in the reaction of $H^{\bullet}$ with water.

The repulsion of the electron orbitals of the atoms forming the reaction centre ΔE_R plays an important role in all the radical abstraction reactions. In the interaction of radicals with molecules, the contribution of this repulsion ranges from 25 to 46 kJ mol^{-1}. In reactions of molecules with hydrogen atoms, the contribution is naturally smaller, varying from 8 to 16 kJ mol^{-1}.

Thus Eqns (36) and (37) make it possible to estimate the quantities r_e and E_{e0} for classes of reactions which have not been investigated.

VIII. The causes of the high reactivity of antioxidants

The considerations concerning the influence of physical factors on the heights of activation barriers in radical reactions of compounds in different classes, described above, may be used also to account for the kinetics of specific processes. Two such processes will be examined below: oxidation processes occurring in the presence of phenols and aromatic amines. Phenols and aromatic amines (antioxidants) react very rapidly with peroxyl radicals, whereas $RO_2^{\bullet}$ interaction with hydrocarbons is comparatively slow.[57] We shall compare three reactions: (*a*) $RO_2^{\bullet}$ + $C_6H_5CH_2CH_3$, (*b*) $RO_2^{\bullet}$ + 4-$CH_3C_6H_4OH$, and (*c*) $RO_2^{\bullet}$ + $(4\text{-}CH_3C_6H_4)_2NH$, where $RO_2^{\bullet}$ is a secondary peroxyl radical.[28, 38, 39]

Reaction	k(333 K) /litre mol^{-1} s^{-1}	ΔH /kJ mol^{-1}	$10^{-7}A$ /litre mol^{-1}s^{-1}	E /kJ mol^{-1}
(*a*)	2.0	−8.5	2.0	44.6
(*b*)	1.4×10^4	−7.7	3.0	21.4
(*c*)	3.0×10^5	−8.0	3.0	16.1

Evidently the peroxyl radical reacts with the O–H bond of *p*-cresol faster by four orders of magnitude and with the N–H bond of bis(*p*-tolyl)amine faster by five orders of magnitude than with the C–H bond of ethylbenzene. Furthermore the enthalpies ΔH of these reactions are very similar and so are the pre-exponential factors. The large difference between the rate constants is determined exclusively by the inequality of the activation energies E, which indicates in its turn that the quantities E_{e0} are different. This question has been analysed using the IP[58] and MPC[59] models. The correlation equation (36) makes it possible to establish the causes of this difference. The values of E_{e0} (kJ mol^{-1}), $10^{-11}b\,(1+\alpha)^{-1}$ (kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}), $10^{11}\,r_e$ (m), and the increments ΔE_R, ΔE_T, and ΔE_{EA} (kJ mol^{-1}) calculated by Eqn (36) are presented below.

HY	E_{e0},	$10^{-11}\,b(1+\alpha)^{-1}$	r_e	ΔE_R	ΔE_T	ΔE_{EA}
RH	61.5	1.87	3.80	32	37	−7
ArOH	45.3	2.33	2.88	45	~0	0
AmH	39.0	2.16	2.80	44	15	−20

The activation energy for the thermally neutral reaction of $RO_2^{\bullet}$ with the C–H bond is indeed greater than in the interaction of the same radical with the O–H bond of the phenol and the N–H bond of the amine. In the case of the phenol, the comparatively low value of E_{e0} is caused by the absence of triplet repulsion (the ArO–OAr bond is very weak), while in the case of the amine the large difference between the electronegativities of the N and O atoms, which leads to the polarisation of the N...H...O reaction centre and a decrease in the activation energy for low triplet repulsion, may be regarded as such a cause. On the other hand, the high value of E_{e0} in the reactions of $RO_2^{\bullet}$ with the C–H bond of the hydrocarbon is caused primarily by the strong triplet repulsion

(ΔE_T = 37 kJ mol^{-1}) and also by the comparatively slight polarisation of the C–O bond (ΔE_{EA} = −7 kJ mol^{-1}).

Aminyl radicals interact extremely rapidly with the O–H bond.[60,61] For example, the rate constants for the abstraction of the H atom from phenol at 294 K is 1×10^6 litre mol^{-1} s^{-1}, whereas the enthalpy of this reactions is only 2 kJ mol^{-1}. The high selective reactivity of aminyl radicals in the abstraction of H atoms from the O–H bond is indicated by the comparison of the values of E_{e0} for the Am$^{\bullet}$ + HY reactions:[43]

HY	RH	ArOH	AmOH	ROOH
E_{e0} /kJ mol^{-1}	81.7	27.6	33.2	41.1

It is seen from the data presented that the activation energy for the thermally neutral reaction involving the abstraction of H from the O–H bond is smaller by 40–54 kJ mol^{-1} than for the abstraction of H from a C–H bond of the hydrocarbon. The reason for this difference is the high polarity of the O–N bond in the transition state for weak triplet repulsion. By virtue of this precise factor, aromatic amines are effective catalysts of the reaction of the phenoxyl radical with a hydroperoxide.[62]

$$ArO^{\bullet} + Ar'_2NH \rightleftharpoons ArOH + Ar'_2N^{\bullet},$$

$$Ar'_2N^{\bullet} + ROOH \longrightarrow Ar'_2NH + RO_2^{\bullet},$$

$$RO_2^{\bullet} + ArO^{\bullet} \longrightarrow Q(\text{quinone}) + ROH.$$

This process is faster than the forward reaction

$$ArO^{\bullet} + HOOR \longrightarrow ArOH + RO_2^{\bullet}.$$

For the same reason (the polarity of the N–O bond), aromatic amines can ensure multiple chain termination in the oxidation of alcohols, alkenes, and polymers, where the $>C(OH)O_2^{\bullet}$ and $HO_2^{\bullet}$ radicals participate in chain propagation. This is not observed in the oxidation of hydrocarbons. This question has been discussed in detail in another review by the present author.[63]

IX. The influence of the π-bond and the steric effect

An aromatic ring and a double or triple bond in the α-position relative to a C–H bond weaken the latter by virtue of the delocalisation of the unpaired electron in its interaction with the π-bond. The weakening of the C–H bond is very considerable: for example, D(C–H) is 418 kJ mol^{-1} in ethane, 363 kJ mol^{-1} in the methyl group of propene, and 368 kJ mol^{-1} in the methyl group of toluene. Such decrease in the strength of the C–H bond diminishes the enthalpy of the radical abstraction reaction and hence its activation energy. This effect is illustrated below in relation to the reactions of the methyl radical with hydrocarbons.[27]

Hydrocarbon	C_2H_6	$CH_3CH=CH_2$	$C_6H_5CH_3$
ΔH /kJ mol^{-1}	−20.0	−75.2	−70.2
E /kJ mol^{-1}	52.4	37.4	39.3

Comparative analysis of the kinetics of the reactions of atoms and radicals with paraffinic (R^1H), olefinic (R^2H), and aromatic alkyl-substituted (R^3H) hydrocarbons within the framework of the IP and MPC models permitted a new important conclusion. It was found that the π-C–C bond occupying the α-position relative to the attacked C–H bond increases the activation energy for thermally neutral reaction.[27] The corresponding results are presented in Table 7. Evidently the activation energy for a thermally neutral reaction with participation of a hydrogen atom or a radical (alkyl, alkoxyl, *etc.*) is higher in those cases where there is a π-bond or an aromatic ring next to the attacked C–H bond. This result is independent of the method used to calculate (IP or MPC) the parameters br_e and E_{e0}. Evidently this effect is a property of the structures themselves and the π-bond exerts a dual effect on the reaction centre. On the one hand, by weakening the C–H bond the π-bond in the α-position lowers the enthalpy and hence the activation energy for the reaction. On the other hand, by interacting with the electrons of the reacting bonds, the π-orbital increases the strength of the C–Y bond in the Y$^{\bullet}$ + HR reaction, which increases the energy of the non bonding C–Y orbital and intensifies triplet repulsion.

The influence of bulky substituents, for example tertiary alkyl groups, on the kinetics of diverse chemical reactions is well known. A steric effect occurs also in radical reactions. Such substituents usually influence both the enthalpy of the reaction and its activation energy. The IP and MPC models examined in the present review make it possible to separate these effects and to estimate separately the contribution of steric hindrance to the activation energy.[27] We shall examine the thoroughly investigated radical reactions in which a radical attacks the O–H group of a sterically hindered phenol (Ar^2OH) containing two *tert*-alkyl (as a rule *tert*-butyl) groups in the *ortho*-position relative to the phenolic group. Comparison of the energies E_{e0} for isotypical reactions involving both sterically unhindered (Ar^1OH) and sterically hindered (Ar^2OH) phenols makes it possible to estimate the contribution of steric hindrance ΔE_S to the activation energy:

$$\Delta E_S = E_{e0}(Ar^2OH) - E_{e0}(Ar^1OH). \quad (38)$$

The results of the comparison are presented in Table 8. The steric hindrance increases the activation energy for a thermally neutral reaction by 8.2±2.0, 8.2±1.5, and 24 kJ mol^{-1} when oxygen-centred, nitrogen-centred, and alkyl radicals are involved respectively. The data obtained with the aid of the IP and MPC

Table 7. The influence of the π-C–C bond on the activation thermally neutral radical abstraction reactions.[14,27,64–68]

Radical	RH	IP model			MPC model		
		br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	ΔE_π /kJ mol^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	ΔE_π /kJ mol^{-1}
H$^{\bullet}$	R^1H	14.49	57.9		19.45	66.1	
	R^2H	15.58	66.9	9.0	20.44	71.4	5.3
	R^3H	15.34	64.9	7.0	19.91	69.1	3.0
R$^{\bullet}$	R^1H	17.23	74.2		21.86	71.3	
	R^2H	18.86	88.9	14.7	24.87	82.9	11.6
	R^3H	18.11	82.0	7.8	22.53	73.3	2.0
RO$^{\bullet}$	R^1H	13.37	55.2		16.98	58.5	
	R^2H	14.41	64.1	8.9	19.99	75.4	16.9
	R^3H	14.16	61.9	6.7	18.17	65.1	6.6
$RO_2^{\bullet}$	R^1H	14.23	61.5		18.24	61.8	
	R^2H	15.68	74.7	13.2	20.37	72.9	11.1
	R^3H	14.74	66.0	4.5	19.21	66.8	5.0
AmO$^{\bullet}$	R^1H	13.72	58.0				
	R^2H	15.66	75.5	17.5			
	R^3H	14.42	64.0	6.0			

Table 8. The contributions of the steric effect (ΔE_S) to the activation energies for thermally neutral reactions of sterically hindered phenols, phenoxyl radicals, and diphenylpicryl hydrazyl.[38,41,43,59]

Reaction	IP method			MPC method		
	br_e /kJ$^{0.5}$ mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	ΔE_S /kJ mol^{-1}	br_e /kJ$^{0.5}$mol$^{-0.5}$	E_{e0} /kJ mol^{-1}	ΔE_S /kJ mol^{-1}
$RO_2^{\bullet}$ + Ar^1OH	13.76	45.3		16.58	45	
$RO_2^{\bullet}$ + Ar^2OH	14.40	51.8	6.5	18.26	52.0	7.0
$CH_3^{\bullet}$ + Ar^1OH	17.38	59.8				
$CH_3^{\bullet}$ + Ar^2OH	18.92	84.2	24.4			
$Ar^1O^{\bullet}$ + Ar^1OH	12.61	39.7				
$Ar^1O^{\bullet}$ + Ar^2OH	13.31	44.3	4.6	17.19	48.5	
$Am^{\bullet}$ + Ar^1OH	10.93	27.6		12.84	28.0	
$Am^{\bullet}$ + Ar^2OH	12.15	34.2	6.6	14.99	36.0	8.0
$AmO^{\bullet}$ + Ar^1OH	12.93	41.8		16.22	43.8	
$AmO^{\bullet}$ + Ar^2OH	14.54	52.9	11.1	19.05	55.8	12.0
$Ar^1O^{\bullet}$ + HOOR	13.46	45.3		15.86	43.1	
$Ar^2O^{\bullet}$ + HOOR	14.40	51.8	6.5	18.26	52.0	
$Ar^2O^{\bullet}$ + Ar^2OH	14.37	51.6	7.3	19.13	56.7	8.2
$Ar^1O^{\bullet}$ + AmH	10.13	27.6		11.90	28.0	
$Ar^2O^{\bullet}$ + AmH	11.59	36.2	8.6	14.49	38.8	10.8
$Am^{\bullet}$ + RH	16.87	81.7		22.57	80.6	
$DPPH^{\bullet}$ + RH	18.59	99.3	17.6	26.76	98.7	18.1
$DPPH^{\bullet}$ + Ar^1OH	14.85	51.0	23.4	18.71	51.9	23.9
$DPPH^{\bullet}$ + Ar^2OH	16.74	64.8	30.6	21.63	64.3	28.3

models in most cases agree. The steric effect is manifested similarly also in the reactions of sterically hindered ($Ar^2O^{\bullet}$) phenoxyl radicals with various substrates (Table 8). The reactions of the sterically hindered diphenylpicryl radical ($DPPH^{\bullet}$) and the unhindered diphenylaminyl radical may serve as another example (Table 8). In the reactions of $DPPH^{\bullet}$ with phenols, the contribution of the steric effect to E_{e0} ranges from 23 to 30 kJ mol^{-1}, *i.e.* is very considerable.

X. The polar effect in radical reactions

An extensive literature has been devoted to polar effects in chemical reactions.[69–72] The IP and MPC models permit a fresh approach to this important problem. The introduction of a functional group into a hydrocarbon molecule alters the dissociation energy of the neighbouring C–H bonds, which is indicated by the examples presented below (the bond strengths taken from the review of McMillen and Golden [73]).

Compound	C_2H_6	C_2H_5OH	CH_3CHO	$C_2H_5OC_2H_5$
D /kJ mol^{-1}	418.4	392.5	365.3	383.7

The change in the C–H bond strength affects the enthalpies and through them the activation energies for radical abstraction reactions. If a molecule is attacked by a nonpolar group (hydrogen atom, alkyl radical), then the influence of the polar group on the activation energy is confined to a change in ΔH. This has been confirmed by data on the reactions of the methyl radical with the C–H bonds of hydrocarbons and their derivatives (alcohols, ethers, *etc.*),[12] which are characterised by a virtually identical parameter br_e = 17.23 kJ mol^{-1}. A similar result has been obtained when the MPC model was used.[47] Thus a polar group (OH, OR, *etc.*) influences only the enthalpy of reaction and not the energy of the reaction centre of a transition state of the type C...H...C and H...H...C.

A different picture is observed when a polar radical reacts with a C–H bond of a polar molecule. For example, the reaction of an oxygen atom with a methane C–H bond is characterised by the parameter br_e = 13.11 kJ$^{0.5}$ mol$^{-0.5}$ while the reaction with a methanol C–H bond is characterised by the corresponding parameter of 12.55 kJ$^{0.5}$ mol$^{-0.5}$. For these values of br_e, the difference between the activation energies is 4.6 kJ mol^{-1}. The decrease in activation energy can be explained by the fact that the polar OH group in the O...H...C–OH transition state interacts with the O...H...C polar reaction centre.

The IP and MPC models make it possible to isolate from the overall effect of the substituent its contribution to E. In the calculation, use is made of the values of ΔH and the activation energy for a thermally neutral reaction of the given group (reaction series), because the activation energy can be represented by the sum $E_e = E_{e0} + \Delta E_H$ (see above), where the second term takes into account only the influence of enthalpy. The polar interaction in the transition state may be inferred by comparing the values of E_{e0} in various reactions involving a hydrocarbon and the corresponding polar molecule. The contribution of the polar interaction to the activation energy (ΔE_μ) can be estimated [27] from the formula

$$\Delta E_\mu = \frac{(br_e)_\mu^2 - (br_e)_{RH}^2}{(1+\alpha)^2}\ , \qquad (39)$$

where the parameters $(br_e)_\mu$ and $(br_e)_{RH}$ refer to reactions involving a polar compound YH and a reference hydrocarbon RH respectively. The results of the calculation of the energy ΔE_μ (in kJ mol^{-1}) for the $X^{\bullet}$ + HY gas-phase reactions are presented below:[74]

$X^{\bullet}$	HY				
	CH_3OH	CH_2O	RCHO	CH_3COCH_3	$(CH_3)_2O$
$O^{\bullet}$	4.6	−4.6	−7.9	−9.4	−5.1
$HO^{\bullet}$	2.4	1.8	1.5	−11.4	2.8
$CH_3O^{\bullet}$	−6.0	0	−12.2	–	–
$(CH_3)_3CO^{\bullet}$	–	−4.2	−3.1	−17.8	–

Extensive data concerning the influence of polar groups on the activation energies for abstraction reactions have been obtained by analysing experimental data on reactions with participation of alkoxyl and peroxyl radicals in the liquid phase.[75–77] These data are presented in Table 9. As can be seen from the table, the interaction of a polar group with a O...H...C or O–O...H...C polar reaction centre can both diminish and increase the activation energy. A very marked decrease in activation energy (from −11 to −19 kJ mol^{-1}) has been observed in the reactions of $RO^{\bullet}$ and $RO_2^{\bullet}$ with aldehydes and ketones. The alcoholic group diminishes slightly the height of the activation barrier (by 1–3 kJ mol^{-1}), the reaction of $RO^{\bullet}$ with benzyl alcohol being

Table 9. Kinetic parameters of the reactions of alkoxyl and peroxyl radicals with the C–H bonds of oxygen-containing compounds YH.[74–77]

YH	$RO^{\bullet}$		$RO_2^{\bullet}$		$YO_2^{\bullet}$		
	br_e /kJ$^{0.5}$ mol$^{-0.5}$	ΔE_μ /kJ mol^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	ΔE_μ /kJ mol^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	ΔE_μ /kJ mol^{-1}	$\Delta\Delta E_\mu$ /kJ mol^{-1}
AlkOH	13.36	−1.5	13.71	−2.2	14.52	−5.8	−3.6
cyclo-$C_6H_{11}OH$	13.41	−1.1	13.63	−2.2	14.55	−5.6	−3.4
$C_6H_5CH_2OH$	13.03	−8.8	15.02	−2.8	41.75	−12.7	−9.9
C_6H_5CHO	11.76	−19.0	13.69	−8.2	13.53	−15.8	−7.6
RCHO	12.56	−12.2	12.83	−8.8	11.76	−15.8	−7.0
$RC(O)CH_2R$	13.17	−10.6	13.66	−15.4	13.96	−13.0	−2.4
$RC(O)CHR_2$			13.65	−15.7	12.96	−21.2	−5.5
$C_6H_5CH_2C(O)R$	13.82	−5.2	14.19	−11.2	13.91	−12.9	−1.7
$(RCH_2)_2O$	13.34	−1.7	14.30	3.4	14.52	5.7	2.3
$(R_2CH)_2O$	13.81	2.3	14.57	6.3	14.25	3.5	−2.8
$(C_6H_5CH_2)_2O$			14.55	−1.4			
$(C_6H_5RCH)_2O$			15.49	6.1	15.21	3.7	−2.4
$(RO)_2CH_2$	13.07	−3.9	14.06	1.8	14.00	1.4	−0.4
$(RO)_2CHCH_3$	13.50	−0.4	14.52	6.2	14.25	3.8	−2.4
cyclo-$C_6H_{11}OCH_3$			14.76	8.4			
			13.43	−3.8	13.43	−3.8	0.0
			13.42	−3.4	13.20	−5.3	−1.9
			13.54	−2.4	13.81	−0.2	2.2
$CH_3OC(O)R$	14.28	6.3	15.10	8.7			
$RCH_2OC(O)R$	14.47	8.0	15.00	8.9	13.48	−11.2	−20.1
cyclo-$C_6H_{11}OC(O)CH_3$	12.79	−6.1	14.89	8.8			–
$C_6H_5CH_2OC(O)R$	13.77	−2.7	15.11	4.5	14.04	−17.6	−22.1
$CH_3C(O)OH$			15.33	11.5			
$RCH_2C(O)OH$			14.92	7.9			
$(CH_3)_2CHC(O)OH$			15.08	10.6			
$RCH_2C(O)OR$			13.82	−2.7			
$(CH_3)_2CHOR$			14.36	2.7			
$C_6H_5CH_2C(O)OR$	13.17	−3.1	13.80	−7.6			

an exception. In the reactions with ethers, an increase in activation energy is observed.

XI. The effect of multidipole interaction

Yet another effect, namely multidipole interaction, is manifested in the reactions of polar radicals with polyfunctional compounds.[78] This effect consists in the unequal reactivities of the same group, for example $\rangle$CH(OH), in compounds with one and several functional groups. Factual data concerning multidipole interactions have been examined in a review.[79] The corresponding kinetic data have been analysed within the framework of the IP model.[77] The multidipole interaction is manifested, in particular, in the reactions of peroxyl radicals $RO_2^{\bullet}$, containing functional groups,with oxygen-containing compounds YH (Table 9). The magnitude of this effect in the transition state may be inferred from the change in the activation energy for a thermally neutral reaction on passing from a monofunctional compound YH to a polyfunctional compound ZH:

$$\Delta\Delta E_\mu = \frac{(br_e)^2_{ZH} - (br_e)^2_{YH}}{(1+\alpha)^2}.$$

As can be seen from Table 9, the highest values of $\Delta\Delta E_\mu$ correspond to the transition from $RO_2^{\bullet}$ to $YO_2^{\bullet}$ containing a carbonyl or ester group. Apparently this effect is induced by the dipole–dipole interaction in the transition state. Table 10 presents data concerning the influence of ester groups on the reactivity of CH_2 groups in reactions with peroxyl radicals. The multidipole effect always reduces the activation energy for reactions of this group and in certain cases the decrease is extremely significant (down to −10 kJ mol^{-1} and even further).

XII. Solvation of the reactants in radical abstraction reactions

Yet another important effect, observed when reactions take place in the liquid phase, is associated with the solvation of the reactants.Theoretical comparison has shown that the collision frequencies of the species in a gas and in a liquid are different, the difference being due to the difference between the free volumes.[80] In a gas, the free volume is virtually equal to the volume occupied by the gas species ($V_f \approx V$), while in a liquid it is much smaller than the volume of the liquid species ($V_f \ll V$). Since the motion and collision of the species occur in the free volume, the collision frequency in a liquid is higher than in a gas by an amount $(V/V_f)^{1/3} \approx 4-2$. The activation energies for the reactions of radicals and atoms with hydrocarbon C–H bonds in a gas and in a liquid are virtually identical, that in a liquid being independent of the solvent polarity. This also applies to the parameter br_e (the IP model), which can be seen from the following examples referring to the interaction of the hydroxyl radical with hydrocarbons:[74]

RH	C_2H_6	C_3H_8
br_e (gas) /kJ$^{0.5}$ mol$^{-0.5}$	13.74	13.52
br_e (H_2O) /kJ$^{0.5}$ mol$^{-0.5}$	13.48	13.40

Table 10. Kinetic parameters of the reactions of cumenylperoxyl radicals with compounds containing ester groups.[77]

Ester	ΔH_e /kJ mol^{-1}	E_e /kJ mol^{-1}	br_e /kJ$^{0.5}$ mol$^{-0.5}$	ΔE_μ /kJ mol^{-1}	$\Delta\Delta E_\mu$ /kJ mol^{-1}
$[CH_3OC(O)]_2$	31.7	72.5	13.70	−3.6	−12.3
$[CH_3(CH_2)_4C(O)OCH_2]_2$	23.7	71.0	14.02	0.3	−8.6
$[CH_3(CH_2)_4C(O)OCH_2CH_2]_2O$	23.7	68.8	13.73	−0.4	−9.3
$CH_3O(O)C(CH_2)_3C(O)OCH_2CH_3$	23.7	74.8	14.46	2.2	−6.7
$[CH_2C(O)O(CH_2)_2CH_3]_2CH_2$	23.7	76.6	14.67	6.0	−2.9
$[CH_2C(O)O(CH_2)_3CH_3]_2CH_2$	23.7	76.1	14.61	5.5	−3.4
$[CH_3CH_2C(O)OCH_2]_2C(CH_3)_2$	23.7	78.6	14.89	8.0	−0.9
$[CH_3(CH_2)_3C(O)OCH_2]_4C$	23.7	76.8	14.69	6.2	−2.7
$[CH_3(CH_2)_6C(O)OCH_2CH_2]_2O$	23.7	77.3	14.72	6.5	−2.4
$[CH_3C(O)OCH_2]_4C$	23.7	77.6	14.78	7.0	−1.9
$[CH_3CH_2C(O)OCH_2]_4C$	23.7	75.8	14.55	5.1	−3.8
$[CH_3(CH_2)_8C(O)OCH_2]_4C$	23.7	69.6	13.85	−1.1	−10.0
$[CH_3CH_2C(O)OCH_2]_3CCH_2CH_3$	23.7	77.4	14.76	6.8	−2.1

A different picture is observed when a polar molecule is attacked by a polar radical ($HO^\bullet$, $RO^\bullet$, $RO_2^\bullet$). The reaction in a polar solvent is slower than in a nonpolar hydrocarbon solution or in the gas phase. From the change in the parameter br_e, it is possible to estimate the extent to which the activation energy increases as a result of the solvation of the polar reactants:[74]

$$\Delta E_{sol} = \frac{(br_e)_l^2 - (br_e)_g^2}{(1+\alpha)^2}. \quad (40)$$

The subscripts l and g in Eqn (40) refer to the liquid and gas phases respectively. The results of the comparison are presented in Table 11. If the $HO^\bullet$ + YH reaction takes place in aqueous solution and not in the gas phase, the parameter br_e and hence the activation energy increase. This is associated with the solvation of the reactants and the need to overcome the solvation shell by the reacting component in order to effect the elementary step. The contribution of ΔE_{sol} is particularly large in the reaction of the hydroxyl radical with aldehydes.

When a radical or atom attacks a polar O–H or N–H bond, the reactant Y forms a hydrogen bond of the type O–H...Y or N–H...Y in polar solvents.[81, 82]

The hydrogen bond shields the reactant and slows down the reaction regardless of what kind of radical — polar or nonpolar — attacks it. A universal kinetic scale has been proposed [83] for the estimation of the effectiveness of such shielding. This problem has been examined in detail in a monograph.[84]

Table 11. The contributions of the solvation effect to the activation energies for radical reactions.[74]

RH	$(br_e)_g$ /kJ$^{0.5}$ mol$^{-0.5}$	$(br_e)_l$ /kJ$^{0.5}$ mol$^{-0.5}$	ΔE_{sol} /kJ mol^{-1}
$HO^\bullet$ + RH reaction (in water)			
CH_3OH	13.91	14.26	3.1
CH_3CH_2OH	13.48	14.01	4.6
$(CH_3)_2CHOH$	13.31	14.12	7.1
$(CH_3)_3COH$	13.39	14.13	6.5
CH_3OCH_3	13.95	14.70	6.8
$(C_2H_5)_2O$	13.47	14.33	7.6
CH_2O	13.84	14.98	10.4
CH_3CHO	13.81	14.99	10.8
CH_3COCH_3	13.81	14.50	6.3
CH_3COOCH_3	14.38	14.97	5.5
$(CH_3)_3CO^\bullet$ + RH reaction (in CH_3COCH_3)			
CH_3COCH_3	12.67	13.17	7.2

XIII. Estimation of bond strength from kinetic data

The IP and MPC methods make it possible to calculate correctly the dissociation energies of bonds subjected to radical attack.[85, 86] The parameter br_e and the enthalpy of reaction $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$ (see above) are used in such calculations. In order to increase the accuracy of the calculation, the rate constants for two different reactions (1 and *i*) are measured by one method. Within the limits of the same reaction series, the pre-exponential factor calculated per reacting bond remains constant, so that the difference between the activation energies for reactions with participation of the reactants R^1H and R^iH is

$$\Delta E_{e,i} = E_{e,i} - E_{e,1} = RT \ln \frac{n_i k_1}{n_1 k_i}. \quad (41)$$

In the IP model, the relation between E and ΔH is described by Eqns (2)–(4). The following relation between the bond strength difference $\Delta D_i = D_i - D_1$ and $\Delta E_{e,i}$ follows from them:

$$\Delta D_i = \frac{2br_e}{\alpha^2}(E_{e,i}^{1/2} - E_{e,1}^{1/2}) - \left(\frac{1}{\alpha^2} - 1\right)\Delta E_{ei}. \quad (42)$$

For $\alpha = 1$, where the force constants of the reacting bonds are identical and $\Delta E_{e,i} \ll E_{e,1}$, we obtain

$$E_{e,i}^{1/2} = \tfrac{1}{2} br_e + \frac{\Delta H_e}{2br_e} \quad \text{and} \quad E_{e0}^{1/2} = \tfrac{1}{2} br_e.$$

For a single reaction series, $\Delta D_i = \Delta H = \Delta H_e$, whereupon

$$E_{e,i}^{1/2} - E_{e,1}^{1/2} = \frac{\Delta D_i}{2br_e} = \frac{\Delta D_i}{4E_{e0}^{1/2}}.$$

Since

$$E_{e,i}^{1/2} = (E_{e,1} + \Delta E_i)^{1/2} = \left[E_{e,1}\left(1 + \frac{\Delta E_i}{E_{e,1}}\right)\right]^{1/2} \approx$$

$$\approx E_{e,1}^{1/2}\left(1 + \frac{\Delta E_i}{2E_{e,1}}\right),$$

it follows that

$$E_{e,i}^{1/2} - E_{e,1}^{1/2} = \frac{\Delta E_i}{2E_{e,1}^{1/2}}.$$

Hence

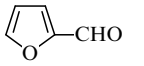
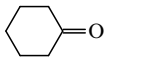
$$\frac{\Delta E_i}{2E_{e,1}^{1/2}} = \frac{\Delta D_i}{4E_{e0}^{1/2}},$$

and the following simple formula is obtained:

$$\Delta D_i = 2\left(\frac{E_{e0}}{E_{e,1}}\right)^{1/2}\Delta E_{ei}\,. \qquad (43)$$

Eqns (42) and (43) are applicable to reactions in the same reaction series for which $\Delta H_{e,\min} < \Delta H_e < \Delta H_{e,\max}$ [Eqns (28) and (29) and Table 3]. In the case of very exothermic reactions ($\Delta H_e < \Delta H_{e,\min}$), the activation energy is independent of the enthalpy, while for endothermic reactions ($\Delta H_e > \Delta H_{e,\max}$) we have $\Delta E = \Delta D_i$. This method has been used to estimate the strength of the C–H bonds in hydrocarbons[85] and oxygen-containing compounds,[86] the O–H bonds in phenols[87] and hydroxylamines,[45] the N–H bonds in amines,[46] and the C–Cl, C–Br, and C–I bonds in halogen-containing compounds.[88]

Table 12. Dissociation energies of the C–H bonds in oxygen-containing compounds estimated by the IP[87] and MPC[90] methods.

Compound	D /kJ mol^{-1}		
	IP	MPC	literature data
CH_3CH_2OH	391.7±1.1	389.1±0.5	392.5
$(CH_3)_2CHOH$	382.2±1.2	376.6±0.8	380.7
$HOCH_2CH_2OH$	390		385.3
$HOCH_2(CH_2)_2CH_2OH$	389.5		
cyclo-$C_6H_{11}OH$	375.4	378.6±0.8	
$C_6H_5CH_2OH$	363.8±0.5	355.3	
$C_6H_5CH(CH_3)OH$	353.8±2.1	353.7	
CH_3COCH_3	394.1±0.9	395.9±0.7	389.1
$CH_3COCH_2CH_3$	386.1±2.1		386.2
$CH_3COCH(CH_3)_2$	381.8±2.4		
	377.8	379.6	
$C_6H_5COCH_3$		372.8	
$C_6H_5COCH_2CH_3$		367.3±0.1	
$C_6H_5COCH(CH_3)_2$	336.8	358.2	
$(C_6H_5CO)_2CH_2$	343.9		
$(C_6H_5CH_2)_2CO$	356.1		
$C_6H_5COCH(OH)C_6H_5$	329.1		
	382.6±2.7	385.3±1.1	
HCHO	377.1	379.7	369.4
CH_3CHO	377.9	376.7	365.3
C_6H_5CHO	339.6±1.5		
CH_3COOH	390.7±0.5	391.8±1.3	
$(CH_3)_2CHCOOH$	378.7±0.5	380.4±0.7	
cyclo-$C_6H_{11}COOH$	377.8		
$(CH_3CH_2)_2O$	386.8		386.2
$ROCOCH_3$	394.8	395.0±0.3	389.1
$ROCOCH_2R$	388.3±0.7	388.4	
$ROCOCHR_2$	384.1	381.1±0.6	

A similar method has been developed on the basis of the MPC model.[86] In order to calculate the dissociation energy of the attacked bond, a system of two equations , one of which refers to the ith reaction and the other to the reference reaction 1, is solved numerically (for $D_{e,i}$):

$$br_e + D_{e,1}^{1/2}\ln\left[1-\left(\frac{E_{e,1}}{D_{e,1}}\right)^{1/2}\right] + \qquad (44)$$

$$+\alpha D_{ef}^{1/2}\ln\left[1-(E_{e,1}-\Delta H_{e,1})^{1/2}\right] = 0\,,$$

$$br_e + D_{e,i}^{1/2}\ln\left[1-\left(\frac{E_{e,i}}{D_{e,i}}\right)^{1/2}\right] + \qquad (45)$$

$$+\alpha D_{ef}^{1/2}\ln\left[1-(E_{e,i}-\Delta H_{e,i})^{1/2}\right] = 0\,.$$

By solving Eqn (45), the value of $E_{e,i}$ is found and then $D_{e,i}$ is obtained taking into account the equality $E_{e,i} = E_{e,1} + \Delta E_{e,i}$. The m has been used to calculate the dissociation energies of the C–H bonds in hydrocarbons[89] and oxygen-containing compounds.[90] Table 12 presents the values of D(C–H) calculated by the two methods from experimental data. These results agree well with one another. The average error in the estimation of ΔD_i by the IP and MPC methods is 2 and 1.6 kJ mol^{-1} respectively. The estimate by the MPC method is more accurate, but it is applicable to a narrower range of variation of ΔE_i (from −20 to +25 kJ mol^{-1}) than in the IP method (from −30 to +50 kJ mol^{-1}). Both methods make it possible to estimate ΔD_i more accurately than by the Polanyi–Semenov method.

XIV. Characteristic features of bimolecular reactions with high absolute enthalpies

The activation energies for highly exothermic radical reactions are known to be virtually zero. The disproportionation of alkyl radicals belongs to such reactions. The rate constants for reactions of this kind and the temperature ranges in which k = const are presented below.

Reaction	$10^{-9}\,k$ /litre mol^{-1}	T/K	Ref.
$Me^{\bullet} + Et^{\bullet}$	1.15	300–800	91
$Me^{\bullet} + Me_2CH^{\bullet}$	4.53	300–2500	92
$Et^{\bullet} + Et^{\bullet}$	1.40	300–1200	93
$Et^{\bullet} + Me_2CH^{\bullet}$	2.51	300–2500	92

In a liquid, such fast reactions are limited by the frequency of the diffusional encounters and their activation energies are characteristic of the diffusion of species in a liquid. The IP and MPC models agree with this observation. According to the IP model, each group of reactions is characterised by the parameter br_e = const. The lower the value of ΔH_e, the lower the position of the point of intersection of the parabolic potential curves on the potential energy axis (Fig. 4). For $\Delta H_{e,\min} = \Delta H_e$ the curves intersect at the point corresponding to the zero-point vibration energy of the ruptured ith bond. At this point, $E_{e0} + 0.5hLv_i$ and $E = 0.5RT$. Such activation energy is retained for all reactions with $\Delta H_e < \Delta H_{e,\min}$. Analysis within the framework of the MPC model also leads to a similar result.

The question of the pre-exponential factors for such reactions has been recently examined.[45] For a separate group of reactions, the quantity A calculated for a single attacked bond is virtually constant. For example, for all reactions of the type $RO_2^{\bullet} + R^1H$, occurring in a hydrocarbon solution (R^1H is an aliphatic hydrocarbon), we have $A = 10^8 n$ litre mol^{-1}s^{-1}, where n is the number of C–H bonds with equivalent reactivities. This is valid for reactions with $\Delta H_{e,\min} < \Delta H_e < \Delta H_{e,\max}$. For $\Delta H_e < \Delta H_{e,\min}$, the parameter r_e increases with increase in ΔH_e, since the potential curves cannot intersect below point C (Fig. 4). With increase in r_e, the cross-section for the collision of a radical and a molecule and hence also the pre-exponential factor A increase. The dependence of A on ΔH is described by the formula[45]

$$\left(\frac{A}{A_0}\right)^{1/2} = 1 + \beta(|\Delta H_e|^{1/2} - |\Delta H_{e,\min}|^{1/2})\,, \qquad (46)$$

where A_0 is a pre-exponential factor typical for the given group of reactions.

The same happens with increase in ΔH_e. When the curves intersect at point L (Fig. 4), there comes a time when the $\Delta H_e > \Delta H_{e,\max}$ curves intersect at a distance exceeding the con-

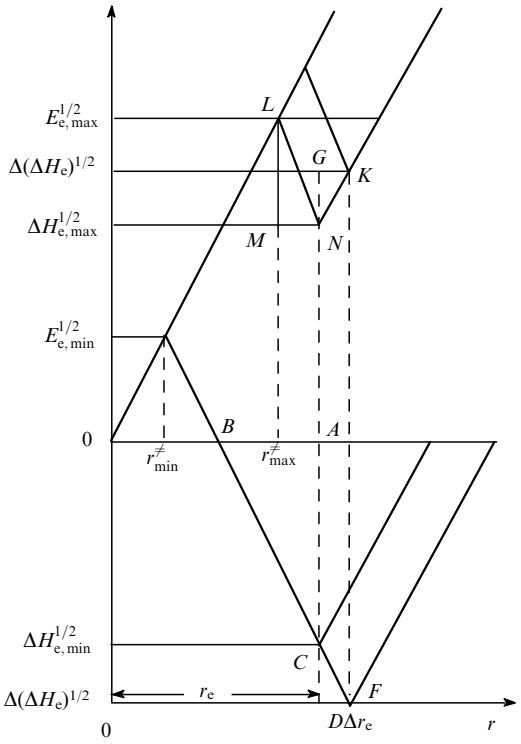


Figure 4. The energy profile for radical abstraction reactions over a wide range of variations of ΔH_e (IP model).[45] For $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$, the parameter r_e = const. Beyond these limits, r_e increases by Δr_e (parabolas with vertices at points K and F).

stant value of r_e for the given group of reactions. For such reactions, $E = \Delta H_e + 0.5RT$, while the pre-exponential factor depends on ΔH_e (Fig. 5).[45]

$$\left(\frac{A}{A_0}\right)^{1/2} = 1 + \beta(|\Delta H_e|^{1/2} - |\Delta H_{e,max}|^{1/2}) \,. \qquad (47)$$

The coefficient β = 1.0 and 1.6 for reactions with C...H...C and O...H...O reaction centres respectively. Table 3 presents the values of $\Delta H_{e,min}$ and $\Delta H_{e,max}$ calculated by Eqns (28) and (29).

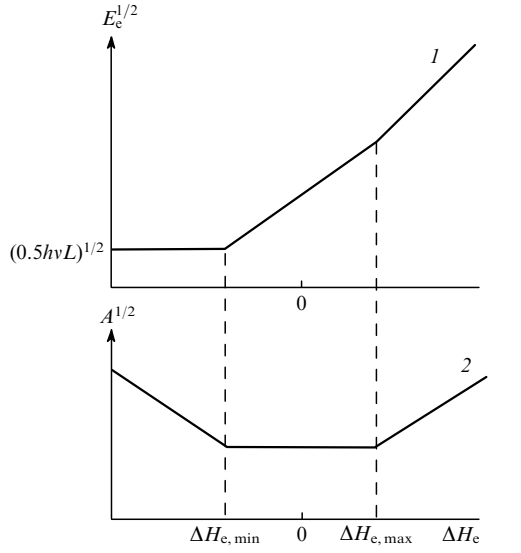


Figure 5. Dependence of E_e (*1*) and A (*2*) on ΔH_e according to the IP model.[45]

Evidently the range of H_e in which $A = A_0$ = const depends on the parameter br_e and varies within wide limits. Eqns (46) and (47) make it possible to calculate the rate constants for highly exothermic and highly endothermic reactions. As an example, Table 13 presents the results of the calculation of the quantities ΔH, A, and k (at 400 K) for the reactions of a stable nitroxyl radical — 2,2,6,6-tetramethylpiperidinyloxyl — with a series of phenols.

Table 13. Dissociation energies of the O–H bonds of phenols and the kinetic parameters of the reactions of 2,2,6,6-tetramethylpiperidinyloxyl with various phenols calculated by the Arrhenius equation taking into account Eqn (47).

Phenol	D	E	$10^{-8}A$	k (400 K)
	/kJ mol^{-1}		/litre mol^{-1} s^{-1}	
p-Cresol	357.8	68.3	9.32	1.12
Hydroquinone	350.3	60.8	10.54	12.12
1-Naphthol	341.4	51.9	1.77	29.65
2-Naphthol	351.8	62.3	6.01	4.40
1-Hydroxy-phenanthrene	352.7	63.2	6.47	3.62
Phenol	367.0	77.5	15.41	0.12
4-Acetylphenol	369.5	80.0	17.25	6.17×10^{-2}
4-Aminophenol	354.7	65.2	7.54	2.31
4-Benzyloxy-phenol	347.5	58.0	4.00	10.69
4-Bromophenol	370.6	81.1	18.09	4.65×10^{-2}
4-Butoxyphenol	345.8	56.3	3.31	14.71
4-*tert*-Butyl-phenol	356.9	67.4	8.79	1.39
4-Methoxyphenol	349.0	59.5	4.66	7.93
3,4-Dimethylphenol	352.6	63.1	6.42	3.70
2,6-Dimethylphenol	354.9	65.4	7.65	2.21
4-Nitrophenol	369.7	80.2	17.41	5.86×10^{-2}
4-Phenylphenol	357.4	67.9	9.08	1.24
Pentamethylphenol	338.5	49.0	1.00	39.95
Resorcinol	365.8	76.3	29.12	0.32

XV. Conclusion

Thus the successive employment of the IP and MPC models for the analysis of the reactivities of the reactants in radical abstraction reactions yield very similar results. These models make it possible to divide all radical abstraction reactions into classes and to characterise quantitatively each class by a pair of force constants for the ruptured and generated bonds (b_i and b_f). In both models, these parameters are naturally identical. Each class of reactions may consist of one or several groups of reactions. All the reactions of a given group are characterised by a single parameter r_e and the energy of a thermally neutral reaction E_{e0}. The parameters r_e in the IP and MPC models differ but the values of E_{e0} are very similar. Each individual reaction is additionally characterised by the enthalpy. Thus an individual radical reaction is characterised in both models by four parameters: b_i, b_f, E_{e0}, and ΔH_e. Their number can be reduced to three: $\alpha = b_i/b_f$, $b_i r_e$, and ΔH_e.

Analysis with the aid of the IP and MPC models of extensive experimental data on the kinetics of radical reactions has shown that the reactivities of the interacting molecules and radicals are determined by diverse physical factors. The following 10 factors which determine the height of the potential barrier in radical abstraction reactions have been revealed.

1. The enthalpy of reaction ΔH_e. For low values of this enthalpy, the dependence of the activation energy E_e on ΔH_e assumes the form $E_e^{1/2} = E_{e0}^{1/2} + \alpha\Delta H_e$.

2. The force constants of the ruptured and generated bonds. A correlation between E_{e0} and the force constant of the C–X bond

has been established for the first time in relation to the reactions of a hydrogen atom and alkyl radicals with alkyl halides.

3. The strength of the X–Y bond in the $X^{\bullet}$ + HY reactions. The stronger this bond, the higher the activation energy. This relation is due to triplet repulsion in the transition state when one of three electrons occupies the nonbonding X–Y orbital.

4. The electronegativities of the fragments (radicals) X and Y. The difference between the electronegativities of these fragments (ΔEA) induces their attraction in the transition state, which lowers the activation energy. The quantity ΔE_{e0} is proportional to $-\Delta EA$.

5. The radii of the atoms X and Y, between which a hydrogen atom or some other atom is transferred. The greater the radii, *i.e.* the longer the X–Y bond, the stronger the repulsion in the transition state, and the greater the activation energy. It has been established empirically that the quantity ΔE_{e0} is proportional to $r_{X-Y}^{1/2}$.

6. The presence of a polar group in the molecule or radical. It influences the activation energy if the reaction centre is also polar ($\Delta EA \neq 0$). Both models make it possible to separate the influence of the polarity of the X–Y bond on the enthalpy of reaction (the polar factor) and the influence of the polar group on the activation energy for a thermally neutral reaction and also to estimate the contribution of each factor to the activation energy.

7. The presence of several polar groups in the molecule. In this case, the multidipole interaction effect, influencing the activation energy, arises. This effect differs significantly from the influence of a single polar group on the activation energy.

8. The presence of a π-bond or an aromatic ring in the α-position relative to the attacked C–H bond. The activation energy E_{e0} increases in their presence apparently as a result of the increase in the triplet repulsion between X and Y.

9. The presence of bulky groups next to the reaction centre. These groups exert a steric effect, increasing E_{e0}.

10. The solvent polarity. The solvation effect is manifested in a polar solvent if both reactants incorporate polar groups.

Some of the factors enumerated, which influence the activation energy, were not examined previously. They include the force constants of the reacting bonds, the electronegativites of the fragments X and Y, the radii of the atoms X and Y, and the presence of a π-bond next to the reaction centre. The parameters found from experimental data may be used to estimate the activation energy and the rate constants of radical abstraction reactions. The existence of correlation equations for E_{e0} or r_e makes it possible to estimate these parameters for new classes of reactions which have not yet been investigated. The bond dissociation energies can also be calculated from kinetic data with the aid of the IP and MPC methods. Overall, the models described above constitute an effective instrument for the analysis of kinetic parameters of radical reactions.

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