Kinetics and Catalysis, Vol. 43, No. 1, 2002, pp. 10–18. Translated from Kinetika i Kataliz, Vol. 43, No. 1, 2002, pp. 14–22.

Reactivity of the Ge–H, Sn–H, P–H, and Se–H Bonds in Radical Abstraction Reactions

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Received April 12, 2001

Abstract—The experimental data for the liquid- and gas-phase reactions of atoms and radicals with organoelement compounds $R_{n-1}E–H$

$$X^{\bullet} + H - ER'_{n-1} \longrightarrow XH + R'_{n-1}E^{\bullet},$$

where E = Ge, Sn, P, and Se, are analyzed within the framework of the parabolic model of radical abstraction reactions. The parameters characterizing the activation energies of such reactions involving H, O, and F atoms and $R^{\bullet}$, $RO^{\bullet}$, aryl ($Ar^{\bullet}$), $RO_2^{\bullet}$, and nitroxyl ($AmO^{\bullet}$) radicals are determined. The activation energies for thermally neutral reactions $E_{e,0}$ are calculated. Reactions of a hydrogen atom with the H–element bond are characterized by the close $E_{e,0}$ (kJ/mol) values: 51.4 (GeH_4), 52.8 (PH_3), and 52.6 (SeH_2). The $E_{e,0}$ values for the reactions of alkyl radicals with the Ge–H and Sn–H bonds are also close: $E_{e,0}$ (kJ/mol) = 62.7 (R'_3GeH) and 63.2 (R'_3SnH). Low $E_{e,0}$ values are typical of the reactions of alkoxy radicals ($E_{e,0}$ (kJ/mol) = 43.9 (GeH_4), 46.2 (R'_3GeH), 48.9 (R'_3SnH), 43.8 (PH_3) and oxygen atoms ($E_{e,0}$ (kJ/mol) = 41.0 (GeH_4) and 47.3 (SeH_2). Higher $E_{e,0}$ values are found for the reactions of peroxy radicals ($E_{e,0}$ (kJ/mol) = 62.8 (R'_3GeH) and 60.6 (R'_3SnH)) and nitroxyl radicals ($E_{e,0}$ (kJ/mol) = 81.3 (R'_3GeH) and 77.4 (R'_3SnH). The atomic radius of element E affects the activation energy of a thermally neutral reaction. The E–H bond dissociation energies for seven germanium and two tin compounds, as well as for five phosphites, are calculated from the kinetic data in terms of the parabolic model.

INTRODUCTION

Germanium and tin compounds containing the Ge–H and Sn–H bonds are reducing agents [1] that are widely used in the radical reactions of organic synthesis. They are also often used in kinetic experiments when applying the method of competitive reactions. Kinetic data on radical reactions involving these compounds are scarce, but it is interesting to analyze the rate constants and activation energies of such reactions. Recent analysis of radical abstraction from the C–H, N–H, and O–H bonds of organic compounds in the framework of the parabolic model showed that the X–Y bond strength in the $X^{\bullet}$ + HY reaction and the electronegativities and radii of the X and Y atoms strongly influence the reactivity of these compounds [2]. All these factors are also important in radical abstraction involving organoelement compounds.

CALCULATION PROCEDURE

For the kinetic analysis of the bimolecular radical reactions of hydrogen atom abstraction from the germanium, tin, phosphorus, and selenium compounds

$$R^{\bullet} + R'_3GeH \longrightarrow RH + R'_3Ge^{\bullet}$$

we used the parabolic model [2] and characterized such reactions by the following parameters:

1. The reaction enthalpy

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

where D_i and D_f are the dissociation energies of breaking Ge–H and forming R–H bonds, respectively; ν_i and ν_f are the frequencies of their stretching vibrations, respectively; and h and N_A are the Planck and Avogadro constants, respectively.

2. The activation energy E_e, which is related to the experimental activation energy $E = -RT\ln(Alk)$, where

Table 1. Kinetic parameters for the liquid- and gas-phase radical reactions involving germanium, tin, phosphorus, and selenium compounds

No.	Reaction	α	$0.5hN_A\nu$, kJ/mol	$0.5hN_A(\nu_i - \nu_f)$, kJ/mol	A, l mol^{-1} s^{-1}
1	$\mathrm{GeH_3{-}H + H^{\bullet}}$	0.673	12.6	–13.7	2×10^{10}
2	$\mathrm{GeH_3{-}H + O^{\bullet}}$	0.577	12.6	–9.7	6×10^{9}
3	$\mathrm{GeH_3{-}H + F^{\bullet}}$	0.518	12.6	–12.2	4.4×10^{10}
4	$\mathrm{GeH_3{-}H + RO^{\bullet}}$	0.595	12.6	–9.1	2×10^{8}
5	$\mathrm{R'_3GeH + R^{\bullet}}$	0.746	12.6	–4.8	1×10^{9}
6	$\mathrm{R'_3GeH + Ar^{\bullet}}$	0.706	12.6	–5.8	1×10^{9}
7	$\mathrm{R'_3GeH + RO^{\bullet}}$	0.595	12.6	–9.1	1×10^{9}
8	$\mathrm{R'_3GeH + RO_2^{\bullet}}$	0.608	12.6	–8.6	1×10^{8}
9	$\mathrm{R'_3GeH + AmO^{\bullet}}$	0.599	12.6	–8.9	1×10^{9}
10	$\mathrm{R'_3SnH + R^{\bullet}}$	0.720	12.1	–5.3	1×10^{9}
11	$\mathrm{R'_3SnH + Ar^{\bullet}}$	0.681	12.1	–6.3	1×10^{9}
12	$\mathrm{R'_3SnH + RO^{\bullet}}$	0.573	12.1	–9.6	1×10^{9}
13	$\mathrm{R'_3SnH + RO_2^{\bullet}}$	0.586	12.1	–9.1	1×10^{8}
14	$\mathrm{R'_3SnH + AmO^{\bullet}}$	0.578	12.1	–9.4	1×10^{9}
15	$\mathrm{H_2PH + H^{\bullet}}$	0.736	13.9	–12.4	2×10^{10}
16	$\mathrm{H_2PH + RO^{\bullet}}$	0.650	13.9	–7.8	2×10^{8}
17	$\mathrm{HSeH + H^{\bullet}}$	0.750	14.0	–12.3	2×10^{10}
18	$\mathrm{HSeH + O^{\bullet}}$	0.643	14.0	–8.3	6×10^{9}

Note: $\mathrm{R^{\bullet}}$, $\mathrm{Ar^{\bullet}}$, and $\mathrm{AmO^{\bullet}}$ represent the hydrocarbon, aryl, and nitroxyl radicals, respectively.

A is the preexponential factor for a given reaction group, as follows:

$$E_e = E + 0.5hN_A\nu - 0.5RT. \quad (2)$$

3. The r_e parameter, which is a sum of the amplitudes of the vibrations of breaking Ge–H and forming R–H bonds in the transition state.

4. The b_i and b_f dynamic parameters of breaking ($b_i = \pi\nu_i(2\mu_i)^{1/2}$) and forming ($b_f = \pi\nu_f(2\mu_f)^{1/2}$) bonds, respectively; and μ_i and μ_f are the reduced weights of atoms forming these bonds, respectively.

The stretching vibrations of the relevant bonds were taken from [3]. For E–H bonds, we obtained the following values of $b = b_i$ ($b \times 10^{-11}$ (kJ/mol)$^{1/2}$ m^{-1}): 2.795 (Ge–H), 2.697 (Sn–H), 3.055 (P–H), and 3.113 (Se–H). For the forming R–H bonds, the b_f values were taken from [2]. Table 1 presents the parameters $\alpha = b_i/b_f$.

The radical reactions of hydrogen atom abstraction involving germanium, tin, phosphorus, and selenium compounds were subdivided into groups (classes) of similar reactions with the same α, b, and r_e parameters (see Table 1). Each reaction class is characterized by the constant br_e parameter. This parameter was calculated by the following equation:

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

The activation energy of a thermally neutral reaction (at $\Delta H_e = 0$) $E_{e,0}$ was determined by the formula

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

The intersection point of the parabolas for the reaction with $E_e = E_{e,0}$ is characterized by the parameter $r^{\neq} = r_e(1+\alpha)^{-1}$. Table 1 gives the parameters used to calculate the br_e, E, and $E_{e,0}$ values. The partial preexponential factors A (per one bond being attacked) was set equal to those for the relevant reactions involving the C–H bonds [2].

The reaction enthalpies ΔH_e were calculated by Eq. (1) using the following dissociation energies for the breaking bonds D (kJ/mol): 348.9 (H_3Ge–H) [4], 347.3 $(C_4H_9)_3$Ge–H [5], 334.7 $(C_6H_5)_3$Ge–H [5]; 309.6 $(C_4H_9)_3$Sn–H [5], 351.0 (H_2P–H) [4], 375.3 for $CH_3(CH_2)_7$PH–H as for C_2H_5PH–H [6]; and D (HSe–H) = 334.9 [5]. For the forming bonds we have

D (H–H) = 436 kJ/mol [4], $D(\text{H–O}^\bullet)$ = 427.5 kJ/mol [3], and D(H–F) = 570.7 kJ/mol [4]. The D (RO–H) and D (AmO–H) values were taken from [3] and [8], respectively, and the bond dissociation energies for the R–H and Ar–H bonds were taken from [7].

For certain R'_3EH compounds with unknown E–H bond dissociation energies (D_i), we estimated them from the rate constants for hydrogen atom abstraction by radicals for two compounds, one of which was a reference with a known bond dissociation energy (D_1). The following equation was used [2]:

$$\begin{aligned}\Delta D_i &= D_i - D_1 \\ &= 2br_e\alpha^{-2}(E_{e,i}^{1/2} - E_{e,1}^{1/2}) - (1-\alpha^2)\alpha^{-2}\Delta E_i,\end{aligned} \quad (5)$$

where α and br_e are the parameters that characterize one reaction class; ΔE_i is the difference in the activation energies of the ith compound (with an unknown bond strength) and the first (reference) compound with the known bond strength D_1. This difference is

$$\Delta E_i = -RT\ln(n_1k_i/n_ik_1), \quad (6)$$

where k_i and k_1 are the reaction rate constants, and n_i and n_1 are the number of equally reactive E–H bonds in the studied (i) and reference (1) compounds, respectively.

RESULTS AND DISCUSSION

Tables 2 and 3 present the initial experimental br_e values and those calculated by Eqs. (1)–(3). Analyzing these data, we subdivided the reactions into the following 20 classes, the br_e, $E_{e,0}$, r_e, and $r^{\neq}/r_e$ parameters for which were summarized in Table 4. This table shows that the activation energy for a thermally neutral reaction $E_{e,0}$ changes within broad limits from 41 (O + GeH_3–H) to 81 kJ/mol ($\text{AmO}^\bullet + R'_3\text{Ge–H}$). The low activation energy $E_{e,0}$ (41–48.9 kJ/mol) of a thermally neutral reaction is typical of abstraction reactions involving oxygen atoms and alkoxy radicals, when the activation energy strongly depends on the substantial difference in the electronegativities of the oxygen atom and the Ge, Sn, P, and Se atoms [2]. For all the reactions considered here, the transition state in the $r_e - E$ coordinates is shifted toward reaction products ($r^{\neq} > 0.5r_e$, Table 4).

Table 5 presents the initial (T, k_i, and k_1) and calculated data (ΔE_i and ΔD_i) used to estimate the E–H bond dissociation energies D_i by Eqs. (5) and (6) for germanium, tin, and phosphorus compounds.

The br_e parameters obtained for hydrogen atom abstraction from the E–H bonds in germanium and tin compounds allows one to analyze and estimate the contribution of the radii of the atoms of the reaction center to the formation of the activation energy. Using the reactions of alkyl radicals with the C–H bonds of hydrocarbons and the Si–H bonds of silanes, we found earlier [38] that the larger the radius of the atom from which the hydrogen atom is abstracted, the higher the activation energy, other conditions being the same. Now we consider this problem for reactions when the transition state contains germanium and tin atoms with much larger radii than those of the silicon and carbon atoms. In this connection, it is convenient to consider the $\text{H}^\bullet + R'_3\text{E–H}$ and $\text{R}^\bullet + R'_3\text{E–H}$ reaction classes, for which the difference in the electronegativities of atoms in the reaction center has little effect on the activation energy. In this case, the activation energy of a thermally neutral reaction mainly depends on two factors: (i) triplet repulsion and (ii) the repulsion of the electron shells of the H and E or C and E atoms in the reaction center of the transition state [2].

The dependence of the $r_e(E_{e,0} \sim r_e^2)$ parameter on the energy of the triplet repulsion and the $r_{\text{E–X}}$ bond length (the F function) for the $\text{X}^\bullet + R'_3\text{E–H}$ reaction [2] is described by the following equation:

$$r_e^2 \times 10^{22} = 13.7\frac{D_e(\text{E–X})}{D_e(\text{H–H})} + F(r_{\text{E–X}}), \quad (7)$$

where $F(r_{\text{E–X}})$ is the desired function and D_e(H–H) = 462.3 kJ/mol [3]. The D(E–H) and D(E–C) bond dissociation energies were taken from [3–5], whereas the energies of the zero-point vibrations of the relevant bonds ($D_e = D + 0.5hN_A\nu$) were calculated with due regard to the frequencies ν of vibrations of the relevant E–H and E–C bonds (Table 1). Table 7 presents the D_e(E–H), D_e(E–C), and r_e (Table 4) values, as well as the $r_{\text{E–H}}$ and $r_{\text{E–C}}$ bond lengths [3]. Comparison of the $r_e^2 \times 10^{22} - 13.7\ [D_e(\text{E–X})/D_e(\text{H–H})]$ and the $r_{\text{E–H}}$ and $r_{\text{E–C}}$ bond lengths suggests that the longer the forming E–C (or E–H) bond, the larger the increment that characterizes the repulsion of the electron shells in the transition state. The dependence of $r_e^2 - 13.7 \times 10^{-22}[D_e(\text{E–X})/D_e(\text{H–H})]$ on the $r_{\text{E–X}}/r_{\text{H–H}}$ ratio, where X = H or R ($r_{\text{H–H}} = 0.746 \times 10^{-10}$ m) is illustrated in the figure as a straight line in the relevant coordinates for ten reactions under consideration. The empirical dependence of the r_e parameter on the D_e and $r_{\text{E–X}}$ values is

$$\begin{aligned}r_e^2 \times 10^{22} &= 13.7\frac{D_e(\text{E–X})}{D_e(\text{H–H})} \\ &+ (9.37 \pm 1.43)\left(\frac{r_{\text{E–X}}}{r_{\text{H–H}}} - 1.31\right).\end{aligned} \quad (8)$$

Table 2. Experimental data (T, k) and calculated parameters (ΔH_e, E, and br_e) for the radical reactions of hydrogen atom abstraction from germanium, selenium, and phosphorus compounds in the liquid and gas phases. Solvents: pentane, cyclohexane, octane, isooctane, decane, benzene, toluene, cumene, tetrahydrofurane, and carbon tetrachloride

No.	Compound	Radical	Experiment		ΔH_e, kJ/mol	E, kJ/mol	br_e, (kJ/mol)$^{1/2}$	Reference
			T, K	k, l mol^{-1} s^{-1}				
1	GeH_4	$H^{\bullet}$ (gas)	298	2.6×10^9	–100.77	8.49	11.85	[9]
2	GeH_4	$H^{\bullet}$ (gas)	305	1.2×10^9	–100.77	10.65	12.14	[10]
3	GeH_4	$O^{\bullet}$ (gas)	298	2.5×10^9	–88.3	5.60	10.04	[11]
4	GeH_4	$O^{\bullet}$ (gas)	298	2.0×10^9	–88.3	6.16	10.12	[12]
5	GeH_4	$O^{\bullet}$ (gas)	300	2.1×10^9	–88.3	6.08	10.11	[13]
6	GeH_4	$F^{\bullet}$ (gas)	298	9.4×10^{10}	–234.0	1.55	11.73	[14]
7	GeH_4	$(CH_3)_3CO^{\bullet}$ (gas)	430.5	1.4×10^8	–99.9	6.24	10.56	[15]
8	$[CH_3(CH_2)_3]_3GeH$	$C^{\bullet}H_3$	298	1.2×10^5	–97.5	22.37	14.35	[16]
9	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	233	1.2×10^4	–79.5	21.90	13.72	[17]
10	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	273	6.9×10^4	–79.5	21.74	13.68	[17]
11	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	303	1.1×10^5	–79.5	23.03	13.82	[17]
12	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	313	1.4×10^5	–79.5	23.02	13.82	[17]
13	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	328	2.1×10^5	–79.5	23.11	13.82	[17]
14	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	353	3.8×10^5	–79.5	23.11	13.81	[18]
15	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	363	4.7×10^5	–79.5	23.14	13.81	[17]
16	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	393	8.5×10^5	–79.5	23.10	13.79	[17]
17	$[CH_3(CH_2)_3]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}HCH_3$	298	1.8×10^4	–69.5	27.04	13.95	[17]
18	$[CH_3(CH_2)_3]_3GeH$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	3.8×10^5	–79.5	23.11	13.81	[18]
19	$(C_6H_5)_3GeH$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	3.8×10^6	–92.1	16.35	13.40	[18]
20	$[CH_3(CH_2)_3]_3GeH$	$C_6H_5^{\bullet}$	302	2.6×10^8	–132.5	3.35	12.40	[19]
21	$[CH_3(CH_2)_3]_3GeH$	$(CH_3)_2C{=}C^{\bullet}H$	300	3.5×10^7	–117.5	8.36	12.71	[19]
22	$[CH_3(CH_2)_3]_3GeH$*	$(CH_3)_3CO^{\bullet}$	295	9.2×10^7	–101.5	5.85	10.63	[20]
23	$(CH_3)_3GeH$*	$(CH_3)_3CO^{\bullet}$	295	6.7×10^7	–105.7	6.63	10.85	[20]
24	$C_6H_5GeH_3^*$	$(CH_3)_3CO^{\bullet}$	295	4.4×10^8	–118.3	4.70	10.91	[20]
25	$(C_6H_5)_2GeH_2^*$	$(CH_3)_3CO^{\bullet}$	295	1.8×10^8	–114.1	5.91	10.98	[20]
26	$[CH_3(CH_2)_3]_3GeH$	$C_6H_5C(O_2^{\bullet})(CH_3)_2$	345.5	1.9×10^1	–19.9	44.40	12.74	[21]
27	$(C_6H_5)_3GeH$	*cyclo*-$[N(O^{\bullet})C(CH_3)_2(CH_2)_3C(CH_3)_2]$	333	1.8×10^{-4}	28.1	81.22	14.42	[22]
28	H_2PH	$H^{\bullet}$ (gas)	298	1.6×10^9	–97.3	8.93	12.67	[23]
29	H_2PH	$H^{\bullet}$ (gas)	298	2.3×10^9	–97.3	8.08	12.55	[24]
30	H_2PH	$(CH_3)_3CO^{\bullet}$ (gas)	430.5	1.9×10^8	–96.5	4.03	10.92	[15]
21	HSeH	$H^{\bullet}$ (gas)	298	7.1×10^9	–113.4	4.28	12.69	[25]
32	HSeH	$O^{\bullet}$ (gas)	298	1.3×10^9	–100.9	5.59	11.30	[11]

* Solvent: di-*tert*-butylperoxide/benzene (2 : 1).

Table 3. Experimental data (T, k) and calculated parameters (ΔH_e, E, br_e) (Eqs. (1)–(3)) for the liquid-phase reactions of the $[CH_3(CH_2)_3]_3SnH$ radical. Solvents: pentane, cyclohexane, isooctane, benzene, toluene, cumene, and tetrahydrofurane

No.	Radical	Experiment		ΔH_e	E	br_e, (kJ/mol)$^{1/2}$	Reference
		T, K	k, l mol^{-1} s^{-1}	kJ/mol			
1	$C^{\bullet}H_3$	274	6.6×10^6	–135.7	11.44	13.78	[26]
2	$C^{\bullet}H_3$	298	5.8×10^6	–135.7	12.78	13.95	[27]
3	$C^{\bullet}H_3$	298	1.0×10^7	–135.7	11.41	13.77	[28]
4	$C^{\bullet}H_3$	300	1.1×10^7	–135.7	11.31	13.76	[26]
5	$CH_3C^{\bullet}H_2$	297	2.2×10^6	–117.7	15.12	13.73	[26]
6	$CH_3C^{\bullet}H_2$	300	2.3×10^6	–117.7	15.16	13.73	[26]
7	$CH_3C^{\bullet}H_2$	303	2.7×10^6	–117.7	14.91	13.69	[19]
8	$CH_3C^{\bullet}H_2$	306	2.8×10^6	–117.7	14.94	13.70	[19]
9	$(CH_3)_2C^{\bullet}H$	300	1.5×10^6	–107.7	16.20	13.56	[26]
10	$(CH_3)_2C^{\bullet}H$	304.5	1.7×10^6	–107.7	16.15	13.55	[26]
11	$CH_3(CH_2)_2C^{\bullet}H_2$	300	2.5×10^6	–117.7	14.99	13.71	[26]
12	$(CH_3)_3C^{\bullet}$	298	7.4×10^5	–95.7	17.86	13.39	[27]
13	$(CH_3)_3C^{\bullet}$	300	1.9×10^6	–95.7	15.68	13.11	[26]
14	$(CH_3)_3C^{\bullet}$	303	1.7×10^6	–95.7	16.07	13.16	[28]
15	$(CH_3)_3C^{\bullet}$	307	2.1×10^6	–95.7	15.69	13.11	[26]
16	$CH_3(CH_2)_4C^{\bullet}H_2$	298	1.0×10^6	–117.7	17.12	13.98	[27]
17	$(CH_3)_3CC^{\bullet}H_2$	272	1.3×10^6	–117.7	15.05	13.73	[19]
18	$(CH_3)_3CC^{\bullet}H_2$	303	3.6×10^6	–117.7	14.15	13.60	[19]
19	$CH_2{=}CHC(CH_3)_2C^{\bullet}H_2$	323	4.9×10^6	–117.7	14.28	13.60	[29]
20	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	298	2.2×10^6	–117.7	15.16	13.73	[26]
21	*cyclo*-$[(CH_2)_5C^{\bullet}H]$	298	1.2×10^6	–104.5	16.66	13.52	[27]
22	*cyclo*-$[(CH_2)_5C^{\bullet}H]$	300	2.2×10^6	–104.5	15.28	13.34	[26]
23	*cyclo*-$[(CH_2)_5C^{\bullet}H]$	327.5	3.9×10^6	–104.5	15.11	13.30	[26]
24	$CH_3($*cyclo*-$C_6H_{10})C^{\bullet}(O)$	353	1.3×10^6	–81.3	19.53	13.10	[30]
25	$CH_3(CH_2)_{10}C^{\bullet}(O)$	348	1.0×10^6	–70.7	19.92	13.15	[31]
26	*cyclo*-$[(CH_2)_3C^{\bullet}H]$	287	7.2×10^7	–114.2	6.26	12.40	[19]
27	*cyclo*-$[(CH_2)_3C^{\bullet}H]$	303	8.5×10^7	–114.2	6.21	12.38	[19]
28	$CH_3(CH_2)_{10}C^{\bullet}(O)$	348	1.0×10^6	–70.7	19.92	13.15	[31]
29	$C_6H_5C^{\bullet}H_2$	298	3.6×10^4	–70.7	25.33	13.46	[28, 32]
30	$C_6H_5C^{\bullet}H_2$	303	4.2×10^4	–70.7	25.41	13.47	[28, 32]
31	$2{-}CH_2CH{=}CH_2{-}C_6H_4C^{\bullet}H_2$	433	6.8×10^5	–70.5	26.28	13.50	[32]

Table 3. (Contd.)

No.	Radical	Experiment		ΔH_e	E	br_e, (kJ/mol)$^{1/2}$	Reference
		T, K	k, l mol^{-1} s^{-1}	kJ/mol			
32	$C_6H_5^{\bullet}$	303	5.9×10^8	–170.7	1.33	12.70	[19]
33	$C_6H_5^{\bullet}$	304	6.5×10^8	–170.7	1.11	12.66	[33]
34	$C_6H_5^{\bullet}$	306	6.2×10^8	–170.7	1.23	12.68	[19]
35	$(CH_3)_2C{=}C^{\bullet}H$	273.5	2.6×10^8	–155.7	3.04	12.61	[19]
36	$(CH_3)_2C{=}C^{\bullet}H$	303	3.5×10^8	–155.7	2.67	12.54	[19]
37	$(CH_3)_2C{=}C^{\bullet}H$	306	3.6×10^8	–155.7	2.58	12.52	[19]
38	$(CH_3)_3CO^{\bullet}$*	295	1.9×10^8	–139.7	4.07	11.0	[34]
39	$C_6H_5C(O_2^{\bullet})(CH_3)_2$	345.5	1.8×10^3	–58.1	31.39	12.35	[21]
40	*cyclo*-$[N(O^{\bullet})C(CH_3)_2(CH_2)_3C(CH_3)_2]$	333	2.5×10^{-2}	2.5	67.58	13.88	[22]

* Solvent: di-*tert*-butylperoxide/benzene (2 : 1).

Table 4. Kinetic parameters for the liquid- and gas-phase reactions of hydrogen atom abstraction from germanium, tin, phosphorus, and selenium compounds by atoms and radicals

No.	Reaction	br_e, (kJ/mol)$^{1/2}$	$E_{e,0}$, kJ/mol	$r_e \times 10^{11}$, m	$(r^{\neq}/r_e)_0$
1	$H^{\bullet} + GeH_4$	12.00 ± 0.15	51.4	4.293	0.598
2	$O^{\bullet} + GeH_4$	10.10 ± 0.03	41.0	3.614	0.634
3	$F^{\bullet} + GeH_4$	11.73	59.7	4.197	0.659
4	$(CH_3)_3CO^{\bullet} + GeH_4$	10.56	43.9	3.778	0.627
5	$R^{\bullet} + R'_3GeH$	13.82 ± 0.12	62.7	4.945	0.573
6	$Ar^{\bullet} + R'_3GeH$	12.56 ± 0.16	54.2	4.494	0.586
7	$(CH_3)_3CO^{\bullet} + R'_3GeH$	10.84 ± 0.11	46.2	3.88	0.627
8	$RO_2^{\bullet} + R'_3GeH$	12.74	62.8	4.558	0.622
9	$AmO^{\bullet} + R'_3GeH$	14.42	81.3	5.159	0.625
10	$R^{\bullet} + R'_3SnH$	13.67 ± 0.13	63.2	5.068	0.581
11	$(CH_3)_3C^{\bullet} + R'_3SnH$	13.13 ± 0.02	58.3	4.868	0.581
12	$RC^{\bullet}(O) + R'_3SnH$	13.13 ± 0.03	58.3	4.868	0.581
13	$Ar^{\bullet} + R'_3SnH$	12.62 ± 0.06	56.4	4.679	0.595
14	$RO^{\bullet} + R'_3SnH$	11.00	48.9	4.079	0.636
15	$RO_2^{\bullet} + R'_3SnH$	12.35	60.6	4.579	0.631
16	$AmO^{\bullet} + R'_3SnH$	13.88	77.4	5.146	0.634
17	$H^{\bullet} + H_2PH$	12.61 ± 0.06	52.8	4.128	0.576
18	$(CH_3)_3CO^{\bullet} + H_2PH$	10.92	43.8	3.574	0.606
19	$H^{\bullet} + HSeH$	12.69	52.6	4.076	0.571
20	$O^{\bullet} + HSeH$	11.30	47.3	3.630	0.609

Note: See Table 1.

Table 5. Estimates of the Ge–H, Sn–H, and P–H bond dissociation energies from the kinetic data (Eqs. (2), (5), and (6))

Compound (R'EH)	Radical ($R^{\bullet}$)	T, K	$n_l k_i / n_i k_l^*$	ΔE, kJ/mol	ΔD, kJ/mol	D, kJ/mol
$R_1H = [CH_3(CH_2)_3]_3GeH$						
$[(CH_3)_3Si]_3GeH$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	39.5 [18]	−10.8	−41.5	305.8
$[(CH_3)_3Si]_3GeH$	$CH_2{=}CH(CH_2)_3C^{\bullet}H_2$	298	39.7 [35]	−9.1	−34.4	312.9
$[(CH_3)_3Si]_3GeH$	$C_6H_5C(O_2^{\bullet})(CH_3)_2$	345.5	206.2 [21]	−15.3	−50.4	296.9
$(C_6H_5)_3GeH$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	10.0 [18]	−6.8	−24.8	322.5
$(C_6H_5CH_2)_3GeH$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	7.9 [18]	−6.1	−22.4	324.9
$C_6H_5CH_2(C_2H_5)GeH_2$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	1.7 [18]	−1.6	−5.7	341.6
$[2,4,6\text{-}(CH_3)_3\text{–}C_6H_2]_2GeH_2$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	2.8 [18]	−3.0	−10.5	336.8
$2,4,6\text{-}(CH_3)_3\text{–}C_6H_2GeH_3$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	2.5 [18]	−2.7	−9.8	337.5
cyclo-$[H_2GeC(C_6H_5){=}C(C_6H_5)H_2GeC(C_6H_5){=}C(C_6H_5)$	*cyclo*-$[C(O)(CH_2)_3C(C^{\bullet}H_2)(C(O)OCH_3)]$	353	12.5 [18]	−7.4	−27.4	319.9
$R_1H = [CH_3(CH_2)_3]_3SnH$						
$(CH_3)_3SnH$	$(CH_3)_3C^{\bullet}$	298	0.4 [27]	2.3	8.9	318.5
$(C_6H_5)_3SnH$	$(CH_3)_3C^{\bullet}$	298	4.2 [27]	−3.6	−15.0	294.6
$(C_6H_5)_3SnH$	$(CH_3)_3CO^{\bullet}$	300	2.7 [34, 36]	−1.7	−12.0	297.6
$(C_6H_5)_3SnH$	$C_6H_5C(O_2^{\bullet})(CH_3)_2$	346	2.7 [21]	−2.9	−11.1	298.5
$R_1H = CH_3(CH_2)_7PH_2$						
$CH_3(CH_2)_7PH_2$	$\sim CH_2C^{\bullet}HC_6H_5$	333	1.1×10^3 [37]			375.3 [6]
$NC(CH_2)_3PH_2$	$\sim CH_2C^{\bullet}HC_6H_5$	333	1.5×10^3 [37]	−0.86	−1.9	373.4
$[NC(CH_2)_3]_2PH$	$\sim CH_2C^{\bullet}HC_6H_5$	333	1.5×10^3 [37]	−2.8	−5.8	369.5
$[CH_3(CH_2)_3]_2PH$	$\sim CH_2C^{\bullet}HC_6H_5$	373	2.7×10^3 [37]	−0.14	−0.3	375.0
$(CH_3CH_2)_2PH$	$\sim CH_2C^{\bullet}HC_6H_5$	373	1.8×10^3 [37]	1.2	2.5	377.8
(*cyclo*-$[(CH_2)_5CH])_2PH$	$C_6H_5C^{\bullet}H_2$	298	2.5×10^3 [32]	−8.0; (−9.1)	−17.7; (−20.2)	357.6; (357.6)
(*cyclo*-$[(CH_2)_5CH])_2PH$	$2\text{-}CH_2CH{=}CH_2C_6H_4C^{\bullet}H_2$	433	6.8×10^4 [32]	−5.4; (−6.6)	−11.8; (−14.2)	363.5; (363.6)

* For these germanium and tin compounds (Ge and Sn), the rate constants k_i (Eq. (6)) for hydrogen atom abstraction by radicals were taken from the papers listed. For the k_1 values for the same radicals in the case of the reference compounds R_1H, see Tables 2 and 3. For phosphorus compounds, the rate constants k_i are given.

The activation energy for thermally neutral reactions of different classes (with due regard to the effect of both the triplet repulsion and electronegativities on the $X^{\bullet} + HY \longrightarrow XH + Y^{\bullet}$ reaction [2]) can be expressed as follows:

$$E_{e,0} = \left(\frac{b \times 10^{-11}}{1+\alpha}\right)^2 \left\{13.7\frac{D_e(\text{Y–X})}{D_e(\text{H–H})} + 9.37\left(\frac{r(\text{Y–X})}{r(\text{H–H})} - 1.31\right) - 22.4\frac{\Delta EA}{D_e(\text{H–H})}\right\}. \tag{9}$$

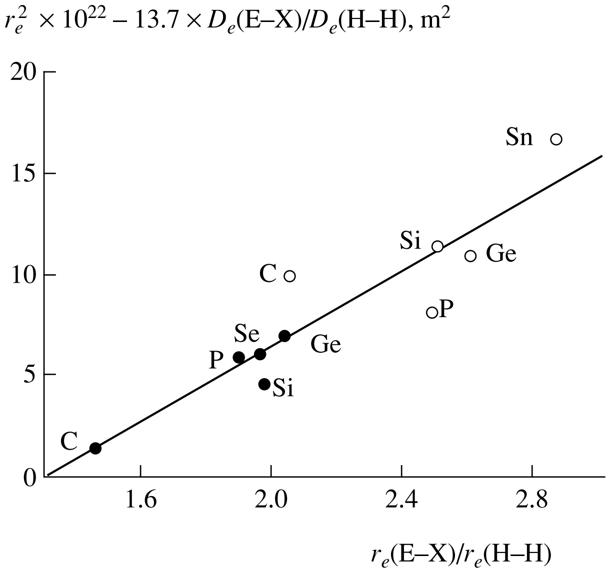
From Eq. (9), we calculated the increment

$$\Delta E_r = \left(\frac{b \times 10^{-11}}{1+\alpha}\right)\left(9.37\frac{r(\text{Y–X})}{r(\text{H–H})} - 12.27\right), \tag{10}$$

which takes into account the influence of the sum of the radii of atoms X and Y between which the hydrogen atom is transferred. The contribution of this factor to the activation energy $E_{e,0}$ for the $R^{\bullet} + \text{H–E}R'_3$ abstraction reaction takes the following values:

E	C	Si	Ge	Sn
$E_{e,0}$, kJ/mol	68.2	57.6	62.7	63.2
ΔE_r, kJ/mol	23.6 ± 1.0	31.2 ± 1.0	31.2 ± 1.4	36.1 ± 2.3
*ΔE_T, kJ/mol	39.8	31.2	26.7	21.9

* ΔE_T is the factor that takes into account triplet repulsion.



$\left(r_e^2 \times 10^{22} - 13.7\frac{D_e(\text{E–X})}{D_e(\text{H–H})}\right)$ vs. $\frac{r(\text{E–X})}{r(\text{H–H})}$ for $X^{\bullet} + R'_3\text{E–H}$ reactions, where X = H (in the gas phase; solid points), X = R (in solution; open points). The E element given in the figure corresponds to the reactant class given in Table 6.

Therefore, the radius of an atom from which the hydrogen atom is abstracted strongly affects the activation energy of an abstraction reaction.

Table 6. Comparison of the r_e parameter for the liquid- and gas-phase $R'_3EH + X^{\bullet} \longrightarrow XH + R'_3E^{\bullet}$ reactions with the strength (D_e) and length (r(E–X)) of the E–X bond in the transition state

Reactant class	$r_e \times 10^{11}$, m	$r(\text{E–X}) \times 10^{10}$, m	D_e(E–X), kJ/mol	$r_e^2 \times 10^{22} - 13.7\frac{D_e(\text{E–X})}{D_e(\text{H–H})}$
		$X^{\bullet} = H^{\bullet}$		
CH_4	3.87	1.091	457.4	1.42
SiH_4	4.09	1.480	408.0	4.64
GeH_4	4.28	1.525	380.4	7.04
PH_3	4.09	1.420	364.9	5.91
SeH_2	4.06	1.470	348.9	6.14
		$X^{\bullet} = R^{\bullet}$		
R'_3CH	4.62	1.536	384.2	9.96
R'_3SiH	4.77	1.870	381.3	11.45
R'_3GeH	4.93	1.945	350.4	10.92
R'_3SnH	5.07	2.144	300.2	16.81
R'_3PH	4.16	1.858	306.6	8.22

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