servations indicate that, qualitatively, the exchange is proceeding preferentially in the non-bridge positions. If we make the assumption that all of the deuterium entering the decaborane molecule by exchange is going into the non-bridge positions, then the per cent. deuterium as determined by thermal conductivity multiplied by 1.4 gives the percentage of non-bridge positions occupied by deuterium. Comparison of this figure with the infrared deduced percentage of non-bridge positions occupied by deuterium shows reasonable quantitative agreement as evidenced from the data in Table I. To within experimental error all of the deuterium that has entered the decaborane molecule by exchange can be accounted for by the amount of deuterium in the non-bridge positions, indicating that the exchange reaction proceeds preferentially into these positions.

TABLE I

DEUTERIUM ANALYSIS OF PARTIALLY DEUTERATED DECABORANE OBTAINED FROM THE B_2D_6–$B_{10}H_{14}$ EXCHANGE

Per cent. deuterium By thermal conductivity[a]	By infrared spectra (5.17 μ) (non-bridge positions)
14.7	16.6
27.4	29.1
41.7	40

[a] Calculated from thermal conductivity measurements assuming that all of the deuterium enters the non-bridge positions.

Another region in the spectrum which can be observed fairly well is an absorption band at 8.72μ due to a B–D–B bridge vibration. For statistical samples this B–D–B band rises almost linearly with increasing deuterium content. However, for exchange samples there is no rise in this peak at all. This fact constitutes further proof that the deuterium entering the decaborane molecule by the exchange reaction is not going into the bridge positions.

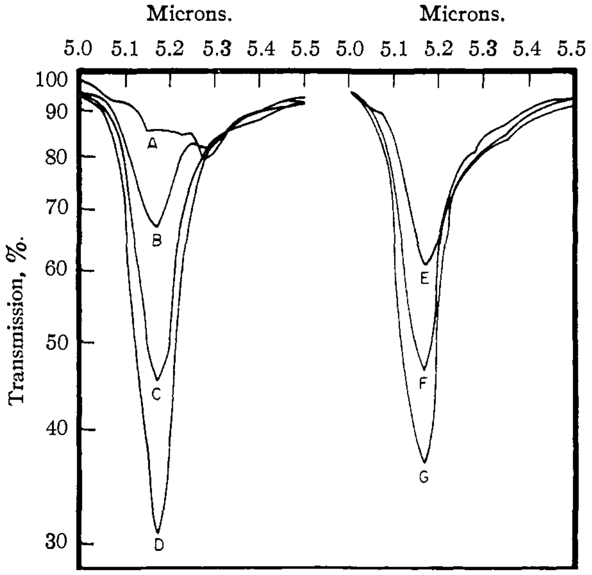

Fig. 1.—Infrared absorption of partially deuterated decaborane: A, $B_{10}H_{14}$ of normal isotopic content; B, C and D are samples of decaborane in which the deuterium is statistically distributed and have 12.9, 30.1 and 48.3% total deuterium, respectively. E, F and G are samples of decaborane prepared by exchange and contain 10.5, 19.6 and 29.8% total deuterium, respectively.

BALTIMORE, MD.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Energetics of the Boranes. II. Kinetic Consequences of the Diborane–Borane Equilibrium. Comments on the Decomposition of OC:BH_3

BY S. H. BAUER

RECEIVED MAY 25, 1956

The equilibrium $B_2H_6 \rightleftarrows 2BH_3$ has been assumed to play a dominant role in many reactions involving diborane. Eight independent kinetic studies have been analyzed to determine whether these data impose mutually consistent conditions on this dissociation. It is demonstrated that if the postulate is introduced that the rate of association of boranes is comparable to that for methyl groups ($k_{\mathrm{assoc}} \approx 10^{14}$ mole^{-1} cc. sec.$^{-1}$) six experiments lead to mutually compatible upper bounds for the heat of dissociation of diborane; the two smallest bracket the previously published thermochemical value of 28.4 ± 2 kcal. The remaining kinetic experiments do not give clear-cut estimates. With the introduction of an additional assumption one of these can be interpreted to give a lower bound which is consistent with the lack of a directly observable equilibrium dissociation pressure, and with the other studies listed above. The published mechanism for the decomposition of OC:BH_3 is shown to be incorrect and an alternate mechanism is proposed which does give the correct form for the observed pressure–time dependence. Comments are appended for the existence of activation energies for some primary acid–base associations.

In the first paper of this series[1] we reported a value for the heat of dissociation $B_2H_6(g) = 2BH_3(g)$, based on measured heats of reaction between diborane and tetramethyldiborane with several amines. Since the entropy increment for this reaction has been computed with adequate certainty (34.2 e.u.),[2] the equilibrium concentration of BH_3 may be estimated readily. This equilibrium has been utilized in eight postulated mechanisms describing the kinetic behavior of mixtures containing diborane. In five of these it is assumed as a first step

$$B_2H_6 \underset{k_d}{\overset{k_a}{\rightleftarrows}} 2BH_3 \qquad \text{(a)}$$

followed by

$$BH_3 + X \underset{k_x}{\longrightarrow} \text{products} \qquad \text{(b)}$$

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[1] R. M. McCoy and S. H. Bauer, THIS JOURNAL, **78**, 2061 (1956).

[2] A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).

so that the measured rate constant is directly related to the product ($k_x K_{eq}^{1/2}$). For this to be valid, the rate of removal of boranes *via* X must be less than their association rate

$$k_a > k_x \frac{(X)}{(BH_3)} = \frac{k_x(X)}{K_{eq}^{1/2}(B_2H_6)^{1/2}} \qquad (1)$$

i.e., a lower limit is indicated. It is possible to test whether these apparently diverse experiments are mutually consistent.

One of several procedures might be followed in comparing the kinetics data. One could start with a roughly estimated value for the enthalpy increment (say 32 kcal.), along with the computed entropy increment for reaction (a), as we had initially attempted,[3] insert the corresponding value for the equilibrium constant in eq. 1, and note the variety of lower limits for k_a thus deduced from the reported data. This procedure proved unsatisfactory because the minimal association rate thus found proved to be orders of magnitude greater than the collision number; for the self-deuteration reaction, the association rate was 10^3 greater than the collision rate, assuming a reasonable diameter for the boranes. Since it is now agreed[4] that the recombination rate of two methyl radicals at relatively high pressures is just that expected from the collision number, with no activation energy and with a steric factor close to unity, it is unreasonable to postulate that boranes could combine appreciably more rapidly. Hence, we chose to make the comparison in the following manner.

Consider the limiting high pressure case. Assume that $k_a = 1 \times 10^{14}$ mole^{-1} cc. sec.$^{-1}$, parallel to the case for methyl recombination. From eq. 1 deduce a lower bound for the magnitude of K_{1c} under initial conditions of the experiment, using the initial rates for k_x. Accept the computed value for the entropy increment for reaction (a): $\Delta S^\circ_{300} = 34.22$ e.u., and thus deduce an upper bound for the magnitude of ΔH° for that dissociation, from

$$\log_{10} K_{1p} = 7.478 - 0.2185\,\Delta H^\circ/T \qquad (2)$$

Since the various experimenters used different units in reporting their rate measurement, care must be exercised in reducing these data to the usual kinetic units (moles cc.$^{-1}$ sec.$^{-1}$) for comparison.

To obtain a feeling for the orders of magnitude involved and for the sensitivity of the method, observe from (1)

$$K_{1p}^{1/2} > k_x \left\{\frac{(X)(RT)^{1/2}}{k_a(B_2H_6)^{1/2}}\right\}$$

so that upon inserting the expression from (2)

$$\Delta H^\circ < \frac{T}{0.2185}\,[7.478 - 2\log_{10} k_x - 2\log_{10}\{\ \}] \qquad (3)$$

If the reported value for k_x were too large by a factor of 10, the deduced upper bound for the enthalpy would be too small by 2.75 kcal., at $T = 300$°K. Note also that since the *initial* rates will be used in the following analysis, the identity of the products formed in (b) or even the correctness of the subsequent mechanism is immaterial.

The Self Deuteration Reaction.[5]—In this case, equilibrium (a) is followed by

$$BH_3 + B_2D_6 \xrightarrow{k_3} B_2H_3D_3 + BD_3 \qquad (c)$$

The experiments were performed with equimolar proportions of B_2H_6 and B_2D_6, and magnitudes of k^m(sec.$^{-1}$) have been tabulated for various initial total pressures and temperatures for the rate of disappearance of B_2D_6. It follows that the quoted rate constants are

$$k^m(\text{sec.}^{-1}) = k_3 K_{1_{1p}}^{1/2} p_{B_2H_6}^{1/2}\,(2RT)^{-1} \qquad (4)$$

and these were indeed demonstrated to vary with the square root of the total pressure. Upon combining eq. 1, 2 and 4

$$k_a > \sqrt{2}\ k^m(\text{sec.}^{-1})(RT/K_{1p})$$

and

$$\Delta H^\circ < 27 \text{ kcal./mole of dimer}$$

based on the reported rate at $T = 297$° and $p_{\text{total}} = 10$ cm.

The Vapor Phase Hydrolysis.[6]—In this case, equilibrium (a) is followed by

$$BH_3 + H_2O \xrightarrow{k_4} BH_2OH + H_2 \qquad (d)$$

and further stepwise hydrolyses to produce $B(OH)_3$. Assuming that the initial observed rate of generation of H_2 is that appropriate for step (d), k_4 (mole^{-1} cc. sec.$^{-1}$) may be expressed in terms of the reported constant (mole$^{-1/2}$ l.$^{1/2}$ sec.$^{-1}$)

$$k_4 = k_{\text{hyd}}\ 10^{3/2}(RT)^{1/2}/K_{1p}^{1/2} \qquad (5)$$

and

$$k_a > [k_{\text{hyd}}\ 10^{3/2}(RT)^{1/2}/K_{1p}]\left(p_{H_2O}/p_{B_2H_6}^{1/2}\right)$$

Since no individual pressures were cited in the paper, we selected the nearly maximal ratio of unity for the last factor. (At 50°, the vapor pressure of water is 0.118 atm.; also, at the maximum ratio of water to diborane, $p_{B_2H_6} = 0.0102$ atm.) From the above it follows that

$$\Delta H^\circ < 30 \text{ kcal./mole}$$

based on the reaction constant at 324°K.

The Pyrolysis of Diborane.[7a,b]—In this case, equilibrium (a) is followed by

$$BH_3 + B_2H_6 \xrightarrow{k_5} B_3H_7 + H_2 \qquad (c)$$

with

$$k_5 = (760)^{1/2}RT\,k^+/K_{1p}^{1/2} \qquad (6)$$

where k^+ is the reported value for the rate constant times the square root of the equilibrium constant, in units of [mm.$^{-1/2}$ sec.$^{-1}$]. At 110°, the value for the latter is 2×10^{-6}. Then

$$k_a > (760)^{1/2}k^+RTp_{B_2H_6}^{1/2}/K_{1p}$$

$$\Delta H^\circ < 38 \text{ kcal./mole}$$

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[3] S. H. Bauer, A. Shepp and R. E. McCoy, This Journal, **75**, 1003 (1953).

[4] G. B. Kistikaowsky and E. K. Roberts, *J. Chem. Phys.*, **21**, 1637 (1953); R. E. Dodd and E. W. R. Steacie, *Proc. Roy. Soc. (London)*, **223A**, 283 (1954).

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

[6] H. G. Weiss and I. Shapiro, This Journal, **75**, 1221 (1953).

[7] (a) R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951); (b) J. K. Bragg, L. V. McCarty and F. J. Norton, *ibid.*, **73**, 2134 (1951).

for an initial pressure of diborane in the neighborhood of 50 mm.

The Diborane–Ethylene Reaction.[8]—In this case the authors propose that equilibrium (a) is followed by the steps

$$BH_3 + B_2H_6 \xrightarrow{k_6} B_3H_9 \qquad (f)$$

$$B_3H_9 + C_2H_4 \longrightarrow B_2H_5Et + BH_3, \text{ etc.} \qquad (g)$$

Assumption (f) is primarily justified by the empirically deduced dependence of the initial rate of pressure fall on the $^3/_2$ power of the diborane pressure

$$-\left(\frac{dp}{dt}\right)_0 = k_{\text{exp}} \frac{p_{B_2H_6}^{3/2}}{1 - a\dfrac{p_{B_2H_6}}{p_{C_2H_4}}}, \text{ with } a = 2.0$$

It follows that

$$k_6 = k_{\text{exp}} \frac{(760)^{1/2}}{5} \frac{RT}{K_{1p}^{1/2}} \qquad (7)$$

and

$$k_a > k_{\text{exp}}\, p_{B_2H_6}^{1/2} \frac{RT}{5K_{1p}}, \text{ with } p \text{ in mm.}$$

Since the object is to set a minimum condition, the smallest value of k_{exp} was taken from Table I[8] reported for $T = 403°K$. Then

$$\Delta H° < 38.4 \text{ kcal. mole}^{-1}$$

The last two upper bounds on $\Delta H°$ check very well, although the reactions and data upon which they are based do not appear to be mutually consistent. Whereas one expects an activation energy for (e), little if any is expected for (f); yet the same author reported

$$\left[\frac{\Delta H°_{\text{diss}}}{2} + E_f\right] > \left[\frac{\Delta H°_{\text{diss}}}{2} + E_e\right]$$

The former is 36.8 kcal. while the latter is 25.5 kcal. This is surprising in view of the reasonable notion that (f) is the activated complex path for (e). Further, since there is little doubt that $\Delta S°_{(a)} = +34.22$ e.u., the pre-exponential factor of K_{1_p} is 3.08×10^7 regardless of the value selected for $\Delta H°$. Whatley and Pease give

$$k_{\text{exp}} = 1.5 \times 10^{15}\, e^{-36800/RT}, \text{ mm.}^{-1/2} \text{ sec.}^{-1} \qquad (7^1)$$

It follows that the pre-exponential factor of k_6 is 5×10^{16}. This is too high for a bimolecular association reaction. These arguments suggest that the mechanism proposed by Whatley and Pease should be reconsidered.

Deuteration of Diborane.—As initially reported by Maybury and Koski[5] the kinetics of this reaction appeared to be complex; the authors suggested that the reaction of borane with deuterium occurred on the walls. Recently these data have been reinterpreted by Marcus[9] who showed that they are consistent with a homogeneous mechanism. Suppose

$$BH_3 + D_2 \underset{k_7}{\overset{k_{-7}}{\rightleftarrows}} BH_2D + HD \qquad (h)$$

$$BH_2D + B_2H_6 \xrightarrow{k_3} H_2DB{\cdot}BH_3 + BH_3, \text{ etc.} \qquad (i)$$

The over-all rate of isotope exchange is

$$R = \frac{6k_7(B_2H_6)^{3/2}K_{1c}^{1/2}}{2k_7/k_3 + 3(B_2H_6)/(D_2)} = 1.67 \times 10^{-5}k^*C_{B_2H_6}^{3/2} \qquad (8)$$

where k^* is the measured rate constant at 55°, and C is in (g. atoms H) liter^{-1}. The condition

$$k_a > \frac{k_7(D_2)}{(BH_3)}$$

gives

$$\Delta H° < 33 \text{ kcal. mole}^{-1}$$

Decomposition of Dimethyl Ether–Borane.—Both the equilibrium pressure and the rate of decomposition of the solid complex have been reported.[10]

$$2(CH_3)_2O{:}BH_3(s) = 2(CH_3)_2O(g) + B_2H_6(g) \qquad (j)$$

$\Delta F°_{195} = 5.08$ kcal./mole of diborane produced; decomposition occurs at an apparent unimolecular rate (in the amount of solid present) of 1.4–1.6% per hour (*i.e.*, 4.2×10^{-6} sec.$^{-1}$). From

$$4.2 \times 10^{-6} = \frac{kT}{h} \exp(-\Delta F^{\pm}/RT) \qquad (9)$$

we deduced that $\Delta F^{\pm} = 16.0$ kcal./mole of complex. We then introduce the following postulates Slow Step

$$Me_2O{:}BH_3(s) \xrightarrow{k_8} \underbrace{Me_2O(g) + BH_3(g)}_{} \qquad (k)$$

$$\text{"transition state"};\ \Delta F^{\pm} \geqslant \Delta F°_{k}$$

The measured free energy of activation is thus to be associated with step (k).

Rapid Association

$$2BH_3(g) \xrightarrow{k_a} B_2H_6(g) \qquad (a)$$

$$\Delta F_a° = (2\Delta F_k° - \Delta F_j°) \leqslant (2\Delta F^{\pm} - \Delta F_j°) = 26.9 \text{ kcal.} \qquad (10)$$

But $\Delta S_a° = 34.22$ e.u.; hence, $\Delta H° \leqslant 33.5$ kcal.

With the above arguments we have demonstrated that six independent kinetic studies led to mutually consistent upper bounds for the enthalpy of dissociation of diborane. The fact that the two lowest values bracket the calorimetric value[1] (28.4 ± 2 kcal.) which involved a "thermochemical extrapolation" lends support to the assumptions introduced therein, as well as to the postulate that the association rate constant for boranes is of the order of 1×10^{14} mole^{-1} cc. sec.$^{-1}$. With respect to the latter, two points need additional discussion. The nuclear magnetic resonance spectrum of diborane in the proton frequency range shows about eight peaks.[11] That well resolved maxima are observed is evidence that the average lifetime of diborane as a dimer is greater than 0.01 sec. This is consistent with the above estimate for the association rate; at the high pressure limit the latter leads to a lifetime for the dimer at 300°K. ($t_{1/2} \approx 1/k_d = 1/K_{1c}\, k_a$) of the order $10^{3.6}$ sec. No difficulty is encountered with the alternate mechanism by means of which a dissociation–association cycle can occur, *i.e.*, *via* a displacement reaction, such as was proposed by Maybury and Koski[5] to account

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[8] A. T. Whatley and R. N. Pease, THIS JOURNAL, **76**, 835 (1954).

[9] R. A. Marcus, *J. Chem. Phys.*, **23**, 1107 (1955).

[10] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 296 (1938).

[11] R. A. Ogg, Jr., *J. Chem. Phys.*, **22**, 1933 (1954); J. N. Shoolery, *Disc. Faraday Soc.*, No. 19, 215 (1955).

for the self-deuteration of diborane. On combining our thermochemical value[1] with their rate data, we deduce

$$k_3 = 3.1 \times 10^{14} \exp(-7600/RT) \text{ moles}^{-1} \text{ cc. sec.}^{-1} \quad (11)$$

For this process, at 300° K. and 1 atm. of diborane

$$t_{1/2} \cong \frac{1}{k_3(\mathrm{BH_3})_{\mathrm{eq}}} \approx 10^2 \text{ sec.}$$

The estimate $k_a \cong 10^{14}$ is thus not contradicted by the nuclear magnetic resonance data.[12]

The second point pertains to the implied efficiency of excitation of diborane by collisions, as per a Lindemann type mechanism. On writing

$$\mathrm{B_2H_6} + \mathrm{M} \underset{k\alpha}{\overset{k_{-\alpha}}{\rightleftarrows}} \mathrm{B_2H_6}^* + \mathrm{M} \quad (1)$$

$$\mathrm{B_2H_6}^* \underset{k\beta}{\overset{k_{-\beta}}{\rightleftarrows}} 2\mathrm{BH_3}$$

The high pressure limiting rate constant for dissociation

$$k_d = \frac{k_\beta k_\alpha}{k_{-\alpha}} = k_{-\beta} K_{1c} \quad (12)$$

Now, $k_{-\beta} = k_a = 10^{14}$ moles^{-1} cc. sec.$^{-1}$; for $T = 500$°K. $K_{1c} = 10^{2.865} \exp(-\Delta H°/RT)$; $(k_\beta/k_{-\alpha}) = 10^{-6}$ to 10^{-7}, by analogy with the case for two methyls (ref. 4). Hence

$$k_\alpha = (10^{21} \text{ to } 10^{23}) \exp(-\Delta H°/RT)$$

From 4 to 6 internal degrees of freedom must be assumed to be effective in the activation process (1).

To complete the bracketing of the magnitude of $\Delta H°$ we looked for systems which set lower bounds. The fact that no appreciable dissociation can be detected in diborane at 400°K., except for a slight pressure increase due to pyrolysis,[13] requires that

$$\log_{10} K_{1p} = \left[7.478 - \frac{0.2185}{T}\Delta H°\right] < -6.0 \quad (13)$$

$$\Delta H° > 25 \text{ kcal.}$$

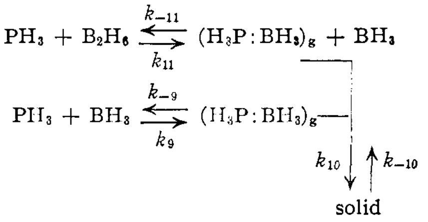
The remaining kinetic experiments unfortunately do not lead clear cut lower bounds.

Diborane with Phosphine.—For the reaction of this Lewis secondary acid and primary base to produce a solid product, Brumberger and Marcus[14] report that their kinetic data cannot be accounted for by the mechanism

$$\mathrm{B_2H_6} \underset{k_a}{\overset{k_d}{\rightleftarrows}} 2\mathrm{BH_3} \quad (a)$$

$$\mathrm{BH_3} + \mathrm{PH_3} \underset{k_9}{\overset{k_{-9}}{\rightleftarrows}} (\mathrm{H_3P{:}BH_3})_g \underset{k_{10}}{\overset{k_{-10}}{\rightleftarrows}} \text{solid} \quad (m)$$

but that another mechanism is satisfactory



$$\mathrm{PH_3} + \mathrm{B_2H_6} \underset{k_{11}}{\overset{k_{-11}}{\rightleftarrows}} (\mathrm{H_3P{:}BH_3})_g + \mathrm{BH_3} \quad (n)$$

$$\mathrm{PH_3} + \mathrm{BH_3} \underset{k_9}{\overset{k_{-9}}{\rightleftarrows}} (\mathrm{H_3P{:}BH_3})_g \quad (n')$$

$$(\mathrm{H_3P{:}BH_3})_g \underset{k_{-10}}{\overset{k_{10}}{\rightleftarrows}} \text{solid}$$

Clearly, reactions (a) + (m) are not quenched by the concurrent imposition of (n) + (m); the kinetic data merely require that the rate of removal of phosphine *via* (n) + (m) is more rapid than that *via* (a) + (m).

$$[2\mathrm{k}_{11}(\mathrm{B_2H_6})(\mathrm{PH_3})] > [k_9(\mathrm{BH_3})_{\mathrm{eq}}(\mathrm{PH_3})]$$

$$\frac{2k_{11}}{k_9} > (K_{1p}/p_{\mathrm{B_2H_6}})^{1/2} \quad (14)$$

$k_{11} = 2.3$ moles^{-1} cc. sec.$^{-1}$ at 0° ; $p_{\mathrm{B_2H_6}} \cong 0.05$ atm. One must make a judicious estimate of k_9; we have assumed it to be a 2.3×10^9 moles^{-1} cc. sec.$^{-1}$, extrapolating from the measured rate constant for $\mathrm{NH_3} + \mathrm{BF_3}$.[15] Then, a very rough lower bound, $\Delta H° > 30.5$ kcal. Preliminary kinetic data obtained in this Laboratory on the rate of reaction between trimethylamine and diborane require only that $\Delta H° > 10$ kcal.; this is not particularly informative.

Decomposition of Carbon Monoxide (C–B) Borane.—If one accepts the mechanism proposed by Burg[16] for the decomposition of "borine carbonyl," a lower bound is set for $\Delta H°$. He assumes that the following equilibrium is rapidly attained

$$\mathrm{OC{:}BH_3} \underset{k_{12}}{\overset{k_{-12}}{\rightleftarrows}} \mathrm{BH_3} + \mathrm{CO} \quad (o)$$

and this is followed by the rate limiting step

$$\mathrm{BH_3} + \mathrm{OC{:}BH_3} \xrightarrow[k_{13}]{} \mathrm{B_2H_6} + \mathrm{CO} \quad (p)$$

If the above is correct, one may argue that under the conditions of this experiment

$$[k_a(\mathrm{BH_3})^2] < [k_{13}(\mathrm{BH_3})(\mathrm{OC{:}BH_3})] \quad (15)$$

since step (p) rather than the association rate of boranes (a) determines the kinetics

$$k_a < k_{13}(\mathrm{OC{:}BH_3})^{1/2} K_{\mathrm{oc}}^{1/2}$$

Burg reported that the increment in standard free energy for the reaction

$$\mathrm{OC{:}BH_3} = 1/2\ \mathrm{B_2H_6} + \mathrm{CO} \quad (q)$$

$$\Delta F° = 4560 - 16.21T \quad (16)$$

from which it follows [by combining (q) with (a)] that for reaction (o)

$$\log_{10} K_{\mathrm{op}} = 7.281 - 996.5/T - 0.1092\ \Delta H°/T \quad (16')$$

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[12] An inconsistency, still to be substantiated, does appear for the tri- and tetramethyl substituted diboranes. For these Ogg reported that only one peak was present [*Disc. Faraday Soc.*, No. 17, 215 (1954)] suggesting that the average lifetime of these dimers is less than 0.01 sec. Since the ($\mathrm{BH_3B}$) bridges in these compounds are at most only 5 kcal. weaker than in diborane,[1] whereas the recombination rate constant for $\mathrm{BHMe_2}$ and $\mathrm{BH_2Me}$ units is still assumed to be $\cong 10^{14}$, the lifetimes for direct dissociation of these dimers must be of the order 10^3 sec. For a displacement type reaction, the lifetime can be reduced to about 10 sec.

The most plausible explanation for the lack of resolution of the nuclear magnetic resonance peaks is that the samples were actually complex mixtures of all (1 to 4) methyl substituted diboranes resulting from disproportionation reactions. Such interconversions are expected to occur extensively and rapidly at room temperatures [see ref. 1 for analyses of data by H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935)].

[13] A. Stock and E. Kuss, *Ber.*, **56B**, 789 (1923).

[14] H. Brumberger and R. A. Marcus, *J. Chem. Phys.*, **24**, 741 (1956).

[15] G. B. Kistiakowsky and R. Williams, *ibid.*, **23**, 334 (1955), reported 2.7×10^{11} for the ammonia–boron trifluoride association rate constant. For other substituted amines, the rates roughly parallel the $\Delta H°$'s for the association reactions. There is considerable evidence that $\mathrm{BH_3}$ is a somewhat stronger acid than $\mathrm{BF_3}$[1] but that $\mathrm{PH_3}$ is a considerably weaker base than $\mathrm{NH_3}$; hence, the reduction of the rate constant by two orders of magnitude. For the reaction of borane with water, the rate constant at 324°K. was measured[6]: $k_4 = 1.7 \times 10^1$ mole^{-1} cc. sec.$^{-1}$.

[16] A. B. Burg, THIS JOURNAL, **74**, 3482 (1952).

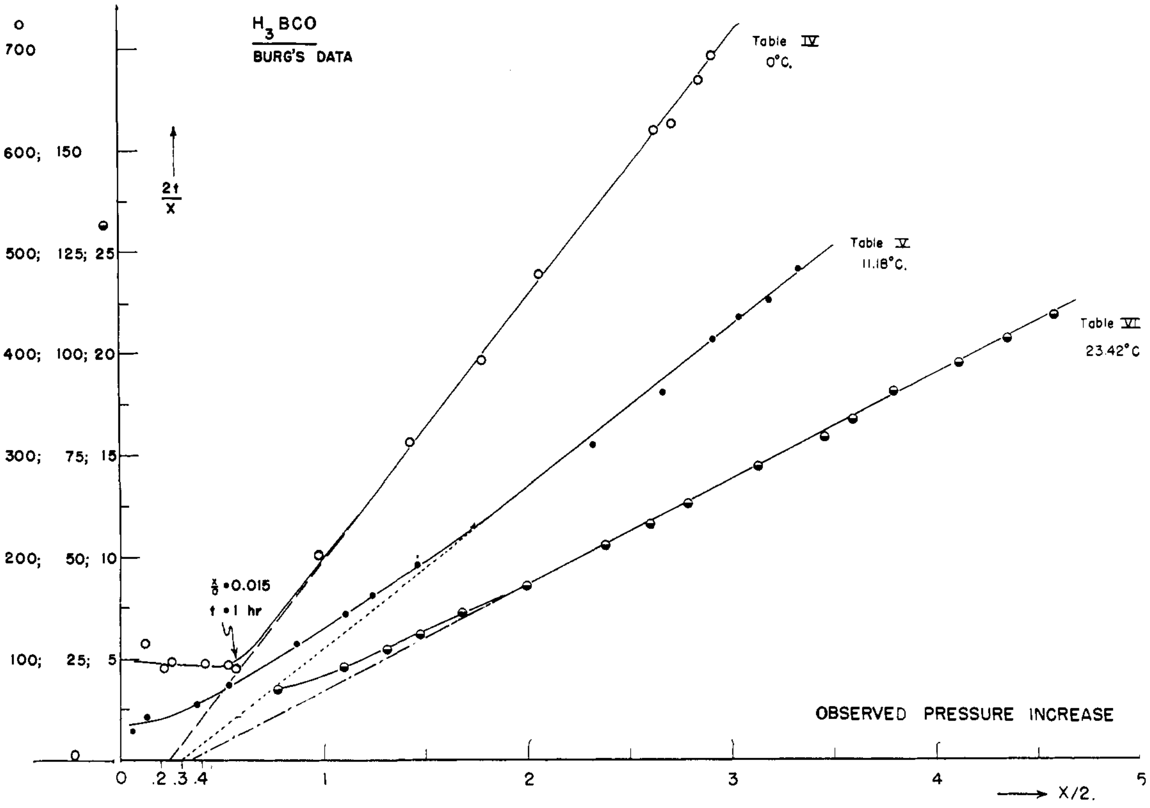

Fig. 1.—Pressure increase *vs.* (time/pressure increment) for the decomposition of carbon monoxide (C–B) borane.

He also reported a value for the product of K_{op} by the rate constant k_{13} (units sec.$^{-1}$); call that quantity $k^{\#}$. Then

$$k_a < RTk^{\#}\,(p^{1/2}_{OC:BH_3}\,K^{1/2}_{op}) \qquad (17)$$

$$\Delta H^\circ > 41 \text{ kcal./mole}$$

This is clearly incompatible with the other kinetic data. As indicated in the introduction, to maintain that ΔH° is greater than 41 kcal. would require that the six rate constants cited above as measured for different reactions by independent investigators were all in error by many orders of magnitude. Further, this value is inconsistent with our thermochemical data. Hence, we concluded that the above mechanism is not correct. Reservations regarding the cited mechanism were expressed by Burg who presented the simplest account consistent with the data available for the later parts of the experiments; the early pressure measurements were clearly not reproduced by his rate equations.

Three items remain: demonstration that Burg's pressure data are not consistent with the mechanism (o) + (p); presentation of an alternate satisfactory mechanism; and a justification of the conclusion that (o) does not reach equilibrium rapidly even though this represents a Lewis acid–base reaction.[17]

To test how well Burg's mechanism fits the data, expand his rate expression

$$2k^{\#}t = \frac{x}{a-x} + \ln\frac{a-x}{a};\quad a = \text{initial } p_{OC:BH_3}$$

x = instantaneous p_{CO}
$x/2$ = obsd. pressure increase

Since $(x/a) << 1$

$$2k^{\#}t = \frac{1}{2}(x/a)^2 + \frac{2}{3}(x/a)^3 + \ldots \qquad (18)$$

The maximum value for (x/a) in most of the experiments cited in his Table V is about 0.10; neglect of $(x/a)^4$ and higher terms introduces a maximum error of 1%. Upon rearrangement

$$\frac{2t}{x} = \frac{x}{2k^{\#}a^2} + \frac{2x^2}{3k^{\#}a^3} + \ldots \qquad (19)$$

Hence, a plot of $(2t/x)$ *vs.* $(x/2)$ should give a curve which *passes through the origin*, and is initially *linear*, with a slope of $(1/k^{\#}a^2)$. Three sets of data are plotted in Fig. 1.[18] Inspection shows that neither condition is fulfilled. One cannot force an agreement even by taking the extrapolated $(x/2)$ value as the initial pressure, on the assumption that all the pressure readings were high by 0.26 mm. and using either the given time scale or a corrected time scale $(t - 25)$. It is significant that as $x \rightarrow 0$, $(2t/x) \rightarrow$ a constant, and that during the first hour $(2t/x)$ changes slowly. This is clearly incompatible with the assumption of an initial rapidly attained equilibrium.

We now propose that the rate-limiting step is

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[17] Prof. R. W. Parry informed me that his preliminary rate data on the decomposition of $F_3P:BH_3$ are very similar to those presented by Burg for $OC:BH_3$, suggesting that the same mechanism was operative in both cases. We must argue that the analogous reaction

$$F_3P:BH_3 \rightleftarrows PF_3 + BH_3 \qquad (r)$$

also does not rapidly attain equilibrium.

[18] We are indebted to Prof. A. B. Burg who sent us two sets of unpublished data (the 11.18 and 23.42° runs) for inclusion in this graph.

the production of boranes *via* eq. (o); that k_{-12} does involve an activation energy, and that the activation energy for the decomposition of $OC:BH_3$ is indeed larger than the B–C bond dissociation energy. The latter is 18.8 kcal.[1] whereas Burg found 27.5 kcal. for the activation energy for the over-all decomposition; hence, k_{-12} has an activation energy of about 8.7 kcal. The slow step (o) can occur either through a Lindemann mechanism or through a three body collision, and is followed by the relatively rapid reactions

$$BH_3 + OC:BH_3 \underset{k_{13}}{\overset{k_{-13}}{\rightleftarrows}} B_2H_6 + CO \qquad (p)$$

$$BH_3 + BH_3 \underset{k_a}{\overset{k_d}{\rightleftarrows}} B_2H_6 \qquad (a)$$

This postulate implies that the activation energies for the forward step in (p) and the association (a) are both less than for k_{-12}.

From *stoichiometry*, the gain in pressure at time t (Burg's $x/2$) is half of the integrated rate of disappearance of $OC:BH_3$ or rate of appearance of CO

$$-\frac{d(OC:BH_3)}{dt} = [k_{12} + k_{13}(H_3B)](OC:BH_3) - \{k_{-12}(H_3B) + k_{-13}(B_2H_6)](CO) = \frac{d(CO)}{dt} \qquad (20)$$

During the early and intermediate stages of the reaction, the amount of diborane generated *via* (a) is negligible; also

$$k_{13}(H_3B) << k_{12};\; k_{-12}(H_3B) << k_{-13}(B_2H_6)$$

Using Burg's definitions of x and a, the kinetic equation reduces to

$$-\frac{dx}{dt} = \frac{k_{-13}}{2}(x^2 + \mu x - \mu a);\; \mu \equiv \frac{2k_{12}}{k_{-13}};\quad \theta \equiv \sqrt{\mu^2 + 4\mu a} \qquad (21)$$

$$\frac{2t}{x} = \frac{8}{\theta k_{-13}x}\left[\tanh^{-1}\left(\frac{2x+\mu}{\theta}\right) - \tanh^{-1}\frac{\mu}{\theta}\right] \qquad (22)$$

Equation 22 has the form which matches the experimental points in Fig. 1. On expansion of the right member

$$\frac{2t}{x} = \frac{16}{k_{-13}\theta^2} + \frac{8}{3k_{-13}\theta^4}[8x^2 + 12x\mu + 6\mu^2] + \ldots \qquad (23)$$

$x \rightarrow 0$ a constant positive value is approached; as x increases, the magnitude of $(2t/x)$ begins to increase first slowly and then rapidly in a manner dependent both on the initial concentration of $OC:BH_3$ and on the ratio (k_{12}/k_{-13}). This represents the well established inhibition of the reaction by the accumulated B_2H_6 and CO. Evaluation of the constants will not be attempted at this time due to the lack of sufficient data. It is clear, however, that the kinetics of the decomposition of $OC:BH_3$ as interpreted herein imposes no restriction on the magnitude of $\Delta H°$.

On Acid–Base Reactions.—It is generally accepted that the association rate is high for molecules which in their ground state have a non-bonding electron pair with a relatively low ionization potential, with molecules which in their ground state are lacking two or more electrons to complete a stable shell; the reaction may be too rapid to be followed with the usual kinetic techniques. This has led to the tacit assumption that all such primary acid–base reactions occur with no activation energy.[19] Recently, using an ingenious adaptation of the flame diffusion technique, Kistiakowsky, *et al.*,[15,20] measured the rates for typical acid–base pairs and found that even in the fastest of these reactions, boron trifluoride with pyridine, only about $^1/_{100}$ of the collisions are effective in association; for the same acid with a slightly weaker base (NH_3) this factor goes down to $^1/_{1000}$. In contrast, the association of two methyls appears to occur at every collision.[4] The implication is (this we hope to check by direct experiment) that in the association even of strong acids and bases small activation energies may be present, and for weaker pairs larger barrier must be overcome. This is consistent with a qualitative theoretical analysis of the association process.[21]

The potential surface for the adiabatic transition from the ground levels of the uncomplexed states at large intermolecular separations to the lowest bound valence state for the complex may be considered to be synthesized from two surfaces. At very large r there is no interaction (taken as the zero of potential); as r decreases there is an initial van der Waals attraction, but on further decrease in r repulsion sets in between the outermost electronic envelopes, and the potential rises steeply. There would be no bonding if it were not that in this region the non-bonding surface is intersected by a second downward sloping potential surface corresponding to the attractive interactions between electronically excited donor and acceptor molecules, this excitation being equivalent to their valence states in the complex. When the system is on the latter bonding potential surface the nuclear configurations of the molecules is approximately that found in the complex. The two surfaces belong to the same symmetry species, and cannot cross. Hence, for further decrease in r the adiabatic path follows the downward sloping attractive potential surface and a stable complex results. The potential at the region around the crossover may be below or above zero (absence or presence of an activation energy) depending on the detailed shapes of the two surfaces. As yet no quantitative theory is available which permits the plotting out of this region. It is obvious, however, that if the dissociation energy for the donor–acceptor bond following the hypothetical isovalent curve is not large, while the excitation energy required to bring the stable separated molecules from their ground states to the electronic states appropriate for bonding is large, the ΔH for complex formation will be numerically small, and the association process will have to pass over an activation hump. One would expect ΔH and E_{act} to be roughly parallel but not necessarily directly proportional to one another. A large electronic excitation is a consequence of a relatively high ionization potential for the non-bonding electrons in the base, or a low electron affinity of the acid. A small dissociation energy in the isovalent curve is a

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(19) G. N. Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

(20) D. Garvin, V. P. Quinn and G. B. Kistiakowsky, *Disc. Faraday Soc.*, **17**, 32 (1954).

(21) R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

TABLE I

Reaction	*A*	E_{act} (kcal.)	Remarks
$BH_3 + B_2D_6 \rightarrow H_2B\overset{H}{\underset{D}{}}BD_2 + BD_3$	14.49	7.6	Ref. 5
$BH_3 + HD \rightarrow BH_2D + H_2$	~11.60	~7	Ref. 9
$BH_3 + H_2O \rightarrow BH_2OH + H_2$	~11.28	~6 (Our estm.)	Ref. 6. Authors did not measure *E*; they gave $k_4 = 10^{7.232}$ at 324°K.
$BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2$	11.15	11.5	Ref. 7a and 7b differ somewhat; we took for measured $E_{\text{act}} = 25.5$ kcal.
$PH_3 + B_2H_6 \rightarrow H_3P{:}BH_3(g) + BH_3$	9.47	11.4	Ref. 14
$BH_3 + CO \rightarrow OC{:}BH_3$	...	8.7	Ref. 16 and this paper; rate constants for new mechanism not available
$OC{:}BH_3 \rightarrow BH_3 + CO$	...	27.5	
$BH_3 + BH_3 \rightarrow B_2H_6$	14.00	0	Assumed in this paper
$B_2H_6 \rightarrow BH_3 + BH_3$	$(10^{19.56})/T$	28.4	Based on K_{1p} (ref. 1) and above assumption

consequence of the necessity for extensive configurational adjustments in the uncomplexed molecules (particularly in the acid), for the quenching of resonance energies which may be present in the uncomplexed molecules, and of steric repulsions brought about when the coördination number of both the acid and base atoms is increased by one. In addition, there is the expected variation of dissociation energy with inductive effects due to various substituents on the acid and base atoms, and on their atomic size, decreasing in magnitude as the electrons involved in bonding occupy orbitals with large principal quantum numbers.

The above permits us to account for the following observations. The association of H_3B with CO or PF_3 requires an activation energy of roughly 9 kcal.; although many attempts have been made,[22] no complex has been prepared from BF_3 with either of these bases; in contrast, PH_3 forms complexes with both the acids, BH_3 and BF_3.[23,24]

That the reaction between carbon monoxide and a strong acid should require an activation energy is not unreasonable. Carbon monoxide has two nonbonding molecular orbitals with an electron pair in each. The ionization potential for the electrons in the ($s\sigma$) orbital, with most of the electron density external to the C–O bond on the oxygen end, has been computed to be 20.011 volts; for the electrons in the ($u\sigma$) orbital, with most of the electron density on the carbon end, it has been computed to be 13.373 volts.[25] It is thus obvious that the basic properties of CO must be associated with the carbon atom, but these are weak by comparison with methyl ether, trimethylamine, or dimethyl thioether, for which the ionization potentials for the non-bonding electrons are 10.5, 9.4 and 9.4 v., respectively. When BH_3 and CO approach the crossover region must occur at rather small intermolecular separations, when stabilization of the complex due to $B \leftarrow C$ bonding begins to compensate for the destabilization of the CO due to partial electron abstraction and loss of resonance energy; the hump in the adiabatic path is appreciable.

There is an abundance of evidence that CO is a very weak base, and that when it does act in this manner an activation energy is required. It adds to carbonium ions (generated by acid catalysts, such as BF_3), but somewhat elevated temperatures and relatively high pressures are needed.[26] Alternatively, a heterogeneous step, such as adsorption on surfaces of metals known to be good catalysts, provide sufficient activation; metal ions act as acceptors only when additional orbitals (π or d) can participate in bonding.[27] Boron trifluoride is about 5 kcal. weaker as an acid (as measured by ΔH° association with amines) than is BH_3. For BF_3 + CO, we estimate

$$(\Delta F^\circ) = -14 + 0.036T, \text{ kcal.}$$

This would not fully account for the failure of several serious attempts to prepare the complex $OC{:}BF_3$. We believe that due to the quenching of resonance (which stabilizes the planar configuration of BF_3) and the necessity for large structural adjustments in the acid as the donor–acceptor bond is formed, the boron and carbon atoms must approach even more closely than in $OC{:}BH_3$ before the crossover to the attracting potential can occur. As much as 15 kcal. may be required as activation energy, so that the preparation must be undertaken at elevated temperatures. But, under such conditions, the positive $T\,\Delta S^\circ$ term makes the free energy increment unfavorably positive.

Phosphorus trifluoride seems to behave in a manner analogous to CO; regrettably its ionization potential is not known. PF_3 is indeed a weak base due to the strong inductive effects by the three fluorine atoms; in contrast, PH_3 is a considerably stronger base. The activation energy measured (reaction n) for k_{11} is 11.4 kcal.[14] whereas the activation energy associated with k_{13} (reaction p) we estimate to be about 15 kcal. Hence, phosphine forms stable complexes with both borane and trifluoroborane.

Summary of Rate Constants.—On the basis of the available thermochemical and kinetic data it appears that the best value for the heat of dissociation of diborane is 28.4 ± 2 kcal. For dissociation,

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(22) A. W. Laubengayer and later R. M. McCoy were unsuccessful in the preparation of $OC{:}BF_3$ (private communications). For attempts on $F_3P{:}BF_3$ refer to H. S. Booth and J. H. Walkup, THIS JOURNAL, **65**, 2334 (1943).

(23) E. L. Gamble and P. Gilmont, *ibid.*, **62**, 717 (1940).

(24) H. C. Brown and R. B. Johannesen, *ibid.*, **72**, 852 (1950).

(25) R. C. Sahni, *Trans. Faraday Soc.*, **49**, 1246 (1953).

(26) C. R. Noller, "Chemistry of Organic Compounds," Saunders, 1952, p. 159; D. V. N. Hardy, *J. Chem. Soc.*, 358, 364 (1936); T. A. Ford, H. W. Jacobson and F. C. McGrew, THIS JOURNAL, **70**, 3793 (1948); J. W. Reppe, *et al.*, *Ann. (Liebig)*, **582**, 1 (1953).

(27) J. Chatt, *Nature*, **165**, 637 (1950).

the equilibrium constant, per mole of diborane, is

$$\log_{10} K_{1p\,(\text{atm})} = 7.478 - 6205/T$$

The measured kinetic constants which were cited by the various authors in the form of $(k_x K_{\text{eq}}^{1/2})$ now can be evaluated separately. These have been assembled in Table I for ready reference, expressed in the form $10^A \exp(-E/RT)$, with concentration units in [moles cc.$^{-1}$].

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[CONTRIBUTION FROM McPHERSON CHEMICAL LABORATORY, THE OHIO STATE UNIVERSITY]

Investigation of the Complexes of Mercury(II) with Ethylenediaminetetraacetic Acid Using the Mercury Electrode

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Mercury(II) forms complexes with ethylenediaminetetraacetate ion which are reversibly reduced at the dropping mercury electrode in the acidic *p*H range and to a *p*H of 10 if a relatively large excess of the ligand is present. The composite anodic–cathodic polarographic waves with excess ligand have slopes of 0.030 volt corresponding to a reversible 2 electron transfer. The relative magnitudes of the anodic and cathodic diffusion currents as well as the 0.030 volt shift in the wave for a tenfold change in the ethylenediaminetetraacetic acid concentration prove the complexes contain one mercury(II) and one ethylenediaminetetraacetate ion. The mercury pool electrode rapidly reaches equilibrium with the complexes in solutions containing excess ligand from a *p*H of 10 to at least 2. The potential of the electrode as a function of *p*H and ligand concentration has permitted the interpretation of the equilibrium and the evaluation of the equilibrium constants. Below a *p*H of 3.5, the association of one hydrogen ion by the bound ligand occurs while above a *p*H of 8, the association of one hydroxyl ion occurs. The predominant species in the *p*H range of 4 to 8 is Hg(enta)^{2-}, with $K_{100} = 10^{21.64 \pm 0.02}$ at 25° and $\mu = 0.1$. In more acidic solutions Hg(Henta)^- also occurs with $K_{110} = 10^{14.62 \pm 0.10}$. In more basic solutions the second species is Hg(OH)(enta)^{3-} with $K_{101} = 10^{26.60 \pm 0.15}$.

Introduction

After the completion of the polarographic portion of the present investigation a similar study was reported by Matyska and Kossler.[2] In agreement with our results they found three complexes Hg(enta)^{2-}, Hg(Henta)^- and Hg(OH)(enta)^{3-} where enta indicates the ethylenediaminetetraacetate ion. However, their complexity constants were consistently smaller than ours. It was concluded that the difference was caused by an unreliable saturated mercury(I) sulfate reference electrode to which they assigned a potential of 0.417 volt instead of the theoretical 0.65 volt. More recently Goffart, Michel and Duychaerts[3] as well as Schwarzenbach, Gut and Anderegg[4] have studied the complex polarographically. The former authors studied the system by the conventional polarographic method in the *p*H range of 4.5 to 9.2. Their data indicated a single complex Hg(enta)^{2-} in this *p*H range with a complexity constant of $10^{22.15}$ at 25° and $\mu = 0.065 \pm 0.02$. Schwarzenbach, Gut and Anderegg[4] obtained polarograms of a solution containing two metal ions and insufficient enta to completely complex them. From the wave height of one metal ion in the uncomplexed form the known complexity constant of one of the complexes, and the known total concentrations, they calculated the concentrations of all metal species and finally the unknown equilibrium constant. In this way the complexity constants for a large number of cations were calculated. Although the method did not succeed for mercury(II), they included equilibrium constants presumably calculated on the basis of the shift of half wave potential. For the simple and the acid complexes of mercury(II) at $\mu = 0.1$ and 20° their values, $K_{100} = 10^{21.80}$ and $K_{110} = 10^{14.64}$, are in good agreement with ours.

Theoretical

The general mathematical procedure used in the present study was presented in an earlier paper.[5] Since all of the complexes contained mercury(II) and the ligand in a (1:1) ratio, the calculations were relatively simple. The various equilibria involving the association of hydrogen ion with the bound ligand were first considered in terms of the concentration of ethylenediaminetetraacetate ion and the activities of hydrogen ions, instead of ions such as Henta^{3-} and $\text{H}_2\text{enta}^{2-}$, since this greatly simplified the calculations. These constants, indicated by primes, were finally converted to the desired forms.

In the following equations, parentheses indicate concentrations while brackets indicate activities.

$$\text{Hg}^{2+} + \text{enta}^{4-} \rightleftharpoons \text{Hg(enta)}^{2-};\quad K_{100} = \frac{(\text{Hg(enta)}^{2-})}{(\text{Hg}^{2+})(\text{enta}^{4-})} \tag{1}$$

$$\text{Hg}^{2+} + s\text{H}^+ + \text{enta}^{4-} \rightleftharpoons \text{Hg(H}_s\text{enta)}^{(2-s)-};\quad K'_{1s0} = \frac{(\text{Hg(H}_s\text{enta)}^{(2-s)-})}{(\text{Hg}^{2+})[\text{H}^+]^s(\text{enta}^{4-})} \tag{2}$$

$$\text{Hg}^{2+} + t\text{OH}^- + \text{enta}^{4-} \rightleftharpoons \text{Hg(OH)}_t\,\text{enta}^{(2+t)-};\quad K_{10t} = \frac{(\text{Hg(OH)}_t\text{enta}^{(2+t)-})}{(\text{Hg}^{2+})[\text{OH}^-]^t(\text{enta}^{4-})} \tag{3}$$

In terms of these equilibria, eq. 8 for Leden's[6]

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[1] Presented in part before the Division of Physical and Inorganic Chemistry, American Chemical Society, at Kansas City, Mo., April 1, 1954. Taken in part from a thesis by J. G. Mason submitted in partial fulfillment of the requirements for the Ph.D. degree, The Ohio State University, 1955.

[2] B. Matyska and I. Kossler, *Collection Czech. Chem. Commun.*, **16**, 221 (1951).

[3] J. Goffart, G. Michel and G. Duychaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

[4] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, **37**, 939 (1954).

[5] J. I. Watters and John G. Mason, THIS JOURNAL, **78**, 285 (1956).

[6] I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).