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The Preparation and Properties of the Boranocarbonates

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The H_3B group and the oxygen atom are isoelectronic, suggesting that H_3BCO and CO_2 might exhibit certain chemical similarities. Development of these similarities has resulted in the synthesis, by four different methods, of metal salts of the boranocarbonate anion, $M^{+}{}_2[H_3BCO_2]^{2-}$. The gross structure of the anion is that of a carbonate in which one oxygen atom is replaced by the isoelectronic H_3B group. The above replacement gives the symmetry of the acetate ion; this fact is revealed in a comparison of the infrared spectra. The salts are stable indefinitely in dry air. Both water and methanol solutions can be prepared. Titration, solubility, infrared, and nmr data are presented and analyzed in terms of the above model. Treatment of $M_2[H_3BCO_2]$ salts with 85% H_3PO_4 regenerates high-purity H_3BCO; thus, boranocarbonate salts now provide an easily transported source of high-purity H_3BCO.

The compound carbon monoxide borane diammoniate, $H_3BCO \cdot 2NH_3$, was first reported by Burg and Schlesinger.[1] Recent evidence[2] establishes its structure unequivocally as that of a carbamate, with an H_3B group replacing an isoelectronic oxygen atom. If the isoelectronic analogy used in determining the structure of $H_3BCO \cdot 2NH_3$ is pursued one step further, an analogy between H_3BCO and CO_2 emerges. Pursuit of this analogy has resulted in the synthesis of a boranocarbonate anion which is an analog of the carbonate ion. A surprising similarity in the chemistries of H_3BCO and CO_2 has been developed which suggests that entire families of oxyacids and organic compounds might be prepared with a BH_3 group replacing an oxygen atom. A reasonable possibility of property prediction for such structures emerges as a result of this study. Several such acid analogs have been synthesized.

The Synthesis of Boranocarbonate Salts

It is well known that CO_2, when added to an alcoholic solution of KOH, reacts to give K_2CO_3.[3a] Direct extrapolation of this reaction suggests the process

$$H_3BCO + 2KOH \xrightarrow{\text{alcohol}} K_2H_3BCO_2 + H_2O \qquad (1)$$

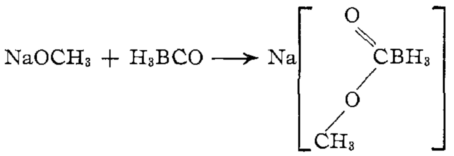
The reaction goes precisely as expected, giving high-purity[3b] potassium boranocarbonate as an insoluble precipitate from the alcohol; indeed, this process works so well that crude H_3BCO can be separated easily from the excess CO–B_2H_6 mixture used in H_3BCO preparation. This process (described in more detail in the Experimental Section) is the best method now available for preparation of boranocarbonate salts and makes them relatively easily available in moderate amounts.

The CO_2–H_3BCO analogy suggests other procedures for the synthesis of boranocarbonate salts. When CO_2 is allowed to come in contact with CaO, no reaction occurs unless a trace of water is present. If a very small amount of water is present, $CaCO_3$ is easily formed.[3c] An exactly comparable set of reactions is observed for H_3BCO; dry H_3BCO will not react with dry CaO, but CaO containing a small amount of water will pick up H_3BCO readily to give CaH_3BCO_2. It is also of interest to note that commercial Ascarite (NaOH and asbestos), used to absorb CO_2 in gas analysis, will pick up H_3BCO quantitatively at room temperature in the absence of air.

$$CaO + H_3BCO \xrightarrow[25°]{\text{trace } H_2O} CaH_3BCO_2 \qquad (2)$$

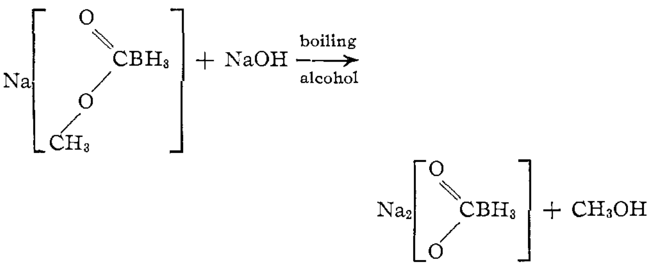
$$NaOH + H_3BCO \xrightarrow[\text{Ascarite, } 25°]{\text{commercial}} NaH[H_3BCO_2] \qquad (3)$$

Comparable to the reaction of H_3BCO with KOH is the reaction between H_3BCO and $NaOCH_3$ in alcoholic solution. The expected product is sodium O-methylboranocarbonate, $Na[CH_3OC(O)BH_3]$



(4)

The reaction proceeds as expected to give the sodium O-methylboranocarbonate in good yield.[4] Hydrolysis of $Na[CH_3OC(O)BH_3]$ by NaOH in boiling alcohol gives $Na_2H_3BCO_2$ as an insoluble precipitate



This procedure appears to be the least desirable one of those described for the synthesis of boranocarbonates.

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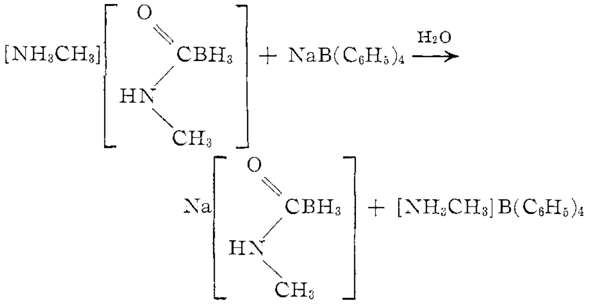
[1] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1937).

[2] (a) J. C. Carter and R. W. Parry, *ibid.*, **87**, 2354 (1965); (b) R. W. Parry, C. E. Nordman, J. C. Carter, and G. Ter Haar, Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1964, p 302.

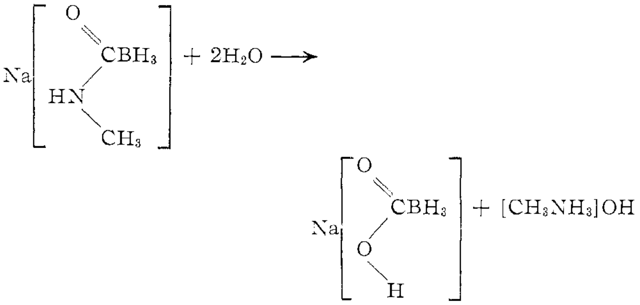
[3] (a) H. Remy, "Treatise on Inorganic Chemistry," Vol. I, Elsevier Publishing Co., New York, N. Y., 1956, p 196; (b) obviously the CO used to prepare H_3BCO should be free from CO_2 or contamination with K_2CO_3 will result; (c) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Clarendon Press, Oxford, 1950, p 247.

[4] This reaction was first carried out by Professor James C. Carter at the University of Pittsburgh. It was done independently in this laboratory.

The first procedure to give evidence for boranocarbonates was the hydrolysis of boranocarbamates, but this method is now recognized as being inferior to other procedures as a synthesis route. Carter, working in this laboratory,[2a] found that when methylammonium N-methylboranocarbamate was allowed to react with $NaB(C_6H_5)_4$, 1 mole of $[CH_3NH_3]B(C_6H_5)_4$ precipitated rapidly for each mole of the boranocarbamate used. The reaction can be represented as


(5)

Upon standing, additional $[NH_3CH_3]B(C_6H_5)_4$ slowly precipitated and the pH of the solution increased. The latter set of observations was tentatively interpreted[2] in terms of the reactions



$$[CH_3NH_3]OH + NaB(C_6H_5)_4 \longrightarrow [CH_3NH_3]B(C_6H_5)_4\downarrow + NaOH$$

It should be noted that the sodium boranocarbonate was never isolated or characterized further in the original study. The foregoing interpretation of these reactions has now been verified. As expected, the hydrolysis of methylammonium N-methylboranocarbonate is greatly accelerated by the presence of sodium tetraphenylborate in the solution.

The Chemistry of Boranocarbonate Salts

(1) Conversion to Other Salts. Solubility Trends.—Sodium *or* potassium boranocarbonate dissolves in distilled water to give a solution which decomposes slowly. About 20% decomposition was observed over a 10-day period at 25°. It is possible to use cation-exchange resins (Dowex 50) to convert the sodium or potassium compound to the lithium, calcium, or similar compound. By adding potassium boranocarbonate to an aqueous $PbCl_2$ solution at 25°, one can precipitate lead boranocarbonate. The alkali metal boranocarbonates can be dehydrated completely by heating to 50° under vacuum. Decomposition was not detected as a result of the drying. Solubility data for various salts and solvents are given in Table I.

The boranocarbonates represent an interesting compromise between carbonates and acetates. The anion has a charge of 2 comparable to the carbonate ion and a symmetry or molecular geometry comparable to that of the univalent acetate ion. Thus lattice energies, heats of hydration of ions, entropy changes for the solution process, and other factors of significance in determining solubility might well fall between the values for the corresponding acetates and carbonates. That the general solubility patterns are intermediate between acetates and carbonates is seen in Table I.

Table I

Selected Properties of the Boranocarbonate Salts. A Comparison with Acetates and Carbonates[a]

Cation	Salt	Decompn temp, °C	Solubility		
			H_2O	CH_3OH	C_2H_5OH
	Acetate		VS	VS	S
Li	Boranocarbonate	230	VS	S	SlS
	Carbonate		S	Ins	Ins
	Acetate		VS	S	S
Na	Boranocarbonate	400	VS	S	Ins
	Carbonate		S	Ins	Ins
	Acetate		VS	S	S
K	Boranocarbonate	400	VS	S	Ins
	Carbonate		VS	Ins	Ins
	Acetate		VS	SlS	SlS
Ca	Boranocarbonate	100	S	SlS	Ins
	Carbonate		Ins	Ins	Ins
	Acetate		VS	SlS	SlS
Ba	Boranocarbonate	150	S	Ins	Ins
	Carbonate		Ins	Ins	Ins
	Acetate				
Pb	Boranocarbonate	...	Ins	Ins	Ins
	Carbonate		Ins	Ins	Ins

[a] VS = very soluble = 20 g/100 g of solvent; S = soluble = 1–20 g/100 g of solvent; SlS = slightly soluble = 0.5–1.0 g/100 g of solvent; Ins = insoluble = <0.05 g/100 g of solvent.

(2) Pyrolysis of the Boranocarbonates.—The pyrolysis of the boranocarbonates is still under study in this laboratory, but the temperatures at which decomposition first ensues are recorded in Table I. As expected, large cations of low charge give the most stable compounds. The alkaline earth boranocarbonates decompose more easily than the corresponding alkali metal salts. (Compare decomposition of carbonates.)

(3) The Reaction of Boranocarbonates with Acids. (a) Titration of Aqueous Solution with Dilute HCl.—Titration of a solution (0.023 *M*) of sodium boranocarbonate with 0.05 *N* HCl at 25° gives a curve which is very close to the first half of the titration curve of Na_2CO_3 at comparable concentration. The second ionization constant of the hypothetical acid $H_2[H_3BCO_2]$ can be estimated as $(6 \pm 3) \times 10^{-11}$ from the titration curve. The literature value of K_2 for H_2CO_3 is 4.8×10^{-11}.[5]

Addition of the second equivalent of acid caused some gas evolution and erratic pH readings in the pH range 7.5–5.5. Below pH 5.0 the titration curve broke sharply and an end point could be determined easily

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(5) The K_2 value measured in this laboratory by a procedure identical with that used for boranocarbonate was 7.5×10^{-11}.

at pH 4.5. By using this end point, experimental values for the equivalent weights of the Li, Na, K, Ca, and Ba salts were determined. Since freezing point measurements in aqueous solution had indicated that the equivalent weight of $K_2H_3BCO_2$ is half of the formula weight, the formula weights could be calculated. The experimental values are summarized as: (a) equivalent weight measured, (b) formula weight measured, (c) formula assigned, (d) formula weight calculated for assigned formula: (a) 40.2, (b) 80.4, (c) $Li_2H_3BCO_2 \cdot 0.5H_2O$, (d) 80.7; (a) 53.2, (b) 106.4, (c) $Na_2H_3BCO_2$, (d) 103.8; (a) 69.9, (b) 139.8, (c) $K_2H_3BCO_2$, (d) 136.0; (a) 60.4, (b) 120.8, (c) $CaH_3BCO_2 \cdot H_2O$, (d) 115.9; (a) 95.5, (b) 191.0, (c) BaH_3BCO_2, (d) 195.2. Since some acid is used in side reactions in the pH range 7.5–5.5, analytical precision is not to be expected. Reasonable agreement is observed in all cases, however.

The first ionization constant for $H_2[O_2CBH_3]$ can be estimated from the pH of the $NaH[O_2CBH_3]$ solution as about 10^{-8}. This value is subject to the same set of uncertainties found in the measurement of the first ionization constant of carbonic acid. If one corrects[6] for the fact that in aqueous solution only part of the CO_2 is present as H_2CO_3, the value of K_1 for H_2CO_3 changes from the apparent value of 4.5×10^{-7} to the theoretically expected value of 1.32×10^{-4}. Direct measurement of the free H_3BCO dissolved in solution is more difficult than is the same measurement with CO_2, since H_3BCO reacts with water to give hydrogen and boric acid. The experimental problem of measuring dissolved H_3BCO has not yet been resolved; hence, an absolute first ionization constant is not now available. One significant fact which does emerge, however, is the relatively slow speed of the hydrolysis reaction between H_3BCO and aqueous acid. It has usually been assumed that this reaction is instantaneous, yet some H_3BCO was isolated from the gases above the water solution after 4 hr!

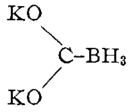
(b) The Strength of Boranocarbonic Acid.—The question of the acid strength of $H_2[O_2CBH_3]$ is an interesting one. Nearly all available chemical observations suggest that the H_3B group is less electronegative or is a poorer electron-withdrawing group than is the oxygen atom. If one then uses the formal charge concept frequently used to correlate the acid strength of oxyacids,[7] strong electron withdrawal by attached groups should increase acid strength. Since a BH_3 group is less effective than an oxygen atom in the removal of negative charge from the carbon, this model would then indicate that the boranocarbonic acid should be somewhat weaker than regular carbonic acid.

The similarity in the second pK values of carbonic acid and of boranocarbonic acid is an experimental fact. Whether this fact is a result of competing inductive and charge delocalization effects is still speculative at best.

(c) The Reaction with 85% H_3PO_4. The Regeneration of H_3BCO.—When a dry boranocarbonate salt was treated with 85% H_3PO_4, H_3BCO was isolated in yields above 95%. This completely unexpected fact and the synthetic procedures cited earlier provide an easy method for separating H_3BCO from its original reaction mixture, storing it as $K_2H_3BCO_2$, and regenerating pure H_3BCO on demand. The use of more dilute acid promotes decomposition of H_3BCO. These observations are being considered by one of us in a more general mechanistic analysis of the hydrolysis of $H_3BCO_2^{2-}$ and H_3BCO.

(d) An Attempted Reaction of Solid $K_2H_3BCO_2$ with Gaseous BF_3.—The unexpected possibility that BF_3 might displace BH_3 from $K_2H_3BCO_2$ was checked by allowing BF_3 to stand at a partial pressure of about 2 atm above dry powdered $K_2H_3BCO_2$. No reaction was detected after 4 days at 25°. Boron trifluoride will *not* displace the borane group from the boranocarbonates under the conditions used here.

(e) Acid Reactions in Nonaqueous Solution.—When 1 equiv of HCl in aqueous solution was added to an aqueous solution at 25° containing 1 mole of $Na_2H_3BCO_2$, the boranobicarbonate, $H_3BCO_2H^-$, was formed, and *no hydrogen* was evolved from the system. On the other hand, when 1 equiv of an ether–alcohol (3:1 by volume) solution of HCl was added to an ether–alcohol solution containing 1 mole of $K_2H_3BCO_2$, 1 and only 1 mole of gaseous H_2 was evolved. Additional HCl, when added to the solution, gave no more H_2. This was true even when excess HCl was used and the temperature was varied during the measurement over the range −196 to 25°. The reaction between HCl and boranocarbonate is strongly dependent upon the nature of the solvent used. In another experiment it was shown that $KH[O_2CBH_3]$, prepared independently, is stable in nonacidic ether–methanol solution, so the mechanism does not involve formation and decomposition of $[H_3BC(O)OH]^-$ in the ether–methanol solution. The data suggest that in a strongly ionizing solvent such as water, transfer of a proton from H_3O^+ to the anion $H_3BCO_2^{2-}$ is easily accomplished to give the stable boranobicarbonate. On the other hand, in the ether–alcohol solvent of low dielectric constant, the boranocarbonate probably exists as the un-ionized unit or as an ion cluster.



Acid attack then takes place directly on one of the hydrogens of the BH_3 group to give H_2. As soon as one of the hydrogens is removed, rapid shifting of H to carbon and of O to boron followed by interaction with solvent[8] would be expected to give products such as H_3COCH_3 and KHO_2BOCH_3. As expected, the solid remaining after removal of the solvent showed no B–H stretching frequencies. An equation consistent with the currently available evidence is

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(6) O. Berg and A. Patterson, *J. Am. Chem. Soc.*, **75**, 5197 (1953).

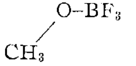
(7) B. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry," Blaisdell Publishing Co., New York, N. Y., 1965, p 191.

(8) D. H Campbell, T. C. Bissot, and R. W. Parry, *J. Am. Chem. Soc.*, **80**, 1868 (1958).

$$K_2H_3BCO_2 + 2CH_3OH + HCl \longrightarrow KCl + KHO_2BOCH_3 + CH_3OCH_3 + H_2$$

The rapid shifting of hydrogens after removal of the first hydrogen would account for the unexpected stoichiometry. More detailed mechanistic studies are in progress.

The Lewis acid BF_3, when placed in the alcohol–ether solution (1:3 by volume), reacted with $K_2H_3BCO_2$ in a manner exactly analogous to the HCl reaction described above: 1 mole of H_2/mole of $K_2H_3BCO_2$ was liberated when BF_3 was in excess, and 1 mole of H_2/mole of BF_3 was liberated when $K_2H_3BCO_2$ was in excess. Since BF_3 and alcohol would be expected to react to give



the reaction can be considered analogous to that involving $H^{\delta+}$–$Cl^{\delta-}$ in alcohol–ether solution.

Physical Properties and Characterization of Boranocarbonate Salts

(1) **X-Ray Powder Patterns.**—The X-ray powder patterns for the Li, Na, and K salts are shown in the Experimental Section; they could not be indexed in either the cubic or the tetragonal systems. Lower crystal symmetry is indicated.

(2) **The Infrared Spectrum.**—The boranocarbonate ion has only a plane of symmetry at best if the ion is considered to be rigid. It is the structural analog of nitromethane and of the acetate ion. Crawford and Wilson,[9] in an analysis of nitromethane, showed that if certain force constants of nitromethane are treated as independent of the angle of twist about the C–N bond or are restricted to certain functions of this angle, the symmetry C_{2v} can be applied. The same simplification was used by Jones and McLaren[10a] and subsequent workers[10b,c] in their treatment of acetate ion. It is appropriate to the boranocarbonate ion if the force constants for cross terms, such as those involving C–B–H and B–C–O, are treated as constants independent of the angle of twist about the B–C bond. With this simplifying assumption to give point group C_{2v}, 15 fundamental frequencies are expected, 2 of which (B–H stretching modes) should be degenerate and 1 of which (B–C torsional mode) is not considered here since the corresponding C–C torsional mode is not seen in sodium acetate.[10b] As seen in Table II, 10 of the expected 13 fundamentals can be assigned, while the remaining 3 bands would be expected below the limit of the measurement made here (600 cm^{-1}).

The spectra for lithium, sodium, and potassium boranocarbonates are shown in Table II. The data reveal clearly that a single anion is being considered in the three salts, but the spectra are not of a quality to permit detailed comparisons between different cations. Such a study with better instrumentation is currently underway and will be reported later. The assignments listed in Table II result from comparisons with the spectra of sodium acetate[10] and potassium carbonate[11] taken from the literature. Assignments above 2000 cm^{-1} recognize the expected B–H stretching frequencies and two combination bands. The doublet around 1400 cm^{-1} is interpreted as the asymmetric C–O stretching mode which has been split by local field effects. As a precedent for this interpretation, the splitting of $\nu_{as(CO)}$ in $K_2CO_3{\cdot}H_2O$ is particularly marked, and the anhydrous K_2CO_3 shows some evidence of splitting in vaseline mull.[11b] The strong peak at 1218 cm^{-1} is assigned to $\nu_{s(CO)}$. The comparable value in sodium acetate is given as 1414 cm^{-1}, but the very weak, normally infrared-inactive $\nu_{s(CO)}$ in K_2CO_3 shows up as a very weak band at 1060 cm^{-1} (made weakly active by site symmetry). The boranocarbonate value of 1218 cm^{-1} lies between these extremes (1414 and 1060 cm^{-1}). Peaks at 1190 and 1150 cm^{-1} in the spectrum of boranocarbamate have been assigned to B–H deformation modes[2a] and serve as a model for δ_{B-H} modes at 1193 and 1150 cm^{-1} in the present case. The lower frequency assignments are made on the basis of direct comparisons to the sodium acetate case (Table II).

Table II

Infrared Frequencies (cm^{-1}) and Assignments of Boranocarbonate Salts

Legend:
ν = stretching mode
δ = deformation or in plane bending,
π = out of plane vibration
ρ = rock
s = symmetric
as = asymmetric

$Li_2[H_3BCO_2]$ (C_{2v})	$Na_2[H_3BCO_2]$ (C_{2v})	$K_2[H_3BCO_2]$ (C_{2v})	Assignment	K_2CO_3[11b] (D_{3h})	Assignment[11]	$Na[H_3CCO_2]$[10b] (C_{2v})	Assignment[10]
						2989 (S)	$\nu_{as(CH)}$
						2936 (S)	$\nu_{s(CH)}$
				2520 (VW)	$\nu_{s(CO)}+\nu_{as(CO)}$		
				2445 (W)			
		2384 (W)	2 × 1193				
		2300 (S)	2 × 1150				
2290 (S)	2280 (S)	2275 (S)	$\nu_{as(BH)}$				
Broad	Broad	2226 (S)	ν_{s} (BH)	2165 (VVW)	$\nu_{as(CO)}+\delta_{(OCO)}$		
				2083 (VVW)			
				1751 (W)	$\nu_{s(CO)}+\delta_{(OCO)}$		
1420 (VS)*	1450 (VS)*	1428 (VS)*	$\nu_{as(CO)}$	1412 (VS)	$\nu_{as(CO)}$*	1578 (S)	$\nu_{as(CO)}$
Broad	1410	1398		Evidence for splitting $\nu_{as(CO)}$ in $K_2CO_3{\cdot}H_2O$		1498 (W)	$\delta_{(CH)}$
1370 (VS)*	1380 (VS)*	1380 (VS)*				1443 (W)	
						1430 (W)	
1230 (M)	1200 (M)	1218 (M)	$\nu_{s(CO)}$	1060 (VVW)	$\nu_{s(CO)}$	1414 (M)	$\nu_{s(CO)}$
1200 (M)	1160 (M)	1193 (M)	$\delta_{(BH)}$			1042 (W)	ρ_{CH_3}
1115 (S)	1150 (S)	1150 (S)	$\delta_{(BH)}$			1009 (MW)	
		925 (W)	ρ_{BH_3}?				
895 (M)	900 (M)	900 (M)					
				880 (M)	$\pi_{(XY_3)}$		
870 (M)	855 (M)	855 (M)	$\nu_{(CB)}$ or $\pi_{(CO_2B)}$	855 (VW)	$\pi_{(XY_3)}$ (lattice)	924 (MW)	$\nu_{(C-C)}$
		615 (W)	$\delta_{(OCO)}$	691 (W)	$\delta_{(OCO)}$	646 (M)	$\delta_{(OCO)}$
				685 (W)			
						615 (S)	$\rho_{(CO_2)}$
						460 (M)	

*Normal $\nu_{as(CO)}$ split under crystal site symmetry.

A more careful analysis of the B–H stretching modes is also of interest. Wyma and Taylor[12] found that as the strength increases for a Lewis base coordinated to a BH_3 group, the weighted average[13] of the symmetrical and unsymmetrical B–H stretching frequencies shifts toward lower frequencies. The averages for all of the borane adducts studied ranged from 2430 cm^{-1} for H_3BPF_3 (weak base) to 2245 cm^{-1} for H_3BH^- (strong base). The weighted average for the boranocarbonate

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[9] B. L. Crawford and E. B. Wilson, *J. Chem. Phys.*, **9**, 323 (1941).

[10] (a) L. H. Jones and E. McLaren, *ibid.*, **22**, 1796 (1954); (b) K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956); (c) K. J. Wilmhurst, *J. Chem. Phys.*, **23**, 2463 (1955).

[11] (a) J. C. Decius, *ibid.*, **22**, 1946 (1954); (b) C. J. H. Schulte and K. Buijs, *Spectrochim. Acta*, **17**, 921 (1961).

[12] R. J. Wyma, Ph.D. Dissertation, University of Michigan, 1964. Work done in the laboratory of Dr. R. C. Taylor.

[13] Weighted average = (2 × asymmetric frequency + symmetric frequency)/3.

is 2251 cm^{-1}, suggesting that the CO_2^{2-} is about equal in base strength to the H^- ion. As will be noted later, nmr data lead to the same conclusion.

(3) **The Nmr Spectrum of $Na_2H_3BCO_2$.**—The proton resonance of $H_3BCO_2^{2-}$ ion in D_2O shows four peaks (J_{BH} = 81 cps) resulting from ^{11}B coupling. The seven small peaks are the result of coupling with ^{10}B (I = 3). The area under the quartet is about 4.0 times the area under the septet, a result which agrees with the known analysis of 81.2% ^{11}B and 18.8% ^{10}B in the boron used. The quotient of the coupling constants $J_{^{11}B-H}$ and $J_{^{10}B-H}$ is 3.00 as predicted by the quotient $\gamma_{^{11}B}/\gamma_{^{10}B}$.

The J_{B-H} coupling constant of 81 cps is of special interest. If the widely quoted[14,15] correlation between J_{B-H} and s character of the bond is assumed, the value of 81 cps for $J_{^{11}B-H}$ can be interpreted as indicating that $Na_2H_3BCO_2$ has the same high degree of electrical symmetry at the boron nucleus as does the BH_4^- ion ($J_{^{11}B-H}$ = 80 cps). The sharpness of the signals is also significant. As shown by Ogg and Ray[16] nuclear quadrupole line broadening for protons is dependent upon the electrical field symmetry at the nucleus containing the quadrupole. Thus the NH_4^+ spectrum showed sharp peaks while the NH_3 spectrum consisted of a broad signal. Since high electrical field symmetry at the boron nucleus is clearly indicated by the sharp peaks (Figure 1), it is reasonable to conclude that the CO_2^{2-} ion is comparable in electron-donating power to the H^- ion; this fact was also suggested from the infrared data.

The ^{11}B spectrum shows the expected 1:3:3:1 quartet (J_{B-H} = 81 cps) with δ = 50 ppm relative to $B(OCH_3)_3$.

Experimental Section

The Preparation of Boranocarbonate Salts. (1) The Reaction of H_3BCO with Alcoholic KOH Solution. (a) Apparatus.—A 500-ml reaction flask was equipped with an outer 24/40 standard taper joint. A gas exit tube and a gas entry tube equipped with a coarse sintered-glass dispersion head were sealed through the inner part of the 24/40 standard taper joint. The reaction system could be fastened to a conventional vacuum line by means of ball joints attached to both gas exist and entry tubes. Temperature was controlled by a slush bath and stirring was effected by a Teflon-covered bar magnet.

(b) **Procedure.**—A 40-mmole sample of B_2H_6 was condensed into a 75-ml stainless steel cylinder; then a 160-mmole sample of CO was condensed into the system as described earlier.[2] The pressure dropped overnight from an initial value of 1200 psi to a final value of 900 psi. A 400-ml aliquot of absolute alcohol containing 8–9 g of dissolved KOH was placed in the 500-ml round-bottom reaction flask and cooled to −78°. The crude H_3BCO–CO–B_2H_6 mixture was then passed slowly through the gas-dispersing head and into the stirred alcoholic KOH solution.

After all of the gas had passed through the solution (about 2 hr), the flask was removed from the vacuum line and the cloudy solution was boiled for 15 min. As the system was cooled in an ice bath, a white precipitate settled. The supernantant liquid was poured off; the white solid was washed three times with 100 ml of cold ethanol, washed once with 150 ml of diethyl ether, and dried for 3 hr under vacuum. About 8.3 g of dry $K_2H_3BCO_2$ was isolated. *Anal.* Calcd for $K_2H_3BCO_2$: K, 57.6; C, 8.8; H, 2.2; H_3BCO, 42.4. Found:[17] K, 57.5; C, 8.8; H, 2.3; H_3BCO, 40.3 recovered.[17] The yield is 75% based on the original amount of B_2H_6 taken. The apparent molecular weight of $K_2H_3BCO_2$ was determined by freezing point depression over the concentration range as indicated: 0.15 *m*, 47.8; 0.185 *m*, 48.1; 0.222 *m*, 48.8. Extrapolation of these values to infinite dilution gives a measured molecular weight of 45.5. Theory for three ions of $K_2H_3BCO_2$ in water is 45.3; equiv wt by titration, 69.9; theory, 68.0.

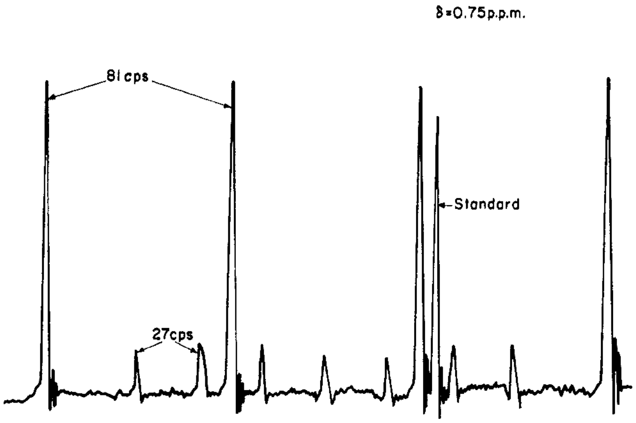

Figure 1.—Proton nmr of $Na_2H_3BCO_2$ in D_2O.

The solid $K_2H_3BCO_2$ gave the following X-ray powder pattern. The *d* values (in A) are recorded: 6.11 w, 5.28 m, 4.35 vw, 4.21 vw, 3.58 vw, 3.45 m, 3.26 m, 3.10 s, 3.04 m, 2.94 ms, 2.83 m, 2.76 w, 2.63 w, 2.51 ms, 2.47 ms, 2.41 w, 2.34 vw, 2.22 m, 2.09 w, 1.96 m, 1.94 m, 1.79 w, 1.72 w, 1.65 vw, 1.60 vw; intensity designations: w, weak; m, medium; s, strong; v, very.

(c) **Other Salts.**—The use of NaOH in the above procedure instead of KOH gives $Na_2H_3BCO_2$. Equivalent weight data and spectroscopic data have been cited. The X-ray powder data (in A) for the sodium salt are: 4.96 vs, 3.39 m, 3.29 s, 2.92 w, 2.77 s, 2.68 m, 2.48 m, 2.37 m, 2.22 w, 2.09 w, 1.93 w, 1.91 vw, 1.84 w, 1.80 w, 1.77 w, 1.70 m, 1.68 w, 1.61 w, 1.50 w, 1.48 vw, 1.42 w. The above X-ray powder pattern is identical with that of dry samples prepared from $K_2H_3BCO_2$ by ion-exchange procedures. The infrared data (Table II) establish the integrity of the $H_3BCO_2^{2-}$ ion in the salt.

The anhydrous lithium boranocarbonate, prepared from the potassium salt by ion-exchange procedures, displayed the following X-ray powder pattern (in A): 10.91 vs, 7.02 s, 4.77 vw, 4.67 w, 3.97 w, 3.66 s, 3.56 w, 3.38 w, 3.14 w, 3.11 w, 3.01 w, 2.82 vw, 2.58 w, 2.53 vw, 2.28 w.

(2) **The Reaction of H_3BCO with CaO and with NaOH.**—Finely powdered commercial CaO (100 mg) was dispersed on glass wool in a tube which was then attached to the vacuum line. The system was carefully evacuated; then 0.25–0.5 ml of water was distilled onto the CaO at −196° along with enough H_3BCO to give a final pressure of about 400 mm. The temperature was then raised slowly to 25°. The system was allowed to stand 2 hr at 25°. Then all volatile components were removed. The solid remaining liberated H_3BCO on acid hydrolysis and gave an infrared spectrum characteristic of the boranocarbonate ion. The infrared spectrum was also identical with that obtained from the calcium salt prepared from $K_2H_3BCO_2$ by ion exchange.

A similar procedure using *dry* Ascarite (NaOH on asbestos) gave $Na_2H_3BCO_2$.

(3) **The Reaction of H_3BCO with $NaOCH_3$. The Synthesis of Sodium O-Methylboranocarbonate and Its Hydrolysis.**—A 65-

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[14] H. S. Gutowsky, O. W. McCall, and C. P. Slichter, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

[15] (a) W. D. Phillips, H. C. Miller, and E. C. Muetterties, *ibid.*, **81**, 4496 (1959); (b) T. T. Onak, H. Landesman, R. E. Williams, and J. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

[16] R. A. Ogg and J. D. Ray, *J. Chem. Phys.*, **26**, 1339 (1957).

[17] Potassium was determined by precipitation as $K[B(C_6H_5)_4]$. Borane carbonyl was determined by treating a weighed sample of $K_2H_3BCO_2$ with 85% H_3PO_4 in the vacuum system, then catching, measuring, and identifying (infrared spectra; vapor pressure = 25 mm at −112°) the H_3BCO released. Values are a little low and correspond to 95% gas recovery.

mg (1.20-mmole) sample of $NaOCH_3$ was weighed into a reaction tube and dissolved in 2 ml of anhydrous methyl alcohol. About 6 ml of diethyl ether was added leaving a clear solution. The reaction tube was placed on the vacuum line and the contents frozen to $-196°$. The system was evacuated; then a 2-mmole sample of H_3BCO and 1 additional ml of ether were frozen on the sides of the reaction tube. The temperature was raised slowly to $-112°$ (CS_2 slush) and then to $-78°$ (Dry Ice and isopropyl alcohol) over a 3-hr period. The system was held at $-78°$ overnight.

Removal of solvent from the clear solution at $-78°$ gave an amorphous solid with infrared bands at 2950, 2830, 2260, and 1635 cm^{-1}. The assigned formula for the ethanol-soluble solid is $Na[CH_3OC(O)BH_3] \cdot x$(solvent).

To a 100-mg sample of $Na[H_3BC(O)OCH_3]$, dissolved in 5 ml of absolute ethanol, was added 100 mg of NaOH, dissolved in 5 ml of absolute ethanol. The mixture was heated to boiling. The precipitate which formed was filtered off, washed with 5 ml of ethanol, and dried under vacuum. The X-ray powder pattern of the solid product was identical with that cited earlier for $Na_2H_3BCO_2$.

(4) **The Preparation of Boranocarbonates from N-Methylboranocarbamates.** (a) **Preparation of N-Methylboranocarbamate Salts.**—Literature methods[2] were used. Larger amounts could be prepared when H_3BCO was carried into an ether solution of methylamine on an N_2 stream. A 20-mmole quantity of H_3BCO was thermostated at $-95°$ (toluene slush) in a vacuum line trap (vapor pressure of H_3BCO 100 mm at $-95°$). A stream of dry N_2 was passed slowly through the trap where H_3BCO was entrained and then carried through a coarse glass frit into a stirred solution containing 50 mmoles of methylamine in 100 ml of diethyl ether, all at $-112°$ (CS_2 slush). Pressure above the reaction vessel was maintained at about 400–500 mm by control of stopcocks leading to the vacuum pump. A blowout manometer prevented pressure increases above 1 atm. From 85 to 90% of the H_3BCO can be converted to $[H_3NCH_3][H_3BC(O)NHCH_3]$ if 25% excess of the amine is used.

(b) **Conversion of N-Methylboranocarbamate Salts to Boranocarbonate Salts.**—A 1.90-g sample (18.2 mmoles) of $H_3BCO \cdot 2NH_2CH_3$ was weighed into a 300-ml round-bottom flask equipped with a 24/40 standard taper joint. A 200-ml aliquot of absolute ethanol containing about 2.5 g of dissolved KOH was added. The solution was boiled gently and stirred for 4–5 hr (additional C_2H_5OH was added to replace that lost by boiling). When the resulting solution was cooled in an ice bath for 10 min, a precipitate formed. The supernatant liquid was decanted, the precipitate was washed once with 100 ml of diethyl ether, the flask was attached to the vacuum line, and the product was dried under vacuum for about 30 min. The resulting solid was 1.44 g (10.6 mmoles) of high-purity $K_2H_3BCO_2$ which was identified by X-ray powder pattern and analysis. About 58% of the $H_3BCO \cdot 2NH_2CH_3$ was converted to $K_2H_3BCO_2$.

An aqueous solution of NaOH was also used to prepare $Na_2H_3BCO_2$ from $H_3BCO \cdot 2NH_2CH_3$ by a similar procedure. After evaporation of the water solution, excess NaOH was washed out with ethyl alcohol, and the remaining solid was dried under vacuum for 2 hr at 100°.

The Properties of Boranocarbonate Salts. (1) **The Reaction of $K_2H_3BCO_2$ with 85% Phosphoric Acid.**—A 136-mg (1.00-mmole) sample of $K_2H_3BCO_2$ was placed in a reaction tube (22 cm long) equipped with a 24/40 joint. An approximately 3-ml aliquot of 85% phosphoric acid was added to a small test tube and then frozen in liquid nitrogen. The test tube and its frozen contents were inverted and dropped into the reaction tube containing the $K_2H_3BCO_2$. The reaction tube was immediately attached to the vacuum line and the air pumped out of the system. When the phosphoric acid began to melt, it reacted with the $K_2H_3BCO_2$. The gas that evolved from this reaction was led through a trap on the vacuum line at $-78°$ to a trap at $-196°$. During the reaction, little or no noncondensable gas evolved. When the reaction was complete, a 0.95-mmole quantity of H_3BCO was found in the trap at $-196°$ (95% yield of H_3BCO from the $K_2H_3BCO_2$). The H_3BCO was identified by its infrared spectrum and by its vapor pressure of 25 mm at $-112°$.

(2) **The Reaction of $K_2H_3BCO_2$ with HCl or BF_3 in Methanol–Ether Solution.**—A 67.6-mg sample of $K_2H_3BCO_2$ was dissolved in 2 ml of methanol in the reactor; then 6 ml of diethyl ether was added. The reactor, containing a magnetic jump stirrer, was attached to the vacuum system and cooled to $-196°$. A sample of BF_3 (0.52 mmole) or an equivalent sample of HCl was frozen above the frozen boranocarbonate solution. The system was surrounded by a slush at $-112°$ (CS_2) and then allowed to warm, with periodic stirring, to $-78°$. No noncondensable gas was detected at $-78°$. As the solution warmed to room temperature, a 0.51-mmole sample of H_2 (measured mol wt, 4; adsorbable on Pd) was evolved over a 24-hr period.

When a 0.58-mmole sample of $K_2H_3BCO_2$ was treated with 0.73 mmole of HCl, a 0.58-mmole sample of H_2 was evolved. The solid remaining after reaction had no B–H stretching frequencies.

(3) **Instrumentation.**—A Perkin-Elmer Model 21 and a Perkin-Elmer 337 infrared grating spectrometer were used.

A Varian A-60 nmr spectrometer was used with D_2O as a solvent and sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal standard.

Standard X-ray powder techniques were used on samples in 0.3-mm glass capillaries (0.01-mm wall). Nickel-filtered copper K radiation with a weighted average wavelength of 1.5418 A was used.

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