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Theoretical Analysis of the Alternative Additions of Radicals to Multiple Bonds

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Abstract—The alternative additions of the hydrogen atom and methyl, aminyl, and methoxyl radicals to the double bond of CH_2=Y (Y = CHR, CR_2, CHCH=CH_2, CHPh, NH, O) compounds are theoretically analyzed using the intersecting parabolas method and DFT. The enthalpies, activation energies, and geometric parameters of the transition state in the reactions $R^{\bullet} + CH_2{=}Y \longrightarrow RCH_2Y^{\bullet}$ and $R^{\bullet} + CH_2{=}Y \longrightarrow RYC^{\bullet}H_2$ are calculated. The results obtained by the two methods are compared with experimental data. The competing alternative radical additions to the multiple bonds are governed by the enthalpies of the reactions.

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INTRODUCTION

The addition of a free atom or a radical to a CH_2=Y (Y = CHR, CR_2, NH, O) bond can always take place in alternative ways: the radical can add either to the CH_2 group or to Y:

$$R^{\bullet} + CH_2{=}Y \longrightarrow RCH_2Y^{\bullet},$$

$$R^{\bullet} + CH_2{=}Y \longrightarrow C^{\bullet}H_2YR.$$

What are the factors in the competition between these reactions? Experimental data relevant to this issue are scarce and unsystematized [1–5]. The alternative additions of radicals to the C=C bond are of great importance in polymerization, oligomerization, polymer cross-linking, syntheses using free-radical addition reactions, and photochemical and radiochemical reactions of unsaturated compounds. In free-radical polymerization, a polymer results primarily from head-to-tail addition (1,3-addition). Nevertheless, head-to-head addition (1,2-addition) is sometimes observed. For instance, polyvinyl alcohol contains 99% monomeric units formed by 1,3-addition ($\sim CH_2CH(OH)CH_2CH(OH)\sim$) and ~1% monomeric units formed by 1,2-addition ($\sim CH_2CH(OH)CH(OH)CH_2\sim$) [6]. Polymonofluoroethylene contains up to 5% monomeric units formed by head-to-head addition ($\sim CH_2CHFCHFCH_2\sim$) [6]. Poly(vinyl acetate) also contains 1,2-addition fragments, and their content increases from 1.2% at 298 K to 2% at 383 K [3]. The proportion of these fragments has an effect on the properties and thermal stability of the polymer.

We have recently developed an algorithm for the semiempirical calculation of the energy and geometric parameters of the transition state (TS) in the addition of atoms and radicals to unsaturated compounds [8–11]. This algorithm was constructed using the intersecting parabolas model (IPM) in combination with density functional theory (DFT). In the present work, these two approaches were used to examine the alternative additions of a hydrogen atom or a free radical to C=C, C=O, C=N, and C≡N bonds. The results obtained by the different methods were intercompared and compared to experimental data. The factors in the competition between the alternative addition reactions were analyzed.

THEORETICAL METHODS FOR CALCULATING THE ACTIVATION ENERGY AND GEOMETRIC PARAMETERS FOR ALTERNATIVE FREE-RADICAL ADDITION REACTIONS AT MULTIPLE BONDS

IPM Calculations

This model was fitted to a large body of experimental data for the addition of radicals and atoms to double bonds in the gas and liquid phases [8, 12, 13]. The method allows one to calculate the activation energy and rate constant of the reaction

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

from its enthalpy ΔH_e. The enthalpy includes the algebraic sum of the zero-point vibration energies (ZPEs) of the breaking and forming bonds [8]:

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

where h is the Planck constant, N_A is Avogadro’s number, and ν is the bond stretching frequency. The classical potential barrier E_e, which is related to the Arrhenius activation energy E by the equation

$$E_e = E + 0.5hN_A\nu_{Y=Z} - 0.5RT, \qquad (2)$$

Table 1. Parameters of the chemical bonds involved in the addition reactions [8, 13]

Bond	$r \times 10^{10}$, m	$b \times 10^{-10}$, kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$0.5hN_A\nu$, kJ/mol
>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=O	1.210	59.91	10.3
C=N	1.280	56.50	10.0
C≡N	1.136	59.91	13.5

is calculated by the formula [8]

$$\sqrt{E_e} = B\left\{\alpha\sqrt{1+\frac{\Delta H_e}{Bbr_e}}-1\right\}. \qquad (3)$$

In this formula, $b = 2\pi\nu_{Y=Z}\mu_{Y=Z}^{1/2}$; $2b^2$ is the force constant of the attacked bond, μ is the reduced mass of the bonded atoms, $\alpha = b_{Y=Z}/b_{X-Y}$, r_e is the total elongation of the X–Y and Y–Z bonds in the TS, and $B = br_e/(\alpha^2 - 1)$. The parameter br_e is preliminarily calculated from the experimental kinetic data using the formula [12]

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

The bond parameters used in this work—bond length r, coefficient b, and zero-point stretching vibration energy $0.5hN_A\nu$—are presented in Table 1. The parameters α and br_e characterizing this reaction are given in Table 2.

For some addition reactions, experimental data are lacking. For example, the experimental data available on the addition of a hydrogen atom to the carbonyl group are limited to addition to the oxygen atom:

$$H^{\bullet} + CH_2(O) \longrightarrow C^{\bullet}H_2OH.$$

This reaction is characterized by the following parameters: $\alpha = 1.247$, $br_e = 20.37$ (kJ/mol)$^{1/2}$, and $0.5hN_A\nu_{C=O} = 10.3$ kJ/mol. The parameters α and br_e for the alternative addition of $H^{\bullet}$ to the carbon atom,

$$H^{\bullet} + CH_2(O) \longrightarrow CH_3O^{\bullet}$$

were calculated. $\alpha = b_{C=O}/b_{C-H} = 59.91 \times 10^{10}/37.43 \times 10^{10} = 1.601$. The value of r_e for this reaction is typical of $H^{\bullet}$ addition reactions at the C=C bond ($br_e = 21.99$ (kJ/mol)$^{1/2}$) and can be derived from the proportion

$$br_e(H^{\bullet} + C{=}O) = br_e(H^{\bullet} + C{=}C)\frac{b_{C=O}}{b_{C=C}}, \qquad (5)$$

whence it follows that $br_e(H^{\bullet} + C{=}O) = 24.45$ (kJ/mol)$^{1/2}$.

The decay of alkoxyl radicals with C–C bond cleavage is characterized by $br_e = 13.38$ (kJ/mol)$^{1/2}$ and $\alpha = 0.748$. Accordingly, the reverse reaction, which is alkyl addition to the C atom of the carbonyl group, is characterized by $\alpha = 1/0.748 = 1.337$ and $br_e = 13.38 \times 1.337 = 17.87$ (kJ/mol)$^{1/2}$. Experimental data on the addition of alkyl radicals to the oxygen atom of the carbonyl group are lacking. For these reactions, br_e was taken to be the same as for alkoxyl addition to a C=C bond with a structurally similar reaction center (O…C…C) and the correction for the difference in b was applied:

$$br_e(R^{\bullet} + C{=}O) = br_e(RO^{\bullet} + C{=}C)\frac{b_{C=O}}{b_{C=C}}. \qquad (6)$$

The reaction $R^{\bullet} + O{=}C\!< \longrightarrow ROC^{\bullet}\!<$ is characterized by $\alpha = 1.571$ and $br_e = 18.62$ (kJ/mol)$^{1/2}$. The α and br_e values calculated within this approximation are listed in Table 2.

To calculate the interatomic distance in the TS of an addition reaction, we used the reduced intersecting parabolas model (RIPM) [9]. In distinction to IPM, RIPM treats activation energy as the intersection point between the parabola characterizing the elongation of the Y=Z bond and the parabola characterizing the elongation of the X…Y or X…Z bond with a reduced $b_f^{\#}$ value. This parameter is calculated using the empirical equation [9]

$$b_f^{\#} = aD_{ef}^{\#} - cD_{ef}^{\#2}, \qquad (7)$$

where the reduced bond dissociation energy is $D_{ef}^{\#} = E_e - \Delta H_e$. The method used to calculate the empirical coefficients a and c and their calculated values are reported elsewhere [9]. In order to determine the interatomic distance elongations in the TS (the same as are calculated in DFT), we introduced two correlation parameters, namely, $\beta = r_e(\mathrm{DFT})/r_e$ (RIPM) and $b_m = E_e^{1/2}/r^{\#}$ (DFT). The values of these parameters and of the parameters a and c (see formula (7)) are presented in Table 2. The TS structures were calculated using DFT for some of the reactions considered (the results are detailed below).

The r(X…Y) and r(X…Z) values for the TS in the alternative addition reactions

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

and

$$X^{\bullet} + Y{=}Z \longrightarrow XZY^{\bullet}$$

are calculated as follows. The enthalpies ΔH and ΔH_e of a given reaction are calculated from thermochemical data using formula (1). Next, the classical potential barrier E_e is determined using formula (3). The coefficient $b_f^{\#}$ characterizing the elongation of the Y…X bond in

Table 2. Kinetic (α, br_e) and geometric (β, b_m, a, c) parameters of the addition reactions [8–11]

Reaction	α	br_e, (kJ/mol)$^{0.5}$	β	$b_m \times 10^{10}$, kJ$^{0.5}$ mol$^{-0.5}$ m^{-1}	$a \times 10^8$, mol$^{0.5}$ kJ$^{-0.5}$ m^{-1}	$c \times 10^6$, mol$^{1.5}$ kJ$^{-1.5}$ m^{-1}
$H^{\bullet} + CH_2{=}CHR \longrightarrow CH_3C^{\bullet}HR$	1.440	21.99	1.231	133	12.12	0.818
$H^{\bullet} + (CH_2{=}CH)_2 \longrightarrow CH_3C^{\bullet}HCH{=}CH_2$	1.440	25.33	1.322	215	12.12	0.818
$H^{\bullet} + CH_2{=}CHPh \longrightarrow CH_3C^{\bullet}HPh$	1.440	24.18	1.350	160	12.12	0.818
$C^{\bullet}H_3 + CH_2{=}CHR \longrightarrow CH_3CH_2C^{\bullet}HR$	1.202	19.24	1.287	217	16.40	1.24
$C^{\bullet}H_3 + (CH_2{=}CH)_2 \longrightarrow MeCH_2C^{\bullet}HCH{=}CH_2$	1.202	20.42	1.806	253	16.40	1.24
$C^{\bullet}H_3 + CH_2{=}CHPh \longrightarrow CH_3CH_2C^{\bullet}HPh$	1.202	19.62	1.752	202	16.40	1.24
$N^{\bullet}H_2 + CH_2{=}CH_2 \longrightarrow NH_2CH_2C^{\bullet}H_2$	1.410	18.27	0.936	157	14.80	1.24
$N^{\bullet}H_2 + (CH_2{=}CH)_2 \longrightarrow NH_2CH_2C^{\bullet}HCH{=}CH_2$	1.410	19.45	1.457	182	14.80	1.24
$N^{\bullet}H_2 + CH_2{=}CHPh \longrightarrow NH_2CH_2C^{\bullet}HPh$	1.410	18.65	1.312	146	14.80	1.24
$CH_3O^{\bullet} + CH_2{=}CH_2 \longrightarrow CH_3OCH_2C^{\bullet}H_2$	1.413	16.75	1.305	102	22.80	3.32
$CH_3O^{\bullet} + (CH_2{=}CH)_2 \longrightarrow MeOCH_2C^{\bullet}HCH{=}CH_2$	1.413	17.93	1.831	184	22.80	3.32
$CH_3O^{\bullet} + CH_2{=}CHPh \longrightarrow MeOCH_2C^{\bullet}HPh$	1.413	17.13	1.776	95	22.80	3.32
$H^{\bullet} + O{=}CH_2 \longrightarrow CH_3O^{\bullet}$	1.600	24.45	1.111	454	12.12	0.818
$H^{\bullet} + O{=}CH_2 \longrightarrow C^{\bullet}H_2OH$	1.274	20.37	1.725	159	19.50	1.99
$C^{\bullet}H_3 + Me_2C{=}O \longrightarrow Me_3CO^{\bullet}$	1.336	17.87	0.841	185	16.40	1.24
$C^{\bullet}H_3 + Me_2C{=}O \longrightarrow Me_2C^{\bullet}OMe$	1.571	18.62	0.826	124	22.80	3.32
$H^{\bullet} + N{\equiv}CCH_3 \longrightarrow NH{=}C^{\bullet}Me$	1.768	22.32	0.720	62	13.71	0.818

the TS is calculated by empirical equation (7) using the E_e and ΔH_e values. The distance $r(Y...Z) = r(Y{=}Z) + r^{\#}$ is determined from the formula [9]

$$r^{\#}(Y...Z) = r(Y{=}Z) + \frac{\sqrt{E_e}}{b_m}, \qquad (8)$$

where b_m is the reduced coefficient b, which ensures the coincidence of the RIPM and DFT interatomic distances for this class of reactions. The interatomic distance $r(Y...X)$ in the TS is calculated by the formula [9]

$$r^{\#}(X...Y) = r(X{-}Y) + \frac{\beta\sqrt{E_e - \Delta H_e}}{a(E_e - \Delta H_e) - c(E_e - \Delta H_e)^2}. \qquad (9)$$

As will be demonstrated below, the addition reactions are very exothermic. The activation energy of a very exothermic reaction is $0.5RT$, and its classical barrier is $E_e = 0.5hN_A\nu$ [13]. The transition from $E_e > 0.5hN_A\nu$ to $E_e = 0.5hN_A\nu$ occurs at $\Delta H_e < \Delta H_{e,\,min}$. This threshold enthalpy depends on α, br_e, and the ZPE of the attacked bond ($0.5hN_A\nu$) [13]:

$$\Delta H_{e,\,min} = -\left(\frac{br_e}{\alpha}\right)^2 + \frac{2br_e\sqrt{0.5hN_A\nu}}{\alpha^2} + \frac{0.5hN_A\nu}{\alpha^2}(\alpha^2 - 1). \qquad (10)$$

The $\Delta H_{e,\,min}$ values (in kJ/mol) calculated by formula (10) for addition reactions of the 12 classes considered here are given below.

$X^{\bullet}$	$H^{\bullet}$	$C^{\bullet}H_3$	$N^{\bullet}H_2$	$CH_3O^{\bullet}$
$CH_2{=}CHR$	161.3	169.4	105.1	82.8
$CH_2{=}CHCH{=}CHR$	227.4	196.6	123.8	99.6
$CH_2{=}CHPh$	203.4	117.9	111.0	88.0

The dependence of the TS interatomic distance on the enthalpy of reaction also changes at $\Delta H_e < \Delta H_{e,\,min}$. The $r(X...Y)$ distance depends on the enthalpy and other characteristics of the reaction according to the equation

$$r^{\#}(\mathrm{X}\ldots\mathrm{Y}) = r(\mathrm{X{-}Y}) + \frac{\beta\sqrt{D^{\#}_{\mathrm{ef}}}}{aD^{\#}_{\mathrm{ef}} - cD^{\#2}_{\mathrm{ef}}} + \beta\frac{br_{\mathrm{e}} - \sqrt{0.5hN_{\mathrm{A}}\nu}}{b}\,\frac{\sqrt{-\Delta H_{\mathrm{e}}} - \sqrt{-\Delta H_{\mathrm{e,\,min}}}}{\sqrt{-\Delta H_{\mathrm{e,\,min}}} + \sqrt{0.5hN_{\mathrm{A}}\nu}}. \quad (11)$$

Note that the activation energies of the free-radical addition reactions in the gas and liquid phases coincide if the liquid phase is a nonpolar solvent. Furthermore, they coincide for any solvent if both reactants are nonpolar particles [8, 13]. In these cases, the bimolecular rate constants of the gas- and liquid-phase reactions differ only by a collision frequency factor. For the free-radical addition reactions, this factor is four times higher in the liquid phase than in the gas phase [8, 13]. In view of this, we ignored the solvation effects in the quantum-chemical calculations for the alternative addition reactions.

DFT Calculations

The hybrid B3LYP DFT method was used in the theoretical analysis of the alternative additions of radicals to molecules with double bonds. Theoretical studies [14, 15] have demonstrated that this method in combination with the use of an extended basis set in energy calculations provides close fits for the energy barriers in the addition of radicals to double bonds. The calculations were performed using the Gaussian 98 program [16]. The geometry of stationary points was determined by optimization in the 6-31G* basis set. As compared to the extended basis set 6-31+G(2d,2p) [17, 18], this basis set leads to somewhat overestimated lengths of the forming bond in the TS. In very early studies of the TS of H atom addition to ethylene, taking a more rigorous account of electron correlation in terms of the CCSD(T)/6-311G(d,p) coupled-cluster method [19] led to an overestimated C–H distance in the TS. However, for the less "loose" TS's in H atom addition reactions, the incorrect description of the long distance van der Waals asymptotics for the reactants is expected to have a weaker effect on the TS geometry. The molecular geometries found by the B3LYP/6-31G* method were used in the calculation of the energy of the system taking into account ZPE in the 6-311++G(d,p) basis set within the B3LYP/6-31G* approximation. When comparing calculated and experimental data, temperature corrections to the heat and activation energy of the reaction at 298 K were derived from statistical sums in the harmonic oscillator–rigid rotator model.

The following additions of the H atom and $\mathrm{Me}^{\bullet}$, $\mathrm{MeO}^{\bullet}$, and $\mathrm{NH}_2^{\bullet}$ radicals to multiple bonds (30 reactions) were considered:

$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{CH_3C^{\bullet}Me_2}$	$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{C^{\bullet}H_2CHMe_2}$
$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{CH_3C^{\bullet}HCH{=}CH_2}$	$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{C^{\bullet}H_2CH_2CH{=}CH_2}$
$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CHPh} \longrightarrow \mathrm{CH_3C^{\bullet}HPh}$	$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}CHPh} \longrightarrow \mathrm{C^{\bullet}H_2CH_2Ph}$
$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}O} \longrightarrow \mathrm{C^{\bullet}H_2OH}$	$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}O} \longrightarrow \mathrm{CH_3O^{\bullet}}$
$\mathrm{H}^{\bullet} + \mathrm{Me_2C{=}O} \longrightarrow \mathrm{Me_2CHO^{\bullet}}$	$\mathrm{H}^{\bullet} + \mathrm{Me_2C{=}O} \longrightarrow \mathrm{Me_2C^{\bullet}OH}$
$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}NH} \longrightarrow \mathrm{C^{\bullet}H_2NH_2}$	$\mathrm{H}^{\bullet} + \mathrm{CH_2{=}NH} \longrightarrow \mathrm{CH_3N^{\bullet}H}$
$\mathrm{H}^{\bullet} + \mathrm{MeC{\equiv}N} \longrightarrow \mathrm{MeCH{=}N^{\bullet}}$	$\mathrm{H}^{\bullet} + \mathrm{MeC{\equiv}N} \longrightarrow \mathrm{MeC^{\bullet}{=}NH}$
$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{MeCH_2C^{\bullet}Me_2}$	$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{C^{\bullet}H_2CMe_3}$
$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{MeCH_2C^{\bullet}HCH{=}CH_2}$	$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{C^{\bullet}H_2CHMeCH{=}CH_2}$
$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CHPh} \longrightarrow \mathrm{CH_2MeC^{\bullet}HPh}$	$\mathrm{Me}^{\bullet} + \mathrm{CH_2{=}CHPh} \longrightarrow \mathrm{C^{\bullet}H_2CHMePh}$
$\mathrm{Me}^{\bullet} + \mathrm{Me_2C{=}O} \longrightarrow \mathrm{Me_3CO^{\bullet}}$	$\mathrm{Me}^{\bullet} + \mathrm{O{=}CMe_2} \longrightarrow \mathrm{Me_2C^{\bullet}OMe}$
$\mathrm{MeO}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{MeOCH_2C^{\bullet}Me_2}$	$\mathrm{MeO}^{\bullet} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{C^{\bullet}H_2CMe_2(OMe)}$
$\mathrm{MeO}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{MeOCH_2C^{\bullet}HCH{=}CH_2}$	$\mathrm{MeO}^{\bullet} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{C^{\bullet}H_2CH(OMe)CH{=}CH_2}$
$\mathrm{N^{\bullet}H_2} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{NH_2CH_2C^{\bullet}Me_2}$	$\mathrm{N^{\bullet}H_2} + \mathrm{CH_2{=}CMe_2} \longrightarrow \mathrm{C^{\bullet}H_2CMe_2NH_2}$
$\mathrm{N^{\bullet}H_2} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{NH_2CH_2C^{\bullet}HCH{=}CH_2}$	$\mathrm{N^{\bullet}H_2} + \mathrm{CH_2{=}CHCH{=}CH_2} \longrightarrow \mathrm{C^{\bullet}H_2CH(NH_2)CH{=}CH_2}$

The results of the DFT calculations are presented in Tables 3 and 4 and in Fig. 1.

In Table 4, the calculated enthalpies of the alternative addition reactions are compared with experimental data and the calculated activation energies are compared to IPM data. In some cases, to estimate the accuracy of the DFT method, the electronic energies of the reactants and TS were determined using a combined procedure based on many-body perturbation theory (MBPT). The essence of this procedure is calculating,

Table 3. Energy and geometric characteristics of the reactants and transition states

System	Geometric parameters**		Energy, Hartree units		
	(bond length) × 10^{-10}, m	angle, deg	B3LYP/6-31G*	ZPE*	B3LYP/6-311++G**
H			–0.50027		–0.50226
$CH_3^{\bullet}$	C–H = 1.0833		–39.83829	0.02981	–39.85517
$NH_2^{\bullet}$	N–H = 1.034	H–N–H = 102.1	–55.87262	0.01898	–55.90038
$CH_2{=}O$	C–O = 1.207		–114.50047	0.02682	–114.54174
$CH_3O^{\bullet}$	C–O = 1.369 C–H = 1.103		–115.05046	0.03738	–115.09221
$H{-}CH_2O^{\bullet}$ TS	C–O = 1.219 C–H = 1.957	H–C–O = 103.8	–114.99847	0.02841	–115.04133
$HOC^{\bullet}H_2$	C–O = 1.370 O–H = 0.969		–115.05203	0.03752	–115.10230
$H{-}OC^{\bullet}H_2$ TS	O–H = 1.568 C–O = 1.236	H–O–C = 121.2	–114.99200	0.02779	–115.03573
$(CH_3)_2C{=}O$	C–O = 1.216 C–C = 1.521		–193.15569	0.08407	–193.21818
$(CH_3)_2CHO^{\bullet}$	C–O = 1.375 C–H = 1.106	H–C–O = 110.5	–193.68868	0.095316	–193.750951
$(CH_3)_2CHO^{\bullet}$ TS	C–O = 1.236 C–H = 1.795	H–C–O = 94.8	–193.64713	0.086532	–193.711400
$(CH_3)_2C^{\bullet}OH$	O–H = 0.969 C–O = 1.385	H–O–C = 108.5	–193.69798	0.09460	–193.76819
$(CH_3)_2C^{\bullet}O{-}H$ TS	O–H = 1.522 C–O = 1.248	H–O–C = 116.6	–193.64663	0.08543	–193.71199
$(CH_3)_3C{-}O^{\bullet}$	C–O = 1.382 C–C = 1.541		–233.00617	0.12310	–233.07878
$CH_3^{\bullet} + (CH_3)_2C{=}O$ TS	C–C = 2.158 C–O = 1.251 C–C = 1.534	C–C–O = 92.5	–232.94989	0.11931	–233.05414
$(CH_3)_2C^{\bullet}OCH_3$	C–O = 1.418 O–$C^{\bullet}$ = 1.381 $C^{\bullet}$–C = 1.498	C–O–C = 117.8	–233.00355	0.12323	–233.07615
$CH_3^{\bullet} + O{=}C(CH_3)_2$ TS	C–O = 1.903 O=C = 1.271 C–C = 1.509	C–C–O = 119.1	–232.97039	0.11770	–233.04571
$HN{=}CH_2$	C=N = 1.271 N–H = 1.027		–94.62721	0.04005	–94.66244
$NH_2C^{\bullet}H_2$	C–N = 1.402 N–H = 1.015		–95.19561	0.05052	–95.23741
$H^{\bullet} + HN{=}CH_2$ TS	N–H = 1.960 C–N = 1.275 N–H = 1.025	H–N–C = 122.3	–95.12774	0.04129	–95.16440
$CH_3NH^{\bullet}$	C–N = 1.445		–95.19086	0.049073	–95.22566
$H^{\bullet} + CH_2{=}NH$ TS	C–H = 2.077 C–N = 1.281	H–C–N = 104.7	–95.12610	0.04141	–95.16243
CH_3CN	C–N = 1.160 C–C = 1.461		–132.75493	0.04564	–132.79604
$CH_3C^{\bullet}NH$	C–N = 1.244 C–C = 1.493 N–H = 1.025	H–N–C = 116.5	–133.29207	0.05539	–133.33858
$H^{\bullet} + NCCH_3$ TS	N–H = 1.589 C–N = 1.175 C–C = 1.460	H–N–C = 118.6	–133.24736	0.04649	–133.29122
$CH_3CHN^{\bullet}$	C–N = 1.252 C–C = 1.516 C–H = 1.104	H–N–C = 118.7	–133.30593	0.05510	–133.34686
$H^{\bullet} + CH_3CN$ TS	C–H = 1.862 C–N = 1.172 C–C = 1.473	H–C–N = 100.8	–133.24870	0.04725	–133.29131
$CH_2{=}C(CH_3)_2$	C–C = 1.337 C–C = 1.509		–157.2273	0.10852	–157.27507
$CH_3C^{\bullet}(CH_3)_2$	C–H = 1.106 C–$C^{\bullet}$ = 1.498	H–C–C = 112.1	–157.7983	0.11727	–157.84552
$C^{\bullet}H_2CH(CH_3)_2$	C–H = 1.108 C–C = 1.496 C–C = 1.539	H–C–C = 108.3	–157.78565	0.11715	–157.83433
$CH_2^{\bullet}CH(CH_3)_2$ TS	C–H = 1.953 C–C = 1.365 C–C = 1.514	H–C–C = 94.4	–157.72385	0.110530	–157.773343
$MeCH_2C^{\bullet}(CH_3)_2$	C_m–C = 1.549 C–C = 1.503 C–C = 1.499	C_m–C–C = 114.0	–197.11082	0.146297	–197.168448
$MeCH_2C^{\bullet}(CH_3)_2$ TS	C_m–C = 2.370 C–C = 1.361 C–C = 1.506	C_m–C–C = 109.6	–197.05857	0.141275	–197.120893
$CH_2C^{\bullet}(CH_3)_3$	C_m–C = 1.553 C–C = 1.503 C–C = 1.543	C_m–C–C = 109.3	–157.22729	0.108516	–157.275063
$CH_2C^{\bullet}(CH_3)_3$ TS	C_m–C = 2.314 C–C = 1.370 C–C = 1.519	C_m–C–C = 110.2	–197.05002	0.141847	–197.112454
$NH_2CH_2C^{\bullet}(CH_3)_2$	C–N = 1.472 C–C = 1.503 C–C = 1.496	N–C–C = 111.9	–213.13775	0.135492	–213.20940
$NH_2CH_2C^{\bullet}(CH_3)_2$ TS	C–N = 2.182 C–C = 1.368 C–C = 1.502	N–C–C = 105.4	–213.09532	0.130868	–213.170040
$C^{\bullet}H_2C(CH_3)_2(NH_2)$	C–N = 1.497 C–C = 1.500 C–C = 1.536	N–C–C = 110.4	–213.13161	0.134511	–213.204415
$C^{\bullet}H_2C(CH_3)_2(NH_2)$ TS	C–N = 2.174 C–C = 1.370 C–C = 1.513	N–C–C = 95.1	–213.09709	0.131706	–213.171112
$CH_3OCH_2C^{\bullet}(CH_3)_2$	C–O = 1.411 O–C = 1.436 C–C = 1.494 C–C = 1.497	C–O–C = 112.3 O–C–C = 109.5	–272.31049	0.151088	–272.394162
$CH_3OCH_2C^{\bullet}(CH_3)_2$ TS	C–O = 1.386 O–C = 2.100 C–C = 1.364 C–C = 1.503	C–O–C = 111.2 O–C–C = 102.0	–272.27753	0.148140	–272.364979

Table 3. (Contd.)

System	Geometric parameters**		Energy, Hartree units		
	(bond length) × 10^{-10}, m	angle, deg	B3LYP/6-31G*	ZPE*	B3LYP/6-311++G**
$C^{\bullet}H_2C(CH_3)_2(OCH_3)$	C–O = 1.413 O–C = 1.440 C–C = 1.498 C–C = 1.545	C–O–C = 117.8 O–C–C = 104.2	–272.29964	0.149411	–272.383603
$C^{\bullet}H_2C(CH_3)_2(OCH_3)$ TS	C–O = 1.391 O–C = 2.038 C–C = 1.377 C–C = 1.509	C–O–C = 117.2 O–C–C = 96.6	–272.27423	0.148089	–272.361261
$CH_2=CHCH=CH_2$	C=C = 1.341 C–C = 1.458		–155.99212	0.085492	–156.040790
$CH_3C^{\bullet}HCH=CH_2$	H–C = 1.100 $C–C^{\bullet}$ = 1.496 $C^{\bullet}$–C = 1.389 C=C = 1.385	H–C–C = 111.6	–156.58064	0.094797	–156.62830
$C^{\bullet}H_2CH_2CH=CH_2$	H–C = 1.101 $C^{\bullet}$–C = 1.497 C–C = 1.510 C=C = 1.333	H–C–C = 109.2	–156.54800	0.093693	–156.597458
$C^{\bullet}H_2CH_2CH=CH_2$ TS	H–C = 1.957 C–C = 1.358 C–C = 1.467 C–C = 1.338	H–C–C = 99.9	–156.48868	0.086923	–156.538800
$MeCH_2C^{\bullet}HCH=CH_2$	C_m–C = 1.541 C–C = 1.498 C–C = 1.389 C–C = 1.386	C_m–C–C = 113.1	–195.89411	0.123770	–195.952384
$MeCH_2C^{\bullet}HCH=CH_2$ TS	C_m–C = 2.502 C–C = 1.359 C–C = 1.448 C–C = 1.345	C_m–C–C = 109.2	–195.82673	0.118088	–195.890197
$C^{\bullet}H_2CHMeCH=CH_2$	C_m–C = 1.540 C–C = 1.500 C–C = 1.520 C–C = 1.334	C_m–C–C = 111.8	–195.86253	0.122240	–195.922475
$C^{\bullet}H_2CHMeCH=CH_2$ TS	C_m–C = 2.290 C–C = 1.372 C–C = 1.471 C–C = 1.338	C_m–C–C = 105.0	–195.81725	0.118534	–195.880370
$NH_2CH_2C^{\bullet}HCH=CH_2$	C–N = 1.472 C–C = 1.497 C–C = 1.388 C–C = 1.387	N–C–C = 110.5	–211.91968	0.112882	–211.992217
$NH_2CH_2C^{\bullet}HCH=CH_2$ TS	C–N = 2.414 C–C = 1.356 C–C = 1.450 C–C = 1.345	N–C–C = 101.7	–211.86691	0.107803	–211.941816
$C^{\bullet}H_2CHNH_2CH=CH_2$	C–N = 1.479 C–C = 1.495 C–C = 1.516 C–C = 1.334	N–C–C = 109.1	–211.89097	0.111391	–211.964333
$C^{\bullet}H_2CHNH_2CH=CH_2$ TS	C–N = 2.118 C–C = 1.375 C–C = 1.471 C–C = 1.337	N–C–C = 99.8	–211.85900	0.108441	–211.933587
$CH_3OCH_2C^{\bullet}HCH=CH_2$	C–O = 1.411 O–C = 1.421 C–C = 1.493 C–C = 1.387 C–C = 1.386	C–O–C = 112.5 O–C–C = 109.3	–271.09144	0.128331	–271.175521
$CH_3OCH_2C^{\bullet}HCH=CH_2$ TS	C–O = 1.380 O–C = 2.276 C–C = 1.357 C–C = 1.446 C–C = 1.346	C–O–C = 111.1 O–C–C = 100.8	–271.04462	0.124994	–271.132992
$C^{\bullet}H_2CHOMeCH=CH_2$	C–O = 1.414 O–C = 1.427 C–C = 1.496 C–C = 1.513 C–C = 1.337	C–O–C = 113.5 O–C–C = 112.2	–271.06310	0.126938	–271.147774
$C^{\bullet}H_2CHOMeCH=CH_2$ TS	C–O = 1.393 O–C = 2.003 C–C = 1.379 C–C = 1.446 C–C = 1.337	C–O–C = 111.4 O–C–C = 96.0	–271.03464	0.124947	–271.122593
$CH_2=CHC_6H_5$	C–C = 1.337 C–C = 1.473 C_k–C_k = 1.407		–309.64827	0.133722	–309.730768
$CH_3C^{\bullet}HC_6H_5$	C_H–C = 1.100 C–C = 1.497 C–C = 1.415 C_k–C_k = 1.426	C_H–C–C = 112.2	–310.23337	0.14324	–310.31552
$C^{\bullet}H_2CH_2C_6H_5$	C_H–C = 1.097 C–C = 1.499 C–C = 1.529 C_k–C_k = 1.401	C_H–C–C = 110.0	–310.20669	0.142368	–310.290116
$C^{\bullet}H_2CH_2C_6H_5$ TS	H–C = 1.983 C–C = 1.356 C–C = 1.480 C_k–C_k = 1.405	C_H–C–C = 100.5	–310.14544	0.135177	–310.229548
$MeCH_2C^{\bullet}HC_6H_5$	C_m–C = 1.544 C–C = 1.498 C–C = 1.415 C_k–C_k = 1.427	C_m–C–C = 112.8	–349.54646	0.172352	–349.639055
$MeCH_2C^{\bullet}HC_6H_5$ TS	C_m–C = 2.489 C–C = 1.357 C–C = 1.462 C_k–C_k = 1.410	C_m–C–C = 108.7	–349.48285	0.166377	–349.580146
$C^{\bullet}H_2CHMeC_6H_5$	C_m–C = 1.546 C–C = 1.497 C–C = 1.526 C_k–C_k = 1.401	C_m–C–C = 111.4	–349.52098	0.170537	–349.614681
$C^{\bullet}H_2CHMeC_6H_5$ TS	C_m–C = 2.300 C–C = 1.370 C–C = 1.484 C_k–C_k = 1.405	C_m–C–C = 105.8	–349.47440	0.166778	–349.571476

*Zero-point vibration energy.

**C_m is the C atom of the methyl group, and C_k is a C atom in the benzene ring.

Table 4. Activation energies and enthalpies of the addition reactions calculated by the IPM and DFT methods

Reaction	$-\Delta H$, kJ/mol			E, kJ/mol		
	thermochemical method	DFT	MPT	IPM	DFT	MPT
$H^\bullet + CH_2{=}CMe_2 \longrightarrow CH_3C^\bullet Me_2$	162.5	152.3	–	1.2	0	–
$H^\bullet + CH_2{=}CMe_2 \longrightarrow C^\bullet H_2CHMe_2$	140.5	124.9	–	5.1	17.0	–
Difference	22.0	28.3	–	3.9	17.0	–
$H^\bullet + CH_2{=}CHCH{=}CH_2 \longrightarrow CH_3C^\bullet HCH{=}CH_2$	206.5	197.1	–	4.6	0	–
$H^\bullet + CH_2{=}CHCH{=}CH_2 \longrightarrow C^\bullet H_2CH_2CH{=}CH_2$	133.3	118.7	–	28.9	16.7	–
Difference	73.2	79.0	–	24.3	16.7	–
$H^\bullet + CH_2{=}CHPh \longrightarrow CH_3C^\bullet HPh$	199.2	189.9	–	1.2	0	–
$H^\bullet + CH_2{=}CHPh \longrightarrow C^\bullet H_2CH_2Ph$	141.3	124.8	–	17.8	14.7	–
Difference	57.9	65.1	–	16.6	14.7	–
$H^\bullet + O{=}CH_2 \longrightarrow C^\bullet H_2OH$	110.2	123.9	–	12.6	26.8	–
$H^\bullet + CH_2{=}O \longrightarrow CH_3O^\bullet$	97.2	99.4	–	21.0	12.7	–
Difference	13.0	24.5	–	8.4	–14.1	–
$H^\bullet + Me_2C{=}O \longrightarrow Me_2C^\bullet OH$	100.5	97.1	–	17.0	27.6	–
$H^\bullet + Me_2C{=}O \longrightarrow Me_2CHO^\bullet$	59.4	51.3	–	38.4	30.5	–
Difference	41.1	45.8	–	21.4	2.9	–
$Me^\bullet + Me_2C{=}O \longrightarrow Me_3CO^\bullet$	26.0	–2.2	36.3	33.4	57.3	34.0
$Me^\bullet + O{=}CMe_2 \longrightarrow Me_2C^\bullet OMe$	9.5	–10.9	10.9	36.3	78.3	74.0
Difference	16.5	8.7	25.4	2.9	19.6	40.0
$H^\bullet + HN{=}CH_2 \longrightarrow C^\bullet H_2NH_2$	138.3	162.2	–	–	6.3	–
$H^\bullet + CH_2{=}NH \longrightarrow CH_3N^\bullet H$	119.9	135.0	–	–	11.4	–
Difference	19.2	27.2	–	–	5.1	–
$H^\bullet + N{\equiv}CCH_3 \longrightarrow NH{=}C^\bullet Me$	53.1	79.1	–	18.2	23.4	–
$H^\bullet + CH_3C{\equiv}N \longrightarrow MeCH{=}N^\bullet$	–	101.8	–	–	11.4	–
Difference	–	–22.7	–	–	–12.0	–
$Me^\bullet + CH_2{=}CMe_2 \longrightarrow MeCH_2C^\bullet Me_2$	102.4	83.9	125.2	18.5	27.0	9.7
$Me^\bullet + CH_2{=}CMe_2 \longrightarrow CH_2C^\bullet Me_3$	94.2	61.0	109.6	21.4	51.4	23.8
Difference	8.2	22.9	15.6	2.9	24.4	14.1
$Me^\bullet + CH_2{=}CHCH{=}CH_2 \longrightarrow MeCH_2C^\bullet HCH{=}CH_2$	146.9	131.8	–	12.0	19.1	–
$Me^\bullet + CH_2{=}CHCH{=}CH_2 \longrightarrow C^\bullet H_2CHMeCH{=}CH_2$	80.7	56.2	–	35.4	45.1	–
Difference	66.2	75.6	–	23.4	26.0	–
$Me^\bullet + CH_2{=}CHPh \longrightarrow CH_2MeC^\bullet HPh$	144.7	122.2	–	7.7	19.4	–
$Me^\bullet + CH_2{=}CHPh \longrightarrow C^\bullet H_2CHMePh$	87.0	62.2	–	26.8	42.2	–
Difference	57.7	60.0	–	19.1	22.8	–
$MeO^\bullet + CH_2{=}CMe_2 \longrightarrow MeOCH_2C^\bullet Me_2$	74.4	57.5	71.3	2.3	11.6	20.1
$MeO^\bullet + CH_2{=}CMe_2 \longrightarrow C^\bullet H_2CMe_2(OMe)$	75.7	34.3	66.6	1.9	20.5	18.3
Difference	–1.3	23.2	4.7	–0.4	8.9	–1.8
$MeO^\bullet + (CH_2{=}CH)_2 \longrightarrow MeOCH_2C^\bullet HCH{=}CH_2$	166.8	99.2	–	0.0	5.1	–
$MeO^\bullet + (CH_2{=}CH)_2 \longrightarrow C^\bullet H_2CH(OMe)CH{=}CH_2$	96.8	29.3	–	0.6	31.9	–
Difference	70.0	69.9	–	0.6	26.8	–
$N^\bullet H_2 + CH_2{=}CMe_2 \longrightarrow NH_2CH_2C^\bullet Me_2$	83.0	72.7	73.1	6.7	20.0	30.9
$N^\bullet H_2 + CH_2{=}CMe_2 \longrightarrow C^\bullet H_2C^\bullet Me_2NH_2$	86.4	63.0	80.4	5.5	17.4	16.4
Difference	–3.4	9.7	–6.5	–2.2	–2.6	–14.1
$N^\bullet H_2 + (CH_2{=}CH)_2 \longrightarrow NH_2CH_2C^\bullet HCH{=}CH_2$	127.5	117.6	–	0.0	3.4	–
$N^\bullet H_2 + (CH_2{=}CH)_2 \longrightarrow C^\bullet H_2CH(NH_2)CH{=}CH_2$	68.7	47.6	–	18.9	25.6	–
Difference	58.8	70.0	–	18.9	22.2	–

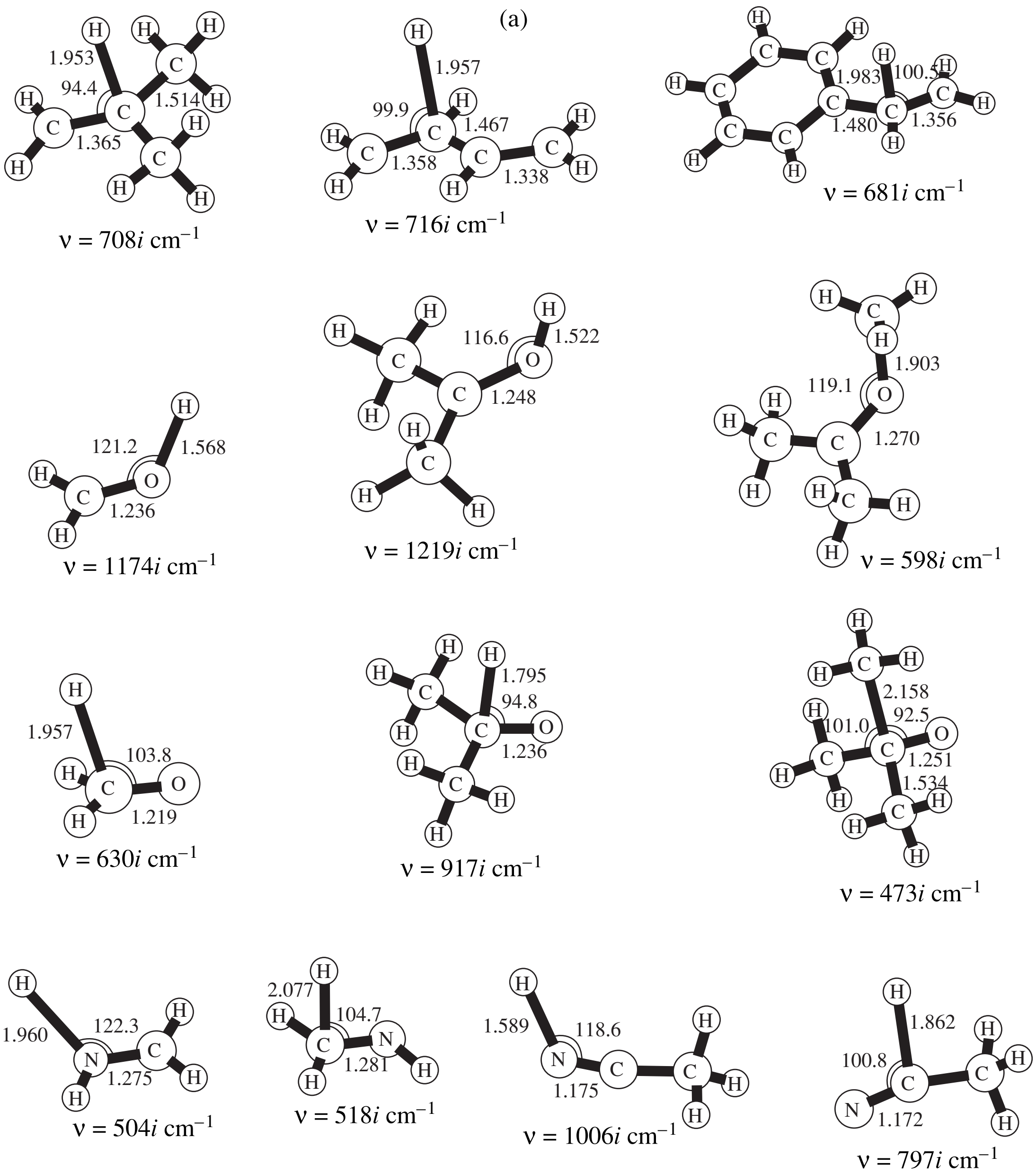

Fig. 1. B3LYP/6-31G* transition state geometries: (a) H addition to C=C, C=O, C=N, and C≡N bonds and methyl addition to the C=O bond; (b) $^{\bullet}CH_3$, $^{\bullet}NH_2$, and $^{\bullet}OCH_3$ addition to C=C bonds. The bond lengths are in Å, and the angles are in degrees.

by the CCSD(T) coupled-cluster method with the 6-31G* basis set and by the MP2 method with the 6-311++G** and 6-31G* basis sets, the algebraic sum E(CCSD(T)/6-31G*) – E(MP2/6-31G*) + E(MP2/-311++G**) for the B3LYP/6-31G* geometry. The results of these calculations are presented in Table 4.

RESULTS AND DISCUSSION

The IPM enthalpies, activation energies, and TS interatomic distances for the addition of $H^{\bullet}$, $^{\bullet}CH_3$, $^{\bullet}NH_2$, and $MeO^{\bullet}$ are listed in Tables 5–8. The mean estimation error for the IPM activation energy is ±1.5 kJ/mol [13], and, hence, the alternative addition reactions differ in activation energy by ±3.0 kJ/mol.

As follows from the data in Table 5, in the reactions with $\Delta H_e > \Delta H_{e,\min}$ $H^{\bullet}$ adds mainly to the CH_2 group of CH_2=CHY. This finding is in agreement with experimental data [2]. The difference between the activation energies of hydrogen atom addition to the CHY and CH_2 groups (ΔE) is positive and varies between

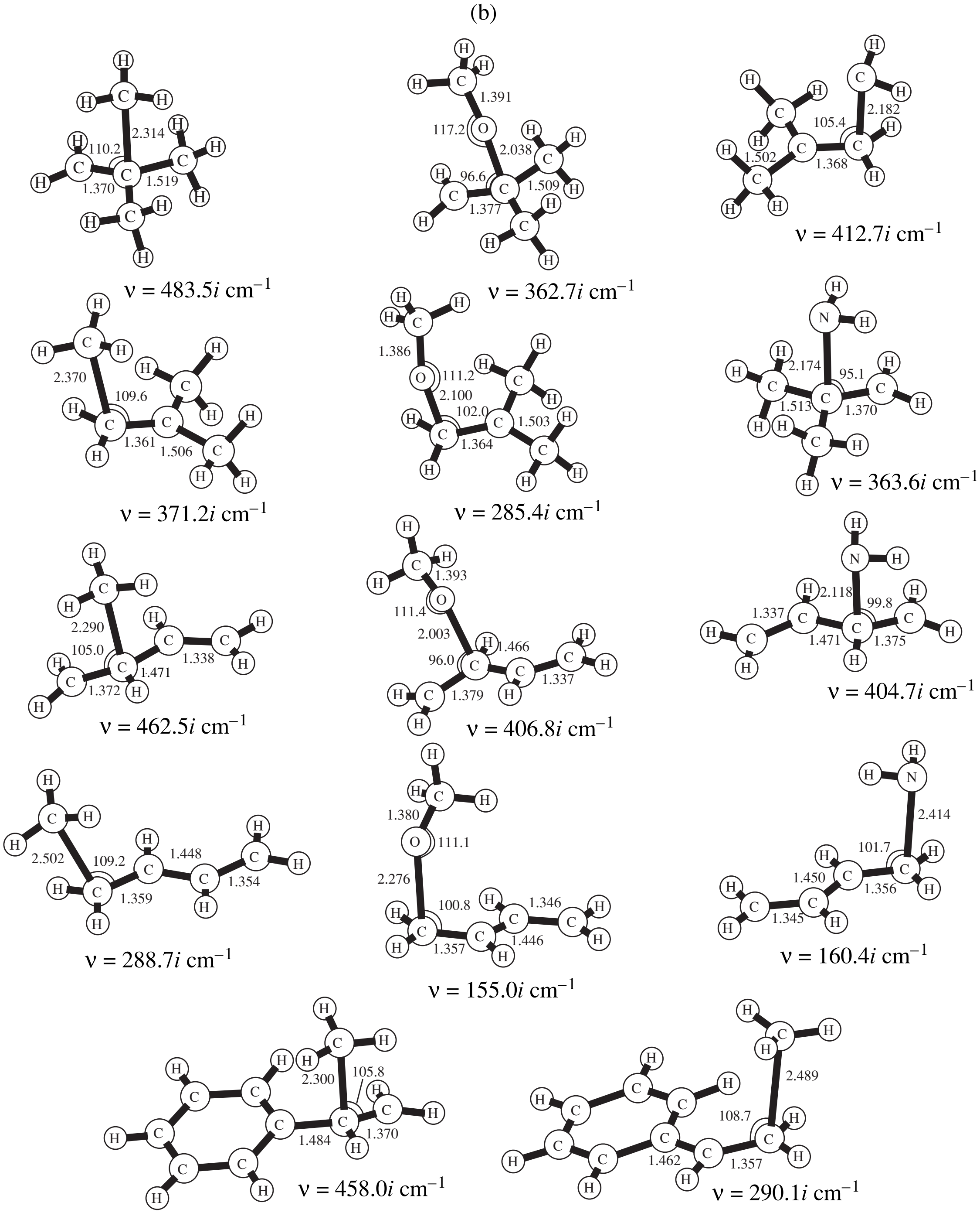

Fig. 1. (Contd.)

3.9 kJ/mol ($H^{\bullet}$ + CH_2=CHMe) and 24.3 kJ/mol ($H^{\bullet}$ + CH_2=CHCH=CH_2). The difference is particularly large if the addition reaction yields a stabilized radical such as $CH_3C^{\bullet}HCH=CH_2$ or $CH_3C^{\bullet}HPh$. The determining factor here is the enthalpy of the reaction (compare the ΔH_e and E_e values). An increase in ΔE is accompanied by an elongation of the TS C…H distance ($\Delta\Delta r^{\#}$) within 6×10^{-12} m. A linear correlation is observed between these values:

$$\begin{aligned}&\Delta\Delta r^{\#}(\mathrm{C\ldots H}) \times 10^{13}\ (\mathrm{m})\\ &= (8.13 \pm 0.53)\Delta E\ (\mathrm{kJ/mol}).\end{aligned} \tag{12}$$

The double bond elongates insignificantly (by only $(1-3) \times 10^{-13}$ m).

Table 5. Enthalpy, activation energy, and TS geometry in the alternative addition of the hydrogen atom to saturated compounds

Reaction	$-\Delta H_e$	E_e	ΔE	$r^{\#}$(C…H) $\times 10^{10}$	$r^{\#}$(C…C) $\times 10^{10}$
	kJ/mol			m	
$\mathrm{CH_2{=}CMe_2 + H^{\bullet} \longrightarrow CH_3C^{\bullet}Me_2}$	169.3	9.9		1.971	1.323
$\mathrm{CH_2{=}CMe_2 + H^{\bullet} \longrightarrow C^{\bullet}H_2CHMe_2}$	147.3	13.8	3.9	1.989	1.327
$\mathrm{CH_2{=}CMeCl + H^{\bullet} \longrightarrow CH_3C^{\bullet}MeCl}$	188.2	9.9		1.973	1.323
$\mathrm{CH_2{=}CMeCl + H^{\bullet} \longrightarrow C^{\bullet}H_2CHMeCl}$	161.7	9.9	0.0	1.970	1.323
$\mathrm{CH_2{=}CHOAc + H^{\bullet} \longrightarrow CH_3C^{\bullet}HOAc}$	181.0	9.9		1.970	1.323
$\mathrm{CH_2{=}CHOAc + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2OAc}$	158.5	10.6	0.7	1.973	1.324
$\mathrm{CH_2{=}CHC(O)OMe + H^{\bullet} \longrightarrow CH_3C^{\bullet}HC(O)OMe}$	174.0	9.9		1.971	1.323
$\mathrm{CH_2{=}CHC(O)OMe + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2C(O)OMe}$	146.9	13.9	4.0	1.990	1.327
$\mathrm{CH_2{=}CMeC(O)OMe + H^{\bullet} \longrightarrow CH_3C^{\bullet}MeC(O)OMe}$	169.4	9.9		1.971	1.323
$\mathrm{CH_2{=}CMeC(O)OMe + H^{\bullet} \longrightarrow C^{\bullet}H_2CHMeC(O)OMe}$	137.9	16.7	6.8	2.003	1.330
$E\text{-}\mathrm{MeCH{=}CHC(O)OH + H^{\bullet} \longrightarrow MeCH_2C^{\bullet}HC(O)OH}$	178.1	9.9		1.972	1.323
$E\text{-}\mathrm{MeCH{=}CHC(O)OH + H^{\bullet} \longrightarrow MeC^{\bullet}HCH_2C(O)OH}$	161.0	10.0	0.1	1.969	1.323
$Z\text{-}\mathrm{MeCH{=}CHC(O)OH + H^{\bullet} \longrightarrow MeCH_2C^{\bullet}HC(O)OH}$	182.3	9.9		1.972	1.323
$Z\text{-}\mathrm{MeCH{=}CHC(O)OH + H^{\bullet} \longrightarrow MeC^{\bullet}HCH_2C(O)OH}$	165.2	9.9	0.0	1.970	1.323
$\mathrm{CH_2{=}CHCH_2OAc + H^{\bullet} \longrightarrow CH_3C^{\bullet}HCH_2OAc}$	148.5	13.4		1.987	1.326
$\mathrm{CH_2{=}CHCH_2OAc + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2CH_2OAc}$	138.5	15.6	2.2	2.004	1.329
$\mathrm{CH_2{=}CHCN + H^{\bullet} \longrightarrow CH_3C^{\bullet}HCN}$	202.4	16.3		1.897	1.318
$\mathrm{CH_2{=}CHCN + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2CN}$	162.3	29.2	12.9	1.934	1.324
$\mathrm{CH_2{=}CMeCN + H^{\bullet} \longrightarrow CH_3C^{\bullet}MeCN}$	190.5	19.8		1.908	1.320
$\mathrm{CH_2{=}CMeCN + H^{\bullet} \longrightarrow C^{\bullet}H_2CMeHCN}$	135.1	39.6	19.8	1.962	1.328
$\mathrm{CH_2{=}CHCH{=}CH_2 + H^{\bullet} \longrightarrow CH_3C^{\bullet}HCH{=}CH_2}$	213.3	13.3		1.946	1.316
$\mathrm{CH_2{=}CHCH{=}CH_2 + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2CH{=}CH_2}$	140.1	37.6	24.3	2.020	1.327
$\mathrm{MeCH{=}CHCH{=}CHMe + H^{\bullet} \longrightarrow MeCH_2C^{\bullet}HCH{=}CHMe}$	209.4	14.4		1.949	1.317
$\mathrm{MeCH{=}CHCH{=}CHMe + H^{\bullet} \longrightarrow MeC^{\bullet}HCH_2CH{=}CHMe}$	138.5	38.3	23.9	2.022	1.328
$\mathrm{CH_2{=}CHPh + H^{\bullet} \longrightarrow CH_3C^{\bullet}HPh}$	206.0	9.9		1.981	1.319
$\mathrm{CH_2{=}CHPh + H^{\bullet} \longrightarrow C^{\bullet}H_2CH_2Ph}$	148.1	26.5	16.6	2.048	1.331
$\mathrm{CH_2{=}CMePh + H^{\bullet} \longrightarrow CH_3C^{\bullet}MePh}$	206.5	9.9		1.981	1.319
$\mathrm{CH_2{=}CMePh + H^{\bullet} \longrightarrow C^{\bullet}H_2CHMePh}$	138.5	30.1	20.2	2.060	1.333
$\mathrm{CH_2{=}O + H^{\bullet} \longrightarrow C^{\bullet}H_2OH}$	128.2	21.3		1.821	1.239
$\mathrm{CH_2{=}O + H^{\bullet} \longrightarrow CH_3O^{\bullet}}$	110.9	29.7	8.4	1.946	1.222
$\mathrm{Me_2C{=}O + H^{\bullet} \longrightarrow Me_2C^{\bullet}OH}$	118.5	25.7		1.934	1.242
$\mathrm{Me_2C{=}O + H^{\bullet} \longrightarrow Me_2CHO^{\bullet}}$	73.1	47.1	21.4	2.184	1.225
$\mathrm{MeC{\equiv}N + H^{\bullet} \longrightarrow MeC^{\bullet}{=}NH}$	67.0	26.9		1.583	1.220

In the case of $\Delta H_e < \Delta H_{e,\min}$, the activation energies of the alternative addition reactions do not differ. However, the reaction with a lower enthalpy will proceed at a higher rate owing to the influence of the reaction enthalpy on the preexponential factor [13].

The experimental ratio of the rate constants of the alternative hydrogen atom additions to vinyl chloride,

$$H^{\bullet} + CH_2{=}CHCl \longrightarrow CH_3C^{\bullet}HCl, \quad (I)$$

$$H^{\bullet} + CH_2{=}CHCl \longrightarrow C^{\bullet}H_2CH_2CHCl, \quad (II)$$

is reported to be $k_1/k_2 = 179$ [20] and 32 [21]. These values differ markedly from one another and from the calculated value of 5.4 derived from the enthalpies of the reactions (Table 5, [13]). These discrepancies are most likely to arise from the errors in both the experimental data and their theoretical estimates.

For the above alternative H atom additions to substituted olefins, DFT predicts the absence of an activation barrier for the interaction of an H atom with the terminal carbon atom (Fig. 2), as do the IPM calculations. The calculated heat of H atom addition to the C=C bond is always less exothermic than the corresponding experimental value by 7–15 kJ/mol. This discrepancy does not exceed the mean error in DFT calculations, which is 12–20 kJ/mol.

The enthalpy data calculated for H atom addition to the carbonyl group involve smaller errors of different signs. In the case of addition to the C=N and C≡N bonds, the theoretical values of the heat of the reaction are systematically overestimated. The IPM and DFT activation energies are rather close, the average difference being approximately 8 kJ/mol. The only qualitative discrepancy is observed for H atom addition to formaldehyde: according to the quantum-chemical calculation, the activation energy of the thermodynamically less favorable addition to the C atom is lower. Apparently, this discrepancy is due in part to the specific features of the TS structure in the alternative additions to the oxygen atom. This structure has a symmetry plane passing through the reacting H atom and carbonyl group, as opposed to the structure of the resulting

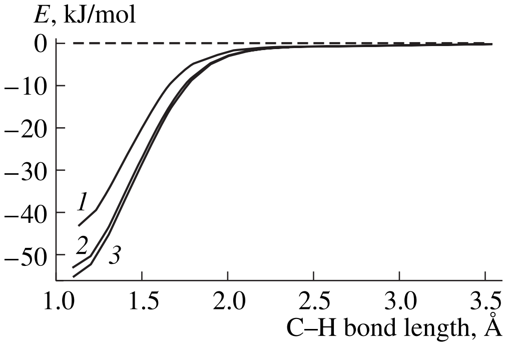

Fig. 2. Change in the energy upon C–H bond elongation in the (*1*) $H{-}CH_2C^{\bullet}HPh$, (*2*) $H{-}CH_2C^{\bullet}HCH{=}CH_2$, and (*3*) $H{-}CH_2C^{\bullet}Me_2$ radicals.

$HOC^{\bullet}H_2$, whose molecule is flat. The nonplanar structure of $HOC^{\bullet}H_2$ with the OH group turned by 90°, which has the same symmetry as the TS, is characterized by a 14.4 kJ/mol higher energy than the planar structure.

IPM data for the alternative additions of the methyl radical to different C atoms at the double bond are presented in Table 6.

The alternative additions of $CH_3^{\bullet}$ to alkyl-substituted olefins differ slightly in both enthalpy (2.1–12.2 kJ/mol) and activation energy (0.8–2.9 kJ/mol). The experimental data concerning the addition of the methyl radical to the CH_2 and CHMe groups of propylene indicate a considerable difference between the reactivities of these groups. The ratio of the rate constants of these reactions is 9 (at 410 K), which implies an activation energy difference of $\Delta E = RT\ln 9 = 7.5$ kJ/mol [2]. This value is much higher than the calculated value ($\Delta E = 0.8$ kJ/mol, see Table 4). However, the experimental activation energies of the alternative additions of the cyclohexyl radical to methyl crotonate ($CH_3CH{=}CHCOOMe$) are in good agreement with calculated data [22].

$$R^{\bullet} + YCH{=}CHC(O)OMe \longrightarrow RYCHC^{\bullet}HC(O)OMe \quad (III)$$

$$R^{\bullet} + YCH{=}CHC(O)OMe \longrightarrow YC^{\bullet}HCHRC(O)OMe \quad (IV)$$

$R^{\bullet}$	$C^{\bullet}H_3$ (calculated data; see Table 3)	*cyclo*-$C_6H_{11}^{\bullet}$ (experimental data [17])
k_3/k_4 ($T = 293$ K)	24.6	11.0
ΔE, kJ/mol	7.8	5.8

As can be seen, the difference between the activation energies of the alternative addition reactions is, on average, $\Delta E = 6.8 \pm 1.0$ kJ/mol; i.e., it does not exceed the measurement error.

A very different situation is observed for the addition of $CH_3^{\bullet}$ to a C=C bond in the α-position with respect to the vinyl group (1,3-dienes) or benzene ring (styrenes). Because of the stabilization of the allyl (or benzyl) radical resulting from β-addition, the difference in ΔH between the alternative $CH_3^{\bullet}$ addition reac-

Table 6. Enthalpy, activation energy, and TS geometry in the alternative additions of the methyl radical to unsaturated compounds

Reaction	$-\Delta H_e$	E_e	ΔE	$r^{\#}$(C…Me) $\times 10^{10}$	$r^{\#}$(C…C) $\times 10^{10}$
	kJ/mol			m	
$\mathrm{CH_2{=}CHMe + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}HMe}$	106.5	28.0		2.266	1.323
$\mathrm{CH_2{=}CHMe + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CHMe_2}$	104.4	28.8	0.8	2.269	1.323
$\mathrm{CH_2{=}CMe_2 + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}Me_2}$	108.9	27.2		2.263	1.323
$\mathrm{CH_2{=}CMe_2 + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CMe_3}$	100.7	30.1	2.9	2.274	1.324
$\mathrm{MeCH{=}CMe_2 + C^{\bullet}H_3 \longrightarrow Me_2CHC^{\bullet}Me_2}$	106.3	28.1		2.266	1.323
$\mathrm{MeCH{=}CMe_2 + C^{\bullet}H_3 \longrightarrow MeC^{\bullet}HCMe_3}$	101.4	29.9	1.8	2.273	1.324
$\mathrm{CH_2{=}CHOEt + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}HOEt}$	104.7	28.7		2.269	1.322
$\mathrm{CH_2{=}CHOEt + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CHMeOEt}$	96.6	31.6	2.9	2.280	1.324
$\mathrm{CH_2{=}CMeOMe + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}MeOMe}$	117.2	24.3		2.252	1.322
$\mathrm{CH_2{=}CMeOMe + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CMe_2OMe}$	87.2	35.2	10.9	2.295	1.326
$\mathrm{CH_2{=}CHC(O)OMe + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}HCOOMe}$	111.2	26.4		2.260	1.323
$\mathrm{CH_2{=}CHC(O)OMe + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CHMeCOOMe}$	92.3	33.2	6.8	2.287	1.325
$\mathrm{CH_2{=}CMeC(O)OMe + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}MeCO_2Me}$	112.5	25.9		2.258	1.322
$\mathrm{CH_2{=}CMeC(O)OMe + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CMe_2CO_2Me}$	91.9	33.4	7.5	2.287	1.326
$\mathrm{MeCH{=}CHC(O)OMe + C^{\bullet}H_3 \longrightarrow Me_2CHC^{\bullet}HCO_2Me}$	135.8	18.5		2.228	1.319
$\mathrm{MeCH{=}CHC(O)OMe + C^{\bullet}H_3 \longrightarrow MeC^{\bullet}HCHMeCO_2Me}$	111.3	26.3	7.8	2.260	1.323
$\mathrm{CH_2{=}CHCN + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}HCN}$	137.9	17.9		2.226	1.318
$\mathrm{CH_2{=}CHCN + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CHMeCN}$	109.8	26.9	9.0	2.262	1.323
$\mathrm{CH_2{=}CHCH{=}CH_2 + C^{\bullet}H_3 \longrightarrow MeCH_2C^{\bullet}HCH{=}CH_2}$	153.4	20.7		2.474	1.317
$\mathrm{CH_2{=}CHCH{=}CH_2 + C^{\bullet}H_3 \longrightarrow C^{\bullet}H_2CHMeCH{=}CH_2}$	87.2	44.1	23.4	2.580	1.325
$\mathrm{MeCH{=}CHCH{=}CHMe + C^{\bullet}H_3 \longrightarrow Me_2CHC^{\bullet}HCH{=}CHMe}$	144.9	23.3		2.486	1.318
$\mathrm{MeCH{=}CHCH{=}CHMe + C^{\bullet}H_3 \longrightarrow MeC^{\bullet}HCHMeCH{=}CHMe}$	87.0	44.2	20.9	2.580	1.326
$\mathrm{C^{\bullet}H_3 + CH_2{=}CHPh \longrightarrow MeCH_2C^{\bullet}HPh}$	151.2	16.4		2.458	1.319
$\mathrm{C^{\bullet}H_3 + CH_2{=}CHPh \longrightarrow C^{\bullet}H_2CHMePh}$	93.5	35.5	19.1	2.555	1.328
$\mathrm{C^{\bullet}H_3 + CH_2{=}CMePh \longrightarrow MeCH_2C^{\bullet}MePh}$	147.2	17.5		2.464	1.320
$\mathrm{C^{\bullet}H_3 + CH_2{=}CMePh \longrightarrow C^{\bullet}H_2CMe_2Ph}$	84.3	39.2	21.7	2.573	1.330
$\mathrm{C^{\bullet}H_3 + Me_2C{=}O \longrightarrow Me_3CO^{\bullet}}$	30.5	42.1		2.150	1.245
$\mathrm{C^{\bullet}H_3 + Me_2C{=}O \longrightarrow Me_2C^{\bullet}OMe}$	12.4	45.0	2.9	1.937	1.264

tions is as large as 60–73 kJ/mol and the difference between the ΔE values is approximately 19–22 kJ/mol. Accordingly, the Me…C bond elongation increases from 3×10^{-13} m for the alternative additions to olefins to 7×10^{-12} m for the alternative additions to dienes or phenylethylenes.

For the addition of the aminyl radical $^{\bullet}NH_2$ to the C=C bond, there is only a slight difference between the attacks on the CH_2 and CR^1R^2 groups (see Table 7). Regardless of whether $E(CH_2) < E(CR^1R^2)$ or $E(CH_2) > E(CR^1R^2)$, the difference between the activation energies is within ±2 kJ/mol. A radically different situation is observed for the addition of $^{\bullet}NH_2$ to dienes and styrenes: the attack on the β-position dominates, yielding a stabilized allyl or benzyl radical. In these reactions, the difference between the activation energies of the alternative additions is 10–20 kJ/mol.

A similar situation is observed for the alternative additions of the methoxyl radical at the double bond in the reactions for which $\Delta H_e > \Delta H_{e,\,min}$ (Table 8). The activation energies of the additions of $CH_3O^{\bullet}$ to the CHMe group of propylene and to the CMe_2 group of isobutylene are, respectively, 0.4 and 1.4 kJ/mol lower than the activation energy of addition to the terminal CH_2 group. The addition of the radical to the conjugated double bonds of styrene primarily yields a stabilized benzyl radical.

Table 7. Enthalpy, activation energy, and TS geometry in the alternative additions of the aminyl radical to unsaturated compounds

Reaction	$-\Delta H_e$	E_e	ΔE	$r^{\#}(C\ldots N) \times 10^{10}$	$r^{\#}(C{=}C) \times 10^{10}$
	kJ/mol			m	
$CH_2{=}CHMe + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}HMe$	85.7	16.3		2.154	1.325
$CH_2{=}CHMe + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CHMeNH_2$	91.0	14.4	–1.9	2.145	1.323
$CH_2{=}CMe_2 + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}Me_2$	88.1	15.4		2.150	1.324
$CH_2{=}CMe_2 + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2C^{\bullet}Me_2NH_2$	91.5	14.2	–1.2	2.144	1.323
$MeCH{=}CMe_2 + N^{\bullet}H_2 \longrightarrow NH_2MeCHC^{\bullet}Me_2$	92.9	13.8		2.141	1.323
$MeCH{=}CMe_2 + N^{\bullet}H_2 \longrightarrow MeC^{\bullet}HC^{\bullet}Me_2NH_2$	92.2	14.0	0.2	2.143	1.323
$CH_2{=}CHOEt + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}HOEt$	83.9	16.9		2.157	1.325
$CH_2{=}CHOEt + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CH(OEt)NH_2$	83.2	17.2	0.3	2.158	1.325
$CH_2{=}CMeOMe + N^{\bullet}H_2 \longrightarrow NH_2CMeC^{\bullet}HOMe$	96.4	12.6		2.136	1.322
$CH_2{=}CMeOMe + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CMe(OMe)NH_2$	78.0	19.1	2.2	2.168	1.327
$CH_2{=}CHC(O)OMe + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}HC(O)OMe$	90.4	14.6		2.146	1.323
$CH_2{=}CHC(O)OMe + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CH(NH_2)C(O)OMe$	78.9	18.8	4.2	2.166	1.327
$CH_2{=}CMeC(O)OMe + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}MeC(O)OMe$	91.7	14.2		2.143	1.323
$CH_2{=}CMeC(O)OMe + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CMe(NH_2)C(O)OMe$	82.7	17.4	3.2	2.159	1.326
$E\text{-}MeCH{=}CHC(O)OH + N^{\bullet}H_2 \longrightarrow Me(NH_2)CHC^{\bullet}HC(O)OH$	122.4	9.9		2.110	1.319
$E\text{-}MeCH{=}CHC(O)OH + N^{\bullet}H_2 \longrightarrow MeC^{\bullet}HCH(NH_2)C(O)OH$	97.9	12.1	2.2	2.133	1.321
$CH_2{=}CHCH{=}CH_2 + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}HCH{=}CH_2$	132.6	9.9		2.422	1.316
$CH_2{=}CHCH{=}CH_2 + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CH(NH_2)CH{=}CH_2$	73.8	27.6	17.7	2.537	1.332
$MeCH{=}CHCH{=}CHMe + N^{\bullet}H_2 \longrightarrow NH_2CHMeC^{\bullet}HCH{=}CHMe$	131.5	9.9		2.423	1.316
$MeCH{=}CHCH{=}CHMe + N^{\bullet}H_2 \longrightarrow MeC^{\bullet}HCH(NH_2)CH{=}CHMe$	73.6	27.7	19.8	2.538	1.328
$CH_2{=}CHPh + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}HPh$	130.4	9.9		2.351	1.321
$CH_2{=}CHPh + N^{\bullet}H_2 \longrightarrow C^{\bullet}H_2CH(NH_2)Ph$	80.1	20.4	10.5	2.434	1.330
$CH_2{=}CMePh + N^{\bullet}H_2 \longrightarrow NH_2CH_2C^{\bullet}MePh$	126.4	9.9		2.354	1.321
$CH_2{=}CMePh + N^{\bullet}H_2 \longrightarrow CH_2C^{\bullet}Me(NH_2)Ph$	75.1	22.4	12.5	2.447	1.331

The DFT values of $-\Delta H$ for the addition of the $Me^{\bullet}$, $MeO^{\bullet}$, and ${}^{\bullet}NH_2$ radicals are systematically underestimated by 18–33, 8–41, and 10–23 kJ/mol, respectively, as in the case of $H^{\bullet}$ addition. Apparently, the general cause of these deviations exceeding the deviations for the $H^{\bullet}$ atom addition reactions is that the correlation effects contributing to the noncovalent interactions of atomic groups (which are equivalent to van der Waals interactions) are inadequately taken into account. These effects are due to the dispersion interactions between the radical and the unsaturated molecule, which are not taken into account explicitly by DFT. As a consequence, the activation energy calculated by the DFT method is, on average, systematically overestimated by 16 kJ/mol relative to the activation energy calculated by the IPM.

This point can be illustrated using the alternative additions of the methyl radical to acetone as an example. For C–O bond formation, all C and O atoms in the $(CH_3)_2C^{\bullet}OCH_3$ radical are virtually in one plane, resulting in a short (2.39×10^{-10}-m-long) contact between hydrogen atoms of the nearest neighbor methyl groups. In the symmetric radical $(CH_3)_3CO^{\bullet}$, the steric strain is lower, because the short H–H contacts have a longer length of 2.54×10^{-10} m. As a consequence, the O-centered radical is more stable than the C-centered radical according to both calculated and experimental data. However, DFT leads to slightly endothermic enthalpies for the methyl addition reactions, because it does not take into account the correlation effects adequately, while, in fact, these reactions are slightly exothermic. In more precise calculations using MBPT, the enthalpy of methyl addition to the C and O atoms of the carbonyl group of acetone at 298 K appears to be –36.3 and –10.9 kJ/mol, respectively, while the corresponding experimental values are –26.0 and –9.5 kJ/mol. In the calculation of activation ener-

Table 8. Enthalpy, activation energy, and TS geometry in the alternative additions of the methoxyl radical to unsaturated compounds

Reaction	$-\Delta H_e$	E_e	ΔE	$r^{\#}(C\ldots O) \times 10^{10}$	$r^{\#}(C\ldots C) \times 10^{10}$
	kJ/mol			m	
$CH_2{=}CHMe + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}HMe$	81.5	10.3		2.105	1.400
$CH_2{=}CHMe + MeO^{\bullet} \longrightarrow C^{\bullet}H_2CH(OMe)Me$	85.9	9.9	−0.4	2.102	1.447
$CH_2{=}CMe_2 + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}Me_2$	79.3	11.0		2.109	1.331
$CH_2{=}CMe_2 + MeO^{\bullet} \longrightarrow C^{\bullet}H_2CH(OMe)Me_2$	80.6	10.6	−0.4	2.107	1.331
$MeCH{=}CMe_2 + MeO^{\bullet} \longrightarrow Me(MeO)CHC^{\bullet}Me_2$	80.0	10.8		2.108	1.331
$MeCH{=}CMe_2 + MeO^{\bullet} \longrightarrow MeC^{\bullet}HC(MeO)Me_2$	68.3	14.9	4.1	2.130	1.337
$CH_2{=}CMeOMe + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}(OMe)Me$	74.6	12.6		2.118	1.334
$CH_2{=}CMeOMe + MeO^{\bullet} \longrightarrow C^{\bullet}H_2C(OMe)_2Me$	95.5	9.9	−2.7	2.100	1.330
$CH_2{=}CHCH{=}CH_2 + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}HCH{=}CH_2$	171.7	9.9		2.395	1.316
$CH_2{=}CHCH{=}CH_2 + MeO^{\bullet} \longrightarrow C^{\bullet}H_2CH(OMe)CH{=}CH_2$	101.7	9.9	0	2.329	1.316
$MeCH{=}CHCH{=}CHMe + MeO^{\bullet} \longrightarrow MeOCHMeC^{\bullet}HCH{=}CHMe$	173.7	9.9		1.400	1.316
$MeCH{=}CHCH{=}CHMe + MeO^{\bullet} \longrightarrow MeC^{\bullet}HCH(OMe)CH{=}CHMe$	107.9	9.9	0	2.331	1.316
$CH_2{=}CHPh + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}HPh$	113.6	9.9		2.337	1.332
$CH_2{=}CHPh + MeO^{\bullet} \longrightarrow C^{\bullet}H_2CH(OMe)Ph$	59.4	20.3	10.4	2.403	1.343
$CH_2{=}CMePh + MeO^{\bullet} \longrightarrow MeOCH_2C^{\bullet}MePh$	101.7	9.9		2.333	1.332
$CH_2{=}CMePh + MeO^{\bullet} \longrightarrow C^{\bullet}H_2CMe(OMe)Ph$	67.8	17.0	7.1	2.381	1.339

gies, this refined approach does not lead to such a large difference (Table 4). This is likely to be explained by the sensitivity of the calculation method to the structure of the loose TS. The residual discrepancy between the IPM and MPT activation energies of methyl addition to the oxygen atom of acetone, which is 38 kJ/mol, is likely to indicate that the true activation energy has some intermediate value.

As for the addition of the $Me^{\bullet}$, $MeO^{\bullet}$, and $NH_2^{\bullet}$ radicals to isobutylene, the DFT and MPT methods lead to similar discrepancies of 10–24 kJ/mol between calculated and experimental ΔH data, and the same is true for the DFT and MPT values of E as compared to IPM data (Table 4). There are only a few exceptions in which the error of the theoretical calculation of ΔH is insignificant.

Thus, the theoretical approaches suggest the simple inference that this is the enthalpy of the addition reaction that is the main factor determining the atom to be attacked. The lower the enthalpy of the addition of a radical to a certain C atom at the double bond, the lower the activation energy and, accordingly, the higher the rate constant of the addition reaction.

Using the results of a similar theoretical study of the addition of these radicals to ethylene [10], we can formulate the following rules concerning relative energies and TS structures (Table 3, Fig. 1). Due to the high strength of the C–H bond compared to the C–C bond, the additions of the hydrogen atom to the C=C bond are 70–80 kJ/mol more exothermic than the additions of the $^{\bullet}CH_3$ radical and are characterized by a ~30 kJ/mol lower activation barrier. This rule is also valid for addition to the terminal C atom in substituted olefins: the energy barrier is 22–32 kJ/mol for the methyl radical and is equal to zero for $H^{\bullet}$.

It is noteworthy that, in the alternative addition reactions of the methyl radical at the C=C bond, the average C–C distances in the TS and the activation energies of $^{\bullet}CH_3$ addition to the α- and β-carbon atoms are very close to the corresponding values for the addition of the same radicals to ethylene. Under the assumption that the same rule is also valid for the $H^{\bullet}$ atom, the addition of $H^{\bullet}$ to the terminal C atom will occur with a zero activation energy. According to calculated data, the C…..H distance in the β-addition of $H^{\bullet}$ to terminal olefins ($\sim(1.95\text{–}1.98) \times 10^{-10}$ m) is much shorter than the same distance in the TS of $H^{\bullet}$ addition to ethylene (2.33×10^{-10} m). Therefore, a long C…..H distance of 2.75×10^{-10} m should formally be expected for the TS of $H^{\bullet}$ α-addition, and this value is close to the van der Waals minimum for the H + olefin system. Thus, the energy of this structure must be lower than the energy of the reactants.

A specific feature of the addition of the methyl radical, as distinct from the hydrogen atom, is a change in the structure of the coordination polyhedron around the C atom caused by a decrease in the H–C–H angle from 120° in the $^\bullet CH_3$ radical to ~109° in the products. This distortion of the methyl group, which is necessary for the rehybridization of the *s* and *p* orbitals, increases the activation energy and decreases the heat of the reaction. The appearance of a directed valence in the distorted methyl radical favors tighter interaction between the radical center and the double bond in the TS, which is not the case for the hydrogen atom. As a consequence, the relative elongation of the C–C bond in the TS is smaller than the C–H bond elongation by $\sim 0.2 \times 10^{-10}$ m in spite of the less favorable thermodynamics of the methyl addition.

The addition of oxymethyl and aminyl radicals to the double bond virtually does not change the geometry of the structure around the reaction center O or N. Therefore, the activation barriers in this case are, as a rule, lower than those in methyl addition. The conjugation of the resulting radical center with the double bond or with a system of double bonds increases the heat of the reaction, results in an earlier TS than in the case of the alternative additions in the absence of conjugation, and lengthens the C–C, O–C, and N–C distances by $(0.2–0.3) \times 10^{-10}$ m.

Thus, a simultaneous analysis of the enthalpy and activation energy differences between the alternative addition reactions has demonstrated that the higher the enthalpy, the faster the addition reaction. The quantitative results obtained by the IPM and DFT methods are in satisfactory agreement. The difference between the activation energies of alternative addition reactions is most pronounced (15–20 kJ/mol) for the addition to the carbonyl group. In this case, the accuracy of the DFT calculation is lower, because, in this method, it is more difficult to take into account the correlation effects associated with the change in the number of lone electron pairs at the oxygen atom. Similar differences are observed for the addition of $^\bullet CH_3$ to 2-methylpropene (10 kJ/mol) and of $H_3CO^\bullet$ to butadiene (25 kJ/mol). In the addition of the hydrogen atom and methyl, methoxyl, and aminyl radicals to the C=C bond, the difference is 8–12, 3, 9, and 2 kJ/mol, respectively. For H addition to the C=N bond and to the N atom of acetonitrile, the difference does not exceed 10 kJ/mol.

The use of both calculation methods has shown that, in the 17 reaction classes considered, the addition $X^\bullet + Y{=}Z \longrightarrow XYZ^\bullet$ and the alternative addition $X^\bullet + Y{=}Z \longrightarrow XZY^\bullet$ are governed by the enthalpy of the reaction: the process is dominated by the addition reaction with a lower enthalpy.

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