

TABLE II
ELECTRONIC CHARGE ON THE PHOSPHORUS ATOM FROM
INTERPRETATION OF ^{31}P NMR CHEMICAL SHIFTS

R		R_3P	R_3PO	R_3PS	R_3PSe
C_6H_5	σ	+0.30	+0.58	+0.38	+0.37
	π^a	-0.00	-0.12	-0.05	-0.04
		+0.30	+0.46	+0.33	+0.33
$\text{C}_6\text{H}_5\text{O}$	σ		+1.17	+0.97	+0.96
	π		-0.45	-0.36	-0.29
				+0.72	+0.61
$\text{C}_6\text{H}_5\text{S}$	σ	+0.27		+0.35	
	π	-0.10		-0.15	
		+0.17		+0.20	

^a In ref 23 and 24, the numerical values shown for the number of π electrons is effectively the total number of such electrons, not just those associated with the phosphorus. A number of as yet unpublished electron density maps made in our laboratory show that the π bonds to phosphorus are at least as polar as the σ bonds and in the same direction. Therefore the value of the parameter^{23,24} $f(v)$ has been set to $f(3) = 0.0055$ and $f(4) = 0.0045$ for these charge calculations in order to include the same π -bond polarity, h_z , as was employed for the σ bonds.

energy is constant for each coordination number exhibited by the phosphorus and, indeed, varies by only a small fixed amount from one coordination number (*e.g.*, R_3P) to another (*e.g.*, R_3PM). However, they do show qualitatively how important the π contribution is to the total charge, particularly for the phenoxyl derivatives.

In each row of Table II the charge per phosphorus is substantially constant and is quite different from that in the other rows. It is also clear that, as the positive charge on the phosphorus calculated for the σ orbitals becomes smaller, the absolute value of the opposing negative charge attributable to the π orbitals also diminishes (*i.e.*, π -bond feedback) so that we can consider that the value of a measured inner-orbital binding energy for phosphorus (and also for other second- and third-row main-group elements) is the result of considerable charge compensation between the σ -bond polarity and the π -bond feedback. This probably explains the

difficulties in data interpretation encountered by the authors of the first study¹⁶ of phosphorus "2p" binding energies and is in accord with their suggestion that such measurements should be useful in interpreting p_π - d_π bonding.

The small decrease in phosphorus "2p" binding energy going from $(\text{C}_6\text{H}_5\text{S})_3\text{P}$ to $(\text{C}_6\text{H}_5\text{S})_3\text{PS}$ is now understandable although the rather high values of these two binding energies relative to those of the other compounds is not in agreement with the charges presented in Table II. For the other compounds of Table II, the usual⁸ essentially linear relationship of increasing binding energy with increasing electron-withdrawing power (in this case, σ and π together) of the substituents is found. The atomic calculations treated in the preceding section indicate that the effect of the charge due to the σ electrons ought to be considerably different than the effect of the π -electron charge. However, simply multiplying the σ -bond charge by 2 before adding it to the π -bond "charge" turns out not to be an appropriate way of handling the numbers of Table II.

Final Remarks.—Our original hopes that measurements of inner-orbital binding energies might prove to be a useful method for identifying and subtly classifying phosphorus compounds has not worked out, since a vast number of phosphorus derivatives will surely exhibit binding energies in a narrow middle-range band around 133 eV.¹⁶ In other words, X-ray photoelectron spectroscopy will probably never turn out to be as useful to phosphorus chemists as ^{31}P nmr.²⁴ However, the measurement of inner-orbital binding energies throws new light on the electronic structure of the compounds of second-row elements and this is leading to a valuable reevaluation of chemists' working concepts concerning these matters and to increased efforts toward the practical application of quantum mechanics to chemistry.

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The Aminolysis and Basic Hydrolysis of the *O*-Ethylboranocarbonate Ion

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Aminolysis of the *O*-ethylboranocarbonate ion ($\text{K}^+\text{H}_2\text{BCOOC}_2\text{H}_5^-$) occurs in ethanol solution leading to the formation of boranocarbamates. Of special interest is the formation of the ethylenediaminetris(boranocarboxylate) ion. In addition to this work, a study of the kinetics of the basic hydrolysis of potassium *O*-ethyl boranocarbonate in aqueous solution shows that the reaction follows a first-order rate law. Analogy to the isoelectronic monoethylcarbonate ion is indicated.

Introduction

Certain chemical similarities between a borane adduct and an isoelectronic oxygen compound were first dem-

onstrated by Parry and Bissot.² This relationship was also shown to apply to carbon monoxide-borane (H_3BCO) and carbon dioxide in the preparation of car-

(1) Author to whom correspondence should be addressed.

(2) R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, **78**, 1524 (1956).

bamates,³ carbonates,⁴ and monoalkylcarbonates.⁵ In the last case, the relative ease of preparation of potassium *O*-ethyl boranocarbonate ($K^+H_3BCOOC_2H_5^-$) makes available a compound well suited to further studies emphasizing this chemical relationship between iso-electronic systems. In particular, this study is concerned with the aminolysis of $KH_3BCOOC_2H_5$ and with the mechanism of the basic hydrolysis of $KH_3BCOOC_2H_5$.

Experimental Section

Potassium *O*-Ethyl Boranocarbonate.—The $KH_3BCOOC_2H_5$ was prepared by published procedures.⁵ It was recrystallized from absolute ethanol before use.

Potassium Boranocarbamate.—Approximately 0.5 g (4 mmol) of $KH_3BCOOC_2H_5$ was added to an absolute ethanolic solution containing a large excess of dissolved NH_3 at room temperature. After about 20 min about 30 ml of diethyl ether was added to the solution precipitating the boranocarbamate. The precipitate was filtered and dried on the vacuum line. *Anal.* Calcd for KH_3BCONH_2 : C, 12.37; H, 5.19; N, 14.45; equiv wt, 48.5. Found: C, 11.64; H, 4.25; N, 9.92; equiv wt, 49.7. The infrared spectrum of the solid was typical of boranocarbamates previously reported.³

Potassium *N*-Methylboranocarbamate.—The same procedure as was used. *Anal.* Calcd for $KH_3BCONHCH_3$: C, 21.64; H, 6.36; N, 12.62; equiv wt, 55.5. Found: C, 15.13; H, 5.48; N, 10.84; equiv wt, 56.7.

Potassium *N,N*-Dimethylboranocarbamate.—The same procedure as was used. *Anal.* Calcd for $KH_3BCON(CH_3)_2$: C, 28.82; H, 7.26; equiv wt, 62.5. Found: C, 29.03; H, 7.50; equiv wt, 62.4.

Potassium Morpholineboranocarbamate.—A 0.5-ml (5.7-mmol) quantity of previously distilled morpholine was added to 0.5 g (4.0 mmol) of $KH_3BCOOC_2H_5$ dissolved in 40 ml of absolute ethanol at room temperature. In about 2 hr a precipitate began to form. The reaction mixture was allowed to stand overnight before separation of the precipitate. A 0.32-g (2-mmol) quantity of the boranocarbamate was separated or about a 50% yield based on the amount of $KH_3BCOOC_2H_5$ used. *Anal.* Calcd for $KH_3BCON(CH_2)_2O$: C, 35.9; H, 6.58; equiv wt, 83.5. Found: C, 35.8; H, 6.34; equiv wt, 83.9.

Potassium Ethylenediaminetris(boranocarboxylate).—A 12.6-g (0.100-mol) sample of $KH_3BCOOC_2H_5$ was weighed into a 500-ml round-bottomed flask and dissolved in 250 ml of absolute ethanol. The solution was equipped with a magnetic stirrer and cooled to 0° by an ice bath. From a buret, approximately 25 ml of absolute ethanol containing 0.18 ml (25 mmol) of ethylenediamine was added dropwise to the solution over a period of about 1 hr. Precipitation occurred within a few minutes after the ethylenediamine solution was added; however, the solution was stirred for 1 additional hr after all the reactants had been mixed. The product was then separated and washed with absolute ethanol. Based on the amount of ethylenediamine, the yield was about 93%. *Anal.* Calcd for $K_3(H_3BCO)_2NCH_2CH_2NH(H_3BCO)$: C, 20.1; H, 4.68; B, 10.81; N, 9.34; K, 39.1; equiv wt, 60.0. Found: C, 19.6; H, 4.96; B, 10.30; N, 9.34; K, 38.4; equiv wt, 59.7.

Potassium Monoethyl Carbonate and Potassium *O*-Ethyl Thiocarbonate.—Addition of CO_2 to ethanolic solutions of KOH at room temperature produces a mixture of $KCO_3C_2H_5$ and K_2CO_3 .⁶ However, in this work, chips of Dry Ice were added to an ethanolic solution of KOH cooled to -78° resulting in precipitation of $KCO_3C_2H_5$. The precipitate was separated from the cold solution and recrystallized from absolute ethanol before use. The same procedure was used to prepare $KSCO_3C_2H_5$ except that carbonyl sulfide gas from a lecture bottle was bubbled into the cold ethanolic solution of KOH.

Potassium Ethylenediaminebis(carboxylate) and Potassium Ethylenediaminebis(thiocarboxylate).—The same procedure was used as in the preparation of the ethylenediaminetris(boranocarboxylate) ion as reported above. In these preparations, however, the reactants were allowed to stand overnight to allow complete precipitation. *Anal.* Calcd for $K_2(CO_2)NHCH_2CH_2$

$NH(CO_2)$: C, 21.40; H, 2.68; N, 12.50; K, 35.0; equiv wt, 56.0. Found: C, 21.49; H, 2.73; N, 12.04; K, 34.8; equiv wt, 57.4. Calcd for $K_2(COS)HNCH_2CH_2NH(COS)$: C, 18.80; H, 2.34; N, 10.90; K, 30.5; equiv wt, 64.0. Found: C, 19.49; H, 2.77; N, 10.90; K, 31.4; equiv wt, 65.8.

The Kinetic Study of the Basic Hydrolysis of $KH_3BCOOC_2H_5$.—The kinetics of the basic hydrolysis in aqueous solution were followed by measurement of the conductivity of the solution. This method assumes that the change in conductance is due mainly to the disappearance of the highly conductive hydroxide ion.

In a typical experiment a 0.126-g (1.00-mmol) sample of $KH_3BCOOC_2H_5$ was weighed into a 50-ml volumetric flask. Into this flask was pipetted 10.0 ml of 0.100 *N* aqueous KOH which had been equilibrated to the experimental temperature. This solution was then diluted to 50 ml with distilled water which was also at the experimental temperature. The solution was then rapidly transferred to a conductivity cell. The cell was placed in a constant-temperature bath and the electrodes were connected to a conductance bridge. Readings were taken every 2 or 3 min until the conductivity changed so little in the interval that readings could be taken less frequently, *i.e.*, every 15 min. This was continued until a constant value was obtained in three successive readings. Time was measured from the moment of addition of the KOH solution to the flask.

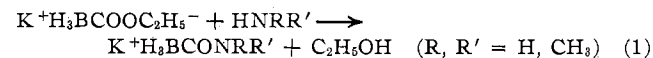
The half-life was calculated as the time required for the conductance to change by half the total change found during the course of the reaction.

The Basic Hydrolysis Reaction in Ethanol.—To determine the effect of the presence of water on the reaction in ethanol solution a 0.50 *M* ethanolic solution of $KH_3BCOOC_2H_5$ was made from fresh absolute ethanol. A 0.50 *M* ethanolic solution of KOH was made from fresh reagent grade pellets and absolute ethanol. This solution was filtered to remove potassium carbonate. Aliquots of 10 ml of each of these solutions were added to small flasks. Water and additional absolute ethanol were added to bring the volume to about 25 ml. Cloudiness was defined as the inability to see lines on a loose-leaf paper through the solution.

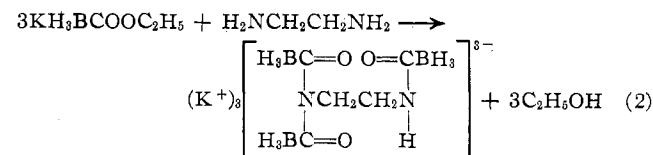
A similar series of experiments was carried out where the amounts of $KH_3BCOOC_2H_5$ and H_2O were held constant but the concentration of KOH was varied.

Results and Discussion

Aminolysis reactions occur in ethanol solution as shown in



It was hoped that this procedure would lead to a comparatively easy preparation of alkali boranocarbamate salts by use of NH_3 , NH_2CH_3 , or $NH(CH_3)_2$. However, only the dimethylamine yielded a high-purity boranocarbamate suitable for further use. The boranocarbamate and the *N*-methylboranocarbamate apparently were formed but analyses indicative of high purity were not obtained. On the other hand, morpholine and ethylenediamine gave boranocarbamates that precipitated from ethanol in high purity. The reaction with ethylenediamine proceeded as in



The potassium ethylenediaminetris(boranocarboxylate) was characterized as follows. (1) The infrared spectrum of the product as a Nujol mull produced strong absorptions at 2380 and 2275 cm^{-1} typical of the BH_3 group and at 1588 cm^{-1} for the carbonyl stretching which is comparable to previous reports for boranocarbamates.³ In addition there was a single sharp absorp-

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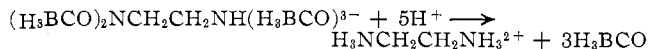
(4) L. J. Malone and R. W. Parry, *Inorg. Chem.*, **6**, 817 (1967).

(5) L. J. Malone, *ibid.*, **7**, 1039 (1968).

(6) C. Faurholt, *Z. Phys. Chem.*, **126**, 211 (1927).

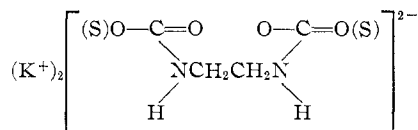
tion at 3370 cm^{-1} in the N-H region indicating the presence of a secondary amide structure.⁷

(2) As is also the case with potassium boranocarbonate⁴ this compound can be titrated to a sharp endpoint with standard acid despite decomposition of the compound in water. The equivalent weight found in this manner was 59.7 g/equiv. The value expected from the reaction



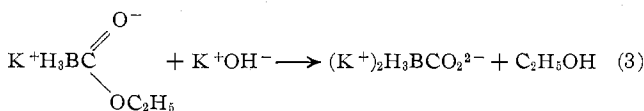
is 59.9 g/equiv. The H_3BCO produced above reacts with water without effect on the titration.⁸

(3) Analytical data shown in the Experimental Section are in good agreement with the proposed formula. Nmr was not useful in this case because of the lack of solubility of the compound in appropriate solvents. It is of interest to compare the above product with that produced from the reactions of potassium monoethyl carbonate or potassium *O*-ethyl thiocarbonate with ethylenediamine under similar conditions. In these cases only two of the amine hydrogens of ethylenediamine are replaced by carboxylate groups giving the compound



The symmetrical structure of the potassium ethylenediaminebis(carboxylate) and the potassium ethylenediaminebis(thiocarboxylate) was inferred from infrared and nmr spectra. Both compounds exhibited a sharp singlet at 3200 cm^{-1} in the infrared spectra indicative of secondary amide structure.⁷ Also proton nmr spectra in D_2O showed one sharp peak (in addition to H_2O). More complicated spectra would be expected from the unsymmetrical structure. The preparation of the symmetrical ethylenediaminebis(dithiocarboxylate) ion has been reported previously.⁹

Reaction 3 is also known to occur in both aqueous and ethanolic solutions.⁵ The resemblance of the *O*-



ethylboranocarbonate ion structurally to ethylacetate and isoelectronically to the monoethylcarbonate ion invites comparison with the hydrolysis of these two compounds. The basic hydrolysis of ethyl acetate in aqueous solution provides the textbook example of second-order kinetics and of an $\text{S}_{\text{N}}2$ mechanism. On the other hand, the basic hydrolysis of monoethyl carbonate proceeds by first-order kinetics and is usually assigned an $\text{S}_{\text{N}}1$ mechanism.⁶

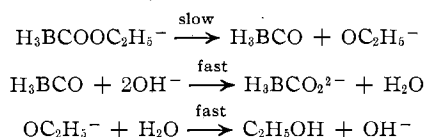
The results of this work show that reaction 3 follows a first-order rate law in aqueous solution under the conditions of these experiments. Table I gives the half-life of $\text{K}^+\text{H}_3\text{BCOOC}_2\text{H}_5^-$ with various ratios of hydroxide at 20°. The variation of ± 0.5 min indicates that the reaction is independent of the hydroxide ion concentrations. In addition, graphs of the log of the

Expt	[KOH]/ [KH ₃ BCOOC ₂ H ₅]	$t^{1/2}$, min	Expt	[KOH]/ [KH ₃ BCOOC ₂ H ₅]	$t^{1/2}$, min
1	1.00	16.0	3	1.36	15.5
2	1.24	16.5	4	1.49	16.5

conductance as a function of time were linear confirming first-order kinetics. The rate constants at different temperatures are given in Table II.

Temp, °C	k , min ⁻¹	Temp, °C	k , min ⁻¹	Temp, °C	k , min ⁻¹
25.0	0.093	20.0	0.047	15.0	0.037

The results in water would be consistent with a basic hydrolysis mechanism similar to that proposed by Faurholt for monoethyl carbonate,⁶ *i.e.*



Some observations, however, indicate that this mechanism may not be appropriate. First, as mentioned earlier, reaction 3 also takes place in ethanol. In this case the $\text{K}_2\text{H}_3\text{BCO}_2$ precipitates. However, the time it takes for a precipitate to become evident in ethanol, although not dependent on the amount of hydroxide present (Table III), is dependent on the amount of water present (Table IV). In the case where precau-

Sam- ple ^a	[KOH]/ [KH ₃ BCOOC ₂ H ₅]	Results	Sam- ple ^a	[KOH]/ [KH ₃ BCOOC ₂ H ₅]	Results
1	1/1	Cloudiness at 29 min	3	2/1	Cloudiness at 19 min
2	1.5/1	Cloudiness at 20 min	4	3/1	Cloudiness at 20 min

^a All samples contained 2 drops of H_2O and 0.5 mmol of $\text{KH}_3\text{BCOOC}_2\text{H}_5$ in a total volume of 25 ml of ethanol.

Sam- ple ^a	Amt of H_2O added, ml	Amt of $\text{C}_2\text{H}_5\text{OH}$ added, ml	Results	Sam- ple ^a	Amt of H_2O added, ml	Amt of $\text{C}_2\text{H}_5\text{OH}$ added, ml	Results
1	None	25	No precipitate after 55 hr	3	0.5	24.5	Cloudiness at 6 min
2	0.2	25	Cloudiness at 60 min	4	1.0	24	Cloudiness at 2 min

^a All samples contained 0.5 mmol of KOH and $\text{KH}_3\text{BCOOC}_2\text{H}_5$.

tions were taken to avoid the presence of as much water as possible (sample 1), a precipitate had not formed after more than 2 days. It would appear then that the *O*-ethylboranocarbonate ion actually reacts initially with H_2O rather than the OH^- ion in the ethanol. It is also possible that changes in the dielectric of the solvent and in the activity of the hydroxide as water is added to these samples may account for the observed results.

A second observation concerns the aminolysis reactions of $\text{KH}_3\text{BCOOC}_2\text{H}_5$ in ethanol solution discussed above. Aminolysis occurs rapidly with ethylenediamine as compared to the case when morpholine is the reacting amine. This observation indicates that the nature of the nucleophile is important in the rate of aminolysis in ethanol.

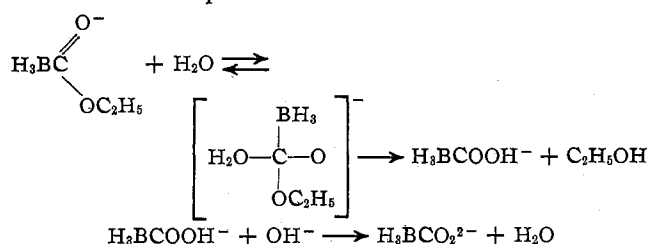
Extrapolation of observations from one solvent medium to another is, of course, not necessarily valid. However, the strong possibility of a pseudo-first-order

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(8) L. J. Malone and M. R. Manley, *Inorg. Chem.*, **6**, 2260 (1967).

(9) H. Amatsu and S. Iwanaga, Japanese Patent 9564 (1957) to Nissan Chemical Industries, Ltd.; *Chem. Abstr.*, **52**, 15572f (1958).

reaction in water is suggested. In this case, the mechanism may involve an intermediate with the solvent water and subsequent reactions as shown in



In any case these results indicate that the *O*-ethylboranocarbonate ion and the normal monoethylcarbonate ion hydrolyze by the same rate law with comparable rate constants (*i.e.*, for $\text{OCO}_2\text{C}_2\text{H}_5$ at 0° , $k = 0.00102 \text{ min}^{-1}$).⁶

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Four- and Five-Coordination in Tetraphenyl Derivatives of Phosphorus(V), Arsenic(V), and Antimony(V). An Investigation Employing Laser-Raman Spectroscopy¹

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The laser-Raman spectra of a number of crystalline tetraphenylphosphorus(V), tetraphenylarsenic(V), and tetraphenylantimony(V) compounds are measured in order to differentiate tetracoordinate species from those that are pentacoordinate. Structural conclusions are based on the spectra in the low-frequency ("X-sensitive") region, and the crystalline P(V) and As(V) compounds appear to be four-coordinate. This is also true for $(\text{C}_6\text{H}_5)_4\text{SbClO}_4$, but there is evidence that the other Sb(V) derivatives are pentacoordinate and probably trigonal bipyramidal in the solid state. All compounds studied are tetracoordinate in methanolic solution, with the exception of the molecular species $(\text{C}_6\text{H}_5)_4\text{SbF}$. The existence of the five-coordinate cations $(\text{C}_6\text{H}_5)_4\text{SbOH}_2^+$ and $(\text{C}_6\text{H}_5)_4\text{AsOH}_2^+$ in aqueous solutions of the corresponding salts is possible.

An examination of earlier literature reveals X-ray diffraction studies that demonstrate the existence of discrete tetrahedra for the $(\text{C}_6\text{H}_5)_4\text{P}^+$ and $(\text{C}_6\text{H}_5)_4\text{As}^+$ cations in the solid state.³⁻⁵ Several recent observations^{6,7} suggest that five-coordination is a general phenomenon in tetraphenylantimony derivatives, contrasting with the ionic structures of the stoichiometrically similar arsenic and phosphorus salts. Within the last year, structural studies of methoxytetraphenylantimony⁸ and hydroxytetraphenylantimony⁹ have shown that both molecules are pentacoordinate trigonal bipyramids with OCH_3 and OH groups, respectively, in one of the axial positions. An additional question that warrants investigation is whether a square-pyramidal or trigonal-bipyramidal coordination polyhedron is adopted, since the sole pentacoordinate com-

pound among those formed by P(V), As(V), and Sb(V) that has been shown to deviate from trigonal-bipyramidal geometry is pentaphenylantimony.^{10,11}

The cations are useful as potentiometric and amperometric titrants,¹²⁻¹⁵ and it is interesting to note that while both $(\text{C}_6\text{H}_5)_4\text{P}^+$ and $(\text{C}_6\text{H}_5)_4\text{As}^+$ exhibit single, two-electron polarographic waves,^{16,17} the reduction of $(\text{C}_6\text{H}_5)_4\text{Sb}^+$ proceeds through two discrete one-electron transfers.¹⁸ The key to this anomalous polarographic behavior may be in the geometries adopted by these species in solution.

In this investigation we employ vibrational measurements in the region below 700 cm^{-1} to differentiate between four- and five-coordination in tetraphenyl derivatives of P(V), As(V), and Sb(V) in the crystalline state and in aqueous and methanolic solutions. Structural conclusions are based on the number and symmetries of fundamentals involving phenyl-central atom motions (termed "X sensitive" by Whiffen¹⁹), which are deter-

(1) Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

(2) U. S. Public Health Service Predoctoral Fellow, 1968-1969.

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