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Model of the Radical Addition Reaction As the Superposition of Three Potential Curves

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Abstract—A new semiempirical model of the reaction of radical addition to molecules with multiple bonds has been developed. In the framework of this model, the transition state (TS) of the reaction $X^{\bullet} + Y{=}Z \longrightarrow XYZ^{\bullet}$ is considered as the result of the intersection of the potential curve of the stretching vibration of the forming bond X–Y with the curve that is the difference between the amplitudes of stretching vibrations of the Y–Z and Y=Z bonds and the stretching vibrations are considered harmonic. The kinetic parameters describing the activation energy as a function of the enthalpy of the reaction were calculated for 34 classes of addition reactions using the new model. The factors determining the activation energy of the addition reactions are analyzed: triplet repulsion in the TS, the π electrons in the α position to the reaction center, the electronegativity of atoms of the reaction center of the TS, the steric factor, the interaction of polar groups in the TS, and the force constants of the reacting bonds. The increments characterizing the contribution of these factors to the activation energy are calculated. The model is also used to describe the energy of 12 classes of cyclization reactions and 16 classes of radical decomposition reactions. The parameters that make it possible to estimate the activation energy of the reaction from its enthalpy are calculated for these classes of reactions.

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INTRODUCTION

The model considering the addition of a radical to a molecule with a multiple bond as a result of the intersection of two parabolic potential curves (intersecting parabolas model, IPM) describes well the activation energy at different reaction enthalpies [1–3]. The IPM provides a method for the kinetic classification of these reactions, analysis of the factors determining the activation barrier, and description of the activation energy as a function of the reaction enthalpy [2–5]. However, when applying the IPM to radical addition reactions, an error is observed: the transition state is considered as a result of the intersection of the potential curves of the stretching vibrations of only two bonds, whereas three bonds are involved in the rearrangement. Some corrections should be introduced into this simplified consideration of the radical addition. In particular, when calculating the classical potential barrier E_e and the classical enthalpy of the reaction ΔH_e, the IPM takes into account the algebraic sum of the zero-point stretching vibrations of only two bonds, whereas it is more reasonable to take into account the contribution from the stretching vibrations of all three reacting bonds. The following deviation from quantum chemical data appears for the TS geometry in the framework of the IPM [6]. Since the IPM ignores the transition from the vibrational motion of atoms to their translational motion at the top of the potential barrier, the extension of the reacting bonds in the TS calculated according to the IPM is always less than that in more rigorous quantum chemical calculations. This is observed in calculations for the radical abstraction reactions [7]. However, an anomaly is observed for the extension of a multiple bond in the TS for the addition reactions: according to the IPM, this bond is elongated several times more as compared to the same bond in the quantum-chemical calculation [6].

To eliminate the discrepancies associated with the use of the IPM in the description of the energy and geometry of the radical addition reactions, in the present work we suggest a new model of the addition reaction. In this model, the TS is viewed as the combination of three potential curves (3PC model). Using this model, we consider experimental data on the radical addition reactions analyzed earlier in the framework of the IPM [2–5], identify the factors determining the activation barrier of the reaction, and calculate the parameters for the estimation of the activation energy as a function of the reaction enthalpy. The 3PC model is also used in the description of the energy of the cyclization and radical decomposition reactions.

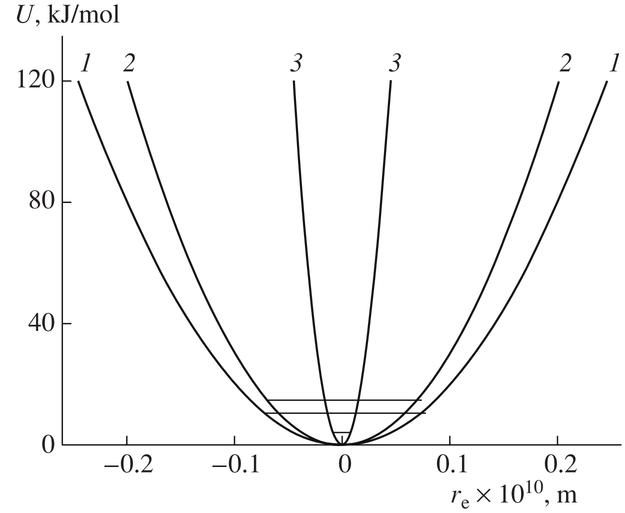

Fig. 1. Potential energy of the stretching vibration of the bond as a function of the amplitude of its harmonic vibration: (*1*) for the C–C bond, (*2*) for the C=C bond, and (*3*) as a function of the difference of the vibration amplitudes $\Delta r_{C-C} - \Delta r_{C=C}$.

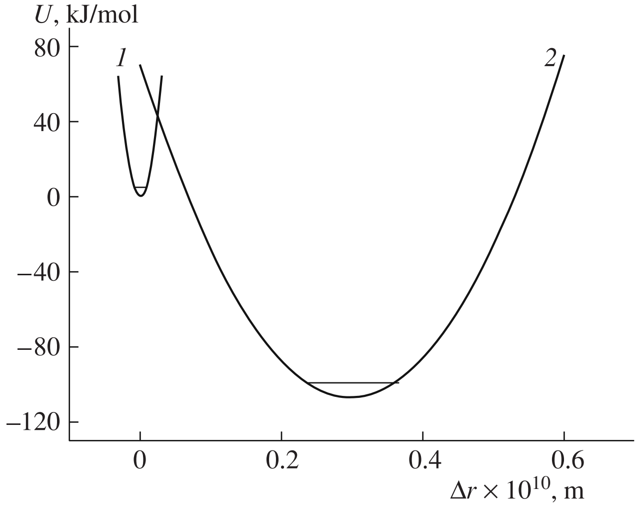

Fig. 2. The 3PC model for the reaction $C^{\bullet}H_3 + CH_2{=}CH_2 \longrightarrow CH_3CH_2C^{\bullet}H_2$. The dependences of the (*1*) potential energy of stretching vibrations of the attacked C–C bond on the difference of the vibration amplitudes $\Delta r_{C-C} - \Delta r_{C=C}$ and (*2*) forming C–C bond on the amplitude of its vibration.

MODEL OF THE RADICAL ADDITION REACTION AS A RESULT OF THE COMBINATION OF THREE POTENTIAL CURVES

In the reaction of $X^{\bullet}$ addition to the multiple bond Y=Z,

$$X^{\bullet} + Y{=}Z \longrightarrow (X\cdots Y\cdots X)^{\neq} \longrightarrow XYZ^{\bullet},$$

this bond is transformed from a double bond into an ordinary bond: $Y{=}Z \longrightarrow Y\overset{\cdots}{-}Z \longrightarrow Y{-}Z$ (or from a triple bond into a double bond: $Y{\equiv}Z \longrightarrow Y{=}Z$). The potential energy of the stretching vibration of the bond is a function of the amplitude of its vibration. If the bond vibration is considered harmonic, then its potential energy will be the following parabolic function: $U_{Y=Z}^{1/2} = b\Delta r_{Y=Z}$, $U_{Y-Z}^{1/2} = b_{Y-Z}\Delta r_{Y-Z}$, where U is the potential energy of the stretching vibration of the bond, $2b^2$ is its force constant, $b = b_{Y=Z}$, and Δr is the amplitude of its stretching vibration. Since in the TS the Y=Z bond elongates and the $Y\overset{\cdots}{-}Z$ distance is intermediate between Y=Z and Y–Z, it can reasonably be described by a combination of two potential curves. The combination characterizes the bond extension from the Y=Z state to the Y–Z state rather than the simple elongation of the Y=Z bond (Fig. 1). This extension can be presented as the difference of amplitudes of vibrations of two bonds, namely, Y=Z and Y–Z. Considering the stretching vibration of atoms of each bond as harmonic (see Fig. 1), we have

$$\sqrt{U} = b_{\Sigma}(\Delta r_{Y-Z} - \Delta r_{Y=Z}). \quad (1)$$

The expression for the coefficient b_{Σ} is found taking into account the equations for the description of the harmonic vibration of each Y=Z and Y–Z bond: $\sqrt{U} = b\Delta r_{Y=Z}$, $\sqrt{U} = b_{Y-Z}\Delta r_{Y-Z}$. We obtain

$$\sqrt{U} = b_{\Sigma}(\Delta r_{Y-Z} - \Delta r_{Y=Z}) = \sqrt{U} b_{\Sigma}(b_{Y-Z}^{-1} - b^{-1}) \quad (2)$$

and

$$b_{\Sigma} = bb_{Y-Z}/(b - b_{Y-Z}). \quad (3)$$

Since the Y=Z bond disappears and the Y–Z ordinary bond appears in $X^{\bullet}$ addition to Y=Z, this should also be taken into account when calculating the classical potential barrier E_e, which should be considered equal to $E + 0.5hN_A(\nu_{Y=Z} - \nu_{Y-Z})$. Let us consider the TS of the addition reaction as the intersection point of the new parabola describing the extension of Y=Z to the Y–Z bond with the parabola describing the potential energy of the forming X–Y bond vibration (Fig. 2).

The classical potential barrier E_e in the 3PC model thus takes the following form:

$$E_e = E + 0.5hN_A(\nu_{Y=Z} - \nu_{Y-Z}) - 0.5RT, \quad (4)$$

and the classical enthalpy is

$$\Delta H_e = \Delta H + 0.5hN_A(\nu_{Y=Z} - \nu_{Y-Z} - \nu_{X-Y}); \quad (5)$$

i.e., it is completely consistent with the method of calculation of the enthalpy for the radical addition reactions. For the reverse reaction of $XYZ^{\bullet}$ decomposition (reaction (d)), we obtain $\Delta H_d = -\Delta H$, $E_d = E - \Delta H$, $E_{e,\,d} = E_d + 0.5hN_A(\nu_{X-Y} + \nu_{Y-Z} - \nu_{Y=Z}) - 0.5RT$, and $\Delta H_e = E_e - E_{e,\,d}$. Thus, no contradiction in the calculation of E_e and ΔH_e for the forward and reverse reaction appears in

Table 1. Characteristics of bonds in molecules: frequency ν and zero-point stretching vibration energy $0.5hN_A\nu$ of the bond, coefficient b, and r_{X-Y} bond length [8]

Bond	ν, cm^{-1}	$0.5hN_A\nu$, kJ/mol	$b \times 10^{-10}$, (kJ/mol)$^{1/2}$ m^{-1}	$r_{X-Y} \times 10^{10}$, m
C–H	2914	17.4	37.43	1.092
N–H	3337	20.0	43.07	1.009
RO–H	3625	21.7	46.98	0.967
C–C	1375	8.2	44.83	1.513
C=C	1653	9.9	53.89	1.340
C≡C	2120	12.7	69.12	1.183
C–N	1130	6.8	38.23	1.469
C=N	1670	10.0	56.50	1.279
C≡N	2250	13.4	76.12	1.136
C–OR	1125	6.7	39.21	1.416
C–OOR	890	5.3	31.02	1.437
>C=O	1719	10.3	59.91	1.210
C≡O	2170	13.0	75.63	1.128
N–N	1587	9.5	55.89	1.449
N=N	1800	10.8	63.39	1.240
C–S	650	3.9	25.56	1.789

the 3PC model, while it exists in the IPM. For bond extension in the TS, we have the following equation (Fig. 2):

$$r_e = \Delta r^{\neq}_{Y-Z} - \Delta r^{\neq}_{Y=Z} + \Delta r^{\neq}_{X-Y}. \qquad (6)$$

After the insertion of $E_e^{1/2} = b_{\Sigma}(\Delta r^{\neq}_{Y-Z} - \Delta r^{\neq}_{Y=Z})$ and $\sqrt{E_e - \Delta H_e} = b^{\neq}_{X-Y}\Delta r^{\neq}_{X-Y}$, we obtain

$$br_e = \gamma\sqrt{E_e} + \alpha\sqrt{E_e - \Delta H_e}, \qquad (7)$$

where $\gamma = (b - b_{Y-Z})/b_{Y-Z}$, $\alpha = b/b_{X-Y}$.

The frequencies (ν), zero-point stretching vibration energies ($0.5hN_A\nu$), and coefficients $b = 2\pi N_A\nu\mu^{1/2}$, where μ is the reduced mass of the atoms forming the bond and $2b^2$ is the force constant of the bond, are presented in Table 1.

In the IPM the br_e parameter characterizes the whole class of reactions. Does it retain this property in the 3PC model when Eq. (7) is used? To check this fact, we processed the data for the addition of methyl radicals to olefins using Eq. (7). For this reaction $\alpha = 1.202$ and $\gamma = 0.202$, $0.5hN_A\nu_{Y=Z} = 9.9$ kJ/mol, and $0.5hN_A\nu_{X-Y} = 0.5hN_A\nu_{Y-Z} = 8.2$ kJ/mol (see Table 1). The initial data (ΔH_e, E_e, and the parameter br_e (the result of the calculation by formula (7))) are given in Table 2.

The column of br_e values shows that all of them are very similar for the reactions of methyl radical addition to olefins and the average value is $br_e = 14.97 \pm 0.25$ (kJ/mol)$^{1/2}$. In the framework of the IPM, $r_e = \Delta r^{\neq}_{Y=Z} + \Delta r^{\neq}_{X-Y}$ and $br_e = 20.01 \pm 0.40$ (kJ/mol)$^{1/2}$ [16]. Thus, Eq. (7) in the 3PC model characterizes the whole class of reactions and makes it possible to calculate the activation energy of each individual reaction from the parameters (br_e, α, and γ) and the reaction enthalpy (ΔH). Each class of reactions can be characterized by a classical potential barrier $E_{e,0} = E_e$ at $\Delta H_e = 0$. The potential barrier bears information on the role of other factors (along with the reaction enthalpy) in the formation of the activation energy.

$$E_{e,0} = \left\{\frac{br_e}{\alpha + \gamma}\right\}^2. \qquad (8)$$

For one class of reactions, the br_e, α, and γ parameters are constant values and the activation energy can be calculated through the enthalpy. The transformation of Eq. (7) gives the following equation for the calculation of the activation energy of addition:

$$\sqrt{E_e} = B\left\{\alpha\sqrt{1 + \frac{\Delta H_e}{Bbr_e}} - \gamma\right\}, \qquad (9)$$

where $B = br_e/(\alpha^2 - \gamma^2)$. At rather low enthalpy of the reaction ($\Delta H_e \ll Bbr_e$), its activation energy can be calculated by the equation

$$\sqrt{E_e} = \frac{br_e}{\alpha + \gamma} + \frac{\alpha\Delta H_e}{2br_e}. \qquad (10)$$

Table 2. Enthalpy, activation energy, and br_e for methyl radical additions to olefins

Olefin	$-\Delta H_e$, kJ/mol	E_e, kJ/mol	br_e, $(kJ/mol)^{1/2}$	Reference
$CH_2=CH_2$	106.7	29.7	15.14	[9, 10]
$CH_2=CHMe$	104.3	28.8	14.95	[11]
$CH_2=CHMe$	104.3	28.6	14.94	[12]
$CH_2=CHEt$	104.8	27.8	14.91	[12]
$CH_2=CMe_2$	106.5	27.5	14.97	[12]
cyclo-C_8H_{14}	95.5	34.2	14.87	[13]
$CH_2=CHCl$	112.5	25.4	15.13	[12]
CH_2CClMe	102.5	24.0	14.51	[12]
$CH_2=CCl_2$	125.5	19.4	15.36	[12]
$CH_2=CHF$	108.5	24.0	14.83	[14]
$CH_2=CHOAc$	113.0	27.1	15.28	[12]
$CH_2=CHOEt$	104.7	26.3	14.79	[12]
$CH_2=C(Me)OMe$	117.2	26.7	15.46	[12]
$CH_2=CHCOOMe$	110.2	18.4	14.50	[12]
$CH_2=CHCH_2OAc$	110.5	26.7	15.12	[15]
$CH_2=CHOC(O)CH_2Ph$	113.0	21.6	14.88	[15]

The Arrhenius activation energy of the reaction (E) is related to the classical potential E_e through Eq. (4).

As already mentioned [6], the IPM calculations give a very long multiple bond extension in the TS of the addition reaction as compared to the quantum chemical calculations. Let us compare the interatomic distances in the TS for three addition reactions obtained according to the 3PC model, IPM, and quantum-chemical calculation (Table 3).

It can be seen that, unlike the IPM data, the results of the calculation according to the 3PC model lead to the inequality $\Delta r^{\neq}_{X-Y}(3PC) < \Delta r^{\neq}_{X-Y}$ (quantum chemistry) and, hence, are consistent with the quantum chemical calculations. In this respect, the 3PC model naturally supplements the earlier reduced model proposed for the addition reaction (RIPM) and allows one to exclude (in this model) the correlation parameter for the double bond extension [17].

Table 3. Interatomic distances X–Y in the TS obtained by quantum chemical calculations and by the 3PC and IPM methods

Reaction	$\Delta r^{\neq}_{X-Y} \times 10^{10}$, m		
	quantum chemistry [6]	3PC model	IPM [6]
$C^{\bullet}H_3 + CH_2=CH_2$	0.026	0.020	0.098
$N^{\bullet}H_2 + CH_2=CH_2$	0.025	0.015	0.073
$MeO^{\bullet} + CH_2=CH_2$	0.031	0.016	0.073

Thus, the new model eliminates the contradictions noted above for the IPM as applied to addition reactions. The following relationship is observed between the br_e parameters in the IPM [2] and the 3PC model:

$$br_e(3PC) = br_e(IPM) - E_e(IPM)^{1/2} + \gamma[E_e(IPM) - 0.5hN_A\nu_{Y-Z}]^{1/2}. \quad (11)$$

For correct calculation of the geometric parameters of the TS of the addition reactions, the 3PC model can be combined with the reduced intersecting parabolas model [17].

FACTORS IN THE ACTIVATION ENERGY OF RADICAL ADDITION

In the framework of the IPM, the influence of a number of physicochemical factors on the activation barrier of the radical addition reactions was found [2–5]. What is the behavior of these factors in the framework of the new 3PC model? The parameters α, γ, br_e, $E_{e,0}$, and r_e for 34 classes of the addition reactions in the framework of the 3PC model are given in Table 4. Let us consider the influence of various physicochemical factors on the activation energy by comparison of $E_{e,0}$ and r_e for different classes of the addition reactions.

Table 4. Kinetic parameters of the classes of addition reactions in the 3PC model

Class of reactions	α	γ	br_e, $(\mathrm{kJ/mol})^{1/2}$	$E_{e,0}$, kJ/mol	$r_e \times 10^{10}$, m	$-\Delta H_{e,\min}$, kJ/mol	Reference
$\mathrm{H}^{\bullet} + \mathrm{C{=}C}$	1.440	0.202	20.50	155.8	0.380	195.7	[18]
$\mathrm{H}^{\bullet} + \mathrm{C{=}CC{=}C}$	1.440	0.202	22.59	189.2	0.419	238.6	[18]
$\mathrm{H}^{\bullet} + \mathrm{C{=}CPh}$	1.440	0.202	22.14	181.8	0.411	229.1	[18]
$\mathrm{H}^{\bullet} + \mathrm{C{=}CCN}$	1.440	0.202	21.60	173.2	0.401	217.8	[18]
$\mathrm{H}^{\bullet} + \mathrm{C{\equiv}C}$	1.745	0.283	27.64	185.8	0.400	241.4	[18]
$\mathrm{H}^{\bullet} + \mathrm{O{=}C}<$	1.275	0.528	23.19	165.5	0.387	299.3	[18]
$\mathrm{Cl}^{\bullet} + \mathrm{C{=}C}$	1.639	0.202	15.86	74.2	0.294	88.8	[18]
$\mathrm{Br}^{\bullet} + \mathrm{C{=}C}$	2.280	0.202	13.91	31.4	0.258	34.1	[18]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{C{=}C}$	1.202	0.202	14.97	113.2	0.278	147.7	[16]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{C{=}C{=}C}$	1.202	0.202	16.54	138.8	0.307	181.7	[16]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{C{=}CPh}$	1.202	0.202	16.36	135.7	0.303	177.6	[16]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{C{\equiv}C}$	1.542	0.283	20.35	124.4	0.294	166.3	[16]
$\mathrm{Me_2C}^{\bullet}\mathrm{H} + \mathrm{C{=}C}$	1.202	0.202	14.43	105.6	0.268	137.2	[16]
$\mathrm{Me_3C}^{\bullet} + \mathrm{C{=}C}$	1.202	0.202	12.86	83.9	0.239	108.1	[16]
$\mathrm{Ph}^{\bullet} + \mathrm{C{=}C}$	1.202	0.202	17.01	146.8	0.316	192.4	[16]
$\mathrm{Ph}^{\bullet} + \mathrm{C{=}C{=}C}$	1.202	0.202	18.85	180.3	0.350	237.6	[16]
$\mathrm{Ph}^{\bullet} + \mathrm{C{=}CPh}$	1.202	0.202	18.27	169.4	0.339	222.8	[16]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{O{=}C}<$	1.352	0.528	15.76	70.3	0.263	122.7	[19]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{Q}^*$	1.531	0.528	20.37	97.9	0.349	163.6	[20]
$\mathrm{RO}^{\bullet} + \mathrm{C{=}C}$	1.413	0.202	15.16	88.1	0.281	109.5	[19]
$\mathrm{RO}^{\bullet} + \mathrm{C{=}CPh}$	1.413	0.202	17.45	116.8	0.323	146.3	[19]
$\mathrm{N}^{\bullet}\mathrm{H}_2 + \mathrm{C{=}C}$	1.410	0.202	14.76	83.9	0.274	104.0	[21]
$\mathrm{N}^{\bullet}\mathrm{H}_2 + (\mathrm{C{=}C})_2$	1.410	0.202	16.52	105.1	0.307	131.3	[21]
$\mathrm{RS}^{\bullet} + \mathrm{C{=}C}$	2.108	0.202	13.29	33.1	0.247	36.5	[21]
$\mathrm{RS}^{\bullet} + \mathrm{C{=}CPh}$	2.108	0.202	17.38	56.6	0.323	64.3	[21]
$\mathrm{RS}^{\bullet} + \mathrm{C{=}CCN}$	2.108	0.202	16.49	50.9	0.306	57.5	[21]
$\mathrm{RO}_2^{\bullet} + \mathrm{C{=}C}$	1.737	0.202	19.48	100.9	0.361	120.6	[22]
$\mathrm{RO}_2^{\bullet} + \mathrm{C{=}CPh}$	1.737	0.202	21.08	118.2	0.384	141.9	[22]
$\mathrm{H}^{\bullet} + \mathrm{RCN}$	1.767	0.347	19.78	87.5	0.260	117.9	[23]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{RCN}$	1.991	0.347	16.86	52.0	0.222	66.2	[23]
$\mathrm{C}^{\bullet}\mathrm{H}_3 + \mathrm{CO}$	1.687	0.262	16.36	70.4	0.216	88.4	[24]
$\mathrm{HO}^{\bullet} + \mathrm{CO}$	1.929	0.262	23.32	113.3	0.308	140.2	[25]
$\mathrm{MeO}^{\bullet} + \mathrm{CO}$	1.929	0.262	25.13	131.6	0.332	163.5	[25]
$\mathrm{RO}_2^{\bullet} + \mathrm{CO}$	2.044	0.262	22.73	97.2	0.301	118.3	[25]

* Q is quinone.

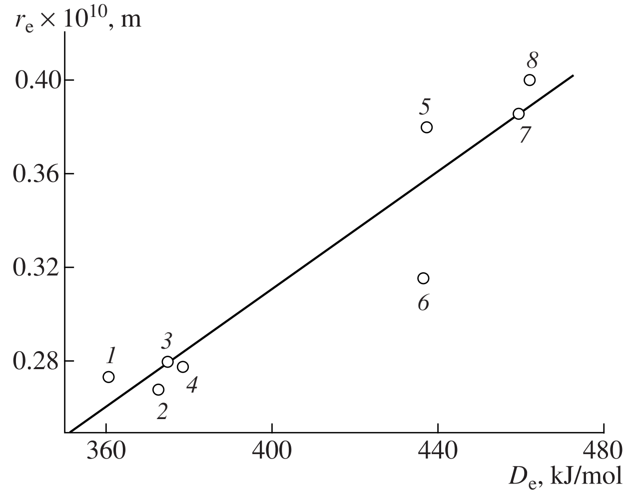

Fig. 3. Dependences of the r_e parameter on the dissociation energy of the forming bond (D_e) in the radical addition reaction as a result of the triplet repulsion in the TS of the reactions: (*1*) $N^{\bullet}H_2$ + C=C, (*2*) $Me_2C^{\bullet}H$ + C=C, (*3*) $RORO^{\bullet}$ + C=C, (*4*) $C^{\bullet}H_3$ + C=C, (*5*) $Ph^{\bullet}$ + C=C, (*6*) $H^{\bullet}$ + C=C, (*7*) $H^{\bullet}$ + O=C<, and (*8*) $H^{\bullet}$ + C≡C.

Triplet Repulsion

The triplet repulsion manifests itself as the fact that the stronger the forming X–Y bond, the higher the classical potential barrier of the thermally neutral reaction, $E_{e,0}$ (see Eq. (8)). However, the expression for $E_{e,0}$ includes b, α, and γ, which reflect the influence of the force constants of the bonds on the activation energy. Therefore, for estimation of the effect of the triplet repulsion on the activation energy, it is reasonable to compare the bond strength D_e(X–Y) with the parameter r_e. This comparison is presented in Fig. 3.

It can be seen that, for eight classes of reactions, namely, $C^{\bullet}H_3$ + C=C, $Me_2C^{\bullet}H$ + C=C, $N^{\bullet}H_2$ + C=C, $C^{\bullet}H_3$ + O=C<, $Ph^{\bullet}$ + C=C, $H^{\bullet}$ + C=C, $H^{\bullet}$ + O=C<, and $H^{\bullet}$ + C≡C, a linear extension of r_e is observed as D_e increases. This should be considered as empirical evidence that the nonbonding orbital of X–Y is involved in the formation of the activation barrier for $X^{\bullet}$ + Y=Z. The contribution from the triplet repulsion to the activation energy is described by the empirical equation

$$r_e \times 10^{10}\ [\mathrm{m}] = -0.19 + (1.25 \pm 0.002) \times 10^{-3}(D_e(\mathrm{X{-}Y})\ [\mathrm{kJ/mol}]). \quad (12)$$

This relationship somewhat differs from the relationship $r_e \times 10^{10}$ [m] = $0.98 \times 10^{-3}(D_e$(X–Y) [kJ/mol]), which was obtained in the framework of the IPM [2]. The larger proportionality coefficient (1.25×10^{-3} instead of 0.98×10^{-3}) indicates a higher sensitivity of the 3PC model to the influence of the triplet repulsion on the activation energy.

Influence of π-Bonds Adjacent to the Reaction Center

If bonds with π electrons are localized near the reaction center of the TS, they raise the activation energy [2–5]. This is due to the interaction of the π electrons with the electrons of the reaction center, the increase in the electron density on the reaction center, and, accordingly, the increase in the TS energy [26]. Table 5 contains $E_{e,0}$ and $\Delta E_{\pi} = E_{e,0\pi} - E_{e,0}$(C=C) data that characterize the contribution from the π interaction in the TS for the corresponding classes of addition reactions (see Table 4).

It can be that $E_{e,0}$ increases by 21–34 kJ/mol upon the formation of the α-C=C bond and the phenyl ring in the α position increases $E_{e,0}$ by 17–29 kJ/mol. Thus, the earlier mentioned [2–5] effect of the α–π-bond appears in the framework of the 3PC model.

Force Constants of the Y=Z, Y–Z, and X–Y Bonds

According to Eq. (10), the effect of the force constants on $E_{e,0}$ reflects the combination from the $b^2(\alpha + \gamma)^{-2}$ coefficients. The values of this factor (in kJ mol^{-1} m^{-2} $\times 10^{-23}$) for 12 classes of reactions are given below.

$H^{\bullet}$ + C=C,	$Cl^{\bullet}$ + C=C	$R^{\bullet}$ + C=C	$RO^{\bullet}$ + C=C	$N^{\bullet}H_2$ + C=C	$R^{\bullet}S$ + C=C
1.080	0.856	1.473	1.113	1.118	0.544
$H^{\bullet}$ + C≡C	$C^{\bullet}H_3$ + C≡C	$H^{\bullet}$ + N≡C	$C^{\bullet}H_3$ + N≡C	$C^{\bullet}H_3$ + C≡O	$RO^{\bullet}$ + C≡O
1.162	1.434	1.297	1.060	1.506	1.192

These values of the $b^2/(\alpha + \gamma)^2$ factor show that it varies in a wide range of $b^2/(\alpha + \gamma)^2 \times 10^{-23}$ = 0.544 – 1.506 kJ mol^{-1} m^{-2} and, thus, exerts a strong effect on the activation barrier of the addition reaction. This agrees with the conclusion made in the framework of the IPM [2–5].

Electronegativity of the Atoms of the Reaction Center

Another factor affecting the activation energy of abstraction and addition radical reactions is the different electron affinity of atoms of the reaction center. The asymmetric electron density distribution on the atoms of the TS that appeared due to this factor decreases the

Table 5. The values of $E_{e,0}$ (kJ/mol) for selected classes of addition reactions

Radical	C=C	C=C–C=C		C=C–Ph	
	$E_{e,0}$	$E_{e,0}$	ΔE_π	$E_{e,0}$	ΔE_π
$H^\bullet$	155.8	189.2	33.4	181.8	26.0
$C^\bullet H_3$	113.4	138.8	25.4	135.7	22.3
$Ph^\bullet$	146.8	180.3	33.6	169.4	22.6
$N^\bullet H_2$	83.9	105.1	21.2	–	–
$RO^\bullet$	88.1	–	–	116.8	28.7
$RO_2^\bullet$	100.9	–	–	118.2	17.3

TS energy and, hence, the activation energy [27]. The important role of the electron affinity (EA) in the addition reactions is illustrated by a comparison of the r_e parameter in the reactions of methyl radical addition to ethylene, acetone, and CO. For all these reactions, the dissociation energies of the forming bond (see below) are very similar and, therefore, the contribution from the triplet repulsion to the activation energy is almost the same (see above). Since these reactions are characterized by different force constants of the reacting bonds, the values of r_e should be compared and the contribution of the electron affinity to the activation energy should be calculated using the formula

$$\Delta E_{EA} = \left\{\frac{b_{XYZ}}{\alpha+\gamma}\right\}^2 (r^2_{e,\,XYZ} - r^2_{e,\,0}). \qquad (13)$$

The initial data and the results of the calculation are given below.

Reaction	$C^\bullet H_3 + CH_2{=}CH_2$	$C^\bullet H_3 + O{=}CMe_2$	$C^\bullet H_3 + C{\equiv}O$
Reaction center	$C\cdots C\overset{\cdots}{-}C$	$C\cdots C\overset{\cdots}{-}O$	$C\cdots C^\bullet{=}O$
D_e(Me–C), kJ/mol [8]	378	365	373
$r_e \times 10^{10}$, m	$r_{e,0} = 0.278$	0.263	0.216
ΔE_{EA}, kJ/mol	0	–9.1	–46.1

It follows from the obtained data that the difference in the electronegativity of the atoms of the reaction center decreases the activation energy and the contribution of ΔE_{EA} to the activation is rather high. Note that the influence of the electronegativity on the activation energy was not found in the framework of the IPM [2].

Steric Effect

In the reactions of methyl radical addition to olefins $CH_2{=}CHR$, where the addition takes place at the $CH_2{=}$ group, and to RCH=CHR, where the radical adds to the RCH= group, a difference between the $E_{e,\,0}$ values is observed (Table 6).

This indicates additional growth of the activation barrier $E_{e,\,0}$ (by 6–8 kJ/mol) upon the attack of the $X^\bullet$ radical on the RCH= group compared to the attack on the $CH_2{=}$ group. It should be mentioned that an analysis of the experimental data on methyl radical addition to olefins in the framework of the IPM revealed no steric effect: the addition of $C^\bullet H_3$ to the $CH_2{=}$ and RCH= groups is characterized by the same $E_{e,\,0}$ value [16].

Interaction of Polar Groups

The interaction of polar groups manifests itself when the monomer containing a polar group X ($CH_2{=}CHX$) is attacked by a polar radical [22]. The peroxy radical has a high dipolar moment: μ = 1.94 D for $HO_2^\bullet$, μ = 2.40 D for $Me_3CO_2^\bullet$ [28]. Table 7 shows

Table 6. Kinetic parameters of the reactions of the $C^\bullet H_3$ radicals with $CH_2{=}CHR$ and RCH=CHR [16, 21]

Reaction	–Δ*H*, kJ/mol	E_e, kJ/mol	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol
$C^\bullet H_3 + CH_2{=}CHR$			14.95	113.4
$C^\bullet H_3$ + *E*-MeCH=CHMe	103.8	44.3	15.43	120.8
$C^\bullet H_3$ + *Z*-MeCH=CHMe	107.2	42.0	15.45	121.1
$C^\bullet H_3$ + *cyclo*-C_5H_8	108.0	42.9	15.55	122.7
				$\Delta E_s = 8.3 \pm 0.8$ kJ/mol

Table 7. Kinetic parameters of the reactions with polar monomers and ΔE_μ values characterizing the polar effect (Eq. (16)) [22, 29]

CH_2=CHR	$RO_2^{\bullet}$*	ΔH_e, kJ/mol	E_e, kJ/mol	br_e, $(kJ/mol)^{1/2}$	$E_{e,0}$, kJ/mol	ΔE_μ, kJ/mol
CH_2=CMeOOR	$HO_2^{\bullet}$	–73.6	46.4	20.39	110.6	9.7
CH_2=CMeOOR	*sec*-$RO_2^{\bullet}$	–70.1	50.9	20.53	112.2	11.2
CH_2=CMeOOR	*tert*-$RO_2^{\bullet}$	–63.2	55.9	20.45	111.3	10.4
CH_2=CMeOOR	$R^1O_2^{\bullet}$	–63.2	54.5	20.32	109.8	8.9
CH_2=CMeOOR	$R^2O_2^{\bullet}$	–70.1	52.8	20.71	114.1	13.2
CH_2=CMeOOR	$R^3O_2^{\bullet}$	–70.1	49.6	20.41	110.8	9.9
CH_2=CMeOOR	$R^4O_2^{\bullet}$	–70.1	47.8	20.24	109	8.1
CH_2=CHOAc	$HO_2^{\bullet}$	–40.6	51.1	18.06	86.8	–14.1
CH_2=CHOAc	*sec*-$RO_2^{\bullet}$	–37.1	55.2	18.17	87.9	–13.1
CH_2=CHOAc	*tert*-$RO_2^{\bullet}$	–30.2	61.5	18.20	88.1	–12.8
CH_2=CHOAc	$R^3O_2^{\bullet}$	–37.1	53.3	17.98	85.9	–15.0
CH_2=CHOAc	$R^2O_2^{\bullet}$	–37.1	54.6	18.11	87.2	–13.7
CH_2=CHOAc	$R^4O_2^{\bullet}$	–37.1	52.1	17.85	84.7	–16.2
CH_2=CHOAc	$R^1O_2^{\bullet}$	–30.2	55.4	17.56	82	–18.9
CH_2=CHCN	$HO_2^{\bullet}$	–82.6	46.7	21.12	118.6	17.7
CH_2=CHCN	*sec*-$RO_2^{\bullet}$	–79.1	49.7	21.12	118.7	17.8
CH_2=CHCN	*tert*-$RO_2^{\bullet}$	–72.2	55.2	21.09	118.3	17.4
CH_2=CHCN	$R^4O_2^{\bullet}$	–79.1	49.7	21.12	118.7	17.8
CH_2=CHCN	$R^2O_2^{\bullet}$	–79.1	47.5	20.93	116.4	15.5
CH_2=CHCN	$R^3O_2^{\bullet}$	–79.1	49.8	21.13	118.8	17.9
CH_2=CHCN	$R^1O_2^{\bullet}$	–72.2	49.7	20.59	112.7	11.8

* $R^1O_2^{\bullet}$ = ~$CH_2CMe(COOMe)O_2^{\bullet}$, $R^2O_2^{\bullet}$ = ~$CH_2CH(COOMe)O_2^{\bullet}$, $R^3O_2^{\bullet}$ = ~$CH_2CH(OAc)O_2^{\bullet}$, $R^4O_2^{\bullet}$ = ~$CH_2CH(CN)O_2^{\bullet}$.

the E_e values calculated for the addition of $RO_2^{\bullet}$ to CH_2=CHX using Eq. (8), the parameters br_e and $E_{e,0}$, and the ΔE_μ values calculated using the equation

$$\Delta E_\mu = E_{e,0}(CH_2{=}CHX) - E_{e,0}(CH_2{=}CHR). \qquad (14)$$

It can be seen that the polar interaction enhances the activation energy of the reactions of the peroxy radicals with methyl methacrylate and acrylonitrile by 8.1–13.2 and 11.8–17.8 kJ/mol, respectively, and decreases the activation energy in the reactions of $RO_2^{\bullet}$ with vinyl

Table 8. Kinetic parameters of the cyclization reactions of the radicals (n is the number of atoms in the cycle) [30–32]

Radical	n	α	γ	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	$r_e \times 10^{10}$, m
$RCH{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	3	1.202	0.202	7.64	29.6	0.142
$RCH{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	4	1.202	0.202	8.24	34.4	0.153
$RCH{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	5	1.202	0.202	10.97	61.0	0.204
$RCH{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	6	1.202	0.202	12.64	81.1	0.235
$RCH{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	7	1.202	0.202	11.19	63.5	0.208
$RN{=}CH(CH_2)_{n-2}C^{\bullet}H_2$	5	1.478	0.478	14.91	58.1	0.264
$RN{=}N(CH_2)_{n-2}C^{\bullet}H_2$	5	1.658	0.134	13.16	53.9	0.208
$RN{=}N(CH_2)_{n-2}C^{\bullet}H_2$	6	1.658	0.134	14.97	69.8	0.236
$RCH{=}CH(CH_2)_{n-2}N^{\bullet}R$	5	1.410	0.202	12.94	64.4	0.240
$RCH{=}CH(CH_2)_{n-2}N^{\bullet}R$	6	1.410	0.202	12.00	55.4	0.223
$RC(O)(CH_2)_{n-2}C^{\bullet}H_2$	5	1.336	0.528	5.60	9.0	0.093
$RC(O)(CH_2)_{n-2}C^{\bullet}H_2$	6	1.336	0.528	8.25	19.6	0.138

acetate by a value from –12.8 to –18.9 kJ/mol. Thus, all factors affecting the activation energy and marked earlier [2–5] manifest themselves also in the analysis of the experimental data in the framework of the new 3PC model.

CYCLIZATION OF FREE RADICALS

The new model of the addition reaction can be used in the description and analysis of the cyclization reactions of radicals containing multiple bonds (C=C, C=N, N=N, C=O). These reactions were analyzed previously using the IPM [30–32]. Table 8 contains the α, γ, br_e, $E_{e,0}$, and r_e parameters for 12 classes of these reactions obtained using the 3PC model.

It is noteworthy that the activation energy of the thermally neutral reaction ($E_{e,0}$) depends on the strain energy of the forming cycle (E_{rcs}). The values of the $E_{e,0}(6) - E_{e,0}(n)$ difference at different cycle sizes, where n is the number of atoms forming the cycle, are presented in Table 9.

It can be seen that the higher the cycle strain energy, the lower the $E_{e,0}$ value. A linear correlation is observed for the cyclization of the alkyl radicals containing the double bond.

$$E_{e,0}(6) - E_{e,0}(n) = 17.5 \pm 4.4 + (0.28 \pm 0.05)E_{rcs}. \quad (15)$$

Thus, the conclusion that the activation energy of cyclization depends on E_{rcs}, which was drawn in the framework of the IPM [32], holds true for the analysis of the data by the 3PC model.

A comparison of $E_{e,0}$ for the cyclization of carbon-centered radicals with the attack to the C=C, N=N, and C=O bonds to form the six-membered cycle for which $E_{rcs} \approx 0$ indicates the influence of the electronegativity of atoms of the double bond on the activation energy of the radical cyclization reactions.

Bond	C=C	N=N	C=O
$E_{e,0}$, kJ/mol	81.1	69.1	19.6

The lowest $E_{e,0}$ value is observed for the cyclization with the addition of the C atom bearing the free energy to the carbonyl group, whose oxygen atom possesses the highest electron affinity (in the order C < N < O).

Table 9. Dependence of $E_{e,0}(6)$–$E_{e,0}(n)$ (kJ/mol) on the cycle size (n)

	Number of atoms in cycle (n)				
Reaction	3	4	5	6	7
$R^{\bullet}$ + C=C	51.5	46.7	20.1	0	17.5
$R^{\bullet}$ + N=N	–	–	15.9	0	–
$R^{\bullet}$ + C=O	–	–	10.6	0	–
E_{rcs}, kJ/mol [33]	115.1	110.9	26.7	0.7	26.8

Table 10. Kinetic parameters of the decomposition reactions of the radicals with the formation of molecules with multiple bonds

Reaction	α	γ	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	$r_e \times 10^{10}$, m	Reference
$\mathrm{RCH_2C^{\bullet}H_2 \longrightarrow H^{\bullet} + RCH{=}CH_2}$	1.440	0.202	19.68	143.6	0.365	[34]
$\mathrm{CH_2{=}CHC^{\bullet}H_2 \longrightarrow H^{\bullet} + CH_2{=}C{=}CH_2}$	1.440	0.202	23.77	209.6	0.441	[34]
$\mathrm{PhC^{\bullet}HCH_2R \longrightarrow PhCH{=}CHR + H^{\bullet}}$	1.440	0.202	22.28	184.1	0.413	[34]
$\mathrm{CH_2{=}C^{\bullet}R \longrightarrow HC{\equiv}CR + H^{\bullet}}$	1.745	0.283	27.09	178.4	0.392	[34]
$\mathrm{C^{\bullet}H_2CHRMe \longrightarrow CH_2{=}CHR + Me^{\bullet}}$	1.202	0.202	14.92	112.9	0.277	[35]
$\mathrm{C^{\bullet}H_2CH_2CHMe_2 \longrightarrow CH_2{=}CH_2 + Me_2C^{\bullet}H}$	1.202	0.202	14.55	107.4	0.270	[35]
$\mathrm{C^{\bullet}H_2CH_2CMe_3 \longrightarrow CH_2{=}CH_2 + Me_3C^{\bullet}}$	1.202	0.202	14.70	109.6	0.273	[35]
$\mathrm{C^{\bullet}H_2CH_2Ph \longrightarrow CH_2{=}CH_2 + Ph^{\bullet}}$	1.202	0.202	18.21	168.2	0.338	[35]
$\mathrm{C^{\bullet}H_2CH{=}CHCH_2Me \longrightarrow CH_2{=}CHCHCH_2 + C^{\bullet}H_3}$	1.202	0.202	16.86	144.2	0.313	[35]
$\mathrm{C^{\bullet}H{=}CHCH_3 \longrightarrow CH{\equiv}CH + C^{\bullet}H_3}$	1.543	0.283	18.69	104.8	0.270	[35]
$\mathrm{R_2CHO^{\bullet} \longrightarrow R_2C(O) + H^{\bullet}}$	1.601	0.528	20.10	89.1	0.335	[36]
$\mathrm{R_3CO^{\bullet} \longrightarrow R_2C(O) + R^{\bullet}}$	1.256	0.528	14.10	62.5	0.235	[36]
$\mathrm{PhCH_2CMe_2O^{\bullet} \longrightarrow PhCH_2^{\bullet} + Me_2C(O)}$	1.256	0.528	14.57	66.7	0.243	[36]
$\mathrm{MeC^{\bullet}(O) \longrightarrow C^{\bullet}H_3 + C{\equiv}O}$	1.687	0.262	16.48	71.5	0.218	[24]
$\mathrm{RCH_2C^{\bullet}(O) \longrightarrow RC^{\bullet}H_2 + C{\equiv}O}$	1.687	0.262	15.15	60.4	0.200	[24]
$\mathrm{R_3CC^{\bullet}(O) \longrightarrow R_3C^{\bullet} + C{\equiv}O}$	1.687	0.262	13.85	50.5	0.183	[24]

DECOMPOSITION OF RADICALS WITH DOUBLE BOND FORMATION

Radical decomposition of the type

$$\mathrm{XYZ^{\bullet} \longrightarrow (X\cdots Y \overset{\cdots}{\cdots} Z)^{\neq} \longrightarrow X^{\bullet} + Y{=}Z} \qquad (d)$$

is the reverse of the $X^{\bullet}$ addition to the Y=Z molecule. The activation energy of this decomposition is $E_d = E + \Delta H_d$ and $\Delta H_d = -\Delta H$, where E and ΔH concern the addition reaction, and E_d and ΔH_d are attributed to the decomposition reaction. In the decomposition reaction, the X–Y bond is cleaved and the Y–Z ordinary bond is transformed into the multiple bond Y=Z. The above model of the reaction as a result of the combination of three parabolas is quite applicable to the description of the energy of these reactions (see Figs. 1, 2). For these reactions, the extension of three reacting bonds r_e in the TS can be presented as the algebraic sum

$$r_e = \Delta r^{\neq}_{\mathrm{X\cdots Y}} + \Delta r^{\neq}_{\mathrm{Y\cdots Z}} - \Delta r^{\neq}_{\mathrm{Y=Z}}. \qquad (16)$$

After the insertion $E^{1/2}_{\mathrm{e,\,d}} = b^{\neq}_{\mathrm{X-Y}}\Delta r^{\neq}_{\mathrm{X\cdots Y}}$, $(E_{\mathrm{e,\,d}} - \Delta H_{\mathrm{e,\,d}})^{1/2} = b_{\Sigma}(\Delta r^{\neq}_{\mathrm{Y-Z}} - \Delta r^{\neq}_{\mathrm{Y=Z}})$, and $b_{\Sigma} = b_{\mathrm{Y-Z}}b_{\mathrm{Y=Z}}/(b_{\mathrm{Y=Z}} - b_{\mathrm{Y-Z}})$, we obtain the equation

$$br_e = \alpha\sqrt{E_{\mathrm{e,\,d}}} + \gamma\sqrt{E_{\mathrm{e,\,d}} - \Delta H_{\mathrm{e,\,d}}}, \qquad (17)$$

where $= b_{\mathrm{Y=Z}}$, $\alpha = b_{\mathrm{X-Y}}/b_{\mathrm{Y=Z}}$, $\gamma = (b_{\mathrm{Y=Z}} - b_{\mathrm{Y-Z}})/b_{\mathrm{Y-Z}}$, $\Delta H_{\mathrm{e,\,d}} = \Delta H_d + 0.5hN_A(\nu_{\mathrm{X-Y}} + \nu_{\mathrm{Y-Z}} - \nu_{\mathrm{Y=Z}})$. This equation can also be obtained from Eq. (7) after $E_{\mathrm{e,\,d}} = E_e - \Delta H_e$ and $\Delta H_{\mathrm{e,\,d}} = -\Delta H_e$ were inserted into it. The kinetic parameters of the decomposition reactions [34–36] analyzed in the framework of the new 3PC model are presented in Table 10.

For the same class of decomposition and addition reactions, the br_e parameters calculated from the experimental data for the addition and decomposition reactions are rather similar (see Tables 4 and 10, br_e is expressed in (kJ/mol)$^{1/2}$).

Transition state	$\mathrm{H\cdots CH_2{-}CH_2}$	$\mathrm{Me\cdots CH_2{-}CH_2}$	$\mathrm{Me\cdots C{\equiv}O}$
br_e for addition (kJ/mol)$^{1/2}$	20.50	14.97	16.36
br_e for decomposition (kJ/mol)$^{1/2}$	19.68	14.92	16.48

Table 11. Contribution of the electronegativity of atoms of the reaction center to the activation energy of radical decomposition

Reaction	$E_{e,0}$, kJ/mol	$r_e \times 10^{10}$, m	$\{br_e/(\alpha + \gamma)\}^2$, kJ/mol	$-\Delta E_{EA}$, kJ/mol
$\mathrm{RCH_2C^{\bullet}H_2 \longrightarrow H^{\bullet} + RCH{=}CH_2}$	143.6	0.365	1077	0.0
$\mathrm{R_2CHO^{\bullet} \longrightarrow H^{\bullet} + R_2C(O)}$	89.1	0.335	1104	23.2
$\mathrm{C^{\bullet}H_2CH_2CH_3 \longrightarrow CH_2{=}CH_2 + C^{\bullet}H_3}$	112.9	0.277	1473	0.0
$\mathrm{R_3CO^{\bullet} \longrightarrow R_2C(O) + R^{\bullet}}$	62.5	0.235	1016	21.8
$\mathrm{MeC^{\bullet}(O) \longrightarrow C^{\bullet}H_3 + C{\equiv}O}$	71.5	0.218	822	24.0

The TS of the decomposition reactions are affected by the same factors as the TS of the addition reactions, namely, the triplet repulsion, the electronegativity of atoms of the reaction center, the π-bonds in the α position to the double bond, the force constants of the bonds involved in the rearrangements, and the interaction of polar groups. Due to this, the $E_{e,0}$ value changes in a wide range on going from one class of reactions to another: $E_{e,0} = 36$–210 kJ/mol. The increments calculated by formula (15), which characterize the contribution from the electronegativity of atoms of the reaction center to the activation energy, are given in Table 11. As can be seen, this contribution is rather high.

Thus, the 3PC model correctly describes the energy of the addition, cyclization, and decomposition of free radicals and eliminates contradictions, which appear when these reactions are considered in the framework of the IPM. In the framework of the 3PC model, the earlier established classification of the reactions is retained and this model is more "sensitive" to the influence of physicochemical factors on the activation barrier of the reaction. The 3PC model makes it possible to calculate the activation energy of the radical addition reaction, depending on its enthalpy (formula (9)). In combination with the reduced model, the 3PC model allows one to calculate the geometric parameters of the TS of the addition reactions that coincide with the results of the quantum-chemical calculation.

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