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The Reaction of Carbon Monoxide–Borane with Potassium Glycinate

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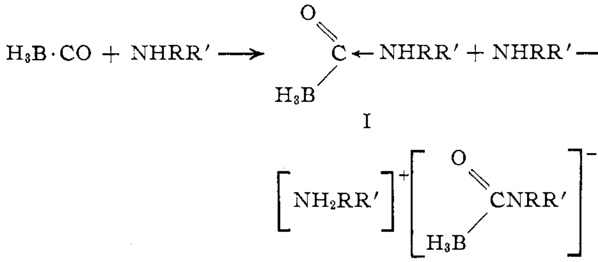
Carbon monoxide–borane ($H_3B \cdot CO$) reacts with potassium glycinate in ethanol solution to produce a 1:1 adduct. This result is in contrast to similar previously reported reactions and to the behavior of its isoelectronic analog, carbon dioxide. In these cases, reactions typical of carbamate formation occur. This study is also concerned with the boranocarboxylation of the glycinate ion by its reaction with potassium *O*-ethylboranocarbonate.

Introduction

Carbon monoxide–borane ($H_3B \cdot CO$) has been shown to be analogous to carbon dioxide in its reactions with primary and secondary amines[1] as shown in



I

(1)

In more recent studies[2] attempts at isolation of the proposed intermediate (I) were unsuccessful presumably because the hydrogen on the nitrogen has become acidic with reference to the original amine. Thus a second molecule of amine removes the proton, leaving an amide ion which is a stronger base than the free amine. The carbamate structure is therefore stabilized.[3] If trimethylamine which has no removable protons is used, an adduct similar to I is formed at very low temperatures but is unstable above $-45°$.[2] No reaction is observed with the weak base pyridine.[2] On the other hand, if methylphosphine is used, there is some evidence of adduct formation at low temperatures but since the phosphine is a poor proton acceptor, proton transfer cannot take place and stabilization does not occur.[3]

This study is mainly concerned with the reaction of H_3BCO with the glycinate ion ($H_2NCH_2CO_2^-$) with the purpose of further elucidating the phenomenon described above as well as providing more information on the compared reactivity of the $H_3B \cdot CO$ and CO_2 systems.

Experimental Section

Preparation of Potassium Glycinate.—The $KH_2NCH_2CO_2$ was prepared by stirring a large excess of glycine in 200 ml of a 1 *M* ethanolic KOH solution for about 1 hr. The potassium glycinate was then precipitated from the ethanol solution with diethyl ether, vacuum dried, and identified by its equivalent weight. The equivalent weight calculated for $KH_2NCH_2CO_2$ is 113; the found value was 114.

The Reaction of CO_2 with $KH_2NCH_2CO_2$.—In one experiment, a 0.927-g (8.2-mmol) quantity of $KH_2NCH_2CO_2$ was dissolved in 30 ml of absolute ethanol in a 100-ml round-bottomed flask equipped with a ₸ joint. This was attached to a vacuum system and a 6.0-mmol quantity of CO_2 was allowed to come into contact with the solution held at room temperature. After 2.5 hr it was found that a total of 3.1 mmol of CO_2 had been absorbed giving a glycinate:CO_2 ratio of 2.6. The precipitate from the reaction was filtered in a drybox and dried. Infrared spectra of this compound and of those reported below were obtained in Nujol and Fluorolube mulls. The precipitate was then extracted with ethanolic KOH and the residue was then dried. Diethyl ether was added to the ethanol solution and the resulting precipitate was identified as potassium glycinate. The reaction of CO_2 and the glycinate ion gave approximately the same results when carried out in water except that the products were soluble.

The Reaction of $H_3B \cdot CO$ with $KH_2NCH_2CO_2$.—In a typical reaction a 25-g (240-mmol) quantity of $KH_2NCH_2CO_2$ was dissolved in approximately 250 ml of absolute ethanol and placed in a 500-ml three-necked flask equipped with ₸ joints. The center joint was attached to the vacuum-line system with a gas dispersion system[4] extending into the solution. One neck of the flask was stoppered while the other contained a separatory funnel with additional ethanol. The solution was stirred by means of a magnetic stirring bar. Approximately 140 mmol of carbon monoxide–borane (prepared and purified by previously published procedures)[1] was placed in a trap on the vacuum line and allowed to warm with a stream of nitrogen passing over the liquid $H_3B \cdot CO$ and into the reaction solution. The total pressure within the system was held between 300 and 400 Torr. Since the reaction was carried out at room temperature at low pressure, solvent was lost during the course of the reaction and was replaced from the separatory funnel. Evaporation of the $H_3B \cdot CO$ kept the liquid $H_3B \cdot CO$ cool and thus no problem with bumping was incurred. In any case, all aspects of this reaction must be closely and carefully monitored because of the inherent danger in the use of $H_3B \cdot CO$.

The white precipitate produced by this reaction was stable in dry air but deliquesced rapidly on contact with atmospheric moisture with subsequent decomposition. The reaction flask was removed under nitrogen, filtered under suction in a drybox, washed with absolute ethanol and ether, and dried on the vacuum line. A 12-g (77.4-mmol) quantity was produced or a yield of approximately 55% based on the amount of carbon monoxide–borane was used. Although the compound decomposed rapidly in water, it produced a basic solution which could be titrated with standard HCl. *Anal.* Calcd for $KH_3BCONH_2CH_2CO_2$: C, 23.2; H, 4.56; N, 9.04; K, 25.2; equiv wt 155. Found: C, 23.1; H, 4.69; N, 10.1; K, 25.7: equiv wt 153.

A 0.5-g sample of the precipitate was stirred with 20 ml of an ethanol solution of KOH for about 15 min at room temperature. The resulting solid was then filtered, washed, and dried. An infrared spectrum of this compound was identical with that of $K_2H_3BCONHCH_2CO_2$ prepared as described below. The ethanol solution did not contain potassium glycinate.

The Reaction of $H_3B \cdot CO$ with $KH_3CNHCH_2CO_2$.—The potassium sarcosinate ($KCH_3NHCH_2CO_2$) used in this reaction was prepared in the same manner as described above for potassium glycinate. The reaction of $H_3B \cdot CO$ and potassium sarcosinate was carried out under similar conditions as described above. The product in this case was soluble in ethanol and separation of a pure compound was not effected. If 2-propanol was used as the solvent, a sticky precipitate was formed, but a compound suitable for analyses was not obtained.

The Reaction of Potassium Monoethylcarbonate and Potassium *O*-Ethylboranocarbonate with Potassium Glycinate.—Both of these reactions occur with such ease to produce a pure product that special techniques are unnecessary. Generally, about a

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[1] J. C. Carter and R. W. Parry, *J. Amer. Chem. Soc.*, **87**, 2354 (1965).

[2] A. L. Moye, Ph.D. Dissertation, University of Pittsburgh, 1968.

[3] L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 176 (1967).

[4] L. J. Malone and R. W. Parry, *ibid.*, **6**, 817 (1967).

1-g sample of $KCO_3C_2H_5$[5] or $KH_3BCOOC_2H_5$[6] in about 25 ml of absolute ethanol was mixed with 25 ml of ethanol containing about 1 g of $KH_2NCH_2CO_2$. At room temperature a precipitate began to form after a few seconds. After about 10 min the product was filtered, washed with ethanol and ether, and dried on a vacuum line. The borane compound decomposed rapidly in water producing a basic solution that could be titrated with standard acid. The borane compound was stable indefinitely in dry air. *Anal.* Calcd for $K_2O_2CNHCH_2CO_2$: C, 18.4; H, 1.55; K, 40.0. Found: C, 18.4; H, 1.69; K, 38.4. Calcd for $K_2H_3BCONHCH_2CO_2$: C, 18.6; H, 3.13; N, 7.24; K, 40.5; equiv wt 101. Found: C, 18.6; H, 3.23; N, 7.60; K, 40.1; equiv wt 96.6.

Potassium *N*-methyl-*N*-boranocarboxalatoaminoacetate was prepared by the same method. In this case, however, 1 hr was needed to complete the precipitation. *Anal.* Calcd for $K_2H_3BCO(CH_3)NCH_2CO_2$: C, 23.2; H, 3.87; N, 6.77; K, 37.8; equiv wt 106. Found: C, 23.1; H, 3.87; N, 6.56; K, 38.2; equiv wt 104.

The Reaction of Potassium *O*-Ethylboranocarbonate with Glycine.—A 150-mg (2.0-mmol) quantity of glycine and a 504-mg (4.0-mmol) quantity of $KH_3BCOOC_2H_5$ were weighed into a 100-ml round-bottomed flask with a $\overline{\$}$ joint and attached to a vacuum system. After evacuation of air, a 10-ml quantity of absolute ethanol was distilled into the flask and the mixture was allowed to warm to room temperature. The slurry was then stirred for 3 hr at room temperature with a magnetic stirring bar. At that time 2.1 mmol of noncondensable gas had evolved. The ethanol solution was distilled through a small, detachable U trap held at −23°.

The ethyl ester of hydroxymethylboronic acid was identified in this trap.[6] The solid residue remaining in the round-bottomed flask was identified as $K_2H_3BCONHCH_2CO_2$.

Results and Discussion

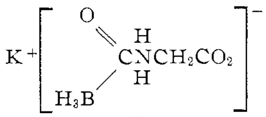
The reaction of carbon dioxide with the glycinate ion has been studied but not fully characterized.[7-9] It was confirmed in this study, however, that the reaction is typical of carbamate formation as shown by

$$CO_2 + 2K^+H_2NCH_2CO_2^- \xrightarrow[H_2O]{C_2H_5OH\ or} H_3NCH_2CO_2 + \underset{II}{(K^+)_2(O_2CNHCH_2CO_2)^{2-}} \qquad (2)$$

In ethanol solution both of the products glycine and II (potassium *N*-carboxalatoaminoacetate) precipitate. This was shown to be a mixture of these two compounds by the facts that (1) infrared spectra of glycine and II (prepared by an independent method described below) superimposed on a spectrum of the precipitate and (2) the glycine could be extracted from the mixture with ethanolic KOH leaving II undissolved and potassium glycinate in the ethanol solution.

In this case, the presumed intermediate $K^+O_2CNH_2CH_2CO_2^-$ is acidic with respect to the glycinate ion and thus reacts further to form the observed products.

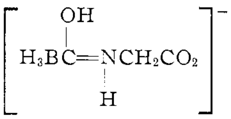
In comparison to this reaction, when $H_3B \cdot CO$ is allowed to react with excess potassium glycinate under similar conditions, the results are unique in this type of reaction. In this case, the 1:1 adduct (potassium *N*-boranocarboxalatoaminoacetic acid) shown below is isolated as the final product.



III

The formula for III was supported by the following data. (1) Elemental analyses and equivalent weight data as shown in the Experimental Section were in good agreement with those of the proposed structure. As with other boranocarboxalates, titration to a sharp end point is possible despite decomposition in water.[4,5] The results are in agreement with the assumption of 1 equiv/mol for III. (2) The infrared spectrum of III was unique compared to that of glycine or $K_2H_3BCONHCH_2CO_2$ (which was prepared by independent methods described below).

The infrared spectrum of the compound, however, indicates the possibility that a hydrogen on the nitrogen has migrated to the adjacent oxygen forming the enol structure



$$\left[H_3B\overset{\overset{\displaystyle OH}{|}}{C}{=}\underset{\underset{\displaystyle H}{\vdots}}{N}CH_2CO_2\right]^-$$

There are two broad peaks at 3320 and 3090 cm^{-1} that could be assigned to NH_2^+ [10] as would be present in III or could be due to bonded OH and NH[11] as would be present in the structure shown above. Of more consequence is the absence of an absorption around 1800 cm^{-1} as would be expected for the keto structure III and as indeed found for $H_3B \cdot CO \cdot N(CH_3)_3$.[2] This latter compound is the only other reported example where $H_3B \cdot CO$ is coördinated to an amine. There is a broad band at 1600 cm^{-1} but this is in the region usually found for a carboxylate group as well as for a C=N group.[11] A strong broad absorption found at 2280 cm^{-1} is typical of other boranocarboxylates.[1,5] Solubility and stability problems prohibited resolution of this question by nmr techniques.

The possibility that III precipitates so completely and rapidly from the ethanol solution that further reaction with the glycinate ion could not occur was considered. However, the following reaction occurs easily under the same conditions

$$KH_3BCONH_2CH_2CO_2 + KOH \longrightarrow \underset{IV}{K_2H_3BCONHCH_2CO_2} + H_2O \qquad (3)$$

This indicates that the following order of acidities is real under these reaction conditions: $O_2CNH_2CH_2CO_2^- > H_3NCH_2CO_2 > H_3BCONH_2CH_2CO_2^-$. Although III does not protonate the glycinate ion, there was no evidence that the reverse reaction (protonation of IV by glycine) occurs in ethanol slurry as would be predicted by the above order of acidities. However, in the latter case, since both reactants have very low solubility in ethanol, the lack of a reaction is inconclusive.

This order of acidities could be explained if one assumes that the $H_3B \cdot CO$ moiety is less electronegative than the CO_2 moiety in these compounds. The following two reactions have been reported[6] which lend some support to this

$$3H_3BCOOC_2H_5^- + H_2NCH_2CH_2NH_2 \longrightarrow (H_3BCO)_2NCH_2CH_2NH(H_3BCO)^{3-} + 3C_2H_5OH$$

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[5] B. D. Hoewe, L. J. Malone, and R. M. Manley, *Inorg. Chem.*, **10**, 930 (1971).

[6] L. J. Malone, *ibid.*, **7**, 1039 (1968).

[7] A. Jensen and C. Faurholt, *Acta Chem. Scand.*, **6**, 385 (1952).

[8] A. Jensen and C. Faurholt, *ibid.*, **6**, 395 (1952).

[9] A. Jensen and C. Faurholt, *ibid.*, **18**, 377 (1964).

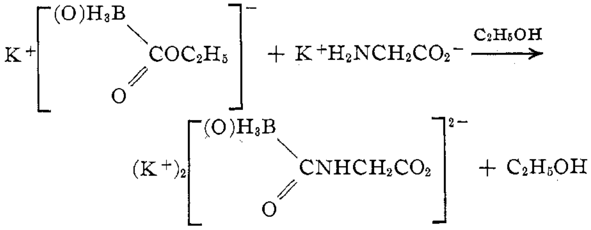
[10] A related example is the compound $H_3B \cdot NH_2CH_2CO_2CH_3$ (methylglycinate–borane) which has two absorptions at 3410 and 3210 cm^{-1}: E. F. Rothgery, Ph.D. Dissertation, St. Louis University, 1969.

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1962.

$$2OCOOC_2H_5^- + H_2NCH_2CH_2NH_2 \longrightarrow (CO_2)HNCH_2CH_2NH(CO_2)^{2-} + 2C_2H_5OH$$

Since these reactions appear to proceed stepwise by an S_N2 mechanism, the difference in reactivity of these isoelectronic analogs should be effected by the difference in the effect of the $H_3B \cdot CO$ and CO_2 moieties on the nitrogen environment. If the $H_3B \cdot CO$ is less electronegative than CO_2, this should render the nitrogen more nucleophilic in the former reaction and thus rationalizing the more extensive substitution.

$K_2O_2CNHCH_2CO_2$ and the $K_2H_3BCONHCH_2CO_2$ were also prepared as shown in



(4)

This reaction procedure has been reported previously for the preparation of boranocarbamates.[5]

The structure proposed for these compounds was consistent with elemental analyses and equivalent weight data as reported in the Experimental Section and with infrared spectra which showed a sharp peak at 3421 cm^{-1} for the oxygen compound and at 3380 cm^{-1} for the borane analog which is consistent with the N–H stretching vibration usually found for secondary amides.[11] The borane compound also had strong absorptions at 2280 and 1618 cm^{-1} typical of boranocarboxylate groups.[1,5]

If glycine is stirred with an ethanol solution of $KH_3BCOOC_2H_5$, the same borane compound described above is produced as shown in

$$2KH_3BCOOC_2H_5 + H_3NCH_2CO_2 \longrightarrow K_2H_3BCONHCH_2CO_2 + (C_2H_5O)_2BCH_2OH + H_2 \quad (5)$$

The fact that III is not produced by this reaction by substitution of $H_3B \cdot CO$ for an H^+ is further evidence that such a reaction would require a lone pair of electrons on the nitrogen so as to proceed by an S_N2 mechanism.[5] In this reaction glycine apparently protonates the $H_3BCOOC_2H_5^-$ ion producing the ethyl ester of hydroxymethylboronic acid and hydrogen as in reactions previously observed.[6] The glycinate ion then reacts as shown in (4).

Carbon monoxide–borane also reacted with potassium sarcosinate $K(CH_3)HNCH_2CO_2$ under the same conditions but a pure product was not isolated. Potassium *N*-methyl-*N*-boranocarboxylatoaminoacetate ($K_2H_3BCO(CH_3)NCH_2CO_2$) was prepared, however, in a similar manner as shown in reaction 4.

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Preparation and Spectral Characterization of Unsymmetrically Substituted Borazines

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The ten possible *B*-phenyl-, -methyl-, and -chloro-substituted derivatives of *N*-trimethylborazine, as well as $(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3$, $[(CH_3)_5C_6](CH_3)_2B_3N_3(CH_3)_3$, $[(CH_3)_3N_3B_3(CH_3)_2]_2$, and $[(CH_3)_3N_3B_3(CH_3)_2]_2O$, have been synthesized and characterized, and their infrared spectra have been determined. Correlation techniques are used to establish the characteristic frequencies associated with the absorptions of the B and N substituents.

Introduction

It is well known that substitution reactions occur at the boron site of a borazine nucleus more readily than at the nitrogen position. Thus, *B*-halogeno[1] and *B*-H[2] substituents react with Grignard reagents or organolithium reagents to yield the corresponding *B*-alkyl or -aryl derivatives. Evidence is available to show that *B*-alkyl and *B*-aryl substituents can also react with Grignard reagents to form a different B-substituted derivative.[3] The hydridic nature of a *B*-H moiety in borazines can be used to form the corresponding *B*-Cl substituents.[4–6] We present here several synthetic routes to a series of unsymmetrically B-substituted borazines which are potentially useful intermediates for other compounds containing the borazine nucleus.

Experimental Section

All reactions were carried out under an inert atmosphere (N_2 or Ar) using conventional techniques developed for the preparation of air-sensitive, volatile compounds. Melting points are uncorrected.

Preparation of Compounds. $Cl_3B_3N_3(CH_3)_3$.—This compound was prepared by the method of Haworth and Hohnstedt[7] in 78.7% yield based on the amount of $CH_3NH_2 \cdot HCl$ taken; mp 150–153°, lit.[8] mp 153–156°.

$Cl(CH_3)_2B_3N_3(CH_3)_3$.—This compound was prepared by the following modification of the method of Wagner and Bradford.[9] Methylmagnesium bromide (0.68 mol in 250 ml of ether) was

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[1] D. T. Haworth and L. F. Hohnstedt, *J. Amer. Chem. Soc.*, **82**, 3860 (1960).

[2] J. H. Smalley and S. F. Stafiej, *ibid.*, **81**, 582 (1959).

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[9] R. T. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 93 (1962).