The reactivity of silanes in free-radical reactions: analysis in terms of the parabolic model of the transition state

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Rate constants and activation energies of free-radical reactions of silanes and silyl radicals were analyzed in terms of the parabolic model of the transition state. The kinetic parameters were estimated for 16 groups of reactions of silanes and silyl radicals. These parameters were used to calculate the activation energies for 112 free-radical reactions and to estimate the dissociation energies of the Si—H bond for 21 compounds and those of the C—Cl bond for 12 substituted benzyl chlorides. Triplet repulsion, electronegativity, and radii of atoms of the reaction center of the transition state were shown to play an important rôle in the formation of the activation barrier.

Key words: activation energy, atomic radius, bond dissociation energy, electronegativity, free-radical reactions, parabolic model, silanes, silyl radicals, triplet repulsion.

Radical reactions of silanes are widely used in synthesis, technique, and chemical technology.[1] Silanes are very active as reducing agents and react readily in various radical reactions.[2]

It is interesting and important to know which structural factors determine the reactivity of silanes in radical reactions. The parabolic model of the bimolecular radical reaction is an efficient method for analysis of reactivity at the semi-empirical level.[3–6] This model makes it possible to divide radical reactions into classes, and each class into groups to compare these groups and reveal the structural factors that determine the activation barrier for the reactions of a particular group. Analysis of reactions of radicals with C—H, N—H, and O—H bonds in organic compounds indicates the important role of such factors as the triplet repulsion in the transition state, the electron affinity, and the force constants of reacting bonds.[4,5] Since silicon appears after carbon in Group IV in the Periodical table, it is of interest to analyze the reactivity of silanes and silyl radicals and compare it to that of hydrocarbons and alkyl radicals. Several structural distinctions between silanes and hydrocarbons are evident. Elements C and Si differ in atomic radius, electron affinity, and force constants of C—H and Si—H bonds. However, it is not clear to what extent these factors affect the reactivity of silanes and hydrocarbons in radical reactions. In this work, we attempted to answer these questions using the parabolic model.

Parabolic model of bimolecular radical reaction

In the parabolic model,[3] a reaction of radical cleavage such as the reaction

$$R^{\cdot} + R'_3SiH \rightarrow RH + R'_3Si^{\cdot},$$

is considered to be the result of intersection of two potential energy curves. One of them describes the dependence of the potential energy on the amplitude of vibration of the attacked Si—H bond, and another describes the same dependence for the forming C—H bond. It is assumed that the transition state can be considered as the intersection of these curves, and the vibration of atoms along the bond line is harmonic. In this case, the elementary radical reaction is characterized by the parameters presented below.

1. Enthalpy of the reaction ΔH_e, which includes the difference between the zero energies of reacting bonds:

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

where D_i and D_f are the dissociation energies of the Si—H and R—H bonds, ν_i and ν_f are the frequencies of their stretching vibrations, respectively; h is Planck's constant; and L is Avogadro's number.

2. Activation energy E_e, which includes the energy of the zero vibration of the attacked bond and is related to the experimentally determined activation energy (E) by the simple relation

$$E_e = E + 0.5hL\nu - 0.5RT. \qquad (2)$$

3. Distance r_e between minimum points of two potential curves of reacting bonds.

4. Parameters b_i and b_f, which are dynamic characteristics ($2b^2$ is the force constant of the bond) of the reacting Si—H ($b_i = \pi\nu_i(2\mu_i)^{1/2}$) and R—H bonds ($b_f = \pi\nu_f(2\mu_f)^{1/2}$); μ_i and μ_f are the reduced masses of atoms forming these bonds.

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The parameters listed above are related to each other by the following relation ($\alpha = b_i/b_f$, $b = b_i$):

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \qquad (3)$$

For this consideration, all reactions of radical cleavage can be divided into classes, and each class is characterized by a pair of coefficients b_i and b_f or $b = b_i$ and α. Each class is divided into groups, and a particular group of reactions is characterized by the parameter r_e or activation energy of the thermoneutral reaction $E_{e,0}$ ($\Delta H_e = 0$):

$$E_{e,0} = (br_e)^2(1 + \alpha)^{-2}. \qquad (4)$$

All the experimentally studied reactions,[3] which were collected and analyzed in this work, can be grouped in 11 classes (see Table 1, α values) and 16 groups (see Table 1, br_e values). Within each group, the parameter br_e = const within the range of inaccuracy caused by the spread of experimental data associated with the errors in determining the rate constant and activation energy. In calculating E from the value of the rate constant k using the Arrhenius equation ($E = -RT\ln(A/k)$), the pre-exponential factor A is assumed to be constant when related to one Si—H bond for each group of radical reactions (see Table 1).

As can be seen in Table 1, the parameter br_e varies from one group to another within a wide range from 9.5 to 25 (kJ mol^{-1})$^{1/2}$, and the $E_{e,0}$ values vary from 35 to 100 kJ mol^{-1}. The parameter r_e also varies substantially (from 3.3 to 7.4 $\cdot$ 10^{-11} m). Since the E_e values for the reactions of atoms and radicals with C—H bonds are lower than those for the reactions with Si—H bonds, it can be assumed that the Si—H bond is more susceptible to attack than C—H. This specific feature will be considered in detail below.

Determination of dissociation energies of C—H and Si—H bonds

The equations of the parabolic model can be used for estimation of the bond dissociation energy from the kinetic data.[44] If the ratio of rate constants of two reactions is experimentally measured

$$R^{\cdot} + R_3'SiH \rightarrow RH + R_3'Si^{\cdot} \ (k_i),$$

$$R^{\cdot} + R_3''SiH \rightarrow RH + R_3''Si^{\cdot} \ (k_1),$$

the difference between the activation energies of these reactions can be calculated from this ratio using the Arrhenius equation, since the pre-exponential factor A is the same for the reactions of one group:

$$\Delta E_i = E_i - E_1 = -RT\ln(k_1/k_i). \qquad (5)$$

The difference in enthalpies of reactions (1) and (i) $\Delta(\Delta H_{e,i})$ is equal to the difference in bond strengths D_i and D_1: $\Delta(\Delta H_{e,i}) = \Delta H_i - \Delta H_1 = D_i - D_1$. In turn, $\Delta\Delta H_{e,i}$ is related to $E_{e,i}$ and $E_{e,1}$ by the following equation:[44]

$$\Delta D_i = 2br_e\alpha^{-2}(E_{e,i}{}^{1/2} - E_{e,1}{}^{1/2}) - (1 - \alpha^{-2})\alpha^{-2}\Delta E_i. \qquad (6)$$

Thus, using the known parameter br_e and experimentally measured activation energies E_1 and E_i (for the transition from E to E_e, see relation (2)), we can calculate $\Delta D_i = D_i - D_1$, and $D_i = D_1 + \Delta D_i$ can be determined if D_1 is known. The results of the determination of the Si—H bond strength are presented in Table 2. The D_1 values for several silanes were taken from the previously published work.[2] For diphenylsilane, the D_{Si-H} values calculated from the results of two different measurements are very close (365.3 and 366.8 kJ mol^{-1}). For phenylsilanes, the D_{Si-H} value decreases as the number of phenyl groups increases from 377 kJ mol^{-1} for $PhSiH_3$

Table 1. Kinetic parameters of reactions of atoms and radicals with silanes

Reaction	α	br_e /(kJ mol^{-1})$^{1/2}$	$E_{e,0}$ /kJ mol^{-1}	$r_e \cdot 10^{11}$/m	$(r^{\#}/r_e)_0$	$A \cdot 10^{-8}$ /L mol^{-1} s^{-1}	Ref.
$H^{\cdot} + SiH_4$	0.692	11.69±0.32	47.7	4.086	0.591	200	7
$O + SiH_4$	0.604	10.83±0.20	45.6	3.785	0.623	100	8—15
$Br^{\cdot} + SiH_4$	0.814	11.14±0.10	37.7	3.894	0.551	600	16—18
$HO^{\cdot} + SiH_4$	0.591	9.45	35.3	3.303	0.628	870	8,11
$H^{\cdot} + R_3SiH$	0.668	11.29±0.32	45.8	4.096	0.599	200	7
$H^{\cdot} + PhR_2SiH$	0.668	11.63	47.2	4.220	0.591	20	19
$R^{\cdot} + SiH_4$	0.750	13.65±0.26	60.8	4.771	0.571	10	7, 20—23
$R^{\cdot} + R'_3SiH$	0.723	13.18±0.32	58.5	4.782	0.580	10	7, 20, 22, 24—29
$CX_3^{\cdot} + R_3SiH$	0.723	12.10±0.29	49.3	4.390	0.580	1.0	30—32
$CX_3^{\cdot} + PhR_2SiH$	0.723	12.82	55.4	4.481	0.580	1.0	31
$RO^{\cdot} + R_3'SiH$	0.581	10.13±0.15	41.1	3.676	0.632	10	33—39
$RO_2^{\cdot} + R_3'SiH$	0.599	12.41	60.2	4.503	0.625	1.0	2
$R_3Si^{\cdot} + R_3'SiH$	1.00	13.69	46.9	4.967	0.500	20	39
$R_3Si^{\cdot} + R_3'CCl$	1.500	23.74±1.0	90.2	7.007	0.400	25	34, 36, 40—42
$R_3Si^{\cdot} + ArCH_2Cl$	1.500	24.77	98.6	7.311	0.400	25	36, 40, 42, 43
$R_3Si^{\cdot} + ClCH_2CH{=}CH_2$	1.500	25.00	100.0	7.379	0.400	25	40

Table 2. Estimation of dissociation energies of Si—H bonds from kinetic data (formulas (5) and (6))

Silane	R_1H	$R^\cdot$	T/K	n_jk_i/n_ik_j	ΔE	ΔD	D	Ref.
					kJ mol^{-1}			
$Bu^t{}_2MeSi—H$	Et_3SiH	$C_6F_{13}CF_2^\cdot$	303	21.7	−7.8	−25.2	372.8	45
$Bu^t{}_3Si—H$	Et_3SiH	$C_6F_{13}CF_2^\cdot$	303	68.0	−10.6	−35.7	362.3	45
$PhMe_2Si—H$	Ph_3SiH	n-$C_{16}H_{33}^\cdot$	363	0.37	3.0	9.2	371.0	46
$Ph_2HSi—H$	$PhSiH_3$	$PhMe_2CCH_2^\cdot$	383	2.90	−3.4	−10.2	366.8	29
$Ph_2HSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.66	1.2	3.5	365.3	47
$Ph_2MeSi—H$	Ph_3SiH	n-$C_{16}H_{33}^\cdot$	363	0.63	1.4	4.4	366.2	46
$Ph_3Si—H$	$PhSiH_3$	$PhMe_2CCH_2^\cdot$	383	4.77	−5.0	−15.2	361.8	29
$PhMeFSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.05	8.5	23.6	385.4	47
$PhMeClSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.17	5.2	14.8	376.6	47
$Ph(C_6F_5)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.19	4.8	13.7	375.5	47
$Ph(Ph_3Si)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	4.83	−4.6	−14.1	347.7	47
$(Me_3CCH_2)PhMeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.60	1.5	4.4	366.2	47
$(3\text{-}CF_3C_6H_4)Me_2Si—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.76	0.8	2.4	364.2	47
$(3\text{-}CF_3C_6H_4)_3Si—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.24	4.2	12.0	373.8	47
1-NpPhMeSi—H	Ph_3SiH	$Cl_3C^\cdot$	350	0.68	1.1	3.2	365.0	47
$1\text{-}Np(3\text{-}FC_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.43	2.5	7.4	369.2	47
$1\text{-}Np(3\text{-}MeOC_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.59	1.5	4.4	366.2	47
$1\text{-}Np(3\text{-}CF_3C_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.39	2.7	7.8	369.6	47
$1\text{-}Np(3\text{-}MeC_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.82	0.6	1.8	363.6	47
$1\text{-}Np(4\text{-}CF_3C_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.35	3.1	8.9	370.7	47
$1\text{-}Np(4\text{-}MeOC_6H_4)MeSi—H$	Ph_3SiH	$Cl_3C^\cdot$	350	0.92	0.2	0.6	362.4	47

Note. Np is naphtyl.

to 362 kJ mol^{-1} for Ph_3SiH. The C—Cl bond dissociation energies for chlorotoluenes were calculated from the kinetic data for the reactions of silyl radicals with substituted chlorotoluenes (Table 3). For different substituents, the D_{C-Cl} values vary from 277 to 292 kJ mol^{-1}. Electronegative substituents weaken and electropositive substituents strengthen the C—Cl bond in benzyl chloride.

Estimation of activation energy for radical reactions of silanes

The kinetic parameters of the radical reactions of silanes calculated from the kinetic data (see Table 1) make it possible to calculate activation energies for a wide range of reactions involving silanes. The activation energy E_e is related to ΔH_e and parameters br_e and α by the following relation:[4]

$$E_e{}^{1/2} = br_e(1 - \alpha^2)^{-1}\{1 - \alpha[1 - (br_e)^{-2}(1 - \alpha^2)\Delta H_e]^{1/2}\}.(7)$$

At $b_i = b_f$, $\alpha = 1$ and the equation takes the form

$$E_e{}^{1/2} = 0.5br_e + 0.5(br_e)^{-1}\Delta H_e. \qquad (8)$$

The results of the calculation of the activation energies (T = 300 K) are presented in Table 4. The energy of the zero vibration of the Si—H bond for SiH_4 is 13.1 kJ mol^{-1}, and for silanes with alkyl substituents, it is 12.6 kJ mol^{-1} (these values were used for the calculations of E from E_e and ΔH_e from ΔH with equations (1) and (2)). The enthalpies of the corresponding reactions were determined using the D_{Si-H} values in Ref. 2 and Table 3. The activation energies calculated in this work and measured experimentally are compared in Table 5. In most cases, these values are similar: the mean value $\Delta E = |E_{exp} - E_{calc}|$ = 1.3 kJ mol^{-1}. Thus, the experimental and calculated E values agree well.

Structural and physical factors determining reactivity of silanes

The analysis of activation energies for the reactions with radicals attacking C—H and O—H bonds showed that along with the enthalpy of the reaction, triplet repulsion and electron affinity strongly affect the activation energy.[5] In the case where

$$X^\cdot + HY \rightarrow XH + Y^\cdot,$$

the hydrogen atom in the transition state moves from Y to X along the bond line X—Y. Since three electrons

Table 3. Estimation of dissociation energies of the C—Cl bond in substituted benzyl chlorides from kinetic data[43]

RCl	k/k_j	E	ΔH	D
		kJ mol^{-1}		
$3\text{-}MeC_6H_4CH_2Cl$	1.47	−1.0	−3.5	289.0
$4\text{-}MeC_6H_4CH_2Cl$	0.98	0.0	0.0	292.5
$4\text{-}Me_3CC_6H_4CH_2Cl$	1.07	−0.2	−0.6	291.9
$3,5\text{-}(CF_3)_2C_6H_3CH_2Cl$	4.89	−3.9	−14.9	277.6
$3,5\text{-}Cl_2C_6H_3CH_2Cl$	4.13	−3.5	−13.3	279.2
$4\text{-}CNC_6H_4CH_2Cl$	3.69	−3.2	−12.2	280.3
$3\text{-}CF_3C_6H_4CH_2Cl$	2.00	−1.7	−6.3	286.2
$3\text{-}FC_6H_4CH_2Cl$	1.87	−1.5	−5.7	286.8
$4\text{-}FC_6H_4CH_2Cl$	1.47	−1.0	−3.5	289.0
$3\text{-}ClC_6H_4CH_2Cl$	1.64	−1.2	−4.5	288.0
$3\text{-}MeOC_6H_4CH_2Cl$	1.38	−0.8	−2.9	289.6
$3,4\text{-}Cl_2C_6H_3CH_2Cl$	2.13	−1.9	−6.9	285.6

Table 4. Activation energies (*E*) for abstraction of the H atom from silanes (calculated from relations (2), (7), and (8)

Silane	E/kJ mol^{-1}						
	$Me^{\cdot}$	$Et^{\cdot}$	$Me_2HC^{\cdot}$	$Me_3C^{\cdot}$	$Cl_3C^{\cdot}$	$Me_3CO^{\cdot}$	$Et_3Si^{\cdot}$
SiH_4	27.1	33.8	39.7	43.8	30.8	10.8	28.8
$MeSiH_3$	26.3	32.9	38.7	42.7	31.6	11.3	29.7
Me_3SiH	30.0	37.0	43.1	47.3	36.1	14.0	35.2
Et_3SiH	30.2	37.2	43.3	47.6	36.3	14.2	35.5
$(Me_3Si)Me_2SiH$	23.9	30.2	35.7	39.5	28.6	9.5	26.0
$(Me_3Si)_3SiH$	16.3	21.8	26.6	29.9	19.6	4.2	15.0
$(MeS)_3SiH$	20.4	26.3	31.5	35.1	24.4	7.0	20.9
$PhSiH_3$	23.6	29.9	35.4	39.2	34.2	9.3	25.6
$PhMeSiH_2$	25.1	31.5	37.2	41.1	36.1	10.4	27.8
$PhMe_2SiH$	21.8	27.9	34.9	36.9	32.0	8.0	23.0
Ph_2SiH_2	20.2	26.1	31.3	34.9	30.0	6.9	20.6
Ph_3SiH	19.2	25.0	30.1	33.6	28.8	6.2	19.1
$PhMeFSiH$	26.1	32.7	38.4	42.4	37.4	11.2	29.4
$PhMeClSiH$	23.4	29.7	35.2	39.0	34.1	9.2	25.4
$(Ph_3Si)PhMeSiH$	15.5	20.9	25.6	27.3	24.3	3.6	13.7
$(Me_3CCH_2)PhMeSiH$	20.4	26.4	31.6	35.2	30.4	7.0	20.9

involved in the bond rearrangement cannot be localized on the bonding orbital of X—Y (Pauli rule), the antibonding orbital of the X—Y bond participates in the formation of the transition state, and the stronger the bond, the higher the activation energy of the thermoneutral reaction $E_{e,0}$.[4,5] Since in the parabolic model of transition state $E_{e,0}$ depends on both the distance r_e and force constants of the X—H and Y—H bonds (b and α, see formula (4)), the effect of D_{X-Y} on $E_{e,0}$ can be estimated from the value of parameter r_e.[5] Thus, for the individual reaction, the transition from $E_{e,i}$ to $E_{e,0}$ rules out the effect of the enthalpy, and the transition from $E_{e,0}$ to r_e eliminates the effect of the force constants on the activation energy. Let us compare the r_e values in the symmetrical transition states X...H...X (D are given in kJ mol^{-1}):

	$r_e^2 \cdot 10^{22}$/m	D_{X-Y}	$r_{X-Y} \cdot 10^{11}$/m
O...H...O	8.3	~0	14.6
C...H...C	19.4	376	15.1
Si...H...Si	24.7	354	23.6

It can be seen that for reactions with H atom transfer from oxygen to oxygen, the r_e^2 value is much lower than those for reactions with X = C and X = Si. Comparison of the two latter reactions shows that the triplet repulsion is not the only factor affecting the energy of the symmetrical transition state X...H...X. In fact, for the Si...H...Si configuration, D_{X-Y} is somewhat lower than that for the C...H...C configuration, whereas r_e^2 and, accordingly, $E_{e,0}$ are higher. Thus, the symmetrical transition state is also affected by other factors. One of them is the radius of the atoms between which hydrogen is transferred: the longer the radius, the stronger the repulsion and the longer the r_e distance. Comparison of r_e with the bond length r_{X-X} indicates just this parallelism. A similar dependence is observed in the reactions $X^{\cdot}$ + RH, where X = Cl, Br, and I[5] ($r_e^2 \sim r_X^{1/2}$). As shown by correlation analysis, parameter r_e depends on D_{X-Y} and bond length r_{X-Y} for the reaction groups $R^{\cdot} + SiH_4$, $R^{\cdot} + R_3SiH$, $R_3Si^{\cdot} + R'_3SiH$, and $R^{\cdot}$ + RH as follows:

$$r_e^2 \cdot 10^{22} = 18[(r_{X-Y}/r_{H-H})^{1/2} - 1] + \\ + 13.7(D_{X-Y}/D_{H-H}), \qquad (9)$$

where $r_{H-H} = 7.46 \cdot 10^{-11}$ m is the bond length in the hydrogen molecule, and D_{H-H} = 436 kJ mol^{-1}. The empirical equation (9) proves the important role of the triplet repulsion (D_{X-Y}) and repulsion of electronic shells of X and Y atoms, which changes the bond length r_{X-Y} and the transition state energy.

There is another factor affecting the activation energy with the asymmetrical transition state (X...H...Y), namely, the electron affinity of atoms (radicals) X and

Table 5. Comparison of calculated (see Table 4) and experimental[7—43] values of activation energies (*E*) of free-radical reactions of silanes

Reaction	E_{calc}	E_{exp}	ΔE
	kJ mol^{-1}		
$Me^{\cdot} + SiH_4$	27.1	28.8—30.0	−1.7
$Et^{\cdot} + SiH_4$	33.8	31.6	2.2
$RC^{\cdot}H_2 + Et_3SiH$	37.2	35.6	1.6
$RC^{\cdot}H_2 + PhSiH_3$	29.9	29.4	0.5
$RC^{\cdot}H_2 + PhMe_2SiH$	27.9	27.5	0.4
$RC^{\cdot}H_2 + Ph_2SiH_2$	26.1	26.0	0.1
$RC^{\cdot}H_2 + Ph_3SiH$	25.0	22.4	2.6
$RC^{\cdot}H_2 + (Me_3Si)_3SiH$	21.8	19.6	2.2
$Cl_3C^{\cdot} + Et_3SiH$	39.4	36.2	3.2
$Cl_3C^{\cdot} + Ph_2SiH_2$	30.0	32.4	−2.4
$Cl_3C^{\cdot} + Ph_3SiH$	28.8	28.8	0.0
$RO^{\cdot} + Et_3SiH$	14.2	12.2	2.0
$RO^{\cdot} + PhSiH_3$	9.3	9.5	−0.2
$RO^{\cdot} + Ph_2SiH_2$	7.2	6.8	0.4
$RO^{\cdot} + Ph_3SiH$	6.2	5.5	0.7
$RO^{\cdot} + (Me_3Si)_3SiH$	4.2	5.4	−1.2
$RO^{\cdot} + (MeS)_3SiH$	7.0	7.8	−0.8

Y.[5] Let us compare the r_e values for the reactions with asymmetrical configurations of the transition state (*D* and *EA* are given in kJ mol^{-1}):

	D_{X-Y}	$r_e \cdot 10^{11}/m$	ΔEA
C...H...Si	376	4.78	11
RO...H...Si	477	3.68	221
HO...H...Si	536	3.30	275

On going from X = R to X = RO and HO, the D_{X-Si} value increases and, hence, the triplet repulsion rises, whereas the parameter r_e decreases. This inverse relationship between r_e and D_{X-Si} is the result of the strong effect on the transition state attraction caused by the large difference between the electronegativities (ΔEA) of the O and Si atoms. The antiparallelism between r_e and ΔEA is seen from the ΔEA values presented above: the higher ΔEA, the lower r_e. The same dependence is observed for the reactions of O-centered radicals with hydrocarbons.[5] The difference between the electronegativities of X and Y was estimated from the classical Pauling formula: $\Delta EA = D_{X-Y} - 0.5(D_{X-X} + D_{Y-Y})$. The complete list of the classes of reactions used for the determination of the multi-parametric correlation dependences between r_e and r_{X-Y}, D_{X-Y} and ΔEA is presented in Table 6, included also are the values of parameters taken for the correlation. The following correlation equation was obtained for reactions of various radicals with silanes and hydrocarbons:

$$r_e^2 \cdot 10^{22}/m = 18[(r_{X-Y}/r_{H-H})^{1/2} - 1] + 13.7(D_{X-Y}/D_{H-H}) - 22.4(\Delta EA/D_{H-H}). \qquad (10)$$

For the reactions of hydrogen and bromine atoms with SiH_4 and R_3SiH another correlation equation can be derived:

$$r_e^2 \cdot 10^{22}/m = 12.8[(r_{X-Y}/r_{H-H})^{1/2} - 1] + 13.7(D_{X-Y}/D_{H-H}) - 22.4(\Delta EA/D_{H-H}). \qquad (11)$$

The obtained correlations make it possible to estimate the contribution of each of the physical factors listed above to the activation energy of the thermoneutral reaction for each reaction class. For this purpose, the dependences of $E_{e,0}$ on the force constants of the X—H and Y—H bonds (relation (4)) should be taken into account. The contribution (increment) of orbitals of the X and Y atoms, which depends on the X—Y bond length, is described by the equation

$$\Delta E_R/\text{kJ mol}^{-1} = Bb^2(1 + \alpha)^{-2} \times [(r_{X-Y}/r_{H-H})^{1/2} - 1], \qquad (12)$$

where B = $18 \cdot 10^{-22}$ m for radical reactions and $12.8 \cdot 10^{-22}$ m for atomic reactions. The contribution of the triplet repulsion to $E_{e,0}$ is described by the equation

$$\Delta E_T/\text{kJ mol}^{-1} = 13.7b^2(1 + \alpha)^{-2} \times (D_{X-Y}/D_{H-H}) \cdot 10^{-22}, \qquad (13)$$

and for the contribution of the electron affinity of X and Y, we can write

$$\Delta E_{EA}/\text{kJ mol}^{-1} = -22.4b^2(1 + \alpha)^{-2} \times (\Delta E_{EA}/D_{H-H}) \cdot 10^{-22}. \qquad (14)$$

Table 6. Values of r_e, r_{X-Y}, D_{X-Y}, and ΔEA used for development of correlation equations

Reaction	$r_e \cdot 10^{11}$	$r_{X-Y} \cdot 10^{11}$	$r_e \cdot 10^{11}$*	D_{X-Y}	ΔEA
		m		kJ mol^{-1}	
$H^{\cdot} + SiH_4$	4.086	14.83	4.087	384.4	12.4
$H^{\cdot} + R_3SiH$	4.096	14.76	4.193	397.4	2.4
$Br^{\cdot} + SiH_4$	3.894	21.60	3.728	402.0	151.5
$HO^{\cdot} + SiH_4$	3.303	16.33	3.383	536.0	275.5
$R^{\cdot} + SiH_4$	4.771	18.70	4.552	369.0	27.0
$R^{\cdot} + R'_3SiH$	4.782	18.70	4.665	376.0	11.0
$RO^{\cdot} + R'_3SiH$	3.676	16.33	3.516	477.0	221.3
$R_3Si^{\cdot} + R'_3SiH$	4.967	23.59	5.013	354.0	0.0
$H^{\cdot} + H_2$	3.692	7.461	3.703	436.0	0.0
$H^{\cdot} + RH$	3.762	10.59	3.946	438.4	32.4
$R^{\cdot} + R'H$	4.414	15.13	4.411	376.1	0.0
$RO^{\cdot} + R'H$	3.553	14.16	3.668	361.1	92.3
$RO_2^{\cdot} + R'H$	3.687	14.26	3.701	272.0	34.0

* The values were calculated from formulas (10) and (11).

It follows from the results of calculations of the increments presented in Table 7 that the triplet repulsion makes a great contribution to the activation energy of the radical reactions involving silanes. In the case of the reactions of silanes with oxygen-centered radicals, the great difference between the electron affinities of Si and O atoms reduces considerably the activation barrier of the thermoneutral reaction.

Let us compare the reactions of alkyl and silyl radicals with C—H and Si—H bonds (*E* and *D* are presented in kJ mol^{-1}):

	$R^{\cdot}$+HR	$R^{\cdot}+R'_3SiH$	$R_3Si^{\cdot}+R'_3SiH$
$b(1 + \alpha)^{-1}$	1.87	1.60	1.38
$r_e \cdot 10^{11}/m$	4.41	4.78	4.97
$r_{X-Y} \cdot 10^{11}/m$	1.46	1.87	2.36
D_{X-Y}	376.0	376.0	354.0
$\Delta E_{e,0}$	55.6	58.5	46.9

It is seen that on going from reactions of the class $R^{\cdot}$ + RH to $R_3Si^{\cdot}$ + R'_3SiH, the parameter r_e increases mainly due to the increasing radii of atoms in the reaction center (values r_{X-Y}). However, this does not result in a corresponding increase in $E_{e,0}$, because, first,

Table 7. Contributions of various physical factors in the activation energy $E_{e,0}$

Reaction	$b(1 + \alpha)^{-1}$ /(kJ $mol^{-1})^{1/2}$	ΔE_R	ΔE_T	ΔE_{EA}	$\Delta E_R+\Delta E_T+$ $+ \Delta E_{EA}$
		kJ mol^{-1}			
$H^{\cdot} + SiH_4$	1.69	15	34	−2	47
$Br^{\cdot} + SiH_4$	1.58	22	32	−19	35
$H^{\cdot} + R_3SiH$	1.65	14	34	0	48
$R^{\cdot} + SiH_4$	1.63	28	31	−1	58
$R^{\cdot} + R'_3SiH$	1.60	27	30	−3	54
$R_3Si^{\cdot} + R'_3SiH$	1.38	27	18	0	45
$RO^{\cdot} + R'_3SiH$	1.74	26	45	−34	37
$HO^{\cdot} + SiH_4$	1.80	28	55	−45	38

Note: R is repulsion of atomic orbitals; T is triplet repulsion; *EA* is electron affinity.

the contribution of the triplet repulsion decreases in this row (values ΔE_T); second, the factor $b(1 + \alpha)^{-1}$, which reflects the role of force constants in the formation of the activation barrier, decreases in the same row. Due to the same reason, the contribution of the triplet repulsion to the $E_{e,0}$ value decreases in this row, although its influence on the r_e parameter remains nearly unchanged.

* * *

The analysis of the kinetic parameters of the radical reactions of silanes showed that their activation energies are determined, along with the reaction enthalpy, by the triplet repulsion and electronegativity of the X atom in the transition state with the reaction center Si...H...X. Both of these factors are also important for the reactions of atoms and radicals with C—H bonds in organic compounds. In the reactions of radicals with Si—H bonds, another factor plays an important role, namely, the radii of atoms forming the reaction center of the transition state (Eqs. (10) and (11)). Compared to carbon, silicon is characterized by a larger atomic radius and a higher energy of repulsion. Accordingly, when other factors remain unchanged, the activation energy of the abstraction of the H atom from the Si—H bond is higher. However, another factor, namely, the force constant of the Si—H bond, has an opposite effect. The lower values of the b coefficient for the Si—H bond than that for the C—H bond explains the enhanced reactivity of the Si—H bond. As a result of the opposite effects of these factors, the activation energies of the thermoneutral reactions $R^{\cdot} + RH$ and $R^{\cdot} + R_3'SiH$ are similar.

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