

# The Ammonia and Alkylamine Addition Compounds of Carbon Monoxide Borane<sup>1</sup>

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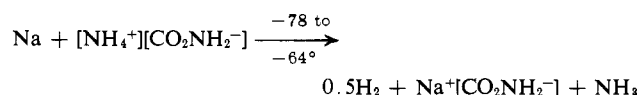
Contribution from the Department of Chemistry, University of Michigan, Ann Arbor, Michigan. Received November 19, 1964

The new compounds  $H_3BCO \cdot 2CH_3NH_2$ ,  $H_3BCO \cdot 2(CH_3)_2NH$ , and  $NaH_3BCONHCH_3$  have been prepared and characterized. The compound  $H_3BCO \cdot 2CH_3NH_2$  has been shown to be a relatively stable 1:1 electrolyte in water, to contain one methylammonium ion per formula weight, and to yield  $NaH_3BCONHCH_3$  when allowed to react with sodium in liquid ammonia or with sodium tetraphenylborate in water. The results of this research support the structure  $[H_2NRR'^+][H_3BCONRR'^-]$ , where  $R$  and  $R'$  may be either  $H$  or  $CH_3$ , for the 1:2 adducts obtained when carbon monoxide borane is allowed to react with ammonia, methylamine, or dimethylamine in ether. The suggested structures of the two sodium salts obtained when  $H_3BCO \cdot 2NH_3$  and sodium are allowed to react in liquid ammonia are  $[Na^+][H_3BCONH_2^-]$  and  $[2Na^+][H_3BCONH_2^-]$ . The carbamate type structure is also supported by infrared data.

Burg and Schlesinger<sup>2</sup> found that the reaction of carbon monoxide borane with trimethylamine at room temperature liberates carbon monoxide and forms trimethylamine-borane rapidly. In contrast, direct interaction of  $H_3BCO$  with ammonia at low temperatures does not liberate carbon monoxide but instead a "triammoniate,"  $H_3BCO \cdot 3NH_3$ , is initially formed. On warming to room temperature this material loses ammonia forming the "diammoniate of carbon monoxide borane." The latter substance is a relatively stable white solid at room temperature which reacts with an excess of sodium in liquid ammonia to produce rapidly at  $-77^\circ$  1 equiv. of hydrogen per formula weight of  $H_3BCO \cdot 2NH_3$ . A second equivalent of  $H_2$  is liberated over a 12-hr. period at  $-49^\circ$ . On the basis of their original information, Burg and Schlesinger suggested that  $H_3BCO \cdot 2NH_3$  was either a diammonium salt or a mixture of ammonium salts, but the structure of the solid has never been established. The present research investigates further the reactions of carbon monoxide borane with ammonia and the methylamines and establishes the structures of the resulting products.

Carbon monoxide borane is isoelectronic with carbon dioxide. The latter has been shown to react with ammonia in the gas phase or at low temperatures in suitable solvents such as absolute alcohol or petroleum ether to yield ammonium carbamate,  $[NH_4^+][O_2CNH_2^-]$ . The direct reaction of  $[NH_4^+][O_2CNH_2^-]$  with sodium in liquid ammonia was first reported by Rengade<sup>3</sup> and confirmed by Shore,<sup>4</sup> who isolated ammonium carbamate, redissolved it in liquid ammonia,

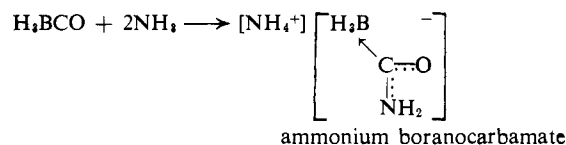
added sodium metal in excess, and noted that the following reaction occurs. Only the monosodium salt was



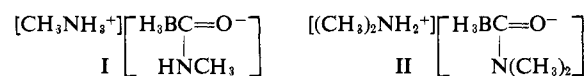
produced.

Blair<sup>5</sup> studied the reaction of ammonium carbamate with  $KNH_2$  in liquid ammonia and found that two products could be obtained. The first reaction formed a monopotassium salt. Potassium carbamate would react further with  $KNH_2$  yielding a dipotassium salt,  $K_2O_2CNH$ . The latter product was never completely characterized.

The foregoing reactions of ammonium carbamate with potassium amide and sodium are qualitatively similar to the results obtained by Burg and Schlesinger when they allowed the "diammoniate of carbon monoxide borane" to react with sodium. The structure supported by the present research for  $H_3BCO \cdot 2NH_3$  is formally analogous to that of ammonium carbamate and the reaction is represented as



wherein one oxygen is replaced by the isoelectronic  $BH_3$  group. Carbon monoxide borane could then react with methylamine and dimethylamine with a similar proton shift and with formation of methylammonium N-methylboranocarbamate (I) and dimethylammonium N,N-dimethylboranocarbamate (II), respectively.



The inability of trimethylamine to react by a proton shift would suggest a different mode of reaction for trimethylamine.

The sodium salts resulting from the reaction of sodium in liquid ammonia with the "diammoniate of borane carbonyl" would be  $Na[H_3BCONH_2]$  and  $Na_2[H_3BCONH]$ .

*Reaction of Carbon Monoxide Borane with Ammonia, Methylamine, or Dimethylamine.* The observations of Burg and Schlesinger concerning the *direct* interaction of  $H_3BCO$  and  $NH_3$  were verified in this study. The resulting product decomposed erratically at room temperature in an inert atmosphere. The compound  $H_3BCO \cdot 2NH_3$ , formed by loss of  $NH_3$  from the "triammoniate," gave no X-ray powder pattern and a real question about its homogeneity remained.

(1) This study is described in more detail in the Ph.D. Dissertation of James C. Carter, submitted to the Horace H. Rackham School of Graduate Studies, University of Michigan, 1960.

(2) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

(3) E. Rengade, *Bull. soc. chim. France*, **31**, 565 (1904).

(4) S. G. Shore, Ph.D. Dissertation, University of Michigan, 1956.

(5) J. S. Blair, *J. Am. Chem. Soc.*, **48**, 96 (1926).

Table I. X-Ray Powder Diffraction Data<sup>a</sup>

[NH <sub>4</sub> <sup>+</sup> ][H <sub>3</sub> BCONH <sub>2</sub> <sup>-</sup> ]		[CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> ][H <sub>3</sub> BCONHCH <sub>3</sub> <sup>-</sup> ]		[(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> <sup>+</sup> ][H <sub>3</sub> BCON(CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup> ]		[Na <sup>+</sup> ][H <sub>3</sub> BCONHCH <sub>3</sub> <sup>-</sup> ]	
<i>d</i> , Å.	Intensity	<i>d</i> , Å.	Intensity	<i>d</i> , Å.	Intensity	<i>d</i> , Å.	Intensity
7.344	w	6.575	s	8.874	s	8.294	vs
5.356	ms	6.223	s	5.668	vs	6.673	vs
5.126	w	4.901	ms	5.126	vs	6.000	vs
4.770	m	4.695	m	4.476	vs	4.910	m
4.210	w	3.963	vvs	3.668	ms	4.679	m
3.850	vs	3.791	vvw	3.557	ms	4.469	vvw
3.708	s	3.712	ms	3.351	s	4.291	s
3.414	mw	3.516	w	3.018	m	4.139	vvw
3.225	s	3.423	vs	2.953	m	3.986	vs
2.940	w	3.335	vvw	2.834	m	3.431	m
2.876	m	3.228	vw	2.760	ms	3.267	m
2.822	vvw	3.146	ms	2.554	m	3.082	ms
2.722	mw	3.001	mw	2.479	w	3.001	ms
2.652	vvw	2.906	mw	2.434	vvw	2.943	w
2.462	mw	2.772	vw	2.360	m	2.867	s
2.386	w	2.714	vvw	2.306	vw	2.783	vvw
2.265	m	2.642	m	2.258	vvw	2.675	ms
2.176	mw	2.597	vvw	2.208	mw	2.600	ms
2.103	mw	2.536	mw	2.055	w	2.529	w
2.053	mw	2.411	m	1.999	vw	2.481	mw
1.941	vvw	2.291	w	1.960	vvw	2.449	w
1.841	vvw	2.220	mw	1.905	w	2.358	mw
1.710	vvw	2.184	w	1.829	vw	2.298	vvw
1.667	w	2.124	vvw	1.782	vw	2.219	m
1.645	w	2.091	w	1.742	vvw	2.153	ms
1.397	w	2.012	vvw	1.698	vvw	2.114	m

<sup>a</sup> s = strong, m = moderate, w = weak, v = very.

On the other hand, the use of diethyl or dimethyl ether<sup>6</sup> as a low temperature reaction medium produced relatively stable, white, *crystalline* diadducts of borane carbonyl with the bases NH<sub>3</sub>, NH<sub>2</sub>CH<sub>3</sub>, or NH(CH<sub>3</sub>)<sub>2</sub>. The products are of the form H<sub>3</sub>BCO·2base. Neither H<sub>2</sub> or CO was evolved during the reactions. X-Ray powder diffraction data on the solid products are given in Table I.

The compound H<sub>3</sub>BCO·2NH<sub>3</sub> produced in ether is significantly more stable than the product of direct addition; it is not vigorously hydrolyzed by water, but can be quantitatively hydrolyzed by 6 N HCl in a sealed tube at 175°. No evidence for formation of a triammoniate in ether was obtained and the fact that the product obtained from diethyl ether was identical with that obtained from dimethyl ether eliminated the possibility that an ether molecule replaced the third ammonia in the solid product.

The apparent stability order for the three base adducts is, in order of *decreasing* stability, H<sub>3</sub>BCO·2NH<sub>2</sub>CH<sub>3</sub> > H<sub>3</sub>BCO·2NH(CH<sub>3</sub>)<sub>2</sub> > H<sub>3</sub>BCO·2NH<sub>3</sub>. The methylamine compound is stable for at least 24 hr. in air and can be dissolved in water for at least 30 min. without any gas evolution. The solid product, H<sub>3</sub>BCO·2NH<sub>2</sub>CH<sub>3</sub>, which could be separated after 4 hr. from an aqueous solution, had the same X-ray powder pattern as the starting material; however, after the solution had been standing for *more than* 4 hr., it became cloudy indicating decomposition of solute.

On standing for 6 weeks in an evacuated tube at 25°, solid H<sub>3</sub>BCO·2NH<sub>2</sub>CH<sub>3</sub> underwent a slow decomposition process

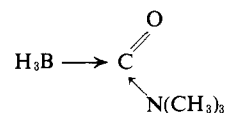


(6) Advantages due to use of ether as a reaction medium are well known: M. Steindler and H. I. Schlesinger, *J. Am. Chem. Soc.*, **75**, 756 (1953); D. H. Campbell, T. C. Bissot, and R. W. Parry, *ibid.*, **80**, 1949 (1958); E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *ibid.*, **81**, 3550 (1959).

Both the ammonia<sup>7</sup> and dimethylamine adducts underwent similar decomposition processes. Since H<sub>3</sub>BCO·2NH(CH<sub>3</sub>)<sub>2</sub> has a *slight sublimation pressure*, it was not possible to separate the amine borane by sublimation as in the first two cases, but the production of CO and (CH<sub>3</sub>)<sub>2</sub>NH as volatile decomposition products argued for the same type of decomposition.<sup>8</sup>

*The Reaction of Carbon Monoxide Borane with Trimethylamine.* Burg and Schlesinger<sup>2</sup> reported no observable displacement of CO by N(CH<sub>3</sub>)<sub>3</sub> at -80°, but found that a displacement reaction proceeded rapidly at room temperature.

In this research an 0.62-mmole sample of H<sub>3</sub>BCO was mixed with a 3.4-mmole sample of N(CH<sub>3</sub>)<sub>3</sub> in 6 ml. of dimethyl ether at -100°. A white precipitate formed which dissolved on warming to -80°; small amounts of CO were evolved. A solid product was isolated at -80° by distillation of the solvent. In one case further warming of the solid to room temperature produced small amounts of CO and H<sub>3</sub>BN(CH<sub>3</sub>)<sub>3</sub> along with an unidentified nonvolatile oil. In a subsequent run, good yields of H<sub>3</sub>BN(CH<sub>3</sub>)<sub>3</sub> and CO were obtained. The reactions of H<sub>3</sub>BCO and other amines suggest that the original white solid, isolated at -80°, was



The solid presumably underwent decomposition comparable to that noted for the other amine adducts

(7) The ammonia adduct gave H<sub>3</sub>NBH<sub>3</sub>. Schlesinger and Burg<sup>2</sup> reported the formation of a small amount of a slightly volatile white solid in the preparation of H<sub>3</sub>BCO·2NH<sub>3</sub> from the triammoniate. The solid obtained by us under these conditions was H<sub>3</sub>BNH<sub>3</sub>.

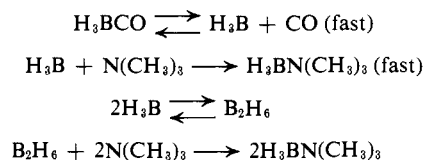
(8) Since completion of this research, it has been called to our attention that Professor A. B. Burg has also studied the reaction of carbon monoxide-borane and dimethylamine (NACA 6940-286, 1949), but no report has been published in the open literature.

Table II. A Comparison of Infrared Frequencies (cm.<sup>-1</sup>) for H<sub>3</sub>BCO · 2NH<sub>2</sub>CH<sub>3</sub> and Related Molecules<sup>a</sup>

[CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> ]Cl <sup>-</sup>	[CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup> ]- [H <sub>3</sub> BCONHCH <sub>3</sub> <sup>-</sup> ]	Na <sup>+</sup> [H <sub>3</sub> BCONHCH <sub>3</sub> <sup>-</sup> ]		H <sub>3</sub> CCONHCH <sub>3</sub>	
		Freq.	Assign.	Freq.	Assign. <sup>b</sup>
3420	3400 (s)	3400 (s)	ν(N-H)	3300 (s)	ν(NH...O)
3100	3190 (s)			3100 (s)	ν(NH...O)
	2940 (s)	2940 (m)	ν(CH <sub>3</sub> )	2960 (m)	ν(CH <sub>3</sub> )
	2850 (s)	2870 (w)	ν(CH <sub>3</sub> )	2900 (m)	ν(CH <sub>3</sub> )
	2270 (s)	2290 (s)	ν(B-H)		
	1640 (m)	1635 (m)	ν(C=O)	1640 (s)	ν(C=O)
1538	1545 (m)	1550 (s)	δ(NH)	1550 (s)	δ(NH)
	1510 (s)	1515 (s)	δ(BH <sub>3</sub> )	1440 (s)	δ(CH <sub>3</sub> )
1428	1400 (m)	1408 (s)	δ(CH <sub>3</sub> )	1410 (s)	δ(CH <sub>3</sub> )
	1280 (w)	1280 (m)	δ(CH <sub>3</sub> )	1370 (s)	δ(CH <sub>3</sub> )
	1190 (m)	1190 (m)	δ(B-H)	1290 (s)	δ(CH <sub>3</sub> )
	1150 (m)	1170 (s)	ν(C-N)?		
	1130 (m)	1130 (w)	δ(B-H)	1160 (s-)	ν(C-N)
	1030 (w)			1095 (m)	δ(CH <sub>3</sub> )
1003	1000 (w)	1040 (m)	ν(N-CH <sub>3</sub> )	1040 (m-)	ν(N-CH <sub>3</sub> )
	990 (w)			995 (m)	δ(CH <sub>3</sub> )
958	965 (m)				
	930 (w)	920 (w)			
	890 (m)	880 (s)	ν(C-B)?	880 (s)	ν(C-C)
	835 (w)	845 (w)			
	740-660 (w)	740-760 (w)	π?	710	π

<sup>a</sup> Frequencies in units of cm.<sup>-1</sup>; ν is the stretching vibration, δ is the deformation vibration, π is the perpendicular vibration. <sup>b</sup> See ref. 12.

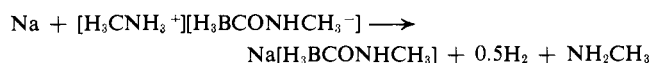
as the system was warmed to room temperature. This system is under further study. Since H<sub>3</sub>BCO is strongly dissociated at room temperature, it is probable that the room temperature reaction of Burg and Schlesinger involved the reaction of trimethylamine with the dissociation products



This assumption would explain the marked difference in the results obtained at 25 and -80°. The foregoing scheme would appear to be consistent with current information on the decomposition of H<sub>3</sub>BCO.

### The Structure and Reactions of Carbon Monoxide Borane Bis(monomethylamine)

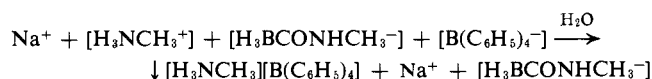
1. *The Reaction with Sodium. Evidence for the Ionic Nature of the Product.* As with the comparable diammoniate described by Burg and Schlesinger,<sup>2</sup> carbon monoxide borane bis(monomethylamine) reacts rapidly with sodium in liquid ammonia in accordance with the equation



In contrast to the ammonia adduct, the methylamine compound gave no additional hydrogen on standing in ammonia with an excess of sodium at -78°. This difference may be properly attributed to the less acidic nature of the proton on the methylamide group, resulting from the inductive effect of the methyl group.

The sodium N-methylboranocarbamate, isolated as a crystalline white solid from the above reaction, is stable for several hours at room temperature in air or water. X-Ray powder diffraction data are given in Table I. It is a strong electrolyte in water solution.

2. *The Reaction of Carbon Monoxide Borane Bis(monomethylamine) with Sodium Tetraphenylborate.* The insolubility of methylammonium tetraphenylborate<sup>9</sup> in aqueous solution suggested synthesis of the compound Na[H<sub>3</sub>BCONHCH<sub>3</sub>] by metathesis. Mixing stoichiometric quantities of the reagents gave the reaction



Removal of the insoluble [H<sub>3</sub>NCH<sub>3</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] by filtration and removal of the solvent water under vacuum at room temperature left the white crystalline Na[H<sub>3</sub>BCONHCH<sub>3</sub>]. Its X-ray diffraction pattern was identical with that of the salt prepared by the previously described sodium reaction in liquid ammonia.

When an excess of Na[B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] was used, 1 mole of methylammonium tetraphenylborate precipitated rapidly for each mole of H<sub>3</sub>BCO · 2NH<sub>2</sub>CH<sub>3</sub> used. When the filtrate containing excess tetraphenylborate was allowed to stand, additional [CH<sub>3</sub>NH<sub>3</sub>][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] formed slowly; this fact suggests slow hydrolysis of the anion.<sup>10</sup>

3. *Infrared Studies.* Infrared spectral data for solid samples of [CH<sub>3</sub>NH<sub>3</sub>]Cl, [CH<sub>3</sub>NH<sub>3</sub>][H<sub>3</sub>BCONHCH<sub>3</sub>], and Na[H<sub>3</sub>BCONHCH<sub>3</sub>] in KBr pellets are shown in Table II. Also included in Table II are the spectral data and assignments of Mizushima and co-workers<sup>11</sup> for liquid N-methylacetamide which is isostructural and isoelectronic with the boranocarbamate anion. From the assignments of both N-methylacetamide and known borane adducts, tentative assignments for the boranocarbamate anion can be made; these are shown in Table II.

(9) F. E. Crane, Jr., *Anal. Chem.*, **28**, 1794 (1956); **30**, 1426 (1958).

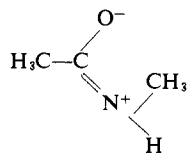
(10) (a) R. W. Parry, C. E. Nordman, J. C. Carter, and G. TerHaar, *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington D. C., 1964, p. 305; (b) J. C. Carter, Ph.D. Dissertation, University of Michigan, 1964.

(11) S. Mizushima, T. Simanouti, S. Nagakura, K. Kuratani, M. Tsuboi, H. Baba, and O. Fujioka, *J. Am. Chem. Soc.*, **72**, 3490 (1950).

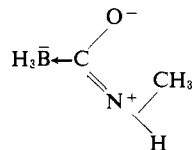
The infrared absorption spectrum of  $[\text{CH}_3\text{NH}_3^+][\text{H}_3\text{BCONHCH}_3^-]$  may be obtained by combining the spectra of  $[\text{CH}_3\text{NH}_3^+][\text{Cl}^-]$  and  $[\text{Na}^+][\text{H}_3\text{BCONHCH}_3^-]$ , the sodium and chloride ions being inactive in the infrared. The result agrees both in frequency and intensity and accounts for each band observed in the original adduct. This is proof that the anion has undergone the metathesis reaction without internal rearrangement. The bands at 1640 in  $[\text{CH}_3\text{NH}_3^+][\text{H}_3\text{BCONHCH}_3^-]$  and at 1635  $\text{cm}^{-1}$  in  $\text{Na}[\text{H}_3\text{BCONHCH}_3]$  are of major interest since they may be unambiguously assigned to the carbonyl group and they compare almost exactly with the  $>\text{C}=\text{O}$  stretching frequency in  $\text{CH}_3\text{CONHCH}_3$ . The 1640- $\text{cm}^{-1}$  band is unchanged in the deuterated species  $[\text{CH}_3\text{NH}_3^+][\text{D}_3\text{BCONHCH}_3^-]$ , and therefore cannot be associated with the  $\text{BH}_3$  group. The bands at 2270, 1190, and 1130  $\text{cm}^{-1}$  are absent in  $[\text{CH}_3\text{NH}_3^+][\text{D}_3\text{BCONHCH}_3^-]$  and are assigned to the boron-hydrogen modes. The  $\nu_{\text{B-D}}$  band appears at 1731  $\text{cm}^{-1}$  as expected.

Several more detailed points are of interest in comparing the spectrum of the boranocarbamate anion with that of the isoelectronic N-methylacetamide. According to Mizushima and collaborators<sup>11</sup> N-methylacetamide in the liquid form is associated in long chains by  $>\text{N}-\text{H}\cdots\text{O}=\text{C}<$  hydrogen bonds. Such hydrogen bonding causes a drop in the N-H stretching frequency from 3480  $\text{cm}^{-1}$  in the nonbonded state to 3300  $\text{cm}^{-1}$  in the pure liquid. An N-H stretching frequency of 3400  $\text{cm}^{-1}$  in solid  $\text{Na}[\text{H}_3\text{BCONHCH}_3]$  could be interpreted as indicative of reduced hydrogen bonding between anions in the solid state.

A more detailed analysis of the  $>\text{C}=\text{O}$  stretching frequency is also of interest. In  $\text{CH}_3\text{CONHCH}_3$  the  $>\text{C}=\text{O}$  stretch at 1640  $\text{cm}^{-1}$  is significantly lower than the normal carbonyl stretch in saturated ketones (1705–1725  $\text{cm}^{-1}$ ). This decrease from 1700 to 1640  $\text{cm}^{-1}$  in  $\text{CH}_3\text{CONHCH}_3$  has been attributed to increased contributions by the structure containing a single-bonded oxygen<sup>12</sup>



In view of the anionic nature of the boranocarbamate one might well anticipate that this anion would exhibit structures with even greater single-bonded oxygen participation. If normal conventions are followed, the anion would then be represented as



Such a formulation would imply a  $>\text{C}=\text{O}$  stretch *below* 1640  $\text{cm}^{-1}$ . Since hydrogen bonding does not usually shift the  $>\text{C}=\text{O}$  frequency in ketones and aldehydes by more than about 10  $\text{cm}^{-1}$ ,<sup>12</sup> an increase due to reduced hydrogen bonding seems unlikely and one is led to

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 209.

conclude that the multiplicities of the  $>\text{C}=\text{O}$  bonds in the boranocarbamate anion and N-methylacetamide are comparable.

Finally the infrared data shown in Table III show unequivocally that  $\text{H}_3\text{BCO}\cdot 2\text{NH}_3$ ,  $\text{H}_3\text{BCO}\cdot 2\text{NHCH}_3$ , and  $\text{H}_3\text{BCO}\cdot 2\text{NH}(\text{CH}_3)_2$  are structurally similar. The only spectral differences observed are those which would be expected from required minor structural features. All available evidence is entirely in agreement with the carbamate structure. The absence of a C-H stretching vibration in  $\text{H}_3\text{BCO}\cdot 2\text{NH}_3$  argues strongly against a model involving shift of a hydrogen from  $\text{BH}_3$  to C in the anion.

Table III. Infrared Spectral Data<sup>a</sup>

$[\text{NH}_4^+][\text{H}_3\text{BCONH}_2^-]$	3420(s), 3240(s), 2290(s), 1630(s); 1510(w), 1460(m), 1410(s), 1270(m), 1190(m), 1160(m), 1120–1090(w), 1020(w), 890– 860(w), 760(w)
$[(\text{CH}_3)_2\text{NH}_2^+][\text{H}_3\text{BCON}(\text{CH}_3)_2^-]$	3400(m), 3000(m), 2920(s), 2760(s), 2280(s), 1630(m), 1510(m), 1470(s), 1430(w), 1380(s), 1260(s), 1220(w), 1150(m), 1110(s), 1030(m), 940(m), 900(w), 860(s), 700(m)

<sup>a</sup> s = strong, m = moderate, w = weak.

Since the completion of this research, a single crystal X-ray diffraction study completed by Professor Nordman<sup>13</sup> has verified the structure supported here by chemical and physical evidence.

## Experimental

Standard vacuum techniques were used throughout.

**Reagents.** Carbon monoxide borane was prepared by the reaction of  $\text{B}_2\text{H}_6$  and CO at high pressure and room temperature.  $\text{B}_2\text{H}_6$  (50–100 mmoles) was condensed at  $-196^\circ$  into a 30-cc. Hoke 1800 p.s.i. test, stainless steel, single outlet cylinder equipped with a gauge, a packless diaphragm valve, and a tubing connection. The cylinder was attached to a standard high vacuum line. Carbon monoxide was placed in a 5-l. bulb at 1 atm. It was then condensed into the steel cylinder until its vapor pressure of approximately 400 mm. was reached. The cylinder valve was closed, the 5-l. bulb refilled to an atmosphere, and the process repeated until the desired ratio of  $\text{CO}/\text{B}_2\text{H}_6$  was obtained. The cylinder valve was then closed and the cylinder warmed to room temperature while the pressure was observed closely to see that it did not exceed 1800 p.s.i. In most cases 1000 to 1600 p.s.i. were the maximum pressures observed. If the pressure built up to too high a value, the cylinder was cooled with liquid nitrogen and some of the CO removed. After 3 to 6 hr. the pressure became constant; the cylinder was cooled to  $-196^\circ$ ; and the excess CO was passed very slowly through three  $-196^\circ$  traps, then pumped out. The  $\text{H}_3\text{BCO}$  was then fractionated and its vapor pressure checked with literature values.<sup>2</sup> Yields were nearly quantitative based on the diborane used. All other reagents were of the highest purity and appropriately dried.

(13) C. E. Nordman, private communication.

*Reaction of  $H_3BCO$  and  $NH_3$ .* Ammonia (4 to 5 mmoles) was condensed into the reaction tube; an approximately 5-ml. sample of methyl or ethyl ether was added, and the mixture was warmed to  $-80^\circ$  and stirred. The ammonia-ether mixture was then frozen into the bottom of the reaction tube ( $-196^\circ$ ) and approximately 1 mmole of  $H_3BCO$  condensed above it. The reactor was then surrounded with a methylcyclohexane slush ( $-126^\circ$ ) and the magnetic stirrer started. After 6 hr. the temperature was approximately  $-70$  to  $-80^\circ$  and a white precipitate was present. No noncondensable gas formed during the reaction. The tube was surrounded with Dry Ice and the solvent ether and excess ammonia were distilled away over a 12-hr. period. The samples for X-ray and infrared analysis were removed in a drybox under a nitrogen atmosphere. With ethyl ether the initial reaction temperature was raised from  $-126$  to  $-111^\circ$  because of the higher melting point of ethyl ether.

*Reaction of  $H_3BCO$  and  $CH_3NH_2$ .* In a typical reaction, 13.26 mmoles of  $CH_3NH_2$  and 10 ml. of ethyl ether were thoroughly mixed and frozen in a reaction tube at  $-196^\circ$  with 3.29 mmoles of carbon monoxide borane. The mixture was stirred for 2 hr. while the temperature rose from  $-111$  to  $-90^\circ$ . The mixture was stirred an additional 3 hr. and allowed to stand overnight at  $-80^\circ$ . On cooling to  $-196^\circ$ , only a trace of noncondensable gas was present. The solvent and excess methylamine (6.88 mmoles) were distilled out; excess amine was converted to methylammonium chloride with HCl and weighed. The  $CH_3NH_2/H_3BCO$  ratio was 6.38:3.29 or 1.94:1.00. Similar reactions in methyl ether were started at  $-126^\circ$ . The product was shown to be identical with that formed in ethyl ether by comparing their X-ray powder patterns. The reaction conducted using a 1:1 ratio of  $H_3BCO$  to  $CH_3NH_2$  yielded only the diadduct and excess  $H_3BCO$  with no evidence for a monoadduct.

*Anal.* Calcd. for  $[CH_3NH_3^+][H_3BCONHCH_3^-]$ : C, 34.65; H, 12.60; N, 26.95; B, 10.41; mol. wt. (calcd. for two ions), 52. Found: C, 34.6; H, 12.4; N, 26.7; B, 10.3; mol. wt. (in water), 51.3.

*Reaction of  $H_3BCO$  and  $(CH_3)_2NH$ .* The reaction was conducted in ethyl ether in a manner similar to that described above for  $H_3BCO$  and  $CH_3NH_2$ . The solid  $H_3BCO \cdot 2(CH_3)_2NH$  could not be easily recovered from water.

*Anal.* Calcd. for  $[(CH_3)_2NH_2^+][H_3BCON(CH_3)_2^-]$ : C, 45.48; H, 12.98; N, 21.22; B, 8.20. Found: C, 45.3; H, 13.1; N, 21.1; B, 8.1.

*Reaction of  $[CH_3NH_3^+][H_3BCONHCH_3^-]$  and  $NaB(C_6H_5)_4$ .* A 0.132-mmole sample of methylammonium N-methylboranocarbamate was weighed into a microbeaker with attached sintered glass frit, 1 ml. of water was added with a syringe, the beaker was swirled to thoroughly mix the solutions, and the mixture was

immediately filtered. The elapsed time between mixing and filtering was 5 to 10 sec. After drying *in vacuo*, the precipitate was found to be 0.132 mmole of  $[CH_3NH_3^+][B(C_6H_5)_4^-]$ . On standing, the filtrate became cloudy and further precipitate formed. Repetition of the reaction using equimolar quantities of reagents (0.55 mmole) in 5 ml. of  $H_2O$  permitted isolation of  $Na[H_3BCONHCH_3]$ .

*Anal.* Calcd. for  $[Na^+][H_3BCONHCH_3^-]$ : C, 25.31; H, 7.43; N, 14.76; B, 11.40; Na, 24.23; mol. wt. (calcd. for two ions), 47.5. Found: C, 25.3; H, 7.3; N, 14.7; B, 11.3; Na, 24.2; mol. wt. (in water), 46.2.

*Reaction of  $[CH_3NH_3^+][H_3BCONHCH_3^-]$  and Sodium in Liquid Ammonia.* Methylammonium N-methylboranocarbamate (1.05 mmoles) and sodium metal (1.03 mg.-atoms) in 10 ml. of liquid ammonia gave 0.51 mmole of  $H_2$  and the blue color of the sodium was discharged. Removal of the solvent left a white solid,  $[Na^+][H_3BCONHCH_3^-]$ , identical with that prepared in water.

When a large excess (30:1) of sodium metal was used and the reaction allowed to stand 20 hr. at  $-75^\circ$  and 16 hr. at  $-45^\circ$ , only 1 equiv. of hydrogen was evolved per formula weight of  $H_3BCO \cdot 2NH_2CH_3$ .

*Physical Procedures.* Standard X-ray powder techniques were used on samples in 0.3-mm. diameter glass capillaries (0.01-mm. wall thickness). Nickel filtered Cu  $K\alpha$  radiation with a weighted average wave length of 1.5418 Å. was used.

A Perkin-Elmer Model 21 double beam spectrophotometer with NaCl or  $CaF_2$  optics was used to examine solid samples pressed in KBr disks.

*Analysis.* Hydridic hydrogen was determined by hydrolysis of the sample with 6 N HCl in a sealed tube at  $150$ – $175^\circ$  for a minimum time of 24 hr. Boron and nitrogen were determined by standard methods.<sup>14</sup>

*Molecular Weight Determinations.* Standard freezing point depression methods were used in water in a concentration range of  $10^{-3}$  to  $10^{-2}$  m. Results were extrapolated to infinite dilution; extrapolated values are reported.

*Conductivity Determinations.* The apparatus used has been described by Atkinson.<sup>15</sup> The equivalent conductance of a water solution of  $[CH_3NH_2][H_3BCONHCH_3]$  at a molar dilution of 1024 l. was 150 mhos. Under the same conditions methylammonium carbamate shows an equivalent conductance of 185 mhos.

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(14) D. R. Schultz and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 4 (1958).

(15) G. Atkinson, *ibid.*, **82**, 818 (1960).