The deposition of manganese on the surface is corroborated visually by the fact that no colloidal manganese dioxide formed in the solutions during the tests, whereas similar tests in which no manganese dioxide surfaces were introduced showed increasing quantities of colloid in the solutions as the peroxide decomposed.

These results are interpreted as confirming the conclusion drawn from the electrode potential measurements that the solution adjacent to the manganese dioxide surface is saturated with manganous hydroxide.

Acknowledgment.—The authors are indebted to Dr. T. K. Sherwood and Dr. E. R. Gilliland for many helpful suggestions, and to the Naval Bureau of Ordnance for support and release of this work.

Summary

The electrode potential of a manganese dioxide electrode was measured in hydrogen peroxide solutions of various peroxide and ion concentrations. Of a number of possible electrode reactions, the results were in most consistent agreement with the assumption that the potential was controlled by the reaction

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{++} + 2H_2O$$

and that the solution immediately adjacent to the manganese dioxide surface was saturated with manganous hydroxide, even though the bulk of the solution was not.

Measurements of the change of manganese concentration in hydrogen peroxide solutions decomposing in contact with macroscopic manganese dioxide surfaces gave results supporting the assumption that the solution adjacent to the surface was saturated with manganous hydroxide.

The inconsistency between the conclusion drawn in the first paper of this series (that catalysis of hydrogen peroxide decomposition by manganese dioxide will not occur unless the solution is saturated with manganese dioxide) and the fact that macroscopic manganese dioxide surfaces act catalytically in solutions having bulk concentrations below saturation is thus removed.

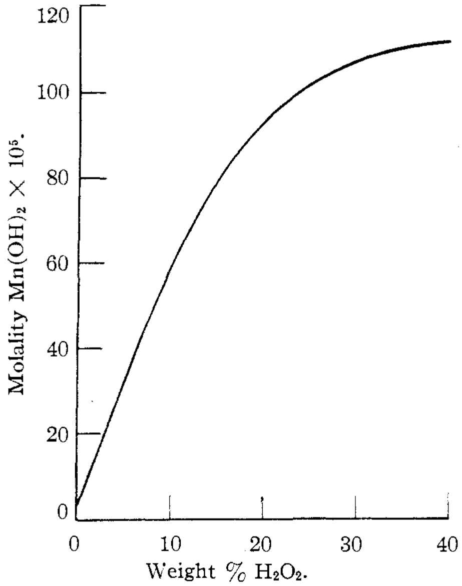

Fig. 5.—Solubility of manganous hydroxide in hydrogen peroxide solutions.

CAMBRIDGE, MASS. RECEIVED JUNE 3, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF SOUTHERN CALIFORNIA]

Proton–Deuteron Exchange between Ammonia and Ammoniated Diborane

BY ANTON B. BURG

Earlier publications[1,2,3,4] brought forth several kinds of experimental evidence pointing uniquely to the idea that diborane (B_2H_6) behaves toward bases (electron donors) as if it consisted of separable pairs of borine (BH_3) radicals, able to share electrons furnished by other molecules. Thus the volatile solid material of the composition $B_2H_6{\cdot}2N(CH_3)_3$ proved to be the borine complex $(CH_3)_3N:BH_3$[1,5] and $B_2H_6{\cdot}2NH_3$ (if prepared carefully by an addition reaction at $-120°$), behaved as one would expect of the structure $NH_4^+(BH_3)_2NH_2^-$.[2] The latter reacted further with liquid ammonia, evidently drifting toward the equilibrium $NH_4(BH_3)_2NH_2 + 2xNH_3 \rightleftarrows 2BH_3NH_3{\cdot}xNH_3$, probably not appreciably complicated by $(NH_4)_2(BH_3)_3NH$ or $(NH_4)_3(BH_3)_4N$. There was no evidence which could reasonably be interpreted to favor the formula $(NH_4)_2B_2H_4$.[6]

Although the borine theory of the base-reactions of diborane appears to be fairly generally accepted, there has recently been a tendency to revive the di-protic acid hypothesis, because of its simple relation to the protonated double bond idea of the structure of diborane.[7] It therefore became necessary to seek new evidence bearing on the subject—evidence preferably simple and yet decisive enough to eliminate all doubt.

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[1] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1937).

[2] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 290 (1938).

[3] H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 673 (1939).

[4] H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

[5] S. H. Bauer, *ibid.*, **59**, 1804 (1937).

[6] E. Wiberg, *Z. anorg. allgem. Chem.*, **173**, 210 (1928).

[7] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945).

Such evidence was found in the study of the proton–deuteron exchange reaction between free ammonia and ammoniated diborane. The experiments were planned in two ways: (1) treatment of $B_2H_6\cdot 2NH_3$ with known proportions of nearly pure ND_3, and observing the rate and final extent of substitution of H for D in the ND_3; (2) dissolving $B_2H_6\cdot 2ND_3$ in liquid ND_3 and retesting the ND_3 for purity.

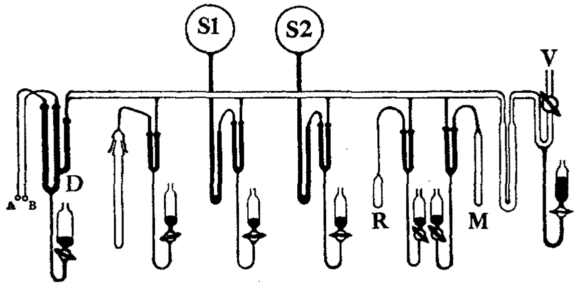

Fig. 1.—Silhouette of apparatus.

Experiments of type (1) showed that the exchange reaction reaches equilibrium within a few seconds after the solid $B_2H_6\cdot 2NH_3$ and ND_3 form a liquid solution at −78°. The composition of the free ammonia then corresponds to a mixture of all the ammonia (bound and free). This agrees with the borine theory, according to which only the N–H links in $NH_4(BH_3)_2NH_2$ should be able to exchange with ND_3. The transfer of protons from diborane to ammonia to form $(NH_4)_2B_2H_4$ would imply one-third more proton-contamination of the ND_3 than is observable.

An experiment of type (2) showed no exchange. The recovered ND_3 had received no appreciable contamination by protons from diborane, even though the solution had been allowed to warm to 18° during many hours. The formula $(ND_3H)_2$-B_2H_4 would have implied an easily detectable 5% substitution of H for D in the ND_3, occurring rapidly at −78°. Again there was no H–D exchange when B_2H_6 and ND_3 were suddenly brought to reaction at room temperature, with extensive ammonolysis.

It thus is no longer within reason to assume that protons can be transferred directly from diborane to a base. The only possible alternative is that the acidic character of diborane is due to the electron-receptor character of the boron atom.

Since the discovery of the borohydrides,[8,9,10] it has become necessary to admit a theoretical alternative to the idea that the base reactions of diborane are all due to the borine radical. One may consider also the reaction form $BH_2^+BH_4^-$. The diammoniate thus would be $(NH_3)_2BH_2^+BH_4^-$, in logical symmetry to $NH_4^+(BH_3)_2NH_2^-$. However, such a borammonium borohydride structure seems to be eliminated by a formidable array of facts,[2] and, in any case, the strong proton-donor character of the quaternary nitrogen atoms should render the proton-sensitive BH_4^- ion incapable of existence.

Experimental

Apparatus.—A completely greaseless high-vacuum system was constructed in the form silhouetted in Fig. 1. It was attached at V to the main high-vacuum manifold, from which purified diborane or ammonia could be delivered. The 200-cc. bulbs S1 and S2 were used for storage of gaseous samples or for measurement of gas volumes of ND_3 (employing the mercury float-valves as null manometers). The ammoniation of diborane and the subsequent exchange reaction were carried out in the small reaction tube R. The deuterium content of the recovered ammonia then could be estimated by comparison of its vapor tension with that of a known mixture, in the differential tensiometer D. Comparison samples of mixed ammonias could be stored temporarily in tube M.

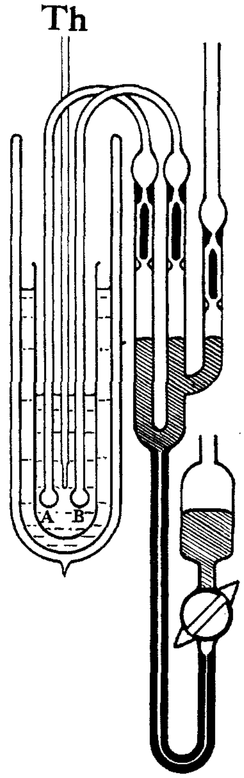

Fig. 2.—The differential tensiometer.

The tensiometer was as shown more clearly in Fig. 2. It was essentially a three-way mercury float-valve, with two arms ending in bulbs A and B. The standard ND_3-NH_3 mixture was condensed into bulb A (at −183°; B at room temperature) and a small part sublimed away, in order to clear out any possible trace of noncondensable gases. Next the mercury level was raised to cut off access to A, and the test sample was condensed into B, again with return sublimation. Then with all three glass plugs floated into place, A and B were immersed in ether, contained in a test-tube dipping into propane near its boiling point. Finally, the mercury was lowered half-way, and the differences of pressure could be read. The tip of the ammonia vapor tension thermometer[11] served as a stirrer for the final approach to thermal equality.

Sources of Materials.—*Ammonia-d_3* was prepared by the reaction of D_2O (99.9% according to label by Stuart Oxygen Co.) with magnesium nitride. The procedure was the same in almost every detail as that described by Kirschenbaum and Urey[12]; the reaction took place in tube I, from which the product was distilled directly into the vacuum system and resublimed. Comparison with pure ammonia in the differential manometer showed a vapor tension difference of 62 ± 0.3 mm. at −42.3°. Calculation from the equations[12] gave 62.1 mm. for ND_3 assaying 98% deuterium. It thus seemed reasonable to base assay calculations upon 98% original purity of the ND_3, and to estimate the probable error as 0.5%. In later experiments, the error of reading was lowered to about 0.1 mm., or 0.2%.

Diborane was freed of hydrogen by trapping from the pump-stream at −183°, and then distilled *in vacuo* from a tube at −155°. Its vapor tension was 225 mm. at

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[8] H. I. Schlesinger, R. T. Sanderson and A. B. Burg, This Journal, **61**, 536 (1939); **62**, 3421 (1940).

[9] A. B. Burg and H. I. Schlesinger, *ibid.*, **62**, 3425 (1940).

[10] H. I. Schlesinger and H. C. Brown, *ibid.*, **62**, 3429 (1940).

[11] A. Stock, *Z. Elektrochem.*, **29**, 354 (1923).

[12] I. Kirschenbaum and H. C. Urey, *J. Chem. Phys.*, **10**, 714 (1942).

−111.9° (melting CS_2). The original sample had been made seven years earlier, by the boron trichloride–hydrogen discharge method,[13] and several times repurified at wide intervals.

First Experiment, Plan (1).—A sample of diborane amounting to 5.43 cc. (gas at S. C.) was condensed in tube R (Fig. 1), the lower walls of which were coated with solid ammonia (25.6 cc. gas). The diborane was absorbed at −120 to −115°, and the excess ammonia was sublimed off as the temperature rose to −80° (recovered NH_3, 14.4 cc.; formula of residue $B_2H_6 \cdot 2.06NH_3$). Ammonia-d_3 (15.9 cc. gas, 98%D) now was condensed upon the residue and warmed to −80° without forming a solution. The ammonia was removed at intervals, assayed, and returned for further reaction. After the first approach to equilibrium, 9.1 cc. more ND_3 was brought in, and equilibrium again was approached. Comparisons were made against a mixed ammonia containing 70% of the 98% ND_3. The data and calculated results are given by Table I.

TABLE I

ND_3 EXCHANGE WITH SOLID $B_2H_6 \cdot 2.06NH_3$

Total time, hr.	Temp., °C.	Gas cc.[a] D atoms	Gas cc.[a] H atoms	Δpmm. at −42.5°	% H in free ammonia	Calcd. % H if solid exchanges		
						$4H^+$	$6H^+$	$8H^+$
12	−80	46.7	34.6	1	31	33.7	42.6	49.3
23	−80	46.7	34.6	7	42.6	33.7	42.6	49.3
35	−80	46.7	34.6	6.7	42.1	33.7	42.6	49.3
47	−73	46.7	34.6	6.5	41.8	33.7	42.6	49.3
57	−42	46.7	34.6	7	42.6	33.7	42.6	49.3
59	−42[b]	73.5	34.6	1	33.0	24.5	32.0	38.2
75	−42	73.5	34.6	0.5	32.2	24.5	32.0	38.2

[a] For convenience in calculation, the quantities of deuterium and of hydrogen are here computed as though each were a monatomic gas at standard conditions. Hydrogen atoms in diborane are not here included. [b] Liquid state.

Although these first results lacked precision because of some uncertainty of temperature control, there can be no doubt of the main conclusion, that $B_2H_6 \cdot 2NH_3$ exchanges six and only six protons with ND_3. The extent of exchange after only twelve hours corresponds to exchange of four protons, attributable to the ammonium ion of $NH_4(BH_3)_2NH_2$, but this cannot be taken as evidence of such a structure because the latter stages of a heterogeneous reaction often are much slower than the earlier course of reaction. In any case, the observation times were too far apart for genuine estimation of exchange-rate.

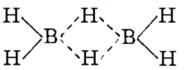
Second Experiment, Plan (1).—In an attempt to discern stages in the exchange reaction in the liquid phase, a sample of the diammoniate containing 7.67 cc. of B_2H_6 and 15.5 cc. of NH_3 was washed down the tube-wall by 98% ND_3 (23.7 cc. gas at S. C.), deliquescing at −80°, and the resulting mixed ammonia was removed after seventeen seconds (reaction tube at −183° during assay). The vapor tension of this mixture at −42° was 0.5 mm. less than that of the standard mixture (68.6% D); hence it contained 30.6% H (calcd. for four-proton exchange, 31.7). This could mean a primary exchange on one NH_4^+ ion only, except that the final equilibrium was almost attained during the next 70 seconds at −80°: the new mixed ammonia showed 5.0 mm. more pressure (at −41.5°) than the standard—hence contained 39.0% H (calcd. for exchange only of N–H, 40.8% H). The final equilibrium (ammonia assay 40.9% H) was established within ten minutes at −42°; a further ten hours at −42° showed no change. Thus again the exchange could not be made to involve any hydrogen except that originally belonging to ammonia. The liquid-phase reaction was much too fast for definite recognition of stages.

Third Experiment, Plan (2).—A 9.92-cc. sample of diborane was brought to reaction at −120° with 64.3 cc. of 98% ND_3. The temperature was allowed to rise during sixty hours to 18°. The glassy solution now was cooled to −183° and 0.10 cc. of uncondensed gas (probably HD) was pumped off. Comparison of the recovered ND_3 with fresh 98% ND_3 showed no difference of vapor tension at −46° (readings ±0.2 mm.). An exchange reaction involving even one proton from diborane should have increased the proton content of the ND_3 from 2 to 4.4%, a change which would have been easily detectable as a pressure difference of 1.3 mm. at −46°.

This experiment disposed of any doubt that it was only nitrogen–hydrogen bonds which were involved in the previously observed exchange. Any exchange involving protons from diborane must be indescribably slow even at room temperature. This result cannot be reconciled with any theory which requires transfer of protons from diborane to a base.

Fourth Experiment.—As a final check, it was considered essential to carry out a more violent reaction between diborane and ND_3, such as would occur if the two were suddenly mixed at room temperature. Accordingly a 28.2-cc. sample of pure diborane and 74.7 cc. of 98% ND_3 were condensed together in the reaction tube (R, Fig. 1) at −183° and suddenly warmed by a beaker of water at 40°. The tube was at once filled with a dense fog and a viscous liquid appeared. After five minutes at room temperature, the non-condensable gas was pumped off through a trap at −183°, and measured as 19.5 cc. Taking this to be HD, it represented one-stage ammonolysis of nearly half of the available BH_3 groups. The recovered ammonia amounted to 19.7 cc.—hence the residue contained one N per B. This ammonia proved to have the same vapor tension (within 0.1 mm.) at −40° as the original 98% ND_3—hence no exchange with the diborane occurred even during the extensive ammonolysis reaction. The borine theory thus applies as well at room temperature as at −120°.

Discussion

The results of these experiments evidently remove the last doubt of the validity of the borine theory of the base-reactions of diborane, but they do not directly support any specific theory of its structure. If one assumes the two-proton bridge  originally proposed by Dilthey[14] and strongly favored by Longuet-Higgins and Bell,[15,16] it must now be recognized that the bridge protons are not directly removable, as would be implied by the designation "protonated double bond."[7] It thus would become a difficult necessity to explain why the B_2H_2 bridge, held together by only four electrons, breaks two resonating H–B bonds instead of losing at least one proton. It is especially difficult to account for the ease with which a base molecule adds (fast at −120°) to a boron atom as nearly tetrahedrally-surrounded by hydrogen as the two-proton bridge structure implies.

This bridge structure might be accepted if all of the conceivable alternative models were proved to be wrong, but several possibilities seem to have been neglected. Proponents of an ethane-like structure usually have assumed a symmetry strictly like that of ethane, whereas a pseudo-

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(13) H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **53**, 4321 (1931).

(14) W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

(15) H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943).

(16) R. P. Bell and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A183**, 357 (1945).

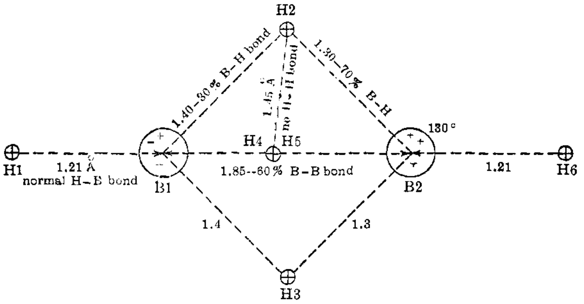

Fig. 3.—A possible four-proton-bridge model for diborane (H4 and H5 lie above and below the plane, and correspond to H2 and H3).

ethane structure in which two protons interact a little more or less than the other four would be easier to reconcile with two strong Raman lines as far apart as 2101 and 2523.[17] One thus visualizes a trigonal antiprism consisting of two sp^2 planar BH_3 groups, held together by B–B and B–H partial cross-linkages, using electrons originally assigned only to the sp^2 orbitals. Such resonance cross-linkage would account for the high barrier against internal rotation[18] quite as would the two-proton bridge, and a slight tipping of one BH_3 prism-face would provide increased or diminished cross-linkage of two protons.

Another method of varying this pseudo-ethane structure would be to slide one triangular face in the direction of the median line from a vertex through the opposite base. Two widely separated protons thus approach each other and four others adjust out of their planes, until the symmetrical two-proton bridge model results. Along the course of this change of models, one finds an infinite number of different possible structures for diborane. Another continuous variable is introduced if one permits the boron atom to depart from the sp^2 plane when cross-linkage first is established, or during the plane-sliding.

Quite as difficult to overthrow as the pseudo-ethane possibilities would be many others involving what might be described as a four-proton bridge. The example shown in Fig. 3 would be consistent with the theory of partial bond orders[19] (roughly extrapolated to orders less than unity), for the total bond order of each proton would be 1.0 and of each boron atom, 3.6. Each boron atom would have a total bonding of 0.6 outside the original BH_3 plane. Such structures, as well as most of the pseudo-ethane types, offer adequate electronic "bareness" on boron to account for the unhindered addition of base molecules.

In view of so many possible and inadequately considered alternatives, it would seem quite inappropriate to accept at this time any specific model as equivalent to the real structure of diborane.

Summary

The H–D exchange reaction between ND_3 and $B_2H_6 \cdot 2NH_3$ reaches equilibrium very rapidly in liquid ND_3 solution at −78°. The extent of exchange corresponds only to the N–H links in $B_2H_6 \cdot 2NH_3$, even at temperatures up to 18°. The reaction between B_2H_6 and ND_3 is not such as to contaminate the excess ND_3 with protons; this is equally true, whether the reaction is carried out at low temperatures (and followed by soaking in liquid ND_3) or at relatively high temperatures, with extensive ammonolysis. Diborane thus fails to yield protons to bases and the borine-complex theory of its base reactions is justified. Possible structural models for diborane are briefly discussed.

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[17] T. F. Anderson and A. B. Burg, *J. Chem. Phys.*, **6**, 586 (1938).

[18] F. Stitt, *J. Chem. Phys.*, **8**, 981 (1940).

[19] J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.*, **35**, 817 (1939).

Los Angeles, Calif. Received November 9, 1946

[Contribution from the Chemical Laboratories of The Johns Hopkins University]

The Nature of the Non-Porphyrin Bonding in Derivatives of Ferriheme[1]

By J. Gordon Erdman[2] and Alsoph H. Corwin

The nature of the bonding in the ferric hemin enzymes such as catalase and the peroxidases requires further study. These enzymes are believed to form, in addition to their protein links, complexes with hydrogen peroxide which are intermediates in the enzymatic processes. In our consideration of the peculiarities of the chemistry of hemoglobin,[1] we have postulated that some, at least, of these phenomena might find an explanation if we assume that globin is bound to ferroheme by two iron to protein links, whereas a single linkage would not permit advancing a geometric argument of the type proposed. If we extend this speculation to the enzymes containing ferriheme, assuming two bonds to the protein, we are faced with the objection that we must assume seven bonds to iron, one more than the usual coordination number of iron. We may refer to the fact that the assumption of the heptavalence of iron in isolated cases is not a new one,[3] and in the

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[1] Studies in the Pyrrole Series, XIX. Paper XVIII, Corwin and Erdman, This Journal, **68**, 2473 (1946).

[2] Present address: Mellon Institute, University of Pittsburgh, Pittsburgh, Pennsylvania.

[3] Pauling and Coryell, *Proc. Nat. Acad. Sci.*, **22**, 210 (1936).