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The reactivity of organoboranes in radical substitution reactions

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The parameters characterizing substitution reactions of the types $R^\bullet + BR_3$, $RO^\bullet + BR_3$, $ROO^\bullet + BR_3$, and $RS^\bullet + BR_3$ were calculated from the experimental data using the parabolic model of bimolecular radical reaction. Along with the enthalpy of the reaction, the following factors affect the activation energy: triplet repulsion in the transition state, difference in electronegativities of the atoms forming the reaction center, π-bonds in the α-position to the reaction center, steric hindrances, and force constants of the reacting bonds. The change in the dissociation energy of the B—C bond in organoboranes, in which alkyl substituents were replaced by alkoxyl and thiyl substituents, was estimated from the kinetic data. The parameters obtained make it possible to calculate the activation energies of individual reactions of four types under study.

Key words: organoboranes, parabolic model, radical substitution reaction, force constant, steric effect, triplet repulsion, electronegativity of atoms, activation energy, bond energy.

An important feature of the radical chemistry of organoboranes is their ability of actively entering into various radical substitution reactions in which one radical ($Y^\bullet$) reacts BR_3 to displace another radical ($R^\bullet$). These reactions involve alkyl,[1—3] alkoxyl,[4—7] and thiyl[8—10] radicals

$$Y^\bullet + BR_3 \rightarrow YBR_2 + R^\bullet$$

$$(Y^\bullet = R'^\bullet,\ R'O^\bullet,\ R'S^\bullet).$$

Organoboranes are oxidized *via* the chain mechanism

$$ROO^\bullet + BR_3 \rightarrow ROOBR_2 + R^\bullet, \qquad (a)$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet.$$

According to this, chain propagation (*a*) is the radical substitution reaction.[11—13]

Discussions and comparison of the reactivity of organoboranes in radical substitution reactions were restricted up to date by the comparison of their rate constants. The question what factors and to which extent affect the reactivity of organoboranes in these reactions was not considered.[1—17] This work is aimed at bridging this gap.

In our opinion, the semiempirical model of intersecting parabolas[18] is the most efficient among various empirical methods and approaches to the description of bimolecular reactions. Using this model, we examined the data on radical elimination,[19,20] addition,[21,22] and cyclic chain termination during oxidation.[23] We have previously applied this model for the experimental results of studying radical substitution at the O—O bond in peroxides[24] and at the S—S bonds in disulfides.[25]

Calculation Procedure

The parabolic model considers the substitution reaction of the type

$$Y^\bullet + BR_3 \rightarrow YBR_2 + R^\bullet$$

as a result of intersecting of two potential curves, one of which describes the potential energy of the system as a parabolic function of the amplitude of the stretching vibration of the cleaved B—C bond (i), and another curve reflects it as a similar function of the amplitude of the stretching vibration of the formed B—Y bond (f) (Y = O, S, C).[18]

The reaction is characterized by the following parameters:

(1) enthalpy of the reaction ΔH_e, which includes the difference of zero energies of the reacting bonds

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

(D_i and D_f are the dissociation energies; ν_i and ν_f are the frequencies of stretching vibrations of the i and f bonds, respectively; h is the Planck constant; and L is Avogadro's number);

(2) activation energy E_e, which includes the energy of zero vibrations of the attacked bond and is related to the experimentally determined activation energy E by a simple correlation ($\nu = \nu_i$)

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

(R is the gas constant, R = 8.314 J mol^{-1} K^{-1}, and T is temperature in K);

(3) distance r_e between the vertices of two intersecting parabolas;

(4) parameters b_i and b_f ($2b_i^2$ is the force constant of the i bond), which are the dynamic characteristics of the cleaved ($b_i = \pi\nu_i(2\mu_i)^{1/2}$) and formed ($b_f = \pi\nu_f(2\mu_f)^{1/2}$) bonds ($\mu_i$ and μ_f are the reduced masses of atoms participating in the formation of these bonds).

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The above five parameters are related to each other by the following correlation:

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

where $\alpha = b_i/b_f$, $b = b_i$.

As shown previously,[24,25] radical substitution reactions can be classified, each class being characterized by a couple of coefficients b and α. The class is grouped, and a particular group of reactions is characterized by the br_e parameter or the activation energy of the thermoneutral reaction E_{e0} ($\Delta H_e = 0$)

$$E_{e0} = (br_e)^2\,(1 + \alpha)^{-2}. \qquad (4)$$

As a rule, the reactions of the same group is characterized by the constant pre-exponential factor A, which allows E to be calculated from the k rate constant using the Arrhenius formula

$$E = RT\ln(A/k). \qquad (5)$$

Substitution under the action of oxygen-centered radicals

It has been proved using various procedures[5—7,11—13] that the radical substitution at the B atom in trialkylboranes involves oxygen-centered radicals

$$\mathrm{Bu^tO^{\bullet} + BR_3 \rightarrow Bu^tOBR_2 + R^{\bullet}},$$

$$\mathrm{ROO^{\bullet} + BR_3 \rightarrow ROOBR_2 + R^{\bullet}}$$

(R is alkyl, and R in the radical corresponds to R in trialkylborane).

These reactions occur with the B—C bond cleavage and formation of the B—O bond. The enthalpy of this reaction is $\Delta H = D(\mathrm{B—C}) - D(\mathrm{B—O})$. To estimate $\Delta\overline{H}$, we used the average dissociation energies of the $\overline{D}$(B—C) and $\overline{D}$(B—O) bonds, which were calculated from the enthalpies of formation ΔH_f°

for BR_3 compounds (R is alkyl)

$$3\overline{D}(\mathrm{B—C}) = 3\Delta H_f^\circ(\mathrm{R^{\bullet}}) + \Delta H_f^\circ(\mathrm{B}) - \Delta H_f^\circ(\mathrm{BR_3}), \qquad (6)$$

for $B(Bu^nO)_3$ compounds

$$3\overline{D}(\mathrm{B—O}) = 3\Delta H_f^\circ(\mathrm{R^{\bullet}}) + \Delta H_f^\circ(\mathrm{B}) - \Delta H_f^\circ(\mathrm{B(Bu^nO)_3}). \qquad (6a)$$

The ΔH_f° values used for the calculation (for the boron atom, $\Delta H_f^\circ(\mathrm{B}) = 562.7$ kJ mol^{-1})[27] and the calculated $\overline{D}$(B—C) and $\overline{D}$(B—O) values are presented in Table 1. We accepted the average dissociation energy of the B—C bond of trialkylboranes (R are linear alkyl substituents) to be 357.3 kJ mol^{-1} (the average value between two consistent in magnitudes dissociation energies of the B—C bond for BEt_3 and BBu^n_3). The dissociation energies of the B—C bond of other compounds in Table 1 were ignored for the following reasons. We believe that the value for BPr^n_3 is somewhat overestimated. In the case of the methyl substituent (BMe_3), the dissociation energy of the B—C bond is higher that those for other alkyl substituents (the same regularity is observed for the C—C bond, for example, Me—Et and Me—Pr^n are characterized by dissociation energies of the C—C bond of 370 and 373 kJ mol^{-1}, and Et—Et and Et—Pr have 364 and 365 kJ mol^{-1}, respectively[26]). The dissociation energy of the B—C bond for BPr^i_3 was ignored due to the influence of chain branching on D, which follows from the comparison of the $\overline{D}$(B—C) values for BPr^n_3 and BPr^i_3 (366.2 and 361.9 kJ mol^{-1}, respectively): the introduction of one methyl group into the α-position to the B atom decreases the bond strength by ~4 kJ mol^{-1}.

Table 1. Enthalpies of formation (ΔH_f°) of the R$^{\bullet}$ radicals[26,27] of organoboranes BR_3[28,29] and calculated average dissociation energies ($\overline{D}$) of the B—C and B—O bonds in molecules of BR_3

BR_3	$\Delta H_f^\circ(\mathrm{R^{\bullet}})$	$-\Delta H_f^\circ(\mathrm{BR_3})$	$\overline{D}$(B—C)
	kJ mol^{-1}		
BMe_3	147.0	122.5	375.1
BEt_3	119.0	152.6	357.4
BPr^n_3	100.0	236.0	366.2
BPr^i_3	90.0	253.0	361.9
BBu^n_3	75.3	283.0	357.2
$B(OBu^n)_3$	−69.5	1151.0	501.7*

* Average dissociation energy of the B—O bond.

The dissociation energy of the C—C bond for the compounds with the benzyl substituent $PhCH_2$—C is by 54 kJ mol^{-1} lower than that for the compound with the methyl substituent Me—C due to the stabilization of the free valence in the benzyl radical.[26] We used this value to calculate the dissociation energy of the B—C bond in $B(CH_2Ph)_3$. From this $\overline{D}$(B—C) for $B(CH_2Ph)_3$ = 375.1 ($\overline{D}$(B—C) for BMe_3) − 54 = 321.1 (kJ mol^{-1}).

In calculations of the enthalpy of the reaction, we used $\overline{D}$(B—O) = 501.7 kJ mol^{-1} obtained for $B(OEt)_3$, assuming that the dissociation energy of the B—O bond in the $B(OR)_3$ compounds (R is linear alkyl) is almost independent of R.[27,29]

For the B—OO bond, we accepted $\overline{D}$(B—OOR) = $\overline{D}$(B—OR) − ΔD, where the ΔD increment reflects a weakening of the B—O bond when the OR group is replaced by OOR. The average value ΔD = 68 kJ mol^{-1} was determined by the comparison of the dissociation energies of the bond in the hydrocarbon analogs of boroxyalkanes[27]: D(OO—C) = 281.0 and 284.4 kJ mol^{-1} for MeOOMe and EtOOEt, respectively; D(O—C) = 346.0 and 355 kJ mol^{-1} for MeOMe and EtOEt, respectively. This gives $\overline{D}$(B—OOR) = 433.7 kJ mol^{-1}. The dissociation energy of the C—OO bond (D) for the peroxide compounds discussed above was calculated from ΔH_f° using the equation

$$D(\mathrm{OO—C}) = \Delta H_f^\circ(\mathrm{ROO^{\bullet}}) + \Delta H_f^\circ(\mathrm{R^{\bullet}}) + \Delta H_f^\circ(\mathrm{ROOR}) \qquad (7)$$

(R = Me, Et).

The ΔH_f° values[26,30] used in the calculation are presented below

	MeOOMe	EtOOEt	MeOO$^{\bullet}$	EtOO$^{\bullet}$
$-\Delta H_f^\circ$ /kJ mol^{-1}	125.9	192.8	−9.0	27.4

Table 2. Rate constants (k),[5—7,11,13] enthalpies (ΔH_e), and kinetic parameters (E_e, E_{e0}, br_e, r_e, ΔE_H) of the reaction $Y^{\bullet} + BR_3 \rightarrow YBR_2 + R^{\bullet}$

BR_3	T/K	$k \cdot 10^{-6}$ /L mol^{-1} s^{-1}	E_e	$-\Delta H_e$	br_e /kJ$^{1/2}$ mol$^{-1/2}$	$r_e \cdot 10^{11}$ /m	E_{e0}	$-\Delta E_H$
			kJ mol^{-1}				kJ mol^{-1}	
			$Y^{\bullet} = Bu^tO^{\bullet}$					
BBu^n_3	313	10	15.6	145.7	13.89	3.918	60.7	45.1
BBu^s_3	313	0.4	24.0	150.7	15.25	4.303	73.2	49.2
BBu^i_3	313	0.3	24.7	145.7	15.19	4.286	72.6	47.9
$B(CH_2Bu^t)_3$	313	0.04	29.9	145.7	15.84	4.467	78.9	49.0
$B(CH_2Ph)_3$	313	30	12.7	181.9	14.49	4.087	70.2	53.3
			$Y^{\bullet} = ROO^{\bullet}$ (R coincides with R in BR_3)					
BBu^n_3	303	2	19.3	77.7	12.1	3.411	46.0	26.7
BBu^s_3	303	0.08	27.4	82.7	13.45	3.793	56.9	29.5
$B(CH_2Ph)_3$	303	5	17.0	131.7	13.67	3.856	58.5	41.5
			$Y^{\bullet} = Bu^nS^{\bullet}$					
BBu^n_3	323	780	7.92	28.4	9.16	2.584	19.9	12.0
BBu^s_3	323	11	19.4	33.4	11.98	3.380	34.1	14.7
BBu^i_3	323	33	14.3	28.3	10.65	3.000	26.9	12.6
			$Y^{\bullet} = Me^{\bullet}$					
BEt_3	298	0.05	26.4	17.7	11.78	3.323	34.7	8.3

For the B—C bond in trialkylboranes, the energy of zero vibrations is $0.5hL\nu_i = 6.7$ kJ mol^{-1}, and for the B—O bond $0.5hL\nu_f = 8.0$ kJ mol^{-1} ($\nu_i = 1120$ cm^{-1},[14] $\nu_f = 1340$ cm^{-1} [15]), in this case, $\Delta H_e = \bar{D}(\text{B—C}) - \bar{D}(\text{B—O}) - 1.3$ (kJ mol^{-1}).

For the calculation of E_e using formula (2) and E_{e0} using formula (4), we used the increment $0.5(hL\nu_i - RT) = 5.4$ kJ mol^{-1} and coefficients $\alpha = 0.783$, $b_i = 3.545 \cdot 10^{11}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}, $b_f = 4.525 \cdot 10^{11}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1} calculated, in all cases, using $\nu_f = 1340$ cm^{-1} for symmetrical vibrations of the B—O bond.

The activation energy was calculated from the rate constant k (Table 2) by formula (5) using the pre-exponential factor $A = 5 \cdot 10^8$ L mol^{-1} s^{-1}.[5] The results of calculation of ΔH_e, E_e, and parameters br_e and r_e are presented in Table 2.

The reactions of substitution of the alkyl radical at the B atom by oxygen-centered radicals are exothermic ($\Delta H_e = -77.7$—-181.9 kJ mol^{-1}) and occur with a low activation energy (see Table 2). However, activation energies of the thermoneutral reactions are rather high ($E_{e0} = 46.0$—78.9 kJ mol^{-1}).

The enthalpy makes a considerable contribution to the activation energy. This contribution (ΔE_H) can be estimated as a difference between the activation energy of the considered (jth) and thermoneutral reactions[20]:

$$\Delta E_H = E_{ej} - E_{e0}. \qquad (8)$$

The ΔE_H values thus calculated are presented in Table 2.

Estimation of the dissociation energy of the B—O bond in boroxines and boroxyalkanes

Oxyl ($RO^{\bullet}$) and peroxyl ($ROO^{\bullet}$) radicals also enter into radical substitution reactions with cyclic boron compounds containing oxygen, for example, boroxines[5,7]

$$RO^{\bullet} + cyclo\text{-}(R'BO)_3 \rightarrow R'^{\bullet} + cyclo\text{-}ROR'_2(BO)_3,$$

and boroxyalkanes[11,13]

$$ROO^{\bullet} + BR'(OR'')_n \rightarrow ROOB(OR'')_n + R'^{\bullet}.$$

These reactions occur by an order of magnitude more slowly and with a higher activation energy than the reactions involving trialkylboranes (see Tables 2 and 3). The authors[5,7,11,13] assume that the presence of the O atom linked with the B atom results in the p_π—p_π interaction of the vacant orbital of the B atom with the orbital of a lone electron pair of the O atom, which affects the dissociation energy of the B—C bond and strengthens it.

The method of intersecting parabolas makes it possible to estimate quantitatively the effect of oxygen on the dissociation energy of the B—C bond in these compounds. Within the same group of reactions (br_e = const, A = const, α = const), the difference in activation energies of the reactions ("increment of activation energy" ΔE_{ej}) involving trialkylboranes BR_3 (1st reaction) and boroxines $cyclo$-$(R^1BO)_3$ or boroxyalkanes $BR^1(OR^2)_n$ (jth reaction) is the following[18]:

$$\Delta E_{ej} = E_{ej} - E_{e1} = RT\ln(k_1/k_j). \qquad (9)$$

The difference in dissociation energies of the B—C bonds in these compounds ("increment of bond strength" ΔD_j) was calculated by the equation[20]

$$\Delta D_j = (2br_e/\alpha^2)(E_{ej}{}^{1/2} - E_e{}^{1/2}) - (\alpha^{-2} - 1)\Delta E_{ej}. \qquad (10)$$

The results of calculations are presented in Table 3.

As can be seen in Table 3, the dissociation energy of the B—C bond increases in compounds also bearing

Table 3. Rate constants k,[5,11] activation energies (E_e), increment of the activation energy (ΔE_{ej}), and B—C bond strengths (ΔD_j) calculated for reactions of boroxines and boroxyalkanes with oxygen-centered radicals[a]

Compound	k /L mol^{-1} s^{-1}	E_e	ΔE_{ej}	ΔD_j
		kJ mol^{-1}		
$Bu^tO^\bullet$ + *cyclo*-$(RBO)_3 \rightarrow$ *cyclo*-$Bu^tOR_2(BO)_3$ + $R^\bullet$ [b]				
BBu^n_3	$1 \cdot 10^7$	10.2		
cyclo-$(Bu^nBO)_3$	$1 \cdot 10^6$	19.0	8.8	39.3
cyclo-$(Bu^sBO)_3$	$6 \cdot 10^5$	20.4	10.2	44.7
cyclo-$(Bu^tBO)_3$	$1 \cdot 10^6$	19.0	8.8	39.3
$ROO^\bullet$ + *cyclo*-$(RBO)_3 \rightarrow$ *cyclo*-$ROOR_2(BO)_3$ + $R^\bullet$				
BBu^n_3	$2 \cdot 10^6$	11.3		
cyclo-$(Bu^nBO)_3$	$1 \cdot 10^3$	35.8	21.9	66.1
cyclo-$(Bu^sBO)_3$	$5 \cdot 10^4$	26.0	12.1	40.17
$B(CH_2Ph)_3$	$5 \cdot 10^6$	11.6		
cyclo-$(PhCH_2BO)_3$	$1 \cdot 10^6$	18.4	6.8	29.4
$ROO^\bullet + RB(OR')_n \rightarrow ROOB(OR')_n + R^\bullet$				
$Bu^n_2BOOBu^n$	$3 \cdot 10^4$	24.5	10.6	35.7
$Bu^s_2BOOBu^s$	$1.5 \cdot 10^4$	26.2	12.3	40.7
Bu^n_2BOEt	$5 \cdot 10^3$	29.0	15.1	48.6
$Bu^s_2BOBu^s$	$2 \cdot 10^3$	31.3	17.4	54.7
$Bu^nB(OEt)_2$	4	47.0	33.1	91.4
$PhCH_2B(OMe)_2$	21	42.8	31.2	106.0
$PhCH_2B(OCH_2)_2$	20	42.9	31.3	106.3
$PhCH_2B(OBu^n)_2$	18	43.8	32.2	108.6

[a] The corresponding values for some trialkylboranes are presented for comparison.

[b] In all cases, R coincides with R in organoborane.

B—O bonds. For example, in the series BBu^n_3, Bu^n_2BOEt, and $Bu^nB(OEt)_2$ the increments of dissociation energies of the B—C bond (ΔD) are 0, 48.6, and 91.4 kJ mol^{-1}, respectively.

Substitution under the action of sulfur-centered radicals

Trialkylboranes react with butane-1-thiol *via* the free-radical chain mechanism in which the chain propagation stage is the homolytic substitution of the alkyl radical at the B atom by the butylthiyl radical[10]

$$Bu^nS^\bullet + BR_3 \rightarrow Bu^nSBR_2 + R^\bullet.$$

The activation energies of the reactions (see Table 2) were calculated by the kinetic data[10] using the pre-exponential factor $A = 2 \cdot 10^9$ L mol^{-1} s^{-1} (found from the correlation $A = 5 \cdot 10^8 r_1{}^2 r_2{}^{-2}$, where r_1 and r_2 are the radii of the S and O atoms, respectively[31]).

The enthalpy of this reaction is $\Delta H_e = D(B—C) - D(B—S) + 0.5hL(\nu_i - \nu_f)$. The average dissociation energies of the bonds were used in the calculation: $\bar{D}(B—C) = 357.2$ kJ mol^{-1} for BBu^n_3, $\bar{D}(B—C) = 353.2$ kJ mol^{-1} for BBu^s_3 (by 4 kJ mol^{-1} lower, taking into account the effect of the Me substituent in the α-position to the B atom), $\bar{D}(B—C) = 357.3$ kJ mol^{-1} for BBu^i_3 (the isobutyl substituent can be considered as pseudo-linear because the branching is remote from the B atom at a distance of two bonds), as well as $\bar{D}(B—S) = 387.0$ kJ mol^{-1}, which is constant for various thiyl radicals.[32]

The value[15] $\nu_f = 890$ cm^{-1} was taken for the frequency of the stretching vibration of the B—S bond. The b coefficients for this reaction are the following: $b = b_i = 3.545 \cdot 10^{11}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}, $b_f = 3.364 \cdot 10^{11}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}, coefficient $\alpha = 1.053$, the difference in zero energies of vibrations of the B—C and B—S bonds is $0.5hL(\nu_i - \nu_f) = 6.7 - 5.3 = 1.4$ (kJ mol^{-1}). To calculate E_e by formula (2), we used the increment $0.5(hL\nu_i - RT) = 5.4$ kJ mol^{-1}.

The results of calculation of ΔH_e, br_e, E_{e0}, and r_e are summarized in Table 2.

As can be seen from Table 2, the alkylthiylation reaction is exothermic ($\Delta H_e = -28.4$—-32.4 kJ mol^{-1}), and the activation energy of the thermoneutral reaction is low, for example, for the reaction of $Bu^nS^\bullet$ with BBu^n_3 $E_{e0} = 19.9$ kJ mol^{-1} and increases with the branching of the alkyl substituent at the B atom (*i.e.*, the steric factor is manifested in these reactions as well).

Using the kinetic data, parameter $br_e = 9.16$ kJ$^{1/2}$ mol$^{-1/2}$ for this series of alkylthiylation reactions, and formulas (9) and (10), we estimated the influence of the S atom on the strength of the B—C bond in $Bu^n_2BSBu^n$ compared to that in BBu^n_3. The bond strength increases when one S atom is introduced. The calculated value is $\Delta D = 31.0$ kJ mol^{-1}.

Substitution under the action of carbon-centered radicals

The substitution reaction occurs under photolysis of azomethane in the presence of triethylborane in the gas phase[1—3,16]:

$$Me^\bullet + BEt_3 \rightarrow MeBEt_2 + Et^\bullet.$$

Table 2 contains the rate constant k and activation energy E_e of this reaction. Its pre-exponential factor is $A = 2.3 \cdot 10^8$ L mol^{-1} s^{-1} ($A = 1 \cdot 10^8 r_1{}^2 r_2{}^{-2}$, where r_1 and r_2 are the atomic radii of C and O, respectively[31]).

To calculate the br_e parameter by formula (3), we used the following parameters: $b = b_i = 3.545 \cdot 10^{11}$ kJ$^{1/2}$ mol$^{-1/2}$ m^{-1}, $\alpha = 1$, $\Delta E_e = 5.5$ kJ mol^{-1}. The enthalpy of the reaction is $\Delta H_e = \bar{D}(B—C)$ (for BEt_3) $- \bar{D}(B—C)$ (for $MeBEt_2$) $= 357.4 - 375.1 = -17.7$ (kJ mol^{-1}) (see Table 2). For $MeBEt_2$, we used the value of dissociation energy of the B—C bond of 375.1 kJ mol^{-1} (as in BMe_3) instead of the average value equal to 357.3 kJ mol^{-1} because the Me—B bond was formed in the latter.

Structural and physical factors influencing on the activation energy of substitution

Naturally, the enthalpy of the process ΔH_e affects the activation energy of the considered reactions and other reactions of radical elimination and substitution.[18—25] As can be seen from Table 2, the more exothermic the reaction, the higher the contribution of the enthalpy to the activation energy (ΔE_H). However, the comparison of the E_{e0} values shows that even inside the same class of reactions (for example, $R'O^{\bullet} + BR_3$) the activation energy is also influenced by other factors.

Energy of the nonbonding orbital of the formed bond (triplet repulsion). In radical elimination reactions

$$X^{\bullet} + HY \rightarrow X...H...Y \rightarrow XH + Y^{\bullet}$$

the H atom in the transition state removes from Y to X along the line of the X...Y bond. Since three electrons participating in the rearrangement of bonds cannot dispose on the bonding orbital of X...Y (Pauli exclusion principle), the X...Y bond participates in the formation of the transition state. The stronger this bond, the higher the energy of the nonbonding orbital and the activation energy of the thermoneutral reaction.[20] The same interrelation was established for the addition of atoms and radicals at multiple bonds.[21,22] Does triplet repulsion manifest itself in radical substitution reactions? Compare the r_e values for two classes of reactions with the same O...B...C reaction center and different from one another only by the strength of the forming bond.

Reaction	E_{e0}	D(B—O)	$r_e \cdot 10^{11}$ /m	$r_e/D \cdot 10^{13}$ /m mol kJ^{-11}
	kJ mol^{-1}			
$Bu^nO^{\bullet} + BBu^n_3$	60.7	501.7	3.92	0.781
$Bu^nOO^{\bullet} + BBu^n_3$	46.0	433.7	3.41	0.786

It can be seen that the strength of the forming bond has an effect on the r_e parameter and, hence, on E_{e0} (see formula (4)). Therefore, it is more correct to consider the r_e/D ratios rather than r_e values. It is seen from the above data that the r_e/D ratio remains almost unchanged: $r_e/D = 0.78 \cdot 10^{-13}$ m mol kJ^{-1}. Thus, triplet repulsion also affects the activation energy of substitution. As in the case of addition reactions,[21] the r_e/D ratio remains unchanged.

Influence of π-bonds on the activation energy. The comparison of the br_e and E_{e0} parameters for the reactions of $R'O^{\bullet}$ and $R'OO^{\bullet}$ with tributylborane and tribenzylborane, the replacement of the butyl radical by benzyl increases the activation energy of the thermoneutral reaction (see Table 2). The same effect is observed in radical elimination,[20] addition,[21] and substitution at the S—S bond.[25] Their E_{e0}/kJ mol^{-1} are presented below.

Reaction	E_{e0}		ΔE_π
	R = Alk	R = Ph	
$R'O^{\bullet} + B(CH_2R)_3$	60.7	70.2	9.5
$R'OO^{\bullet} + B(CH_2R)_3$	46.0	58.5	12.5
$R''^{\bullet} + RSSR$	44.0	50.0	6.0
$R''^{\bullet} + HCH_2R$	74.2	82.0	7.8
$CH_3^{\bullet} + CH_2{=}CHR$	82.6	90.0	7.4

The increment $\Delta E_\pi = E_{e0}$ (R = Ph) − E_{e0} (R = Alk) stipulated by the influence of the benzyl ring in the α-position to the reaction center is a magnitude of the same order for all reaction types listed and ranges within 6—12 kJ mol^{-1}.

The benzyl group at the B atom has a dual effect on the activation energy. On the one hand, the B—C bond in tribenzylborane is weaker than that in tributylborane, and this decreases the enthalpy of the reaction (*cf.* ΔH_e). On the other hand, when R is replaced by $PhCH_2$ the delocalization of π-electrons enhances the bond between the atoms of the reaction center, which increases the energy of the nonbonding orbital and, correspondingly, the activation energy. Below we present the energy balance (E/kJ mol^{-1}) for the reactions $Bu^tO^{\bullet} + BBu^n_3$ and $Bu^tO^{\bullet} + B(CH_2Ph)_3$.

Reagent	$-\Delta H_e$	$-\Delta E_H$	ΔE_π	E_{e0}	E_e
BBu^n_3	145.7	45.1	0	60.7	15.6
$B(CH_2Ph)_3$	181.9	57.5	9.5	70.2	12.7

Despite a great difference in enthalpies of these reactions ($\Delta\Delta H_e = -181.9 + 145.7 = -36.2$ (kJ mol^{-1})), their activation energies (E_e) differ by 3 kJ mol^{-1} only. So small difference in E_e along with a considerable difference in ΔH_e is a result of the compensation effect at which a decrease in the activation energy due to the enthalpy is compensated for an increase in the activation energy E_{e0} due to the delocalization of π-electrons in the transition state.

Electronegativity of atoms of the reaction center. The difference in electronegativity of the atoms of the reaction center (ΔEA) also affects radical elimination reactions: the greater the difference, the lower the activation barrier.[18] This factor is also manifested for substitution at the O—O bond.[24] Does it affect the activation energy of the radical substitution of organoboranes? Compare the parameters of the substitution reactions $Y^{\bullet} + BR_3$ ($Y = Me^{\bullet}, Bu^nO^{\bullet}$).

$Y^{\bullet}$	$r_e \cdot 10^{11}$ /m	D(Y—B) /kJ mol^{-1}	r_e/D(Y—B)$\cdot 10^{13}$ /m mol kJ^{-1}	ΔEA[32] /eV
$Me^{\bullet}$	3.32	375.1	0.885	0.97 (C—B)
$Bu^nO^{\bullet}$	3.92	501.7	0.781	1.18 (O—B)

The comparison of the parameters (see above) shows that the r_e/D(Y—B) ratio for the reaction of the alkoxyl radical is lower than that for the methyl radical, and the difference in electronegativities (ΔEA) of the couple of B and O atoms is much greater than that for the B and C couple. The difference in r_e/D(Y—B) is most likely the result of the influence of the electronegativity of the atoms of the reaction center on the activation energy of the substitution reactions of organoboranes.

Steric effect. As can be seen from the data in Table 2, the E_{e0} values differ for the reactions of $R'O^{\bullet}$ and $R'OO^{\bullet}$ with boranes bearing linear and branched alkyl substituents. The introduction of the methyl group into both the α- and β-positions to the B atom increases br_e

Table 4. Activation energy (E_{e0}/kJ mol^{-1}) and contributions of the steric effect (ΔE_s/kJ mol^{-1}) for the reactions of boranes BR_3 with the R′O$^{\bullet}$, R′OO$^{\bullet}$, and R′S$^{\bullet}$ radicals

BR_3	E_{e0}			ΔE_s		
	R′O$^{\bullet}$	R′OO$^{\bullet}$	R′S$^{\bullet}$	R′O$^{\bullet}$	R′OO$^{\bullet}$	R′S$^{\bullet}$
$BBu^n{}_3$	60.7	46.0	19.9	0	0	0
$BBu^s{}_3$	73.2	56.9	34.5	12.5	10.9	14.6
$BBu^i{}_3$	72.6	—	26.9	11.9	—	7.0
$B(Bu^tCH_2)_3$	78.9	—	—	18.2	—	—

and, correspondingly, E_{e0}. The contribution (increment) of the steric influence on the activation reaction can be estimated from the difference in E_{e0}:

$$\Delta E_s = E_{e0}\,(\text{branched}) - E_{e0}\,(\text{linear}). \qquad (12)$$

The obtained values are presented in Table 4.

The steric effect (ΔE_s) is of the same order of magnitude (see Table 4) in all cases (for the branched substituent with one methyl group in the α- or β-position relatively to the B atom and for two methyl groups in the β-position). A similar effect was also observed[25] for substitution at the S—S bond.

Influence of force constants. The force constants of reacting bonds also contribute to the activation energy of the thermoneutral reaction, which is seen from the comparison of the $b^2(1 + \alpha)^{-2}$ coefficients (see formula (4) for E_{e0}) for three reaction centers.

Reaction center	$b^2(1 + \alpha)^{-2} \cdot 10^{22}$ /kJ m^2 mol^{-1}	E_{e0} /kJ mol^{-1}
O...B...C	3.95	60.7
C...B...C	3.14	34.7
S...B...C	2.98	19.9

Thus, the analysis of the experimental data on the kinetics of radical substitution involving trialkylboranes showed that the activation energy of the reaction $Y^{\bullet} + BR_3$ is influenced by its enthalpy, triplet repulsion in the transition state, electronegativity of the Y and B atoms, the presence of π-electrons in the vicinity of the reaction center, degree of branching of alkyl substituents bound to the B atom, and the value of force constants of the formed and cleaved bonds. The parameters obtained in our work make it possible to estimate the activation energies of other reactions of four analyzed classes and they agree well with the regularities of radical substitution at the O—O and S—S bonds.

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