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Transition state geometry in radical hydrogen atom abstraction

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Abstract. The interatomic distances in the transition states of radical hydrogen atom abstraction reactions $X^{\bullet} + HY \longrightarrow XH + Y^{\bullet}$ determined by quantum chemical calculations are systematized and generalized. It is shown that depending on the reaction centre structure, these reactions can be subdivided into classes with the same X...Y interatomic distance in each class. The transition state geometries found by the methods of intersecting parabolas and intersecting Morse curves are also presented. The X...H...Y fragments are almost linear, the hydrogen atom position being determined by the reaction enthalpy. The effects of triplet repulsion, electronegativities and radii of X and Y atoms, the presence of adjoining π-bonds, and steric effects on the X...Y interatomic distances are analyzed and characterized. The bibliography includes 62 references.

I. Introduction

The energy and structure parameters such as atom positions, bond lengths and angles between the bonds are important characteristics of molecules, radicals, ions and radical ions. The transition state (TS) of a chemical reaction is characterized by the activation enthalpy, energy and entropy, on the one hand, and by the geometry of the reaction centre atoms, on the other hand. The energy characteristics of chemical reactions can be measured by experimental methods. Available data for radical reactions are collected in reference books and databases.[1–10]

The situation with geometric characteristics of TSs of radical reactions is different. Quantum chemical calculations remain the only source of these data. The number of radical reactions for which the TS geometries are known is not large in comparison with the number of reactions for which the activation energies and enthalpies have been determined. A new semiempirical method for calculation of interatomic distances in TSs of radical reactions was developed recently.[11] It consists in a combination of quantum chemical calculations and intersecting parabolas model and opens up the possibility for fast assessment of geometric parameters of TSs using the experimental enthalpy and activation energy values for a reaction. The geometric parameters obtained in this way practically coincide with those resulting from quantum chemical calculations. A considerable work was performed in this direction and the geometries were determined for a large number (>500) of radical reaction TSs.[12–20] Analysis of the data obtained revealed the factors affecting the geometries of TSs of radical hydrogen atom abstraction and made it possible to characterize the contribution of each of them to the interatomic distances in the reaction centre quantitatively by an increment or a correlation coefficient.

The present review gives account of the results of quantum chemical calculations and calculations according to the intersecting parabolas and intersecting Morse curves models and analyses various factors influencing the geometry of TSs of the radical hydrogen atom abstraction.

II. Quantum chemistry of the transition state geometry for radical abstraction reactions

Hydrogen atom abstraction plays an important role in chemical and biological processes.[21] Due to the fundamental significance of these reactions, repeated attempts at their

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systematic theoretical description were undertaken in order to elucidate the effects on their TSs from such key factors as energies of breaking and forming bonds, the Pauli repulsion and polar and steric effects.[22,23] The Evans–Polanyi approach was historically the first one,[24] it was extended by Semenov[25] to the radical hydrogen atom abstraction reactions. This approach predicts a linear dependence between the activation energy (E_a) and the reaction enthalpy (ΔH)

$$E_a = E_0 + \alpha \Delta H \quad (1)$$

where the coefficient α can be considered as a measure of the TS position on the reaction coordinate.[26] The value $\alpha \approx 0$ corresponds to a reactant-like TS, while $\alpha \approx 1$ means a product-like TS. The Polanyi–Semenov equation (1) has a clear physical meaning if the notions of chemical inertia and chemical driving force introduced by Evans and Polanyi[27] are used. The chemical inertia is characterized by the intrinsic barrier or the activation energy (E_0) of a thermoneutral reaction, whereas the driving force is the difference between the energies of breaking and forming bonds (ΔH). However, the linear correlations are inaccurate. Attempts to improve the situation using additional theoretical parameters and supplementary empirical correlative relations (see, for instance, Ref. 28) resulted in rather complicated expressions.

The fundamental importance of the Polanyi–Semenov equation consists in separation of kinetic and thermodynamic contributions to the activation energy of a reaction. This idea is also contained in the known Marcus equation[29] for the electron transfer

$$\Delta G^{\neq} = E_r\left(1 + \frac{\Delta G}{4E_r}\right)^2 \quad (2)$$

which relates the free activation energy ($\Delta G^{\neq}$) to the free energy of a reaction (ΔG) and kinetic factor (E_r).

Being simple in its form, nonlinear relationship (2) is quite precise. Its modified version was suggested by Marcus for the atom transfer reactions.[30] There are also other nonlinear models,[31] for example, the intersecting-state model.[32,33] The latter is based on the bond energy–bond order principle and the postulate of total bond order conservation along the reaction coordinate. This model enables one to calculate E_a and to determine the geometry of TS from experimental bond energies and spectroscopic data. The results obtained using sophisticated models that go beyond simple linear correlations between the kinetic and thermodynamic parameters are in rather good agreement with the data of the precise calculations and experiments. However, the use of such models requires extra experimental data besides specific calculations using experimentally obtained reaction enthalpies.[34]

Nevertheless, the experience of chemical studies indicates that small changes in the molecular structure result in small variations in reactivity, and this fact is substantiated theoretically.[35] It is therefore necessary to search for simpler phenomenological approaches. These include the generalized Polanyi–Semenov model[36] and the intersecting parabolas model,[37,38] resulting in parabolic dependence of E_a on ΔH. In both models, there is a structural aspect that implies the possibility of finding the geometrical parameters of TSs.

The generalized Polanyi–Semenov model follows from analysis of TSs of radical hydrogen atom abstraction reactions in terms of the valence bond method with simplifying assumptions.[39,40] In this method, the cross-section of a potential energy surface in the TS region along the reaction coordinate is formed by pseudo-intersection of terms E_1 and E_2 (Fig. 1). Taking into account the resonance energy B, which determines the matrix element of interaction between diabatic terms E_1 and E_2, the lower adiabatic term E in the vicinity of TS has the form

$$E = \frac{E_1 + E_2}{2} - \sqrt{B^2 + \left(\frac{E_1 - E_2}{2}\right)^2} \approx \quad (3)$$

$$\approx \frac{E_1 + E_2}{2} - B - \frac{(E_1 - E_2)^2}{8B}$$

The positions of the initial terms E_1 and E_2 in the terminal points of the dimensionless reaction coordinate (q) are determined by the excited state energies of reactants at $q = 0$

$$E_1(0) - E_2(0) = E_r$$

and products at $q = 1$

$$E_2(1) - E_1(1) = E_p,$$

as well as by the reaction enthalpy

$$E_1(1) - E_2(0) = \Delta H$$

For simplicity, it can be assumed that the terms are linear throughout (calculations using the valence bond method showed little deviation from linearity)[41]

$$-\frac{dE_1}{dq} = E_r - \Delta H = \text{const} \quad (4)$$

$$\frac{dE_2}{dq} = E_p + \Delta H = \text{const}$$

The location of the intersection point for the terms E_1 and E_2

$$q_0 = \frac{E_r}{E_r + E_p}$$

does not depend on the reaction enthalpy,[42] although the barrier height E_a and location of TS (coordinate $q^{\neq}$) are dependent on ΔH. This follows from Eqn (3), which can be represented in the canonical form taking into account Eqns (4)

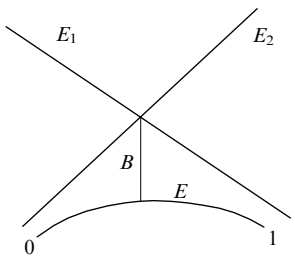


Figure 1. Cross-section of the potential energy surface in the vicinity of TS along the reaction coordinate.

$$E(\Delta H, q) = E_0 + \Delta H q - \frac{W(q - q^{\neq})^2}{2} \quad (5)$$

where the parameters

$$E_0 = \frac{E_r E_p}{E_p + E_r} - B + \frac{1}{2W}\left(\frac{E_p - E_r}{2}\right)^2$$

$$W = \frac{(E_p + E_r)^2}{4B}$$

determine the activation energy of the thermoneutral reaction and the potential barrier steepness, respectively. In the general case, the TS coordinate of the thermoneutral reaction

$$q^{\neq} = q_0 + \frac{E_p - E_r}{2W} \quad (6)$$

differs from the coordinate of the intersection point of the terms. It is important that the dependence of $E(\Delta H,q)$ on ΔH is linear. Under the adopted assumptions, this is a direct consequence of the fact that the difference between the terms $(E_1 - E_2)$ does not depend explicitly on ΔH. Taking reactions of alkyl radicals with alkanes as an example, it was demonstrated [36] that the reaction energy profile obtained in quantum chemical calculations as a function of the reduced reaction coordinate q corresponds to Eqn (5) in the vicinity of TS.

Analytical dependence (5) can be used to analyze the influence of the reaction enthalpy on TS characteristics. Due to the ΔHq term, the potential energy maximum shifts along the reaction coordinate

$$q^{\neq}(\Delta H) = q^{\neq} + \frac{\Delta H}{W} \quad (7)$$

that is, the increase in the reaction heat leads to earlier TSs, while its decrease results in later TSs in accordance with the Hammond principle. The energy at the maximum point (reaction barrier) is

$$E_a(\Delta H) = E_0 + \Delta H q^{\neq} + \frac{\Delta H^2}{2W} \quad (8)$$

This equation is a generalization of the Polanyi–Semenov equation. It can be represented in the following form:

$$E_a(\Delta H) = E_0 + \Delta H\left(q^{\neq} + \frac{\Delta H}{2W}\right) \quad (9)$$

This expression explains why in terms of the Polanyi–Semenov equation (1), the α values are considerably lower for exothermic reactions ($\Delta H < 0$) than for endothermic ones ($\Delta H > 0$). When using Eqn (9), bear in mind that E_a and ΔH do not include the contribution of zero-point vibrations.

The constancy of E_0 and W in Eqn (5) is necessary for applying expression (9) to comparison of different reactions with different enthalpies. Obviously, this situation arises if series of related reactions $X^{\bullet}$ + YH with a similar reaction centre are considered. If the reaction is symmetric, *i.e.*, X = Y, the transition state is symmetric as well. Then it can be taken that $q^{\neq} = 1/2$, and Eqn (9) acquires a simple two-parametric form

$$E_a = E_0 + \frac{1}{2}\Delta H + \frac{\Delta H^2}{2W} \quad (10)$$

The equality $q^{\neq}(\Delta H) = 1/2$ holds for any thermoneutral reaction (Ref. 43); therefore, Eqn (10) may also be fulfilled for non-symmetric reactions. Theoretical analysis has shown [36] that the key parameter W determining the parabolic form of the potential barrier can be explicitly related to some characteristics of the potential energy surface in the vicinity of TS, namely to the TS geometry, the force constant of the vibration with imaginary frequency $k^{\neq}$ and also to the form of this vibration. In a particular case, if its form mainly implies migration of only a hydrogen atom, then

$$W \approx k^{\neq}(\Delta r_{X-H} + \Delta r_{Y-H})^2 \quad (11)$$

where Δr_{X-H} and Δr_{Y-H} represent the change in the breaking and forming bond lengths, respectively, in the TS. The feasibility of this relation was examined for a series of radical reactions of hydrogen atom abstraction.[44] The direct calculation of W by Eqn (11) and calculation of the term curvature as a function of q in the vicinity of TS gave comparable results.

The phenomenological intersecting parabolas model developed for reactions with symmetric reaction centre [22,23] also leads to the square-law dependence of the activation energy on the reaction enthalpy

$$E_a(\Delta H) = E_0 + \frac{\Delta H}{2} + \frac{\Delta H^2}{16 E_0} \quad (12)$$

which involves a single parameter, namely, the activation energy E_0 of the thermoneutral reaction. An advantage of this one-parameter equation consists in possibility to obtain the E_0 value for each particular reaction (with known activation energy and enthalpy) directly from experimental data according to the equation

$$\sqrt{E_0} = \frac{1}{2}\left(\sqrt{E_a} + \sqrt{E_a - \Delta H}\right) \quad (13)$$

Thus, one can easily find reaction classes with approximately equal E_0 values.

In the intersecting parabolas model, the activation energy of a thermoneutral reaction can be considered not only as an empirical parameter. It is determined analytically from the force constants k of the X–H and Y–H stretching vibrations and total elongation Δr_{X-H} and Δr_{Y-H} of these bonds in the reaction centre of TS

$$E_0 = \frac{k}{8}\left(\Delta r_{Y-H} + \Delta r_{X-H}\right)^2 \quad (14)$$

As can be seen from Eqn (12), the $8E_0$ value in the intersecting parabolas model is an analogue of W. Taking into account expression (14), the relation between W and E_0 is the following:

$$W \approx \frac{k^{\neq}}{k} 8 E_0 \quad (15)$$

Typically, $k^{\neq} < k$; therefore, the calculation of total bond elongation in the TS from the E_0 value results in

some error. Nevertheless, Eqn (14) can be used as a basis of an empirical approach for assessment of TS characteristics from the reaction enthalpy and activation energy of a thermoneutral reaction. Indeed, it was demonstrated [11–13, 45] that the sums $\Delta r_{X-H} + \Delta r_{Y-H}$ obtained using the intersecting parabolas model and quantum chemical calculations are constant for reactions of the same class, their ratio is characterized by a coefficient β. Thus, a new semi-empirical method of calculation of interatomic distances in the reaction centre of radical reaction TS can be suggested, which is able to estimate both the total elongation of bonds in the TS and the partial elongations Δr_{X-H} and Δr_{Y-H} with a good accuracy. This approach with the variable quantity β is more flexible than the approach using a fixed ratio of the total bond elongation to the sum of their equilibrium values [46]

$$1 + \frac{\Delta r_{Y-H} + \Delta r_{X-H}}{r_{Y-H} + r_{X-H}} = 1.25 \pm 0.04 \qquad (16)$$

During the hydrogen atom transfer, the current distance $r_{Y-H}(q)$ increases as compared to its equilibrium value $r_{Y-H}(0) = r_{Y-H}$ to a value of about the van der Waals contact $r_{Y-H}(1)$ in the post-reaction complex. Similarly, the current distance $r_{X-H}(q)$ decreases from the value of about the van der Waals contact $r_{X-H}(0)$ in the pre-reaction complex to its equilibrium value $r_{X-H}(1) = r_{X-H}$. Therefore, the difference $r_{Y-H}(q) - r_{X-H}(q)$ changes considerably, being an alternating function of q. Obviously, the sum $r_{Y-H}(q) + r_{X-H}(q)$ also varies during the reaction, and it is expected to increase when $q \to 0$ or $q \to 1$. As a result, the sum $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ may increase for reactions with large heat evolution and reactant-like TS and for reactions with large heat consumption and product-like TS relative to this sum for analogous reactions with small heats. To elucidate the magnitude of this effect, the data of theoretical calculations of TS structures for hydrogen atom transfer reactions with C...H...C and O...H...C reaction centres were analyzed. [11, 12, 20, 47–54]

These data were mainly obtained either by DFT B3LYP calculations using the 6-31G* basis set or extended basis sets with additional diffuse and polarisation functions by the QCISD [47, 49] calculations with the same basis sets. It was shown [11, 47, 50] that the method of account for electron correlation [density functional theory, Møller–Plesset perturbation theory (MP2 and MP4), the coupled cluster method] has insignificant effect on the TS geometry (maximum variation in the bond lengths is within a few hundredths of an angstrom). In the case of extended basis sets, the effect of completeness of the basis set on the TS geometry is even smaller. Unfortunately, the necessary data are available not in all theoretical studies of radical hydrogen atom abstraction reactions. It is especially true for recent theoretical studies of temperature dependences for such reactions in the wide temperature range. It is worth noting also that the values $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ and $r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq})$ reflect the trends in the variations of the sum and the difference of the bond lengths in TSs because of insignificant substituent effect on the element–H bond length (of the order of a few thousands of an angstrom).

The dependences of the calculated $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ and $r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq})$ values in TSs on the enthalpy changes in the reactions with the C...H...C and O...H...C reaction centres are shown in Figs 2 and 3.

The sum of bond lengths of the C...H...C reaction centre can accept one of three values close to 2.57, 2.73 and 2.80 Å (see Fig. 2). The maximum value is typical of reactions with

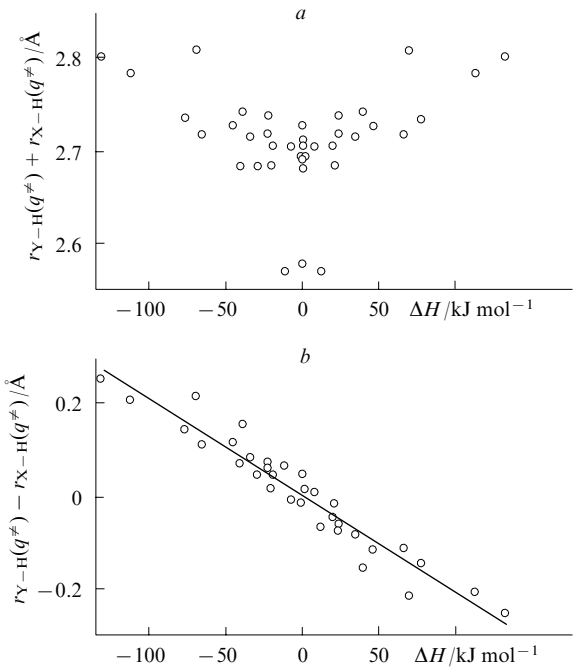


Figure 2. Dependences of the sum $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ (*a*) and the difference $r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq})$ (*b*) on ΔH for the hydrogen atom abstraction reaction with the C...H...C reaction centre.

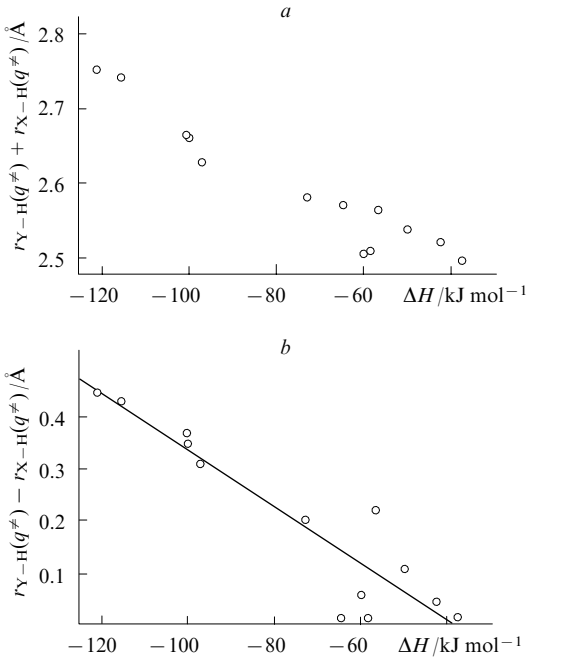


Figure 3. Dependences of the sum $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ (*a*) and the difference $r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq})$ (*b*) on ΔH for the hydrogen atom abstraction reaction with the O...H...C reaction centre.

strongly activated C−H bonds. In the group of thermoneutral reactions with $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ of about 2.57 Å (this group includes the reaction HCN + CN$^{\bullet}$, particularly), hybridization of carbon atoms in the reaction centre changes. For all the reactions, the following correlation is fulfilled rather well:

$$r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq}) = -\frac{2.8\,\Delta H}{1000}. \quad (17)$$

For the group of reactions of hydrogen atom abstraction from C−H bonds by O-centred radicals, including peroxyl radicals, a larger range of variation is also observed in the $r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq})$ values than in the $r_{Y-H}(q^{\neq}) + r_{X-H}(q^{\neq})$ values (see. Fig. 3). This scattering is due to simultaneous consideration of quite different reactions with participation of hydroxyl and peroxyl radicals, which belong to different reaction classes. In addition, the energy differences for the systems with O−O bonds are more sensitive to the method of calculations. One could also observe the following approximately linear dependence:

$$r_{Y-H}(q^{\neq}) - r_{X-H}(q^{\neq}) = -0.215 - \frac{5.47\,\Delta H}{1000}, \quad (18)$$

indicating a stronger effect of the reaction enthalpy on the TS geometry in these series of reactions in comparison with the reactions with the C...H...C reaction centre.

Thus, in accordance with the data of theoretical calculations of the TS geometries, linear dependence of the difference between bond lengths in the reaction centres on the reaction enthalpy is generally fulfilled

III. The parabolic model of radical abstraction

In the intersecting parabolas model, the abstraction reaction of the type

$$X^{\bullet} + HY \longrightarrow XH + Y^{\bullet}$$

is considered as an intersection point of two potential energy curves U_{Y-H} and U_{X-H}, each describig the stretching vibration of the corresponding bond depending on the vibration amplitude.[37,38,55] The vibrations are considered as harmonic and described by parabolic dependences

$$U_{Y-H} = (b\,\Delta r_{Y-H})^2$$

$$U_{X-H} = (b_f\,\Delta r_{X-H})^2$$

where $2\,b^2$ and $2\,b_f^2$ are the force constants of the Y−H and X−H bonds, respectively, Δr_{Y-H} and Δr_{X-H} are the changes in the bond lengths.

Each reaction in the intersecting parabolas model is characterized by the following parameters:[37,38]

— classical enthalpy

$$\Delta H_e = \Delta H + 0.5\,hN_A\,(\nu_{Y-H} - \nu_{X-H})$$

where ΔH is the reaction enthalpy, h is the Planck constant, ν_{Y-H} and ν_{X-H} are the Y−H and X−H stretching vibration frequencies, N_A is Avogadro's number;

— classical potential barrier

$$E_e = E + 0.5\,hN_A\nu_{Y-H} - 0.5\,RT$$

where E is activation energy, R is the absolute gas constant, T is temperature;

— coefficient b

$$b = 2\pi\nu_{Y-H}\sqrt{\mu_{Y-H}}$$

where μ is the reduced mass of the H and Y atoms;

— coefficient α

$$\alpha = \frac{b}{b_f} = \frac{\nu_{Y-H}\sqrt{\mu_{Y-H}}}{\nu_{X-H}\sqrt{\mu_{X-H}}}$$

— parameter r_e, which is the total elongation of the Y−H and X−H bonds in TS related to the energy characteristics of the reaction, ΔH_e and E_e, by the equation

$$r_e = b^{-1}\left(\sqrt{E_e} + \alpha\sqrt{E_e - \Delta H_e}\right) \quad (19)$$

The characteristics for some bonds are presented in Table 1.

Table 1. Characteristics of bonds which are used in the intersecting parabolas model.[56]

Bond	ν /cm^{-1}	$0.5\,hN_A\nu$ /kJ mol^{-1}	$b\times10^{-10}$ /(kJ mol^{-1})$^{1/2}$ m^{-1}	$r\times10^{10}$ /m
H−H	4401	26.3	41.26	0.741
C−H	2914	17.4	37.43	1.092
Cl−H	2990	17.9	39.01	1.275
Br−H	2649	15.8	35.26	1.414
I−H	2309	13.8	30.73	1.609
HO−H	3756	22.5	48.68	0.957
RO−H	3625	21.7	46.98	0.967
ROO−H	3550	21.2	46.00	0.967
ArO−H	3600	21.5	46.66	0.967
AmO−H	3600	21.5	46.66	0.967
N−H	3337	20.0	43.07	1.009
RS−H	2531	15.1	33.21	1.340
Si−H	2157	13.1	28.71	1.483
Ge−H	2100	12.6	27.95	1.525
Sn−H	2026	12.1	26.97	1.711

Note. The following designations are used: R is alkyl radical, Ar is aryl radical, Am is aminyl radical.

Table 2. The C−C bond elongations in reactions of alkyl radicals determined using the intersecting parabolas model (r_e) and quantum chemical calculations ($\Delta r^{\neq}_{C...C}$).[12]

Reaction	$r_e\times10^{10}$ /m	$\Delta r^{\neq}_{C...C}\times10^{10}$ /m	β
Alkyl radical + alkane			
$H_3C^{\bullet} + C_2H_6$	0.462	0.520	1.13
$MeH_2C^{\bullet} + C_2H_6$	0.462	0.520	1.13
$H_3C^{\bullet} + Me_2CH_2$	0.462	0.529	1.15
$H_3C^{\bullet} + Bu^nH$	0.462	0.537	1.16
$H_3C^{\bullet}$ + MeC(O)Me	0.462	0.521	1.13
Allyl radical + alkyl aromatic hydrocarbon			
$H_3C^{\bullet}$ + MePh	0.475	0.538	1.13
Alkyl radical + alkene			
$H_3C^{\bullet}$ + MeCH=CH$_2$	0.479	0.546	1.14

Note. The average value of the β coefficient is 1.14 ± 0.01.

Equation (19) provides the possibility of estimating interatomic distances in the TS from ΔH_e and E_e. It is highly important that r_e = const for reactions of the same class.[37, 38] However, comparison of the bond elongations in TSs determined from the intersecting parabolas model and by quantum chemical calculations (QCCs) demonstrated that $r_e < \left(\Delta r^{\neq}_{Y...H} + \Delta r^{\neq}_{X...H}\right)_{QCC}$,[11] although the following ratio is constant within the same reaction class:

$$\beta = \frac{\left(\Delta r^{\neq}_{H...Y}\right)_{QCC}}{r_e}$$

This is evident from comparison of these distances for the three classes of reactions (Table 2).

This constancy made it possible to correlate the r_e distances found using the intersecting parabolas model with the distances $\Delta r^{\neq}_{X...Y}$ determined by quantum chemical calculations. Thus, a simple semiempirical method for calculating geometric characteristics of the TS reaction centre *via* the reaction enthalpy and activation energy was suggested [the β coefficient is introduced into Eqn (19)].

In the case of abstraction reactions with symmetric reaction centres $X_i...H...X_f$ (the subscripts i and f refer to the breaking and forming bonds, respectively), the equations describing the distances $r^{\neq}_{X_i...H}$ and $r^{\neq}_{X_f...H}$ acquire the following simple form ($\Delta H_e = \Delta H$ and $\alpha = 1$ for such reactions):[11–13]

$$r^{\neq}_{X_i...H} = r_{X_i-H} + \frac{\beta r_e}{2} + \frac{\beta \Delta H}{2 b^2 r_e} \quad (20)$$

$$r^{\neq}_{X_f...H} = r_{X_f-H} + \frac{\beta r_e}{2} - \frac{\beta \Delta H}{2 b^2 r_e} \quad (21)$$

$$r^{\neq}_{X_i...X_f} = 2 r_{X-H} + \beta r_e \quad (22)$$

The parameters necessary for calculations of such reactions are presented in Table 3.

In the case of reactions with an asymmetric reaction centre X...H...Y, the equations describing the distances

Table 3. Geometric parameters of TSs for reactions with the symmetric X...H...X reaction centres.[12]

Reaction	$r_e \times 10^{10}$ /m	$(\Delta r^{\neq}_{X...H})_0 \times 10^{10}$ /m	$(\Delta r^{\neq}_{X...H})_{min} \times 10^{10}$ /m	$(\Delta r^{\neq}_{X...H})_{max} \times 10^{10}$ /m	$\frac{\beta}{2 b^2 r_e} \times 10^{14}$	ΔH_{max} /kJ mol^{-1}
H...H...H, β = 1.056						
H + H_2	0.354	0.177	0.124	0.230	8.79	63.6
C...H...C, β = 1.140						
$(R^1)^{\bullet}$ + HR^1	0.462	0.263	0.111	0.416	8.81	155.0
$(R^1)^{\bullet}$ + HR^2	0.497	0.283	0.111	0.455	8.19	190.8
$(R^1)^{\bullet}$ + HR^3	0.476	0.271	0.111	0.431	8.55	168.3
$(R^2)^{\bullet}$ + HR^2	0.500	0.285	0.111	0.459	8.14	194.3
$(R^2)^{\bullet}$ + HR^3	0.498	0.284	0.111	0.457	8.17	192.0
$(R^3)^{\bullet}$ + HR^3	0.420	0.239	0.111	0.367	9.69	116.0
N...H...N, β = 1.125						
$H_2N^{\bullet}$ + HNH_2	0.420	0.236	0.104	0.368	7.22	145.3
$H_2N^{\bullet}$ + HNHR	0.453	0.255	0.104	0.406	6.69	186.7
$H_2N^{\bullet}$ + HNR^2	0.474	0.267	0.104	0.429	6.40	216.8
$RHN^{\bullet}$ + HNHR	0.488	0.274	0.104	0.445	6.21	236.9
$RHN^{\bullet}$ + HNR^2	0.508	0.286	0.104	0.468	5.97	273.4
$R^2N^{\bullet}$ + HNR^2	0.527	0.296	0.104	0.489	5.75	314.4
$Ar^2N^{\bullet}$ + $HNAr^2$	0.270	0.152	0.104	0.200	11.23	31.2
HO...H...OH, β = 1.529						
$HO^{\bullet}$ + HOH	0.253	0.193	0.097	0.289	12.75	129.1
RO...H...OR, β = 1.547						
$RO^{\bullet}$ + HOR	0.290	0.224	0.099	0.350	12.08	61.3
O...H...O, β = 1.514						
$RO_2^{\bullet}$ + HOOR	0.285	0.216	0.100	0.331	12.55	51.5
$Ar^1O^{\bullet}$ + $HOAr^1$	0.270	0.204	0.099	0.310	12.88	42.1
$Ar^2O^{\bullet}$ + $HOAr^1$	0.283	0.214	0.099	0.329	12.29	51.8
$Ar^2O^{\bullet}$ + $HOAr^2$	0.308	0.233	0.099	0.367	11.29	73.2
β = 1.224						
R^3Si + $HSiR^3$	0.477	0.238	0.126	0.458	15.57	90.2

Note. The following notation is accepted here and below: R^1H are alkanes, R^2H are alkenes, R^3H are alkyl aromatic hydrocarbons, Ar^1OH are sterically unhindered phenols, Ar^2OH are sterically hindered phenols; zero as a subscript indicates that the parameter is referred to the thermoneutral process.

Table 4. Geometric parameters of the TSs for radical abstraction reactions with asymmetric reaction centres.[11, 13–16, 19]

Reaction	α	β	$\Delta r^{\neq}_{Y\ldots X} \times 10^{10}$ /m	$\frac{\Delta r^{\neq}_{Y\ldots H}}{\Delta r^{\neq}_{Y\ldots H}}$ (%)	$(\Delta r^{\neq}_{Y\ldots H})_{min} \times 10^{10}$ /m	$(\Delta r^{\neq}_{X\ldots H})_{min} \times 10^{10}$ /m	$\left(\frac{dr^{\neq}_{Y\ldots H}}{d\Delta H}\right) \times 10^{12}$ /m mol J^{-1}
$H^{\bullet}$ + R^1H	0.907	1.14	0.442	52.4	0.111	0.124	0.953
$H^{\bullet}$ + NH_3	1.044	1.12	0.456	48.9	0.104	0.124	0.773
$H^{\bullet}$ + H_2O	1.180	1.36	0.451	45.9	0.097	0.124	1.021
$H^{\bullet}$ + SiH_4	1.696	1.14	0.448	59.0	0.126	0.124	1.224
$H^{\bullet}$ + HSR	1.805	1.20	0.425	55.4	0.117	0.124	1.237
$(R^1)^{\bullet}$ + HSR	0.887	1.78	0.722	53.0	0.117	0.111	1.763
$(R^1)^{\bullet}$ + $HSiR^3$	0.767	1.43	0.655	56.6	0.126	0.111	1.446
$(R^1)^{\bullet}$ + $HGeR^3$	0.747	1.52	0.753	57.2	0.127	0.111	1.446
$(R^1)^{\bullet}$ + $HSnR^3$	0.721	1.70	0.861	58.1	0.129	0.111	1.658
$H_2N^{\bullet}$ + R^1H	0.868	1.12	0.410	53.5	0.111	0.104	0.949
$H_2N^{\bullet}$ + R^2H	0.868	1.12	0.449	53.5	0.111	0.104	0.866
$H_2N^{\bullet}$ + R^3H	0.868	1.12	0.433	53.5	0.111	0.104	0.899
$RO^{\bullet}$ + R^1H	0.797	1.73	0.588	55.6	0.111	0.099	1.447
$RO^{\bullet}$ + R^2H	0.797	1.73	0.645	55.6	0.111	0.099	1.319
$RO^{\bullet}$ + R^3H	0.797	1.73	0.626	55.6	0.111	0.099	1.360
$RO^{\bullet}$ + $HSiR^3$	0.611	1.60	0.564	62.1	0.126	0.099	1.681
$RO^{\bullet}$ + HSR	0.707	1.62	0.569	58.6	0.117	0.099	1.478
$RO_2^{\bullet}$ + R^1H	0.814	1.44	0.524	55.1	0.111	0.100	1.150
$RO_2^{\bullet}$ + R^2H	0.814	1.44	0.585	55.1	0.111	0.100	1.030
$RO_2^{\bullet}$ + R^3H	0.814	1.44	0.551	55.1	0.111	0.100	1.093
$RO_2^{\bullet}$ + HOAr	1.014	1.49	0.420	49.6	0.099	0.100	1.230
$RO_2^{\bullet}$ + HAm	0.936	1.44	0.405	51.6	0.104	0.100	1.291
$RO_2^{\bullet}$ + $HSiR^3$	0.624	1.60	0.692	61.6	0.126	0.100	1.401
$RO_2^{\bullet}$ + HSR	0.722	1.39	0.518	58.1	0.117	0.100	1.220

$r^{\neq}_{Y\ldots H}$ and $r^{\neq}_{X\ldots H}$ have the form shown below if $\Delta H_e(1-\alpha^2) < (br)^2$ (Refs 11 and 13),

$$r^{\neq}_{Y\ldots H} = r_{Y-H} + \frac{\beta r_e}{1+\alpha} + \frac{\alpha\beta\Delta H_e}{2b^2 r_e} \tag{23}$$

$$r^{\neq}_{X\ldots H} = r_{X-H} + \frac{\alpha\beta r_e}{1+\alpha} - \frac{\alpha\beta\Delta H_e}{2b^2 r_e} \tag{24}$$

$$r^{\neq}_{X\ldots Y} = r_{X-H} + r_{Y-H} + \beta r_e \tag{25}$$

The parameters needed to calculate the geometries are summarized in Table 4.

IV. The Hammond postulate

The Hammond postulate relates to the TS geometries of elementary reactions and states that TS structure is close to that of reactants for strongly exothermic reactions and to that of products for endothermic reactions.[57] This postulate is qualitative. The intersecting parabolas model can make the postulate quantitative;[11–13] the same can be achieved with the use of the model of intersecting Morse curves.[58]

1. Abstraction reactions with symmetric transition states

In the intersecting parabolas model, the hydrogen atom abstraction reactions with symmetric reaction centre, for instance, C...H...C, form the same class if their b = const and r_e = const.[59] Equations (20)–(22) are applicable to the description of TSs of these reactions. The parameters v, $0.5\,hN_Av$ and b and the bond lengths for the reactions under consideration are summarized in Table 1. For a thermoneutral reaction characterized by $\Delta H = 0$, the following simple expression for the $X_f\ldots H$ and $X_i\ldots H$ distances in TSs can be obtained [see Eqns (20) and (21)].

$$\left(r^{\neq}_{X_f\ldots H}\right)_0 = \left(r^{\neq}_{X_i\ldots H}\right)_0 = r_{X-H} + \frac{\beta r_e}{2} \tag{26}$$

Since the $X_i\ldots H\ldots X_f$ distance is equal to $2\,r_{X-H} + \beta r_e$, the hydrogen atom in the TS of the thermoneutral reaction is located exactly in the middle between the X_i andX_f atoms. Equation (26) holds for abstraction reactions with enthalpy in the range $\Delta H_{min} \leqslant \Delta H \leqslant \Delta H_{max}$.[38] In the case of the reactions with symmetric reaction centre, $\Delta H_{max} = |\Delta H_{min}|$, while ΔH_{max}, depends on the parameter br_e and on the zero point energy of the X−H bond vibration in the following way:[38]

$$\Delta H_{max} = |\Delta H_{min}| = (br_e)^2 - 2\,br_e\sqrt{0.5\,hN_Av} \tag{27}$$

The transition state for a reaction with $\Delta H = \Delta H_{min}$ is characterized by a minimum X_i-H bond elongation, which is equal to (Fig. 4)

$$(\Delta r^{\neq}_{X_i\ldots H})_{min} = b^{-1}\sqrt{0.5\,hN_Av}$$

$$(r^{\neq}_{X_i\ldots H})_{min} = r_{X_i-H} + b^{-1}\sqrt{0.5\,hN_Av} \tag{28}$$

Simultaneously, $\Delta r^{\neq}_{X_f\ldots H}$ reaches its threshold value.

$$(\Delta r^{\neq}_{X_f\ldots H})_{max} = \beta r_e - b^{-1}\sqrt{0.5\,hN_Av} \tag{29}$$

Accordingly, for a reaction with $\Delta H = \Delta H_{max}$, the change in the $X_i\ldots H$ distance acquires the threshold value $(\Delta r^{\neq}_{X_f\ldots H})_{max}$ [see Eqn (29) and Fig. 4], whereas the distance $\Delta r^{\neq}_{X_f\ldots H}$ takes the minimum value $(r^{\neq}_{X_i\ldots H})_{min}$ [see Eqn (28) and Fig. 4].

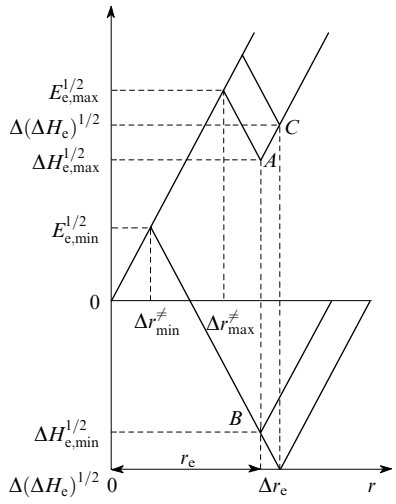


Figure 4. Dependence of the TS energy on the interatomic distances for radical abstraction reactions with different enthalpies according to the intersecting parabolas model.[18]
AB corresponds to reactions with enthalpies in the range from $\Delta H_{e,min}$ to $\Delta H_{e,max}$ and with $\Delta r_{X_i...H}^{\neq} + \Delta r_{X_f...H}^{\neq} = r_e$; the coordinates of point *C* show the increment of r_e (Δr_e) with the increase in $|\Delta H_e|$.

Thus, as ΔH decreases, the TS configuration indeed approaches that of reactants, whereas the increase in ΔH results in TS approaching the products, as predicted by the Hammond postulate. However, the TS configuration always differs from that of both reactants and products for any ΔH values [see Eqns (28) and (29)]. The interatomic distances for reactions of isopropyl, allyl and benzyl radicals with a series of hydrocarbons calculated according to Eqns (20) and (21) are summarized in Table 5.

The following regularities can be formulated on the basis of the above analysis of the TS geometries of radical abstraction reactions with symmetric reaction centres performed in the framework of the intersecting parabolas model:

— the hydrogen atom in the reaction centre of TS for a reaction with $\Delta H = 0$ is located exactly in the middle of the $X_i...X_f$ segment;

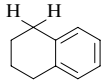
— with increasing ΔH, the $r_{X_i...H}^{\neq}$ distance increases, whereas the $r_{X_f...H}^{\neq}$ distance decreases;

— dependences $r_{X_f...H}^{\neq}$ and $r_{X_i...H}^{\neq}$ on ΔH are linear [see Eqns (20), (21)]; the linear dependence holds in the enthalpy range $\Delta H_{min} \leqslant \Delta H \leqslant \Delta H_{max}$.

The values of the derivative

$$\frac{dr_{C...H}^{\neq}}{d(\Delta H)} = \frac{\beta}{2b^2 r_e}$$

Table 5. Interatomic distances (Å) in the TSs for reactions of isopropyl, allyl and benzyl radicals with hydrocarbons and oxygen-containing compounds calculated using Eqns (20) and (21).[12, 18]

Compound	$Me_2HC^{\bullet}$		$CH_2{=}CHH_2C^{\bullet}$		$PhH_2C^{\bullet}$	
	$r_{R_i...H}^{\neq}$	$r_{R_f...H}^{\neq}$	$r_{R_i...H}^{\neq}$	$r_{R_f...H}^{\neq}$	$r_{R_i...H}^{\neq}$	$r_{R_f...H}^{\neq}$
EtMeCH−H	1.358	1.356	1.413	1.314	1.397	1.332
Me_3C-H	1.346	1.368	1.403	1.351	1.386	1.343
	1.354	1.360	1.410	1.344	1.393	1.336
	1.343	1.371	1.399	1.355	1.382	1.347
$CH_2{=}CHCH_2-H$	1.341	1.413	1.379	1.371	1.384	
$CH_2{=}CHCH(Me)-H$	1.326	1.428	1.364	1.393	1.358	1.399
$CH_2{=}CHCHMe_2$	1.318	1.436	1.356	1.402	1.350	1.407
(Z)-$MeCH{=}CHCH(Me)-H$	1.321	1.433	1.359	1.398	1.354	1.404
$Me_2C{=}CHCH(Me)-H$	1.312	1.442	1.350	1.408	1.344	1.413
$Me_2C{=}C(Me)C(Me_2)-H$	1.304	1.450	1.342	1.415	1.337	1.421
$CH_2{=}CHC(Me)(CH{=}CH_2)-H$	1.291	1.463	1.330	1.428	1.324	1.433
	1.319	1.435	1.357	1.400	1.352	1.406
$MeC{\equiv}CC(Me_2)-H$	1.309	1.444	1.348	1.410	1.342	1.415
PhMeCH−H	1.324	1.405	1.376	1.382	1.323	1.109
$PhMe_2C-H$	1.316	1.413	1.268	1.389	1.314	1.118
	1.308	1.421	1.361	1.397	1.305	1.126
$Me_2C(OH)-H$	1.338	1.376	1.395	1.359	1.378	1.352
$MeCH{=}C(Me)C(Me)(OH)-H$	1.306	1.448	1.344	1.413	1.339	1.419
PhC(O)−H	1.310	1.419	1.363	1.395	1.307	1.124
$Me_2CHOC(Me_2)-H$	1.338	1.376	1.395	1.359	1.378	1.351
$(CH_2{=}CHCH-H)_2O$	1.334	1.420	1.372	1.385	1.366	1.391
$Ph_2C(OMe)-H$	1.315	1.414	1.368	1.390	1.313	1.118

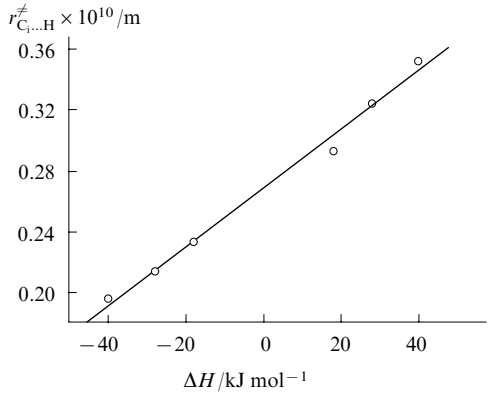


Figure 5. Dependence of the elongation of the C...H distance in the TS for the reaction $R_i^{\bullet} + R_fH$ on the reaction enthalpy (ΔH) according to quantum chemical calculations.[12]

[see Eqn (20)] are presented in Table 3. Thus, the Hammond postulate becomes strictly quantitative. Analogous conclusions were made upon consideration of the reactions with symmetric TS within the model of intersecting Morse curves (see below) and from the data of quantum chemical calculations of reactions of alkyl radicals with alkanes.[12] The dependence of changes in the C...H interatomic distances in TSs on the reaction enthalpy is shown in Fig. 5. It is evident that according to quantum chemical calculations, the dependence of this distance on the reaction enthalpy is also linear.

2. Abstraction reactions with asymmetric reaction centre of the transition state

The interatomic distances in TSs of hydrogen atom abstraction reactions

$$X^{\bullet} + HY \longrightarrow X...H...Y \longrightarrow XH + Y^{\bullet}$$

with asymmetric reaction centre Y...H...X are described by Eqns (23)–(25).[59] For these reactions, the distance $\Delta r^{\neq}_{Y...H}$ increases linearly with increasing ΔH_e, whereas $\Delta r^{\neq}_{X...H}$ linearly decreases as in the case of reactions with symmetric reaction centres. However, unlike the hydrogen atom position in the middle of the $X_i...H...X_f$ segment in the symmetric reaction centre, its location in the asymmetric Y...H...X centre is different and is described by the equations

$$(r^{\neq}_{Y...H})_0 = r_{Y-H} + \frac{\beta r_e}{1+\alpha} \qquad (30)$$

$$(r^{\neq}_{X...H})_0 = r_{X-H} + \frac{\alpha\beta r_e}{1+\alpha}$$

The position of hydrogen atom on the Y...X segment depends on bond lengths and coefficient α. As for reactions with symmetric TS, Eqns (30) and expressions derived from them hold for reactions with enthalpies in the range $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$. However, the boundary values $|\Delta H_{e,min}|$ and $\Delta H_{e,max}$ for reactions with asymmetric TS are different.[38]

At $\Delta H_e = \Delta H_{e,max}$, the minimum value of $\Delta r^{\neq}_{X...H}$ and maximum (threshold) value of $\Delta r^{\neq}_{Y...H}$ are reached.

$$(\Delta r^{\neq}_{X...H})_{min} = \alpha b^{-1}\sqrt{0.5\,hN_A\nu_{X-H}} \qquad (31)$$

$$(\Delta r^{\neq}_{Y...H})_{max} = \beta r_e - \alpha b^{-1}\sqrt{0.5\,hN_A\nu_{X-H}}$$

The $\Delta r^{\neq}_{Y...H}$ value for exothermic reactions linearly decreases with decreasing ΔH_e [see Eqn (23)], and at $\Delta H_e = \Delta H_{e,min}$, it reaches the minimum value, and $\Delta r^{\neq}_{X...H}$ gets its threshold value $(\Delta r^{\neq}_{X...H})_{max}$

$$(\Delta r^{\neq}_{Y...H})_{min} = b^{-1}\sqrt{0.5\,hN_A\nu_{Y-H}} \qquad (32)$$

$$(\Delta r^{\neq}_{X...H})_{max} = \beta r_e - b^{-1}\sqrt{0.5\,hN_A\nu_{Y-H}}$$

Thus, the Hammond principle is also implemented for reactions with asymmetric reaction centre, Y...H...X, while the dependences of $\Delta r^{\neq}_{Y...H}$ and $\Delta r^{\neq}_{X...H}$ on ΔH_e are linear in the range $\Delta H_{e,min} < \Delta H_e < \Delta H_{e,max}$. For the reactions under consideration at $\Delta H_e = 0$, the hydrogen atom is not located in the middle of the Y...H...X segment but is shifted toward the atom with shorter bond and larger force constant [see Eqn (23)]. This shift is equal to

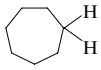
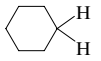
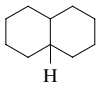
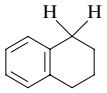
$$(\Delta r^{\neq}_{Y...H})_0 - 0.5\beta r_e = \frac{\beta r_e(1-\alpha)}{2(1+\alpha)} \qquad (33)$$

It is positive when $\alpha < 1$ and negative if $\alpha > 1$. Table 4 presents the α, β, $\Delta r^{\neq}_{Y...X}$ values for some reaction classes. As an example, the results of calculations of the TS geometric parameters for reactions of peroxyl radicals with hydrocarbons by Eqns (23) and (24) are summarized in Table 6.

Table 6. Thermodynamic and geometric parameters of the TSs for the reaction *sec*-$RO_2^{\bullet}$ + RH ⟶ *sec*-ROOH + $R^{\bullet}$ calculated using Eqns (23) and (24).[15,18]

RH	ΔH/kJ mol^{-1}	E_e/kJ mol^{-1}	$r^{\neq}_{C...H} \times 10^{10}$/m	$r^{\neq}_{O...H} \times 10^{10}$/m
$MeCH_2-H$	52.7	83.4	1.442	1.143
$EtMeCH-H$	43.7	78.1	1.432	1.154
Me_3C-H	30.7	71.1	1.416	1.169
	49.2	81.2	1.439	1.147
	39.1	75.6	1.426	1.159

Table 6 (continued).

RH	ΔH /kJ mol^{-1}	E_e /kJ mol^{-1}	$r^{\neq}_{C...H} \times 10^{10}$ /m	$r^{\neq}_{O...H} \times 10^{10}$ /m
	34.6	73.2	1.421	1.165
	26.2	68.8	1.411	1.174
	18.3	64.9	1.402	1.184
$CH_2{=}CHCH_2{-}H$	−1.3	69.6	1.413	1.234
$CH_2{=}CHCH(Me){-}H$	−19.5	61.8	1.394	1.252
$CH_2{=}CHC(Me_2){-}H$	−29.7	57.7	1.384	1.263
Z-$MeCH{=}CHCH(Me){-}H$	−25.3	59.4	1.388	1.258
$Me_2C{=}CHCH(Me){-}H$	−37.3	54.7	1.377	1.270
$Me_2C{=}CMeC(Me_2){-}H$	−46.5	51.2	1.367	1.279
$CH_2{=}CHC(Me)(CH{=}CH_2){-}H$	−62.1	45.6	1.352	1.295
	−27.8	58.4	1.386	1.261
	−38.4	54.2	1.374	1.271
	−56.7	47.5	1.357	1.290
	−68.3	43.5	1.346	1.301
$MeC{\equiv}CC(Me_2){-}H$	−39.3	53.7	1.374	1.273
$PhMeCH{-}H$	−5.2	60.0	1.390	1.223
$PhMe_2C{-}H$	−14.6	56.0	1.380	1.233
	−23.7	52.2	1.370	1.243

V. The model of intersecting Morse curves

The Morse equation describes the relationship between the deviation of the interatomic distance Δr from equilibrium and the bond potential energy U (Ref. 60)

$$\sqrt{U} = \sqrt{D_e}\left[1 - \exp\left(-bD_e^{-1/2}\Delta r\right)\right] \tag{34}$$

where D_e is the bond energy including zero point vibration energy.

The Morse equation describes adequately the vibrational spectra of two- and polyatomic molecules. In accordance with the model of intersecting Morse curves, the TS in radical abstraction reactions is considered as a result of intersection of two curves, one of which describes potential energy of the stretching vibration of the attacked Y−H bond and the other describes the same for the forming X−H bond.[58] Similarly to the intersecting parabola model, all the reactions belonging to the same class are characterized by a parameter $br_e = \text{const}$, where r_e is the total elongation of the Y−H and X−H bonds in the TS. The elongation of these bonds is described by the following equations ($\alpha = b_{Y-H}/b_{X-H}$):

$$\Delta r^{\neq}_{Y...H} = -\frac{\sqrt{D_{e\,Y-H}}}{b_{Y-H}}\ln\left(1 - \sqrt{\frac{E_e}{D_{e\,Y-H}}}\right) \tag{35}$$

$$\Delta r^{\neq}_{X...H} = -\frac{\alpha\sqrt{D_{e\,Y-H}}}{b_{Y-H}}\ln\left(1 - \sqrt{\frac{E_e - \Delta H_e}{D_{e\,Y-H}}}\right) \tag{36}$$

As mentioned above, $\Delta r^{\neq}_{Y...H} + \Delta r^{\neq}_{X...H} = r_e = \text{const}$ for reactions belonging to the same class.

For a thermoneutral reaction ($\Delta H_e = 0$) with a symmetric reaction centre ($\alpha = 1$, $D_{e\,X_i-H} = D_{e\,X_f-H} = D_e$), the following expression is obtained:

$$\left(\Delta r^{\neq}_{X_i...H}\right)_0 = \left(\Delta r^{\neq}_{X_f...H}\right)_0 = -\frac{\sqrt{D_e}}{b}\ln\left(1 - \sqrt{\frac{E_{e\,0}}{D_e}}\right) \tag{37}$$

Hence, like the intersecting parabolas model, the model of intersecting Morse curves, too, predicts that the hydrogen atom in the symmetric reaction centre $X_i...H...X_f$ is located exactly in the middle of the segment r_e.

Consideration of TS geometries for reactions with asymmetric reaction centres in the framework of the model of intersecting Morse curves leads to the conclusions completely analogous to those obtained using the intersecting parabolas model. The activation energies for radical abstraction reactions are much smaller than the bond

dissociation energies ($E_e \ll D_e$), therefore expanding the function $\ln(1-x)$ into the Maclaurin series and considering only the first two terms leads to the following expression:

$$\ln(1-x) \simeq -x-0.5\,x^2$$

Then Eqn (35) takes the following form:

$$\frac{\Delta r^{\neq}_{Y\ldots H}}{r_e} = A + B\,\Delta H_e + C\,\Delta H_e^2 \qquad (38)$$

where

$$A = \frac{1}{1+\alpha}$$

$$B = \alpha A^2 F\left(\frac{1}{\sqrt{D_e E_{e0}}} + \frac{1}{D_e}\right)$$

$$C = \frac{1}{2}\,\frac{\alpha^2 A^3 F}{D_e E_{e0}}$$

$$F^{-1} = \sqrt{\frac{E_{e0}}{D_e}} + \frac{1}{2}\,\frac{E_{e0}}{D_e}$$

$E_{e0} = E_e$ at $\Delta H_e = 0$, the E_{e0} values were reported.[58]

It is follows from equation (38) that the Y...H distance in the TS increases with increasing ΔH_e in accordance with the Hammond postulate. However, this dependence is not linear

$$\frac{d\Delta r^{\neq}_{Y\ldots H}}{d\Delta H_e} = B + 2\,C\,\Delta H_e$$

in contrast to the dependence given by the intersecting parabolas model; it is approximated by a straight line only at $\Delta H_e \ll B/C$. For reactions of alkyl radicals with alkanes ($D_e = 400$ kJ mol^{-1} and $E_{e0} = 74.8$ kJ mol^{-1}), the estimated coefficients are the following: $A = 0.5$, $B = 3.93\times10^{-3}$ mol kJ^{-1}, $C = 3.97\times10^{-6}$ mol^2 J^{-2}, $F = 1.90$. The dependence of $\Delta r^{\neq}_{Y\ldots H}/r_e$ on ΔH_e takes the following form:

$$\frac{\Delta r^{\neq}_{Y\ldots H}}{r_e} = 0.50 + 3.93\times10^{-3}\,\Delta H_e + 3.97\times10^{-6}\,\Delta H_e^2 \qquad (39)$$

When the $|\Delta H_e|$ and E_e values are not large and the expansion of $\ln(1-x)$ into the Maclaurin series may be restricted by the first term $x = (E_{e0}/D_e)^{1/2}$, the equations of the model of intersecting Morse curves turn into equations of the intersecting parabolas model with all the conclusions derived from them.

The model of intersecting Morse curves provides interatomic distances in TSs of radical abstraction reactions close to the distances obtained in quantum chemical calculations.[11] The distances between the terminal atoms determined in the frameworks of different approaches are summarized in Table 7.

The root-mean-square discrepancy between $r^{\neq}$(QCC) and $r^{\neq}$(MIMC) is only $(0.05\pm0.02)\times10^{-10}$ m, whereas that between $r^{\neq}$(QCC) and $r^{\neq}$(IPM) is 0.08×10^{-10} m.

In the case of exothermic disproportionation reactions when $\Delta H_e < \Delta H_{e,\min}$, the model of intersecting Morse curves makes it possible to estimate an additional elongation of interatomic distance in the TS caused by the large difference between the enthalpies of reactants and products.[61] If $\Delta H_e = \Delta H_{e,\min}$, the potential curves U_{Y-H} and U_{X-H} can intersect upon further decrease in ΔH_e only if the X...Y distance is increased (Fig. 6). This is accompanied by the increase in the pre-exponential factor (A) and the reaction rate constant (k) in the Arrhenius equation. In terms of the collision theory, the following simple equation relating k to the interatomic distance elongation $\Delta\Delta r^{\neq}$ is obtained:[61]

$$\sqrt{\frac{k}{n\,A_0}} = 1 + \frac{\Delta\Delta r^{\neq}}{r_{X-H} + r_{Y-H} + r_e} \qquad (40)$$

where n is the number of attacked C–H bonds in the radical, A_0 is the pre-exponential factor for this class of reactions with $\Delta H_e > \Delta H_{e,\min}$ per attacked C–H bond. In turn, analysis of experimental data shows that $\Delta\Delta r^{\neq}$ linearly increases following increase in the difference $\Delta H_{e,\min} - \Delta H_e$. The linear expressions for $\Delta\Delta r^{\neq}$ derived from experimental data analysis, the $(k/nA_0)^{1/2}$ values [calculated using Eqn (40)] and the A_0 and $\Delta H_{e,\min}$ values are presented in Table 8.

Table 7. Interatomic distances determined by quantum chemical calculations (QCC) and using the model of intersecting Morse curves (MIMC) and the intersecting parabolas model (IPM).

Reaction centre	$r^{\neq}$(QCC) $\times 10^{10}$ /m	$r^{\neq}$(MIMC) $\times 10^{10}$ /m	$r^{\neq}$(IPM) $\times 10^{10}$ /m
H...H...H	1.86	1.93	1.86
H...H...Cl	2.42	2.38	2.33
H...H...C	2.31	2.37	2.25
C...H...C	2.73	2.71	2.60
N...H...N	2.50	2.56	2.44
C...H...Si	3.22	3.26	3.12
HOO...H...OOH	2.37	2.29	2.23

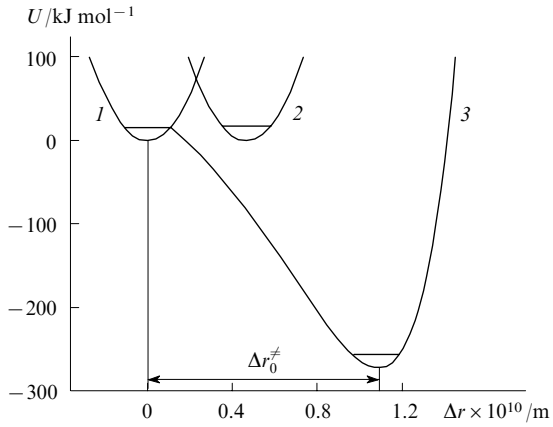


Figure 6. Diagram of the potential energy of the stretching vibration *vs.* change in the interatomic distance for disproportionation of ethyl radicals.
(*1*) Potential energy of the harmonic vibration of the attacked C–H bond; (*2*) potential energy of the harmonic vibration of the forming C–H bond in the thermoneutral reaction of radical hydrogen atom abstraction; (*3*) potential energy of the anharmonic vibration of the forming C–H bond; $\Delta r_0^{\neq}$ is the elongation of the C–H bond in the TS of abstraction reactions when $\Delta H_e = \Delta H_{e,\min}$.

Table 8. Kinetic and geometric parameters for the TSs of disproportionation reactions [see Eqn (40)].[61]

Reaction centre	$-\Delta H_{e,min}$ /kJ mol^{-1}	$\Delta\Delta r^{\neq} \times 10^{13}$ /m	A_0 /litre mol^{-1} s^{-1}	$(k/nA_0)^{1/2}-1$
C...H...C	155.0	3.30 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$1.88\times10^{10}\,\Delta\Delta r^{\neq}$
C=C−C...H...C	190.8	3.59 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$10.6\times10^{10}\,\Delta\Delta r^{\neq}$
C=C...H...C	163.4	3.09 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$1.54\times10^{10}\,\Delta\Delta r^{\neq}$
C...H...C−O	66.6	0.78 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$6.90\times10^{10}\,\Delta\Delta r^{\neq}$
C...H...O...C	66.6	3.34 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^7	$24.0\times10^{10}\,\Delta\Delta r^{\neq}$
C...H...O−O	76.1	2.69 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$32.0\times10^{10}\,\Delta\Delta r^{\neq}$
O...H...C	108.5	2.63 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$6.70\times10^{10}\,\Delta\Delta r^{\neq}$
O...H...O−C	101.7	2.58 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^8	$3.80\times10^{10}\,\Delta\Delta r^{\neq}$
O...H...O−O	117.3	2.18 ($\Delta H_{e,min}-\Delta H_e$)	2.0×10^9	$2.80\times10^{10}\,\Delta\Delta r^{\neq}$

Utilizing the parameters from Table 8, one can estimate the rate constant for disproportionation of radicals on the basis of the reaction enthalpy. For instance, the enthalpy of the disproportionation reaction

$$H_3C^{\bullet} + (CH_3)_2HC^{\bullet} \longrightarrow CH_4 + MeCH{=}CH_2$$

is $\Delta H_e = \Delta H = -291.3$ kJ mol^{-1}. According to the data of Table 8, $\Delta\Delta r^{\neq} = 3.3\times(291.3-155.0)\times10^{-13} = 0.45\times10^{-10}$ m, where $\Delta\Delta r^{\neq}$ is the additional elongation of interatomic distance in the TS. As $(k/nA_0)^{1/2} = 1 + 1.88\times10^{10}\,\Delta\Delta r^{\neq}$, then $(k/nA_0)^{1/2} = 1.85$ and for isopropyl radical with $n = 6$, $k = 6\times2\times10^8\times1.85^2 = 4.1\times10^9$ litre mol^{-1} s^{-1}, *i.e.*, it is very similar to the experimentally measured value $k = 4.0\times10^9$ litre mol^{-1} s^{-1} (Ref. 61).

VI. Factors affecting the transition state geometry

As demonstrated above, the radical abstraction enthalpy influences the hydrogen atom position in the X...H...Y reaction centre (by affecting the values $\Delta r^{\neq}_{X...H}$ and $\Delta r^{\neq}_{Y...H}$). Meanwhile, the X...Y distance does not depend on the enthalpy within the same class of reactions but varies from one class to another (see Tables 2 and 3). The classical potential barrier of the thermoneutral reaction is mainly affected by the following factors:

— triplet repulsion,

— electronegativities and radii of the X and Y atoms,

— the presence of a π-bond nearby the reaction centre.[37, 38, 55]

Do these factors affect the geometry (the X−H and Y−H bond elongations) of TSs of hydrogen atom abstraction reactions?

1. Triplet repulsion

The hydrogen atom in TS moves along the X...Y line. According to the Pauli principle, three electrons cannot occupy the X−Y bonding orbital, therefore, one of them is in the X−Y non-bonding orbital. The stronger this bond, the higher the energy of the non-bonding orbital and higher the activation energy.[38, 55] Does the triplet repulsion affect the X...H and Y...H distances in the TS? Since the activation energy is influenced also by the electronegativity of X and Y atoms, it is reasonable to correlate the X−X bond energies (D_{eX-X}) and the $\Delta r^{\neq}_{X...X}$ distances in the reactions with the symmetric reaction centre (see Table. 3).[11, 62]

Reaction centre	$\Delta r^{\neq}_{X...X} \times 10^{10}$ /m	D_{eX-X} /kJ mol^{-1}
C...H...C	0.519	371.4
N...H...N	0.484	291.5
RO...H...OR	0.446	166.5
ROO...H...OOR	0.429	40.1

For the reaction classes presented, the radii of C, N and O atoms are simular; hence, this factor does not influence the X−H bond elongation in the TS. The dependence of $\Delta r^{\neq}_{X...X}$ on the squared bond energy D_{eX-X} (Fig. 7) is linear and is described by the following correlation equation:

$$\Delta r^{\neq}_{X...X} \times 10^{10} = 0.428 \pm 0.007 + (6.48 \pm 0.90)\times10^{-7} D^2_{eX-X} \quad (41)$$

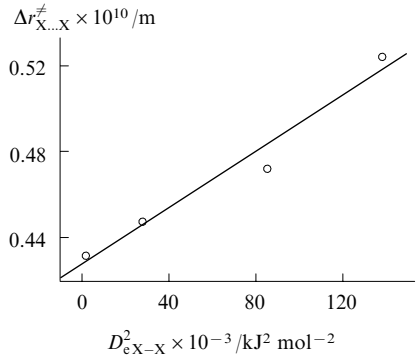


Figure 7. Dependence of $\Delta r^{\neq}_{X...X}$ on the squared dissociation energy of the X−X bond for reactions with symmetric reaction centres.[12]

Thus, the triplet repulsion elongates the interatomic distance in the TS. The dependence of $\Delta r^{\neq}_{X...X}$ on D_{eX-X} is parabolic. Correlation equation (41) helps in elucidating the role of other factors in the radical abstraction TS geometry.

2. The radii of atoms forming the reaction centre

It is known that the atomic number of atom X affects its X−H and X−Y bond characteristics (see Table 1). Since the hydrogen atom migrates along the X...Y pseudo-bond, one can expect that both the X...Y distance and the X−H and Y−H bond elongations in TS depend on the X and Y atomic radii. The strength of the X−Y bond affects $\Delta r^{\neq}_{X...Y}$ (see above), and this is to be taken into account. The values of $\Delta r^{\neq}_{X...Y}$ are presented below for reaction classes in whose TSs, the C−Y bond lengths (Y = C, Si, Ge, Sn) differ

considerably.[14] With the purpose to reveal the dependence of $\Delta r^{\neq}_{X\ldots Y}$, the distances between the atoms were calculated by Eqn (41) taking into account the effect of triplet repulsion (the parameters with subscripts T) on $\Delta r^{\neq}_{X\ldots Y}$. The effect of the X−Y bond length on the distance $\Delta r^{\neq}_{X\ldots Y}$ can be judged by the difference $\Delta r^{\neq} - \Delta r^{\neq}_{T}$.

Reaction	$\Delta r^{\neq}_{X\ldots Y} \times 10^{10}$/m	D_e /kJ mol^{-1}	$\Delta r^{\neq}_{T} \times 10^{10}$ /m	$\Delta r^{\neq}_{X\ldots Y} - \Delta r^{\neq}_{T} \times 10^{10}$/m
R$^{\bullet}$ + RH	0.526	371.4	0.526	0.0
R$^{\bullet}$ + HSiR$_3$	0.655	367.6	0.517	0.138
R$^{\bullet}$ + HGeR$_3$	0.753	329.3	0.500	0.253
R$^{\bullet}$ + HSnR$_3$	0.861	287.8	0.473	0.378

The dependence of the difference $\Delta r^{\neq}_{X\ldots Y} - \Delta r^{\neq}_{T}$ on the X−Y bond length is shown in Fig. 8.[11,14] The linear dependence indicates that the sizes of the electron shells of reaction centre atoms have an influence on $\Delta r^{\neq}_{X\ldots Y}$: the larger are the radii of the X and Y atoms, the more pronounced is the X...Y elongation in the TS. This dependence is described by the following correlation equation:

$$\Delta r^{\neq}_{X\ldots Y} - \Delta r^{\neq}_{T} = -(0.92 \pm 0.19) \times 10^{-10} + (0.59 \pm 0.10) r_{X-Y} \quad (42)$$

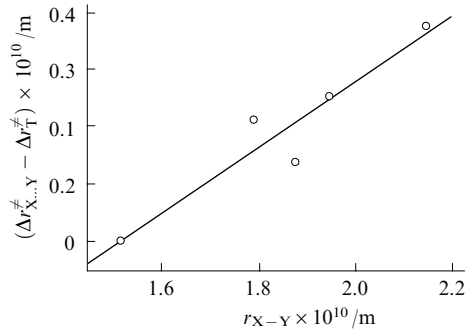


Figure 8. Dependence of the difference $\Delta r_{X\ldots Y}{}^{\neq} - \Delta r_T$ on the X−Y bond length.

3. The electronegativity of the atoms forming the reaction centre

The electronegativities (*EA*) of atoms of the TS reaction centre are yet another factor affecting the activation energies of the radical hydrogen atom abstraction.[38,55] The larger the difference between the electronegativities of X and Y atoms (ΔEA), the lower the classical barrier of thermoneutral abstraction reaction (E_{e0}). Does ΔEA of X and Y atoms affect the change in the X...Y interatomic distance in the TS of the abstraction reaction? Compare the values of $\Delta r^{\neq}_{X\ldots Y}$ for two reactions: H$^{\bullet}$ + CH$_4$ ($\Delta r^{\neq}_{C\ldots H} = 0.442 \times 10^{-10}$ m) and H$^{\bullet}$ + H$_2$O ($\Delta r^{\neq}_{O\ldots H} = 0.451 \times 10^{-10}$ m). The difference between EA(H) = 2.20 eV and EA(C) = 2.55 eV is not large[56] (0.35 eV), whereas that between EA(H) = 2.20 eV and EA(O) = 3.44 eV is 1.24 eV (Ref. 56). When comparing $\Delta r^{\neq}_{X\ldots Y}$, one should take into account the effect of triplet repulsion (see above). Using Eqn (42), one can estimate $\Delta r^{\neq}_{O\ldots H}$ through $\Delta r^{\neq}_{X\ldots H}$ under the assumption that only triplet repulsion operates. The bond energies are D_{eC-H} = 457.4 kJ mol^{-1} for methane and D_{eO-H} = 521.7 kJ mol^{-1} for water.[62] The required value for the reaction H$^{\bullet}$ + H$_2$O can be calculated as follows:

$$(\Delta r^{\neq}_{O\ldots H})_T = \Delta r^{\neq}_{C\ldots H} + 6.62 \times 10^{-17}\left(D^2_{eO-H} - D^2_{eC-H}\right) =$$

$$= 0.484 \times 10^{-10} \text{ m}$$

This would be the H...H...O distance in the TS of the reaction H$^{\bullet}$ + H$_2$O if it was affected only by the triplet repulsion. The difference $\Delta r^{\neq}_{O\ldots H} - (\Delta r^{\neq}_{O\ldots H})_T = -0.033 \times 10^{-10}$ m characterizes the effect of electronegativity on the TS of the hydrogen atom reaction with water.

The influence of ΔEA on the X...Y interatomic distances in TSs is also observed in reactions of O-centred radicals with N−H bonds of aromatic amines. This can be seen from comparison of $\Delta r^{\neq}_{X\ldots Y}$ for reactions of peroxyl, phenoxyl (Ar^{1}O$^{\bullet}$), sterically hindered phenoxyl (Ar^{2}O$^{\bullet}$) and aminoxyl (AmO$^{\bullet}$) radicals with aromatic amines (AmH) and phenols (Ar^{1}OH).[16]

X$^{\bullet}$	$\Delta r^{\neq}_{X\ldots OAr^1} \times 10^{-10}$ /m	$\Delta r^{\neq}_{X\ldots Am} \times 10^{-10}$ /m	$\Delta\Delta r^{\neq}_{EA} \times 10^{-10}$ /m
RO$_2^{\bullet}$	0.441	0.405	0.036
Ar^{1}O$^{\bullet}$	0.389	0.348	0.041
Ar^{2}O$^{\bullet}$	0.407	0.371	0.036
AmO$^{\bullet}$	0.418	0.368	0.050

As can be seen, the interatomic distance in the reaction centre O...H...N is significantly shorter than that in the reaction centre O...H...O: $\Delta\Delta r^{\neq} = (0.041 \pm 0.006) \times 10^{-10}$ m. The triplet repulsion in such TSs is negligibly small because the bonds in ArOOAr and ArOOAm are very weak (actually, stable molecules of these types do not exist). Therefore the interatomic distance shortening on going from TSs with O...H...O to TSs with O...H...N is solely determined by electronegativities of oxygen and nitrogen atoms.

4. Effect of the α-π–bonds

If a radical attacks a C−H bond that has a C=C double bond or an aromatic ring in the α-position, the π-electrons of this bond interact with the reaction centre electrons. As a result, the electron density at the reaction centre increases and, hence, the activation energy also increases.[14,38] This also influences the X...H...C interatomic distances. The $\Delta\Delta r^{\neq}_{\pi} \times 10^{-10}$ m values for TSs of the type X...H...CH$_2$−CH=CHR for some reactions are presented in Table 9.[12–14]

It can be seen that the distance $\Delta r^{\neq}_{X\ldots H}$ increases, on average, by $(0.055 \pm 0.012) \times 10^{-10}$ m in the presence of an α-C=C bond and by $(0.026 \pm 0.006) \times 10^{-10}$ m in the presence of an aromatic ring in the α-position.

Table 9. The $\Delta\Delta r^{\neq}_{\pi}$ values (10^{-10} m) for some reactions with the transition states X...H...CH$_2$−CH=CHR and X...H...CH$_2$−Ar.

X	X...H...CH$_2$−CH=CHR	X...H...CH$_2$−Ar
(R^1)$^{\bullet}$	0.040	0.016
O$_2$N$^{\bullet}$	0.039	0.023
RO$^{\bullet}$	0.057	0.038
RO$_2^{\bullet}$	0.061	0.027
Ar^{1}O$^{\bullet}$	0.063	0.027
AmO$^{\bullet}$	0.070	0.028

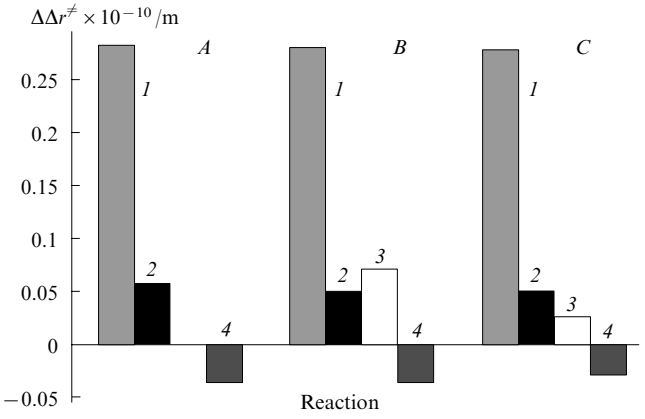


Figure 9. Contributions of different factors to the interatomic distance of the C...H...O reaction centre for three classes of reactions.
Reactions: *A* stands for $RO_2^{\bullet} + H-C$ (alkanes), *B* stands for $RO_2^{\bullet} + H-C$ (alkenes), *C* stands for $RO_2^{\bullet} + H-C$ (alkyl aromatic hydrocarbons); (*1*) effect of the radii of C and O atoms, (*2*) triplet repulsion, (*3*) effect of neighbouring π-electrons, (*4*) effect of the electronegativities of C and O atoms.

The diagram shown in Fig. 9 reflects the contribution of each of the factors mentioned above to the interatomic distance elongation in the C...H...O reaction centres of the reactions of peroxyl radical with C−H bonds of three classes of hydrocarbons, *viz*., alkanes, alkenes and alkyl aromatic hydrocarbons.

5. The steric factor

The presence of bulky substituents in the vicinity of the reaction centre induces additional repulsion and increases the activation energy.[38] Such substituents make the interatomic distances in the TSs longer. This can be followed by comparing $\Delta r^{\neq}_{O...O}$ for reactions of hydrogen atom abstraction from the O−H groups of phenols, Ar^1OH, and sterically hindered phenols, Ar^2OH.[13]

$X^{\bullet}$	$RO_2^{\bullet}$	$Ar^1O^{\bullet}$	$Ar^2O^{\bullet}$	$AmO^{\bullet}$
$\Delta r^{\neq}(X^{\bullet} + Ar^1OH) \times 10^{10}$/m	0.406	0.389	0.407	0.348
$\Delta r^{\neq}(X^{\bullet} + Ar^2OH) \times 10^{10}$/m	0.441	0.407	0.443	0.371
$\Delta\Delta r^{\neq} \times 10^{-10}$/m	0.035	0.018	0.036	0.023

It is evident that the steric repulsion leads to elongation of the interatomic distances in the TSs by, on average, $(0.027 \pm 0.008) \times 10^{-10}$ m. When $Ar^2O^{\bullet}$ reacts with Ar^2OH, the steric repulsion of four *tert*-alkyl groups is summed up; therefore, $\Delta r^{\neq}(Ar^2O^{\bullet} + Ar^2OH) = 0.443 \times 10^{-10}$ m exceeds $\Delta r^{\neq}(Ar^1O^{\bullet} + Ar^1OH)$ by 0.054×10^{-10} m; *i.e*., this is larger than this value for the reaction $Ar^1O^{\bullet}$ + Ar^2 OH by a factor of about 1.5.

VII. The hydrogen bond effect on the transition state geometry

As in the reactions $R^{\bullet} + RH$, the reaction centre configuration in reactions of $RO_2^{\bullet}$ with the C−H bonds of nonpolar hydrocarbons is virtually linear [the O...H...C angle (φ) is 175.9°, Fig. 10 *a*]. The TS configuration changes when $RO_2^{\bullet}$ attacks the α-C−H bond in an alcohol. In this case, the reaction centre in the TS becomes angular (φ = 159.3°, Fig. 10 *b*).[15, 18]

According to quantum chemical calculations, a hydrogen bond between the alcohol O−H group and the oxygen atom of the reaction centre arises in such TS. This fact determines the deviation of the angle φ from 180°. There is no such effect if hydrogen atom is abstracted from the alcohol β-C−H bond (Fig. 10 *c*); no hydrogen bond is formed in the TS in this case. The TS parameters found according to the intersecting parabola model make it possible to calculate the angle φ from experimental data (ΔH_e and E).[15] The calculation is based on the following regularity. As a matter of fact, in the reactions of polar radicals with polar molecules, the interaction of polar groups of the reactants affects the TS energy. As a rule, the interaction of polar groups decreases the activation energy. Also, this has an effect on the TS geometry. An almost linear configuration of the reaction centre (φ = 175.9°) is implemented in the transition state of the reaction of $RO_2^{\bullet}$ with the C−H bond. The presence of polar hydroxyl group in the ethanol molecule changes the TS configuration to φ = 159.3°. At the same time, the sum $\Delta r^{\neq}_{C...O} = \Delta r^{\neq}_{C...H} + \Delta r^{\neq}_{O...H}$ for the TSs of these reactions remains almost invariable

$$\Delta r^{\neq}_{C...O}(EtO_2^{\bullet} + EtH) = 1.115 \times 10^{-10} + 1.470 \times 10^{-10} = 2.585 \times 10^{-10} \text{ m}$$

$$\Delta r^{\neq}_{C...O}(EtO_2^{\bullet} + EtOH) = 1.206 \times 10^{-10} + 1.373 \times 10^{-10} = 2.579 \times 10^{-10} \text{ m}$$

(the error is $\pm 0.005 \times 10^{-10}$ m). Meanwhile, the results obtained using the intersecting parabolas model indicate shortening of the distance $\Delta r^{\neq}_{C...O}$ in the reaction $RO_2^{\bullet}$ + EtOH by 0.159×10^{-10} m as compared to $\Delta r^{\neq}_{C...O} = 2.585 \times 10^{-10}$ m in the reactions $RO_2^{\bullet}$ + R^1H. Clearly, this

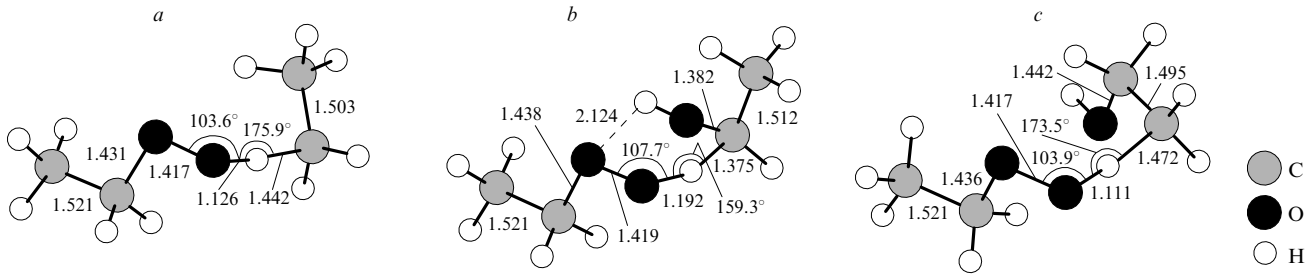


Figure 10. Structures of the TSs for reactions of ethylperoxyl radical with the C−H bonds of ethane (*a*) and ethanol (*b*, *c*).[15]
The bond lengths are in Ångströms and the angles are in degrees.

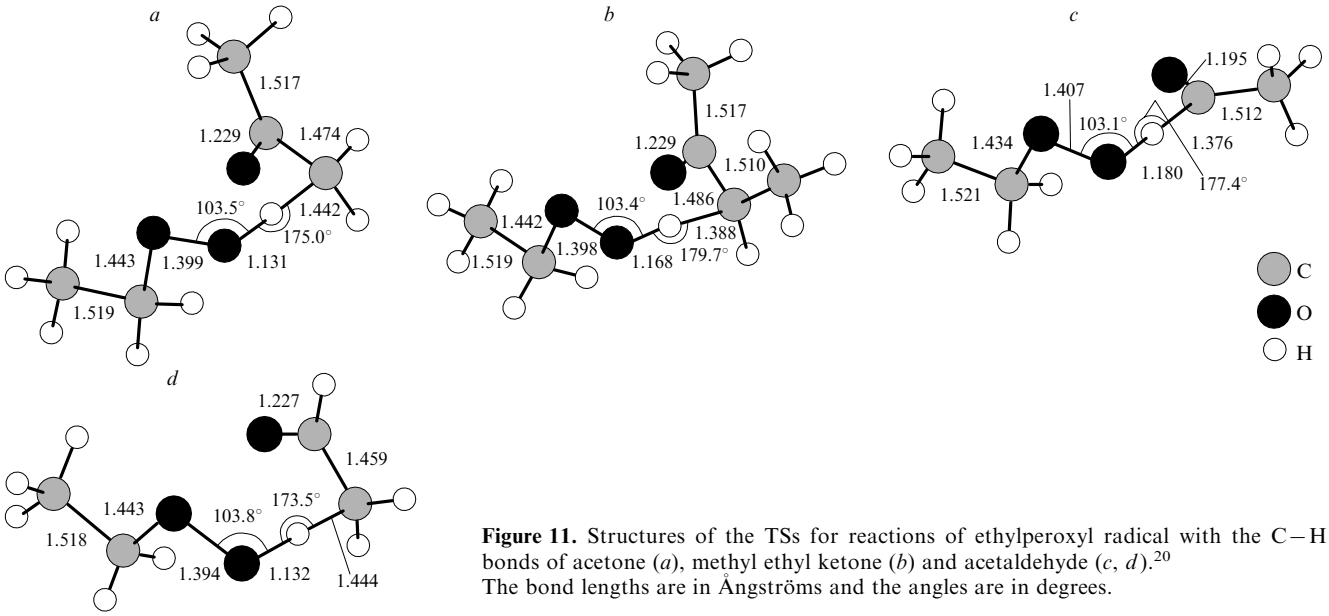


Figure 11. Structures of the TSs for reactions of ethylperoxyl radical with the C—H bonds of acetone (*a*), methyl ethyl ketone (*b*) and acetaldehyde (*c*, *d*).[20]
The bond lengths are in Ångströms and the angles are in degrees.

shortening is a result of an angular configuration of the reaction centre in the TS of the reaction between two species capable of hydrogen bonding. Proceeding from this fact, the following method for estimating the angle φ was suggested.[15] Since the values $\Delta r^{\neq}_{C\ldots H}$ and $\Delta r^{\neq}_{O\ldots H}$ depend on the reaction enthalpy (see Section III), the E and ΔH values for the reaction $RO_2^{\bullet}(X^{\bullet}) + R^1H$ are initially calculated in the framework of intersecting parabolas model using the enthalpy $\Delta H(RO_2^{\bullet} + R^1_{\mu}H)$.† Then, the distances $\Delta r^{\neq}_{C\ldots H}$ and $\Delta r^{\neq}_{O\ldots H}$ in the TS of this reference reaction are calculated using Eqns (23) and (24). The distance $(\Delta r^{\neq}_{C\ldots H})_{\mu}$ for the reaction $RO_2^{\bullet}(X^{\bullet})$ with the polar compound $R_{\mu}H$ is calculated from experimental data (E and ΔH_e). Using the parameters $\Delta r^{\neq}_{C\ldots H}$, $\Delta r^{\neq}_{O\ldots H}$ and $(\Delta r^{\neq}_{C\ldots O})_{\mu}$, $\cos(180^\circ - \varphi)$ is calculated by the following equation:

$$\cos(180^\circ - \varphi) = \frac{\left(r^{\neq}_{C\ldots O}\right)^2 - \left(r^{\neq}_{C\ldots H}\right)^2 - \left(r^{\neq}_{O\ldots H}\right)^2}{2\left(r^{\neq}_{C\ldots H}\right)^2 - \left(r^{\neq}_{O\ldots H}\right)^2} \qquad (43)$$

The following linear correlation between $\cos(180^\circ - \varphi)$ and $\Delta E_{\mu} = E(RO_2^{\bullet} + H^1O) - [RO_2^{\bullet} + E_{\mu}(R^1_{\mu}H)]$ holds:

$$\cos(180^\circ - \varphi) = 1 - (8.14 \pm 0.56) \times 10^{-3} \times \Delta E_{\mu} \qquad (44)$$

Thus, using experimental data (ΔH_e, E), one can estimate not only the elongation of the interatomic distances ($\Delta r^{\neq}_{C\ldots H}$ and $\Delta r^{\neq}_{O\ldots H}$) but also the angle φ if the TS is nonlinear.

VIII. The transition state geometry in the reaction of $RO_2^{\bullet}$ with carbonyl compounds

The angular configuration of the reaction centre in the reaction of $RO_2^{\bullet}$ with alcohol can be due to either hydrogen bonding in the TS or the polar interaction of the reaction centre with hydroxyl group. To distinguish between these effects, quantum chemical calculations of TS configurations were carried out for four reactions of the ethylperoxyl radical with carbonyl compounds.[20] The B3LYP calculations with the use of the 6-31G* basis set were performed using the GAUSSIAN 03 program package. The obtained TS structures are shown in Fig. 11. As can be seen, the reaction centre in all the reactions has a nearly linear configuration.

† The subscript μ refers to the polar compound.

IX. Conclusion

Thus, the following factors affect the X...Y interatomic distance in the TS of hydrogen atom abstraction reaction.

1. Naturally, the X—H and Y—H bond lengths: the longer these bonds, the larger the X...Y distance in TS.

2. Triplet repulsion in the TS: the stronger the X—Y bond, the more pronounced the elongation of the X...Y distance. The correlation between $\Delta r^{\neq}_{X\ldots Y}$ and D_{eX-Y} is given by Eqn (41).

3. Electronegativities of the X and Y atoms of the reaction centre: the larger the difference between the electronegativities of the X and Y atoms, the shorter the X...Y distance.

4. The radii of the X and Y atoms affecting the X—Y bond length: the longer this bond, the larger $\Delta r^{\neq}_{X\ldots Y}$. The dependence between the values of $\Delta r^{\neq}_{X\ldots Y}$ and r_{X-Y} is linear for the C—Y bonds (Y = C, Si, Ge, Sn) and is described by Eqn (42).

5. The proximity of the π-bonds to the reaction centre. The interaction of the reaction centre electrons with the π-electrons in such systems results in elongation of the X...Y distance in the TS. The increments are $(\Delta\Delta r^{\neq}_{X\ldots Y})_{\pi} = 0.055 \times 10^{-10}$ m for the C=C double bond and $(\Delta\Delta r^{\neq}_{X\ldots Y})_{\pi} = 0.026 \times 10^{-10}$ m for an aromatic ring.

6. The steric hindrances caused by bulky substituents adjoining the reaction centre also facilitate the additional elongation of the X...Y distance by $\Delta\Delta r^{\neq}_{s}$.

In the whole, all the factors mentioned above can be expressed by the following equation

$$r^{\neq}_{X\ldots Y} = r_{X-H} + r_{Y-H} + \Delta r^{\neq}_{C\ldots C} + \Delta\Delta r^{\neq}_{T} + \Delta\Delta r^{\neq}_{X-Y} + \\ + \Delta\Delta r^{\neq}_{EA} + \Delta\Delta r^{\neq}_{\pi} + \Delta\Delta r^{\neq}_{s} \qquad (45)$$

where $\Delta\Delta r^{\neq}_{T} = 6.62 \times 10^{-17}(D^2_{eX-Y} - D^2_{eX-Y})$ m, D_e are expressed in kJ mol^{-1}, $\Delta\Delta r^{\neq}_{X-Y} = 0.59(r_{X-H} - r_{C-C})$,

$\Delta\Delta r_{EA}^{\neq}$ depends on EA(X) and EA(Y), $\Delta\Delta r_{\pi}^{\neq} = 0.055 \times 10^{-10}$ m for the C=C bond and 0.026×10^{-10} m for an aromatic ring, and $\Delta\Delta r_{s}^{\neq}$ depends on substituents in the vicinity of the reaction centre.

In addition to the mentioned factors, the TS geometry is also affected by hydrogen bonding, this effect occurs in reactions of peroxyl radicals with the C–H bonds in alcohols. The performed analysis opens up the possibility for a simple and simultaneously quite reliable calculation of the geometric parameters of TSs for radical abstraction reactions on the basis of experimentally obtained enthalpies and activation energies.

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