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Reduced parabolic model for radical addition reactions

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The transition state of addition of free radicals and atoms to multiple bonds is considered as a result of intersecting of two parabolic potential curves. One of them characterizes the stretching vibration of the attacked multiple bond, and another curve characterizes the stretching vibration of the bond formed in the transition state. The force constant of the latter is calculated by an empirical equation that correlates the force constant with the bond dissociation energy. In the framework of this model, the thermally neutral activation energy (E_{e0}) and the elongation of the attacked and formed bonds (r_e) in the transition state were calculated from the experimental data (activation energy (E_e) and enthalpy of reaction (ΔH_e)) for the addition of an H atom and methyl, alkoxyl, aminyl, triethylsilyl, and peroxyl radicals to the C=C bond and the addition of $H^{\bullet}$ and $^{\bullet}CH_3$ to the C=O and C≡C bonds. Analysis of the data obtained showed that E_{e0} depends linearly on the $|\Delta H_e| + E_e$ sum, *i.e.*, $E_{e0}/\mathrm{kJ\ mol^{-1}} = 14.2 + 0.61 \cdot (E_e - \Delta H_e)$, and the bond elongation in the transition state for addition of the most part of radicals to ethylene and acetylene vary within $(0.65—0.87) \cdot 10^{-10}$ m. The factors affecting the activation energy of the radical addition reactions are discussed.

Key words: atom, double bond, reduced intersecting parabolas model, transition state, radical addition, force constant of chemical bond, free radical, triplet repulsion, triple bond, bond elongation, activation energy, bond dissociation energy, electronegativity of atoms, enthalpy of reaction.

Reactions of radical addition to molecules with multiple bonds have previously[1—6] been analyzed in the framework of the intersecting parabolas model (IPM). This approach turned out to be rather fruitful and made it possible to identify structural and physical factors, whose combination determines the reactivity of participants of these reactions.[7—9] In the framework of IPM, the addition reactions are characterized by the following three parameters (along with enthalpy and activation energy)[9]: force constant of the attacked multiple bond, force constant of the formed bond, and the total elongation of the reacting bonds in the transition state (TS). In the earlier version of IPM, the force constant of the formed bond was accepted equal to that in the radical formed.[1—6] This model, which can conventionally be named the "rigid" IPM, describes well the energy of addition reactions but predicts strongly shortened interatomic distances for the TS. For example, according to the quantum-chemical calculation, the elongation of the C_{Me}—C bond for methyl radical addition to the ethylene molecule is $0.75 \cdot 10^{-10}$ m, whereas the IPM gives only $0.26 \cdot 10^{-10}$ m.[9]

In this work, aimed at converging the geometric parameters obtained by the IPM and quantum-chemical calculations, we proposed a new model of intersecting parabolas. According to this model, the TS is also considered as a result of intersecting of two parabolic potential curves. One of them relates to the multiple bond vibration, and another curve concerns the vibration of the bond formed in the TS. The strength and the force constant of this bond are much lower than those in the target molecule. This model of the addition reaction can be named a reduced intersecting parabolas model (RIPM). In this model, the bond vibration is considered as harmonic. The present work considers the experimental data on addition of atoms and radicals in the framework of the RIPM.

Calculation procedure

In the framework of IPM, the radical addition reaction

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

is characterized by the following parameters[6—9]:

(1) enthalpy ΔH_e including the difference between the zero-point vibrational energies of the attacked (Y=Z) and formed (X—Y and Y—Z) bonds

$$\Delta H_e = \Delta H + 0.5hL[\nu(Y{=}Z) - \nu(X{-}Y) - \nu(Y{-}Z)], \qquad (1)$$

where h and L are the Planck constant and Avogadro´s number, respectively;

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(2) classical potential reaction barrier E_e, which differs from the Arrhenius activation energy E by the mean kinetic energy of particle motion

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

(rigidly speaking, this difference also contains the difference between the zero-point vibrational energies of the multiple bond in the starting molecule and in the TS, although the difference between the latter is so insignificant that can be neglected);

(3) parameter r_e, which is equal to the total elongation of the attacked (Y=Z) and formed (X—Y) bonds in the TS;

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

(5) parameter b_f ($2b_f^2$ is the force constant of the formed bond in the TS) or coefficient $\alpha = b/b_f$;

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

The reaction rate constant (k) is related to the activation energy E and A_0 by the Arrhenius equation

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

where n is the number of equally reactive atoms in the reactant molecule (for instance, in propylene $n = 1$, whereas in ethylene $n = 2$). The above parameters are related to each other by the correlation[9]

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

The br_e parameter, in turn, makes it possible to calculate the classical barrier of the thermally neutral reaction (E_{e0}), which is analogous to the reaction under consideration with $\Delta H_e = 0$, $br_e = \text{const}$, and $\alpha = \text{const}$

$$E_{e0} = [br_e/(1 + \alpha)]^2. \tag{5}$$

The force constant of the bond between atoms in a molecule (k^*) depends on the stretching vibrational frequency (ν_f) and reduced weight (μ_f) of the atoms forming the bond[1]

$$k^* = 2b_f^2 = 4\pi^2\nu_f^2\mu_f. \tag{6}$$

The higher the stretching vibrational frequency (ν_f), the stronger the bond formed in the TS, which characterized by the dissociation energy ($D_{ef}^{\neq}$). Therefore, to determine $b_f^{\neq}$ from the $D_{ef}^{\neq}$ value, we constructed the correlations between b and D_e. These relationships have the form

$$b_f^{\neq}/D_{ef}^{\neq} = a - c\cdot D_{ef}^{\neq}, \tag{7}$$

where a and c are the empirical coefficients characteristic of each pair of the bond-forming atoms. The bonds, vibrational frequencies, coefficients b, bond dissociation energies, and correlations for calculation of $b_f^{\neq}$ from the energy of the formed bond are presented in Table 1. The energy of the bond formed in the TS ($D_{ef}^{\neq}$) is equal to $E_e - \Delta H_e$. The method for calculation of the enthalpies of addition reactions has been described previously.[1—6] The energies of the H atom and radical addition to a multiple bond are also known.[10]

The parabolas characterizing the plot of E_e *vs.* r_e for the IPM and RIPM in methyl radical addition to the ethylene molecule are shown in Fig. 1.

The results of calculation of the parameters for various addition reactions are presented in Tables 2—5.

Results and Discussion

Contribution of the enthalpy to the activation energy. This contribution (ΔE_H) can be estimated by comparison of the classical potential barrier (E_e) with that for the thermally neutral ($\Delta H_e = 0$) reaction (E_{e0})

$$\Delta E_H = E_e - E_{e0}. \tag{8}$$

Table 1. Parameters D_e and ν and correlations for estimation of the force constants of bonds (coefficient b) in the TS of addition reactions

Bond	Molecule	ν/cm^{-1}	$b\cdot10^{-10}$ /kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}	D_e (ΔD_e) /kJ mol^{-1}	$(b/D_e)\cdot10^{-8}$ /kJ$^{-1/2}$ mol$^{1/2}$ m^{-1}
$b/D_e = 12.12\cdot10^8 - 0.818\cdot10^6D_e$					
C—H	CH_3CH_3	2910	37.43	439.4 (17.4)	8.518
C—H	$CH_2=CH_2$	3085	39.60	482.4 (18.4)	8.209
C—H	$CH\equiv CH$	3374	43.31	603.5 (20.2)	7.176
$b/D_e = 19.50\cdot10^8 - 1.99\cdot10^6D_e$					
O—H	ROOH	3550	46.00	386.7 (21.2)	11.90
O—H	ROH	3625	46.98	455.5 (21.7)	10.31
$b/D_e = 16.40\cdot10^8 - 1.24\cdot10^6D_e$					
C—C	CH_3CH_3	1375	44.83	386.2 (8.2)	11.61
C—C	$CH_2=CH_2$	1643	53.57	729.8 (9.9)	7.34
$b/D_e = 14.80\cdot10^8 - 1.24\cdot10^6D_e$					
C—N	CH_3NH_2	1130	38.23	378.0 (6.8)	10.11
$b/D_e = 22.80\cdot10^8 - 3.32\cdot10^6D_e$					
C—O	CH_3OCH_3	1125	39.21	349.5 (6.7)	11.22
C—O	$CH_2(O)$	1719	59.91	749.8 (10.3)	8.00
$b/D_e = 12.86\cdot10^8 - 1.24\cdot10^6D_e$					
C—Si	CH_3SiH_3	800	30.87	378.0 (4.8)	8.17

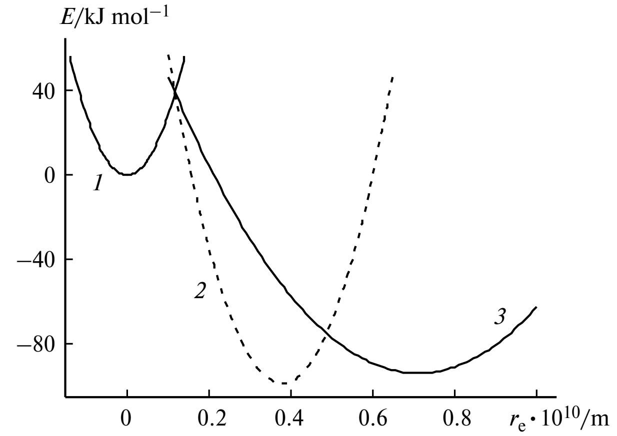


Fig. 1. Potential curves of stretching vibrations of the reacting bonds in the TS of methyl radical addition to ethylene: C=C bond (*1*), formed C—C bond in the IPM (*2*), and formed C—C bond in the RIPM (*3*).

The E_e, E_{e0}, and ΔE_H values for 9 classes of addition reactions are presented in Table 6.

The data presented (see Table 6) show that this contribution is high and changes from −31 kJ mol^{-1} for peroxyl radical addition to the ethylene molecule to −112 kJ mol^{-1} for H$^{\bullet}$ addition to the acetylene molecule. In percentage (see $\Delta E_e/\Delta H_e$ in Table 6), this contribution varies from 84% (for methyl radical addition to ethylene) to 61% (for H atom addition to the carbonyl group).

Triplet repulsion in the TS. Comparison of the activation energy (E_{e0}) with the strength of the bond formed in the TS ($D_{ef}{}^{\neq}$) shows that the stronger the formed bond, the higher E_{e0}. This can be seen from comparison of the E_{e0} and $D_{ef}{}^{\neq}$ values for addition of H atom to ethylene and acetaldehyde molecules and methyl radical to ethylene and acetylene molecules.

Reaction	E_{e0}	$D_{ef}{}^{\neq}$
	kJ mol^{-1}	
$H^{\bullet} + CH_2{=}CH_2$	111.9	174.8
$H^{\bullet}$ + MeCH=O	94.7	144.5
$^{\bullet}CH_3 + CH_2{=}CH_2$	98.1	134.7
$^{\bullet}CH_3 + CH{\equiv}CH$	95.3	129.6

The E_{e0} and $D_{ef}{}^{\neq}$ values change in parallel, reflecting an important role of triplet repulsion in the TS of addition reactions, which has already been mentioned in the stud-

Table 2. Kinetic parameters (ΔH_e, E_e, α, br_e, r_e, and E_{e0}) of H atom addition to olefins in the RIPM (calculated from the experimental data[11—25])

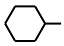
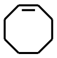
Olefin	$-\Delta H_e$	E_e	α	br_e /kJ$^{1/2}$ mol$^{-1/2}$	$r_e \cdot 10^{10}$ /m	E_{e0} /kJ mol^{-1}
	kJ mol^{-1}					
$CH_2{=}CH_2$	166.1	8.7	2.885	41.09	0.762	111.9
$CH_2{=}CHMe$	169.3	7.1	2.862	40.68	0.755	110.9
$CH_2{=}CHEt$	170.2	6.1	2.864	40.49	0.751	109.8
$CH_2{=}CMe_2$	172.9	4.2	2.852	40.01	0.742	107.9
$CH_2{=}CHPr$	169.7	6.8	2.870	40.61	0.754	110.7
cis-MeCH=CHEt	162.5	10.1	2.917	41.50	0.770	112.2
trans-MeCH=CHEt	158.2	10.3	2.978	41.87	0.777	110.8
$CH_2{=}CEtMe$	174.3	5.5	2.815	40.90	0.744	110.4
$MeCH{=}CMe_2$	173.5	10.6	2.758	40.69	0.755	117.2
$CH_2{=}CMePr$	177.3	9.5	2.725	40.32	0.748	117.2
$CH_2{=}CEt_2$	172.9	9.5	2.781	40.64	0.754	115.5
$EtCH{=}CMe_2$	169.9	10.9	2.802	40.98	0.760	116.2
MeCH=CHPr	162.5	11.5	2.896	41.60	0.772	114.0
$Me_2CH{=}CMe_2$	181.7	11.3	2.650	40.17	0.745	121.2
MeCH=CHBu	162.5	11.5	2.896	41.60	0.772	114.0
$MeCH{=}CEt_2$	167.3	10.7	2.840	41.16	0.764	114.9
$CH_2{=}CH(CH_2)_4Me$	169.7	10.4	2.811	40.95	0.760	115.5
$CH_2{=}CH(CH_2)_5Me$	169.7	10.5	2.810	40.96	0.760	115.6
$CH_2{=}CH(CH_2)_7Me$	169.7	10.4	2.814	40.95	0.760	115.5
	162.3	11.4	2.901	41.61	0.772	113.8
	163.7	9.8	2.904	41.38	0.768	112.3
 $-CH{=}CH_2$	167.6	10.8	2.834	41.14	0.763	115.1
$CH_2{=}CHCH_2OH$	170.5	5.7	2.865	40.42	0.750	109.4
$CH_2{=}CHC(O)OH$	186.0	7.5	2.644	39.52	0.733	117.6
trans-HOOCCH=CHCOOH	188.3	5.0	2.646	39.03	0.724	114.6

Table 3. Kinetic parameters (ΔH_e, E_e, α, br_e, r_e, and E_{e0}) of methyl radical addition to olefins in the RIPM (calculated from the experimental data[26—32])

Olefin	ΔH_e	E_e	α	br_e /kJ$^{1/2}$ mol$^{-1/2}$	$r_e \cdot 10^{10}$ /m	E_{e0} /kJ mol^{-1}
	kJ mol^{-1}					
$CH_2=CH_2$	106.7	28.0	2.716	36.81	0.683	98.1
$CH_2=CHMe$	104.3	27.0	2.778	37.03	0,687	96.1
$CH_2=CHEt$	104.8	26.1	2.786	36.98	0.686	95.4
$CH_2=CMe_2$	106.5	25.8	2.760	36.82	0.683	95.9
trans-MeCH=CHMe	103.8	34.4	2.655	37.08	0.688	102.9
cis-MeCH=CHMe	107.2	32.1	2.637	36.78	0.682	102.3
	108.0	33.0	2.609	36.72	0.681	103.5
	95.5	32.5	2.842	37.86	0.702	97.1
$CH_2=CHCl$	112.5	23.7	2.690	36.26	0.673	96.6
$CH_2=CClMe$	102.5	22.3	2.907	37.20	0.690	90.6
$CH_2=CCl_2$	125.5	17.7	2.573	35.00	0.649	95.9
$CH_2=CHF$	108.5	22.3	2.788	36.61	0.679	93.4
$CH_2=CHOAc$	113.0	25.4	2.652	36.24	0.672	98.5
$CH_2=CHOEt$	104.7	24.6	2.817	36.99	0.686	93.9
$CH_2=CMeOMe$	117.2	25.0	2.589	35.87	0.666	99.9
$CH_2=CMeOAc$	125.2	25.0	2.468	35.25	0.654	103.3
$CH_2=CHC(O)OMe$	110.2	16.7	2.864	36.35	0.674	88.5
$CH_2=CMeC(O)OMe$	136.5	15.8	2.438	34.07	0.632	98.2
trans-MeCH=CHCOOH	135.8	15.4	2.454	34.10	0.633	97.5
cis-MeCH=CHCOOH	140.0	12.4	2.437	33.61	0.624	95.6
$CH_2=CHOCOAc$	110.5	25.0	2.702	36.45	0.676	97.0
$CH_2=CHOCOCH_2Ph$	113.0	18.9	2.767	36.13	0.670	92.0
$CH_2=CHCN$	137.9	15.2	2.427	33.93	0.630	98.0
$CH_2=CMeCN$	135.2	15.1	2.466	34.12	0.633	96.9
$CH_2=CHCH=CH_2$	153.4	16.5	2.219	32.99	0.612	105.0
MeCH=CHCH=CHMe	144.9	21.2	2.262	33.76	0.626	107.1
$CH_2=CMeCMe=CH_2$	157.4	16.2	2.179	32.73	0.607	106.0
	167.1	22.2	2.026	32.58	0.605	116.0
	174.0	19.6	1.988	32.09	0.595	115.3
$CH_2=CHPh$	151.2	17.0	2.238	33.15	0.615	104.8
$CH_2=CMePh$	147.2	17.0	2.285	33.40	0.620	103.1

ies[6—9] analyzing experimental data in the framework of the IPM.

The triplet repulsion reflects the relationships between E_{e0} and $D_{ef}^{\neq}$ for each class of addition reactions. These relationships obtained by statistical processing of the data in Tables 2—4 in terms of a linear equation are presented below.

Reaction	E_{e0}/kJ mol^{-1}
$H^{\bullet} + CH_2=CHR$	$45.6\pm5.5 + 0.39D_{ef}^{\neq}$
$^{\bullet}CH_3 + CH_2=CHR$	$-13.9\pm6.7 + 0.83D_{ef}^{\neq}$
$RO_2^{\bullet} + CH_2=CH_2$	$59.3\pm3.6 + 0.30D_{ef}^{\neq}$
$X^{\bullet} + CH_2=CHR$, $X^{\bullet} + CH\equiv CH$	$14.2\pm9.5 + 0.61D_{ef}^{\neq}$

For all classes of reactions under question, E_{e0} increases linearly with an increase in $D_{ef}^{\neq}$, and the plot of the $E_{e0} = A + BD_{ef}^{\neq}$ type has a universal character (Fig. 2).

Triplet repulsion also explains the increase in $D_{ef}^{\neq}$ and E_{e0} on going from the reaction of a radical with olefin to its reaction with conjugated diene and styrene.[9] The data for addition of methyl and peroxyl radicals to such olefins (see Tables 3 and 4) are presented below.

Reaction	$D_{ef}^{\neq}$	E_{e0}	ΔE_{e0}
	kJ mol^{-1}		
$^{\bullet}CH_3 + CH_2=CH_2$	134.7	98.1	0.0
$^{\bullet}CH_3 + CH_2=CHCH=CH_2$	169.9	107.1	9.0
$^{\bullet}CH_3 + CH_2=CHPh$	168.2	104.8	6.7
$RO_2^{\bullet} + CH_2=CHMe$	107.0	92.4	0.0
$RO_2^{\bullet} + CH_2=CHPh$	128.6	97.9	5.5

The increase in E_{e0} on going from olefin to diene and styrene is caused by the formation of a five-electron, five-centered bond in the TS, its higher energy, and, corre-

Table 4. Kinetic parameters (ΔH_e, E_e, br_e, r_e, and E_{e0}) of peroxyl radical addition to olefins in the RIPM (calculated from the experimental data[33])

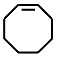
Olefin	$RO_2^{\bullet}$	ΔH_e	E_e	br_e /kJ$^{1/2}$ mol$^{-1/2}$	$r_e \cdot 10^{10}$ /m	E_{e0} /kJ mol^{-1}
		kJ mol^{-1}				
$CH_2{=}CH_2$	*n*-$RO_2^{\bullet}$	44.5	62.0	34.98	0.649	93.0
$CH_2{=}CHMe$	*n*-$RO_2^{\bullet}$	47.6	59.4	34.77	0.645	92.4
$CH_2{=}CHEt$	*sec*-$RO_2^{\bullet}$	49.3	52.4	34.75	0.645	86.9
trans-$MeCH{=}CHMe$	*n*-$RO_2^{\bullet}$	45.7	57.8	34.96	0.649	89.8
$CH_2{=}CMe_2$	*n*-$RO_2^{\bullet}$	51.5	55.5	34.52	0.640	91.1
$MeCH{=}CHMe_2$	*n*-$RO_2^{\bullet}$	56.4	54.4	34.15	0.634	92.9
$MeCH{=}CPr$	$PhC(O)O_2^{\bullet}$	85.6	33.3	31.98	0.593	88.3
$Me_2CH{=}CMe_2$	*n*-$RO_2^{\bullet}$	58.9	52.3	33.98	0.630	92.3
$MeCH{=}C(CH_2)_4Me$	$PhC(O)O_2^{\bullet}$	85.6	33.3	31.98	0.593	88.3
$CH_2{=}CHBu$	*sec*-$RO_2^{\bullet}$	49.3	57.0	34.67	0.643	91.2
$CH_2{=}CHBu$	$PhC(O)O_2^{\bullet}$	89.2	31.8	31.7	0.589	88.5
$CH_2{=}CHCMe_3$	*sec*-$RO_2^{\bullet}$	26.3	77.5	36.13	0.670	96.3
	$PhC(O)O_2^{\bullet}$	89.7	31.4	31.68	0.588	88.4
	*sec*-$RO_2^{\bullet}$	55.3	55.2	34.23	0.635	93.0
	$PhC(O)O_2^{\bullet}$	92.3	32.5	31.56	0.586	90.6
	*sec*-$RO_2^{\bullet}$	52.5	54.4	34.45	0.639	90.6
$CH_2{=}CHPh$	$HO_2^{\bullet}$	90.3	42.5	31.95	0.593	99.3
$CH_2{=}CHPh$	*sec*-$RO_2^{\bullet}$	86.8	41.8	32.11	0.596	96.9
$CH_2{=}CHPh$	*tert*-$RO_2^{\bullet}$	80.1	42.7	32.51	0.603	94.5
$CH_2{=}CMePh$	*sec*-$RO_2^{\bullet}$	92.9	41.7	31.80	0.590	99.7
$MeCH{=}CHPh$	*tert*-$RO_2^{\bullet}$	86.1	47.2	32.28	0.599	101.7
$CH_2{=}CPh_2$	*tert*-$RO_2^{\bullet}$	94.8	45.4	31.8	0.590	104.1

Table 5. Kinetic parameters (ΔH_e, E_e, b_f, α, E_{e0}, and r_e) of addition of atoms and radicals to multiple bonds in the RIPM[9]

Reaction	$-\Delta H_e$	E_e	$b_f \cdot 10^{10}$ /kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}	α	E_{e0} /kJ mol^{-1}	$r_e \cdot 10^{10}$ /m
	kJ mol^{-1}					
$H^{\bullet} + CH_2{=}CH_2$	166.1	8.7	18.68	2.885	111.9	0.762
$H^{\bullet} + CH{\equiv}CH$	160.3	17.3	18.94	3.649	128.9	0.764
$H^{\bullet} + MeCH{=}O$	128.3	16.2	24.02	2.494	94.7	0.567
$^{\bullet}CH_3 + CH_2{=}CH_2$	106.7	28.0	19.84	2.716	98.1	0.683
$^{\bullet}NH_2 + CH_2{=}CH_2$	88.1	15.4	13.99	3.852	78.9	0.800
$CH_3O^{\bullet} + CH_2{=}CH_2$	82.2	16.0	19.19	2.808	69.8	0.590
$Et_3Si^{\bullet} + CH_2{=}CH_2$	105.3	9.5	13.13	4.102	85.0	0.873
$RO_2^{\bullet} + CH_2{=}CH_2$	44.5	62.0	20.52	2.627	93.0	0.649
$^{\bullet}CH_3 + CH{\equiv}CH$	114.3	15.3	19.17	3.606	95.3	0.650

spondingly, a higher contribution to the antibonding C—C orbital (occupied in the TS) to the activation energy.

Electron affinity of atoms of the reaction center in the TS. The difference in electron affinities of atoms forming the TS is pronounced in radical abstraction reactions.[6,10] This difference is also noticeable in radical addition reactions, which can be seen from comparison of E_{e0} with the difference in electron affinities of atoms of the reaction center (ΔEA) for addition of methyl, aminyl, and alkoxyl radical to ethylene.

Radical	E_e	ΔH_e	E_{e0}	ΔE_{e0}	ΔEA
	kJ mol^{-1}				
$^{\bullet}CH_3$	28.0	106.7	98.1	0	0
$^{\bullet}NH_2$	15.4	88.1	78.9	−19.2	28
$MeO^{\bullet}$	16.0	82.2	69.8	−28.3	78

The ΔEA value for the $X^{\bullet}$ and $Y^{\bullet}$ species were calculated using the Pauling method[34]

$$\Delta EA = D_e(X{-}Y) - 0.5[D_e(X{-}X) + D_e(Y{-}Y)]. \qquad (9)$$

Table 6. Comparison of the enthalpies (ΔH_e) and activation energies (E_e and E_{e0}) of the radical addition reactions

Reaction	$-\Delta H_e$	E_e	E_{e0}	$-\Delta E_H$	$\Delta E_e/\Delta H_e$
	kJ mol^{-1}				
$H^{\bullet} + CH_2{=}CH_2$	166.1	8.7	111.9	103.2	0.621
$H^{\bullet} + CH{\equiv}CH$	160.3	17.3	128.9	111.6	0.696
$H^{\bullet} + MeCH{=}O$	128.3	16.2	94.7	78.5	0.612
$^{\bullet}CH_3 + CH_2{=}CH_2$	106.7	28.0	98.1	70.1	0.836
$^{\bullet}NH_2 + CH_2{=}CH_2$	88.1	15.4	78.9	52.9	0.721
$MeO^{\bullet} + CH_2{=}CH_2$	82.2	16.0	69.8	53.8	0.654
$Et_3Si^{\bullet} + CH_2{=}CH_2$	105.3	9.5	85.0	69.0	0.717
$RO_2^{\bullet} + CH_2{=}CH_2$	44.5	62.0	93.0	31.0	0.697
$^{\bullet}CH_3 + CH{\equiv}CH$	114.3	15.3	95.3	80.0	0.700

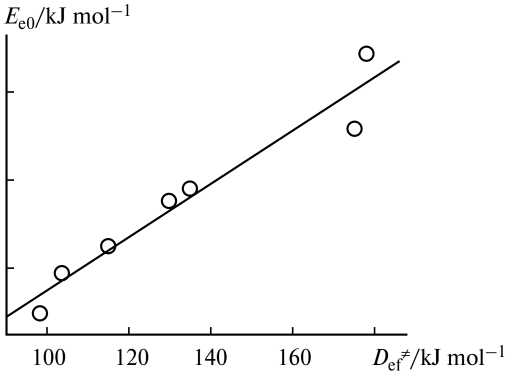


Fig. 2. Plot of the activation energy of thermally neutral addition (E_{e0}) *vs.* bond dissociation energy in the TS ($D_{ef}^{\neq}$) for H atom addition to ethylene, acetaldehyde, and acetylene and addition of the methyl, aminyl, methoxyl, and triethylsilyl radicals to ethylene.

It is seen that the higher ΔEA, the lower E_{e0}.

Bond elongation in the TS. The r_e parameter in the IPM represents the distance between vertices of the parabolas (see Fig. 1) and characterizes the elongation of bonds in the TS. Analysis of the r_e values for reactions of the same class shows (see Tables 3 and 4) that their r_e values are virtually constant within the calculation error.

Reaction	$r_e \cdot 10^{10}$/m
$^{\bullet}CH_3 + CH_2{=}CHR$	0.680±0.010
$^{\bullet}CH_3 + CH_2{=}CHCH{=}CH_2$	0.609±0.010
$^{\bullet}CH_3 + CH_2{=}CHPh$	0.617±0.003
$RO_2^{\bullet} + CH_2{=}CHR$	0.643±0.010
$RO_2^{\bullet} + CH_2{=}CHPh$	0.595±0.005
$PhC(O)O_2^{\bullet} + CH_2{=}CHR$	0.590±0.003

The data presented above and in Table 5 show that the bond elongation r_e in the RIPM is less than 1 Å for all reactions under study. For nine classes of reactions considered (see Table 5), the bond elongation in the TS is within a rather narrow interval, from $0.57 \cdot 10^{-10}$ to $0.87 \cdot 10^{-10}$ Å.

It was found that the r_e bond elongation is affected by the following factors.

(1) Triplet repulsion increases $D_{ef}^{\neq}$ and decreases r_e. It is seen from a comparison of the addition reactions of $H^{\bullet}$ and $^{\bullet}CH_3$ to ethylene and acetylene.

Reaction	$r_e \cdot 10^{10}$/m	$D_{ef}^{\neq}$/kJ mol^{-1}
$H^{\bullet} + CH_2{=}CH_2$	0.762	174.8
$H^{\bullet} + CH{\equiv}CR$	0.764	177.6
$^{\bullet}CH_3 + CH_2{=}CH_2$	0.683	134.7
$^{\bullet}CH_3 + CH{\equiv}CH$	0.650	129.6

(2) π-Bond adjacent to the reaction center in the TS also decreases r_e due to triplet repulsion enhancement.

Reaction	$r_e \cdot 10^{10}$/m	Reaction	$r_e \cdot 10^{10}$/m
$^{\bullet}CH_3 + CH_2{=}CHR$	0.680	$RO_2^{\bullet} + CH_2{=}CHR$	0.643
$^{\bullet}CH_3 + (CH_2{=}CH)_2$	0.609	$RO_2^{\bullet} + CH_2{=}CHPh$	0.595

(3) Difference in the electron affinity decreasing r_e. This follows from comparison of addition reactions with the reaction centers $H\ldots C\overset{\cdots}{-}C$ and $H\ldots O\overset{\cdots}{-}C$, $C\ldots C\overset{\cdots}{-}C$ and $C\ldots C\overset{\cdots}{-}O$.

Reaction	$r_e \cdot 10^{10}$/m	$D_{ef}^{\neq}$/kJ mol^{-1}
$H^{\bullet} + CH_2{=}CH_2$	0.762	174.8
$H^{\bullet} + O{=}CHMe$	0.567	144.5
$^{\bullet}CH_3 + CH_2{=}CH_2$	0.683	134.7
$MeO^{\bullet} + CH_2{=}CH_2$	0.590	98.2

It is of interest that the enhancement of triplet repulsion increases $D_{ef}^{\neq}$ but decreases r_e. On the contrary, the difference in electron affinities for atoms of the TS decreases both $D_{ef}^{\neq}$ and r_e.

(4) Radius of the atom bearing a free valence and attacking the double bond also exerts an effect on r_e: the longer the radius of the atom, the longer r_e. For instance, for methyl radical addition to the ethylene molecule $r_e = 0.683 \cdot 10^{-10}$ m, and for triethylsilyl radical addition $r_e = 0.873 \cdot 10^{-10}$ m.

(5) Force constant of the formed X—C bond plays an important role, which is well seen from a comparison of b_f and r_e for addition of the radicals presented below to ethylene.

Radical	$b_f \cdot 10^{-10}$/kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}	$r_e \cdot 10^{10}$/m
$RO_2^{\bullet}$	20.52	0.649
$^{\bullet}CH_3$	19.84	0.683
$H^{\bullet}$	18.68	0.762
$^{\bullet}NH_2$	13.99	0.800

Comparison of the IPM and RIPM. In the IPM, both coefficients (b and b_f) are constant for the same reaction center.[1—6] Therefore, the coefficient α = const and E_{e0} are characteristics of the whole class of reactions. As a result, such characteristics of the reaction as br_e, E_{e0}, and E_e are determined by simple formulas. In the RIPM described in this work, the b_f coefficient depends on $D_{ef}^{\neq} = -\Delta H_e + E_e$ (see Eq. (7)) and changes from one reaction to another, depending on ΔH_e and E_e, inside the same class. In this model, the only characteristic is the r_e

Table 7. Comparison of the α and E_{e0} parameters of the addition reactions in the RIPM and IPM

Reaction	E_{e0}/kJ mol^{-1}		α	
	RIPM	IPM	RIPM	IPM
$H^{\bullet} + CH_2=CH_2$	111.9	101.6	2.885	1.440
$H^{\bullet} + CH\equiv CH$	128.9	125.1	3.649	1.847
$H^{\bullet} + MeCH=O$	94.7	102.9	2.494	1.600
$^{\bullet}CH_3 + CH_2=CH_2$	98.1	82.6	2.716	1.202
$^{\bullet}NH_2 + CH_2=CH_2$	78.9	61.0	3.852	1.410
$MeO^{\bullet} + CH_2=CH_2$	69.8	65.2	2.808	1.413
$Et_3Si^{\bullet} + CH_2=CH_2$	85.0	76.6	4.102	2.012
$RO_2^{\bullet} + CH_2=CH_2$	93.0	90.5	2.627	1.737
$^{\bullet}CH_3 + CH\equiv CH$	95.3	97.7	3.606	1.542

parameter, which characterizes the bond elongation in the TS. Since b_f depends on ΔH_e, the α coefficient also changes from one reaction to another. The E_e and α values for the series of addition reactions are presented in Table 7.

It can be seen that E_{e0} in the RIPM is higher than or close to E_{e0} in the IPM. An exception is H atom addition to the carbonyl group for which E_{e0}(RIPM) < E_{e0}(IPM). The coefficient $\alpha = b/b_f$ in the RIPM is much higher than that in the IPM for all reactions. As a result, r_e(RIPM) > r_e(IPM). For instance, for methyl radical addition to the ethylene molecule, $r_e(\text{RIPM}) = 0.68 \cdot 10^{-10}$ m, while $r_e(\text{IPM}) = 0.37 \cdot 10^{-10}$ m. It is most likely that the RIPM for addition reactions is more realistic than the IPM. However, the use of the RIPM parameters for calculation of the activation energy from the ΔH_e and r_e values requires multistage calculations because of feedbacks between the parameters. Analysis of the parameters obtained in the framework of the new model gives the same set of physical and structural factors determining the activation energy as that in the IPM,[6] and one more factor is added to them, namely, electron affinity of atoms of the reaction center in the TS.

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