

# Reactivity of Aminyl, Thiyl, and Silyl Radicals in Addition Reactions: A Role of the Radius of an Atom with a Free Valence

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**Abstract**—The experimental data on the addition of aminyl, thiyl, and silyl radicals to olefins as well as on the addition of silyl radicals to carbonyl compounds are analyzed within the framework of the parabolic model of the transition state. The activation energies of thermoneutral reactions  $E_{e,0}$  are calculated: 62.1 for ( $\text{NH}_2^\bullet + \text{CH}_2=\text{CHX}$ ), 31.4 ( $\text{RS}^\bullet + \text{CH}_2=\text{CHX}$ ), 76.6 ( $\text{R}_3\text{Si}^\bullet + \text{CH}_2=\text{CHX}$ ), and 114.5 kJ/mol for ( $\text{R}_3\text{Si}^\bullet + \text{O}=\text{CR}^1\text{R}^2$ ). The radius of the atom bearing the free valence is an important factor that affects the activation energy of these reactions. An empirical formula is derived relating the activation energy of a thermoneutral addition reaction with the strength  $D(\text{C}\dots\text{Y})$  of a forming bond, its length  $r(\text{C}\dots\text{Y})$ , and the force constants of reacting bonds characterized by the  $\alpha$  coefficient:  $(1 + \alpha)(E_{e,0})^{1/2} = 4.78 \times 10^8(r(\text{C}\dots\text{Y}) - 4.2 \times 10^{-11}D(\text{C}\dots\text{Y}))$ . The presence of  $\pi$ -bonds adjacent to the attacked double bond causes an increase in the activation energy  $E_{e,0}$ . The contribution of this factor to the activation energy is evaluated. The addition of silyl radicals to olefins  $\text{RCH}=\text{CHR}$  occurs with a higher activation energy than the addition to  $\text{CH}_2=\text{CHR}$  compounds because of the steric effect of the R substituent.

## INTRODUCTION

The reactivity of radicals and unsaturated compounds in radical addition has actively been discussed in scientific literature since the 1950s [1–8]. The reactions occurring in the chain homopolymerization and copolymerization of various monomers have been a focus. Two important factors, the reaction heat (enthalpy) and the interaction of radical polar groups with a monomer (the polar factor), affect the reaction rate. On this basis, three alternative schemes that took into account these factors were proposed to estimate the reactivity of monomers: the Q–e scheme [9], the  $\alpha$ – $\beta$  scheme, which used the Hammett constants  $\sigma$  [10], and the K–P scheme, which involved the equilibrium and rate constants for thiyl radical addition [11].

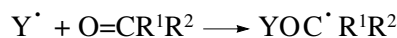
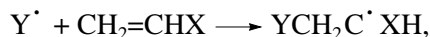
Analysis of kinetic parameters for the addition of atoms [12] and radicals  $\text{R}^\bullet$  [13–15],  $\text{RO}^\bullet$  [16], and  $\text{RO}_2^\bullet$  [17] to multiple bonds in the molecules ( $>\text{C}=\text{C}<$ ,  $-\text{C}\equiv\text{C}-$ , and  $>\text{C}=\text{O}$ ) within the framework of the parabolic model suggested a number of new factors that affect the activation barrier of the addition reaction. These factors are (1) the energy of the nonbonding orbital of a bond resulting from atom or radical addition, (2) the presence of  $\pi$ -bonds adjacent to the reaction center, (3) the force constants of reacting bonds, and (4) the nonlinear structure of the atoms in a reacting molecule. The question arises as to whether the above six parameters are the only essential physical and structural factors that determine the activation barrier of the

addition reaction or there are some other factors that are important for reactant activation in these reactions.

Analysis of abstraction reactions involving silyl radicals within the framework of the parabolic model suggested that the radius of the atom bearing the free valence is an important factor that affects the activation energy of these reactions. This work is devoted to elucidating the effect of this factor. Here, we analyze the experimental kinetic data on the addition of aminyl, thiyl, and silyl radicals to a double  $\text{C}=\text{C}$  bond and the addition of silyl radicals to a carbonyl group. We also compare kinetic parameters for the addition of radicals bearing a free valence on carbon, nitrogen, silicon, and sulfur atoms with different radii.

## CALCULATION PROCEDURE AND RESULTS

Within the framework of the parabolic model [13], the transition state of the addition of a  $\text{Y}^\bullet$  radical ( $\text{NH}_2^\bullet$ ,  $\text{RS}^\bullet$ , or  $\text{R}_3\text{Si}^\bullet$ ) to an olefin  $\text{CH}_2=\text{CHY}$  and a carbonyl compound  $\text{R}^1\text{R}^2\text{C}=\text{O}$



is considered as a result of the intersection of two potential curves corresponding to the potential energy of the stretching vibration of the atoms of the breaking (i) ( $\text{C}=\text{C}$  or  $\text{O}=\text{C}$ ) and forming (f) ( $\text{C}-\text{S}$ ,  $\text{C}-\text{Si}$ ,  $\text{C}-\text{N}$ , or

**Table 1.** Kinetic parameters for the addition of the aminyl  $\text{NH}_2^\bullet$ , thiyl  $\text{C}_6\text{H}_5\text{S}^\bullet$ , and silyl  $\text{R}_3\text{Si}^\bullet$  radicals to multiple C=C and C=O bonds

Parameter	$\text{H}_2\text{N}^\bullet + \text{C}=\text{C}$	$\text{ArS}^\bullet + \text{C}=\text{C}$	$\text{R}_3\text{Si}^\bullet + \text{C}=\text{C}$	$\text{R}_3\text{Si}^\bullet + \text{O}=\text{C}$
$\alpha$	1.410	2.282	2.023	2.518
$b \times 10^{-11} \text{ (kJ/mol)}^{1/2} \text{ m}^{-1}$	5.389	5.389	5.389	5.991
$0.5hN_A\nu_i$ , kJ/mol	9.9	9.9	9.9	10.3
$0.5hN_A(\nu_i - \nu_f)$	3.1	6.3	5.8	7.0
$A$ , $\text{l mol}^{-1} \text{ s}^{-1}$	$8 \times 10^7$	$7 \times 10^8$	$8 \times 10^8$	$8 \times 10^8$

O–Si) bonds. The stretching vibration of atoms along a bond is considered to be harmonic. Its potential energy ( $U$ ) is proportional to the square of the vibration amplitude ( $r$ )  $U = b^2r^2$ , where the coefficient  $b = \pi\nu(2\mu)^{1/2}$ ,  $\nu$  is the frequency of atom vibration along a bond, and  $\mu$  is their reduced weight. Within the framework of this model, radical addition is characterized by the following parameters: a change in the enthalpy  $\Delta H_e$ , the activation energy  $E_e$ , the distance between the minima of two intersecting parabolas  $r_e$ , and the  $b_i$  and  $b_f$  coefficients, which are the dynamic characteristics of breaking and forming bonds ( $2b_i^2$  is the force constant of the  $i$ th bond).

The enthalpy change, including the difference in the energies of the zero vibration of the corresponding bonds, is

$$\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f), \quad (1)$$

where  $D_i$  and  $D_f$  are the dissociation energies of breaking and forming bonds, respectively;  $h$  and  $N_A$  are the Planck and Avogadro constants, respectively; and  $\nu_i$  and  $\nu_f$  are the frequencies of the stretching vibrations of breaking and forming bonds, respectively. The activation energy  $E_e$  with reference to the minimum of the potential curve, which includes the zero vibration energy, is related to the experimental activation energy  $E$  by the equation

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

where  $R$  is the universal gas constant and  $T$  is the experimental temperature. The  $E$  value was calculated by the Arrhenius equation

$$E = RT \ln(A/k), \quad (3)$$

where  $k$  is the experimental rate constant determined at the temperature  $T$  and  $A$  is the preexponential factor

typical of the reaction series of the same structural type. For alkyl radical addition to  $\text{CH}_2=\text{CHX}$  in a hydrocarbon solution,  $A = 5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  [14]. According to collision theory, the  $A$  factor for the addition of other  $\text{Y}^\bullet$  radicals to a C=C bond was calculated by the formula  $A(\text{Y}^\bullet) = A(\text{CH}_3^\bullet)(r_{\text{C}\dots\text{Y}}/r_{\text{C}\dots\text{C}})^2$ .

The  $\Delta H_e$ ,  $E_e$ , and  $b = b_i$  parameters are related as follows [12]:

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

where  $\alpha = b_i/b_f$ . Table 1 lists the  $\alpha$ ,  $b$ ,  $0.5hN_A\nu_i$ , and  $A$  parameters used in the calculations. Using the  $br_e$  parameter, one can calculate the activation energy of the thermoneutral reaction  $E_{e,0}$  ( $E_{e,0} = E_e$  at  $\Delta H_e = 0$ ) for each reaction series with  $br_e = \text{const}$

$$E_{e,0} = (br_e)^2(1 + \alpha)^{-2}. \quad (5)$$

The enthalpy change in the addition of the radical  $\text{Y}^\bullet$  ( $\text{NH}_2^\bullet$ ,  $\text{ArS}^\bullet$ , or  $\text{R}_3\text{Si}^\bullet$ ) to the double C=C bond was calculated by subtracting the difference in the bond dissociation energies  $D(\text{R}\dots\text{Me}) - D(\text{R}\dots\text{Y})$  from the enthalpy of methyl radical addition to this monomer [14]. The enthalpy of  $\text{R}_3\text{Si}^\bullet$  addition to a carbonyl group was calculated in a similar way. Some bond dissociation energies are:  $D(\text{Me}-\text{R}) = 370 \text{ kJ/mol}$ ,  $D(\text{NH}_2-\text{R}) = 353 \text{ kJ/mol}$  [18],  $D(\text{PhS}-\text{R}) = 280.4 \text{ kJ/mol}$  [19],  $D(\text{Et}_3\text{Si}-\text{R}) = 371.4 \text{ kJ/mol}$  [20], and  $D(\text{Et}_3\text{Si}-\text{OR}) = 484 \text{ kJ/mol}$  [21]. Tables 2–4 summarize the calculation results for the  $\Delta H_e$  and  $br_e$  parameters for the addition of aminyl, thiyl, and silyl radicals to olefins and carbonyl compounds.

**Table 2.** Enthalpy ( $\Delta H_e$ ), activation energy ( $E$ ,  $E_e$ ), and  $br_e$  parameters for the addition of  $\text{NH}_2^\bullet$  aminyl radicals to olefins

Olefin	$-\Delta H_e$ , kJ/mol	$E$ , kJ/mol	$E_e(300\text{ K})$ , kJ/mol	$br_e$ , (kJ/mol) <sup>1/2</sup>	Reference
$\text{CH}_2=\text{CH}_2$	77.1	$16.6 \pm 0.6$	25.3	$19.30 \pm 0.10$	[22, 23]
$\text{CH}_2=\text{CHCH}_3$	74.7	$14.8 \pm 0.4$	23.5	$18.82 \pm 0.07$	[22, 24]
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	75.2	14.0	22.7	18.72	[22]
$\text{CH}_2=\text{C}(\text{CH}_3)_2$	76.9	14.4	23.1	18.91	[22]
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	74.2	15.8	24.5	19.01	[22]
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHCH}_3$	77.6	16.1	24.8	19.25	[22]
<i>trans</i> - $\text{CH}_2=\text{CHCH}=\text{CH}_2$	123.8	$6.5 \pm 0.7$	15.2	20.52	[25, 26]

**Table 3.** Enthalpy ( $\Delta H_e$ ), rate constants  $k$  (296 K) [8], activation energies  $E_e$ , and  $br_e$  parameters for the addition of the ( $\text{C}_6\text{H}_5\text{S}^\bullet$ ) phenylthiyl radicals to olefins

Olefin	$-\Delta H_e$ , kJ/mol	$k$ (296 K), $\text{l mol}^{-1} \text{s}^{-1}$	$E_e$ , kJ/mol	$br_e$ , (kJ/mol) <sup>1/2</sup>
$\text{CH}_2=\text{CHOCHMeEt}$	2.3	$1.8 \times 10^5$	29.0	18.15
$\text{CH}_2=\text{CHCOOMe}$	7.8	$4.3 \times 10^5$	26.9	18.63
$\text{CH}_2=\text{CMeCN}$	32.8	$2.3 \times 10^6$	22.8	21.79
$\text{CH}_2=\text{CHOAc}$	12.8	$4.6 \times 10^4$	32.4	21.03
$\text{CH}_2=\text{CMeOAc}$	16.4	$3.5 \times 10^4$	33.1	21.81
$\text{CH}_2=\text{CHPh}$	48.8	$5.1 \times 10^7$	15.1	22.13

**Table 4.** Enthalpy ( $\Delta H_e$ ), rate constants  $k$  (300 K), activation energies  $E_e$ , and  $br_e$  parameters for the addition of the triethylsilyl radicals to olefins and carbonyl compounds

Reactant	$-\Delta H_e$ , kJ/mol	$k$ (300 K), $\text{l mol}^{-1} \text{s}^{-1}$	$E_e$ (300 K), kJ/mol	$br_e$ , (kJ/mol) <sup>1/2</sup>	Reference
$\text{CH}_2=\text{CH}_2$	97.1	$2.2 \times 10^7$	19.4	26.24	[27]
$\text{CH}_2=\text{CCl}_2$	116.0	$2.7 \times 10^8$	11.4	26.21	[27]
$\text{CH}_2=\text{CHBu}$	95.3	$4.8 \times 10^6$	21.5	26.50	[27]
$\text{CH}_2=\text{CHBu}$	95.3	$3.9 \times 10^6$	21.7	26.54	[28]
$\text{CH}_2=\text{CHCMe}_3$	95.3	$3.7 \times 10^6$	22.1	26.62	[27]
<i>cyclo</i> - $\text{C}_6\text{H}_{10}=\text{CH}_2$	99.6	$7.4 \times 10^6$	20.4	26.67	[27]
<i>trans</i> - $\text{EtCH}=\text{CHEt}$	94.4	$9.5 \times 10^5$	27.2	27.51	[27]
<i>cyclo</i> - $\text{C}_5\text{H}_8$	98.5	$2.2 \times 10^6$	25.1	27.50	[27]
<i>cyclo</i> - $\text{C}_6\text{H}_{10}$	95.0	$9.4 \times 10^5$	27.3	27.60	[27]
$\text{CH}_2=\text{CHPh}$	141.7	$2.2 \times 10^8$	11.9	28.52	[27]
$\text{CH}\equiv\text{CCMe}_3$	106.5	$2.3 \times 10^6$	23.3	28.61	[27]
$\text{CH}=\text{CPh}$	141.7	$1.0 \times 10^8$	13.9	28.96	[27]
$\text{EtCHO}$	144.3	$1.2 \times 10^7$	19.6	36.66	[29]
<i>cyclo</i> - $\text{C}_6\text{H}_{10}\text{O}$	140.6	$6.5 \times 10^5$	27.1	37.81	[29]
<i>cyclo</i> - $\text{C}_5\text{H}_8\text{O}$	142.4	$7.2 \times 10^5$	26.9	37.95	[29]
$\text{PhCOMe}$	177.1	$1.2 \times 10^7$	19.6	39.74	[29]
$\text{Ph}_2\text{CO}$	185.3	$3.0 \times 10^7$	17.4	40.02	[29]

PHYSICAL AND STRUCTURAL FACTORS  
AFFECTING THE ACTIVATION ENERGY  
OF RADICAL ADDITION

**Reaction enthalpy.** Using the parabolic model, one can correctly take into account the contribution of the enthalpy of an individual reaction to its activation energy  $\Delta E_H$  by comparing the activation energy of this

reaction with that of the thermoneutral reaction  $E_{e,0}$  at  $br_e = \text{const}$  [15]:

$$\Delta E_H = E_e - (br_e)^2(1 + \alpha)^{-2}. \quad (6)$$

The results of such a comparison for the addition of the  $\text{Et}_3\text{Si}^\cdot$  radical to three unsaturated and two carbonyl compounds are presented below (see Table 3).

Compound	$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CCl}_2$	$\text{CH}_2=\text{CHPh}$	$\text{EtCHO}$	$\text{PhCOMe}$
$-\Delta H_e$ , kJ/mol	97.1	116.0	141.7	144.3	177.1
$E_e$ , kJ/mol	19.4	11.4	11.9	19.6	19.6
$-\Delta E_H$ , kJ/mol	57.2	65.2	64.7	94.9	107.3

For the above highly exothermic reactions, the contribution of the enthalpy to the activation energy of the process is rather high and ranges from  $-57$  to  $-107$  kJ/mol.

**Triplet repulsion.** According to the Pauli principle, the formation of a three-centered three-electron bond  $\text{Y}-\text{C}$  in the transition state for  $\text{Y}^\cdot$  addition to  $\text{CH}_2=\text{CHX}$  involves both the bonding and nonbonding orbitals of the forming  $\text{Y}\cdots\text{C}\cdots\text{C}$  bond. The stronger the  $\text{Y}-\text{C}$  bond, the higher the energy of its nonbonding orbital. This fact is reflected in the parameters of the parabolic model as follows: the stronger the  $\text{Y}-\text{C}$  bond,

the higher the  $r_e$ ,  $E_{e,0}$ , and, consequently,  $E$  values. For alkyl and alkoxy radical addition to a  $\text{C}=\text{C}$  bond, the following empirical relationship between the  $r_e$  value and the strength of the forming bond  $D_e$  was derived [14–16]:

$$r_e = (0.98 \pm 0.04) \times 10^{-13} D_e. \quad (7)$$

Let us consider how the  $r_e$  parameter is related to the  $D_e(\text{C}-\text{N})$  value for  $\text{NH}_2^\cdot$  addition to olefins. The  $r_e$ ,  $D_e$ , and  $r_e/D_e$  values are given below.

Olefin	$\text{CH}_2=\text{CH}_2$	$\text{CH}_2=\text{CHMe}$	$\text{CH}_2=\text{CHEt}$	<i>trans</i> - $\text{MeCH}=\text{CHMe}$	$\text{CH}_2\text{CMe}_2$
$r_e \times 10^{11}$ , m	3.58	3.49	3.47	3.53	3.51
$D_e$ , kJ/mol	360	360	360	361	360
$(r_e/D_e) \times 10^{13}$ , m kJ <sup>-1</sup> mol	0.99	0.97	0.96	0.98	0.98

The fourth line shows that, for  $\text{NH}_2^\cdot$  addition, the  $r_e$  value is related to the strength of the forming bond  $D_e$  by the empirical equation:  $r_e = aD_e(\text{C}-\text{N})$ , where  $a = (0.98 \pm 0.02) \times 10^{-13}$  m kJ<sup>-1</sup> mol, which virtually coincides with the  $a$  value in Eq. (7) for the addition of alkyl radicals [14] and is close to it for the alkoxy radicals [16].

**The radius of the atom bearing a free valence.** The situation with the parameters for thiyl and silyl radical addition is more complicated. Table 5 compares the  $E_{e,0}$  and  $r_e$  values with the dissociation energy  $D_e$  of the forming  $\text{C}-\text{Y}$  bond and shows that the higher the  $D_e(\text{C}-\text{Y})$  value, the higher the  $r_e$  parameter. However, the proportionality  $r_e = \text{const } D_e$ , found earlier for the addition of the carbon-, nitrogen-, and oxygen-centered radicals [14–16], is not observed in this case. As Table 5 shows, the larger the radius of the atom that bears a free valence and attacks a double bond, the higher the  $r_e/D_e$  ratio. The manner in which the  $r_e/D_e$  ratio changes with the length of the forming bond  $r(\text{C}\cdots\text{Y})$  for the addition

of alkyl, aminyl, thiyl, and silyl radicals to the  $\text{C}=\text{C}$  bond is illustrated in the figure. The data of this figure suggest that the empirical equation

$$r_e = (8.81 \pm 0.03) \times 10^{-4}(r(\text{C}\cdots\text{Y}) - 0.42 \times 10^{-10})D_e \quad (8)$$

or

$$br_e = (1 + \alpha)E_{e,0}^{1/2} = (4.78 \pm 0.02) \times 10^8(r(\text{C}\cdots\text{Y}) - 0.42 \times 10^{-10})D_e \quad (9)$$

is true, where the  $r_e$  and  $r(\text{C}\cdots\text{Y})$  parameters are expressed in m, and the  $D_e$  and  $br_e$  values are expressed in kJ/mol and (kJ/mol)<sup>1/2</sup>, respectively. This relationship confirms that the size of an atom bearing a free valence strongly affects the activation barrier of the addition reaction. This is obviously due to the repulsion of electron shells of an attacking atom and an attacked  $\pi$  bond: the larger the atomic radius, the stronger the reactant repulsion. A similar situation is also observed

**Table 5.** Comparison of the activation parameters of the addition of various  $Y^\bullet$  radicals to the C=C bond with the strength  $D_e$  and length  $r(Y...C)$  of the forming bond

Parameter	$Me^\bullet$	$NH_2^\bullet$	$RS^\bullet$	$R_3Si^\bullet$
$E_{e,0}$ , kJ/mol	82.6	61.0	31.4	76.6
$r_e \times 10^{11}$ , m	3.71	3.49	3.41	4.91
$D_e$ , kJ/mol	378	360	284	378
$(r_e/D_e) \times 10^{13} \text{ kJ}^{-1} \text{ mol m}$	0.97	0.97	1.20	1.30
$r(Y...C) \times 10^{10}$ , m	1.52	1.47	1.79	1.89

**Table 6.** Effect of the  $\alpha$ - $\pi$ -bonds on the activation energy of silyl and thiyl radical addition to the C=C and C=O bonds

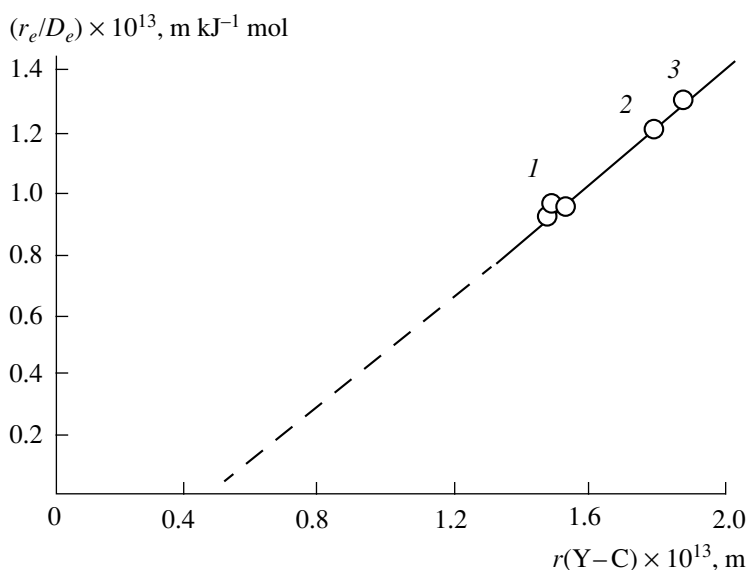
Reaction	$br_e$ , (kJ/mol) <sup>1/2</sup>	$E_{e,0}$ , kJ/mol	$\Delta E_\pi$ , kJ/mol
<i>trans</i> -CH <sub>2</sub> =CHCH=CH <sub>2</sub> + $N^\bullet H_2$	20.52	72.5	10.4
CH <sub>2</sub> =CHPh + $PhS^\bullet$	22.13	45.5	14.1
CH <sub>2</sub> =CHPh + $Et_3Si^\bullet$	28.52	89.0	12.4
CH <sub>2</sub> =CMeCN + $PhS^\bullet$	21.79	44.1	12.7
CH <sub>2</sub> =CHOAc + $PhS^\bullet$	21.03	41.1	9.7
CH <sub>2</sub> =CMeOAc + $PhS^\bullet$	21.81	44.2	12.8
O=CMePh + $Et_3Si^\bullet$	39.74	127.6	13.1
O=CPh <sub>2</sub> + $Et_3Si^\bullet$	40.02	129.3	14.8

for the addition reactions  $RO^\bullet + CH_2=CHX$  [16] and  $R_3Si^\bullet + O = CR^1R^2$ .

Reaction	$r_e \times 10^{11}$ , m	$D_e$ , kJ/mol	$r_e/D_e \times 10^{13}$ , m kJ <sup>-1</sup> mol	$r_{(Y...O)} \times 10^{10}$ , m
$RO^\bullet + CH_2 = CHX$	3.62	359	1.01	1.42
$R_3Si^\bullet + O = CR^1R^2$	6.28	487	1.29	1.64

**Effect of the  $\alpha$ - $\pi$  bond on the activation energy of the addition reaction.** For the addition of the alkyl [14, 15], alkoxy [16], and peroxy [17] radicals to a C=C bond, the effect of triplet repulsion on the activation energy also manifests itself in the fact that the presence of a  $\pi$  bond adjacent to the attacked C=C bond (the  $\alpha$ - $\pi$  bond) causes an increase in the activation energy  $E_{e,0}$ . This is due to the delocalization of  $\pi$  electrons and an

increase in the energy of the nonbonding orbital of the forming C-Y bond in the transition state of the reaction  $Y^\bullet + CH_2 = CHX$ . We also studied whether this effect takes place in the addition of thiyl and silyl radicals. Specifically, Tables 3 and 4 suggest that the  $br_e$  value for the addition of  $PhS^\bullet$  and  $R_3Si^\bullet$  radicals to styrene is higher than to other monomers  $CH_2=CHX$ . The con-



The  $r_e/D_e$  ratio as a function of the length of the forming bond  $r(Y-C)$  for the addition of the  $Y^\bullet$  radical ((1) alkyl, aminyl, and alkoxy; (2) thiyl; and (3) silyl radicals) to  $CH_2=CHX$ .

tribution of the above  $\pi$  bond to the activation barrier of the addition reaction  $\Delta E_\pi$  may be estimated by the equation [15]

$$\Delta E_\pi = [(br_e)_\pi^2 - (br_e)^2](1 + a)^{-2}, \quad (10)$$

where  $(br_e)_\pi$  corresponds to  $CH=CHPh$  or some other compound with a  $\pi$  bond adjacent to the  $C=C$  bond being attacked, whereas  $br_e$  corresponds to  $CH_2=CHX$  with  $X$  lacking any  $\pi$ -bonds. Table 6 lists the  $(br_e)_\pi$  and  $E_{e,0}(\pi)$  parameters, as well as the  $\Delta E_\pi$  values calculated

according to Eq. (10). The  $\pi$  effect was observed for the addition to styrene ( $X = Ph$ ) and compounds with  $X = C\equiv N$  and  $OC(O)CH_3$ . The contribution of the  $\pi$ -bonds to the activation energy is quite significant (ranging from 10 to 15 kJ/mol). In the addition of silyl radicals to the carbonyl group, two phenyl groups have a stronger effect ( $\Delta E_\pi = 15$  kJ/mol) than one ( $\Delta E_\pi = 13$  kJ/mol). The nature of the attacking radical has little effect on the  $\Delta E_\pi$  value, as follows from the comparison of the activation energies  $\Delta E_\pi$  for the addition of different  $Y^\bullet$  radicals to styrene ( $X = Ph$ ):

$Y^\bullet$	$H^\bullet$	$CH_3^\bullet$	$RO^\bullet$	$Et_3Si^\bullet$	$PhS^\bullet$	$RO_2^\bullet$
$\Delta E_\pi$	10.6 [12]	6.8 [14]	14.6 [16]	12.4	14.1	8.5 [15]

The average  $\Delta E_\pi$  value is  $11.2 \pm 2.8$  kJ/mol, and the root-mean-square error (2.8 kJ/mol) is close to the double error in the experimental  $E_{e,0}$  value (1.5 kJ/mol).

**Steric effect.** As Table 4 shows, the  $br_e$  parameter is somewhat higher ( $br_e = 27.54 \pm 0.05$  (kJ/mol) $^{1/2}$ ) for the addition of silyl radicals to olefins  $RCH=CHR$  than for the reactions with olefins  $CH_2=CHR$  ( $br_e = 26.46 \pm 0.18$  (kJ/mol) $^{1/2}$ ). This difference may be due to the additional repulsion in the transition state between the silicon atom, which attacks the double bond, and the carbon atom of the alkyl radical adjacent to the double bond; that is, a steric effect takes place in this case. The

contribution of this effect  $\Delta E_s$  to the activation energy, calculated by the equation [15]

$$\Delta E_s = [(br_e)^2(RCH=CHR) - (br_e)^2(CH_2=CHR)](1 + \alpha)^{-2} \quad (11)$$

is  $\Delta E_s = 6.4 \pm 0.7$  kJ/mol. No steric effect was observed for the alkyl radicals in similar reactions [14, 15]. The steric effect is obviously due to the facts that  $r(C-Si) > r(C-C)$  and that the stronger repulsion in silyl radical addition makes this reaction more sensitive to both the olefin structure and the presence of the alkyl substituents at the carbon atom being attacked.

### The role of the force constants of reacting bonds.

The force constants affect the height of the activation barrier of radical abstraction and addition [15], which also

follows from the expression for the  $E_{e,0}$  parameter (Eq. (5)). The  $b^2(1 + \alpha)^{-2}$  values for the addition of different radicals to the C=C bond [15, 16] are given below.

Radical	$\text{CH}_3^\cdot$	$\text{RO}^\cdot$	$\text{H}^\cdot$	$\text{R}_3\text{Si}^\cdot$	$\text{ArS}^\cdot$
$b^2(1 + \alpha)^{-2} \times 10^{-22}, \text{ kJ mol}^{-1} \text{ m}^{-2}$	6.00	4.99	4.88	3.18	2.70
$E_{e,0}, \text{ kJ/mol}$	82.6	65.4	101.6	76.6	31.4

The parameter  $b^2(1 + \alpha)^{-2}$  ranges from 2.7 to  $6.0 \times 10^{-22} \text{ kJ mol}^{-1} \text{ m}^{-2}$  for the reactions under consideration. Therefore, the  $E_{e,0}$  value nearly doubles on passing from  $\text{ArS}^\cdot$  to  $\text{CH}_3^\cdot$ .

### CONCLUSION

When analyzing the experimental data (the activation energies) for the addition of the aminyl, thiyl, and silyl radicals to molecules with double bonds, we found a new important factor affecting the activation energy of the addition reaction, namely, the radius of the atom bearing a free valence. An empirical equation (see Eqs. (7) and (8)) was derived that allows the estimation of the  $E_{e,0}$  value from the strength and length of the forming bond. With an increase in the radius of the atom bearing a free valence, a steric effect arises, which is observed for the addition of the silyl radicals to 1,2-substituted ethylenes. Moreover, the following important factors also affect the activation energy of thiyl and silyl radical addition: the reaction enthalpy, the force constants of reacting bonds, the energy of the nonbonding orbital of the forming bond, the  $\pi$ -bonds adjacent to the reaction center, and the substituents at the carbon atom being attacked. The parameters that characterize the contribution of each factor to the activation energy of the addition reaction were calculated.

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