

# Reactivity of the Silyl, Germanyl, and Stannyl Radicals in Addition Reactions: The Effect of the Atomic Radius on the Activation Energy

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**Abstract**—Experimental data on the addition of silyl, germanyl, and stannyl radicals to olefins are analyzed in the framework of a three intersecting parabolas model. The parameters characterizing these reactions are calculated. The activation energy of the thermally neutral reaction for this class of reactions depends on both the strength of the formed bond and the radius of the atom bearing the free valence. The dependence is the following:  $E_{e,0}^{1/2} \sim \alpha D_e + b D_e^{3/2} r_{C-X}^{1/2}$ , where  $D_e$  is the strength of the formed bond and  $r_{C-X}$  is its length. Steric repulsion is observed in the reactions of the silyl radicals with symmetrically substituted ethylene derivatives. The presence of a  $\pi$ -bond or aromatic ring near the attacked double bond increases  $E_{e,0}$ . The increments are calculated that characterize the contribution to the activation energy from the following factors: the enthalpy of the reaction, triplet repulsion, steric hindrance, and effect of adjacent  $\pi$  electrons.

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## INTRODUCTION

As was shown by analysis of the data on the radical addition reactions, the activation energy depends on the enthalpy of the reaction, as well as on the triplet repulsion, the presence of a  $\pi$ -bond in the molecule in the  $\alpha$  position to the reaction center, and the polar factor. These factors manifest themselves when both the two intersecting parabolas model [1] and the model with the superposition of three parabolic curves [2] are used. The effect of the radius of the atom that bears the free valence and attacks the molecule is also observed in radical abstraction reactions [3]. Almost all the data on radical addition refer to radical reactions involving C-, N-, and O-centered radicals, and the radii of these atoms are very similar. To answer the question about the effect of the radius of the atom attacking the double bond on the activation energy, in the present work we analyzed the experimental data for the addition reactions involving the silyl, germanyl, and stannyl radicals. The radii of the Si, Ge, and Sn atoms differ substantially from the radius of the carbon atom and from one another. As has been shown by data analysis, the radius of the atom attacking the double bond affects the activation energy. This influence is mutually related to the influence of the formed bond energy, i.e., to the triplet repulsion. The effect of the adjacent  $\pi$  electrons and substituents at the double bond, i.e., steric effect, and other factors on the activation energy were observed in the reactions of the silyl radicals.

## COMPUTATIONAL PROCEDURE

In the addition of an  $X^\bullet$  radical to a  $Y=Z$  multiple bond,



this bond is transformed from double into ordinary:  $Y=Z \longrightarrow Y \cdots Z \longrightarrow Y-Z$ . In the transition state (TS), the  $Y=Z$  bond is elongated and the  $Y \cdots Z$  distance is intermediate between the  $Y=Z$  and  $Y-Z$  bond lengths. This state in the three intersecting parabolas (3IP) model [2] is interpreted as a result of the superposition of three potential curves. The stretching vibration of the Y and Z atoms is considered as harmonic with the effective coefficient  $b_\Sigma = b b_{Y-Z} / (b - b_{Y-Z})$ . The coefficient  $b = 2\pi h N_A v \mu^{1/2}$  characterizes the stretching vibration of the  $Y=Z$  double bond, and  $b_{Y-Z}$  characterizes the  $Y-Z$  bonds ( $h$  is Planck's constant,  $N_A$  is Avogadro's number,  $v$  is the vibration frequency of the  $Y=Z$  bond, and  $\mu$  is the reduced mass of the atoms involved in bond formation,  $2b^2$  being the force constant of the bond). The frequencies of the stretching vibrations of the atoms that form the bond,  $b$  coefficients, and zero-point-vibration energies of the atoms of the bond are given in Table 1.

The transition state of the addition reaction is considered as the intersection point of the parabola describing the extension of the  $Y=Z$  bond to the sizes of the  $Y-Z$  bond with the parabola that describes the potential

**Table 1.** Characteristics of the bonds involved in the reactions considered [4, 6]

Bond	$\nu, \text{cm}^{-1}$	$b, (\text{kJ/mol})^{1/2}$	$0.5hN_A\nu, \text{kJ/mol}$	$r_{\text{C-X}} \times 10^{10}, \text{m}$	$D_e(\text{C-X}), \text{kJ/mol}$
C–C	1375	44.83	8.2	1.513	360.2
C=C	1653	53.89	9.9	1.339	–
C=O	1719	59.91	10.3	1.210	–
Si–C	800	30.87	4.8	1.875	367.6
Ge–C	770	32.89	4.6	1.945	329.0
Sn–C	733	32.21	4.4	2.144	281.4
Si–O	560	23.78	3.3	1.833	515.3

**Table 2.** Parameters of the addition reactions of the alkyl, silyl, germanyl, and stannyl radicals (see Table 1)

Reaction	$\alpha$	$\gamma$	$\Delta\Delta H_e, \text{kJ/mol}$	$\Delta E_e, \text{kJ/mol}$	$A \times 10^{-9}, 1 \text{ mol}^{-1} \text{ s}^{-1}$
$\text{R}_3\text{C}^\cdot + \text{CH}_2=\text{CHR}$	1.202	0.202	-6.5	1.7	1.0
$\text{R}_3\text{Si}^\cdot + \text{CH}_2=\text{CHR}$	1.746	0.202	-3.1	1.7	1.5
$\text{R}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHR}$	1.638	0.202	-2.9	1.7	1.6
$\text{R}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHR}$	1.673	0.202	-2.7	1.7	2.0
$\text{R}_3\text{C}^\cdot + \text{O=CR}_2$	1.336	0.528	-4.6	3.6	1.0
$\text{R}_3\text{Si}^\cdot + \text{O=CR}_2$	1.941	0.528	0.3	3.6	1.5

energy of the stretching vibration of the formed X–Y bond [2].

The addition reaction in the 3IP model is described by the following parameters: the classical enthalpy  $\Delta H_e$ ; the classical potential barrier  $E_e$ ; the coefficients  $b$  (see Table 1),  $\alpha = b/b_{\text{Y-X}}$ , and  $\gamma = (b - b_{\text{Y-Z}})/b_{\text{Y-Z}}$ ; the parameter  $r_e$ ; and the preexponential factor  $A$  [2].

The classical enthalpy of the addition reaction takes the form

$$\begin{aligned} \Delta H_e &= \Delta H + \Delta\Delta H_e \\ &= \Delta H + 0.5hN_A(\nu_{\text{Y=Z}} - \nu_{\text{Y-Z}} - \nu_{\text{X-Y}}), \end{aligned} \quad (1)$$

where  $\Delta H$  is the enthalpy of the reaction;  $\Delta\Delta H_e$  is the algebraic sum of the zero-point vibration energies of the reacting bonds; and  $0.5hN_A\nu_{\text{Y=Z}}$ ,  $0.5hN_A\nu_{\text{Y-Z}}$ , and  $0.5hN_A\nu_{\text{X-Y}}$  are the zero-point vibration energies of the atoms of the corresponding bonds (their values are given in Table 1).

The classical potential barrier  $E_e$  in the 3IP model is related to the Arrhenius activation energy ( $E = RT\ln(A/k)$ ) and to the zero-point vibration energies of the bonds through the following equation (the differ-

ence in the zero-point vibration energies is  $\Delta E_e = 0.5hN_A(\nu_{\text{Y=Z}} - \nu_{\text{Y-Z}})$ :

$$\begin{aligned} E_e &= E + \Delta E_e - 0.5RT \\ &= E + 0.5hN_A(\nu_{\text{Y=Z}} - \nu_{\text{Y-Z}}) - 0.5RT. \end{aligned} \quad (2)$$

The parameter  $r_e$  is the algebraic sum of the extension of the three reacting bonds

$$r_e = \Delta r_{\text{Y-Z}}^\neq - \Delta r_{\text{Y=Z}}^\neq + \Delta r_{\text{X-Y}}^\neq. \quad (3)$$

All these parameters are interrelated by the equation [2]

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

The preexponential factor  $A$  in the addition reaction of alkyl radicals to the double bond is equal to  $1.0 \times 10^9 1 \text{ mol}^{-1} \text{ s}^{-1}$  [1]. According to collision theory [4] applied to the addition of X-centered radicals (X = Si, Ge, Sn), the preexponential factor is calculated by the formula  $A = 1.0 \times 10^9 (r_{\text{C-X}}/r_{\text{C-C}})^2$ . The parameters  $\Delta\Delta H_e = 0.5hN_A(\nu_{\text{Y=Z}} - \nu_{\text{Y-Z}} - \nu_{\text{X-Y}})$  and  $\Delta E_e = 0.5hN_A(\nu_{\text{Y=Z}} - \nu_{\text{Y-Z}})$  and the coefficients  $\alpha = b/b_{\text{Y-X}}$  and  $\gamma = (b - b_{\text{Y-Z}})/b_{\text{Y-Z}}$  for the considered reactions are given in Table 2.

The parameter  $br_e$  characterizes the whole class of reactions. Each class of reactions can be characterized by the classical potential barrier  $E_{e,0} = E_e$  at  $\Delta H_e = 0$  [2]. This value contains information concerning the role of other factors (along with the reaction enthalpy) in the activation of the reactions:

$$E_{e,0} = \left\{ \frac{br_e}{\alpha + \gamma} \right\}^2. \quad (5)$$

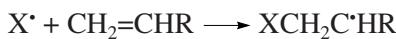
In the framework of one class of the reactions,  $br_e$ ,  $\alpha$ , and  $\gamma$  are constant values. This makes it possible to derive the activation energy from the enthalpy. Transformation of Eq. (4) gives the following equation for calculation of the activation energy of addition through the reaction enthalpy

$$\sqrt{E_e} = B \left\{ \alpha \sqrt{1 + \frac{\Delta H_e}{Bbr_e}} - \gamma \right\}, \quad (6)$$

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

$$\sqrt{E_e} = \frac{br_e}{\alpha + \gamma} + \frac{\alpha \Delta H_e}{2br_e}. \quad (7)$$

The enthalpy of the addition reaction (in kJ/mol)



was calculated using the thermochemical equation

$$\Delta H = \Delta H(\text{CH}_3\text{CH}_2\text{R}) - \Delta H(\text{CH}_2=\text{CHR}) + D(-\text{CH}_2-\text{H}) + D(-\text{CRH}-\text{H}) + D(\text{X}-\text{C}) - 436, \quad (8)$$

where 436 kJ/mol is the dissociation energy of a hydrogen molecule.

The dissociation energy of the X-C bonds was calculated by the thermochemical equation

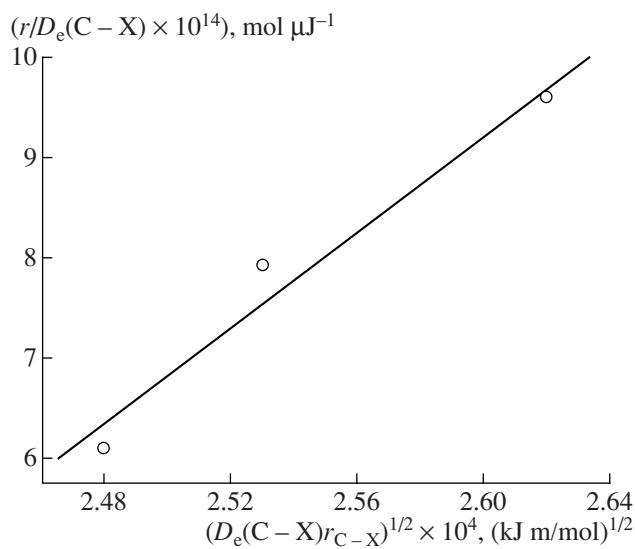
$$\Delta D_{\text{R}-\text{X}} = -\Delta H(\text{R}'\text{X}) + \Delta H(\text{XH}) + D(\text{R}'-\text{H}) + D(\text{X}-\text{H}) - 436. \quad (9)$$

The enthalpies of formation of the molecules were borrowed from a handbook [5], and the dissociation energies of the C-H and X-H bonds were taken from [6].

## RESULTS AND DISCUSSION

The classical enthalpies ( $\Delta H_e$ ), rate constants,  $E_e$ , and the  $br_e$  values calculated by formula (3) for the reactions of addition of  $\text{Et}_3\text{Si}^\bullet$ ,  $\text{Bu}_3\text{Ge}^\bullet$ , and  $\text{Bu}_3\text{Sn}^\bullet$  to various olefins are given in Table 3.

It can be seen that all reactions of  $\text{Et}_3\text{Si}^\bullet$  with  $\text{CH}_2=\text{CHR}$  belong to one class and are characterized by the parameter  $br_e = 18.90 \pm 0.14$  (kJ/mol) $^{1/2}$  and  $E_{e,0} = 94.1 \pm 2.4$  kJ/mol (Eq. (5)). To reveal the influence of



The  $r_e/D_e(\text{C-X})$  ratio versus  $(D_e(\text{C-X})r_{\text{C-X}})^{1/2}$  for the addition of the silyl, germanyl, and stannyl radicals to the double bonds.

the atom bearing the free valence on the activation energy of addition, we compared not  $E_{e,0}$ , which are affected by the force constants of the bonds (the  $\alpha$  and  $\gamma$  coefficients, Eq. (5)), but the  $r_e$  parameters of the reactions of  $\text{Et}_3\text{Si}^\bullet$ ,  $\text{Bu}_3\text{Ge}^\bullet$ , and  $\text{Bu}_3\text{Sn}^\bullet$  with  $\text{CH}_2=\text{CMeCOOMe}$ . The dependence of the  $r_e/D_e$  ratio on the  $(D_e r_{\text{C-X}})^{1/2}$  product is presented in the figure. The dependence is linear and is described by the formula

$$\frac{r_e}{D_e(\text{C-X})} = -5.3 \times 10^{-13} + 2.4 \times 10^{-9} \sqrt{D_e(\text{C-X})r_{\text{C-X}}}. \quad (10)$$

It follows from this formula that the radius of the atom bearing the free valence (it is characterized by the  $r_{\text{C-X}}$  bond length) and the strength of the forming bond  $D_e(\text{C-X})$  exert a mutually dependent effect on  $r_e$  and, hence, on the activation energy (see formula (5) for  $E_{e,0}$ ). This is in qualitative agreement with the Satoh formula [10], which describes the energy of the non-bonding orbital  $U$  as the magnitude that simultaneously depends on the  $D_e$  bond energy and  $r$  interatomic distance

$$U(D_e, r) = D_e \{ \exp(-b D_e^{-1/2} r) + 0.5 \exp(-2b D_e^{-1/2} r) \}, \quad (11)$$

where  $D_e$  is the dissociation energy of the bond,  $2b^2$  is the force constant, and  $r$  is the interatomic distance.

For the reactions of  $\text{Et}_3\text{Si}^\bullet$  with symmetrically substituted ethylene derivatives  $\text{RCH}=\text{CHR}$ , the  $br_e$  and  $E_{e,0}$  parameters are much higher (Table 3):  $br_e = 20.27 \pm 0.67$  (kJ/mol) $^{1/2}$  and  $E_{e,0} = 108.3 \pm 7.2$  kJ/mol (formula (5)). Evidently, this is the result of the steric hindrance to the attack of the silyl radical on the C atoms with the R substituent. The contribution of the

**Table 3.** Enthalpies  $\Delta H_e$ , activation energies  $E_e$ , and parameters  $br_e$  of the additions of the silyl, germanyl, and stanny radicals to unsaturated compounds

Reaction	$-\Delta H_e$ , kJ/mol	$k(300\text{ K})$ , $1\text{ mol}^{-1}\text{ s}^{-1}$	$E_e$ , kJ/mol	$br_e$ , (kJ/mol) $^{1/2}$	Reference
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CH}_2$	94.3	$2.2 \times 10^7$	12.8	18.79	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHBu}$	91.3	$4.8 \times 10^6$	14.8	18.76	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHBu}$	91.3	$3.9 \times 10^6$	15.3	18.82	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCMe}_3$	93.5	$3.7 \times 10^6$	15.5	19.02	[7]
$\text{Et}_3\text{Si}^\cdot + \text{C}_6\text{H}_10=\text{CH}_2$	96.8	$7.4 \times 10^6$	13.7	19.10	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHR}$				Average: $br_e = 18.90 \pm 0.13$	
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CCl}_2$	112.5	$2.7 \times 10^8$	4.8	19.35	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CMeCOOMe}$	100.4	$4.6 \times 10^8$	3.4	18.16	[7]
$\text{Et}_3\text{Si}^\cdot + E\text{-EtCH=CHEt}$	91.6	$9.5 \times 10^5$	20.6	19.41	[7]
$\text{Et}_3\text{Si}^\cdot + \text{C}_6\text{H}_10$	95.7	$2.2 \times 10^6$	18.5	19.53	[7]
$\text{Et}_3\text{Si}^\cdot + \text{C}_6\text{H}_10$	102.7	$9.4 \times 10^5$	20.6	20.30	[7]
$\text{Et}_3\text{Si}^\cdot + \text{C}_6\text{H}_10$	102.7	$1.5 \times 10^7$	14.9	19.71	[7]
$\text{Et}_3\text{Si}^\cdot + E\text{-CHCl=CHCl}$	119.7	$8.9 \times 10^6$	15.0	21.05	[7]
$\text{Et}_3\text{Si}^\cdot + Z\text{-CHCl=CHCl}$	120.1	$2.1 \times 10^7$	12.9	20.86	[7]
$\text{Et}_3\text{Si}^\cdot + \text{MeCH=CHCOOMe}$	127.3	$4.3 \times 10^7$	9.3	21.02	[7]
$\text{Et}_3\text{Si}^\cdot + \text{RCH=CHR}$				Average: $br_e = 20.27 \pm 0.66$	
$\text{Et}_3\text{Si}^\cdot + E\text{-CH}_2=\text{CHCH=CHMe}$	141.7	$1.4 \times 10^8$	6.4	21.76	[7]
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + E\text{-CH}_2=\text{CHCH=CHMe}$	137.0	$7.6 \times 10^7$	7.8	21.01	[8]
$\text{R}_3\text{Si}^\cdot + \text{C}_6\text{H}_10$	149.5	$3.8 \times 10^6$	17.1	21.98	[7]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCH=CHR}$				Average: $br_e = 21.58 \pm 0.41$	
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHPh}$	133.8	$2.2 \times 10^8$	5.3	21.06	[7]
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + \text{CH}_2=\text{CHPh}$	129.1	$5.9 \times 10^7$	8.4	21.06	[8]
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + \text{CH}_2=\text{CPh}_2$	144.4	$1.04 \times 10^8$	7.0	22.02	[8]
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCN}$	136.2	$1.1 \times 10^9$	0.8	20.62	[7]
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + \text{CH}_2=\text{CHCN}$	131.5	$6.3 \times 10^7$	8.2	21.22	[8]
$\text{R}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCN}$				Average: $br_e = 20.92 \pm 0.30$	

Table 3. (Contd.)

Reaction	$-\Delta H_e$ , kJ/mol	$k(300\text{ K})$ , $1\text{ mol}^{-1}\text{ s}^{-1}$	$E_e$ , kJ/mol	$br_e$ , (kJ/mol) $^{1/2}$	Reference
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + \text{CH}_2=\text{CPh}_2$	144.4	$1.04 \times 10^8$	7.0	22.02	[8]
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CMeCOOMe}$	62.1	$1.2 \times 10^8$	6.5	14.08	[9]
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CCl}_2$	73.9	$1.0 \times 10^9$	6.9	15.25	[9]
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHPh}$	95.5	$8.6 \times 10^7$	7.2	17.14	[9]
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHCN}$	97.9	$1.8 \times 10^8$	5.4	17.12	[9]
$\text{Bu}_3\text{Ge}^\cdot + E\text{-CH}_2=\text{CHCH=CHMe}$	103.4	$4.6 \times 10^7$	8.8	17.95	[9]
$\text{Bu}_3\text{Ge}^\cdot + Z\text{-CH}_2=\text{CHCH=CHMe}$	108.7	$4.0 \times 10^7$	9.1	18.39	[9]
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHCH=CHMe}$				Average: $br_e = 18.17 \pm 0.22$	
$\text{Bu}_3\text{Ge}^\cdot +$ 	108.5	$6.4 \times 10^5$	21.9	19.65	[9]
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CMeCOOMe}$	20.6	$1.2 \times 10^8$	7.5	9.42	[9]
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHPh}$	56.0	$9.9 \times 10^7$	7.9	13.73	[9]
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHCN}$	56.4	$8.8 \times 10^7$	8.3	14.04	[9]
$\text{Bu}_3\text{Sn}^\cdot + E\text{-CH}_2=\text{CHCH=CHMe}$	61.9	$6.8 \times 10^7$	8.9	14.68	[9]
$\text{Bu}_3\text{Sn}^\cdot + Z\text{-CH}_2=\text{CHCH=CHMe}$	67.2	$6.8 \times 10^7$	8.9	15.20	[9]
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHCH=CHMe}$				Average: $br_e = 14.94 \pm 0.26$	
$\text{Et}_3\text{Si}^\cdot + \text{EtCHO}$	179.0	$1.2 \times 10^7$	14.4	29.00	[10]
$\text{Et}_3\text{Si}^\cdot + \text{cyclo-C}_6\text{H}_{10}\text{O}$	175.3	$6.5 \times 10^5$	21.7	29.70	[10]
$\text{Et}_3\text{Si}^\cdot + \text{cyclo-C}_5\text{H}_8\text{O}$	177.1	$7.5 \times 10^5$	21.4	29.79	[10]
$\text{Et}_3\text{Si}^\cdot + \text{RCHO}$				Average: $br_e = 29.50 \pm 0.33$	
$\text{Et}_3\text{Si}^\cdot + \text{PhC(O)Me}$	211.8	$1.2 \times 10^7$	14.4	31.20	[10]
$\text{Et}_3\text{Si}^\cdot + \text{Ph}_2\text{C(O)}$	220.0	$3.0 \times 10^7$	12.2	31.42	[10]
$\text{Et}_3\text{Si}^\cdot + \text{PhC(O)R}$				Average: $br_e = 31.31 \pm 0.11$	

steric hindrance to the activation energy is  $\Delta E_s = E_{e,0}(\text{RCH=CHR}) - E_{e,0}(\text{CH}_2=\text{CHR}) = 108.3 - 94.1 = 14.2 \text{ kJ/mol}$ . For comparison we can present  $\Delta E_s$  for the reactions of the methyl radical with  $\text{RCH=CHR}$ :  $\Delta E_s = 8.3 \text{ kJ/mol}$  [2]. We can see that, for the reactions of the silyl radicals with a large atom bearing the free valence,

the contribution of the steric effect to the activation energy is greater:  $\Delta\Delta E_s = 14.3 - 8.3 = 5.9 \text{ kJ/mol}$ .

When the radical attacks the double bond whose  $\alpha$  position is occupied by another double bond or aromatic radical, then in the TS the reaction center begins to interact with the  $\pi$  electrons. As a result of this inter-

**Table 4.** Contribution of the reaction enthalpy ( $\Delta E_H$ ) and the effect of the  $\alpha$ - $\pi$ -bonds ( $\Delta E_\pi$ ) on the activation energy of the addition reactions

Reaction	$E_e$ , kJ/mol	$E_{e,0}$ , kJ/mol	$-\Delta E_H$ , kJ/mol	$\Delta E_\pi$ , kJ/mol
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHR}$	15.3	94.1	78.8	0
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCH}=\text{CHR}$	7.1	122.7	115.6	28.6
$\text{Et}_3\text{Si}^\cdot + \text{CH}_2=\text{CHPh}$	5.3	116.9	111.6	22.8
$(\text{Me}_3\text{Si})_3\text{Si}^\cdot + \text{CH}_2=\text{CPh}_2$	7.0	127.8	120.8	33.7
$\text{R}_3\text{Si}^\cdot + \text{CH}_2=\text{CHCN}$	8.0	115.3	107.3	18.0
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CMeCO}_2\text{Me}$	6.5	58.6	52.1	0
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHCH}=\text{CHR}$	9.0	97.6	88.6	39.0
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHCN}$	8.3	86.6	78.3	28.0
$\text{Bu}_3\text{Ge}^\cdot + \text{CH}_2=\text{CHPh}$	7.9	86.8	78.9	28.2
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CMeCO}_2\text{Me}$	7.5	25.2	17.7	0
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHCH}=\text{CHR}$	8.9	63.5	54.1	38.3
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHPh}$	7.9	53.6	45.7	28.4
$\text{Bu}_3\text{Sn}^\cdot + \text{CH}_2=\text{CHCN}$	8.3	56.1	47.2	30.9
$\text{R}_3\text{Si}^\cdot + \text{RCH}(\text{O})$	21.4	142.8	121.4	0
$\text{R}_3\text{Si}^\cdot + \text{PhC}(\text{O})\text{R}$	14.4	159.7	145.3	16.9
$\text{R}_3\text{Si}^\cdot + \text{Ph}_2\text{C}(\text{O})$	12.2	161.9	149.7	19.1

action, the electron density on the reaction center is enhanced and the activation energy increases [11]. This effect is also observed in the addition reaction of the silyl, germanyl, and stannyl radicals. The contribution of this interaction to the activation energy  $\Delta E_\pi$  achieves 34 kJ/mol for the silyl radicals, 39 kJ/mol for the germanyl, and 38 kJ/mol for the stannyl radicals. The  $\Delta E_\pi$  values and the enthalpy contribution to the activation energy  $\Delta E_H = E_e - E_{e,0}$  are given in Table 4.

Thus, the following factors affect the reactivity of the silyl, germanyl, and stannyl radicals: (1) the reaction enthalpy (see formula (5)), (2) the triplet repulsion, and (3) the radius of the atom bearing the free valence. The latter two factors are mutually related (see Eq. (10)). In addition, the activation energy is affected by (4) the presence of the substituent at the C atom, which is attacked by the radical (steric effect) and (5) the  $\pi$ -bond adjacent to the reaction center of the TS, increasing the activation energy.

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