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Reactions of mono- and bimolecular hydrogen transfer in alkyl radicals: analysis using the parabolic model and density functional calculations

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Experimental data on monomolecular hydrogen transfer in the reactions of the type $RC^{\bullet}H(CH_2)_nCH_2R^1 \longrightarrow RCH_2(CH_2)_nC^{\bullet}HR^1$ (n = 2—4, R and R^1 are alkyl substituents) were analyzed using the parabolic model (PM). The parameters characterizing this class of reactions were calculated. Isomerization of alkyl radicals *via* cyclic transition states (TS) is characterized by the following energy barriers to thermoneutral reaction E_{e0}: 53.5, 65.4, and 63.2 kJ mol^{-1} for the six-, five-, and seven-membered TS, respectively. The E_{e0} energy and the strain energy change in parallel in the series of cycloparaffins C_nH_{2n}. Density functional calculations of intramolecular hydrogen transfer in the n-butyl and n-pentyl radicals and of the bimolecular hydrogen abstraction from the ethane molecule by the ethyl radical were performed. The activation energies of the intra- and intermolecular hydrogen transfer were compared. The parameters of the PM were compared with the interatomic distances in the reaction center of the TS calculated by the density functional method.

Key words: alkyl radical, intramolecular shift of H atom, bimolecular abstraction, activation energy, nonempirical quantum-chemical calculations, density functional theory, parabolic model of bimolecular reaction.

Isomerization of alkyl radicals involving abstraction of H atom from the C—H bond occurs in chain processes of cracking and radiolysis of hydrocarbons,[1] radical polymerization and oligomerization of monomers,[2] and in the thermal and thermooxidative destruction of polymers.[3,4] This reflects both the rate of the chain process and the composition of the products formed. Information on the rates of such reactions is scarce.

Comparison of the parameters of transition states (TS) for reactions of the intra- and intermolecular hydrogen transfer is of great theoretical interest. The matter is that bimolecular abstraction reaction is characterized by linear arrangement of the atoms of the reaction center (C...H...C), whereas a nonlinear (angular) configuration of the same atoms is typical of intraradical hydrogen shift. A higher activation energy (at the same enthalpy of the reaction) can be expected for this process.

In this work, we used the parabolic model (PM) to analyze the available experimental data on radical abstraction reactions and compared the reactions of intra- and intermolecular atom transfer. In addition, we performed density functional (DFT) calculations of similar reactions and compared their parameters obtained using the PM with those calculated quantum-chemically. The influence of the cycle size on the activation energy of intraradical hydrogen transfer was also studied.

Calculation procedure

Calculations of kinetic parameters. Parabolic model of radical abstraction reactions. In the framework of the PM, the isomerization of alkyl radicals

$$RC^{\bullet}H(CH_2)_3CH_2R^1 \longrightarrow RCH_2(CH_2)_3C^{\bullet}HR^1,$$

where R and R^1 are hereinafter alkyl substituents, is a result of intersection of the potential curves of the stretching vibrations of the cleaved (i) and formed (f) bonds plotted in the "potential energy—vibrational amplitude" coordinates.[5,6] The stretching vibrations of the bonds are assumed to be harmonic. Isomerization is described by the following parameters: the enthalpy ΔH_e, activation energy E_e, coefficients b_i and b_f ($2b^2$ is the force constant of the corresponding bond), and the sum of the vibrational amplitudes of the cleaved and formed bonds (r_e) in the TS. The expression for the reaction enthalpy (ΔH_e) includes the difference between the zero-point vibrational energies of the cleaved and newly formed bonds:

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f), \quad (1)$$

and the expression for the activation energy (E_e) includes the zero-point vibrational energy of the cleaved bond

$$E_e = E + 0.5(hL\nu_i - RT), \quad (2)$$

where D_i and D_f are the corresponding bond dissociation energies; ν_i and ν_f are the frequencies of the stretching vibrations of

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these bonds, h is the Planck constant, L is Avogadro´s constant, E is the activation energy of the reaction calculated without inclusion of the zero-point vibrational energy, T is the temperature, and R is the universal gas constant.

Radical reactions belonging to the same class are characterized by the same value of the pre-exponential factor $A_{\text{C—H}}$ calculated per attacked C—H bond.[6] Therefore, the activation energy was calculated from the experimental value of the reaction rate constant k

$$E = -RT\ln(k/n_iA_{\text{C—H}}), \qquad (3)$$

where n_i is the number of the equireactive attacked C—H bonds. In the framework of the PM, each class of radical reactions is characterized by the parameters $\alpha = b_i/b_f$, br_e ($b = b_i$), the energy barrier to thermoneutral reaction E_{e0} (calculated with inclusion of zero-point vibrational energy of the reacting bond), and the position of the TS, $r_0^{\#}$, in the r_e line at $E_e = E_{e0}$, which are calculated for each individual reaction using the following formulas[6]:

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}, \qquad (4)$$

$$\sqrt{E_{e0}} = br_e/(1 + \alpha), \qquad (5)$$

$$r_0^{\#}/r_e = \alpha/(1 + \alpha). \qquad (6)$$

The values of the α, b_i, $0.5hL\nu_i$, and $r_0^{\#}/r_e$ parameters for the reaction classes considered in this work are presented below.

Reaction	α	$b_i \cdot 10^{-11}$ /kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}
$R^{\bullet} \to R^{1\bullet}$	1.000	3.743
$C_6H_4{}^{\bullet}CH_2R \to$ $\to C_6H_5C^{\bullet}HR$	0.945	3.743

Reaction	$0.5hL\nu_i$	$0.5hL\nu_f$	$0.5hL(\nu_i - \nu_f)$	$r_0^{\#}/r_e$
	kJ mol^{-1}			
$R^{\bullet} \to R^{1\bullet}$	17.4	17.4	0.0	0.50
$C_6H_4{}^{\bullet}CH_2R \to$ $\to C_6H_5C^{\bullet}HR$	17.4	18.4	−1.0	0.49

The entropy loss ($-\Delta S^{\#} = R\ln(RT/A_{\text{C—H}}Lh)$ corresponding to the formation of the cyclic TS from the linear aliphatic radical is approximately −53 J (mol K)$^{-1}$ (for the estimation of this value, see below). The pre-exponential factor $A_{\text{C—H}} = 10^{10}$ s^{-1} ($T = 300$ K) corresponds to this entropy loss.

Quantum-chemical calculation. Theoretical study of the intra- and intermolecular hydrogen transfer was carried out using the density functional approach with the B3LYP hybrid functional which provides a good accuracy for simple reactions.[7] Calculations were performed using the GAUSSIAN 98 program package.[8] The optimized geometry corresponding to the stationary point and the zero-point vibrational energy were found in the 6-31G basis set and then the energy of the system was calculated in the 6-311++G(d,p) basis set.

Results and Discussion

The results obtained are presented in Table 1. The calculated C—H bond dissociation energy in the ethane molecule is 403.3 kJ mol^{-1} and the rotation barrier is 867 cm^{-1} (*cf.* experimental values of 422 kJ mol^{-1} [9] and 1008 cm^{-1} [10a], respectively). Using the harmonic vibrational frequencies of the equilibrium structures and TS, we can find the statistical sums and, hence, necessary thermodynamic characteristics for nonzero temperatures. The standard entropy of the ethane molecule calculated in the harmonic approximation is 242.3 J (mol K)$^{-1}$ and its experimental value is 229.5 J (mol K)$^{-1}$.[10b]

The kinetic characteristics of isomerization were determined only for a few alkyl radicals.[11—14] To calculate the br_e parameter, one should know not only the physical characteristics of the bond (see above) but also the enthalpy (ΔH_e) and activation energy of the reaction (Table 2). For the reaction under study in which one C—H bond is cleaved and another C—H bond is formed, we get $\Delta H_e = \Delta H = D_i - D_f$. The dissociation energies of aliphatic C—H bonds were taken from Ref. 15. The activation energy E was calculated using formula (3) with $A_{\text{C—H}} = 10^{10}$ s^{-1} (see above).

From the data listed in Table 2 it can be seen that isomerization of alkyl radicals proceeds *via* cyclic TS and is characterized by different values of the br_e and E_{e0} parameters depending on the cycle size (Table 3). For the most favorable six-membered TS, these are $br_e = 14.63 \pm 0.42$ kJ$^{1/2}$ mol$^{-1/2}$ and $E_{e0} = 53.5 \pm 3.1$ kJ mol^{-1}; for the five- and seven-membered TS, $E_{e0} = 65.4$ and 63.2 kJ mol^{-1}, respectively.

From analysis of experimental data on bimolecular reactions of hydrogen abstraction by alkyl radicals it is known that the aromatic ring in the α-position to the cleaved bond increases the br_e parameter by 0.5 kJ$^{1/2}$ mol$^{-1/2}$, while the double bond increases it by 1.30 kJ$^{1/2}$ mol$^{-1/2}$.[6] This is due to the interaction between π-electrons and three electrons of the reaction center of the TS, and, as a consequence, to the stronger triplet repulsion E_{e0}. These increments were used in the estimations of the br_e parameter for the cyclization of radicals with the corresponding structure (see Table 3).

Comparison of the kinetic parameters of radical reactions of intermolecular[6] hydrogen abstraction and those of intramolecular hydrogen transfer *via* the six-membered TS suggests that the intraradical shift of H atom is characterized by 21.3 kJ mol^{-1} lower activation energy and, correspondingly, by a smaller value of the r_e parameter ($\Delta r_e = 7.1 \cdot 10^{-12}$ m).

Reaction	br_e /kJ$^{1/2}$ mol$^{-1/2}$	E_{e0} /kJ mol^{-1}	$r_e \cdot 10^{11}$ /m
$R^{\bullet} \to R^{1\bullet}$	14.63	53.5	3.91
$R^{\bullet} + R^1H \to$ $\to RH + R^{1\bullet}$	17.30	74.8	4.62

This seems to be a result of different TS geometries. The bimolecular hydrogen abstraction reaction is characterized by the linear arrangement of the C...H...C at-

Table 1. Energies (in Hartree), torsion angles (θ), bond angles (φ), and bond lengths (d) in reactants and transition states

Compound, symmetry	Geometric parameters	B3LYP/6-31G	ZPE[a]	B3LYP/6311++G**
C_2H_6, D_{3d}	θ(H—C—C—H) = 60°	−79.81274	0.07563	−79.85650
C_2H_6, D_{3h}	θ(H—C—C—H) = 0°	−79.80849	0.07526	−79.85218
$C_2H_5^{\bullet}$, C_s	θ(H—C—C—H) = ±86.5°	−79.141136	0.059758[b]	−79.184968
$C_2H_5^{\bullet}$, C_s	θ(H—C—C—H) = 0°	−79.141050	0.059756	−79.184878
TS $C_2H_5^{\bullet}$ + HC_2H_6, C_{2h}	d(C—$H^{\#}$) = 1.353 Å φ(C—$H^{\#}$—C) = 180° φ(C—C—$H^{\#}$) = 107.8°	−158.93046	0.13406	−159.01597
$C_4H_9^{\bullet}$, C_s	θ(C—C—C—C) = 180° θ(C—C—C—H) = ±85.7°	−157.748936	0.117976[b]	−157.833403
$C_4H_9^{\bullet}$, C_s	θ(C—C—C—C) = 180° θ(C—C—C—H) = 0°, 180°	−157.748978	0.117718	−157.833586
$C_4H_9^{\bullet}$, C_1	θ(C—C—C—C) = 178.0° θ(C—C—C—H)= −33.0°, 151.4°	−157.749094	0.117838[b]	−157.833665
$C_4H_9^{\bullet}$, C_1	θ(C—C—C—C) = 178.3° θ(C—C—C—H)= −111.0°, 65.0°	−157.748927	0.118058	−157.833406
$C_4H_9^{\bullet}$, C_1	θ(C—C—C—C) = 66.0° θ(C—C—C—H) = −83.7°, 88.8°	−157.74862	0.117966[b]	−157.833039
TS (1) $C_4H_9^{\bullet}$, C_2	d(C—$H^{\#}$) = 1.377 Å φ(C—$H^{\#}$—C) = 132.5° φ(C—C—$H^{\#}$) = 94.9°	−157.70775	0.11514	−157.79194
TS (2) $C_4H_9^{\bullet}$, C_{2v}	d(C—$H^{\#}$) = 1.361 Å φ(C—$H^{\#}$—C) = 134.7° φ(C—C—$H^{\#}$) = 94.9°	−157.70497	0.11480	−157.78856
$C_5H_{11}^{\bullet}$, C_s	θ(C—C—C—C) = 180° θ(C—C—C—H) = 0°, 180°	−197.05302	0.14712	−197.15772
$C_5H_{11}^{\bullet}$, C_1	θ(H_3C—C—C—C) = 70.6° θ(C—C—C—CH_2) = −74.5° θ(C—C—C—H) = −40.7°, 148.1°	−197.05032	0.14713	−197.15473
TS $C_5H_{11}^{\bullet}$, C_s	d(C—$H^{\#}$) = 1.356 Å φ(C—$H^{\#}$—C) = 153.2° φ(C—C—$H^{\#}$) = 100.8°	−197.02463	0.14416	−197.12781
H		−0.50027		−0.50226

[a] Zero-point vibrational energy.

[b] Ignoring the contribution of the torsional vibration of the terminal CH_2 group.

Table 2. Thermodynamic and kinetic parameters of isomerization of alkyl radicals

Radical	D_i	ΔH_e	T /K	k /s^{-1}	E /kJ mol^{-1}	br_e /$kJ^{1/2}$ $mol^{-1/2}$	Size of cycle	Ref.
	kJ mol^{-1}							
$C^{\bullet}H_2(CH_2)_3$(C—H)HC(O)OMe	398.8	−23.2	313	$1.3 \cdot 10^5$	31.1	15.23	6	13
(C—H)(O)$CH_2CH(CMe_3)CH_2C^{\bullet}H_2$	385.6	−36.4	353	$1.4 \cdot 10^7$	19.2	14.38	6	14
CH(O)(C—H)$HCHCH_2Me_3CCH_2C^{\bullet}H_2$	397.8	−24.2	353	$5.9 \cdot 10^6$	23.8	14.29	6	14
$C^{\bullet}H_2(CH_2)_4$(C—H)HC(O)OMe	398.8	−23.2	313	$1.8 \cdot 10^4$	36.2	15.90	7	13
$C^{\bullet}H_2(CH_2)_2$(C—H)HC(O)OMe	398.8	−23.2	313	$7.8 \cdot 10^3$	38.4	16.17	5	13

Note. The activation energies E were experimentally obtained (formula (3)); the reaction enthalpy ΔH_e and the parameter br_e were calculated using formulas (1) and (4), respectively. The attacked bonds are marked as (C—H); $A_{C-H} = 10^{10}$ s^{-1}, and D_f = 422.0 kJ mol^{-1}.

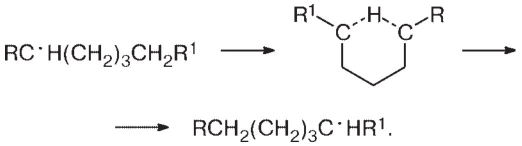
Table 3. Physical characteristics and kinetic parameters of radical isomerization

Radical	br_e /kJ$^{1/2}$ mol$^{-1/2}$	E_{e0} /kJ mol^{-1}	$r_e \cdot 10^{11}$ /m	A_{C-H} /s^{-1}	E_{e0}* /kJ mol^{-1}
$R^{\bullet} \rightarrow R^{1\bullet}$ (six-membered transition state)					
$RC^{\bullet}H(CH_2)_3(C-H)HR'$	14.63	53.5	3.91	10^{10}	74.8
$RC^{\bullet}H(CH_2)_3(C-H)HPh$	15.13	57.2	4.04	10^{9}	79.2
$RC^{\bullet}H(CH_2)_3(C-H)HCH=CH_2$	15.93	63.4	4.26	10^{9}	86.5
$R^{\bullet} \rightarrow R^{1\bullet}$ (five-membered transition state)					
$RC^{\bullet}H(CH_2)_2(C-H)HR'$	16.17	65.4	4.32	10^{10}	74.8
$RC^{\bullet}H(CH_2)_2(C-H)HPh$	16.67	69.5	4.45	10^{9}	79.2
$RC^{\bullet}H(CH_2)_2(C-H)HCH=CH_2$	17.47	76.3	4.67	10^{9}	86.5
$R^{\bullet} \rightarrow R^{1\bullet}$ (seven-membered transition state)					
$RC^{\bullet}H(CH_2)_4(C-H)HR'$	15.90	63.2	4.25	10^{10}	74.8
$RC^{\bullet}H(CH_2)_4(C-H)HPh$	16.40	67.2	4.38	10^{9}	79.2
$RC^{\bullet}H(CH_2)_4(C-H)HCH=CH_2$	17.20	74.0	4.59	10^{9}	86.5

Note. The br_e parameters, energy barriers to thermoneutral reaction E_{e0}, and distances between minima of two intersecting parabolas r_e were calculated using formulas (4)—(6).

* For bimolecular reaction.

oms of the reaction center, while the six-membered cyclic TS is energetically most favorable for isomerization:



Relatively small value of the pre-exponential factor ($A_{C-H} = 10^{10}$ s^{-1}) is also attributed to the cyclic TS.

The energy barriers to intramolecular hydrogen transfer in the *n*-pentyl radical (70.7 kJ mol^{-1}) and to hydrogen abstraction from the ethane molecule by the ethyl radical (62.9 kJ mol^{-1}) obtained from DFT calculations differ insignificantly. Taking into account the temperature dependence of the pre-exponential factor in the framework of the TS theory gives a correction to the activation energy, which has the form $RT^2(\mathrm{d}\ln Q_{TS}/\mathrm{d}T) - RT^2(\mathrm{d}\ln Q_r/\mathrm{d}T)$, where Q_{TS} and Q_r are the partition functions for the transition state and reactants, respectively. The activation energies of intra- and intermolecular hydrogen transfer calculated with inclusion of this correction for $T = 298$ K become virtually equal (65.8 and 62.5 kJ mol^{-1}, respectively). These values agree well with the experimental data for the reaction

$$Me^{\bullet} + CH_4 \longrightarrow CH_4 + Me^{\bullet}.$$

T/K	A_{C-H} /L (mol s)$^{-1}$	E /kJ mol^{-1}	Ref.
473—623	$6.76 \cdot 10^8$	61.29	16
350—600	$6.31 \cdot 10^8$	60.70	17
675—711	$2.58 \cdot 10^9$	55.40	18

The twisted form of the *n*-pentyl radical, whose geometry more closely resembles that of the cyclic TS, is 7.9 kJ mol^{-1} less stable than the main zig-zag structure. Its activation energy of isomerization (51.9 kJ mol^{-1} with inclusion of the thermal energy correction) is close to that predicted by the PM (37.4 kJ mol^{-1}). The results obtained correspond to the absence of steric strain in the six-membered carbocycle because all methylene fragments in the TS, except those "labeled" by the transferred H atom, adopt a mutually non-eclipsed conformation. As a whole, the TS geometry resembles the "chair" conformation of the cyclohexane molecule with the only distinction that the deviation of the transferred H atom from the plane of the "chair" seat is small (the H—C—H angle is ≈153°). The TS structure is less rigid than that of the cyclohexane molecule due to longer C—H distances compared to the equilibrium distances.

Calculations of the entropy change in the harmonic approximation gave a value of 42 J (mol K)$^{-1}$. However, taking into account the anharmonicity effects and especially the unfreezing of internal rotation in the radical increases its entropy. The barrier to rotation of the terminal CH_2 group is particularly low (only 26 cm^{-1} for the ethyl radical[19]; our estimate is 19 cm^{-1}). Assuming this rotation free, we get a contribution of 21.6 J (mol K)$^{-1}$ of the alkyl radical to the entropy for 298 K. This increases the entropy change during the formation of the six- and five-membered cyclic TS to 45 and 40 J (mol K)$^{-1}$, respectively, and makes it possible to estimate the pre-exponential factor at ~$3.8 \cdot 10^{10}$ s^{-1} for 298 K. Since internal rotation in cyclic TS is more hindered than in reactants, the pre-exponential factor decreases due to anharmonicity effects. We consider the value 10^{10} s^{-1} corresponding to the entropy change of 53 kcal (mol K)$^{-1}$ as more realistic estimate. In the case of intermolecular hydrogen abstraction, the internal entropy is almost additive: 207 J (mol K)$^{-1}$ for the TS and 205 J (mol K)$^{-1}$

for the ethane molecule and ethyl radical corrected for free rotation of the CH_2 group.

For the intramolecular transfer of H atom in the *n*-butyl radical, calculations by the DFT method and using the PM lead to different results. For the five-membered cyclic TS, the activation energy noticeably increases to 100.7 kJ mol^{-1} (96.7 kJ mol^{-1} with inclusion of thermal energy correction), which is undoubtedly caused by steric strain. Contrary to expectations, the C_4H_9 cycle in the TS was found to be nonplanar, namely, the C—C—C—C dihedral angle is 35° and the corresponding H—C—C—H dihedral angles are 22° and 41°. The planar structure adopts a fully eclipsed conformation and corresponds to the second-order saddle point. Its energy is 8 kJ mol^{-1} higher than that of the nonplanar TS. The energy of the twisted form of the *n*-butyl radical is slightly higher (by 1.9 kJ mol^{-1}). The energy difference between the structures with different orientation of terminal CH_2 group is also insignificant: only 105 cm^{-1} separate the highest TS and the most stable rotamer.

Below we compare the relative changes in E_{rsc} for the intraradical hydrogen transfer depending on the size of the cycle

Parameter	Number of atoms in cycle		
	5	6	7
ΔE_{e0} ($R \to R^{1\bullet}$)	11.9	0	9.7
E* [16]	26.4	0	26.8
ΔE_{e0} ($R^{\bullet} \to R^{1\bullet}$)**	30.7	0	—

* Strain energy of the cycle.

** Obtained from quantum-chemical calculations.

There is little information on intraradical hydrogen abstraction *via* the five-membered cycle obtained by the method of competitive reactions (see Table 2). Nevertheless, the difference between the results obtained by the DFT method and using the PM is too high to be neglected. We believe that the most important is the circumstance that in the case of intramolecular transfer the free rotation of the terminal Me group in the TS is frozen and the hindered rotation around other C—C bonds is also strongly impeded. As a result, the statistical sum for the activated complex becomes much smaller than that for the initial radical; at the same time, the thermal energy of the activated complex also decreases. This follows from the monotonic increase in the partition function (Q) and the mean thermal energy with temperature. At low temperatures, the correlation is fulfilled

$$RT^2(\mathrm{d}\ln Q/\mathrm{d}T) = RT_{\min}\ln Q,$$

where $T_{\min}$ is the temperature corresponding to the minimum quantum (vibrational) excitation energy of the system. The quadratic law of growth is valid in the high-temperature region:

$$RT^2(\mathrm{d}\ln Q/\mathrm{d}T) = RT^*(\ln Q)^2/N,$$

where N is the number of internal degrees of freedom and T^* is the average characteristic temperature of intramolecular motions determined by the characteristic temperatures of vibrations (T_i^{vib}) and internal rotations (T_i^{rot}):

$$1/T^* = (1 - N_r/N)\sum_i 1/T_i^{\mathrm{vib}} + N_r/(2N)\sum_i 1/T_i^{\mathrm{rot}}.$$

Here N is the number of internal degrees of freedom and N_r is the number of degrees of freedom of internal rotation in the molecule (radical).

Thus, the greater the decrease in the statistical sum during the formation of the cyclic TS due to freezing of internal rotations, the larger the negative correction to the activation energy. Therefore, one should expect a greater decrease in the pre-exponential factor and larger negative thermal corrections to the activation energy for more rigid five-membered cyclic TS. Evidently, it is impossible to describe the crowding of the spectrum due to the intra- and intermode anharmonicity in the harmonic approximation and, hence, to correctly include this effect in the statistical sums. More detailed quantitative study of this problem is beyond the framework of the present work.

For the intermolecular hydrogen abstraction by the $Et^{\bullet}$ radical from the ethane molecule, we calculated the cross section of the potential energy surface in the vicinity of the TS, corresponding to the motion of the H atom along the C...H...C line at fixed position of all C and H atoms of the methylene and methyl fragments (Fig. 1). In this case, the total energy of the system changes insignificantly. It is of interest that at the minima achieved by displacing the H atom by ±0.228 Å, the C—H distance (1.12 Å) is nearly the same as the equilibrium C—H bond length (1.09 Å). This allowed us to estimate the activation energy using a simple model in which the H atom interacts only with the ethyl fragment of the reactant before the TS geometry is achieved, while it reacts only with the ethyl fragment of the product after passing the TS up to the complete displacement of the H atom by 0.456 Å. This method for the estimation of the TS energy is quite satisfactory (see Fig. 1). Approximation of the change in the energy of the ethane molecule during the C—H bond stretch by a parabola makes the estimate of the position of the energy barrier somewhat better. This simplified chemical model completely corresponds to the PM and the quantum-chemical estimate of the displacement of the H atom along the reaction

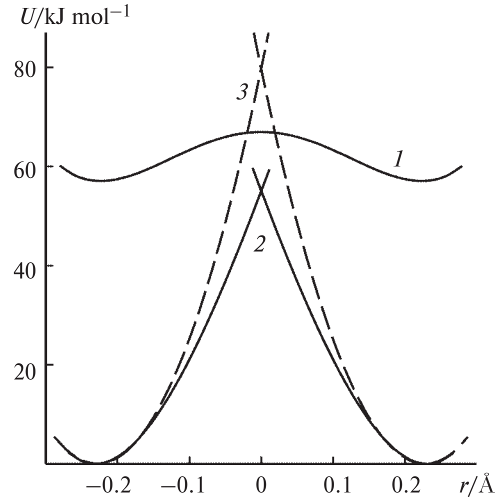


Fig. 1. Cross section of the potential energy surface (U) in the vicinity of the transition state of the reaction $C_2H_5^\bullet + C_2H_6$ along the reaction coordinate (r) C...H...C (*1*) and changes in the energy of the non-interacting reactants during the extension of the C—H bond in the ethane molecule according to calculation using the PM (*2*) and in the harmonic approximation (*3*). Curves *1* and *2* were calculated using the DFT approach, and curves *3* are the parabolic approximation of curves *2*.

coordinate (0.456 Å) is very close to that obtained using the br_e parameter (0.462 Å).

Thus, the results obtained in this work suggest that the geometric parameters of the linear TS calculated by the parabolic model should be rather close to those provided by the quantum-chemical calculations. The calculated C...C distance in the cyclic TS of intraradical hydrogen transfer (2.52 Å for the five-membered cycle and 2.64 Å for the six-membered cycle) is also in reasonable agreement with the estimate found using the PM: $2r_{C-H} + r_e = 2.57$ Å.

Note in conclusion that the activation energy for hydrogen abstraction from the ethane molecule by the $Et^\bullet$ radical calculated by the DFT method (62.9 kJ mol^{-1}) virtually coincides with that estimated from the PM (58.6 kJ mol^{-1}) and with the experimental values (55.4—61.3 kJ mol^{-1})[16—18] for the similar reaction $Me^\bullet + CH_4$. The same holds for the C—C distance in the reaction center of the $Et^\bullet$ + ethane system. Calculations of the activation energy for intraradical hydrogen transfer using the density functional approach and the parabolic model give close values for the six-membered TS and significantly different values for the five-membered cyclic TS.

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