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Radical addition reactions: factors determining the transition-state geometry

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Interatomic distances in the reaction centers of the addition reactions of (i) $H^{\bullet}$ to the C=C, C=O, N≡C, and C≡C bonds, (ii) $^{\bullet}CH_3$ radical to the C=C, C=O, and C≡C bonds, and (iii) alkyl, aminyl, and alkoxyl radicals to olefin C=C bonds were determined using a new semiempirical method for calculating transition-state geometries of radical reactions. For all reactions of the type $X^{\bullet} + Y{=}Z \rightarrow X{-}Y{-}Z^{\bullet}$ the $r^{\#}_{X...Y}$ distance in the transition state is a linear function of the enthalpy of reaction. Parameters of this dependence were determined for seventeen classes of radical addition reactions. The bond elongation, $\Delta r^{\#}_{X...Y}$, in the transition state decreases as the triplet repulsion, electronegativity difference between the atoms X and Y in the reaction center, and the force constant of the attacked multiple bond increase.

Key words: alkyl, alkoxyl, and aminyl radicals; hydrogen atom, acetylene, carbonyl compound, transition-state geometry, quantum chemistry, model of intersecting parabolas, olefin, radical addition, force constant of a chemical bond, triplet repulsion, electronegativity of atoms, activation energy, enthalpy of reaction.

A recently elaborated semiempirical method of estimation of transition-state geometric parameters has made possible fast calculations of these parameters for the reactions of (i) $H^{\bullet}$ addition to C=C, C≡C, C=O, and C≡N bonds; (ii) $^{\bullet}CH_3$ radical addition to C=C, C≡C, and C=O bonds, and (iii) addition of alkoxyl and aminyl radicals to olefin C=C bonds.[1] The method includes treatment of experimental data (enthalpy of and activation energy for a given reaction) in the framework of the intersecting parabolas (IP) model[2—4] and calculations of interatomic distances in the reaction center of transition state according to the reduced intersecting parabolas (RIP) model.[5] The advantage of the method is also that it leads to the same interatomic distances as those found from quantum chemical calculations (GAUSSIAN-98, density functional theory, DFT).[1] Earlier,[3] analysis of experimental data on addition reactions allowed the physical and structural factors determining the activation energy for these reactions to be established. The aim of this study was to calculate the geometric parameters of transition states and to analyze the factors affecting the interatomic distances in the reaction centers of various free radical addition reactions.

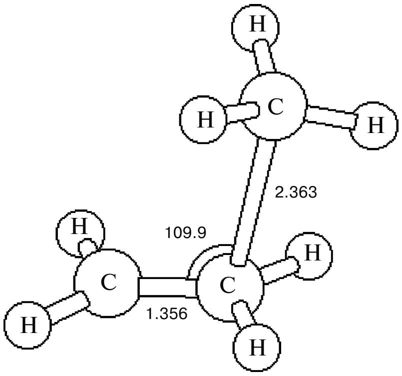

Fig. 1. Transition state of the reaction of methyl radical addition to ethylene.[1] Shown are the interatomic distances (in Å) and the bond angle (in degrees).

Calculaton Procedure

The reaction center of a reaction of radical addition to the multiple bond (C=C, C≡C, C=O, C≡N)

$$X^{\bullet} + Y{=}Z \rightarrow XYZ^{\bullet}$$

has a bent configuration with the φ(X—Y—Z) angle varying from 100 to 110° (Fig. 1).[1]

In the frame of the IP model such a reaction is characterized by the following parameters[2—5]:

1) enthalpy, ΔH_e, which includes the zero-point vibrational energy difference between the attacked bond (Y=Z) and the newly forming bonds (X—Y and Y—Z),

$$\Delta H_e = \Delta H + 0.5hL(\nu_{Y=Z} - \nu_{X-Y} - \nu_{Y-Z}), \quad (1)$$

where h is the Planck constant, L is the Avogadro constant, and $\nu_{Y=Z}$, ν_{X-Y} and ν_{Y-Z} are the corresponding stretching vibration frequencies;

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2) classical potential barrier to the reaction (E_e); in the case of addition reactions E_e differs from the Arrhenius activation energy, E, only by $0.5RT$:

$$E_e = E - 0.5RT; \tag{2}$$

3) total elongation, r_e, of the attacked and forming bonds in the transition state;

4) parameter b ($2b^2$ is the force constant of the Y=Z attacked bond);

5) parameter b_f ($2b_f^2$ is the force constant of the X—Y forming bond in reaction product), or coefficient $\alpha = b/b_f$;

6) pre-exponential factor A_0 calculated per attacked atom in the molecule.

The rate constant for the reaction is related to the activation energy E and the pre-exponential factor A_0 through the Arrhenius relation:

$$k = nA_0\exp[-E/(RT)], \tag{3}$$

where n is the number of chemically equivalent atoms in the reagent molecule, involved in the reaction (*e.g.*, $n = 1$ for formaldehyde and $n = 2$ for ethylene). The parameters mentioned above are interrelated as follows[2]

$$br_e = \alpha\sqrt{E_e - \Delta H_e} + \sqrt{E_e}. \tag{4}$$

According to the IP model,[2—4] the parameters α and br_e are constants for all reactions belonging to the same reaction class. This permits calculations of the classical potential barrier E_e to any reaction from the enthalpy ΔH_e as follows[2]

$$\sqrt{E_e} = \frac{br_e}{\alpha^2 - 1}\left[\alpha\sqrt{1 + \frac{\alpha^2 - 1}{(br_e)^2}\Delta H_e} - 1\right]. \tag{5}$$

The parameters α, br_e, and A_0 for the addition reaction classes considered in this study are listed in Table 1.

The enthalpies of the addition reactions were calculated from thermochemical equations:

$$\Delta H = \Delta H_{\mathrm{XCH_2C^{\bullet}H_2}} - \Delta H_{\mathrm{H_2C=CH_2}} - \Delta H_{\mathrm{e(X^{\bullet})}}, \tag{6}$$

$$\Delta H_{\mathrm{X^{\bullet}}} = \Delta H_{\mathrm{XH}} + D_{\mathrm{X-H}} - \Delta H_{\mathrm{H^{\bullet}}}. \tag{7}$$

The bond dissociation energies, $D_{\mathrm{X-H}}$, were taken from handbooks[6,7] and the enthalpies of formation of molecules were retrieved from a database.[8]

The interatomic distances in transition states were calculated using the RIP model,[5] which treats the activation energy for a reaction as the intersection point of two parabolic potential curves. One parabola describes the stretching vibration of the attacked multiple bond and is characterized by the parameter b (as in the IP model) while the other parabola describes the elongation of the C...X forming bond and is characterized by the parameter $b_f^{\#}$ (the force constant of this bond id $2b_f^{\#}$). The C...X bond energy ($D_{ef}^{\#}$) is equal to the difference between the activation energy for and the enthalpy of the reaction, $D_{ef}^{\#} = E_e - \Delta H_e$. The parameters $b_f^{\#}$ and $D_{ef}^{\#}$ interrelated[5]

$$b_f^{\#} = aD_{ef}^{\#} - c(D_{ef}^{\#})^2, \tag{8}$$

where a and c are empirical coefficients. By comparing the results of calculations using the RIP model with those of DFT quantum chemical calculations using the GAUSSIAN-98[9] program package we obtained correlation equations for estimating the interatomic distances in transition states and found that they lead to the same results as those obtained from quantum chemical calculations.[1,9] The interatomic distances $r^{\#}_{\mathrm{X...Y}}$, $r^{\#}_{\mathrm{Y=Z}}$ and the bond total elongation $\Delta r^{\#}$ in the transition state were calculated using expressions[1]

$$r^{\#}_{\mathrm{X...Y}} = r_{\mathrm{X-Y}} + \beta\sqrt{E_e - \Delta H_e}/b_f^{\#}, \tag{9}$$

$$r^{\#}_{\mathrm{Y=Z}} = r_{\mathrm{Y=Z}} + \sqrt{E_e}/b_m, \tag{10}$$

$$\Delta r^{\#} = \sqrt{E_e}/b_m + \beta\sqrt{E_e - \Delta H_e}/b_f^{\#}. \tag{11}$$

Table 1. Parameters of addition reactions: coefficient α, parameter br_e, parameter $0.5hL(\Delta\nu - \nu_f)$, and pre-exponent A_0 [3]

Reaction	α	br_e /kJ$^{0.5}$ mol$^{-0.5}$	$0.5hL(\Delta\nu - \nu_f)$ /kJ mol^{-1}	$A_0 \cdot 10^{-10}$ /L mol^{-1} s^{-1}
$\mathrm{H^{\bullet} + H_2C{=}CHR}$	1.440	21.99	15.7	10
$\mathrm{H^{\bullet} + H_2C{=}CHCH{=}CHR}$	1.440	25.33	15.7	10
$\mathrm{H^{\bullet} + H_2C{=}CHPh}$	1.440	24.18	15.7	10
$\mathrm{H^{\bullet} + CH{\equiv}CR}$	1.847	28.77	15.6	40
$\mathrm{H^{\bullet} + O{=}CR^1R^2}$	1.274	20.37	18.0	10
$\mathrm{H^{\bullet} + N{\equiv}CR}$	1.768	22.32	16.5	40
$\mathrm{{}^{\bullet}CH_3 + H_2C{=}CHR}$	1.202	19.24	6.5	0.1
$\mathrm{{}^{\bullet}CH_3 + H_2C{=}CHCH{=}CHR}$	1.202	20.42	6.5	0.1
$\mathrm{{}^{\bullet}CH_3 + H_2C{=}CHPh}$	1.202	19.62	6.5	0.1
$\mathrm{{}^{\bullet}CH_3 + CH{\equiv}CR}$	1.542	21.47	5.4	0.1
$\mathrm{{}^{\bullet}CH_3 + O{=}CR^1R^2}$	1.336	15.81	4.5	0.05
$\mathrm{{}^{\bullet}NH_2 + H_2C{=}CHR}$	1.410	18.27	5.1	0.008
$\mathrm{{}^{\bullet}NH_2 + H_2C{=}CHCH{=}CHR}$	1.410	19.45	5.1	0.008
$\mathrm{{}^{\bullet}NH_2 + H_2C{=}CHPh}$	1.410	18.65	5.1	0.008
$\mathrm{RO^{\bullet} + H_2C{=}CHR}$	1.413	16.75	4.9	0.05
$\mathrm{RO^{\bullet} + H_2C{=}CHCH{=}CHR}$	1.413	17.93	4.9	0.05
$\mathrm{RO^{\bullet} + H_2C{=}CHPh}$	1.413	17.13	4.9	0.05

Table 2. Parameters of the chemical bonds involved in the addition reaction under study: bond lengths r, coefficients b, and zero-point vibrational energies ($0.5hL\nu$)[3,10]

Bond	$r \cdot 10^{10}$ /m	$b \cdot 10^{-10}$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$0.5hL\nu$ /kJ mol^{-1}
>C—H	1.092	37.43	17.4
C=CH—H	1.077	39.61	18.4
RO—H	0.967	47.01	21.7
RNH—H	1.009	43.06	20.0
$C—CH_3$	1.513	44.83	8.2
$C—NH_2$	1.469	38.22	6.8
C—OR	1.416	38.14	6.6
C=C	1.299	53.89	9.9
C≡C	1.183	69.12	12.7
C=O	1.210	59.91	10.3
C≡N	1.136	59.91	13.5

The bond lengths, $r_{Y—X}$ and $r_{Y=X}$, in the molecules and the coefficients b and zero-point vibrational energies of these bonds are listed in Table 2 and the coefficients a, b_m, c, and β *are given* in Table 3.

Table 3. Empirical parameters for transition-state geometry calculations from experimental data[1,2]

Reaction	β	$b_m \cdot 10^{-10}$ [a]	$a \cdot 10^{-8}$ [b]	$c \cdot 10^{-6}$ [c]
$H^\bullet + H_2C=CHR$	1.732	421.4	12.12	0.818
$^\bullet CH_3 + H_2C=CHR$	1.143	203.5	16.40	1.24
$^\bullet NH_2 + H_2C=CHR$	1.052	157.0	14.80	1.24
$CH_3O^\bullet + H_2C=CHR$	1.227	102.5	22.80	3.32
$H^\bullet + HC{\equiv}CR$	1.392	520.0	12.12	0.818
$^\bullet CH_3 + HC{\equiv}CR$	1.429	217.3	16.40	1.24
$H^\bullet + H_2C=O$	1.198	249.5	19.50	1.99
$^\bullet CH_3 + R_2C=O$	0.747	156.7	16.40	1.24
$H^\bullet + N{\equiv}CR$	0.708	345.8	13.71	0.818

[a] In kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}.

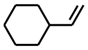
[b] In kJ$^{-0.5}$ mol$^{0.5}$ m^{-1}.

[c] In kJ$^{-1.5}$ mol$^{1.5}$ m^{-1}.

Results and Discussion

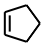
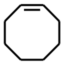
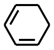
Enthalpy of reaction. The results of calculations of interatomic distances in the transition states of the

Table 4. Enthalpies (ΔH_e), activation energies (E_e)*, and geometric parameters of the reaction centers in the transition states of $H^\bullet$ addition to alkenes

Alkene	$-\Delta H_e$	E_e	$b_f^{\#}$	$\Delta r^{\#}$	$r^{\#}_{C...H}$	$r^{\#}_{C=C}$
	kJ mol^{-1}		/kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	10^{-10} m		
$H_2C=CH_2$	166.1	8.7	18.69	1.232	2.317	1.306
$H_2C=CHMe$	169.3	7.1	18.83	1.228	2.314	1.305
$H_2C=CHEt$	170.2	6.1	18.82	1.228	2.314	1.305
$H_2C=CMe_2$	172.9	4.2	18.90	1.224	2.311	1.304
$H_2C=CHPr$	169.7	6.8	18.84	1.227	2.313	1.305
cis-MeCH=CHEt	162.5	10.1	18.48	1.238	2.323	1.306
trans-MeCH=CHEt	158.2	10.3	18.10	1.250	2.334	1.307
$H_2C=CEtMe$	174.3	5.5	19.15	1.218	2.304	1.305
$MeCH=CMe_2$	173.5	10.6	19.54	1.208	2.295	1.307
$H_2C=CMePr$	177.3	9.5	19.79	1.203	2.288	1.306
$H_2C=CEt_2$	172.9	9.5	19.38	1.213	2.298	1.306
$EtCH=CMe_2$	169.9	10.9	19.24	1.218	2.302	1.307
MeCH=CHPr	162.5	11.5	18.61	1.235	2.319	1.307
$MeCH=CMe_2$	181.7	11.3	20.34	1.191	2.275	1.307
MeCH=CHBu	162.5	11.5	18.61	1.236	2.320	1.307
$MeCH=CEt_2$	167.3	10.7	18.98	1.226	2.310	1.307
$H_2C=CH(CH_2)_4Me$	169.7	10.4	19.17	1.220	2.304	1.307
$H_2C=CH(CH_2)_5Me$	169.7	10.5	19.18	1.219	2.303	1.307
$H_2C=CH(CH_2)_7Me$	169.7	10.4	18.17	1.220	2.304	1.307
	162.3	11.4	18.58	1.236	2.320	1.307
	163.7	9.8	18.56	1.237	2.322	1.306
	167.6	10.8	19.02	1.224	2.308	1.307
$H_2C=CHCH_2OH$	170.5	5.7	18.81	1.228	2.314	1.305
$H_2C=CHC(O)OH$	186.0	7.5	20.39	1.187	2.273	1.305
E-$HOOCCH=CHCO_2H$	188.3	5.0	20.37	1.186	2.273	1.304

* Experimental values of activation energies were taken from Refs 11—26.

Table 5. Enthalpies (ΔH_e), activation energies (E_e)*, and geometric parameters of the reaction centers in the transition states of $^{\bullet}CH_3$ addition to alkenes

Alkene	$-\Delta H_e$	E_e	$b_f^{\#}$ /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$\Delta r^{\#}$	$r^{\#}_{C...Me}$	$r^{\#}_{C=C}$
	kJ mol^{-1}				10^{-10} m	
$H_2C=CH_2$	106.7	28.0	19.84	0.695	2.182	1.325
$H_2C=CHMe$	104.3	27.0	19.39	0.700	2.188	1.324
trans-MeCH=CHMe	103.8	34.4	20.30	0.691	2.175	1.328
cis-MeCH=CHMe	107.2	32.1	20.44	0.688	2.173	1.327
	108.0	33.0	20.66	0.685	2.170	1.327
	95.5	32.5	18.96	0.710	2.195	1.327
$H_2C=CHCl$	112.5	23.7	20.04	0.690	2.179	1.323
$H_2C=CHOAc$	113.0	25.4	20.32	0.687	2.175	1.324
$H_2C=CHOEt$	104.7	24.6	19.13	0.703	2.192	1.323
$H_2C=CMeOMe$	117.2	25.0	20.81	0.680	2.168	1.324
$H_2C=CMeOAc$	125.2	25.0	21.83	0.667	2.165	1.324
$H_2C=CMeC(O)OMe$	136.5	15.8	22.10	0.657	2.151	1.318
trans-MeCH=CHCOOH	135.8	15.4	21.96	0.659	2.153	1.318
cis-MeCH=CHCOOH	140.0	12.4	22.11	0.655	2.151	1.316
$H_2C=CHOCOAc$	110.5	25.0	19.94	0.692	2.180	1.324
$H_2C=CHCN$	137.9	15.2	22.20	0.656	2.150	1.318
$H_2C=CMeCN$	135.2	15.1	21.85	0.660	2.154	1.318
$H_2C=CHCH=CH_2$	153.4	16.5	24.28	0.634	2.127	1.319
MeCH=CHCH=CHMe	144.9	21.2	23.82	0.641	2.131	1.322
$H_2C=CMeCMe=CH_2$	157.4	16.2	24.73	0.629	2.122	1.319
	167.1	22.2	26.60	0.614	2.104	1.322
	174.0	19.6	27.10	0.609	2.100	1.321
$H_2C=CHPh$	151.2	17.0	24.08	0.636	2.129	1.319
$H_2C=CMePh$	147.2	17.0	23.58	0.641	2.134	1.319

* Experimental values of activation energies were taken from Refs 27—34.

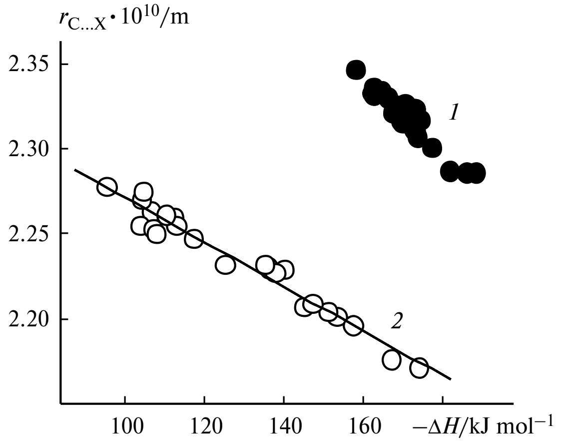


Fig. 2. Interatomic distance in the transition state of reaction plotted *vs.* enthalpy of reaction: $r_{C...H}$ for hydrogen addition to olefins (*1*) and $r_{C...Me}$ for methyl radical addition to olefins (*2*) (see Tables 4 and 5, respectively).

addition reactions of $H^{\bullet}$ and $^{\bullet}CH_3$ radicals to alkenes from experimental data (expressions (1)—(3), (5), and (8)—(11)) are listed in Tables 4 and 5 and shown in Fig. 2.

In the case of addition reactions of the $^{\bullet}NH_2$ and $Me_3CO^{\bullet}$ radicals to olefins and of the $H^{\bullet}$ and $^{\bullet}CH_3$ radicals to the carbonyl group of aldehyde and ketone molecules the interatomic distances were calculated theoretically using the enthalpies of reactions and the RIP model (Eqns (1), (5), and (8)—(10)).[1,5] The results obtained are listed in Tables 6—8.

As can be seen, the higher the enthalpy of addition, the longer the C...X distance in the transition state ($X^{\bullet}$ is the atom, which bears the free valence and attacks the double or triple bond). This is consistent with the Hammond principle,[6] namely, the larger the heat of reaction, the smaller the structural difference between the transition state and initial molecule. The interatomic distance $r^{\#}_{Y...X}$ is a linear function of ΔH_e:

$$r^{\#}_{Y...X} = F + G\Delta H_e. \quad (12)$$

The coefficients *F* and *G* are listed in Table 9.

Table 6. Enthalpies (ΔH_e), activation energies (E_e), and geometric parameters of the reaction centers in the transition states of aminyl radical addition to alkenes (calculated using expressions (1), (2), (5), and (8)—(12))

Alkene	$-\Delta H_e$	E_e	b_f	$\Delta r^{\#}$	$r^{\#}_{C...N}$	$r^{\#}_{C=C}$
	kJ mol^{-1}		/kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}		10^{-10} m	
$H_2C=CH_2$	88.1	15.4	13.99	0.790	2.234	1.324
$H_2C=CHMe$	85.7	16.3	13.81	0.795	2.238	1.325
$H_2C=CMe_2$	86.2	15.5	13.77	0.795	2.239	1.324
trans-MeCH=CHMe	85.2	16.5	13.77	0.796	2.239	1.325
cis-MeCH=CHMe	88.6	15.3	14.04	0.789	2.233	1.324
$H_2C=CHCl$	93.9	13.4	14.45	0.777	2.223	1.322
$H_2C=CMeCl$	83.9	17.0	13.67	0.798	2.241	1.325
$H_2C=CCl_2$	106.9	9.1	15.50	0.750	2.200	1.318
$H_2C=CHF$	89.9	14.8	14.14	0.785	2.230	1.323
$H_2C=CHOAc$	94.4	13.2	14.49	0.777	2.223	1.322
$H_2C=CHOEt$	86.1	16.2	13.84	0.794	2.237	1.325
$H_2C=CMeOMe$	98.6	11.8	14.83	0.767	2.214	1.321
$H_2C=CMeOAc$	106.6	9.2	15.48	0.751	2.201	1.318
$H_2C=CHC(O)OMe$	91.6	14.2	14.27	0.782	2.227	1.323
$H_2C=CMeC(O)OMe$	117.9	7.2	16.57	0.727	2.179	1.316
trans-MeCH=CHC(O)OH	117.2	7.3	16.50	0.729	2.181	1.316
cis-MeCH=CHC(O)OH	121.4	12.2	17.56	0.714	2.161	1.321
$H_2C=CHCH_2OAc$	91.9	14.9	14.39	0.780	2.225	1.323
$H_2C=CHC(O)OCH_2Ph$	94.4	13.2	14.49	0.777	2.223	1.322
$H_2C=CHCN$	119.3	7.1	16.73	0.723	2.175	1.316
$H_2C=CMeCN$	116.6	7.4	16.44	0.730	2.182	1.316
$H_2C=CHCH=CH_2$	134.8	8.7	18.68	0.694	2.144	1.318
MeCH=CHCH=CHMe	126.3	11.6	18.05	0.707	2.154	1.321
$H_2C=CMeCMe=CH_2$	138.8	7.9	19.04	0.687	2.138	1.317
$H_2C=CHPh$	132.6	7.3	18.28	0.698	2.150	1.316
$H_2C=CMePh$	128.6	8.4	17.95	0.704	2.155	1.317

From the data of Table 9 it can be seen that the coefficient G varies from $0.7 \cdot 10^{-10}$ to $2.7 \cdot 10^{-10}$ J^{-1} mol m. The error in determination of the coefficient F is very small, being in most cases no greater than $0.01 \cdot 10^{-10}$ m. The correlation equations obtained may be used for estimation of the $r^{\#}_{C...X}$ distances from the ΔH_e values for the addition reaction classes considered in this work. In the radical addition reactions the multiple bond elongation is small ($(0.009—0.011) \cdot 10^{-10}$ m). As the enthalpy of reaction decreases, the multiple bond is slightly shortened.

Triplet repulsion. Triplet repulsion strongly affects the activation energies for addition reactions[3,35,36] The stronger the forming C—X bond, the stronger the triplet repulsion. The energy characteristics (ΔH_e and E_e) of addition reactions with different structures of reaction centers and the geometric parameters of their transition states are listed in Table 10.

Since these reactions are characterized by different enthalpies and because (as we ascertained) the enthalpy of reaction affects the transition-state geometry, a simple comparison of the interatomic distances in transition states makes it impossible to reveal how other factors influence the transition-state geometry. In order to level the enthalpy effect on the transition-state geometry, we used the following two methods. First, we calculated the barriers E_e and the transition-state geometries of these reactions at the same ΔH_e value ($\Delta H_e = -100$ kJ mol^{-1}) using relationships (5) and (8)—(12). The results are listed in Table 11.

Second, expression (12) was transformed as follows:

$$\Delta r^{\#}_{Y...X} = \Delta r_0{}^{\#}_{Y...X}(1 + \Delta H_e/\Delta H_e{}^{*}), \qquad (13)$$

where $\Delta r_0{}^{\#}_{Y...X}$ is the Y—X bond elongation in the transition state at $\Delta H_e = 0$ and $\Delta H_e{}^{*} = \Delta H_e$ at which $\Delta r_0{}^{\#}_{C...X} = 0$. The parameters $\Delta r_0{}^{\#}_{Y...X}$ and $\Delta H_e{}^{*}$ are listed in Table 9.

The results obtained for the reactions of $H^{\bullet}$ addition to ethylene and acetylene are given below.

Reaction	D_{C-H}	$E_e(100)$	$r^{\#}_{C...H}$[a]	$\Delta r_0{}^{\#}_{C...H}$[b]
	kJ mol^{-1}		10^{-10} m	
$H^{\bullet} + H_2C=CH_2$	422 (ethane)	30.6	2.464	1.646
$H^{\bullet} + HC\equiv CH$	464 (ethylene)	43.8	2.137	1.193

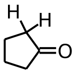
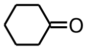
[a] $\Delta H_e = -100$ kJ mol^{-1}.
[b] $\Delta H_e = 0$.

The second reaction is characterized by a higher activation energy $E_e(100)$. This is consistent with the fact that

Table 7. Enthalpies (ΔH_e), activation energies (E_e), and geometric parameters of the reaction centers in the transition states of addition of dimethylethoxyl radical to alkenes (calculated using expressions (1), (2), (5), and (8)—(12))

Alkene	$-\Delta H_e$	E_e	b_f /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$\Delta r^{\#}$	$r^{\#}_{C...X}$	$r^{\#}_{C=C}$
	kJ mol^{-1}			10^{-10} m		
$H_2C=CH_2$	82.2	16.0	19.19	0.673	2.050	1.338
$H_2C=CHMe$	79.8	16.9	18.94	0.677	2.053	1.339
$H_2C=CHEt$	80.3	16.7	18.99	0.676	2.052	1.339
$H_2C=CMe_2$	81.8	16.1	19.14	0.673	2.050	1.338
trans-MeCH=CHMe	79.3	17.1	18.89	0.678	2.054	1.339
cis-MeCH=CHMe	82.7	15.8	19.24	0.672	2.049	1.338
$H_2C=CHCl$	88.0	13.8	19.77	0.662	2.042	1.335
$H_2C=CMeCl$	78.0	17.6	18,76	0.681	2.056	1.340
$H_2C=CCl_2$	101.0	9.2	21.09	0.641	2.027	1.329
$H_2C=CHF$	84.0	15.3	19.37	0.669	2.047	1.337
$H_2C=CHOAc$	88.5	13.6	19.82	0.661	2.041	1.335
$H_2C=CHOEt$	80.2	16.7	18.98	0.667	2.053	1.339
$H_2C=CMeOMe$	92.7	12.1	20.24	0.655	2.037	1.333
$H_2C=CMeOAc$	100.7	9.3	21.06	0.641	2.027	1.329
$H_2C=CHC(O)OMe$	85.7	14.6	19.53	0.666	2.045	1.336
$H_2C=CMeC(O)OMe$	112.0	5.8	22.25	0.621	2.014	1.322
trans-MeCH=CHC(O)OH	111.3	6.0	22.18	0.623	2.015	1.323
cis-MeCH=CHC(O)OH	115.5	4.7	22.61	0.616	2.011	1.320
$H_2C=CHCH_2OAc$	86.0	14.5	19.56	0.666	2.045	1.336
$H_2C=CHC(O)OCH_2Ph$	88.5	13.6	19.82	0.661	2.041	1.335
$H_2C=CHCN$	113.4	5.4	22.40	0.620	2.013	1.322
$H_2C=CMeCN$	110.7	6.2	22.11	0.624	2.016	1.323
$H_2C=CHCH=CH_2$	128.9	10.8	25.37	0.604	1.988	1.331
MeCH=CHCH=CHMe	120.4	13.5	24.58	0.614	1.994	1.335
$H_2C=CMeCMe=CH_2$	132.9	9.5	25.73	0.599	1.985	1.329
$H_2C=CHPh$	126.7	9.6	24.91	0.605	1.991	1.329
$H_2C=CMePh$	122.7	10.9	24.53	0.610	1.994	1.331

Table 8. Enthalpies (ΔH_e), activation energies (E_e), and geometric parameters of the reaction centers of $H^\bullet$ and $^\bullet CH_3$ radical additions to carbonyl compounds (calculated using expressions (1), (2), (5), and (8)—(12))

Carbonyl compound	$-\Delta H_e$	E_e	$b_f^{\#}$ *	$\Delta r^{\#}$	$r^{\#}_{O...H}$	$r^{\#}_{C=O}$
	kJ mol^{-1}			10^{-10} m		
$H^\bullet + R^1R^2C=O \rightarrow R^1R^2C^\bullet OH$						
$H_2C=O$	128.2	22.4	24.86	0.618	1.565	1.230
MeC(O)H	122.6	24.3	24.35	0.624	1.570	1.231
PrC(O)H	124.4	23.7	24.51	0.622	1.569	1.231
$Me_2C=O$	118.5	25.7	23.98	0.628	1.574	1.231
$H_2C=CHC(O)H$	144.2	17.4	26.32	0.603	1.552	1.228
$H_2C=CHC(O)Me$	145.9	16.9	26.47	0.601	1.551	1.227
	113.8	27.4	23.56	0.633	1.578	1.232
	130.0	21.8	25.02	0.617	1.564	1.230
PhC(O)H	150.7	15.5	26.92	0.597	1.548	1.227
PhC(O)Me	148.2	16.2	26.69	0.599	1.549	1.227
PhC(O)Et	145.0	17.2	26.39	0.602	1.552	1.228
$Ph_2C=O$	168.0	11.0	28.53	0.582	1.535	1.224
$^\bullet CH_3 + R^1R^2C=O \rightarrow R^1R^2MeCO^\bullet$						
$H_2C=O$	56.5	17.2	11.41	0.588	2.075	1.236
MeC(O)H	44.0	23.0	10.43	0.617	2.099	1.241
$Me_2C=O$	29.6	30.1	9.35	0.652	2.130	1.245
EtC(O)H	35.4	27.2	9.78	0.637	2.117	1.243
EtC(O)Me	26.1	32.0	9.11	0.661	2.138	1.246
$Et_2C=O$	25.1	32.5	9.03	0.664	2.141	1.246

* In kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}.

Table 9. Dependence of the interatomic distance $r_{Y...X}$ and Y—X bond elongation ($\Delta r^{\#}_{Y...X}$) in the transition state on the enthalpy of reaction (ΔH_e) for reactions of radical addition to the multiple bonds

Reaction	Distance Y...X	$F \cdot 10^{10}$ /m	$G \cdot 10^{13}$ /kJ^{-1} mol m	$\Delta r_0{}^{\#} \cdot 10^{10}$ /m	$\Delta H_e{}^{*}$ /kJ mol^{-1}
$H^{\bullet} + H_2C{=}CHR$	C...H	2.738	2.74	1.646	600.7
$H^{\bullet} + H_2C{=}CHCH{=}CHR$	C...H	2.559	1.84	1.467	797.3
$H^{\bullet} + H_2C{=}CHPh$	C...H	2.616	2.12	1.524	718.9
${}^{\bullet}CH_3 + H_2C{=}CHR$	C...C	2.336	1.46	0.823	563.7
${}^{\bullet}CH_3 + H_2C{=}CHCH{=}CHR$	C...C	2.299	1.26	0.786	623.8
${}^{\bullet}CH_3 + H_2C{=}CHPh$	C...C	2.323	1.38	0.810	587.0
${}^{\bullet}NH_2 + H_2C{=}CHR$	C...N	2.426	2.08	0.951	457.2
${}^{\bullet}NH_2 + H_2C{=}CHCH{=}CHR$	C...N	2.376	1.79	0.907	506.7
${}^{\bullet}NH_2 + H_2C{=}CHPh$	C...N	2.407	1.98	0.938	473.7
$RO^{\bullet} + H_2C{=}CHR$	C...O	2.210	1.74	0.794	456.3
$RO^{\bullet} + H_2C{=}CHCH{=}CHR$	C...O	2.173	1.46	0.757	518.5
$RO^{\bullet} + H_2C{=}CHPh$	C...O	2.199	1.66	0.783	471.7
$H^{\bullet} + HC{\equiv}CR$	C...H	2.270	1.33	1.193	899.0
${}^{\bullet}CH_3 + HC{\equiv}CR$	C...C	2.554	1.68	1.041	620.4
$H^{\bullet} + N{\equiv}CR$	N...H	1.613	0.82	0.604	738.4
$H^{\bullet} + R^1R^2C{=}O$	O...H	1.658	0.73	0.691	950.5
${}^{\bullet}CH_3 + R^1R^2C{=}O$	C...C	2.197	2.27	0.684	300.9

Table 10. Enthalpies (ΔH_e), activation energies (E_e), and transition-state geometries of $H^{\bullet}$, ${}^{\bullet}CH_3$, ${}^{\bullet}NH_2$, and ${}^{\bullet}OCH_3$ radical addition reactions to the multiple bonds[1]

Reaction	$-\Delta H_e$	E_e	b_f	$\Delta r^{\#}$	$r^{\#}_{Y...X}$	$r^{\#}_{Y=Z}$
	kJ mol^{-1}		/kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}		10^{-10} m	
$H^{\bullet} + H_2C{=}CH_2$	166.1	8.7	18.69	1.232	2.317	1.306
${}^{\bullet}CH_3 + H_2C{=}CH_2$	106.7	28.0	19.84	0.695	2.182	1.325
${}^{\bullet}NH_2 + H_2C{=}CH_2$	88.1	15.4	13.99	0.790	2.234	1.324
${}^{\bullet}OCH_3 + H_2C{=}CH_2$	82.2	16.0	19.19	0.673	2.050	1.338
$H^{\bullet} + HC{\equiv}CH$	160.3	17.3	18.95	0.980	2.057	1.191
${}^{\bullet}CH_3 + HC{\equiv}CH$	114.3	15.3	19.17	0.849	2.362	1.201
$H^{\bullet} + H_2C{=}O$	128.3	16.2	24.02	0.626	1.577	1.226
${}^{\bullet}CH_3 + Me_2C{=}O$	29.6	30.1	9.35	0.652	2.130	1.245
$H^{\bullet} + N{\equiv}CMe$	67.0	26.9	12.15	0.564	1.558	1.151

the C—H bond at the C(sp^2) atom is stronger than the C—H bond at the C(sp^3) atom (*cf.* the D_{C-H} values for ethane and ethylene). How does this influence the transition-state geometry? The data presented above show that on going from ethylene to acetylene the C...H interatomic distance in the transition state is shortened. Therefore, an increase in the triplet repulsion causes shortening of the interatomic distance $r^{\#}_{C...H}$ in the transition states of addition reactions.

Triplet repulsion also manifests itself in the reactions of radical addition to conjugated double bonds and to the double bonds in α-position to the aromatic ring. Transition states of these reactions are characterized by the occurrence of an additional interaction between π-electrons and electrons of the reaction center, which makes the triplet repulsion stronger and increases the activation energy.[3] How do π-electrons in the vicinity of the reaction center affect its geometry? The $\Delta r_0{}^{\#}{}_{C...CH_3}$, $r^{\#}{}_{C...CH_3}$, and $r^{\#}{}_{C...H}$ distances for the methyl radical addition reactions to such olefins with $\Delta H_e = -100$ kJ mol^{-1} are listed below.

Reaction	$E_e(100)$ /kJ mol^{-1}	$\Delta r_0{}^{\#}{}_{C...CH_3}{}^{a}$	$r^{\#}{}_{C...CH_3}{}^{b}$	$r^{\#}{}_{C...C}{}^{b}$
			10^{-10} m	
${}^{\bullet}CH_3 + H_2C{=}CHR$	30.6	0.823	2.190	1.326
${}^{\bullet}CH_3 + H_2C{=}CHPh$	33.1	0.810	2.185	1.327
${}^{\bullet}CH_3 +$ $+ H_2C{=}CHCH{=}CHR$	39.0	0.786	2.174	1.330

[a] $\Delta H_e = 0$.

[b] $\Delta H_e = -100$ kJ mol^{-1}.

It is clearly seen that π-electrons in the vicinity of the reaction center cause an increase in the activation energy, shortening of the C...CH$_3$ distance, and an increase in the elongation of the double bond in the transition state of

Table 11. Activation energies (E_e) and geometric parameters of the reaction centers ($\Delta r^{\#}$, $r_{C...X}$, $r_{C=C}$) for $H^{\bullet}$, $^{\bullet}CH_3$, $^{\bullet}NH_2$, and $^{\bullet}OCH_3$ radical addition to the multiple bonds at the same enthalpy of reaction ($\Delta H_e = -100$ kJ mol^{-1}, see expressions (5) and (8)—(11))

Reaction	E_e /kJ mol^{-1}	b_f /kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$\Delta r^{\#}$	$r_{C...X}$	$r_{C=C}$
			10^{-10} m		
$H^{\bullet} + H_2C{=}CHR$	30.6	14.43	1.385	2.464	1.312
$H^{\bullet} + H_2C{=}CHCH{=}CHR$	54.9	16.81	1.300	2.375	1.317
$H^{\bullet} + H_2C{=}CHPh$	46.0	15.95	1.328	2.404	1.315
$H^{\bullet} + H_2C{=}CPh_2$	68.1	18.06	1.264	2.335	1.320
$^{\bullet}CH_3 + H_2C{=}CHR$	30.4	19.28	0.704	2.190	1.326
$^{\bullet}CH_3 + H_2C{=}CHCH{=}CHR$	39.0	20.40	0.692	2.174	1.330
$^{\bullet}CH_3 + H_2C{=}CHPh$	33.1	19.63	0.700	2.185	1.327
$^{\bullet}NH_2 + H_2C{=}CHR$	11.4	14.95	0.764	2.212	1.320
$^{\bullet}NH_2 + H_2C{=}CHCH{=}CHR$	17.4	15.67	0.754	2.196	1.326
$^{\bullet}NH_2 + H_2C{=}CHPh$	13.3	15.18	0.761	2.207	1.322
$^{\bullet}OCH_3 + H_2C{=}CHR$	5.1	20.30	0.667	2.036	1.321
$^{\bullet}OCH_3 + H_2C{=}CHCH{=}CHR$	9.8	21.03	0.641	2.027	1.329
$^{\bullet}OCH_3 + H_2C{=}CHPh$	6.5	20.52	0.642	2.033	1.324
$H^{\bullet} + HC{\equiv}CR$	43.8	15.74	1.073	2.137	1.196
$^{\bullet}CH_3 + CH{\equiv}CR$	20.6	17.97	0.894	2.386	1.204
$H^{\bullet} + H_2C{=}O$	24.9	24.79	0.560	1.507	1.230
$^{\bullet}CH_3 + R_2C{=}O$	20.6	17.97	0.486	1.970	1.239
$H^{\bullet} + N{\equiv}CR$	12.6	14.40	0.532	1.531	1.146

the addition reaction. A similar picture was also established for the addition of $H^{\bullet}$ to other unsaturated compounds.

Reaction	E_e /kJ mol^{-1}	$\Delta r_0{}^{\#}{}_{C...H}$ [a]	$r^{\#}{}_{C...H}$ [b]	$r^{\#}{}_{C...C}$ [b]
			10^{-10} m	
$H^{\bullet} + H_2C{=}CH_2$	30.6	1.646	2.464	1.312
$H^{\bullet} + H_2C{=}CHPh$	46.0	1.524	2.404	1.315
$H^{\bullet} + H_2C{=}CHCH{=}CH_2$	54.9	1.467	2.375	1.317
$H^{\bullet} + H_2C{=}CPh_2$	68.1	—	2.335	1.320

[a] $\Delta H_e = 0$.

[b] $\Delta H_e = -100$ kJ mol^{-1}.

Such changes are also characteristic of the addition reactions of aminyl and alkoxyl radicals (see Table 11). The formation of α—π-bonds in all addition reactions leads to shortening of the interatomic distances in the transition state, thus making the transition state more compact.

Electronegativity of the atoms of the reaction center. When the reaction center of a radical reaction comprises different atoms, the activation energy for the addition decreases.[5] The larger the difference between electron affinity of the atoms, the lower the activation energies for thermally neutral (E_{e0}) radical abstraction[37] and addition[3,35,36] reactions. It is also interesting to find out how the electron affinity difference, Δ(*EA*), between the atoms of the reaction center affects the bond elongation $\Delta r^{\neq}$ and the interatomic distance $r^{\#}{}_{C...X}$ in the transition state. Below we present the data for the addition of methyl and alkoxyl radicals to ethylene at $\Delta H_e = -100$ kJ mol^{-1}. The Δ(*EA*) values was calculated according to Pauling as the difference[38]

$$\Delta(EA) = D_{C-X} - 0.5(D_{Me-Me} - D_{X-X}). \qquad (14)$$

Reaction	$r^{\#}{}_{C...X}$ [a]	$\Delta r_0{}^{\#}{}_{C...X}$ [b]	Δ(*EA*)	$E_e(100)$
	10^{-10} m		kJ mol^{-1}	
$^{\bullet}CH_3 + H_2C{=}CHR$	2.190	0.823	0	30.4
$RO^{\bullet} + H_2C{=}CH_2$	2.027	0.794	78	5.1

[a] $\Delta H_e = -100$ kJ mol^{-1}.

[b] $\Delta H_e = 0$.

As can be seen, the electronegativity difference, Δ(*EA*), between the atoms of the reaction center leads to shortening of the total elongation $\Delta r^{\neq}$ of the bonds involved in the reaction and the C...X (X = C, O) distance. The same conclusion can also be drawn from comparison of the bond elongations in the transition states of the following reactions: $H^{\bullet}$ addition to ethylene, formaldehyde, acetylene, and acetamide and $^{\bullet}CH_3$ radical addition to ethylene and acetone (see Table 9).

Reaction	$\Delta r_0{}^{\#}{}_{Y...H} \cdot 10^{10}$/m	Reaction	$\Delta r_0{}^{\#}{}_{C...Me} \cdot 10^{10}$/m
$H^{\bullet} + H_2C{=}CH_2$	1.646	$^{\bullet}CH_3 + H_2C{=}CH_2$	0.823
$H^{\bullet} + R^1R^2C{=}O$	0.691	$^{\bullet}CH_3 + Me_2C{=}O$	0.684
$H^{\bullet} + HC{\equiv}CH$	1.193		
$H^{\bullet} + N{\equiv}CMe$	0.604		

So, the larger the electron affinity difference between the atoms of the reaction center, the shorter the interatomic distance $r^{\#}{}_{Y...X}$ in the transition state.

Force constant of the multiple bond. The force constant of the attacked bond also influences the activation energies for abstraction[37] and addition[3] reactions. How does this factor affect the transition-state geometry of radical addition reactions? The stretching vibration frequencies and force constants of the double and triple carbon—carbon bonds are strongly different (see Table 2, coefficients *b*). Let us compare the characteristics of the addition of $^{\bullet}CH_3$ radical to these bonds, calculated for a number of reactions with ΔH_e = const = -100 kJ mol^{-1} (see Table 11) and $\Delta H_e = 0$.

Reaction	$\Delta r^{\#}_{C...Me}$	$\Delta r_0{}^{\#}_{C...Me}$	*b* /(kJ mol)$^{0.5}$ m^{-1}
	10^{-10} m		
$^{\bullet}CH_3 + H_2C{=}CH_2$	2.190	0.823	53.89
$^{\bullet}CH_3 + HC{\equiv}CH$	2.386	1.041	69.12

As can be seen, the larger the coefficient *b* (the force constant of the attacked multiple bond), the more the bond elongation $\Delta r_0{}^{\#}_{C...Me}$ and the longer the total interatomic distance, $r^{\#}_{C...Me}$, in the transition state. Here, the effect of the force constants is superimposed with the influence of triplet repulsion (see above), which in the reaction with acetylene is higher than in the reaction with ethylene.

* * *

Thus, the interatomic distances in the transition states of the radical addition reactions considered in this study is affected by the following factors: the enthalpy of reaction, triplet repulsion in the transition state, electronegativity of atoms of the reaction center, and the force constant of the attacked bond. An increase in the enthalpy of reaction leads to elongation of the Y...X distance (see Table 10). On the contrary, an increase in the force constant of the attacked bond and the electronegativity difference between the atoms of the reaction center cause the $r^{\#}_{C...X}$ distance in the transition state to shorten. Let us compare how these factors influence the bond elongation, $\Delta r^{\#}$, in the transition state and the activation energy for addition reaction.

Factor	Triplet repulsion	Δ(*EA*)	Force constant	ΔH_e
$\Delta r^{\#}$	—	—	—	+
E_e	+	—	+	+

As can be seen, these factors affect the activation energy and bond elongation in the transition state in different fashion. The enthalpy of reaction and the electron affinity difference Δ(*EA*) between the atoms of the reaction center act on the parameters $\Delta r^{\#}$ and E_e in parallel. Contrary to this, the effects of the triplet repulsion and the force constant of the attacked bond are antiparallel.

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