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Thermodynamic and Kinetic Parameters for Borane Exchanges

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Equilibrium compositions and bimolecular exchange rates were measured at two temperatures for the following reactions: $H_3BCO + PF_3 \rightleftarrows H_3BPF_3 + CO$; $B_2H_6 + D_3BPF_3 \rightleftarrows H_3BPF_3 + H_3B{\cdot}BD_3$; $H_3BCO + D_3BPF_3 \rightleftarrows H_3BPF_3 + D_3BCO$. These homogeneous reactions are of unit order in each of the reagents, with activation energies 13–15 kcal mol^{-1}. We included in this summary six analogous reactions for which rate data have been published, to demonstrate the existence of a consistent pattern for the borane exchange steps.

Introduction

To facilitate the development of a mechanism for the laser augmented decomposition[1,2]

$$2H_3BPF_3 \xrightarrow[CO_2\ \text{laser}]{10.6\ \mu\text{m}} B_2H_6 + 2PF_3$$

we found it necessary to review the available thermochemical and kinetic data for reactions wherein BH_3 serves as a Lewis acid, interacting with very weak bases. The experimental procedures consisted of sample preparation and purification, measurement of the rate of exchange of the species BH_3, BD_3, PF_3, and CO between adducts (or dimers), and the determination of equilibrium compositions of their mixtures, utilizing the intensities of absorption of characteristic infrared bands.

We are concerned with three types of reactions, designated: association $\rightleftarrows$ dissociation, displacement, and exchange. For the radicals listed we considered all seven possible pairwise adducts [exclusive of $(PF_3)_2$, $(CO)_2$, and $PF_3{\cdot}CO$]. Since H/D were the only isotopic labels readily available we did not investigate reactions of the types

$$H_3B^{13}CO + {}^{12}CO \rightleftarrows H_3B^{12}CO + {}^{13}CO \quad \text{displacement} \qquad (\alpha)$$

$$H_3{}^{10}BPF_3 + H_3{}^{11}BCO \rightleftarrows H_3{}^{11}BPF_3 + H_3{}^{10}BCO \quad \text{exchange} \qquad (\beta)$$

$${}^{10}B_2H_6 + {}^{11}B_2H_6 \rightleftarrows 2{}^{10}B^{11}BH_6 \quad \text{exchange} \qquad (\gamma)$$

However, since our objective was to establish general trends for this class of reactions rather than to obtain precise rate constants for any specific step, we postulated that H/D isotope effects introduce only small perturbations as long as the B–H and B–D bonds remain intact.[3] Reactions β and γ are essentially equivalent to (8) and (9), respectively; the analogue of (α) is (4). In several cases we measured both the forward and the reverse rate constants; in most cases rate data in one direction were recorded and the reverse rate was deduced from the equilibrium constant.

Experimental Section

The samples were prepared according to standard methods, and their purities were checked via their infrared spectra (Perkin-Elmer No. 521). For the kinetic studies the reactants were separately introduced into two identical cells (constructed from a single Al block) to the desired pressures, at the reaction temperature. One of the reagents was mixed with a substantial excess of Ar. The Al block was wrapped with heating wire, thermally lagged, and fitted with several chrome–alumel thermocouples. With the reactants in separate cells at the desired temperature selected portions of their absorption spectra were quickly recorded. Then ($t = 0$) the metal valve connecting the two cells was rapidly opened. The Ar overpressured reactant jetted into the lower pressure cell, the components mixed, and the reaction was initiated. The extent of conversion was followed by recording the time dependent intensity of transmitted radiation at a present wavelength. The applicability of Beer's law was checked for the pressures and spectral resolution used in these experiments. The rate constants were calculated either on the basis of a second-order reversible mechanism or via a pseudo-first-order equation, depending on the combination of pressures used.

Table I. Thermodynamic Functions[h] (T = 298 K)

Compd	ΔH_f°, kcal/mol	Ref	S°, eu/mol	Ref
BH_3	23.87	*a*	44.88	*b*
B_2H_6	9.80	*b*	55.71	*b, c*
CO	−26.42	*b*	47.21	*b*
PF_3	−224.90	*b*	65.28	*b, d*
H_3BPF_3	−225.52	*e*	74.54	*b*
H_3BCO	−26.53	*f*	59.69	*b, g*

[a] Mean value: R. L. Kuczkowski and D. R. Lide, Jr., *J. Chem. Phys.*, **46**, 357 (1967), and references quoted therein. [b] "JANAF Thermochemical Tables", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 37 (1971). [c] S. Sundaram, *Z. Phys. Chem. (Frankfurt am Main)*, **36**, 376 (1963). [d] E. L. Pace and P. V. Petrella, *J. Chem. Phys.*, **36**, 2991 (1962). [e] Equilibrium for decomposition of H_3BPF_3: A. B. Burg and Y. C. Fu, *J. Am. Chem. Soc.*, **88**, 1147 (1966). [f] Equilibrium for displacement reaction $PF_3 + H_3BCO$, this investigation. [g] S. Sundaram and F. F. Cleveland, *J. Chem. Phys.*, **32**, 166 (1960). [h] See also, T. P. Fehlner, "Boron Hydride Chemistry", Academic Press, New York, N.Y., E. L. Muetterties, Ed., Chapter **4**.

A collection of "best" standard molar enthalpies of formation and entropies at 298 K for the gases (at 1 atm) is presented in Table I; their sources are indicated. We emphasize that these constitute a mutually consistent set of values.

Association $\rightleftarrows$ Dissociation Reactions

None of the following unimolecular dissociation rates were measured directly; indeed, these would be very difficult experiments to perform, since the cross sections for the bimolecular steps are within 10^{-2} of gas kinetic. However, mutually consistent mechanisms for the decomposition of H_3BCO and H_3BPF_3[4] and the various flow experiments of Fehlner[5] lead to reasonable values for k_{diss} (s^{-1}) when equated to $K_{eq}{}^{(c)}k_{\text{assoc}} = (\tilde{R}T)^{-1}K_{eq}{}^{(p)}k_{\text{assoc}}$; units $\tilde{R}$ in cm^3 atm mol^{-1} deg^{-1}

$$B_2H_6 \underset{k_f}{\overset{k_r}{\rightleftharpoons}} 2BH_3 \qquad (1)$$

$K_1^{(p)} = e^{17.136}e^{-19094/T}$ atm
$k_{1r} = 2.0 \times 10^{12}$ mol^{-1} cm^3 s^{-1} [5]
$k_{1f} = 3.4 \times 10^{-13}$ s^{-1} at 298 K

$$H_3BPF_3 \rightleftarrows BH_3 + PF_3 \qquad (2)$$

$K_2^{(p)} = e^{17.901}e^{-12325/T}$ atm
$k_{2r} = 1.3 \times 10^{11}$ mol^{-1} cm^3 s^{-1} [5]
$k_{2f} = 3.5 \times 10^{-4}$ s^{-1} at 298 K

$$H_3BCO \rightleftarrows BH_3 + CO \qquad (3)$$

$K_3^{(p)} = e^{16.306}e^{-12043/T}$ atm
$k_{3r} = 2.0 \times 10^{11}$ mol^{-1} cm^3 s^{-1} [6]
$k_{3f} = 2.8 \times 10^{-4}$ s^{-1} at 298 K

In proposing the above dissociation rate constants we make the usual assumption that for a unimolecular reaction, at the high-pressure limit, the activation energy (identified with the bond dissociation energy) is $[\Delta H° - (RT)^{\Delta n}]$.

Displacement Reactions

We measured the equilibrium constant [here $K^{(p)} = K^{(c)}$] for the reaction

$$H_3BCO + PF_3 \rightleftarrows H_3BPF_3 + CO \qquad (4)$$

at 25 and 51 °C. The observed enthalpy and entropy increments permitted us to establish the heat of formation of the borane carbonyl (Table I): K_2(298 K) = 0.57 ± 0.13; K_2(324 K) = 0.44 ± 0.20. One may visualize this displacement as a Walden type process, for which

k_{4f}(298 K) = 4.96 × 10^3 mol^{-1} cm^3 s^{-1} Av of 8 runs
k_{4f}(324 K) = 4.12 × 10^4 mol^{-1} cm^3 s^{-1} Av of 3 runs
k_{4r}(298 K) = 9.53 × 10^3 mol^{-1} cm^3 s^{-1} Av of 3 runs

Expressed in Arrhenius form: $k_{4f} \approx 10^{13}\exp[-6306 \pm 300/T]$ mol^{-1} cm^3 s^{-1} and $k_{4r} \approx 10^{13}\exp[-6613 \pm 300/T]$ mol^{-1} cm^3 s^{-1}. Our attempts to induce the following exchange failed:

$$H_3BPF_3 + HCN \not\rightarrow H_3B{\cdot}NCH + PF_3$$

No noticeable reaction occurred at room temperatures with a 10/1 ratio of HCN to H_3BPF_3.

The rate constants for the displacement from their adducts of the weak bases PF_3 and CO by BH_3 may be derived from the kinetic data on the decomposition of the adducts.[4] For the general mechanism:

$$AB \underset{k_\alpha}{\overset{k_{-\alpha}}{\leftrightarrows}} A + B \qquad \text{(fast)}$$

$$A + AB \underset{k_\beta}{\longrightarrow} A_2 + B \qquad \text{(rate limiting)} \qquad (\delta)$$

$$-\frac{d[AB]}{dt} = \frac{2k_\alpha k_\beta[AB]^2}{k_{-\alpha}[B] + k_\beta[AB]}$$

Soon after an initial first-order period, the decomposition rate decreases; i.e. when $k_{-\alpha}[B] >> k_\beta[AB]$,

$$-\frac{d[AB]}{dt} \rightarrow 2\frac{k_\alpha k_\beta}{k_{-\alpha}}\frac{[AB]^2}{[B]}$$

Thus, given the equilibrium constant for the dissociation step and the measured rate constant, one can deduce the displacement rate constant. For

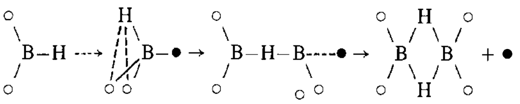
$$H_3B + H_3BCO \rightleftarrows B_2H_6 + CO \qquad (5)$$

$K_5 = e^{-0.830}e^{+7051/T}$
$k_{5f} = 7.2 \times 10^{10}\exp(-1420/T)$ mol^{-1} cm^3 s^{-1}
$k_{5r} = 1.65 \times 10^{11}\exp(-8471/T)$ mol^{-1} cm^3 s^{-1}

$$H_3B + H_3BPF_3 \rightleftarrows B_2H_6 + PF_3 \qquad (6)$$

$K_6 = e^{+0.765}e^{+6769/T}$
$k_{6f} = 2.84 \times 10^{12}\exp(-2421/T)$ mol^{-1} cm^3 s^{-1}
$k_{6r} = 1.32 \times 10^{12}\exp(-9190/T)$ mol^{-1} cm^3 s^{-1}

One may visualize a transition state for these displacement reactions as a transient single –H– bonded structure[7]



There are no data available on the rate of the borane exchange:

$$H_3B + B_2D_6 \rightleftarrows H_3B{\cdot}BD_3 + BD_3$$

In this respect we differ with the interpretation given by Maybury and Koski[8] for their experimental results (see next section).

Radical Exchange Reactions

Our rate data on

$$D_3BPF_3 + B_2H_6 \rightleftarrows H_3BPF_3 + D_3B{\cdot}BH_3 \qquad [K_7 \simeq 2] \qquad (7)$$

demonstrated that the rate is first order in each of the reactants. Two sets of constants were determined (calculated for a reversible bimolecular mechanism):

k_{7f}(299 °K) = 2.34 × 10^3 mol^{-1} cm^3 s^{-1} Av 5 runs
k_{7f}(313 °K) = 9.52 × 10^3 mol^{-1} cm^3 s^{-1} Av 3 runs

Expressed in Arrhenius form: $k_{7f} \approx 10^{13}\exp[-6570 \pm 330/T]$ mol^{-1} cm^3 s^{-1}; $k_{7r} \approx 5 \times 10^{12}\exp[-6570 \pm 330/T]$ mol^{-1} cm^3 s^{-1}. The magnitude of k_7 and its temperature coefficient indicate that this reaction occurs as a direct bimolecular exchange of radicals. If two steps were involved, analogous to (δ), i.e.,

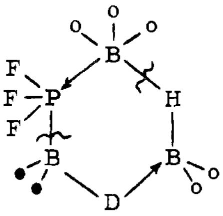
$$D_3BPF_3 \underset{2}{\overset{-2}{\leftrightarrows}} D_3B + PF_3 \qquad \Delta H°_2 = 24.5 \text{ kcal mol}^{-1}$$

$$D_3B + B_2H_6 \rightarrow D_3B{\cdot}BH_3 + BH_3 \qquad E_{est} \simeq 10 \text{ kcal mol}^{-1} \qquad (\epsilon)$$

$$BH_3 + D_3BPF_3 \underset{6}{\rightarrow} D_3B{\cdot}BH_3 + PF_3 \qquad E_6 = 4.8 \text{ kcal mol}^{-1}$$

$$D_3B + D_3BPF_3 \underset{6}{\rightarrow} B_2D_6 + PF_3 \qquad E_6 = 4.8 \text{ kcal mol}^{-1}$$

the observed activation energy would have been ~35 kcal mol^{-1} for the production of $D_3B{\cdot}BH_3$ and substantial levels of B_2D_6 would have been present in the product gas. Also, the overall exchange rate would have been as slow or slower than the decomposition of the adduct, contrary to observation. For the transition state of the bimolecular exchange we propose a six-atom ring:



We did not investigate the analogous exchange $D_3BCO + B_2H_6 \rightarrow H_3BCO + D_3B{\cdot}BH_3$. However, similar to (7) we measured the rates of radical exchange in

$$D_3BPF_3 + H_3BCO \rightleftarrows D_3BCO + H_3BPF_3 \qquad [K_8 \simeq 1] \qquad (8)$$

Here also, the rate is first order with respect to each species, and there is no significant accumulation of B_2H_6, which one would anticipate were the two-step process occurring (indicated by (ϵ)).

k_{8f}(295 °K) = k_{8r} = 1.34 × 10^3 mol^{-1} cm^3 s^{-1}
Av 4 runs

Expressed in Arrhenius form, $k_{8f} \approx 10^{13}\exp[-6744 \pm 100/T]$, mol^{-1} cm^3 s^{-1}.

Finally, we reanalyzed Maybury and Koski's[8] data on

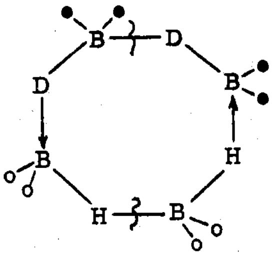
$$B_2H_6 + B_2D_6 \rightleftarrows 2H_3B{\cdot}BD_3 \quad [K_9 \simeq 4] \tag{9}$$

They reported an activation energy of 21.8 ± 3 kcal mol^{-1} and a total order of $^3/_2$. These two results are incompatible. If their proposed mechanism applied (dissociation + three-center displacement) the activation energy would have been (18 + 10) kcal mol^{-1}. Furthermore, their observed exchange rate would have been slower, being limited by the low steady state concentration of borane. We propose that (within their experimental error) their data can be fitted to an overall order of two, with

$$k_{9f} \simeq 10^{15} \exp[-7675 \pm 110/T] \quad \text{mol}^{-1}\,\text{cm}^3\,\text{s}^{-1}$$

$$k_{9r} \simeq 10^{14} \exp[-7675 \pm 110/T] \quad \text{mol}^{-1}\,\text{cm}^3\,\text{s}^{-1}$$

Here one may postulate an eight-atom ring for the transition state,[11]



As mentioned previously,[7] there is experimental evidence for the existence of single –H– bridges between two boron atoms. Also, one can account for the facile production of B_4H_{10} from B_2H_6 via this transition state, which merely has to lose H_2 in a transannular elimination.

It is interesting to note that unlike these fast reactions, the rate of the homogeneous exchange between B_2H_6 and D_2 is in doubt;[9] that for (H_3BCO + D_2) is also unknown. In contrast, Curtis and Porter[10] reported a fast bimolecular rate for

$$HBF_2 + D_2 \rightleftarrows DBF_2 + HD \quad [K_{10} = 4.22 \pm 0.1] \tag{10}$$

$$k_{10f} \simeq 10^{16} \exp[-8900/T] \quad \text{mol}^{-1}\,\text{cm}^3\,\text{s}^{-1}$$

$$k_{10r} \simeq 5 \times 10^{14} \exp[-9100/T] \quad \text{mol}^{-1}\,\text{cm}^3\,\text{s}^{-1}$$

Here a pentacoordinated boron atom characterizes the transition state.

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Registry No. H_3BCO, 13205-44-2; PF_3, 7783-55-3; B_2H_6, 19287-45-7; H_3BPF_3, 14931-39-6.

References and Notes

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(6) Estimated: analogous to reactions 1 and 2.

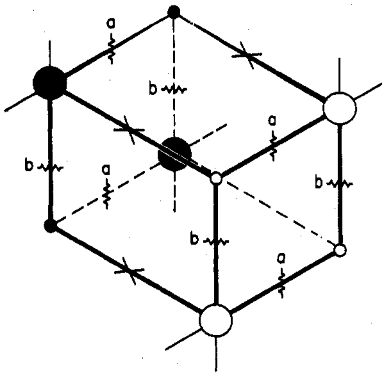
(7) Such structures have been proposed for various B/H compounds: R. E. Williams, H. D. Fisher, and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960); D. F. Gaines, *Inorg. Chem.*, **2**, 523 (1963); R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(8) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

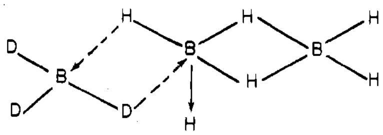
(9) Summary presented by J. D. Odom and R. Schaeffer, "Progress in Boron Chemistry", Vol. 2, R. J. Brotherton and H. Steinberg, Ed., Pergamon Press, Oxford, 1970, Chapter 4. The difficulty with Koski's data for the H/D exchange reaction between B_2H_6 with D_2 was not removed by R. A. Marcus' analysis [*J. Chem. Phys.*, **23**, 1107 (1955)] and the subsequent study by J. S. Rigden and W. S. Koski [*J. Am. Chem. Soc.*, **83**, 3037 (1961)]. We find it unreasonable that at 55 °C borane and D_2 attain a rapid equilibrium and that the overall exchange rate is limited by the rate of $H_2BD + B_2H_6 \rightarrow H_2DB{\cdot}BH_3 + BH_3$.

(10) P. M. Curtis and R. F. Porter, *Chem. Phys. Lett.*, **37**, 153 (1976).

(11) **Note Added in Proof.** Professor R. T. Paine, Jr. (University of New Mexico) proposed a cage structure for this transition state which is quite appealing, based on pentacoordinated boron atoms.



Exchanges occur upon approach of two diboranes along the →← path and then receed after cleavage either at the a∼∼ or b∼∼ bonds, thereby leading to exchange. Through the cage transition state, or via the 8-atom ring, the BH_3 units remain intact, such that in a double labeled experiment [$^{11}B_2D_6$ + $^{10}B_2H_6$], the rates of exchange of the $^{10}B/^{11}B$ and of the H/D are the same. In both cases the breaking away of a borane unit from the B_4H_{12} would be a less likely event, so that unequal B/H scrambling would be slower than borane exchange. On the other hand were the borane displacement to occur via four atom bridges



the integrity of the $^{11}BD_3$ or $^{10}BH_3$ would not be maintained.

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Preparation and Properties of Selenaboranes and Telluraboranes

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In aqueous ammonia Na_2Se_4 and Na_2Te_4 react with decaborane(14) to give $B_{10}H_{11}Se^-$ and $B_{10}H_{11}Te^-$, respectively. These anions form $B_{10}H_{12}Se$ and $B_{10}H_{12}Te$ upon acidification. The electron rich compound $B_9H_9Se_2$ is formed as a by-product in the reaction of polyselenide ion with decaborane. Treatment of $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ with aqueous KOH and $CoCl_2$ or $FeCl_2$ forms $Co(B_{10}H_{10}E)_2^{2-}$ and $Fe(B_{10}H_{10}E)_2^{2-}$ (E = Se or Te), respectively. Triethylamine, cyclopentadiene monomer, $CoCl_2$, and $B_{10}H_{12}Se$ or $B_{10}H_{12}Te$ in tetrahydrofuran solution form $(C_5H_5)Co(B_{10}H_{10}Se)$ and $(C_5H_5)Co(B_{10}H_{10}Te)$, respectively.

The first synthesis of polyhedral thiaboranes was reported nearly a decade ago.[1] To date this chemistry has not been extended to polyhedral insertion of other elements of group 6. This is probably due to the known malodorous and poi-