recently[14] on the basis of Kirkwood's free-volume theory of solutions. This theory gives

$$K = \left(\frac{2\pi\mu kT}{h^2}\right)^{3/2} (gv\sigma) \exp\left(-\frac{E_s}{RT} - \frac{N\epsilon^2}{aRDT}\right) \quad (2)$$

where $\mu = m_+m_-/(m_- + m_+)$, m_i being the mass of the ith ion, $E_s = E_- + E_+ - E_\pm$, E_i being the interaction energy between the ith ion and surrounding solvent, $E_\pm$ being the energy of interaction between solvent and the ion pair, the factor $(gv\sigma) = (g_+g_-v_+v_- \quad \sigma_+\sigma_-)/(g_\pm v_\pm \sigma_\pm)$, g_i being the rotational and vibrational contribution to the partition function of the ith particle, v_i being the free volume available to the ith particle and σ being a factor varying between unity for solids and e for gases. If values of K as a function of T are available, the parameters $(gv\sigma)$ and E_s, characteristic of the solvent and salt, can be chosen so as to give a value of a, the distance of closest approach, which is independent of the temperature and solvent. Using the data obtained in this study, such calculations have been made. The results are shown in Fig. 1, where values of $F = \log K - 3/2 \log T + E_s/T$ are plotted vs. $1/DT$. The values of a, E_s and $(gv\sigma)$ for each salt are given in Table V. At this point, no generalizations can be made concerning the variations in E_s and $(gv\sigma)$, due to their complex nature and the lack of more extensive data. It may be said that the free-volume theory accounts for the observed facts as well as Bjerrum's theory. Certainly a constant value of a is more satisfying than one which varies in an unpredictable manner. It may be noted that the a value for Bu_4NPi in this solvent is the same as that found[14] in the solvents ethylene chloride, ethylidene chloride, propylene chloride and anisole. This work is being extended to other solvent systems in an effort to accumulate data which may lead to some correlation for the values of E_s and $(gv\sigma)$ thus obtained.

TABLE V

SALT PARAMETERS IN o-DICHLOROBENZENE

Salt	$a \times 10^8$, cm.	E_s, cal./mole	$(gv\sigma)$, cm.^{3}
Et_4NPi	1.59	4800	1.2×10^{-13}
Pt_4NPi	1.88	2880	2.4×10^{-17}
Bu_4NPi	2.51	1903	2.2×10^{-19}

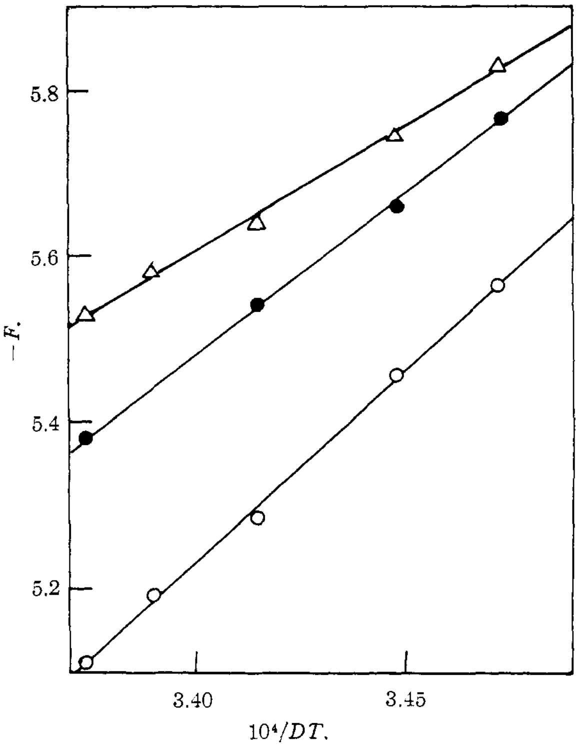

Fig. 1.—Values of the function F are plotted vs. $1/DT$ for the salts Et_4NPi (open circle), Pr_4NPi (closed circle, $F + 1.00$) and Bu_4NPi (triangle, $F + 1.500$) in o-dichlorobenzene.

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COLUMBIA, S. C.

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[14] W. R. Gilkerson, J. Chem. Phys., **25**, 1199 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF HOUSTON]

Further Studies of the Boron Bases: $CaHB(CH_3)_2$[1]

BY GEORGE W. CAMPBELL, JR.[2]

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The reaction of tetramethyldiborane with calcium in liquid ammonia has produced the new compound $CaHB(CH_3)_2 \cdot NH_3$. The Lewis base activity of this salt is lower than that of the comparable sodium salt, as indicated by its inactivity toward $B(CH_3)_3$ in liquid ammonia. $CaHB(CH_3)_2 \cdot NH_3$ reacted with tetramethyldiborane, to produce NH_3-soluble $Ca[H_2B(CH_3)_2]_2 \cdot XNH_3$ and a second product, formulated in speculation as "$Ca[B(CH_3)_2]_2$." In methyl ether solution, $CaHB(CH_3)_2 \cdot NH_3$ reacted with SiH_3Cl to product SiH_4 in equal molal quantity. Cryoscopic and tensiometric measurements of $CaHB(CH_3)_2$ in NH_3 indicate the monomer state of the salt in solution. The identity of $CaHB(CH_3)_2 \cdot NH_3$ as a salt of the $HB(CH_3)_2^=$ anion is argued on the basis of chemical evidence. Attempts to prepare the lithium and potassium salts of the $HB(CH_3)_2^=$ have suggested that the lithium salt can be prepared, but only hinted that the potassium salt can exist. Neither salt was obtained in a state approaching purity. However, these studies have provided a possible explanation for the contamination of the sodium salt with $B(CH_3)_3$, and the formation of $B(CH_3)_3$ in the reactions of tetramethyldiborane with potassium and with sodium in liquid ammonia.

The discovery of the boron base $Na_2HB(CH_3)_2$ and its ability to establish a firm B–B bond by reacting with trimethylboron in liquid ammonia[3] implies the possibility of forming previously unknown bonds by an electron-donor action of boron

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[1] Presented in part at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April 12, 1956.

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[3] A. B. Burg and G. W. Campbell, Jr., THIS JOURNAL, **74**, 3744 (1952).

toward acceptor atoms. The chief difficulty is that the boron base action is not known to occur except in solutions of $Na_2HB(CH_3)_2$ in liquid ammonia, in which most electron-acceptor substances are not free to react as such. In the more weakly basic solvent, liquid dimethyl ether, $Na_2HB(CH_3)_2$ forms a colloid which reacts as a source of hydride ion rather than a boron base.

As a step toward developing a wider range of possible reaction conditions for the $HB(CH_3)_2^=$ unit, and a fuller understanding of the formation of this ion, experiments have been directed toward the reaction of tetramethyldiborane with potassium, lithium and calcium and the possible preparation of the corresponding salts of these metals and the $HB(CH_3)_2^=$ ion. It was not possible to obtain the potassium salt, nor was there more than a slight hint of its existence. The lithium salt probably can be prepared as an ammoniate, but only with unusual difficulty. Although not successful for their original purpose, these experiments served to extend earlier observations concerning the state of the sodium salt in solution in liquid ammonia. The reaction of calcium with tetramethyldiborane has yielded a product that corresponds to the formula $CaHB(CH_3)_2 \cdot NH_3$. Some further knowledge of the reaction of the active metal–ammonia solutions with tetramethyldiborane, with the latter in excess, also was obtained.

Experimental

Materials.—The $(CH_3)_4B_2H_2$ used in these studies was prepared by the reaction of B_2H_6 with $B(CH_3)_3$.[4] It was purified by fractional condensation at −80° until the vapor tension at 0° was 48.0 mm. (literature value 48.0 mm.) prior to each use. Hydrolysis of 0.232 mmole produced 0.452 mmole of H_2 (calculated 0.464) and 0.464 mmole of $(CH_3)_2BOH$ (calculated 0.464).

Anhydrous 99.9% NH_3, purchased from the Matheson Company, was stored *in vacuo* with dissolved Na. The NH_3 was distilled from this solution for use in these experiments.

The dimethyl ether, reported to be 99.9% pure by the manufacturer, contained considerable CO_2, and required NaOH-washing before use. The purified ether had a vapor pressure of 34.0 mm. at −78.6° (literature value 34 mm.).

The SiH_3Cl was prepared by the Al_2Cl_6 catalyzed reaction of SiH_4 with HCl.[5] It was purified by distillation in the high vacuum apparatus.

The Reaction of $(CH_3)_4B_2H_2$ with Calcium in Liquid NH_3.—The addition of approximately one-half mmole of $(CH_3)_4B_2H_2$ to a liquid ammonia solution of calcium (>20 mg.), and the subsequent steps for the isolation of the product were carried out in the same manner as described for the preparation of $Na_2HB(CH_3)_2$,[3] except that the repeated treatments with trimethylamine were found to be ineffective and of no value. Also, it was found that this preparation was far less sensitive to temperature, and the reaction occurred readily and cleanly below −65°. It was further observed that a large excess of calcium was not necessary, but that the mixture required adequate mixing to prevent a local excess of $(CH_3)_4B_2H_2$, which would react with the calcium salt first formed.

After removal of the solvent NH_3, and all volatile (at 50°) components, the non-volatile product of this process, if formulated by analogy to the sodium salt, was $CaHB(CH_3)_2 \cdot NH_3$, and all attempts to remove the remaining ammonia were unsuccessful.

The hydrolysis of the product, in acid solution, produced H_2, $(CH_3)_2BOH$ and NH_3, according to the equation

$$CaHB(CH_3)_2 \cdot NH_3 + 3H_2O \longrightarrow Ca(OH)_2 + (CH_3)_2BOH + NH_3 + 2H_2 \quad (1)$$

On fourteen samples, the ratio H_2 to $(CH_3)_2BOH$ was 1.99 (calculated 2.00), and, on nine samples, the ratio of $(CH_3)_2BOH$ to Ca (determined gravimetrically) was 1.04 (calculated 1.00). The ammonia content was not constant, but always was slightly more than corresponds to the 1-ammoniate, and averaged 1.22 ± 0.26 for six samples. The average of the analyses of two weighed samples, after correcting for ammonia content, gave 41.6% Ca (calculated 48.9); 47.1% $(CH_3)_2B$ (calculated 49.9); ratio of H_2 to $(CH_3)_2B$ was 1.94 (calculated 2.00). These analyses were made on samples of 0.28 and 0.51 mmole, representing sample weights of 23 and 43 mg., respectively. It has not been possible so far to prepare larger samples of relatively pure product apparently because of the high reactivity of $CaHB(CH_3)_2 \cdot NH_3$ toward $(CH_3)_4B_2H_2$. It should be noted, however, that in two experiments, where $(CH_3)_4B_2H_2$ was carefully added in equal molal quantity to approximately 0.5 mmole of calcium, the blue color faded out after approximately 15 minutes at −75°. After removing the volatile components at temperatures up to 50°, the NH_3-soluble residue was found to be $CaHB(CH_3)_2 \cdot NH_3$ by analysis. Due to the extreme sensitivity of the product toward air or moisture, a methyl ether solution of the sample was filtered into a tube and the tube separated from the filter apparatus[3] *in vacuo*. The methyl ether was then distilled away from the sample, and the tube evacuated, removed from the vacuum line and weighed. The tube was then returned to the vacuum line for analysis of the sample, after which the clean evacuated tube was reweighed to determine the sample weight. Since the sample weight never exceeded 50 mg., and the accuracy of measurement of gas volumes was approximately 5%, the estimated accuracy of the analyses was not better than 5%.

Attempts to Prepare the Potassium Salt.—The addition of $(CH_3)_4B_2H_2$ to a liquid ammonia solution of potassium and the subsequent steps for the isolation of the salt product were carried out in the same manner as for the sodium salt,[3] with the difference that the removal of the solvent was far less difficult in this case. However, in the product most nearly approaching the expected formula "$K_2HB(CH_3)_2$," hydrolysis yielded 15% more than the calculated amount of $(CH_3)_2BOH$, 12% too much hydrogen and $B(CH_3)_3$ amounting to 0.23 mole per K_2X unit. Thus it would appear 35% of the expected $HB(CH_3)^=$ units were bonded by the electron acceptors $B(CH_3)_3$ or $HB(CH_3)_2$. In the most deviant experiment the attached $B(CH_3)_3$ amounted to 0.58 mole per K_2X unit, while $(CH_3)_2BOH$ ran 14% low and H_2 24% high—as though some $CH_3BH_2^=$ ions were taking the place of $HB(CH_3)_2^=$ ions.

Attempts to Prepare $Li_2HB(CH_3)_2$.—For the preparation of "$Li_2HB(CH_3)_2$" it was considered necessary to choose an alkali metal solvent which would not solvate the Li^+ ion so strongly as to make it impossible to isolate the desired product. For this purpose methylamine proved to be almost suitable, and certainly far better than ammonia. In the best experiment the supposed "$Li_2HB(CH_3)_2$" was hydrolyzed to give only 56% of the expected $(CH_3)_2BOH$ (based upon a lithium-analysis which might have been somewhat high), while H_2 ran only 8% high. However, no $B(CH_3)_3$ could be found in the products. Thus the disproportionation of the $(CH_3)_2BH$ evidently was important, but it differed sharply from the reactions involving sodium and potassium where the disproportionation was accompanied by methyl group migration. In this respect it is comparable to the reaction of $(CH_3)_4B_2H_2$ with calcium, for in that reaction no $B(CH_3)_3$ was ever formed either.

The Use of Methylamine to Extract the Sodium Salt.—Some advantage was found in the use of methylamine instead of dimethyl ether as a solvent for extracting $Na_2HB(CH_3)_2$ from excess sodium after the removal of the ammonia from the original reaction mixture.[3] The yields varied from 74 to 84% (based upon half the tetramethyldiborane) and the conformity to the ideal formula $Na_2HB(CH_3)_2$ was good. However, it was not possible to remove the methylamine effectively except in very small scale experiments (0.6 mmole or less), and even then a mono-amine solvate was obtained. Hence the product could be used only for chemical studies in solution, as in liquid ammonia.

Hydridic Behavior of $Na_2HB_2(CH_3)_5$.—The salt $Na_2HB_2(CH_3)_5$ reacted with SiH_3Cl in dimethyl ether to form SiH_4 as readily as the original $Na_2HB(CH_3)_2$ had done,[3] indicating that the addition of $B(CH_3)_3$ to the $HB(CH_3)_2^=$ unit had not seriously impaired the hydridic reactivity of the B–H bond.

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[4] H. I. Schlesinger and A. O. Walker, THIS JOURNAL, **57**, 621 (1935)

[5] Stock and Somieski, *Ber.*, **52**, 695 (1919)

The experiment was done with a sample of $Na_2HB_2(CH_3)_5$ which had been formed directly from $(CH_3)_4B_2H_2$ and sodium in liquid ammonia containing $B(CH_3)_3$. The time allowed for completion of the B–B bond was 150 minutes (at −78°); then the last of the ammonia was displaced by trimethylamine and the salt was extracted with methylamine. The sample was suspended in 2 ml. of dimethyl ether and treated with excess SiH_3Cl during 14 hours at −78°. The reaction yielded 0.59 mmole of SiH_4, while the sodium analysis indicated 0.47 mmole of the original salt, $Na_2HB_2(CH_3)_5$. A low sodium analysis and some extra B–H bonds were possible sources of the discrepancy. The recovered $B(CH_3)_3$ (0.26 mmole with the SiH_4 and 0.05 mmole more by hydrolysis of the residue) and $(CH_3)BOH$ were low, for salt residue of such reactions contains boron and methyl groups in a situation which is not yet understood.

In passing, it is worthy of note that the action of C_2H_5Cl upon $Na_2HB(CH_3)_2$ in dimethyl ether (6 days at −78°) was virtually negligible. However, there was an indication of ethane: a 3% yield (0.013 mmole) of a gas having the right volatility. At least the reaction was far slower than the conversion of SiH_3Cl to SiH_4.

Tensiometric Determination of the Molecular Weight of $CaHB(CH_3)_2$ in Solution.—Samples of the calcium salt "$CaHB(CH_3)_2 \cdot NH_3$" were prepared in a suitable bulb which could be attached to a differential manometer for the comparison of the vapor tension of the pure solvent with that of the solution. The two bulbs, one containing the solution and the other the pure solvent, were then immersed in melting chlorobenzene, thus establishing a constant uniform temperature of approximately −46°. In two experiments in liquid ammonia, the results indicated a molecular weight of 87 and 89, respectively, ±10% (formula weight 81.8) at an average molality of 0.27.[6] Although the formula weight and empirical molecular weight agree within the limits of accuracy, the results suggest the possibility of a small amount of association of solute molecules.

When liquid methyl ether was the solvent, an apparent molecular weight of 213 ± 10% was found, corresponding to an average association of 2.6 "$CaHB(CH_3)_2$" units. The clear colorless solution contained 0.50 mmole of "$CaHB(CH_3)_2$" in 1.0 g. of dimethyl ether.

Cryoscopic Determination of the Molecular Weight of the Calcium Salt in NH_3.—The apparatus used in the cryoscopic determination was described in an earlier paper.[3] By comparison with pure ammonia, it was observed that 0.0286 g. of "$CaHB(CH_3)_2$"[6] in 2.73 g. of ammonia lowered the freezing point 0.129 ± 0.006°, indicating a molecular weight value of 79 ± 4 (calculated value 81.8).

The Conductance of the Calcium Salt in NH_3.—The conductance of $CaHB(CH_3)_2$ in liquid ammonia at −70 to −75° was measured by conventional methods. The detailed results are given in Table I.

TABLE I

THE ELECTROLYTIC CONDUCTANCE OF $CaHB(CH_3)_2$ IN LIQUID AMMONIA

Sample	1	2	3
Temp., °C.	−75	−75	−70
Molarity	0.0185	0.0218	0.0272
Specific conductance (ohms^{-1})	8.1×10^{-4}	8.7×10^{-4}	1.03×10^{-3}
Molar conductance (ohms^{-1})	43.0	39.9	37.9

Samples 1 and 2 were prepared by the reaction of $(CH_3)_4B_2H_2$ with calcium (present in excess), followed by a methyl ether extraction of the sample. Sample 3 was prepared by the addition of equal molal quantities of $(CH_3)_4B_2H_2$ and Ca, in liquid ammonia.

These results would compare with an estimated 10% ionization for a uni-univalent salt in this medium, since electrolytes in liquid ammonia at −33° have molar conductances around 300 at infinite dilution. However, an accurate basis for comparison is not available since most di-divalent salts do not dissolve or ionize in liquid ammonia.

The Reaction of the Calcium Salt with Chlorosilane.—A methyl ether solution of 0.45 mmole of $CaHB(CH_3)_2 \cdot NH_3$ was treated with more than an equivalent quantity of chlorosilane at −78° for 48 hours. The reaction produced 0.47 mmole of silane, and the excess chlorosilane was recovered apparently unchanged. It is suggested that the reaction proceeded according to the equation

$$2CaHB(CH_3)_2 + 2SiH_3Cl \longrightarrow \text{“}Ca[B(CH_3)_2]_2\text{”} + CaCl_2 + 2SiH_4 \quad (2)$$

The non-volatile residue from this reaction was found to be 33.6% calcium (calculated 34.3 according to eq. 10). Treatment of this non-volatile residue with aqueous HCl produced only 0.076 mmole of $(CH_3)_2BOH$, but 0.38 mmole of H_2 was produced, corresponding to a ratio of 1.6 moles of H_2 per calculated mole of "$Ca[B(CH_3)_2]_2$." The production of H_2 started rapidly, but slowed down such as to indicate that equilibrium was approached but apparently not quite attained. When the non-volatile portion of this mixture was evaporated to dryness with H_2SO_4, charring was observed indicating the presence of organic carbon, and the typical green flame-test of boron was observed. Hence it seems evident that the residue retained (CH_3)–B groups in a manner not yet understood.

Attempts to Prepare $CaHB(CH_3)_2 \cdot B(CH_3)_3$.—In two experiments $B(CH_3)_3$ was added to solutions of $CaHB(CH_3)_2 \cdot NH_3$ in liquid ammonia at −75°. In one of the experiments the results indicated $B(CH_3)_3$ added to the $CaHB(CH_3)_2 \cdot NH_3$ in the mole ratio of 0.39 to 1 in two days. This could not be repeated in the second experiment, where five days were allowed for reaction, yet no $B(CH_3)_3$ was retained by the "$CaHB(CH_3)_2 \cdot NH_3$."

In two other experiments, $(CH_3)_4B_2H_2$ was brought to reaction with calcium in liquid ammonia with an excess of $B(CH_3)_3$ also present. In these two experiments only $CaHB(CH_3)_2 \cdot NH_3$ was obtained and all of the $B(CH_3)_3$ was recovered as the sublimable $B(CH_3)_3 \cdot NH_3$. Hence it appears that the apparent addition of $B(CH_3)_3$ to $CaHB(CH_3)_2 \cdot NH_3$ was due to incomplete sublimation of the $B(CH_3)_3 \cdot NH_3$, and that no addition reaction occurred with the boron base.

The Reaction of $CaHB(CH_3)_2 \cdot NH_3$ with $(CH_3)_4B_2H_2$.—The reaction of $(CH_3)_4B_2H_2$ with $CaHB(CH_3)_2 \cdot NH_3$ in liquid ammonia produced a clear solution at −75°, but a solid precipitate was formed after 14 hours. The solid residue obtained, after removal of the solvent and all components volatile at 25°, was 28.4% Ca, and released 3.26 moles of H_2 per mole of Ca by hydrolysis (calculated for $Ca(CH_3)_4B_2H_2$; Ca 32.4%; ratio $H_2/Ca = 3.0$). Hydrolysis also produced 1.6 moles of $(CH_3)_2BOH$, but some organic carbon was retained by the non-volatile residue, since evaporation with H_2SO_4 caused charring. The analysis and properties of the non-volatile product obtained in this reaction corresponds in every respect to that produced by the reaction of Ca (in NH_3) with $(CH_3)_4B_2H_2$ when the latter was in excess, as described below.

The Reaction of Calcium with $(CH_3)_4B_2H_2$, the Latter Present in Excess.—When $(CH_3)_4B_2H_2$ was added to a Ca-NH_3 solution (mole ratio = 1.5 to 2.0) at −75°, the blue color of the metal solution faded and a milky suspension was formed which finally dissolved to produce a colorless, clear solution. After standing for several hours, a permanent precipitate was formed from the solution. In one experiment, where the mole ratio of $(CH_3)_4B_2H_2$ to Ca was 2.0, after reaction all volatile components of the mixture were removed at 25°, leaving a solid residue that was 29.6% Ca (calcd. for $Ca(CH_3)_4B_2H_2$, 32.4%) correcting for NH_3 content (mole ratio $NH_3/Ca = 0.24$). Hydrolysis of this residue produced 3.35 moles of H_2 and 1.60 moles of $(CH_3)_2BOH$ per mole of calcium. A wet combustion of this non-volatile portion of the hydrolysis mixture produced CO_2 corresponding to an additional 0.273 mole of $(CH_3)_2B$-groups, to give a total ratio of $(CH_3)_2B/Ca$ of 1.87. Hence it appears that the non-volatile solid obtained from the reaction of $(CH_3)_4B_2H_2$ with Ca corresponds approximately to the speculative formula $Ca(CH_3)_4B_2H_2$.

In three other similar experiments $(CH_3)_4B_2H_2$ and calcium (mole ratio ≧ 1.5) were brought to reaction and the solvent and all volatile products were removed at 25°, but liquid ammonia was then added to the non-volatile residue and the mixture was filtered. The NH_3-soluble product had the empirical formula $Ca[(CH_3)_2BH_2]_2 \cdot XNH_3$ ($X = 1.4$ to 2.4). The results of the three analyses, corrected for NH_3

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[6] In these experiments the sample weight was calculated as "$CaHB(CH_3)_2$" on the basis of the analysis of the sample, since the NH_3 content of this compound is variable, and the solvent was NH_3.

are as follows: Ca, 32.1% (31.8 calcd.); ratio H_2/Ca = 3.99 (4.00 calcd.); ratio R_2B/Ca = 2.04 (2.00 calcd.).

In the further experiments, where the mole ratio of $(CH_3)_4B_2H_2$ to calcium was equal to or greater than 2.5, the reaction resulted in a product that was permanently soluble in NH_3. After removal of all volatile products at 25°, the residue was readily and completely soluble in NH_3. Analysis of the product corresponded to the formula $Ca[(CH_3)_2BH_2]_2 \cdot XNH_3$.

However, when the ratio of $(CH_3)_4B_2H_2$ to calcium was 1.5, almost exactly half of the calcium was converted to $Ca[(CH_3)_2BH_2]_2$, the other half apparently forming the hypothetical $Ca[(CH_3)_2B]_2$. Thus, in one experiment, 0.622 mmole of $(CH_3)_4B_2H_2$ was added to 0.427 mmole of calcium in liquid ammonia, at −75°. The solution turned milky white, then clear within 30 minutes. After 14 hours, however, a precipitate had formed. When all volatile components were removed at 65°, it was possible to extract 0.206 mmole of $Ca[H_2B(CH_3)_2]_2$ from the residue by means of liquid NH_3. The insoluble portion produced less than 0.1 mmole of H_2 and no detectable amount of $(CH_3)_2BOH$ when treated with H_2O-HCl. Examination of the volatile components of the reaction mixture, which were removed by distillation showed that 0.26 mmole of $(CH_3)_2BNH_2$ was present. Since the total mmoles of $(CH_3)_2B$-groups added was 1.24, and 0.41 were found as $Ca[(CH_3)_2BH_2]_2$, and 0.26 as $(CH_3)_2BNH_2$, there remains 0.57 mmole to be accounted for. Due to the low volatility of polymeric $(CH_3)_2BNH_2$, especially in the presence of NH_3, it is conceivable that as much as 0.15 mmole, as an upper limit, could be lost in this analysis. Hence, it would appear that the 0.22 mmole of calcium which was not removed as $Ca[(CH_3)_2BH_2]_2$ was present as NH_3-insoluble "$Ca[(CH_3)_2B]_2$."

Discussion

The Reaction of Tetramethyldiborane with Calcium in Ammonia.—The preparation of the compound which appears to be $CaHB(CH_3)_2 \cdot NH_3$ was accomplished by condensing tetramethyldiborane on a previously prepared and frozen solution of calcium in ammonia, followed by rapid warming to −70 to −75° with thorough mixing. A second product, apparently $(CH_3)_2BHNH_3$, was decomposed thermally, *in vacuo* at 25 to 50°, and the $(CH_3)_2BNH_2$ and H_2 were removed as gases and identified. Hence, it would appear that this reaction parallels that of sodium with tetramethyldiborane,[3] and therefore it would be described by the equation

$$Ca + (CH_3)_4B_2H_2 + NH_3 \xrightarrow[NH_3(l)]{-70°} CaHB(CH_3)_2 \cdot XNH_3 + (CH_3)_2BHNH_3 \quad (3)$$

This system was not as temperature sensitive as that where sodium was the active metal, nor was it necessary that there be a large excess of the active metal to avoid secondary reactions. However, the product does react with tetramethyldiborane, so the mixing of the reactants was quite critical. Based upon this equation, the calcium salt was readily obtained in 80% yield, or higher.

This new calcium salt was soluble in ammonia, dimethyl ether and diethylene-glycol dimethyl ether (diglyme). In most of the experiments dimethyl ether was used to extract this product from the excess calcium in the preparation.

Cryoscopic and tensiometric measurements on the liquid ammonia solutions of $CaHB(CH_3)_2$ clearly indicate the monomeric salt, while conductance measurements suggest some ionization, but considerably less than that indicated for the sodium salt.

In liquid methyl ether the salt formed an aggregate of approximately 2.6 "$CaHB(CH_3)_2$" units, according to the vapor tension of the solution, thus apparently differing from the colloidal state of $Na_2HB(CH_3)_2$ in this medium only in the degree of aggregation.

The Chemical Properties of the Calcium Salt.—In sharp contrast to $Na_2HB(CH_3)_2$, the calcium salt did not react as a Lewis-base toward trimethylboron in liquid ammonia solution. A further attempt to cause such an addition, by bringing tetramethyldiborane to reaction with calcium in the presence of trimethylboron, in liquid ammonia, apparently produced $CaHB(CH_3)_2 \cdot NH_3$ as the only non-volatile product, yet this method did give excellent samples of $Na_2HB(CH_3)_2 \cdot B(CH_3)_3$ when sodium was the active metal.[3]

In liquid dimethyl ether chlorosilane reacted with "$CaHB(CH_3)_2$" to produce an equal molal quantity of silane.

The reaction of $CaHB(CH_3)_2$ with tetramethyldiborane (mole ratio 1:1) in liquid ammonia, produced a water clear solution which did not change visibly for 3 hours at −75°, but after 14 hours at −78° an insoluble product had formed. The analysis of the non-volatile (at 50° *in vacuo*) residue from this reaction corresponded approximately to the formula $Ca(CH_3)_4B_2H_2$, and retained a slight and probably insignificant amount of ammonia. However, a substance empirically formulated as $Ca[H_2B(CH_3)_2]_2$, could be extracted from this solid by liquid ammonia. These results suggest that the mixture consisted of nearly equal molal parts of the substance $Ca[H_2B(CH_3)_2]_2$ and the speculative, probably polymeric, salt "$Ca[B(CH_3)_2]_2$" which would compare with the substance tentatively formulated as "$NaB(CH_3)_2$" in a previous publication.[3] It should be noted further that the products of this reaction of $CaHB(CH_3)_2 \cdot NH_3$ with tetramethyldiborane appear to be identical to those obtained by the reaction of tetramethyldiborane (present in excess) with calcium in liquid ammonia.

The Nature of the Calcium Salt.—On the basis of the analyses alone, the calcium salt can reasonably be formulated as $CaHB(CH_3)_2 \cdot NH_3$ or as the amido salt $H_2NCaH_2B(CH_3)_2$. In accord with the latter postulate, the reaction of tetramethyldiborane with calcium in liquid ammonia might be written as

$$Ca + (CH_3)_4B_2H_2 + NH_3 \longrightarrow H_2NCaH_2B(CH_3)_2 + (CH_3)_2BHNH_3 \quad (4)$$

It appears also that this postulate would be in good agreement with some of the observed chemical and physical properties of this calcium salt. Hence, the failure of this compound to add trimethylboron would be expected if the $H_2B(CH_3)_2^-$ ion were present instead of the boron base, providing also that the amido ion were not available enough from the calcium salt to compete with the ammonia. Also, the moderate electrolytic conductance of the calcium salt would conform well to this interpretation.

On the other hand, the reactions of the calcium salt with tetramethyldiborane and with chlorosilane appear to favor the boron base formulation.

It should be noted that when the calcium salt was brought to reaction with an equal molal quantity of $(CH_3)_4B_2H_2$, the products of the reaction appeared to be identical to those resulting from the reaction of calcium metal with $(CH_3)_4B_2H_2$, when the mole ratio was 1:2, respectively. In both cases a solid mixture was produced with nearly identical composition, and approximately corresponding to the empirical formula $Ca(CH_3)_4B_2H_2$, but from which $Ca[H_2B(CH_3)_2]_2$ could be extracted. Also, if the ratio of $(CH_3)_4B_2H_2$ to calcium metal was reduced to 1.5:1, exactly half of the calcium was converted to NH_3-soluble $Ca[H_2B(CH_3)_2]_2$, the rest of the calcium apparently forming the NH_3 insoluble, apparently polymeric, substance empirically formulated to be $Ca[(CH_3)_2B]_2$. If it is assumed that the reaction of $(CH_3)_4B_2H_2$ with calcium produces the amido-salt $H_2NCaH_2B(CH_3)_2$, according to eq. 4, the formation of $Ca[H_2B(CH_3)_2]_2$ would reasonably be written as

$$(CH_3)_4B_2H_2 + 2NH_3 \longrightarrow (CH_3)_2BNH_2 + NH_4{}^+H_2B(CH_3)_2{}^- \quad (5)^7$$

$$NH_4{}^+H_2B(CH_3)_2{}^- + NH_2CaH_2B(CH_3)_2 \longrightarrow 2NH_3 + Ca[H_2B(CH_3)_2]_2 \quad (6)$$

This interpretation, however, cannot account for the fact that this reaction produced a mixture of $Ca[H_2B(CH_3)_2]_2$ and a second calcium compound $Ca[B(CH_3)_2]_2$." In fact any reaction of $(CH_3)_4B_2H_2$ with $NH_2CaH_2B(CH_3)_2$ to form $Ca[H_2B(CH_3)_2]_2$ and $Ca[B(CH_3)_2]_2$ would require a transfer of B–H hydrogen to N–H hydrogen, which appears quite unlikely in view of the failure of ND_3 to undergo H–D exchange with diborane.[8]

On the other hand, if it is assumed that the formula $CaHB(CH_3)_2{\cdot}NH_3$ represents the correct structure for this salt, the suggested reaction sequence is as

$$2CaHB(CH_3)_2 + (CH_3)_4B_2H_2 \longleftarrow 2\text{“}CaHB(CH_3)_2{\cdot}HB(CH_3)_2\text{”} \quad (7)$$

$$2\text{“}CaHB(CH_3)_2{\cdot}HB(CH_3)_2\text{”} \longrightarrow Ca[H_2B(CH_3)_2]_2 + \text{“}Ca[B(CH_3)_2]_2\text{”} \quad (8)$$

In this postulate, the formation of the hypothetical "$CaHB(CH_3)_2{\cdot}HB(CH_3)_2$" would represent base activity of the $CaHB(CH_3)_2$, and it would further explain the ability of $(CH_3)_4B_2H_2$ to increase the solubility of $CaHB(CH_3)_2$ in NH_3. The disproportionation of this salt according to eq. 8, and probably the polymerization of the $(CH_3)_2B^-$ anion would explain the slow formation of a precipitate in the NH_3 solution. Also, since both of the products of eq. 8 would be non-volatile, the mixture would correspond, in composition, to the formula $Ca(CH_3)_4B_2H_2$.

It was also observed that additional $(CH_3)_4B_2H_2$, beyond that required by eq. 7, produced a higher percentage of the calcium as $Ca[H_2B(CH_3)_2]_2$, with a nearly quantitative conversion of calcium to the borohydride derivative when 2.5 moles of $(CH_3)_4B_2H_2$ is added to one mole of the metal. In explanation of this, it is postulated that the disproportionation of "$CaHB(CH_3)_2{\cdot}HB(CH_3)_2$" in the presence of $NH_4{}^+$ and $H_2B(CH_3)_2{}^-$ ions[7] would reasonably occur as

$$\text{“}CaHB(CH_3)_2{\cdot}HB(CH_3)_2\text{”} + NH_4{}^+H_2B(CH_3)_2{}^- \longrightarrow Ca[H_2B(CH_3)_2]_2 + NH_3HB(CH_3)_2 \quad (9)$$

The reaction of the calcium salt with chlorosilane gives further support to the boron base interpretation, since the non-volatile product of this reaction was apparently $Ca[B(CH_3)_2]_2$. Had the calcium salt been $H_2NCaH_2B(CH_3)_2$, one mole of SiH_4 would have been produced, leaving a dimethylborine group, which would not have reacted further with the chlorosilane,[9] unless it were bonded to the $NH_2{}^-$ group. However, no $(CH_3)_2B^-$ polymer could have been formed without transfer of B–H hydrogen to the NH_2-group and the presence of $(CH_3)_2BH$-groups or $(CH_3)_4B_2H_2$ in the reaction products would not have escaped detection.

On the basis of these arguments, it seems likely that the new calcium salt is best interpreted as another boron base, and an analog of $Na_2HB(CH_3)_2$. However, the chemical properties of $CaHB(CH_3)_2{\cdot}NH_3$ suggest a reduced, yet definite base activity, whereas the availability of the hydride ion from this salt is comparable to that of the sodium salt.

The Preparation of Salts of the $HB(CH_3)_2{}^{=}$ Ion.—It has been reported[3] that the preparation of relatively pure $Na_2HB(CH_3)_2$, by the reaction of Na–NH_3 with $(CH_3)_4B_2H_2$, required an excess of sodium. When this requirement was not met, or when an excess of $(CH_3)_4B_2H_2$ was present, a reaction occurred which always produced some $B(CH_3)_3$. Apparently the same reaction occurred also when $(CH_3)_4B_2H_2$ was added to a solution of $Na_2HB(CH_3)_2$ in liquid NH_3. In all of the attempts to prepare $K_2HB(CH_3)_2$, even with very large excesses of potassium, it was impossible to prevent this further reaction, and considerable $B(CH_3)_3$ was produced in each experiment. In contrast to the sodium and potassium reactions, in the attempts to prepare $Li_2HB(CH_3)_2$, no $B(CH_3)_3$ was produced, although $Li_2HB(CH_3)_2$ was not obtained in a state approaching purity.

The preparation of $CaHB(CH_3)_2$ is particularly noteworthy, for it has been prepared with consistently less contamination than any of the other salts of the $HB(CH_3)_2{}^{=}$ ion, and $B(CH_3)_3$ has never been found in the reaction products. Also, a nearly pure sample of $CaHB(CH_3)_2$ was prepared when neither reactant was in excess.

It appears likely that the reaction of active metals with $(CH_3)_4B_2H_2$, in liquid ammonia, first forms salts of the $HB(CH_3)_2{}^{=}$ ion plus $(CH_3)_2BH{\cdot}NH_3$, as indicated in eq. 3. Further reaction of the $HB(CH_3)_2{}^{=}$ ion with $(CH_3)_4B_2H_2$ can then occur under one or more of the following conditions: if the $(CH_3)_4B_2H_2$ is present in excess; if the stirring is inadequate, leading to local excesses of $(CH_3)_4B_2H_2$; if the rate of reaction of the $HB(CH_3)_2{}^{=}$ with $(CH_3)_4B_2H_2$ is rapid relative to the reaction whereby the $HB(CH_3)_2{}^{=}$ is formed. Since the results suggest that this additional reaction cannot be prevented using potassium, but is progressively easier to prevent when the reactive metals are sodium, (lithium) and calcium, respectively, it appears that the rate of reaction of the salts of $HB(CH_3)_2{}^{=}$ with $(CH_3)_4B_2H_2$ is quite dependent upon the nature of the metal ion, and particularly upon the charge density of the cation.

If it is assumed that the potassium salt of the

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(7) This represents the ammoniation of tetramethyldiborane, corresponding to the ammoniation of diborane as suggested by G. W. Schaeffer, M. D. Adams and J. J. Koenig, THIS JOURNAL, **78**, 725 (1956).

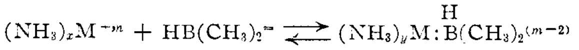
(8) A. B. Burg, *ibid.*, **69**, 747 (1947).

(9) It has been shown in this Laboratory that $Ca[H_2B(CH_3)_2]_2$ reacts with chlorosilane in methyl ether solution according to the equation

$$Ca[H_2B(CH_3)_2]_2 + 2SiH_3Cl \rightarrow CaCl_2 + 2SiH_4 + (CH_3)_4B_2H_2.$$

boron base has some existence, then the great difficulty of avoiding contamination of the potassium salt by donor-acceptor bonding of the $HB(CH_3)_2^{=}$ ion to methylated borine units may be less surprising than the relative ease of making nearly pure $Na_2HB(CH_3)_2$ and $CaHB(CH_3)_2$ in the presence of the complex $(CH_3)_2BH\cdot NH_3$, for a base much stronger than ammonia as the $HB(CH_3)_2^{=}$ ion must be, should quickly capture methylated borine units from their ammonia complexes. Also requiring explanation is the failure of the $HB(CH_3)_2^{=}$ ion to react rapidly with ammonia at low temperatures removing a proton to form amide ion, as various carbon-bases do. Furthermore, it will be recalled,[3] that a relatively clean preparation of $Na_2HB(CH_3)_2$ is possible only when sodium is in large excess, as though it served in some way to block the addition of methylated borine units or ammonia to the $HB(CH_3)_2^{=}$ ion. Finally, it appears that the blocking of such an addition is even more effective if the metal is calcium or lithium instead of sodium.

In explanation of all these facts, it may be suggested that ammonia in the solvation sphere of a metal ion is partly replaced by the stronger boron base ion, so that one may consider the equilibrium



$$(NH_3)_xM^{+m} + HB(CH_3)_2^{=} \rightleftarrows (NH_3)_yM:\overset{H}{B}(CH_3)_2^{(m-2)} \quad \text{(where } x > y) \qquad (10)$$

to lie farthest to the right for ions of highest charge density, and at their highest concentration. Thus, the availability of the free $HB(CH_3)_2^{=}$ ion may be very low in the presence of much sodium ion, but considerably higher if potassium is the positive ion, or if there is no excess of sodium—conditions under which the capture of borine units by the $HB(CH_3)_2^{=}$ ions is hard to prevent. And with calcium or lithium as the positive ion, the electron-donor action of the $HB(CH_3)_2^{=}$ ion would be blocked still more effectively.

Also, it appears likely that $(CH_3)_4B_2H_2$ and possibly the partially ammoniated $(CH_3)_4B_2H_2$ are capable of providing methylated borine units for reaction with the $HB(CH_3)_2^{=}$ ion but that $(CH_3)_2BH\cdot NH_3$ is not able to do so, for reaction mixtures containing the boron base and $(CH_3)_2BH\cdot NH_3$ have been kept in contact as long as 36 hours at $-78°$ without detectable reaction. This failure to react might well be attributed to the absence of a convenient mechanism, and suggests that the di-ammoniate of tetramethyldiborane is not readily converted to $(CH_3)_2BH\cdot NH_3$ and that this is not a component of the tetramethyldiborane–ammonia system.[7] This is further supported by the fact that dimethylborine ammine does not measurably react with sodium in liquid ammonia, in sharp contrast to the behavior of the diammoniate of tetramethyldiborane.

In considering the new compound, $CaHB(CH_3)_2\cdot NH_3$, it appears that the attachment of the calcium ion is quite strong, both on the basis of the chemical properties of this compound and the physical properties in solution, as indicated by the tensiometric and cryoscopic studies. It should also be noted, in this connection, that the liquid ammonia solution of $Na_2HB(CH_3)_2$ and apparently that of "$K_2HB(CH_3)_2$," (assuming by analogy that it is the product of the reaction of tetramethyldiborane with potassium in liquid ammonia) are strongly yellow and show high base activity of the $HB(CH_3)_2^{=}$ ion. In comparison $CaHB(CH_3)_2$ solutions are colorless and it appears that if $Li_2HB(CH_3)_2$ has existence, it is only faintly yellow in liquid ammonia, and both of the latter cases appear to have reduced base activity.

The moderate electrolytic conductance of $CaHB(CH_3)_2$ in liquid ammonia solution, however, would not appear to support the interpretation that the calcium ion is strongly bonded to the boron base. It is possible that this conductance was due to small quantities of highly conducting impurities such as calcium metal or the dimethylborohydride salt. On the other hand, it should be recognized that the solubilities of ionic di-divalent salts in liquid ammonia are generally very low, suggesting that any ionization of $CaHB(CH_3)_2$ would reasonably involve extensive solvation or association. Also, the results of the tensiometric studies suggested that some association was likely since the apparent molecular weight in solution was higher than the formula weight, although within the estimated margin of accuracy. Hence it is suggested, in speculation, that the production of ions necessary for electrolytic conductance might well have proceeded according to the equation

$$2CaHB(CH_3)_2 + xNH_3 \rightleftarrows (CH_3)_2BHCaHB(CH_3)_2^{=} + Ca^{++}\cdot NH_3 \qquad (11)$$

It should be noted that the $HB(CH_3)_2^{=}$ ion is not free on either side of this equation, thus meeting the requirement that the base activity be low. Also, this equilibrium should not affect appreciably the properties of the solution that are based upon the vapor pressure of the solvent.

The Reactions of Active Metals with Tetramethyldiborane, when the Latter Is in Excess.—In previous studies the liquid ammonia reaction of sodium with tetramethyldiborane, when the mole ratio of reactants was less than 2:1, respectively, gave results that were not readily understandable.[3] However, the similar system involving calcium instead of sodium appears to be more easily interpreted in terms of equations 3, 7, 8 and 9 above, and these results suggest a reasonable interpretation for the reactions of all of the active metals with tetramethyldiborane in liquid ammonia.

In considering the reactions observed with sodium and potassium, it is significant that the only observed difference from those involving calcium was that trimethylboron always appeared among the reaction products. In this connection it is also of interest that the reaction of lithium aluminum hydride with trimethylboron according to Wartik and Schlesinger produced dimethylaluminum hydride and lithium monomethylborohydride, but apparently none of the dimethylborohydride.[10] Therefore it appears likely that the dimethylborohydride disproportionates quite easily, and it may well be that the sodium and potassium salts of this anion are incapable of stable existence. In con-

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(10) T. Wartik and H. I. Schlesinger, THIS JOURNAL, **75**, 835 (1953).

trast, lithium appears to behave more like calcium in that no trimethylboron has been found among the reaction products, and the dimethylborohydrides of both of these metals have been isolated.

The explanation of the differences in the apparent stabilities of these salts is not obvious, although the lattice energies of the calcium and lithium salts would certainly be greater than those of the sodium and potassium salts, and the lattice energy may well serve to stabilize the dimethylborohydride ion in the solid state. In solution it could be postulated that ion aggregation, also dependent upon change density, would serve to stabilize the calcium and lithium salts.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Kinetics of Reactions Involving Neptunium(IV), Neptunium(V) and Neptunium(VI) Ions in Sulfate Media[1]

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The rates of the forward and reverse reactions involved in the equilibrium Np(IV) + Np(VI) $\rightleftarrows$ 2Np(V) have been measured in sulfate solution. Both forward and reverse reactions involve multiple parallel reaction paths. The rate of the forward reaction can be expressed in the form $R = k_0'[\mathrm{Np}^{+4}][\mathrm{NpO_2}^{++}][\mathrm{H}^+]^{-2} + \{k_1[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2}^{++}] + k_2[\mathrm{NpSO_4}^{++}][\mathrm{NpO_2SO_4}]\}\{k_3[\mathrm{H}^+]^{-2} + k_4[\mathrm{H}^+]^{-3}\}$. At 25° and $\mu = 2.2$, $k_0' = 2.69$ mole l.$^{-1}$ min.$^{-1}$, $k_1 = 4.27$ mole^{-1} l. min.$^{-1}$, $k_2 = 7.12$ mole^{-1} l. min.$^{-1}$, $k_3 = 3.6$ mole^2 l.$^{-2}$ and $k_4 = 1.7$ mole^3 l.$^{-3}$. The rate of the disproportionation reaction may be represented by $R = \{k_5[\mathrm{NpO_2}^+]^2[\mathrm{HSO_4}^-] + k_6[\mathrm{NpO_2}^+]^2[\mathrm{HSO_4}^-]^2\}\{k_7 + k_8[\mathrm{H}^+]\}$. At 25° and $\mu = 2.2$, $k_5 = 0.30$ mole^{-2} l.^{2} min.$^{-1}$, $k_6 = 0.090$ mole^{-3} l.^{3} min.$^{-1}$, $k_7 = 0.74$, and $k_8 = 0.14$ mole l.$^{-1}$. Apparent activation energies are given. Probable restrictions on the geometrical configurations for the transition state complexes and the mechanism of the electron transfer processes are considered. Relationships of the reactions in sulfate solution to similar reactions occurring in perchlorate media are discussed.

Three prior investigations of the kinetics of the neptunium(IV)–neptunium(VI) reaction have been reported.[2–4] In perchloric acid solution the mechanism of the reaction appears to involve hydrolysis products of neptunium(IV).[2] In mixed ethylene glycol–water media the mechanism is altered, ethylene glycol apparently being present in the activated complex.[3] In sulfate solution the only measurements made were in one molar sulfuric acid.[4] The present research has been carried out to see if alternate paths involving complex ion species are available. The sulfate system has been selected for further investigation for two reasons. First, data on the complexity constants of neptunium(IV) and sulfate are now available.[5] Second, measurement of the reverse reaction, the disproportionation of neptunium(V), is possible in this medium. Interest in the latter reaction is due to the apparent difference in reaction mechanism deduced from kinetic and equilibrium data in perchlorate solution[2] and the reaction which would be expected if the behavior of neptunium(V) paralleled that of uranium(V).

Experimental

The stock solutions of the neptunium ions in perchloric acid were prepared according to previously described methods. The sulfuric acid was reagent grade standardized by titration with sodium hydroxide.

The experimental technique also has been previously described.[2] The only major modification of that technique used in this investigation was the preparation of calibration curves necessary to determine the concentration of Np(IV) in the sulfuric acid–perchloric acid mixtures. The interaction between Np(IV) and bisulfate is reflected in the lowering and slight shift in wave length of the band at 724 mμ which is most useful for analytical purposes.

Results

I. The Np(IV) + Np(VI) ⟶ 2Np(V) Reaction

Effect of Metal Ion.—The stoichiometry of the reaction with respect to each of the metal ions was determined by experiments in which the concentration of Np(IV) and Np(VI) were varied in the reaction mixture. Data were obtained at total sulfuric acid concentrations of 0.0865 and 1.00 molar. At zero bisulfate the reaction is bimolecular.[2] In the bisulfate solutions the data were also found to be consistent for a bimolecular process. The rate constants, k_{obsd}, were computed from the experimental data both by graphical evaluation of the initial rate[6] and by means of the integrated equation for a bimolecular reaction

$$k_{\mathrm{obsd}} = \frac{2.303}{([\mathrm{Np(IV)}]^0 + [\mathrm{Np(VI)}]^0)t} \log \frac{[\mathrm{Np(VI)}]^0}{[\mathrm{Np(IV)}]^0} \left(\frac{[\mathrm{Np(VI)}]^0 - x}{[\mathrm{Np(IV)}]^0 - x}\right) \quad (1)$$

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. C. Hindman, J. C. Sullivan and D. Cohen, THIS JOURNAL, **76**, 3278 (1954).

[3] D. Cohen, E. S. Amis, J. C. Sullivan and J. C. Hindman, *J. Phys. Chem.*, **60**, 701 (1956).

[4] L. B. Magnusson, J. C. Hindman and T. J. LaChapelle, "The Transuranium Elements," edited by G. T. Seaborg, J. J. Katz and W. M. Manning (McGraw-Hill Book Co., New York, N. Y., 1949), National Nuclear Energy Series, Plutonium Project Record, Div. IV, Vol. 14B, paper 15.11, p. 1134.

[5] J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **76**, 5931 (1954).

[6] *Cf.* R. Livingston, "Technique of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 182.