Full Articles

Geometric parameters of transition states of radical abstraction reactions with C...H...C reaction center

E. T. Denisov,★ A. F. Shestakov, T. G. Denisova, and N. S. Emel´yanova

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 511 8910. E-mail: edenisov@icp.ac.ru; as@icp.ac.ru; denisova@icp.ac.ru

An algorithm of calculations of interatomic distances in the transition states (TS) of reactions of hydrogen abstraction by alkyl, allyl, and benzyl radicals from C—H bonds of organic molecules using the enthalpies of the corresponding reactions is proposed. The geometric parameters of the TS of the reactions involving carbon-centered radicals with the C...H...C reaction center, calculated using experimental data, are compared with other characteristics of the reactions and reactants. The r(C...H...C) distance in the TS of the reactions of alkyl radicals with alkanes remains unchanged as the enthalpies of reactions vary, being a characteristic parameter of a given class of reactions. π-Bonds adjacent to the reaction center are responsible for an increase in the parameter r(C...H...C) in the TS.

Key words: alkyl radical, hydrogen atom, abstraction reaction, interatomic distance, parabolic model, quantum-chemical calculations, density functional theory, transition state, hydrocarbon, activation energy, enthalpy of reaction.

Each chemical reaction is characterized by its enthalpy and activation energy. The parabolic model (PM, or the intersecting parabolas method) of a bimolecular radical abstraction reaction uses yet another parameter, namely, the total elongation of the broken and newly formed bonds (r_e) in transition state (TS).[1—5] Correspondence between this empirical parameter and the geometric characteristics of TS calculated using quantum chemistry methods was the subject of earlier studies.[6,7] A comparison of the results of quantum-chemical computations with the parameters of the PM showed that the interatomic distances calculated using both methods are close and can be matched by introducing some corrections to the parameter r_e. This allowed us to derive necessary relationships and to construct a relatively simple algorithm of calculations of interatomic distances for various radical abstraction reactions.[6] The input data for such calculations are the enthalpy of reaction and the PM parameters of a given class of reactions. The aim of this work was to calculate the interatomic distances in the TS of reactions of carbon-centered radicals with the C—H bonds of organic molecules by quantum chemistry methods and using the PM and to compare and analyze the results obtained.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 693—702, April, 2004.

1066-5285/04/5304-0727 © 2004 Plenum Publishing Corporation

Calculation Procedure

The intersecting parabolas method. The characteristic parameters of a radical abstraction reaction of the type

$$^{\bullet}R_f + HR_i \rightarrow R_fH + {^{\bullet}R_i}$$

are as follows[1—5]:

1) enthalpy, ΔH_e, with inclusion of the difference between the zero-point vibrational energies (ZPE) of the broken (C_i—H) and newly formed (C_f—H) bonds; for the reactions with symmetrical TS one has

$$\Delta H_e = \Delta H = D(C_i—H) - D(C_f—H), \quad (1)$$

where $D(C_i—H)$ and $D(C_f—H)$ are the dissociation energies of the broken and the newly formed bonds, respectively;

2) activation energy, E_e, with inclusion of the ZPE of the broken C—H bond; for the reactions under study one has

$$E_e = E + 17.4 - 0.5RT, \quad (2)$$

where 17.4 kJ mol^{-1} is the ZPE of aliphatic C—H bond;[2]

3) parameter r_e equal to the sum of the vibrational amplitudes of the broken and newly formed bonds in the TS;

4) parameter b ($2b^2$ is the force constant of the broken bond and the newly formed bond); for an aliphatic C—H bond, $b = 37.43 \cdot 10^{10}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1};

5) parameter α (α^2 is the force constant ratio of the broken and newly formed bonds); for the reactions with symmetrical TS, $\alpha = 1$; and

6) pre-exponential factor, A_0, per bond involved in the reaction ($n_{C—H}$ is the number of such bonds in the molecule).

The rate constant, k, for a reaction under study is related to the parameters E and A_0 by the Arrhenius equation:

$$k = n_{C—H}A_0\exp[-E/(RT)]. \quad (3)$$

The parameters ΔH_e and E_e characterize individual reactions, while the parameters α, b, A_0, and r_e characterize certain classes of reactions (they have the same values for all reactions belonging to a given class[2]). The parameters mentioned above are related to one another as follows[1]

$$br_e = \sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \quad (4)$$

The parameter br_e makes possible the activation energy, E_{e0}, of a thermally neutral reaction characterized by $\Delta H_e = 0$ to be calculated:

$$E_{e0} = (br_e)^2/(1 + \alpha)^2 = 0.25(br_e)^2. \quad (5)$$

The position of the TS in the r_e line is characterized by the distance $r^{\#}$. In the case of reactions with $\alpha = 1$, the $r^{\#}$ value can be assessed as follows[1]

$$r^{\#} = \frac{r_e\sqrt{E_e}}{\sqrt{E_e - \Delta H_e} + \sqrt{E_e}}. \quad (6)$$

Hydrocarbons involved in reactions with radicals can be placed into three classes (R^1H, R^2H, and R^3H) characterized by different values of the parameter br_e and comprising aliphatic hydrocarbons, olefins, and alkylaromatic hydrocarbons, respectively. The differences in br_e are due to additional triplet repulsion in the TS in the presence of a π-bond adjacent to the attacked C—H bond. The parameters of the PM for the reaction classes $^{\bullet}R^1 + R^1H$, $^{\bullet}R^1 + R^2H$, and $^{\bullet}R^1 + R^3H$ were taken from the literature.[1] The parameters br_e of the reaction classes $^{\bullet}R^2 + R^2H$ and $^{\bullet}R^3 + R^3H$ were calculated from experimental data. The results of calculations are listed in Table 1. The parameter br_e of the reaction classes $^{\bullet}R^3 + R^2H$ and $^{\bullet}R^2 + R^3H$ was assumed to be 18.73 kJ$^{1/2}$ mol$^{-1/2}$, as for the reaction class $^{\bullet}R^2 + R^2H$.

The parameter br_e of the reaction between methyl radical and 1,4-cyclohexadiene appeared to be much larger than the average value (br_e = 19.48 kJ$^{1/2}$ mol$^{-1/2}$). The br_e and E_{e0} values used in this work are listed in Table 2. In the acetone molecule, the attacked C—H bond is in α-position relative to the C=O bond. One could expect that the parameter br_e of the reaction mentioned above will approach that of the reaction class $^{\bullet}R^1 + R^2H$; however, it equals the br_e value characteristic of the reaction class $^{\bullet}R^1 + R^1H$ (see Tables 1 and 2). This means that conjugation of the electrons of the reaction center with π-electrons of the C=O bond in the TS of this reaction is of lesser importance. This is in good agreement with the results of quantum-chemical calculations (see below).

In the framework of the PM the interatomic distances in the TS can be estimated as follows[2]

$$r(C_i...H...C_f) = 2r(C—H) + b^{-1}\left(\sqrt{E_e} + \sqrt{E_e - \Delta H_e}\right), \quad (7)$$

$$r(C_i...H) = r(C—H) + b^{-1}\sqrt{E_e}, \quad (8)$$

$$r(C_f...H) = r(C—H) + b^{-1}\sqrt{E_e - \Delta H_e}. \quad (9)$$

For aliphatic compounds, r(C—H) = $1.096 \cdot 10^{-10}$ m.[14] Knowing the corresponding parameters of the reaction class to which a given reaction belongs and the enthalpy of reaction, ΔH, one can evaluate[2] the activation energy E_e using the PM:

$$\sqrt{E_e} = \frac{br_e}{2} + \frac{\Delta H}{2br_e} = \sqrt{E_{e0}} + \frac{\Delta H}{2br_e}. \quad (10)$$

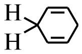
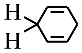
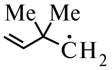
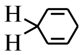
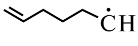
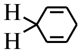
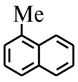
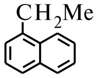
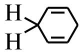
Quantum-chemical calculations. Theoretical study of hydrogen abstraction reactions from double-bonded substrates by the $^{\bullet}CH_3$ radical was carried out using the hybrid density functional method (B3LYP). This approach is a reliable tool of theoretical investigations of radical reactions.[15,16] The average error in determination of the enthalpy and activation energy of reactions is 10 kJ mol^{-1}.[17]

All calculations were carried out using the GAUSSIAN-98 program.[18] Geometric parameters of the structures corresponding to the stationary points on the potential energy surface (PES) were found by optimization in the 6-31G(d) basis set and then used to calculate the energy of the system in the 6-311++G(d,p) basis set with inclusion of ZPE correction in the B3LYP/6-31G(d) approximation. The following reaction systems characterized by conjugation between electrons of the radical center and two C=C bonds were calculated: a) reactions involving the $^{\bullet}CH_3$ and $^{\bullet}CH_2Me$ radicals:

$$^{\bullet}CH_3 + C_2H_6 \rightarrow CH_4 + {^{\bullet}C_2H_5},$$

$$^{\bullet}CH_2Me + C_2H_6 \rightarrow C_2H_6 + {^{\bullet}C_2H_5},$$

Table 1. Parameters br_e of radical reactions with unsaturated and alkylaromatic hydrocarbons (Eqs. (1)—(4)) estimated from experimental data

Reaction	T/K	k /L mol^{-1} s^{-1}	E	$-\Delta H$	br_e	Ref.
			kJ mol^{-1}			
			Reaction class $^{\bullet}R^2 + R^2H$			
$^{\bullet}CH_2Me$ + 	203	$4.9 \cdot 10^2$	26.9	109.4	18.96	8
$^{\bullet}CMe_3$ + 	203	33.0	31.4	87.4	18.56	8
 + 	323	$4.8 \cdot 10^5$	24.2	109.4	18.58	9
 + 	323	$2.5 \cdot 10^5$	26.2	109.4	18.82	9
					18.73±0.17*	
			Reaction class $^{\bullet}R^3 + R^3H$			
$^{\bullet}CH_2Ph + Ph_3CH$	443	$2.95 \cdot 10^4$	21.5	29.0	15.39	10
$^{\bullet}CH_2Ph + Ph_2CH_2$	443	$1.33 \cdot 10^4$	26.9	18.2	15.46	10
$^{\bullet}CH_2Ph + PhCH_2CH_2Ph$	443	$5.65 \cdot 10^3$	32.6	10.8	15.75	10
$^{\bullet}CH_2Ph + PhCH_2CH_2CH_2Ph$	443	$8.10 \cdot 10^3$	31.3	10.9	15.59	10
$^{\bullet}CH_2Ph$ + 	443	$3.68 \cdot 10^3$	33.2	9.9	15.77	10
$^{\bullet}CH_2Ph$ + 	443	$6.14 \cdot 10^3$	29.8	20.8	15.98	10
					15.71±0.20*	
			Individual reactions			
$^{\bullet}CH_3 + Me_2C(O)$	500	$2.05 \cdot 10^4$	45.6	28.2	17.25	11
$^{\bullet}CH_3 + Me_2C(O)$	500	$2.30 \cdot 10^4$	45.2	28.2	17.21	12
$^{\bullet}CH_3 + Me_2C(O)$	500	$2.03 \cdot 10^4$	45.7	28.2	17.27	13
$^{\bullet}CH_3$ + 	273	$5.0 \cdot 10^4$	25.6	127.4	19.48	8

* Average value.

Table 2. Energy characteristics and geometric parameters of symmetrical transition states of radical abstraction reactions[1—4]

Reaction	E_{e0} /kJ mol^{-1}	$br_e \cdot 10^{10}$ /kJ$^{1/2}$ mol$^{-1/2}$	$r(C_i...H...C_f) \cdot 10^{10}$ /m	$[dr(C...H)/d\Delta H] \cdot 10^{10}$ /mol m J^{-1}
$^{\bullet}R^1 + R^1H$	74.8	17.30	2.714	1.75
$^{\bullet}R^1 + R^2H$	86.5	18.60	2.751	1.62
$^{\bullet}R^1 + R^3H$	79.2	17.80	2.729	1.70
$^{\bullet}R^2 + R^1H$	86.5	18.60	2.751	1.62
$^{\bullet}R^2 + R^2H$	87.7	18.73	2.757	1.72
$^{\bullet}R^2 + R^3H$	87.7	18.73	2.757	1.72
$^{\bullet}R^3 + R^1H$	79.2	17.80	2.729	1.70
$^{\bullet}R^3 + R^2H$	87.7	18.73	2.757	1.72
$^{\bullet}R^3 + R^3H$	61.7	15.71	2.666	1.92

$^{\bullet}CH_3 + CH_2Me_2 \rightarrow CH_4 + {}^{\bullet}CHMe_2$,

$^{\bullet}CH_3 + CHMe_3 \rightarrow CH_4 + {}^{\bullet}CMe_3$,

$^{\bullet}CH_3 + PhCH_3 \rightarrow CH_4 + {}^{\bullet}CH_2Ph$,

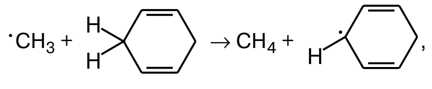
$^{\bullet}CH_3 + MeCH{=}CH_2 \rightarrow CH_4 + {}^{\bullet}CH_2CH{=}CH_2$,

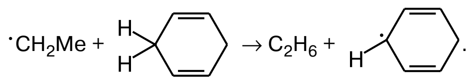
$^{\bullet}CH_3 + MeC(O)Me \rightarrow CH_4 + {}^{\bullet}CH_2C(O)Me$,

and b)

$^{\bullet}CH_2CH{=}CH_2 + MeCH{=}CH_2 \rightarrow$

$\rightarrow MeCH{=}CH_2 + {}^{\bullet}CH_2CH{=}CH_2$,





The results of calculations are listed in Table 3 and shown in Fig. 1. The calculated C—H bond dissociation energies (in kJ mol^{-1}) in the reactants are listed below (for comparison, the experimental D(C—H) values[19—21] are also given in parentheses).

C_2H_6	403 (422)	MeCH—HMe	405 (412)
Me_3C—H	377 (400)	$CH_2{=}CHCH_2$—H	345 (368)
$PhCH_2$—H	357 (375)	$MeC(O)CH_2$—H	383 (375)
	290 (313)		

The activation energies and enthalpies of the reactions under study are compared with the experimental data in Table 4.

Comparison of two computational methods. The results of calculations using the PM can be matched with those of quantum-chemical calculations of interatomic distances in the TS by representing the sum of distances $r(C_i...H) + r(C_f...H) = r(C_i...H...C_f)$ as $2r(R—H) + \beta r_e$, where β is a correction factor. The β values for a number of reactions are listed in Table 5.

With allowance for $\alpha = 1$, $\beta = 1.13\pm0.03$, and $b = 37.43 \cdot 10^{10}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}, the equations for calculating the interatomic distances (r/m) using the quantum-chemically corrected PM take the form

$$r(C_i...C_f) = 2.192 \cdot 10^{-10} + 3.019 \cdot 10^{-12}\left(\sqrt{E_e} + \sqrt{E_e - \Delta H_e}\right), \quad (11)$$

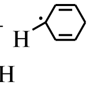
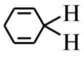
$$r(C_i...H) = 1.096 \cdot 10^{-10} + 3.019 \cdot 10^{-12}\sqrt{E_e}, \quad (12)$$

$$r(C_f...H) = 1.096 \cdot 10^{-10} + 3.019 \cdot 10^{-12}\sqrt{E_e - \Delta H_e}. \quad (13)$$

These equations were used for calculations of geometric parameters of the TS of radical abstraction reactions. The E values were found using the known C—H bond dissociation energies with relationships (1) and (10). The distances $r(C_i...H)$ and $r(C_f...H)$ calculated using Eqs. (12) and (13) are compared with those obtained from quantum-chemical calculations in Table 6.

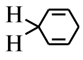
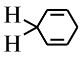
In the case of reactions with $\Delta H \neq 0$, the distances $r(C_i...H)$ calculated by different methods differ by $(3.7\pm2.2) \cdot 10^{-12}$ m, which is comparable with the error in determination of r_e from

Table 3. Energy characteristics and geometric parameters (torsion angles θ, bond angles φ, and bond lengths d) of reactants and transition states

System	E^a/hartree		Geometric parameters^b			
	B3LYP/6-31G(d)	B3LYP/6-311++G(d,p)	Bond	d/Å	Angle	φ/deg
$^{\bullet}CH_3$	−39.83829 (0.02981)	−39.85517	C—H	1.0833		
CH_4	−40.51838 (0.04523)	−40.53395	C—H	1.090		
$^{\bullet}C_2H_5$	−79.15787 (0.05965)	−79.18503			H—C—C—H^c	±86.5
C_2H_6	−79.83042 (0.07524)	−79.85655	C—H	1.096		
$^{\bullet}CH_2CH{=}CH_2$	−117.26035 (0.06636)	−117.29825	C—C	1.386		
$MeCH{=}CH_2$	−117.90756 (0.08009)	−117.94559	C—H	1.097		
			C—C	1.502		
			C=C	1.333		
$^{\bullet}CHMe_2$	−118.47815 (0.08861)	−118.51543	C—C	1.493	C—C—C	121.3
CH_2Me_2	−119.14425 (0.10412)	−119.18110	C—C	1.533	C—C—C	112.9
			C—H	1.098		
$^{\bullet}CMe_3$	−157.79832 (0.11726)	−157.84551	C—C	1.498	C—C—C	118.9
$HCMe_3$	−158.45881 (0.13239)	−158.50644	C—C	1.535	C—C—C	111.1
			C—H	1.101		
CH_4 + 	−232.79339 (0.10906)	−232.85731	C—C	1.419		
			C=C	1.366		
	−233.41850 (0.12259)	−233.48369	C—H	1.103		
			C—C	1.507		
			C=C	1.334		

(*to be continued*)

Table 3 (*continued*)

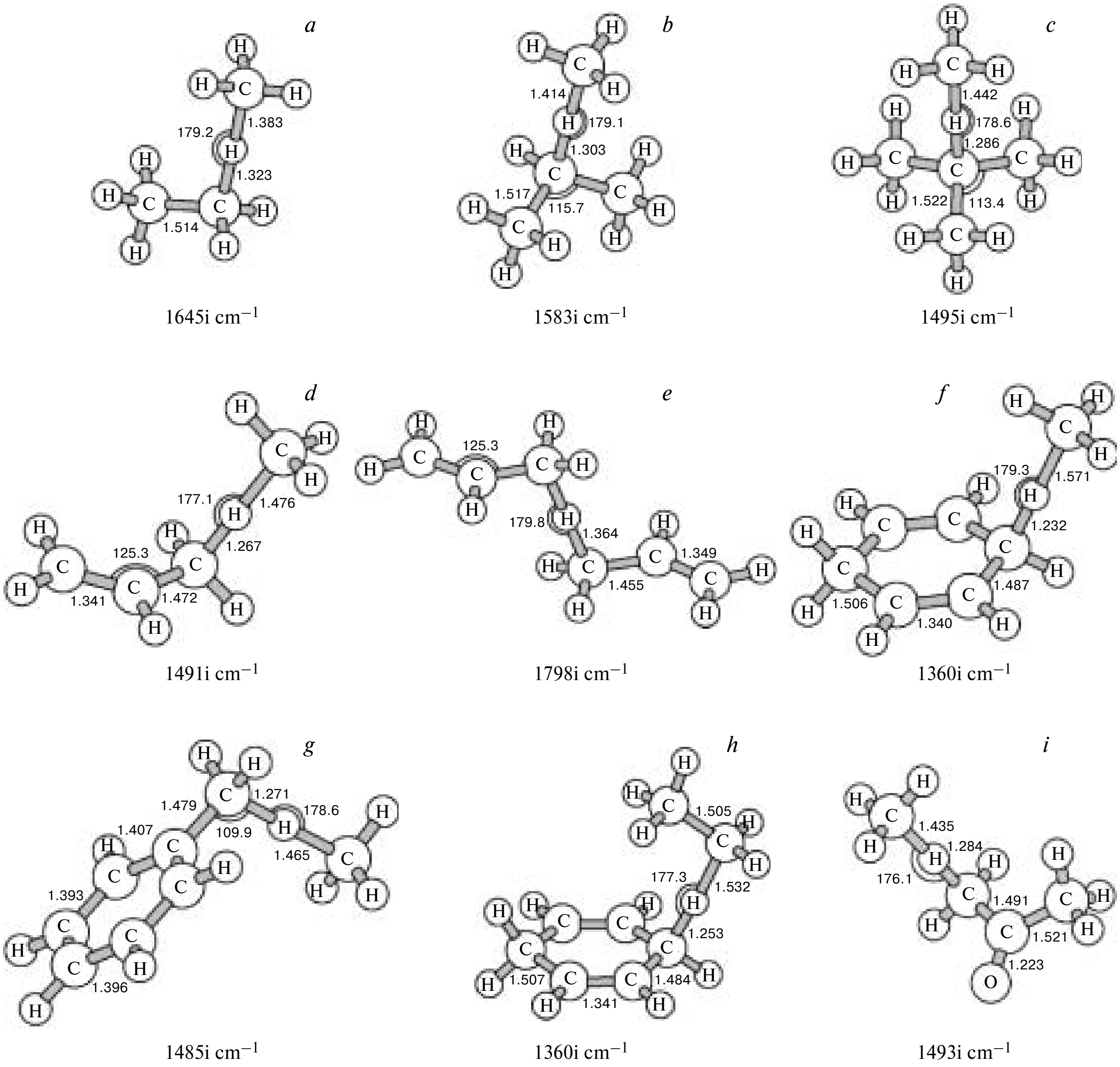
System	E^a/hartree		Geometric parameters^b			
	B3LYP/6-31G(d)	B3LYP/6-311++G(d,p)	Bond	d/Å	Angle	φ/deg
$^{\bullet}CH_2Ph$	−270.91514 (0.11497)	−270.98724	C—C	1.427		
			C=C	1.407		
CH_3Ph	−271.56665 (0.12831)	−271.63882	C—H	1.098	C—H—C	111.3
			C—C	1.511		
			C=C	1.402		
$^{\bullet}CH_2COMe$	−192.49502 (0.07071)	−192.55653	C=O	1.239		
			C—C	1.440		
			C—C	1.522		
MeOMe	−193.15569 (0.08407)	−193.21818	C=O	1.216		
			C—C	1.521		
			C—H	1.097		
$^{\bullet}CH_3 + MeCH_2$—H (TS)	−119.64909 (0.10400)	−119.69040	C_m—H	1.383	C—H—C	179.2
			C—H	1.323		
$^{\bullet}C_2H_5 + MeCH_2$—H (TS)	−158.96444 (0.13323)	−159.01601	C—H	1.356	C—H—C	180
$^{\bullet}CH_3 + Me_2CH$—H (TS)	−158.96569 (0.13256)	−159.01773	C_m—H	1.414	C—H—C	179.1
			C—H	1.303	C—C—C	115.7
			C—C	1.517		
$^{\bullet}CH_3 + Me_3C$—H (TS)	−198.28256 (0.16059)	−198.34554	C_m—H	1.442	C—H—C	178.6
			C—H	1.286	C—C—C	113.4
			C—C	1.522		
$^{\bullet}CH_3 + CH_2{=}CHCH_2$—H (TS)	−157.73213 (0.10915)	−157.78523	C_m—H	1.476		
			C—H	1.267		
			C—C	1.472		
			C=C	1.341		
$^{\bullet}CH_2CH{=}CH_2$ + + $CH_2{=}CHCH_2$—H (TS)	−235.13557 (0.14396)	−235.21048	C—H	1.364	C—H—C	179.8
			C—C	1.455		
			C=C	1.349		
$^{\bullet}CH_3$ +  (TS)	−273.24847 (0.15140)	−273.32874	C_m—H	1.571	C—H—C	179.3
			C—H	1.232		
			C—C	1.487		
			C=C	1.340		
$^{\bullet}CH_2Me$ +  (TS)	−312.56597 (0.18068)	−312.65598	C_m—H	1.532	C—H—C	177.3
			C—H	1.253		
			C—C	1.484		
			C=C	1.341		
$^{\bullet}CH_3 + PhCH_3$—H (TS)	−311.39172 (0.15748)	−311.47891	C_m—H	1.465	C—H—C	178.6
			C—H	1.271		
			C—C	1.479		
			C=C	1.408		
$^{\bullet}CH_3 + MeOCH_2$—H (TS)	−232.97975 (0.11353)	−233.05734	C_m—H	1.434	C—H—C	176.1
			C—H	1.284		
			C—C	1.494		
			C—C	1.521		
			C=O	1.223		

[a] The zero-point vibrational energies of chemical bonds are given in parentheses.

[b] The subscript "m" denotes the C atom in the attacking radical.

[c] Torsion angle θ.

experimental data, namely, $(1.5—2.5) \cdot 10^{-12}$ m. The average error in assessment of the interatomic distance in the TS of hydrogen abstraction reactions by the B3LYP/G-31+G(d,p) method is $7 \cdot 10^{-12}$ m.[31] It should be expected that for the same-type reactions of carbon-centered radicals with hydrocarbon C—H bonds this error is much lower ($(2—3) \cdot 10^{-12}$ m).



1645i cm^{-1} 1583i cm^{-1} 1495i cm^{-1}

1491i cm^{-1} 1798i cm^{-1} 1360i cm^{-1}

1485i cm^{-1} 1360i cm^{-1} 1493i cm^{-1}

Fig. 1. Geometric parameters of the TS of reactions
$^{\bullet}CH_3 + C_2H_6 \rightarrow CH_4 + {}^{\bullet}CH_2CH_3$ (*a*),
$^{\bullet}CH_3 + CH_2Me_2 \rightarrow CH_4 + {}^{\bullet}CHMe_2$ (*b*),
$^{\bullet}CH_3 + CHMe_3 \rightarrow CH_4 + {}^{\bullet}CMe_3$ (*c*),
$^{\bullet}CH_3 + MeCH{=}CH_2 \rightarrow CH_4 + {}^{\bullet}CH_2CH{=}CH_2$ (*d*),
$^{\bullet}CH_2CH{=}CH_2 + CH_3CH{=}CH_2 \rightarrow CH_2{=}CHCH_3 + {}^{\bullet}CH_2CH{=}CH_2$ (*e*),
$^{\bullet}CH_3$ + *cyclo*-$C_6H_8 \rightarrow CH_4$ + *cyclo*-$C_6H_7{}^{\bullet}$ (*f*),
$^{\bullet}CH_3 + PhCH_3 \rightarrow CH_4 + {}^{\bullet}CH_2Ph$ (*g*),
$^{\bullet}CH_2Me$ + *cyclo*-$C_6H_8 \rightarrow C_2H_6$ + *cyclo*-$C_6H_7{}^{\bullet}$ (*h*), and
$^{\bullet}CH_3 + MeC(O)Me \rightarrow CH_4 + {}^{\bullet}CH_2C(O)Me$ (*i*).
Calculations were carried out using the GAUSSIAN-98 program; the geometric parameters of the structures corresponding to the stationary points on the PES were found by optimization in the 6-31G(d) basis set. Given are the imaginary vibrational frequencies for each TS.

Table 4. Enthalpies (ΔH/kJ mol^{-1}) and activation energies (E/kJ mol^{-1}) of the reactions of alkyl radicals with hydrocarbons and acetone obtained from B3LYP/6-31G(d) calculations (I) and experimental values (II)

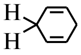
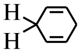
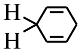
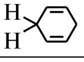
Reaction	$-\Delta H$		E		Ref.
	I	II	I	II	
$^{\bullet}CH_3 + C_2H_6$	19.3	18.0	53.1	50.0	22, 23
$^{\bullet}CH_3 + Me_2CH_2$	34.6	28	45.1	43.1	24
				55.5	25
$^{\bullet}CH_3 + Me_3CH$	46.1	40	38.0	33.8	26
				34.2	27
$^{\bullet}CH_3 + CH_3Ph$	65.7	65.0	38.1	33.5	28
				39.7	29
$^{\bullet}CH_3 + MeCH{=}CH_2$	77.8	72.0	38.9	36.9	30
$^{\bullet}CH_3 + MeC(O)Me$	39.6	28.2	41.1	40.5	11
				40.0	12
				40.3	13
$^{\bullet}CH_3$ + 	132.6	127.4	23.9	25.6	8
$^{\bullet}CH_2Me$ + 	113.1	109.4	29.4	26.9	8
$^{\bullet}CH_2CH{=}CH_2$ + + $CH_2{=}CHCH_2{-}H$	0	0	80.9	70.1	PM

Table 5. Correction factors for a number of reactions, obtained from B3LYP calculations and using the PM

Reaction	PM		B3LYP/6-31G(d)		β
	r_e[a]	r[b]	r_e[a]	r[b]	
$^{\bullet}CH_3 + C_2H_6$	0.462	2.654	0.520	2.706	1.13
$^{\bullet}CH_2Me + C_2H_6$	0.462	2.654	0.520	2.712	1.13
$^{\bullet}CH_3 + MeCH_2Me$	0.462	2.654	0.529	2.717	1.15
$^{\bullet}CH_3 + Bu^tH$	0.462	2.654	0.537	2.728	1.16
$^{\bullet}CH_3 + MeC(O)Me$	0.462	2.654	0.521	2.718	1.13
$^{\bullet}CH_3 + PhCH_3$	0.475	2.668	0.538	2.736	1.13
$^{\bullet}CH_3 + CH_2{=}CHMe$	0.479	2.689	0.546	2.743	1.14
$^{\bullet}CH_2CH{=}CH_2$ + + $CH_2{=}CHMe$	0.500	2.692	0.534	2.728	1.07
$^{\bullet}CH_3$ + 	0.520	2.712	0.610	2.803	1.17
$^{\bullet}CH_2Me$ + 	0.500	2.692	0.586	2.785	1.17

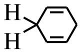
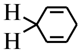
[a] Listed are the values $r_e \cdot 10^{10}$/m.

[b] $r(C_i...H...C_f) \cdot 10^{10}$/m.

Results and Discussion

Constancy of the distance r(C...H...C) for reactions belonging to the same class. The activation energies of the reactions of methyl radical with C—H bonds of various organic molecules and the corresponding interatomic distances calculated using relationships (12) and (13) are listed in Table 7. The C—H bond dissociation energies necessary for calculations were taken from the literature.[19—21]

Table 6. Interatomic distances obtained from B3LYP calculations and using the PM

Reaction	B3LYP		PM	
	r_1[a]	r_2[b]	r_1[a]	r_2[b]
$^{\bullet}CH_3 + C_2H_6$	1.323	1.383	1.341	1.373
$^{\bullet}CH_2Me + C_2H_6$	1.356	1.356	1.357	1.357
$^{\bullet}CH_3 + MeCH_2Me$	1.303	1.414	1.333	1.381
$^{\bullet}CH_3 + Bu^tH$	1.286	1.442	1.392	1.432
$^{\bullet}CH_3 + MeC(O)Me$	1.284	1.435	1.332	1.381
$^{\bullet}CH_3 + PhCH_3$	1.271	1.465	1.321	1.420
$^{\bullet}CH_3 + CH_2{=}CHMe$	1.267	1.476	1.318	1.436
$^{\bullet}CH_2CH{=}CH_2$ + + $CH_2{=}CHMe$	1.364	1.364	1.379	1.379
$^{\bullet}CH_3$ + 	1.232	1.571	1.273	1.481
$^{\bullet}CH_2Me$ + 	1.253	1.582	1.294	1.464

[a] $r(C_i...H) \cdot 10^{10}$/m.

[b] $r(C_f...H) \cdot 10^{10}$/m.

As can be seen from the data listed in Table 7, all reactions of the methyl radical with the C—H bonds of organic molecules are exothermic. Because of this, here we deal with the "early" TS and $r(C...H) < r(Me...H)$. It is known[32] that for all reactions belonging to the same class the parameters br_e and r_e are constants provided that the ΔH values lie within a certain interval, ΔH_{min}—ΔH_{max}. In the case of reactions of alkyl radicals, this range is rather broad (−153—153 kJ mol^{-1}). Is this consistent with the results of quantum-chemical calculations? An answer to this question is provided by the results obtained in this work and reported earlier.[33]

Reaction	$r(C_i...H...C_f) \cdot 10^{10}$/m	$-\Delta H$/kJ mol^{-1}
$Me^{\bullet} + C_2H_6$	2.706	20
$Et^{\bullet} + C_2H_6$	2.712	0.0
$Me^{\bullet} + C_3H_8$	2.717	28
$Me^{\bullet} + Bu^tH$	2.728	40

In spite of large differences between the enthalpies of these reactions the distances C...H...C in the corresponding TS are very similar, namely, $r(C_i...H...C_f) = (2.717\pm0.011) \cdot 10^{-10}$ m. The difference is no greater than the error in estimation of the parameter $r(C_i...H...C_f)$, or $\pm0.02 \cdot 10^{-10}$ m for the PM. Therefore, the conclusion about the constant value of the parameter r_e, which was drawn in the framework of the PM, is additionally confirmed by the results of quantum-chemical calculations. The geometric parameters of the TS of the reactions of ethylmethyl and 1,1-dimethylethyl radicals with hydrocarbons are listed in Table 8.

Table 7. Enthalpies and activation energies of and interatomic distances in the TS of the reactions of methyl radical with hydrocarbons and oxygen-containing compounds

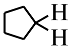
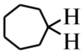
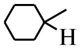
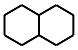
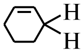
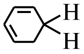
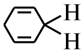
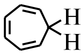
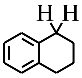
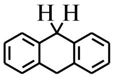
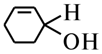
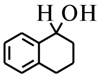
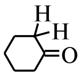
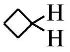
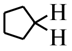
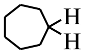
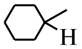
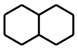
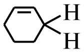
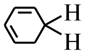
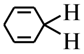
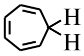
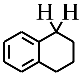
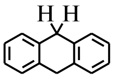
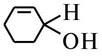
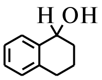
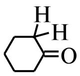
R_iH	E	D_{RH}	$-\Delta H$	E_e	$r(R_i...H)$	$r(Me...H)$
	kJ mol^{-1}				10^{-10} m	
EtMeCH—H	45.8	413.0	27.0	61.8	1.333	1.381
Me_3C—H	40.1	400.0	40.0	56.1	1.322	1.392
	48.4	418.5	21.5	64.4	1.338	1.376
	43.8	408.4	31.6	59.8	1.329	1.385
	41.8	403.9	36.1	57.8	1.326	1.388
	38.1	395.5	44.5	54.1	1.318	1.396
Z- 	34.8	387.6	52.4	50.8	1.311	1.403
CH_2=CHCH_2—H	38.1	368.0	72.0	54.1	1.318	1.436
CH_2=CHCH—HMe	31.2	349.8	90.2	47.2	1.303	1.451
CH_2=CHC—HMe_2	27.5	339.6	100.4	43.5	1.295	1.459
Z-MeCH=CHCH—HMe	29.0	344.0	96.0	45.0	1.299	1.455
Me_2=CHCH—HMe	24.8	332.0	108.0	40.8	1.289	1.465
Me_2C=CMeC—HMe_2	21.7	322.8	117.2	37.7	1.281	1.473
CH_2=CHCMe—HCH=CH_2	16.7	307.2	132.8	32.7	1.269	1.485
	28.2	341.5	98.5	44.2	1.297	1.457
	24.4	330.9	109.1	40.4	1.288	1.466
	18.4	312.6	127.4	34.4	1.273	1.481
	14.8	301.0	139.0	30.8	1.264	1.490
MeC≡CC—HMe_2	23.9	329.4	110.6	39.9	1.287	1.467
PhMeCH—H	29.7	364.1	75.9	45.7	1.300	1.429
PhMe_2C—H	26.2	354.7	85.3	42.2	1.292	1.437
	22.9	345.6	94.4	38.9	1.284	1.445
	15.1	322.0	118.0	31.1	1.264	1.465
Me_2(HO)C—H	36.0	390.5	49.5	52.0	1.314	1.400
	24.0	329.7	110.3	40.0	1.287	1.467
MeCH=CMeC—HMeOH	22.5	325.2	114.8	38.5	1.283	1.471
	20.2	337.5	102.5	36.2	1.278	1.451
PhC(O)—H	23.8	348.0	92.0	39.8	1.286	1.423
	37.5	394.1	45.9	53.5	1.317	1.397
Me_2CHOC—HMe_2	36.1	390.8	49.2	52.1	1.314	1.400
(CH_2=CHCH—H$)_2$O	35.0	360.0	80.0	51.0	1.312	1.442
Ph_2C—HOMe	26.0	354.2	85.8	42.0	1.292	1.437

Table 8. Activation energies and interatomic distances in the TS of the reactions of ethyl and isopropyl radicals with hydrocarbons and oxygen-containing compounds

R_iH	$^\bullet R_f = {}^\bullet CH_2Me$			$^\bullet R_f = {}^\bullet CHMe_2$		
	E_e /kJ mol^{-1}	$r(R_i...H)$	$r(R_f...H)$	E_e /kJ mol^{-1}	$r(R_i...H)$	$r(R_f...H)$
		10^{-10} m			10^{-10} m	
EtMeCH—H	70.3	1.349	1.365	75.2	1.358	1.356
Me_3C—H	64.1	1.338	1.376	68.8	1.346	1.368
	73.0	1.354	1.360	78.0	1.363	1.351
	68.1	1.345	1.369	72.9	1.354	1.360
	66.0	1.341	1.372	70.7	1.350	1.364
	62.1	1.334	1.380	66.7	1.343	1.371
Z- 	58.5	1.327	1.387	63.0	1.336	1.378
CH_2=$CHCH_2$—H	62.0	1.334	1.420	65.8	1.341	1.413
CH_2=CHCH—HMe	54.1	1.318	1.436	58.1	1.326	1.428
CH_2=CHC—HMe_2	50.1	1.310	1.444	54.0	1.318	1.436
Z-MeCH=CHCH—HMe	51.8	1.313	1.441	55.7	1.321	1.433
Me_2=CHCH—HMe	47.2	1.303	1.451	51.0	1.312	1.442
Me_2C=CMeC—HMe_2	43.9	1.296	1.458	47.5	1.304	1.450
CH_2=CHCMe—HCH=CH_2	38.5	1.283	1.471	41.9	1.291	1.463
	50.8	1.311	1.443	54.7	1.319	1.435
	46.8	1.303	1.451	50.6	1.311	1.443
	40.3	1.288	1.466	43.8	1.296	1.458
	36.5	1.278	1.476	39.8	1.286	1.468
MeC≡CC—HMe_2	46.3	1.301	1.453	50.0	1.309	1.444
PhMeCH—H	52.9	1.316	1.413	57.0	1.324	1.405
$PhMe_2C$—H	49.0	1.307	1.422	53.0	1.316	1.413
	45.5	1.300	1.429	49.4	1.308	1.421
	37.0	1.280	1.449	40.5	1.288	1.441
Me_2(HO)C—H	59.8	1.329	1.385	64.4	1.338	1.376
	46.4	1.302	1.452	50.1	1.310	1.444
MeCH=CMeC—HMeOH	44.8	1.298	1.456	48.4	1.306	1.448
	42.5	1.293	1.436	46.2	1.301	1.428
PhC(O)—H	46.4	1.302	1.427	50.3	1.310	1.419
	61.4	1.333	1.381	66.0	1.341	1.373
Me_2CHOC—HMe_2	59.9	1.330	1.384	64.5	1.338	1.376
$(CH_2$=CHCH—$H)_2O$	58.2	1.326	1.428	62.3	1.334	1.420
Ph_2C—HOMe	48.8	1.307	1.422	52.8	1.315	1.414

Effect of adjacent π-bonds. When a radical attacks a C—H bond in α-position with respect to the C=C bond (R^2H) or to the aromatic ring (R^3H), the triplet repulsion is responsible for the increase in both the energy of the thermally neutral reaction and the parameter r_e.[1,2,4] Agreement between the results of B3LYP calculations and those obtained using the PM is illustrated below.

Reaction	PM	
	$r_e \cdot 10^{10}$/m	$\Delta r_e \cdot 10^{10}$/m
$^{\bullet}R^1 + R^1H$	0.462	0.0
$^{\bullet}R^1 + R^2H$	0.497	0.035
$^{\bullet}R^1 + R^3H$	0.475	0.013
	Quantum-chemical calculations	
	$r(C_i...H...C_f) \cdot 10^{10}$/m	$\Delta r(C_i...H...C_f) \cdot 10^{10}$/m
$Et^{\bullet} + EtH$	2.712	0.0
$Me^{\bullet}$ + + $MeCH{=}CH_2$	2.742	0.030
$Me^{\bullet} + PhCH_3$	2.736	0.024

Indeed, the parameters Δr_e (PM) and $\Delta r(C_i...H...C_f)$ (quantum-chemical calculations) of the reactions involving the molecules with π-bonds change in parallel. Therefore, the results of quantum-chemical calculations are consistent with those obtained by the PM. The distances $r(C_i...H...C_f)$ for the reactions belonging to different classes are listed in Table 1. The formation of TS of the reactions involving the molecules with C=C and C=O bonds also causes these bond lengths to change.

Molecule	Radical	$-\Delta H$*	Δr (%)		$r(C_i...H)$ /Å
			C—C	C=C	
C_6H_8	$^{\bullet}CH_3$	127.4	22.7	18.9	1.232
$MeCH{=}CH_2$		72	25.9	15.1	1.266
$PhCH_3$		65	30.8	24	1.270
MeC(O)Me		28.2	33.3	30.4	1.284
C_6H_8	$^{\bullet}CH_2Me$	109.4	26.1	21.9	1.253
$MeCH{=}CH_2$	$^{\bullet}CH_2CH{=}CH_2$	0	40.5	30.2	1.364

* In kJ mol^{-1}.

The lower the enthalpy of reaction, the more "early" is the TS. The more "early" is the TS, the smaller the changes in the carbon—carbon bond lengths. The changes in the carbon—carbon bond lengths also correlate with the change in the distance $r(C_i...H)$.

Effect of the enthalpy of reaction. The distances $r(C_i...H)$ and $r(C_f...H)$ change from one reaction to another, whereas the total distance $r(C_i...H...C_f)$ remains constant for the reactions belonging to the same class (see Tables 7 and 8). If the force constants of the broken and newly formed bonds are equal to each other, the TS of a thermally neutral reaction is at the midpoint of the $r(C_i...H...C_f)$ line, *i.e.*, $r(C_i...H) = r(C_f...H)$, see relations (12) and (13). This is consistent with the results of quantum-chemical calculations of a reaction of Et radical with ethane,[33] according to which $r(C_i...H) = r(C_f...H) = 1.356 \cdot 10^{-10}$ m (see Table 3).

A more sophisticated single-parameter model of intersecting states was also proposed for radical reactions of hydrogen abstraction.[34] In this model a universal parameter, which also includes the effect of zero-point vibrational energies, is introduced in such a way that the activation energies of reactions belonging to different classes be simultaneously reproduced. Because of this, in some cases the error in determination of the activation energy is as high as 20 kJ mol^{-1}. However, the geometric parameters of TS obtained using this model are similar to those found by the PM. For instance, for the reaction of Et radical with ethane one has $r(C_i...H) = r(C_f...H) = 1.33 \cdot 10^{-10}$ m.

For exothermic reactions, $r(C_i...H) < r(C_f...H)$; here we deal with an "early" TS. In contrast to this, for endothermic reactions, $r(C_i...H) > r(C_f...H)$; this is the case of the "late" TS. According to Eqs. (11)—(13), the dependence of the interatomic distances in symmetrical TS on the enthalpy of reaction, ΔH, has the form:

$$\mathrm{d}r(C_i...H)/\mathrm{d}\Delta H = \beta/\left(2b\sqrt{E_{e0}}\right),$$
$$\mathrm{d}r(C_f...H)/\mathrm{d}\Delta H = -\beta/\left(2b\sqrt{E_{e0}}\right). \qquad (14)$$

The activation energies, E_{e0}, and the derivatives, $\mathrm{d}r(C...H)/\mathrm{d}\Delta H$, for the radical reactions involving carbon-centered radicals with symmetrical TS are listed in Table 2. The slope of the straight line in the "distance—enthalpy" coordinates changes slightly on going from one reaction to another (from $1.62 \cdot 10^{-10}$ to $1.92 \cdot 10^{-10}$ mol m J^{-1}) due to minor variation of the activation energy of a thermally neutral reaction for these reaction classes.

Thus, comparison of the results obtained from quantum-chemical calculations and using the PM suggests the following. First, the reactions of alkyl radicals with hydrocarbons are characterized by a constant distance $r(C_i...H...C_f)$ in the TS of all reactions belonging to the same class (see Table 2). This provides a means for comparing the TS geometries of reactions belonging to different classes. Second, a π-bond adjacent to the reaction center is responsible for elongation of the distance $C_i...H...C_f$ in the TS of the reactions of allyl and benzyl radicals with hydrocarbons. Third, the use of corrected PM relationships makes it possible to calculate the interatomic distances in the TS of the reactions of carbon-centered radicals with C—H bonds of organic molecules with the same accuracy as that provided by quantum-chemical computations of these systems.

This work was carried out with the financial support from the Chemistry and Materials Science Branch of the Russian Academy of Sciences in the framework of the

Program No. 1 "Theoretical and experimental investigations on the nature of chemical bonding and mechanisms of the most important chemical reactions and processes."

References

1. E. T. Denisov, *Kinet. Katal.*, 1991, **32**, 461 [*Kinet. Catal.*, 1991, **32** (Engl. Transl.)].
2. E. T. Denisov, *Usp. Khim.*, 1997, **66**, 953 [*Russ. Chem. Rev.*, 1997, **66**, 859 (Engl. Transl.)].
3. E. T. Denisov and T. G. Denisova, *Handbook of Antioxidants*, CRC Press, Boca Raton, 2000.
4. E. T. Denisov, in *General Aspects of the Chemistry of Radicals*, Ed. Z. B. Alfassi, Wiley, Chichester, 1999, 79.
5. E. T. Denisov, T. G. Denisova, and T. S. Pokidova, *Handbook of Free Radical Initiators*, Wiley, New York, 2003.
6. A. F. Shestakov and E. T. Denisov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2003, 306 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 320].
7. T. G. Denisova and N. S. Emel´yanova, *Kinet. Katal.*, 2003, **44**, No. 4 [*Kinet. Catal.*, 2003, **44**, No. 4 (Engl. Transl.)].
8. J. A. Hawari, P. S. Engel, and D. Griller, *Int. J. Chem. Kinet.*, 1985, **17**, 1215.
9. M. Newcomb and S. U. Park, *J. Am. Chem. Soc.*, 1986, **108**, 4132.
10. B. Bockrath, E. Bittner, and J. McGew, *J. Am. Chem. Soc.*, 1984, **106**, 135.
11. N. L. Arthur and P. J. Newitt, *Can. J. Chem.*, 1985, **63**, 3486.
12. H. Arican and N. L. Arthur, *Aust. J. Chem.*, 1983, **36**, 2185.
13. M. J. Duke and K. A. Holbrook, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 1232.
14. *Handbook of Chemistry and Physics*, Ed. D. R. Lide, CRC Press, Boca Raton, 1992, Section 9, p. 2.
15. F. Bernardi, A. Bottoni, and M. Garavelli, *Quant. Struct.-Act. Rel.*, 2002, **21**, 128.
16. R. G. Susnow, A. M. Dean, and W. H. Green, *Chem. Phys. Lett.*, 1999, **312,** 262.
17. J. K. Kang and C. B. Musgrave, *J. Chem. Phys.*, 2001, **115**, 11040.
18. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, *GAUSSIAN-98, Rev. A6*, Gaussian, Inc., Pittsburgh (PA), 1998.
19. V. E. Tumanov, E. A. Kromkin, and E. T. Denisov, *Neftekhimiya*, 2001, **41**, 109 [*Petroleum Chemistry*, 2001, **41** (Engl. Transl.)].
20. E. A. Kromkin, V. E. Tumanov, and E. T. Denisov, *Neftekhimiya*, 2002, **42**, 3 [*Petroleum Chemistry*, 2002, **42** (Engl. Transl.)].
21. V. E. Tumanov, E. A. Kromkin, and E. T. Denisov, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 1508 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1641].
22. W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data*, 1986, **15**, 1087.
23. J. Warnatz, in *Rate Coefficients in the C/H/O System Combusting Chemistry*, Ed. W. C. Gardiner, Jr., Springer-Verlag, New York, 1984, 197.
24. Y. Hidaka, T. Oki, and H. Kawano, *Int. J. Chem. Kinet.*, 1989, **21**, 689.
25. K. J. Mintz and D. J. Le Roi, *Can. J. Chem.,* 1978, **56**, 941.
26. H. X. Zhang and M. H. Back, *Int. J. Chem. Kinet.*, 1985, **17**, 1215.
27. M. Sway, *Ind. J. Chem.*, 1990, **29**, 746.
28. A. N. Dunlop, R. J. Kominar, and S. J. W. Price, *Can. J. Chem.*, 1970, **48**, 1269.
29. M. Cher, C. S. Hollingsworth, and F. Sicilio, *J. Phys. Chem.*, 1966, **70**, 877.
30. A. C. Kinsman and J. M. Roscoe, *Int. J. Chem. Kinet.*, 1994, **26**, 191.
31. B. J. Lynch and D. G. Truhlar, *J. Phys. Chem. A*, 2001, **105**, 2936.
32. E. T. Denisov, *Kinet. Katal.*, 1996, **37**, 553 [*Kinet. Catal.*, 1996, **37** (Engl. Transl.)].
33. A. F. Shestakov, T. G. Denisova, E. T. Denisov, and N. S. Emel´yanova, *Izv. Akad. Nauk*, *Ser. Khim.*, 2002, 559 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 602].
34. A. C. Pais, L. G. Arnaut, and S. J. Formosinho, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2577.

Received April 22, 2003;
in revised form July 28, 2003