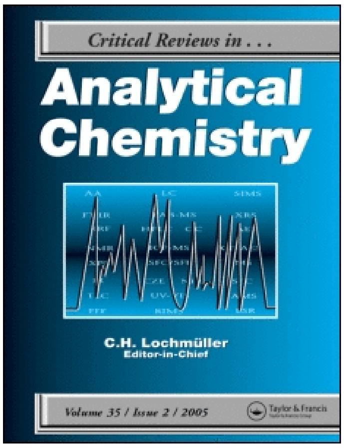

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TETRAARYLBORATES

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I. INTRODUCTION

The literature of the tetraarylborates is still largely confined to the accounts of the chemistry of tetraphenylborate. This very useful analytical reagent has enjoyed an increasingly wide usage and has been applied to many analytical processes other than the detection and determination of potassium, rubidium, cesium, and ammonium, the reasons for its early interest in the field of analytical chemistry.

There has been a proliferation of analytical methods involving the use of tetraphenylborate. These methods are generally adaptations of established analytical methodology designed to meet the conditions imposed by a particular analytical system.

In the literature of the past two decades, there are reports of synthesis of numerous other tetraarylborates. Paradoxically, these compounds received little attention from the analytical chemist despite the intense interest shown in tetraphenylborate. The chemistry of the tetraarylborates appears to be rich in analytical possibilities. This paper is a review of syntheses, applications, and analytical studies of the tetraarylborates.

The literature concerning tetraphenylborate and a few of its analogues has been the subject of several review articles. These vary from reviews of applications in specialized fields of interest to the very comprehensive and exhaustive review of Flaschka and Barnard,[62] which covers the literature up to 1960. This review is especially recommended as the starting point to anyone wishing to embark on new projects in this interesting area of chemistry. Belcher and Wilson[11] critically reviewed the tetraphenylborate chemistry and that of some of the early analogues. Other general reviews of the analytical chemistry of tetraphenylborate have been published by Tamaoku,[226] Buzas,[33] Renault,[188] Montequi,[154] Teijgeler,[229] Kallman,[117] and Heyrovsky.[99] Their use in determinations of alkaloids and synthetic bases was reviewed by Bonnard.[26] Mir[150] has reviewed the analysis of potassium salts with particular regard to mining operations.

II. PREPARATIVE METHODS FOR TETRAARYLBORATES

Considerable attention in this section will be devoted to preparative methods reported for the tetraarylborates because they are usually not commercially available and hence must be synthesized by the investigator. As a historical note, it appears that the first account of the synthesis of an $M(BR_4)$ compound was contained in a note by Thompson and Stevens in 1933.[233] The details reported are insufficient to permit identification of the product obtained. In the previous year, Bent and Dorfman[13] had also synthesized what they considered to be a pentavalent boron compound by reacting tri-α-naphthyl boron in ether solution with a 40% sodium amalgam. However, it was not until 1949 that the tetraarylborates became a reality with the publication by Wittig and co-workers[256] of the first of several papers in which the tetraarylborates were prepared as a part of a more general study. These landmark papers have been reviewed elsewhere, particularly by Flaschka and Barnard,[62] and will be referred to only to the extent that they have bearing on the current chemistry of the tetraarylborates.

The early results of Wittig and co-workers[256] on the determination of potassium are repeated here in Table 1, for from this seed have grown investigations which now number in the hundreds.

It is hard to overemphasize the importance of Wittig's contribution to this area, for he not only originated the first practical synthetic routes to tetraphenylborates but also pointed out many of the more interesting analytical possibilities. Moreover, much of the recent work in tetraarylborate synthesis consists of refinements and adaptations of his original contributions.

A. Nomenclature

At the time sodium tetraphenylborate was coming into use as a reagent, much of the other

TABLE 1

Early Gravimetric Results for
The Determination of Potassium

Given: 3cc 0.1079M KCl solution,
5cc 0.10485M KBr solution, 10cc 0.10485M KBr solution

	mg $(Ph_4B)K$		mg K	
	Calculated	Found	Calculated	Found
(1)	115.9	116.4	12.7	12.7
(2)	187.7	189.6	20.5	20.7
(3)	375.4	376.4	41.0	41.1

boron chemistry was also under investigation. With this borderline element, an unusual chemistry was being experienced which could not be adequately described by the existing nomenclature. The problems which plagued all investigators led to the establishment of the Advisory Subcommittee on the Nomenclature of Boron Compounds to the Nomenclature Committee of the American Chemical Society Division of Organic Chemistry. This first step led to the promulgation of the American Chemical Society Rules on the Nomenclature of Boron Compounds.[273] By these rules, anions of the type BAr_4 are named tetraarylborates(1-). Here borate does not mean derived from boric acid but rather an anion whose central atom is boron. The name tetraarylborate(1-) meets the requirements of the Nomenclature Rules for Coordination Compounds issued in 1960 by the Inorganic Nomenclature Commission of the International Union of Pure and Applied Chemistry (IUPAC).[274] It is suggested that strict adherence to these rules be observed in the naming of new tetraarylborate reagents and that trivial names, where necessary, be carefully chosen and identified with the structures they represent.

B. Improvements in the Synthesis of Tetraphenylborate

Washburn and Billig[247] recommended a synthesis route for the preparation of tetraarylborates which involves (1) preparing the arylsodium compound in an organic solvent, (2) admixing and reacting the arylsodium compound with a boron compound, and (3) a convenient means for recovery of the tetraarylborate from the reaction mixture.

A variety of solvents can be used with the obvious requirement that they not react with the boron compounds under reaction conditions. A polar solvent is needed during the latter stages of the reaction to increase yields and shorten reaction times. The ethers are particularly suitable polar solvents for use in the final stages of the reaction. Solvents recommended are aromatic hydrocarbons (such as benzene, toluene, and xylene) and ethers (such as diethyl ether, tetrahydrofuran, methyltetrahydrofuran, dimethyltetrahydrofuran, the dimethylether of ethyleneglycol, and dibutylether). Solvent mixfures can be used and have the advantage that they permit controlling the temperature of the reaction, which is initially exothermic. This control is accomplished by refluxing a solvent of appropriate boiling point. As examples, the addition of isopentane will limit the temperature of the reaction to about 30°C, while 2,2-dimethylbutane will limit it to about 50°C.

Washburn and Billig characterize this method as particularly desirable for the production of sodium tetraphenylborate. In this process either boron trichloride or boron tribromide is reacted with phenyl sodium, boron trichloride being the preferred reactant.

Other researchers have attempted to improve the synthetic procedures of Wittig by use of different solvents. Kozlova and Pal'm,[126] using the Grignard reagent in tetrahydrofuran, prepared sodium tetraphenylborate in about 30% yield. Holzapfel and Richter[104] made a detailed study of the synthesis of $NaBPh_4$. They developed elegant procedures, used tetrahydrofuran as the solvent, and obtained a very pure product in good yield. They reacted the phenyl Grignard reagent with both the boron trifluoride-etherate and certain alkylesters of boric acid. Their results are summarized in Table 2.

Attention has been given to the development of convenient methods for the preparation of certain tetraphenylborate salts. A recent method[120] consists of preparing $KBPh_4$ by adding crystalline KBF_4 in small excess to an ether solution of the phenyl Grignard reagent. The lithium and sodium salts are then prepared by passing a 0.1N aqueous acetone solution of the potassium salt through a suitably prepared KU-2 ion-exchange resin. Evaporation of the eluates gives the sodium salt containing 0.5% H_2O. After further purification, the lithium salt is obtained as a stable tetrahydrate. The lithium salt has also been prepared by ion exchange from a methylacetate solution of $KBPh_4$, using a KU-2 resin in the lithium form.[189] The product was obtained in a 70% yield and 93

TABLE 2

Yield of Pure Sodium Tetraphenylborate

Boron Compound Used	Solvent	Yield, Percent of Theory
Boron trifluoride-etherate	THF	83
Methyl borate	THF	83
Propyl borate	THF	71
Isoamyl borate	THF	56
Methyl borate	Ether	49

to 98% purity. It was stable in air to 120°C. On heating it was converted quantitatively to $LiBO_2$.

C. Preparation of Arylborates Other Than Tetraphenylborate

This section will deal with the preparation of arylborates other than sodium tetraphenylborate which, because of its great importance, was discussed separately in the previous section. It will include compounds of the BR_4^-type, where R is an aryl group attached directly to the boron atom or where R is an aryl group containing a side chain attached to the boron atom. In addition, anions of the $[BR_3CN^-]$ type will be included because of both their considerable analytical interest and the desire to follow the precedent set in previous reviews in this area. A wide variety of compounds meeting these criteria has been prepared in the course of fundamental and applied research.

The principal routes open to the synthesis of anions as described above will be shown in the reaction sequences to follow. Because most of the preparations are modifications or variations of one of these, the compound under consideration will be referred to as being prepared by reaction schemes I - VI:

I. $4RMgX + NaBF_4 \longrightarrow NaR_4B + 2MgF_2 + 2MgBr_2$

II. $R_3B + MR \longrightarrow R_4BM$

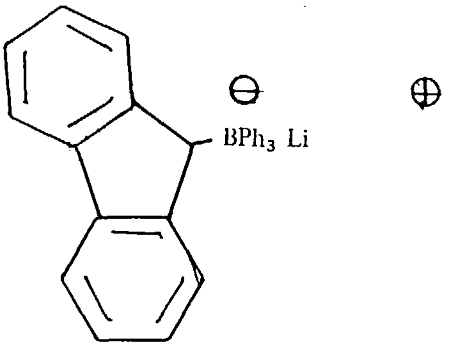
III. $4RM + BX_3 \longrightarrow R_4BM + 3MX$

IV. $4RMgX + 2(RO)_3B \xrightarrow[H_2O]{} Mg(BR_4)_2 + \text{salts}$

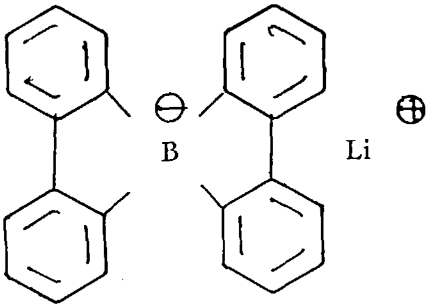
V. $R_3B + NaCN \xrightarrow[\text{melt}]{} (R_3BCN)\,Na$

VI. $BX_3 + RMgX \longrightarrow (R_4B)_2Mg + \text{salts}$

In 1949, in the course of a systematic study of the reaction chemistry of boron compounds, Wittig and co-workers[256] prepared $LiBPh_4$, using reaction II, and noted its analytical possibilities. The following year Wittig and Ruckert[257] reported the synthesis of



using route II. In 1951, apparently in response to the interest generated by tetraphenylborate, Wittig and Raff[258] undertook a fairly extensive study of the preparation of tetraphenylborate and reported isolation techniques extensively used by later workers[38, 146, 152, 240] as well as improved methods of synthesis. In the course of this study, they also prepared $Ph_3BC{\equiv}CPhLi$ and Ph_3BCNNa. The latter was destined to become a compound of considerable analytical interest. In 1955, Wittig and Herwig,[259] because of the analytical significance of the tetraarylborates, prepared the ortho-, meta-, and para-tetratolylborates using method II. They also reported the synthesis of the three tritolylcyanoborate anions: lithium tris(*p*-methylphenyl)cyanoborate, lithium tris(*m*-methylphenyl)cyanoborate, and lithium tris(*o*-methylphenyl)cyanoborate. For the cyano-compounds, they employed procedure V. Their attempt to prepare the lithium tetrakis(*o*-phenylphenyl)borate was not successful. However, they were able to prepare lithium tris(*o*-phenylphenyl)phenylborate. In the course of this work, they prepared the interesting ring compound lithium bis-(2,2'-biphenylenyl)borate,



They also prepared the Li^+, K^+, and $(CH_3)_4N^+$ salts of tetrakis(*p*-N,N-dimethylaminophenyl)borate and tris(*p*-N,N-dimethylaminophenyl)cyanoborate, but they did not report the analytical properties of these compounds.

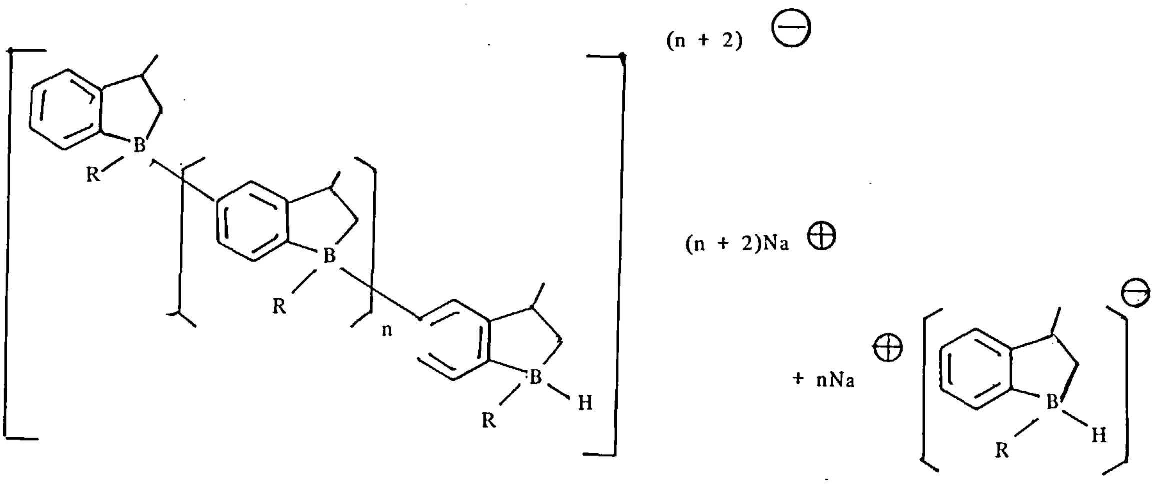
In this series of papers, a number of things were reported that may be of interest to analytical chemists, such as the fluorescence of certain triaryl compounds when exposed to ultraviolet light, the increased stability produced by the introduction of the cyano group into a borate anion, and the steric problems encountered in introducing large ligands into the coordination sphere of boron.

In the early 1950's, Razuvaev and Brilkina[185] were conducting studies on the free-radical reactions of $M(BR_4)$ complexes and reported the use of $Li(BPh_3\,p\text{-tolyl})$ and $NH_4\text{-}B(C_{10}H_7\text{-}1)_3Ph$. There is no indication that they considered the analytical properties of the compounds. In 1957, Mikhailov and co-workers[149] prepared four tetraarylborates in the course of their study of boron compounds with an asymmetric boron atom. These are $(o\text{-}MeC_6H_4)_2BPh_2Li$, $[(1\text{-}C_{10}H_7)\,BPh_2(C_6H_4Me\text{-}o)]\,Li$, $[(o\text{-}MeC_6H_4)(p\text{-}MeC_6H_4)BPh(C_{10}H_7\text{-}1)]\,Li \cdot 2Et_2O$, and $[(o\text{-}MeC_6H_4)(p\text{-}ClC_6H_4)BPh(C_{10}H_7\text{-}1)]\,Li \cdot 2Et^2O$. No analytical studies were reported.

In the late 1950's, Nesmeyanov and co-workers[160] reported on compounds of possible analytical significance. In a study of organo boron heterocycles, they obtained the R_4B^- anions, in which R was the 2-Me-furyl, 2-thenyl, or 2-selenyl group. In a continuation of the work,[199] tetra(2-thienyl)-borate salts of K^+, Rb^+, Cs^+, and Tl^+ were prepared as well as the $KB(C_6H_4\,p\text{-}OCH_3)_4$. It was noted that both anions gave sparingly soluble salts with Rb^+, Cs^+, and Tl^+. In a search for a sodium reagent, they prepared $B(C_6H_4p\text{-}CH_3)_4$. Kruerke[129] prepared $[B(C{\equiv}C\text{-}Ph)_4]_2Mg(H_2O)_6$ in 60% yield and noted that it quantitatively precipitated the ammonium ion.

In the late 1950's and early 1960's, it was beginning to become apparent to many analytical chemists that the preparative chemistry of the tetraarylborates offered many interesting possibilities for totally new reagents through the modification of tetraphenylborate. Using this approach with the intent to improve the stability of tetraphenylborate, Moore and co-workers[157] synthesized the tetrakis(p-tolyl)borate in 1961, using the Grignard route of Equation I, but did not investigate the compound to any extent because of the extensive decomposition of the reagent solutions.

The increasing complexity of the possible four-coordinate boron compounds is shown in the work of Grimme and co-workers.[81] They prepared materials of the following types:



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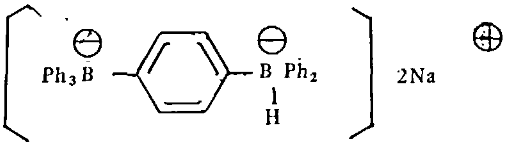
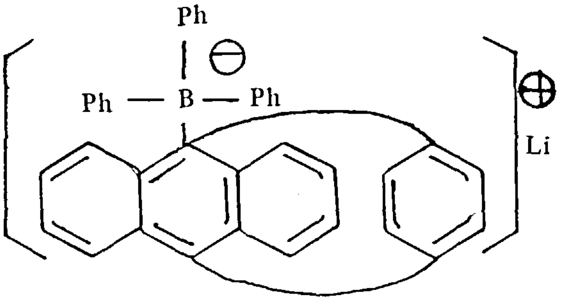
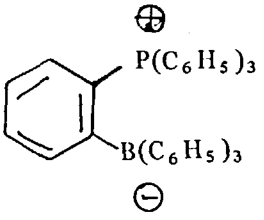


An additional indication of the large and complex structures capable of being coordinated to boron is

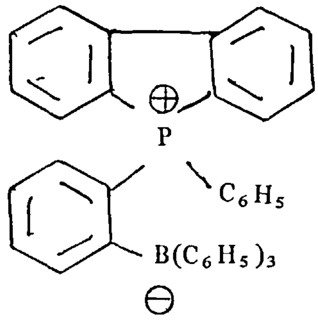


which was prepared by Wittig and Tochtermann[265] in the study of reactions at the bridgehead of triptycene.

In a study of the behavior of dehyrobenzol, Wittig and Benz[261] prepared the salt *o*-ethyl (N,N,N-triethylanilinium)tetraphenylborate and the two betaine compounds that follow:



and

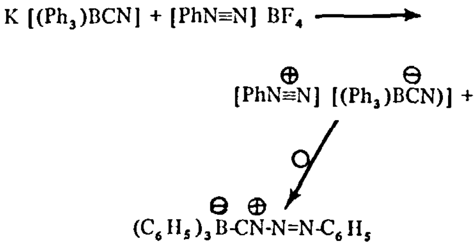


Brehm and co-workers[27] studied reactions of the CN-ligand of potassium triphenylcyanoborate and reported improved preparative methods for KPh_3BCN. The potassium salt was obtained in 75% yield by decomposition of the triphenylborane-β-picoline adduct with KCN. The triphenylborane-ammonia-adduct was also decomposed with KCN to give the K^+ salt. The $(Ph_3BCN)^-$ remaining in solution was precipitated with tetramethylammonium chloride to give a total yield of about 90% of theory. The workers reacted the K^+ salt as follows:

$$K[(Ph_3)BCN] + RX \longrightarrow (Ph_3)B\text{-}CNR$$

$$\text{where } R = \text{-}C(Ph)_3$$

$$R = \text{-}C(CH_3)_3$$



$$K[(Ph_3)BCN] + [PhN{\equiv}N]BF_4 \longrightarrow \overset{\oplus}{[PhN{\equiv}N]}\,\overset{\ominus}{[(Ph_3)BCN)]} + KBF_4 \xrightarrow{} \overset{\ominus\ \oplus}{(C_6H_5)_3B\text{-}CN\text{-}N{=}N\text{-}C_6H_5}$$

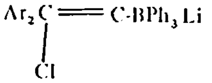
In his attempt to prepare a tetraarylborate more stable in solution than sodium tetraphenylborate, Humecki[109] synthesized the mixed salt sodium magnesium tetrakis(*p*-methoxyphenyl) borate, using routes I and VI. Its solutions proved to be very unstable. Massey and co-workers,[143, 144] using route II, prepared the lithium tetrakis (pentafluorophenyl)borate and found that it precipitated K^+ and NH_4^+ from concentrated aqueous solutions and that the K^+ salt was more soluble than its phenyl analog $KBPh_4$, but that these tetrakis(pentafluorophenyl)borates could not be used for gravimetric analysis. A patent issued in 1963 covered reactions of boron halides and tetrasubstituted compounds claimed numerous tetraarylborates and their salts.[22] Evidence in proof of preparation and characterization does not appear in the patent. Holzapfel and Richter,[104] as a dissertation project, made a critical study of the Wittig method for preparing sodium tetraphenylborate. In their study they located those steps in the process in which loss of yields occurred and suggested remedies to improve the yields. They also prepared sodium tetrakis(*p*-chlorophenyl) borate and the salts lithium and sodium tetrakis(*p*-biphenyl)borate in good yields. They followed both reaction sequences IV and VI, employing tetrahydrofuran in the Grignard preparation. This paper is especially recommended to those interested in doing further synthesis in the area.

The poor stability of the tetrakis(*p*-methylphenyl)borate and the tetrakis(*p*-methoxyphenyl) borate anions in aqueous solution indicated that electron-releasing groups on the ring were not leading to compounds of increased stability. Thus, a series of compounds containing electron-withdrawing groups was synthesized. Moore and co-workers[38] prepared sodium tetrakis(*p*-chlorophenyl)borate, utilizing reaction sequence I. The pure sodium salt was obtained by ion exchange of the mixed sodium-magnesium salt, making use of the sodium form of Dowex-50W-X_4. They then prepared the sodium tetrakis(*p*-fluorophenyl) borate, using route I.[152] As might be expected, the elemental analysis of this compound proved to be extraordinarily difficult and required some special analytical methods research before a satisfactory analysis was achieved. The sodium salt was obtained as a stable dihydrate via ion exchange.

Holzapfel and co-workers[106] prepared sodium tetrakis(*p*-bromophenyl)borate and sodium tetrakis(*p*-fluorophenyl)borate. The bromo compound decomposed so readily that accurate solubility data were difficult to obtain. The authors proposed a mechanism to explain the decomposition. They found the fluoro compound to be a white crystalline material which was soluble in water and gave precipitates with rubidium and cesium. Solutions of the fluoro compound were more stable than solutions of the *p*-bromo and *p*-chloro compounds.

The procedure for producing fluorine-substituted compounds was modified by introducing the aryl halide into an ether solution containing magnesium turnings and $NaBF_4$, thus allowing the Grignard compound to form and react "in situ."[240] The reaction products were separated and recovered as the ammonium or trimethylammonium salts. The sodium salts were conveniently prepared by treating these with sodium methoxide in methanol and pumping off the volatile reaction products. Sodium tetrakis(*p*-trifluoromethylphenyl)borate and sodium tetrakis(*m*-fluorophenyl) borate were prepared in this manner.[146] The sodium tetrakis (*m*-trifluoromethylphenyl)borate was prepared by the "in situ" process described except that ethylamine was found to be a more desirable precipitant.[145] The salt was very hygroscopic and difficult to analyze.

Grisdale and co-workers[82] prepared potassium dimesityldiphenylborate by essentially route III and studied its photolysis products. Koebrich and Merkle,[122] in a study of stable carbenoids, prepared



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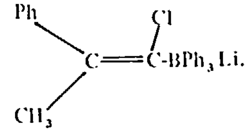


Washburn and Billig,[247] in a patent, claimed the compounds listed in Table 3. It should be noted that no elemental analyses and structural proofs were given. The first column in the table lists the starting boron compound, the second the aryl sodium compound used, the third the solvent system employed, and the fourth the product obtained.

An overview of the tetraarylborate anions clearly indicates that a very wide range of structural possibilities is open to investigation to the researcher interested in the preparation of more selective and advantageous reagents.

III. CHEMICAL AND PHYSICAL PROPERTIES OF THE TETRAARYLBORATES

A. General Chemistry of Boron

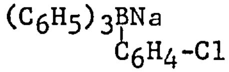
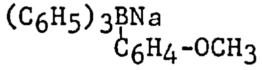
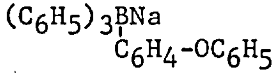
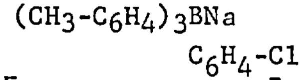
Boron can be considered a rare element, for its concentration in the earth's crust is only 3 ppm. All natural isolable boron compounds contain boron in its trivalent state. The boron atom is small (covalent radius 0.8 Å. Boron is usually considered a metalloid although its cogeners are metals. Its small atomic radius (0.20 Å) makes it more acidic in its oxidized form than the remaining Group III A elements. The neutral boron atom forms trigonal planar bonds when linked to three similar small groups. The availability of the remaining 2p orbital in the oxidized boron atom for bonding results in the strong electron acceptor properties of the tricoordinate boron compounds and the ease with which tetracoordinate structures are formed and tetrahedral configurations assumed. Species containing tetrahedrally coordinated boron may be positively charged $[BH_2[N(CH_3)_3]_2^+]$, neutral $[B_2H_6$ and $BH_3N(CH_3)_3]$, or negatively charged $[(BH_4^-)$ and $B(C_6H_5)_4^-]$ according to the chemical nature of the ligands. The negatively charged species or anions are properly referred to as borates and are the prime consideration of this review.

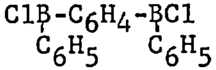
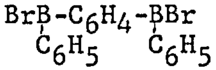
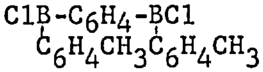
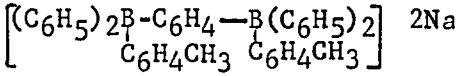
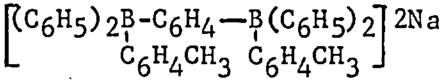
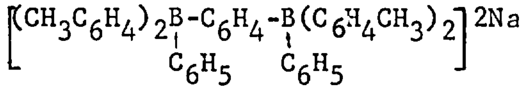
B. Solution Chemistry

The stability of sodium tetraphenylborate solutions has been of especial interest to analytical

TABLE 3

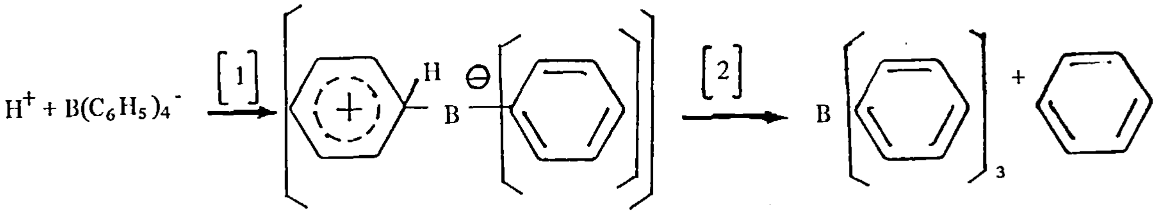
Aryl Boron Compounds Claimed by Washburn and Billig*

Boron Compound	Aryl Sodium	Solvent	Product
BCl_3	$Cl-C_6H_4Na$	CH_3-THF	$(Cl-C_6H_4)_4BNa$
BBr_3	$CH_3-C_6H_4Na$	$C_6H_6+(CH_3OCH_2CH_2)_2O$	$(CH_3-C_6H_4)_4BNa$
BCl_3	$C_2H_5-C_6H_4Na$	$(CH_3OCH_2CH_2)_2O$	$(C_2H_5-C_6H_4)_4BNa$
BCl_3	$Br-C_6H_4Na$	THF	$(Br-C_6H_4)_4BNa$
BCl_3	$C_6H_5O-C_6H_4Na$		$(C_6H_5O-C_6H_4)_4BNa$
$C_6H_5BBr_2$	C_6H_5Na	$C_8H_{10}+(C_2H_5)_2O$	$(C_6H_5)_4BNa$
$Cl-C_6H_4BCl_2$	C_6H_5Na	THF	 $(C_6H_5)_3\underset{C_6H_4-Cl}{B}Na$
$CH_3O-C_6H_4BCl_2$	C_6H_5Na	$CH_3OCH_2CH_2OCH_3$	 $(C_6H_5)_3\underset{C_6H_4-OCH_3}{B}Na$
$C_6H_5O-C_6H_4BCl_2$	C_6H_5Na	$C_6H_5-CH_3+CH_3OCH_2CH_2OCH_3$	 $(C_6H_5)_3\underset{C_6H_4-OC_6H_5}{B}Na$
$Cl-C_6H_4BCl_2$	$CH_3-C_6H_4Na$	$(CH_3OCH_2CH_2)_2O$	 $(CH_3-C_6H_4)_3\underset{C_6H_4-Cl}{B}Na$
$(CH_3-C_6H_4)_3B$	C_6H_5Na	$CH_3OCH_2CH_2OCH_3$	$[(CH_3-C_6H_4)_3BC_6H_5]Na$
$(C_6H_5)_3B$	$Cl-C_6H_4Na$	THF	$[(C_6H_5)_3B(C_6H_4-Cl)]Na$
$(CH_3O-C_6H_4)_3B$	C_6H_5Na	$(CH_3OCH_2CH_2)_2O$	$[(CH_3O-C_6H_4)_3BC_6H_5]Na$
$(C_6H_5)_3B$	$CH_3C_6H_4Na$	CH_3-THF	$[(C_6H_5)_3B(C_6H_4CH_3)]Na$
$(C_6H_5)_2BBr$	C_6H_5Na	$C_6H_6+CH_3OC_2H_4OCH_3$	$(C_6H_5)_4BNa$
$(Cl-C_6H_4)_2BCl$	C_6H_5Na	$CH_3OC_2H_4OCH_3$	$[(ClC_6H_4)_2B(C_6H_5)_2]Na$
$(CH_3OC_6H_4)_2BCl$	C_6H_5Na	THF	$[(CH_3OC_6H_4)_2B(C_6H_5)_2]Na$
$(C_6H_5)_2BCl$	$CH_3C_6H_4Na$	$C_6H_5-CH_3+THF$	$[(CH_3C_6H_4)_2B(C_6H_5)_2]Na$
$Br_2BC_6H_4BBr_2$	C_6H_5Na	$C_6H_5CH_3+CH_3OCH_2CH_2OCH_3$	$[(C_6H_5)_3BC_6H_4B(C_6H_5)_3]2Na$

$Cl_2BC_6H_4OC_6H_4BCl_2$	C_6H_5Na	$C_6H_5CH_3+CH_3$-THF	$[(C_6H_5)_3BC_6H_4OC_6H_4B(C_6H_5)_3]2Na$
$Cl_2BC_6H_4-C_6H_4BCl_2$	C_6H_5Na	$(CH_3)_2$-THF	$[(C_6H_5)_3BC_6H_4-C_6H_4B(C_6H_5)_3]2Na$
$Cl_2BC_6H_4BCl_2$	$CH_3C_6H_4Na$	$C_6H_5CH_3+CH_3OCH_2CH_2OCH_3$	$[(CH_3C_6H_4)_3BC_6H_4B(C_6H_4CH_3)_3]2Na$
 $Cl\underset{C_6H_5}{B}-C_6H_4-\underset{C_6H_5}{B}Cl$	$CH_3C_6H_4Na$	$CH_3OCH_2CH_2OCH_3$	$[(CH_3C_6H_4)_2B-C_6H_4-B(C_6H_4CH_3)_2]2Na$
 $Br\underset{C_6H_5}{B}-C_6H_4-\underset{C_6H_5}{B}Br$	C_6H_5Na	$(CH_3)_2$-THF	$[(C_6H_5)_3B-C_6H_4-B(C_6H_5)_3]2Na$
 $Cl\underset{C_6H_4CH_3}{B}-C_6H_4-\underset{C_6H_4CH_3}{B}Cl$	C_6H_5Na	$(CH_3OCH_2CH_2)_2O$	 $\left[(C_6H_5)_2\underset{C_6H_4CH_3}{B}-C_6H_4-\underset{C_6H_4CH_3}{B}(C_6H_5)_2\right]2Na$
$(C_6H_5)_2BC_6H_4B(C_6H_5)_2$	$CH_3C_6H_4Na$	$CH_3OCH_2CH_2OCH_3$	 $\left[(C_6H_5)_2\underset{C_6H_4CH_3}{B}-C_6H_4-\underset{C_6H_4CH_3}{B}(C_6H_5)_2\right]2Na$
$(CH_3C_6H_4)_2BC_6H_4B(C_6H_4CH_3)_2$	C_6H_5Na	THF	 $\left[(CH_3C_6H_4)_2\underset{C_6H_5}{B}-C_6H_4-\underset{C_6H_5}{B}(C_6H_4CH_3)_2\right]2Na$
$(C_6H_5)_2BC_6H_4-C_6H_4B(C_6H_5)_2$	C_6H_5Na	$(CH_3OCH_2CH_2)_2O$	$[(C_6H_5)_3B-C_6H_4-C_6H_4-B(C_6H_5)_3]2Na$
$(Cl-C_6H_4)_2BC_6H_4B(C_6H_4-Cl)_2$	C_6H_5Na	$CH_3OCH_2CH_2OCH_3$	$[(C_6H_5)_3B-C_6H_4-C_6H_4-B(C_6H_5)_3]2Na$

*The reviewers have corrected certain errors in the structures of several compounds presented. In one case the solvent has been omitted because of inability to determine solvent system intended.

chemists. Flaschka and Barnard[62] reviewed the physical and chemical properties of the metal tetraphenylborates, covering solubility, ultraviolet absorption, thermal and storage stability, conductance of solutions, and crystallography. The mechanism of the acid decomposition of sodium tetraphenylborate was proposed shortly after the compound was first synthesized.[258] Simultaneous studies were reported by Cooper and Powell[44] and by Simon[214] on the acid decomposition of sodium tetraphenylborate. Cooper and Powell proposed an acid decomposition pathway and concluded the following:



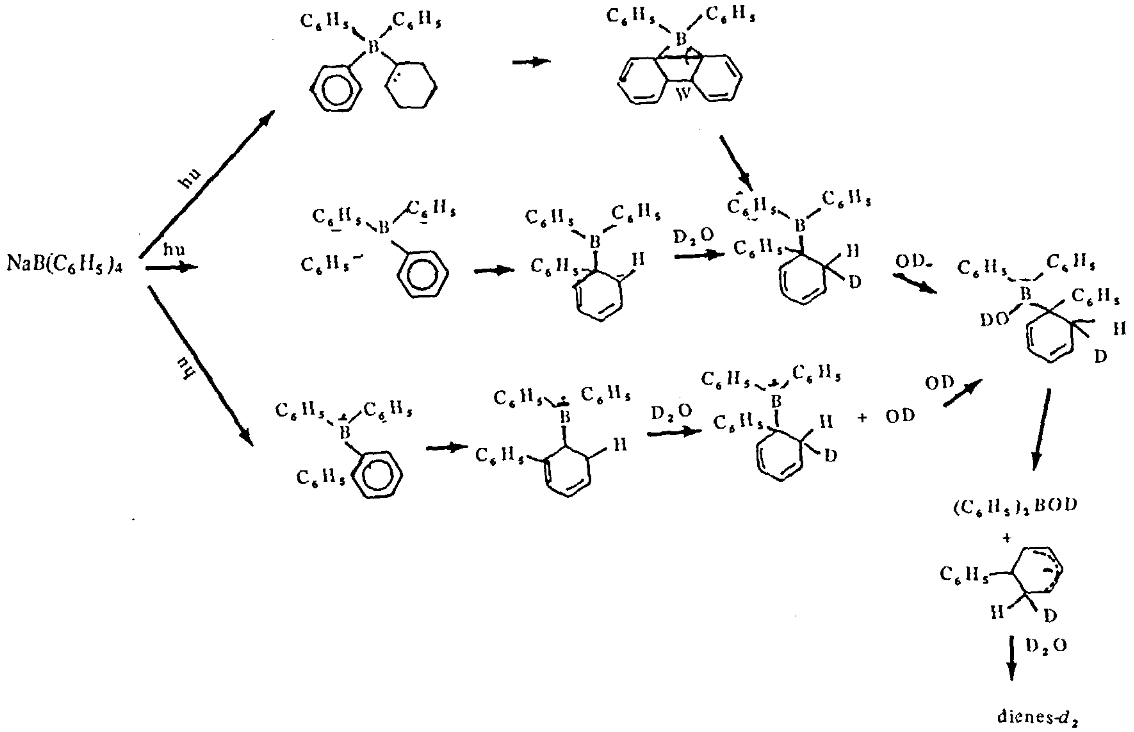
1. the reaction is first order with respect to tetraphenylborate,
2. step [1] is rate determining,
3. the reaction is stoichiometrically correct as written,
4. the reaction might be first order with respect to [H^+] at low concentrations,
5. the reaction is heterogeneous and autocatalytic, and
6. the carbon atom attached to the central boron is the site of the attack.

They also noted that the reaction rates under nitrogen or air are nearly identical. It was reported that appreciable quantities of biphenyl are produced if oxygen was bubbled through the solution and, conversely, that little biphenyl is produced when the reaction is run under nitrogen or air.

Williams and co-workers[266] studied the photochemistry of sodium tetraphenylborate and sodium tetrakis(*p*-methylphenyl)borate in aqueous solutions with radiation in the 253.7-nm region. The products which resulted from the photolysis of sodium tetraphenylborate were biphenyl; 1-phenyl-1, 4-cyclohexadiene; 3-phenyl-1, 4-cyclohexadiene; 1-phenyl-1, 3-cyclohexadiene; and the sodium salt of diphenylboronic acid. The last compound further decomposed to benzene, phenol, and phenylboronic acid. Biphenyl was the principal product in the presence of oxygen, but in its absence 1-phenyl-1,4-cyclohexadiene predominated. The photochemical reaction which led to these products was found to be intramolecular by a study of the irradiation of sodium tetrakis(*p*-methylphenyl)borate and the use of deuterium tagging. A radical pathway was postulated for this process (see next page for illustration).

Williams and co-workers[255] continued to investigate the photochemistry of sodium tetraphenylborate and sodium tetrakis(*p*-methylphenyl)borate by irradiation in alcohol solutions. Photolysis was conducted in methyl, ethyl, isopropyl, and *t*-butyl alcohol solutions. In the presence of air, sodium tetraphenylborate gave biphenyl as the major product in all of the alcohol solutions tested. The yield of biphenyl was correlated with the amount of oxygen present and length of irradiation time. When oxygen was present and isopropyl alcohol the solvent, the products were biphenyl; 1-phenyl;4-cyclohexadiene; *p*-terphenyl; quaterphenyl; 3-phenyl-1,4-cyclohexadiene; and 1-phenyl-1,3-cyclohexadiene. When methyl, ethyl, and isopropyl alcohol solutions under a nitrogen atmosphere were used, the products were biphenyl; 1-phenyl-1,4-cyclohexadiene; 1-phenyl-1,3-cyclohexadiene; 3-phenyl-1,4-cyclohexadiene; and at least three isomeric diphenylhexadienes. Corresponding photoadducts 1-phenyl-1-alkoxy-2-cyclohexenes were isolated in addition to the products mentioned when irradiations were performed in methyl and ethyl alcohols. In *t*-butyl alcohols, no diphenylhexadienes or corresponding 5-butoxy photoadducts were produced.

In 1968, Grisdale and co-workers[82] photolyzed potassium dimesityldiphenylborate in 1,2-dimethoxyethane-water solution in the presence of air. The isolated products were phenol; 2-hydroxymesitylene; 2,4,6-trimethylbiphenyl; and (2,4,6-trimethyl-3-biphenylyl)-mesitylphenylborane. The last photoproduct was confirmatory evidence for the original generation of a phenyl radical and



further proof for the intramolecular free-radical mechanism proposed in their first paper.

The stabilities of dilute aqueous sodium tetraphenylborate solutions stored in glass vessels and kept in diffuse light were investigated.[125] Very dilute solutions decomposed in one month, but the stability increased with increased initial concentration of sodium tetraphenylborate and was also increased by keeping the solutions basic.

The cited investigations indicate quite clearly that both acid and free-radical pathways are available for the decomposition of sodium tetraphenylborate, and also suggest that the decomposition process is very complex.

The hypothesis was made that the sodium tetraarylborates having electron-withdrawing substituents at the meta and para positions on the benzene rings should in aqueous solutions exhibit greater stability than sodium tetraphenylborate.[38,146,152,240] The authors reasoned that inductive effects should reduce the nucleophilic nature of the tetraarylborate and control its susceptibility to proton attack, thereby enhancing the stability of the anion and increasing its usefulness as an analytical reagent. Meisters and co-workers[147] established an order of decreasing resistance toward acid attack in the series of sodium tetraarylborates studied: sodium tetrakis(*m*-fluorophenyl)borate $>$ sodium tetrakis(*p*-fluorophenyl)borate $\geqslant$ sodium tetrakis(*p*-chlorophenyl)borate $\simeq$ sodium tetraphenylborate $\simeq$ sodium tetrakis(*p*-methylphenyl)borate $>$ sodium tetrakis(*p*-methoxyphenyl)borate. As previous studies have indicated, the tetraarylborates appear capable of decomposition by two principal pathways. In the study by Meisters and co-workers, the extents of the acid and free-radical decompositions for several tetraarylborates in aqueous solution were investigated. Sodium tetraphenylborate decomposed almost entirely by acid attack at pH 3.0 and 50.0°C *in air*. Sodium tetrakis(*m*-fluorophenyl)borate did not undergo acid decomposition at pH 2.0 and 50.0°C but was partially decomposed under these conditions via other pathways.

Sodium tetraphenylborate was chosen as a model for the study of the reaction kinetics.[145] Kinetic decomposition data were obtained on separate runs carried out at pH 3.0 and 4.0, and the order of the reaction with respect to tetraphenylborate ion was found to be 1.1 at pH 3.0 and 1.2 at pH 4.0, while the order with respect to hydrogen ion was found to be 1.5 over the same range of pH-values, and the overall order of the reaction was found to be approximately 5/2. This investigation suggested that the acid decompositions of all the tetraarylborates studied probably involve the same general mechanism.

Reports of the solubility of various metal tetraarylborate salts have been made by several authors.[38,62,108,146,152,177,199] Table 4 gives a graphic summary of the solubility values, the pH-values of the equilibrated solutions, and the equilibration times.

The lithium and sodium salts of the tetraarylborates are soluble in water and ether and, in some cases, crystallize from solution as solvates. A change of the *p*-substituent on the phenyl ring of the tetraarylborate ion causes the solubilities of the salts to vary in most solvents. The majority of the tetraarylborates are insoluble in non-polar solvents such as hexane, cyclohexane, carbon tetrachloride, and benzene and are relatively soluble in acetone, dimethylformamide, acetonitrile, dioxane, methanol, and ethanol.

C. Electrochemistry

As indicated in the previous section, a number of diverse studies of the homogenous chemical oxidation of tetraphenylborate have been made. These reports and the observation that tetraphenylborate could be electrolytically oxidized at the platinum electrode in anhydrous acetic acid, N,N-dimethylformamide, and acetone-acetonitrile prompted an extensive investigation by Geske[74] of the electrooxidation of tetraphenylborate. His voltammetric and chronopotentiometric studies with platinum electrodes showed that tetraphenylborate in acetonitrile undergoes a two-electron oxidation. The controlled-potential coulometric data indicated that a secondary chemical process is also consuming tetraphenylborate ion. A reaction scheme was proposed in which the products of the primary electrode process were biphenyl and diphenylboronium ion. A secondary reaction between hydrogen ion (which was generated by

TABLE 4

Solubility of Several Metal Tetraarylborate Salts in Water at 25°C Using Spectrophotometric Measurements

Tetraarylborate Salt	Solution pH	Equilibration Time(Hrs.)	Solubility (moles/1)
$NaB(C_6H_5)_4$			ca. 0.88 [62]
$KB(C_6H_5)_4$			18 x 10^{-5} [177]
$RbB(C_6H_5)_4$			2.3 x 10^{-5} [177]
$CsB(C_6H_5)_4$			2.8 x 10^{-5} [177]
$Tl(1)B(C_6H_5)_4$			5.3 x 10^{-5} [177]
$NH_4B(C_6H_5)_4$			29 x 10^{-5} [108]
$KB(C_6H_4p\text{-}Cl)_4$	3.7		6.0 x 10^{-4} [38]
	6.7		6.5 x 10^{-4} [38]
$CsB(C_6H_4p\text{-}F)_4$	3.3	30	32 x 10^{-5} [152]
	7.3	30	34 x 10^{-5} [152]
	9.5	30	34 x 10^{-5} [152]
$KB(C_6H_4m\text{-}F)_4$	3.5	68	1.21 x 10^{-3} [240]
	6.7	42	1.36 x 10^{-3} [240]
	10.4	42	1.48 x 10^{-3} [240]
$RbB(C_6H_4m\text{-}F)_4$	6.4	68	3.54 x 10^{-4} [240]
$CsB(C_6H_4m\text{-}F)_4$	3.5	68	11 x 10^{-5} [240]
	6.5	68	12 x 10^{-5} [240]
	10.0	68	15 x 10^{-5} [240]
$KB(C_6H_4p\text{-}CF_3)_4$	3.3	68	2.59 x 10^{-4} [240]
	6.2	68	2.66 x 10^{-4} [240]
	10.2	68	2.79 x 10^{-4} [240]
$RbB(C_6H_4m\text{-}CF_3)_4$	2.7		1.25 x 10^{-3} [146]
	10.6		1.59 x 10^{-3} [146]
$CsB(C_6H_4m\text{-}CF_3)_4$	2.6		1.70 x 10^{-4} [146]
	6.5		1.81 x 10^{-4} [146]
	10.5		3.15 x 10^{-4} [146]
$KB(C_6H_4p\text{-}OCH_3)_4$			6.76 x 10^{-4} [199]

reaction of the solvent with diphenylboronium ion) and tetraphenylborate ion produced triphenylboron and benzene. The overall reaction scheme suggested by Geske is shown in the following equations.

$$B(C_6H_5)_4^- \longrightarrow B(C_6H_5)_2^+ + (C_6H_5)_2 + 2e.$$

$$B(C_6H_5)_2^+ + H_2O \longrightarrow (C_6H_5)_2BOH + H^+, \text{and}$$

$$B(C_6H_5)_4^- + H^+ \longrightarrow B(C_6H_5)_3 + C_6H_6.$$

A great interest has been shown in the conductance of salts of tetraphenylborate, especially tetrabutylammonium tetraphenylborate, in non-aqueous solutions. Previous to these studies, single-ion conductances (with the exception of ammonia, methanol, and ethanol) were not available for non-aqueous electrolytic systems because of a lack of reversible electrodes, which are essential for the determination of transport numbers. Theoretical work by Fuoss[68] showed that the conductance of an ionophore can be described in terms of a model in which the ions are represented as charged spheres in a continuum. In that same year, Fuoss and co-workers[69] proposed that tetrabutylammonium tetraphenylborate be a model compound to test their conductance theory. This electrolyte, tetrabutylammonium tetraphenylborate, contains two ions which have centrally located charges and are very large compared to the usual solvent molecules. After the publication of their conductance study of this salt in nitrobenzene, acrylonitrile, propylene carbonate, and acrylonitrile-carbon tetrachloride solvents, a number of publications concerning the conductance of tetrabutylammonium tetraphenylborate in non-aqueous systems appeared. Accascina and co-workers[2] measured the conductance of tetrabutylammonium tetraphenylborate in acetonitrile and in six acetonitrile-carbon tetrachloride mixtures at 25°C, covering the range of dielectric constants from 36.0 to 4.80. In the mixtures having the lowest dielectric constants, triple-ion clustering was evident. The continuum model adequately described the electrostatic effects but was inadequate for explaining the hydrodynamic properties of the electrolyte. The Walden product was found to decrease with increasing carbon tetrachloride content of the solvent. Such a variation showed that Stokes' law must be corrected for the electrostatic interaction between the ions and the dipoles of the polar constituent of the solvent. Conductance measurements on tetrabutylammonium tetraphenylborate in acetonitrile and benzene mixtures at 25°C were performed by Accascina and Petrucci.[1] These results were in agreement with the conductance measurements of tetrabutylammonium tetraphenylborate in mixtures of acetonitrile and carbon tetrachloride. Fuoss and Hirsch[70] measured the conductances of the same salt in propylene carbonate ($D = 65.1$) and in mixtures of nitrobenzene and carbon tetrachloride whose dielectric constants ranged from 34.7 to 7.8. Single ion conductances in these solvents were assumed to be equal to one half the limiting equivalent conductances, $\lambda_0^+ = \lambda_0^- = \Lambda_0/2$, since both ions have nearly identical volumes. The distance parameter, a, which measures the center-to-center distance at cation-anion contact, was found to be 7.1 Å. This value was the average of three independent calculations: from the association constant, from the limiting conductance, and from the limiting curvature of the phoreogram. Brown and Fuoss[29] recognized that tetrabutylammonium tetraphenylborate could be a useful reference electrolyte for exploring a given solvent system. Conductance measurements for tetrabutylammonium tetraphenylborate have also been made in nitriles;[29] in methanol;[132] in mixed solvents prepared by adding water, methanol, acetonitrile, or *p*-nitroaniline to dioxane;[48] and in ethylene chloride and *o*-dichlorobenzene separately.[270]

Bhattacharyya and co-workers[17] summarized the behavior of tetrabutylammonium tetraphenylborate in various non-aqueous solvents. Their report emphasized the validity of the Walden rule when solvents having similar dielectric constants are compared. They showed that the product $\Lambda_0\eta$, where Λ_0 is the limiting equivalent conductance of the salt and η is the viscosity of the solvent, remained constant within ± 1% when ϵ, the dielectric constant of the solvent, varied from 7 to 15 and Λ_0 changed from 50 to 85.

The conductances of tetramethyl-, tetraethyl-, tetrapropyl-, and tetrabutylammonium tetraphenylborate were measured at 25° C in acetonitrile-carbon tetrachloride mixtures having dielectric constants ranging from 36.0 to 10.0.[14] The limiting conductances and association constants of these ammonium tetraphenylborates were found to correlate well with the chemical structures of the salts. Also, it was concluded that the apparent Stokes radius was linear in reciprocal dielectric constant and that the extrapolated values for the hydrodynamic radii of the above cations were 2.37, 2.75, 3.31, and 3.84 Å, respectively. The calculated center-to-center distance for the cation-anion contact in an ion pair was reported to be 0.75 Å larger than the sum of the hydrodynamic radii.

The viscosities and densities of solutions, in acetonitrile and several other solvents, of a series of quaternary tetraphenylborate salts have been measured.[236] Caplan and Fuoss[34] reported the conductances in methanol at 25°C for sodium, potassium, and tetrabutylammonium picrate; tetrabutylammonium tetraphenylborate; and triisoamylbutylammonium iodide, picrate, and tetraphenylborate. Triisoamylbutylammonium tetraphenylborate was shown, in this study, to be an electrolyte for which $\lambda_o+ = \lambda_o- = \Lambda_o/2$ and, therefore, may be used as a reference electrolyte to establish single ion conductances in other solvents. In a later report, these authors[35] measured the conductances of triisoamylbutylammonium iodide, picrate and tetraphenylborate in (nearly) isodielectric methanol, acetonitrile, and nitromethane solvent mixtures. Using the assumption that the conductances of the two ions of triisoamylbutylammonium tetraphenylborate are identical in all solvents, they found that the Walden product for the anion is not constant. They reasoned that the observed changes in the Walden product are caused by selective solvation by monomeric methanol or by acetonitrile in preference to nitromethane.

Conductance measurements of triisoamylbutylammonium tetraphenylborate at 25°C in water were made,[216] and it was shown that the limiting conductances of the two ions are nearly equal. The Walden products of these two ions in water are only about 10% lower than in methanol and in acetonitrile, indicating that they closely approximate Stokes' spheres of nearly equal volume. The authors pointed out that the triisobutylammonium ion has a positive coefficient for the linear term in the conductance function, while the tetraphenylborate ion has a negative one. They stated that current theory cannot explain this fact. The conductance of the tetraphenylborates of lithium, sodium, potassium, cesium, tetrabutylammonium, and triisoamylbutylammonium ions in tetrahydrofuran was investigated at 25°C in the concentration range 2 X 10^{-4}M to 10^{-6}M.[17] The degree of solvation of these salts was found to corroborate the data for K_{dis}. A similar study was made on these salts in dimethoxyethane and tetrahydrofuran in the temperature range +25 to -70°C and a concentration range whose lowest limit was 5 X 10^{-6}M.[37] The respective values of λ_o+, K_{dis}, and $-\Delta H_{dis}$ showed that triisoamylbutylammonium tetraphenylborate forms contact ion pairs in both solvents and dissociates freely into triisoamylbutylammonium cation and tetraphenylborate anion. Although the simple "sphere in continuum" model accounts for the behavior of this salt, the authors had to assume other models to explain the behaviors of other tetraphenylborate salts included in their investigation. Kay and co-workers[118] reported on the conductance and association behavior of the alkali metal perchlorates and tetraphenylborates in anhydrous acetonitrile. Virtanen and co-workers[243] investigated N-methyl-2-pyrrolidone as a medium for chemical reactions by studying the conductance behavior of several alkali metal and ammonium salts of picrate and tetraphenylborate in N-methyl-2-pyrrolidone at 25°C.

Popovych[180] proposed a new method for the estimation of medium effects for single ions in non-aqueous solvents based on the conductance of triisoamylbutylammonium tetraphenylborate. He was able to calculate medium effects for single ions by assuming that log m δ tab = log m δ BPh_4^- = ½ log mδ^2 ± tab BPh_4^-. His values for log m δ H were then used to interpret pH data and to estimate liquid-junction potentials in the two media, water and methanol. The author stated that the use of the compound tetraisoamylammonium tetraphenylborate, proposed by Coetzee and Cunningham,[41] may be an improvement over triisoamylbutylammonium tetraphenylborate for the determination of single-ion conductances in non-aqueous solvents. In a later paper, Popovych and Dill[181] proposed a single scale for ion activities and electrode potentials in ethanol-water solvents based on the triisoamylbutylammonium tetraphenylborate assumption. Medium effects for individual ions enabled them to express standard potentials and ion activities in different solvents on a single aqueous scale and to evaluate liquid-junction potentials of aqueous/non-aqueous interphases. They also summarized the existing methods for the estimation of medium effects of single ions, assuming that the medium effect log mδ of triisoamylbutylammonium tetraphenylborate is equally apportioned between the cation and anion. In ethanol-water mixtures they found that the solvation energy of the proton was lower than in the pure solvents and that it passed through a minimum.

Other workers[84] reported the rate of change of the standard partial molar free energy with changing mole fraction of water as measured in 1/1 wt % dioxane-water solutions for a variety of solutes. In discussing the solvation of the ions, the authors first broke down the rate of change of the standard partial molar free energy with changing mole fraction of water for the electrolytes into separate terms for the individual ions, using an extrathermodynamic approach. The experimental value of the rate of change of the standard partial molar free energy with changing mole fraction of water for the electrolyte tetrabutylammonium tetraphenylborate was found to be in agreement with the value theoretically predicted. Although the highly negative values of the rate of change of the standard partial molar free energy with changing mole fraction of water for the anions were consistent with modes of preferential solvation by water, a chemical method was developed for analyzing the values for small cations because the purely coulombic model could not explain the cation-anion interaction. Compounds having isoelectronic structures such as tetraphenylborate anion and tetraphenylphosphonium cation, which are large organic ions with low density of surface change, were included in this study and believed to have solvation properties similar to analogous uncharged species like tetraphenylmethane.

Alexander and co-workers[3,4,171] discussed the solvent activity coefficients of anions and cations at 25°C for transfer from methanol to other solvents and based their results on an extrathermodynamic assumption regarding the solubility of tetraphenylarsonium tetraphenylborate. In a review, Parker[172] treated protic-dipolar/aprotic solvent effects on rates of bimolecular reactions. Extrathermodynamic assumptions, which included the tetraphenylarsonium tetraphenylborate assumption, were discussed separately.

Conductance measurements on tetraphenylborate salt solutions have given a better understanding of conductance phenomena and solvation properties of non-aqueous solvents. They have been the foundation for the study of polymerization processes and ion-pack phenomena in non-aqueous media. Early reports were concerned with the absolute rate constants of anionic propagation by free ions and ion-pairs of living polystyrene.[19, 71] In both papers the authors reported a common-ion effect when sodium tetraphenylborate was added to a solution of $\sim S^-Na^+$, where $\sim S^-$ is styrene. Subsequent studies of other anionic homo- and co-polymerizations in tetrahydropyran revealed a similar behavior.[16,18,212] Barnikol and Schalz[8] studied the kinetics of the anionic polymerization of styrene in tetrahydrophyran and tetrahydrofuran. They reported that the anionic polymerization of poly(styryl-sodium) is noticeably slower in tetrahydropyran, and the rate constants are a function of the concentration of the active chain ends, with and without the addition of sodium tetraphenylborate. Later Bhattacharyya and co-workers[17] showed that the apparent rate constants of homopropagation of living polystyrene in tetrahydrofuran are inversely proportional to the square root of the concentration of living polymer. They also studied the inhibitory effect of alkali tetraphenylborates on the rate of polymerization and concluded that the free ion is 400 times as reactive as the most reactive ion pair. They found that when cesium was used in the anionic polymerization of polystyrene, poly(styrene-cesium) cyclizes and forms a triple ion. Shimomura and co-workers[213] then investigated the anionic polymerization of sodium and cesium salts of living polystyrene in tetrahydrofuran between -70 and +25°C.

Szwarc[225] evaluated the status and potential of these living polymer investigations. He pointed out that studies of living polymers have greatly enriched our knowledge of the behavior of ions and ion-pairs in organic media and that future studies should also increase our understanding of the intramolecular association or intramolecular solvation by polymer chains.

A significant contribution to analytical chemistry has been the introduction of ion-selective electrodes. The chemical and physical properties of the tetraarylborate salts indicate that these salts could be useful in ion-selective electrodes. Frohliger and Pflaum[67] investigated the analytical applications of the second-order electrodes silver-silver bromide, silver-silver iodide, silver-silver thiocyanate, silver-silver chromate, and silver-silver tetraphenylborate. The indicator electrodes were coupled with a saturated calomel reference electrode. The potentials were measured in various solutions, but suitable electrodes of silver-silver chromate and silver-silver tetraphenylborate were not prepared.

D. Nuclear Magnetic Reasonance Spectroscopy

Boron has two naturally occurring isotopes, B^{10} and B^{11}, and they exist in concentrations of 19.61% and 80.39%, respectively. The availability of isotopically pure boron compounds gives considerable assistance to the analysis of nuclear magnetic resonance and infrared, spectroscopic data. Since both nuclei possess magnetic moments and electric quadrupole moments, NMR and quadrupole studies can be performed on boron compounds to elucidate structures and study rearrangement reactions.

Isotope	Magnetic Moment	Spin	Quadrupole Moment
B^{10}	1.801 ($eh/4\pi Mc$)	($3h/2\pi$)	0.111 ($e \times 10^{-24} cm^2$)
B^{11}	2.689	3/2	0.0355

Relatively little work has been done on the NMR spectroscopy of tetraarylborates. However, B^{11} chemical shifts have been determined for representative examples of most classes of boron-containing compounds,[169,179] including sodium tetraphenylborate. In the study by Onak and co-workers,[169] the B^{11} resonance of tetraphenylborate anion exhibited a paramagnetic shift of 45 ppm relative to tetrahydroborate anion (BH_4^-). The authors stated that the magnitude of the chemical shift is too large to be accounted for on the basis of ring-current shift but may reflect the electronegativity differences between $C_6H_5^-$ and H^-. Chemical shifts for the tetraphenylborate and tetrafluoroborate anions are nearly identical.

Thompson and Davis[232] attempted to correlate B^{11} chemical shifts in tetrahedral BX_4^- ions—where X is H, I, Br, Cl, or F—with substituent electronegativity effects. They observed no direct correlation between the B^{11} chemical shift and the electronegativity of the attached atom. However, using an indirect approach, they showed that the observed B^{11} chemical shifts of these ions may be related to bonding parameters and electronegativities. The B^{11} NMR spectrum of sodium tetraphenylborate was included in this work, and the electronegativity for the phenyl substituent was calculated to be 2.70.

The H^1 and B^{11} nuclear magnetic resonance spectra have been investigated for several potassium para-substituted tetraarylborate compounds, $KB(C_6H_4p\text{-}X)_4$, where X is H, OCH_3, Br, Cl, F, and CF_3.[239] The chemical shift between the centers of the A and X multiplets for the tetraarylborates' phenyl ring proton multiplets, relative to a reference chemical shift for potassium tetraphenylborate, was correlated with the corresponding Hammett σ-values for the para-substituent. The B^{11} chemical shifts for these tetraarylborates also correlate well with corresponding para-substituent σ values. The electronegativity values for the para-substituted phenyl rings ($p\text{-}XC_6H_4\text{-}$) were estimated. It was concluded that electronic substituent effects do not greatly influence the electron density surrounding the central boron atom in the tetraarylborate ions. The reviewers suggest that this conclusion is of significance in the mechanism of acid decomposition of the tetraarylborates. There has been some indication that acid decomposition proceeds through a proton attack on the carbon adjacent to the boron atom. The fact that electronegative groups stabilize tetraarylborates toward acid decomposition while leaving the electron density in the neighborhood of the boron atom virtually unaffected indicates that the proton attack is not on a carbon bonded to the boron atom but probably on the π-cloud of a phenyl ring.

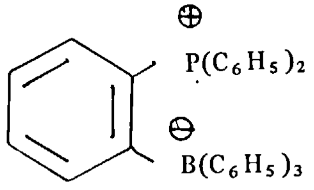
E. Infrared and Raman Spectroscopy

The techniques of infrared and Raman spectroscopy are useful in the structural analysis of the tetraarylborates. Few investigations of the infrared and Raman spectra of salts of tetraphenylborate or related para-substituted tetraarylborates have been reported. Bellamy and co-workers[12] obtained the infrared spectrum of sodium tetraphenylborate but made few vibrational assignments. They found a splitting of the out-of-plane aromatic deformation at approximately 716 cm^{-1} into a doublet and attributed this separation, approximately 20 cm^{-1}, to steric crowding of the hydrogen atoms ortho to the central boron in the tetraphenylborate.

Using infrared spectroscopy, Waddington[245] examined several tetraphenylborates--including those of ammonium, potassium, and rubidium ions and concluded that the NH_4+ ion in ammonium tetraphenylborate is free to rotate within the crystal matrix. He made no assignments for tetraphenylborate.

In their thermal stability study of several analytical standards, Duval and Wadier[55] obtained the infrared spectrum of sodium tetraphenylborate. They recorded the meaningful and strong absorption bands but carried the work no farther.

Wittig and Benz[262] synthesized the two betains whose structures are



A

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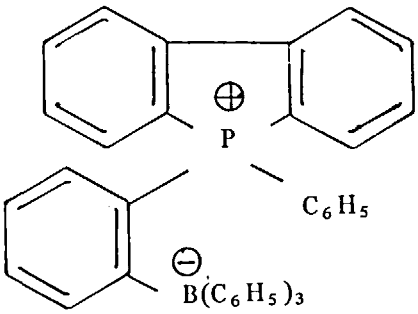


B

As a means of characterization, the authors compared the infrared spectrum of betain A from 700 to 4000 cm^{-1} with the spectra of tetraphenylphosphonium iodide and ammonium tetraphenylborate. Striking similarities were observed and general assignments were made. A detailed analysis of the infrared data was not attempted. After preparing N-benzolazo-nitrilium tetraphenylborate and benzoldiazonium triphenylcyanoborate, Brehm and co-workers[27] obtained their infrared spectra and used the infrared data to determine the structures of these new compounds.

The vibrational spectra of several potassium para-substituted tetraarylborate compounds - $KB(C_6H_4p\text{-}R)_4$, where R is H, OCH_3, CH_3, Br, Cl, F, or CF_3 have been obtained in the solid state from 4000 to 200 cm^{-1} in a study by Vandeberg and co-workers.[241] The X-sensitive modes located between 650 and 200 cm^{-1} were emphasized because they should be influenced by the electronic substituent effects. However, the authors obtained little information on the electron densities in the vicinity of the central boron atom. The absorption bands occurring in the 650 to 200 cm^{-1} region of the parent molecule, potassium tetraphenylborate, were discussed in detail. Tentative assignments for the remaining potassium tetraarylborates were made for absorptions arising from (1) the low-frequency phenyl ring modes, (2) vibrations of the tetrahedral skeleton, and (3) vibrations that are either vibrations of the para-substituent groups or vibrations involving the ring-substituent bond.

F. Thermodynamic Studies

The following thermodynamic studies are closely related to papers reviewed in the preceding section. Arnett and McKelvey[5] found a large solvation-enthalpy effect in highly aqueous t-butyl alcohol solutions. The partial molal heats of solution at infinite dilution ($\Delta\bar{H}_S$) of sodium tetraphenylborate crystals were determined in aqueous t-butyl alcohol solutions at 25°C. The authors noted that a large sharp maximum in $\Delta\bar{H}_S$ occurs at 0.045 mole fraction of the alcohol, where $\Delta\bar{H}_S$ 11.7 ± 0.1 kcal/mole compared to a value of -5.2 ± 0.1 kcal/mole in pure water. The size of the maximum is related to the ion size and is dependent on the ionic charge, but the chief effect was attributed to the reorganization of the solvent structure in the neighborhood of the solute particles.

Heats of solution of several tetraphenylborates, trifluoroacetates, iodides, and perchlorates were determined in water and in propylene carbonate by Wu and Friedman.[268] In addition, these workers reported the relative enthalpies of solvation of the alkali metal ions in propylene carbonate. They measured the heat of solution of sodium tetraphenylborate directly in water. The potassium, rubidium, and cesium salts were studied by measuring the heat of the precipitation reaction which occurred when a solution of sodium tetraphenylborate was mixed with solutions or crystals of the alkali metal chloride. Heats of solution of the other alkali metal tetraphenylborates were measured in propylene carbonate. Values of the heats of solution in water and propylene carbonate permitted the calculation of the standard heats of transfer from water to propylene carbonate. The enthalpies of transfer of the alkali ions from water to propylene carbonate at 25°C, relative to the value for Na^+, were determined calorimetrically and ΔH was found to be 3.17, (0.00), -2.80, -3.43, and -3.96 kcal/mole for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively.

Ionic and molecular rotation in ammonium salts and clathrate compounds was reported by Davies and Staveley[51] and by Staveley and Parsonage.[220] Davies and Staveley investigated the behavior of the ammonium ion in sodium tetraphenylborate by comparing the heat capacities of the ammonium, potassium, and rubidium tetraphenylborates. The molar heat capacity was determined from 20 to 298°K for each of these salts, and the entropies at 298.16°K were evaluated. Davies and Staveley found no transition changes in the heat capacity curve for ammonium tetraphenylborate and reported that the ammonium, potassium, and rubidium salts are isomorphous to at least 20°K. They concluded that ammonium does not freely rotate in the lattice; however, the heat capacity curve for this salt showed an extra energy intake between 20 and 100°K. Staveley and Parsonage studied the motion of the ammonium ion in several selected ammonium salts by attempting to estimate the contributions made to the heat capacity of the salts by the rotational or torsional movements of the ammonium ions. For convenience, they outlined possibilities for ΔC_p as a function of temperature, according to the ammonium salts studied. In the case of ammonium tetraphenylborate, it was concluded that the ammonium ion does not approach the conditions required for free rotation because, at room temperature, ΔC_p is approximately 5 $cal°C^{-1} g\text{-}ion^{-1}$ and increasing. The authors reasoned that ΔC_p can rise to a limiting value of 3R if the barrier to rotation is sufficiently high. It should be noted that the conclusion these authors have drawn regarding the rotation of ammonium ions in ammonium tetraphenylborate does not agree with the conclusions of Waddington[245] which were discussed in the spectroscopy section of this review.

G. Thermochemistry

The thermal stability of the tetraarylborate salts is critical in gravimetric analysis and sometimes very important in volumetric analysis. No thermal analysis studies have been reported for the various salts of the para-substituted tetraarylborates, but the thermochemical behaviors of tetraphenylborate salts have been extensively investigated.

Wittig and Raff[258] observed that ammonium tetraphenylborate decomposes under closed flask distillation conditions at bath temperatures above 240°C forming benzene, triphenylboron, and ammonia. In a similar study, Razuvaev and Brilkina[184, 185] reported that ammonium tetraphenylborate, when heated at 110 to 120°C, decomposes to the ammonia triphenylboron adduct and benzene. Flaschka and co-workers,[63] in the same period, reported that the ammonium salt completely volatilizes when rapidly heated in an open crucible. By thermogravimetry, Wendlandt[249] found a minimum decomposition temperature of 130°C for ammonium tetraphenylborate and concluded that rapid sublimation occurs at this temperature. Howick and Pflaum[108] later confirmed this finding but were able to effect the sublimation of ammonium tetraphenylborate only under reduced pressure.

Thermogravimetric analysis was extended by Wendlandt[252] to the thermal decomposition of 16 amine tetraphenylborates, three cyanotriphenylboron compounds, and the 8-quinolinol tetraphenylborate derivative. He found that in the alkylamine tetraphenylborate series, the thermal stability increases from monomethylamine to triethylamine. A similar but less apparent trend was found in the ethylamine series. Little differences were noted among the thermal stabilities of the isomeric *n*-, *sec*- and *iso-mono*-butylamines. In a further study, Wendlandt and co-workers[254] investigated the thermal properties of 8-quinolinol and several tetraphenylborate salts of substituted 8-quinolinols. The 8-quinolinol and 2-methyl-8-quinolinol salts lose weight at much lower temperatures than the 5,7-dichloro-8-quinolinol; 5,7-dibromo-8-quinolinol; and 5,7-diiodo-8-quinolinol tetraphenylborates. The latter salts apparently undergo thermal decomposition during the initial weight loss period while the 8-quinolinol and 2-methyl-8-quinolinol tetraphenylborates sublime.

Wendlandt[249, 251, 253] investigated the minimum decomposition temperatures of several metal tetraphenylborate salts for which weight loss can be detected. For lithium, sodium, potassium, rubidium, cesium, and thallium(I) tetraphenylborates, the minimum decomposition temperatures are 140, 200, 265, 240, 210, and 180°C, respectively. Under additional heating, these compounds, except for the thallium(I) salt, pyrolyze to a stable metaborate. The pyrolysis of the metal tetraphenylborates proceeds according to the general equation

$$M[B(C_6H_5)_4] + 30O_2 \quad MBO_2 + 24CO_2 + 10H_2O.$$

Silver tetraphenylborate begins to decompose at 65 °C and leaves a metaborate product and silver as the residue. Thermogravimetric studies of mercury(I) and mercury(II) tetraphenylborate have also been carried out.[250,251] Duval and Wadier[55] have used thermal decomposition for studying many analytical standards, including sodium tetraphenylborate.

H. Crystallography

It appears that the first documented crystallographic study of a tetraphenylborate salt was by Webster.[248] From his study of the rubidium and ammonium tetraphenylborate salts, he concluded that in the ammonium salt the tetraphenylborate anions are arranged in parallel columns with an ammonium cation trapped between each pair of neighboring anions in the same column. Crystallographic data for the sodium, potassium, ammonium, rubidium, and cesium tetraphenylborate salts were reported by Arnold and Abraham.[6] Ozols and co-workers[170] have shown by x-ray analysis that rubidium tetraphenylborate forms tetrahedral crystals. They noted that the boron atom is surrounded by four carbon atoms tetrahedrally arranged, and the rubidium ion is likewise surrounded tetrahedrally by four phenyl groups. Levins and co-workers[110] arrived at a similar conclusion regarding the crystal structure of potassium tetraphenylborate. Norment and co-workers[168] published a collection of 21 standard x-ray diffraction powder patterns, mostly of boron compounds, including sodium tetraphenylborate. Their data were collected by both diffractometric and Debye-Scherrer methods.

IV. ANALYTICAL APPLICATIONS OF TETRAPHENYLBORATE

The tetraarylborates have been used in an increasingly wide variety of analytical applications varying from gravimetric determinations of both simple metal cations and complex organic cations. The applications of sodium tetraphenylborate are considered separately in this paper because the literature dealing with this compound is much more extensive than that on the other tetraarylborates. The papers reviewed are organized into categories which to the reviewers seem to contain the main thrust of the contribution. Some papers could well fit into several categories but are covered in only one place in the review.

A. Gravimetric Methods for Metals

The determination of potassium in soils and fertilizers has been the subject of extensive methods development. Rusakova[195] studied the conditions for the determination of potassium in soil and proposed a method in which calcium, magnesium, aluminum, and phosphate do not interfere. He eliminated the interference of ammonium by the use of a formaldehyde solution. Martinek and Gottfreid[138] developed a radiometric determination for potassium in fertilizers based on the natural radioactivity of ^{40}K. They found the tetraphenylborate method to be in good agreement with both flame photometric and radiometric methods.

McCrackan and co-workers[135] studied the tetraphenylborate method and the atomic absorption method for determining potassium in fertilizers and found the tetraphenylborate method to be the more precise. In a collaborative study of the determination of potassium in fertilizers, Ford[65] reported that interferences from organic matter on the tetraphenylborate method can be avoided by the use of decolorizing carbon. Rapoport and co-workers,[183] in the determination of potassium in complex and mixed phosphorus fertilizers with tetraphenylborate, eliminated ammonium interference with a 40% formaldehyde solution and masked other interferences with EDTA in an alkaline solution. Scott and Reed[206-208] used sodium tetraphenylborate in a series of studies on the extraction of potassium from soils and the micaceous minerals biotite and grundite-illite.

Searcy and co-workers[209] devised a simple test for serum potassium in which the potassium was precipitated as the tetraphenylborate and estimated in terms of the length of the precipitate column in a microcapillary tube. Erdey and Kaplar[57] applied tetraphenylborate to the identification and detection of potassium in liquid and solid pharmaceutical preparations. The test was more sensitive than that with tartaric acid. Sodium and calcium did not interfere.

Burglen and Lonquet[31] applied tetraphenylborate to the determination of potassium in raw materials and clinker in cement manufacture and recommended both a gravimetric and a volumetric procedure.

Vecher[242] determined potassium in the Zn-Cr catalyst used in the production of isobutyl alcohol by a gravimetric method employing tetraphenylborate. Zinc was removed prior to the determination of potassium, and chromium did not interfere. Jeczalik and Lis[115] examined and evaluated the precision and accuracy of the perchlorate and tetraphenylborate methods for the determination of potassium in rocks and silicate materials.

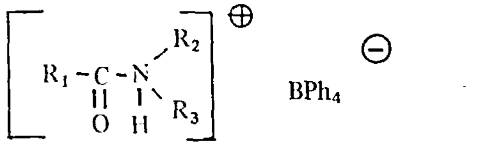
Thomas[231] studied the influence of previously untested foreign ions on the determination of potassium as the tetraphenylborate salt. Salts containing the ions under test were $Na_4P_2O_7$, Na formate, Na citrate, Na_2HPO_3, Na_2HPO_2, Na tartrate, $NaClO_4$, Ca propionate, $VOSO_4$, $Zr(SO_4)_2$, $Mg(H_2PO_2)_2$, $NaIO_4$, and $Na_2S_2O_8$. Kirgintsev and Kozitskii[119] studied the coprecipitation of potassium and cesium tetraphenylborates by adding less than stoichiometric amounts of aqueous sodium tetraphenylborate reagent to a solution containing potassium and cesium chlorides. The precipitate was removed by filtration and the solutions analyzed. The results indicated compound formation of the type $KCs_3(BPh)_4$ and $KCs_9(BPh)_{10}$. Ievins and Peinberga[111] determined small quantities of potassium (0.01-0.25mg) by coprecipitation with ammonium tetraphenylborate. Murakami[156] separated carrier-free Cs from fission products by coprecipitation with ammonium tetraphenylborate.

Iwachido and Toei[114] separated and determined potassium by extraction of potassium dipicrylaminate into nitrobenzene wherein they decomposed it with a strong acid, re-extracted the potassium into water, and precipitated the potassium as potassium tetraphenylborate. Burkser and co-workers[32] used sodium tetraphenylborate to precipitate the potassium in determining the absolute ages of some stone meteorites. Navratil[158] determined macro amounts of ammonium and potassium in plutonium(VI) salts. The plutonium as the anionic chloride complex was adsorbed on an ion exchange resin. The potassium and ammonium ions were precipitated from the resulting solution as the tetraphenylborate salts and weighed. Greenhalgh and co-workers,[80] in a determination of the major cations in sea water, separated the cations by an ion-exchange procedure and found a modified tetraphenylborate gravimetric procedure to be highly acceptable. Attempts to titrate an excess of reagent or the redissolved potassium precipitate with silver nitrate using potentiometric end-point detection gave results inferior in precision and accuracy to the gravimetric method.

Heyrovsky[98] has made use of tetraphenylborate as a means of gravimetrically determining Hg(II) through the formation of diphenylmercury. He found that Ag^+, Tl(I), K^+, Cs^+, Rb^+, NH_4^+ and the anions Cl^-, Br^-, I^-, and SCN^- interfere. Wronski[267] determined the gravimetrically obtained potassium tetraphenylborate by a thiomercurimetric determination, in which he treated the potassium salt with $Hg(ClO_4)_2$ in a methanol solution containing 0.01M $HClO_4$ and titrated with sodium thioglycolate solution.

B. Gravimetric Methods and Qualitative Procedures for Nitrogen-Containing Compounds

Gerrard[73] suggested that an amine must have a basic dissociation constant (K_b) of at least 10^{-11} to undergo quantitative precipitation with tetraphenylborate. Electron-withdrawing groups may make K_b too small to form salts; electron-releasing groups, on the other hand, may make the salt formation easier, as is shown in the acid amides. N-allylpyrrolidone and



acrylamide do not form salts.

Crane and Smith[46] critically studied the variables affecting the precipitation of ammonium ion with tetraphenylborate. These included the pH, the temperature, the volume of the precipitating medium, the concentration of excess tetraphenylborate, the washing conditions, and the effect of extraneous electrolytes. They observed that the precipitation of ammonium ion appears to be more sensitive to variations of conditions than that of potassium ion. As the best conditions for the gravimetric determination of 0.4-0.7 meq of ammonium ion, they recommend: (1) an adjustment of the solution to pH 1.0 to 3.0 before addition of the reagent, (2) use of 25 to 50% excess reagent, (3) presence of a moderate concentration of inert salt, (4) precipitation at room temperature, (5) a total volume of about 60 ml, (6) a digestion time of not more than 1 hour, (7) washing with 1% formic acid followed by a saturated aqueous solution of ammonium tetraphenylborate, and (8) drying to a constant weight at 100°C.

Gracza-Lukacs and co-workers[79] studied the reaction of sodium tetraphenylborate with alkaloids and noted that homatropine methyl bromide and quaternary ammonium compounds can be detected in the presence of tertiary and other amine compounds by their reaction with sodium tetraphenylborate in strongly alkaline media and that the product can be filtered, dried, and weighed. Kranjcevic and Brox-Kaiganovic[127] determined codeine and aminopyrine in mixtures after fractional separation with sodium tetraphenylborate. Amidopyrine in a 0.1M acetic acid medium was determined gravimetrically using sodium tetraphenylborate by Ciogolea and co-workers.[40]

Koehler and Feldmann[123] used sodium tetraphenylborate in a procedure for the qualitative identification of local anesthetics in their dosage forms by preparing derivatives and obtaining their melting points. These are shown in Table 5.

TABLE 6

Local Anesthetic Derivatives

Tetraphenylborates

	Melting Point, ° C.		% N	
No.	Found	Lit. value[123]	Calcd.	Found
1	97-100		4 47	4.37
2	112-115 (90-98)	91.5-108	5.04	4.60
3	143-145		4.74	4.66
4	115-117.5		2.29	2.12
5				
6	154-158		5.06	4.71
7	141-143		2.52	2.41
8	130-132		5.04	4.77
9	106-109	106-109	4.45	4.27
10	72 76	110.5-112.5	4.91	4.65
11	131-134		2.31	2 42
12	127-130 (90-102)	113-116	2.43	2.33
13	168-170 (120-140)	147-151	5 04	4 68
14	143-147	141-143	4.54	4.63
15	127-131		4.56	4.05
16	135-137	119-120	4.81	4.87

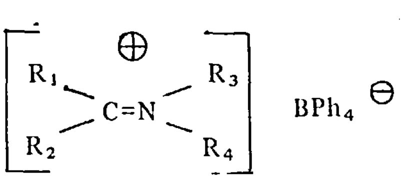
TABLE 5

Local Anesthetics

No.	Generic Name	Chemical Name
1	Butacaine	3′-Dibutylaminopropyl 4-aminobenzoate
2	Butethamine	2-Isobutylaminoethyl 4-aminobenzoate
3	Chloroprocaine	2′-Diethylaminoethyl 2-chloro-4-aminobenzoate
4	Dyclonine	4′-Butoxy-3-N-piperidinopropiophenone
5	Ethyl aminobenzoate	Ethyl 4-aminobenzoate
6	Lidocaine	α-Diethylamino-2,6-acetoxylidide
7	Meprylcaine	2-Methyl-2-propylaminopropylbenzoate
8	Metabutethamine	2′-Isobutylaminoethyl 3-aminobenzoate
9	Metabutoxycaine	2′-Diethylaminoethyl 2-butoxy-3-aminobenzoate
10	Naepaine	2′-Amylaminoethyl 4-aminobenzoate
11	Parethoxycaine	2′-Diethylaminoethyl 4-ethoxybenzoate
12	Piperocaine	3-(2'-Methylpiperidino)propyl benzoate
13	Procaine	2′-Diethylaminoethyl 4-aminobenzoate
14	Proparacaine	2′-Diethylaminoethyl 3-amino-4-propoxybenzoate
15	Propoxycaine	2′-Diethylaminoethyl 2-propoxy-4-aminobenzoate
16	Tetracaine	2′-Dimethylaminoethyl 4-butylaminobenzoate

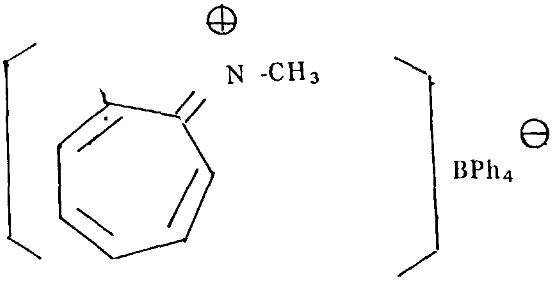
They were not able to prepare a satisfactory derivative of benzocaine, possibly because of its weakly basic properties. The non-aqueous titration procedure was successfully applied to the tetraphenylborate derivatives of metabutethamine, metabutoxycaine, and meprylcaine. The authors noted that their melting points in some cases are substantially higher than previously reported values. The reviewers suggest that the variations in reported values are a possible consequence of contamination by decomposition products of tetraphenylborate, which is subject to both acid and radical decomposition.

Libman,[134] in a study of immonium salts, prepared several salts of the general type



where the R groups are alkyl.

In a study of salts of DL-carnitine and related compounds with tetraphenylborate, Yurkevich and co-workers[269] prepared easily crystallized salts. Dauben and Rhoades,[50] in a study of the synthesis and properties of tropenylidenimmonium(8-aza-troponium) salts, prepared



Tarasenko[227, 228] published two papers on the system $NaBPh_4$-H_2O-$C_{17}H_{19}O_3NHCl$, using the Gibbs' triangle method to clarify the conditions of precipitation of morphine with sodium tetraphenylborate. The solubility of morphine tetraphenylborate in water was found to be 2.8×10^{-4} moles/liter. The precipitation from a solution acidified with HCl was found more satisfactory than precipitation from a non-acidified solution. The data obtained should be useful in establishing conditions for the determination of morphine in pharmaceutical preparations.

C. Volumetric Methods

Improvements in volumetric procedures and new applications of established volumetric methods were the areas in tetraphenylborate chemistry receiving the most attention from analysts during the past decade. The articles reviewed here reflect this interest. Motomizu and co-workers[155] reported a process for the determination of potassium in river water by extraction of the dipicrylamine salt into nitrobenzene. The potassium was then extracted into 1M HCl, the aqueous extract was treated with excess sodium tetraphenylborate, and the excess tetraphenylborate was titrated with benzalkonium chloride using Titan Yellow as the indicator.

A semimicro two-phase titration was reported by Pellerin and co-workers[176] in which the potassium or organic base was precipitated and the excess tetraphenylborate titrated with a quaternary salt. Chloroform was used as the insoluble solvent phase, and bromophenol blue was used as the indicator.

Murakami[156] studied the volumetric determination of potassium in sea water and marine salt using sodium tetraphenylborate and benzalkonium chloride. He investigated the effect of pH on the indirect determination, which employed Titan Yellow or Calmagite and several other indicators.

Imura and co-workers[112] determined triethyllead by precipitating it from an acetic acid solution of pH 4 to 5, removing the precipitate, and titrating the excess tetraphenylborate using benzalkonium chloride and Titan Yellow indicator. Diethyllead and Pb^{++} do not interfere.

Martinez and co-workers[139, 142] published several papers on the applications of the volumetric method to biological and agricultural products. They found the recommended procedure, when applied to samples containing from 5 to 0.011 mg of KCl in 10 ml of solution, to have an error averaging 0.5% and never exceeding 3%, and to fail with concentrations less than 0.01 mg KCl/ml. The potassium was precipitated as the tetraphenylborate salt and removed by filtration, and the filtrate was titrated with a quaternary ammonium salt solution using bromophenol blue as the indicator. The method has been adapted to the determination of potassium in milk, wine, blood serum, and plant material. The sensitivity of the method was later improved and potassium determined at the 5μg/ml level. Iwachido[113] found that the addition of polyvinylpyrrolidone overcame the necessity of removing the precipitated potassium tetraphenylborate before titration of the excess tetraphenylborate with a quaternary ammonium salt.

The analysis of fertilizers led to several studies of the tetraphenylborate reagent. Probably the most noteworthy were those by the Association of Official Agricultural Chemists, who adopted a volumetric procedure as an official method for potassium.[107] The official AOAC method is as follows:

Reagents

(a) Sodium hydroxide solution–approximately 20%. Dissolve 20 g NaOH in 100 ml H_2O.

(b) Formaldehyde solution—37%.

(c) Sodium tetraphenylborate ($NaBPh_4$) solution-approximately 1.2%. Dissolve 12 g $NaBPh_4$ (J. T. Baker Chemical Co., Phillipsburg, N. J.) in ca 800 ml H_2O. Add 20-25 g $Al(OH)_3$, stir 5 minutes, and filter (Whatman No. 42 paper or equivalent) into 1 liter volumetric flask. Rinse beaker sparingly with H_2O and add to filter. Collect entire filtrate, add 2 ml 20% NaOH, dilute to volume with H_2O, and mix. Let stand 48 hours and standardize. Adjust so that the 1 ml $NaBPh_4$=1% K_2O. Store at room temperature.

(d) Quaternary ammonium chloride solution—approximately 0.625%. Dilute 50 ml 12.8% Zephiran chloride (Winthrop-Stearns, Inc., New York, N. Y. 10018), also available at local pharmacies as alkyldimethylbenzyl ammonium chlorides) to 1 liter with H_2O, mix, and standardize. Cetyltrimethylammonium bromide may be substituted for Zephiran chloride. If other concentration is used, adjust volume.

(e) Clayton Yellow (Titan Yellow; Color Index No. 19540)-0.04%. Dissolve 40 mg in 100 ml H_2O.

Standardization of Solutions

(a) Zephiran chloride - To 1.00 ml $NaBPH_4$ solution in 125 ml erlenmeyer, add 20-25 ml H_2O, 1 ml 20% NaOH, 2.5 ml HCHO, 1.5 ml 4% $(NH_4)_2C_2O_4$, and 6-8 drops of indicator, (e). Titrate to pink end-point with Zephiran chloride solution, using 10 ml semimicro buret. Adjust Zephiran chloride solution so that 2.00 ml = 1.00 ml $NaBPh_4$ solution.

(b) Sodium tetraphenylborate solution–Dissolve 2.500 g KH_2PO_4 in H_2O in 250 ml volumetric flask, add 50 ml 4% $(NH_4)_2C_2O_4$ solution, dilute to volume with H_2O, and mix. (It is not necessary to bring to boil.) Transfer 15 ml aliquot (51.92 mg K_2O, 43.10 mg K) to 100 ml volumetric flask; add 2 ml 20% NaOH, 5 ml HCHO, and 43 ml $NaBPh_4$ reagent. Dilute to volume with H_2O, mix thoroughly, let stand 5-10 minutes, and pass through dry filter. Transfer a 50 ml aliquot of filtrate to a 125 ml erlenmeyer, add 6-8 drops of indicator, (e), and titrate excess reagent with Zephiran solution. Calculate titer as follows: F=34.61/(43 ml-ml Zephiran)=% K_2O/ml $NaBPh_4$ reagent. Factor F applies to all fertilizers if 2.5 g sample is diluted to 250 ml and 15 ml aliquot is taken for analysis. If results are to be expressed as K rather than as K_2O, substitute 28.73 for 34.61 in calculation of F.

Determination

Place 2.5 g (1.25 g if $K_2O > 50\%$) sample in 250 ml volumetric flask, add 50 ml 4% $(NH_4)_2C_2O_4$ and 125 ml H_2O, and boil 30 minutes. (If organic matter is present, add 2 g K-free C before boiling.) Cool, dilute to volume with H_2O, mix, and pass through dry filter or let stand until clear. Transfer 15 ml aliquot of sample solution to 100 ml volumetric flask and add 2 ml 20% NaOH and 5 ml HCHO. Add 1 ml standard $NaBPh_4$ solution for each 1% K_2O expected in sample plus additional 8 ml excess to insure complete precipitation. Dilute to volume with H_2O, mix thoroughly, let stand 5-10 minutes, and pass through dry filter (Whatman No. 12 or equivalent). Transfer 50 ml filtrate to 125 ml erlenmeyer, add 6-8 drops of indicator, (e), and titrate excess reagent with standard Zephiran solution.

%K_2O in sample =(ml $NaBPh_4$ added-ml Zephiran) X F, where F=% K_2O/ml $NaBPh_4$ reagent. (Multiply by 2 if 1.25 g sample was used.)

Ford[66] made a critical study of the tetraphenylborate procedure for potassium as an associate referee of the AOAC. He reported the results of 17 participating laboratories doing duplicate determinations on each of two dates. These data are summarized in Table 7.

Ford also studied the effects of organic natural products on the determination of potassium with tetraphenylborate. He found that the negative error in the determination can be eliminated by a pre-treatment of the sample with carbon black. Gehrke and Kramer[72] modified the AOAC meth-

TABLE 7

Standard Deviation and Average Percent K_2O by Sodium Tetraphenylborate Method

	Sample 1	Sample 2	Sample 3
Mean	20.29	20.02	21.56
Standard Deviation	0.21	0.13	0.15

od for potassium so as to apply it to samples containing large amounts of ammonium citrate. Ceresa[39] reported a volumetric method for the extraction and determination of potassium in fertilizer by employing cetyltrimethylammonium bromide and bromophenol blue indicator in an indirect procedure in which the potassium tetraphenylborate was removed by filtration and the excess reagent titrated. Carmo[36] reported a similar method which used Titan Yellow as the indicator and benzalkonium chloride as the titrant.

Riva[190] reported a rapid determination of potassium in common salt and other saline products by precipitation and titration of its tetraphenylborate salt. The potassium tetraphenylborate was dissolved in acetone and decomposed by mercuric chloride in the presence of a known excess of alkali. A solution of KI and a known excess of acid were then added and the acid back titrated to the methyl red end-point. A study by Nogina[166] recommended dissolving the conventionally obtained potassium tetraphenylborate in acetone, treatment with mercuric chloride, removal of the phenylmercuric chloride, and titration of the excess mercuric ion with EDTA.

Geyer and Chojnacki[76] developed a titrimetric procedure for potassium which used thallous nitrate as the titrant and dimethyl yellow as an adsorption indicator. There is a systematic error of about -4%. Large amounts of foreign cations make the end-point less sharp.

Schneer and Hartmann[200] determined tetraphenylborate by an oxidation procedure, employing sodium dichromate in 77% H_2SO_4. The excess dichromate was titrated with $FeSO_4$, using ferroin as the indicator.

Holzapfel and Richter[105] studied the use of fluorescein and substituted fluoresceins as indicators for the determination of potassium, using sodium tetraphenylborate in a back-titration procedure. Several of the indicators gave satisfactory end-points when cetyltrimethylammonium bromide was used as the titrant.

Audidier and Seince[7] determined potassium in foods having a high carbohydrate content, using tetraphenylborate in a back-titration procedure. EDTA was used as a masking agent and the potassium tetraphenylborate weighed or titrated in aqueous acetone with 0.1N silver nitrate, using potassium chromate as the indicator.

Pucher[182] adapted the thallous nitrate method of Schmidt to the determination of small concentrations of potassium by tetraphenylborate. The procedure employed a back-titration of the excess tetraphenylborate, using a "dead stop" technique of end-point detection.

Using variamine blue as the indicator, Rozsa[193] developed a back-titration procedure for potassium which employed silver nitrate as the titrant.

The precipitation titration of sodium, potassium, and rubidium, whose chlorides are insoluble in certain non-aqueous media, was carried out by Henrion and Pungor[97], using lithium chloride as the titrant. The end-point was detected by conductance methods. The method is applicable to tetraphenylborates and certain other insoluble salts.

The titrations of high-molecular-weight quaternary ammonium compounds have been studied by several investigators. Boden[25] reported a two-phase titration of high-molecular-weight quaternary pyridinium halides using 0.01M sodium tetraphenylborate, chloroform as the water immiscible solvent, and neutral red as the indicator. The end-point was indicated by the use of the water soluble cationic dye, which contained the amine functionality. In acidic solution it yielded a colored chloroform-soluble entity with $NaBPh_4$ but only after the $NaBPh_4$ had been completely reacted with the quaternary ammonium ion present. Billow and Baker[20] developed a titrimetric method, using sodium tetraphenylborate as a primary standard, for the determination of aromatic quaternary ammonium salts and long-chain aliphatic sulfates and sulfonates. Later studies on the stability of tetraphenylborate solutions indicate that this compound does not meet several of the criteria usually considered desirable for primary standard substances, and its use for this purpose is no longer recommended.[147]

Metcalfe and co-workers[148] developed a rapid macro titration procedure for the determination of long-chain quaternary ammonium compounds using sodium tetraphenylborate as the titrant. The sample was titrated with 0.06N aqueous reagent, with dichlorofluorescein proving to be the best of several indicators tested. Amine interference was eliminated by pH control, and small amounts of alcohol could be tolerated. The method of Metcalfe compares favorably with the perchloric acid titration and the sodium lauryl sulfate titration methods.

Kaito and Kobayzshi[116] reported a direct two-phase titrimetric method for the determination of organic nitrogen compounds using tetraphenylborate. They found Nile Blue to be superior to bromophenol blue as an indicator.

Uno and co-workers[238] established a volumetric method for the determination of quaternary ammonium salts, using $NaBPh_4^+$ with methyl orange as the indicator. The method is applicable to salts with long (C_{16}) side chains. They reported that methyl orange does not show its acid color when added to these salts, even in acidic solution, but does show its acid color at the end-point when titrated with sodium tetraphenylborate.

Gyenes[85] described several methods for the determination of N-(*o*-bromobenzyl)-N-ethyl-N, N-dimethylammonium *p*-toluene sulfonate by reaction with tetraphenylborate. Gravimetric determination of the precipitate gave an average result equal to 99.8 ± 0.6% of the expected value. The precipitate was also dissolved in a 1:1 mixture of methylethylketone and acetic anhydride and titrated in a back-titration procedure using standard perchloric acid and standard sodium acetate solution. The N(*o*-bromobenzyl)-N-ethyl-N,N-dimethylammonium *p*-toluene sulfonate was also determined in water by extracting it from a basic solution into chloroform, where it was titrated with 0.02M $NaBPh_4$, using Tropoelin 00 indicator.

Cross[47] investigated the direct titrimetric precipitation methods of Uno and of Patel and Anderson at three selected pH values. The resulting precipitates were examined by infrared spectroscopy and chromatography and certain structures classified. By this method, cations can be arbitrarily classified as group–(A): benzethonium, cetyltrimethylammonium, distearyldimethylammonium, cetyldimethylethylammonium, laurylmethylmorpholinium. trimethyl(ethyllauroylamino)ammonium, cetyldimethylbenzylammonium, and phenoctide;(B): laurylisoquinolinium, 2-methyl-4-amino-N-laurylquinolinum, alkylpyridinium, and alkylbiguanidinium; and (C): nonquaternary ammonium compounds that are deprotonated in alkaline solutions.

D. Spectral Methods

Spectral methods have been used for the determination of certain cations following separation as the tetraphenylborate salt. Reed and Scott[187] developed a method for the determination of potassium in $KBPh_4$ by the use of flame photometry. The precipitated $KBPh_4$ was dissolved in a mixture of acetone and water and the resulting solution was analyzed directly. The potassium can also be converted to a water-soluble compound by heating the tetraphenylborate for 20 minutes at 350°C or by boiling in an aqueous solution of mercuric chloride. The methods are suitable for the determination of potassium in soils and micaceous minerals without interference from excess $NaBPh_4$ or other materials. Collins[42] proposed a flame photometric method for determining cesium and rubidium in oil-field waters which enabled them to be detected at concentrations less than 0.05 mg/liter. The tetraphenylborate salts were extracted into nitroethane, and the solutions were aspirated directly into the flame. The effectiveness of the extraction was independently checked, using radiotracer techniques. Schulte and Corey, [203] in the determination of potassium in soils, recommended the extraction of $KBPh_4$ into acetone, acidification with H_2SO_4, evaporation of the acetone, and determination of potassium by the flame photometry of the resulting aqueous solution.

Simon[215] developed a spectrophotometric method for the determination of the tetraphenylborate anion, taking advantage of the fact that it forms an insoluble precipitate with the dye rosaniline. The decrease in the absorbance of a solution containing excess rosaniline was found to be proportional to the amount of tetraphenylborate added to it. Crane and Smith[45] studied the effects of pH, ionic strength, and excess reagent on the completeness of the precipitation of ammonium ion with tetraphenylborate. Their procedure employs ninhydrin to develop a color. with the ammonium ion remaining in solution after precipitation. The color was measured spectrophotometrically.

Korenman and co-workers[124] reported an extraction and photometric procedure for potassium, cesium, and thallium(I); it involves dissolution of the tetraphenylborate precipitate in acetone. treatment with hydrochloric acid and an indicator, extraction with benzene, and measurement of the absorbance of the extract.

Rudnev and co-workers[194] determined small amounts of thallium(I) in mining samples by separating it with the "collectors" Bi_2S_3 and $KBPh_4$ and determining the collected thallium, using rhodamine B. Skinner and Docherty[217] reported an automated ultraviolet absorptimetric method for potassium. The potassium was precipitated with sodium tetraphenylborate and the unconsumed tetraphenylborate determined by measuring its ultraviolet absorption.

Ammonium, potassium, rubidium, and cesium, if present together, will precipitate together upon addition of tetraphenylborate. In a recent investigation, Kiss-Eröss and co-workers[121] recorded the infrared spectra for sodium, potassium, rubidium, cesium, and ammonium tetraphenylborate salts in KBr pellets between 400 and 4000 cm^{-1}. They found that the spectra of the alkali tetraphenylborates are practically identical. Apparently the differences in the electronegativities of the cations have little effect on the absorption bands arising from the tetraphenylborate anion. However, the spectrum of ammonium tetraphenylborate is significantly different. The stretching and bending vibrations of the NH_4^+ group in ammonium tetraphenylborate appear at 3223 and 1405 cm^{-1}, respectively. The authors used the 1405 cm^{-1} band to determine ammonium in the presence of potassium, rubidium, and cesium and showed that ammonium can be determined in the presence of the alkali metals by using infrared spectroscopy without a preliminary separation. Their determination of the ammonium in concentrations ranging from 10.00 to 84.21 wt % gave a standard deviation of ± 4.05% and an error of -3.00%.

Neu[164] developed a colorimetric method for the identification of alkaloids and organic bases by reacting their tetraphenylborate precipitates with 3-hydroxy-phenylbenzo-γ-pyrone, which gave characteristic colors in the orange and red regions. The method is useful for both spot tests and paper chromatography. De LaRubia and Blasco[52] developed a turbidimetric method for potassium, using sodium tetraphenylborate. They overcame the principal difficulty, the turbidity of the reagent solution itself due to decomposition, but preparing it in a suitable buffer solution. The method was highly satisfactory in the concentration range of 5 to 100 μg K_2O/ml of sample solution. Bladh and Gedda[21] determined potassium by precipitation with $NaBPh_4$. The excess reagent was determined by turbidimetric titration with cetyltrimethylammonium bromide.

Bobtelsky and Cohen[24] did a heterometric study of the reactions between alkaloids and other large nitrogen-containing compounds with tetraphenylborate and considered their analytical applications. In general, the method employing tetraphenylborate was less sensitive than the bismuth iodide method, but with acriflavine and rivanol it was more sensitive. The compounds investigated were acriflavine, rivanol, nitron, cinchonine, quinine, strychnine, papaverine, sparteine, phenanthroline, pyramidone, antipyrine, atropine, and oxine. A method for their determination was proposed.

A method for the determination of ^{137}Cs in radioactive wastes was described by Testemale and Girault.[230] The radioactive sample was mixed with a natural cesium carrier, extracted into isoamyl alcohol containing 0.05M $NaBPh_4$, and subjected to gamma-ray spectrometry. Bastian and Liser[9] determined potassium in rubidium and cesium salts by activation analysis. The alkali metal ions were sorbed on a column of $TiFe(CN)_6$. The potassium was determined by irradiation in a neutron flux of 10^{11}-10^{13} neutrons/cm^2/sec for 8 to 24 hours. Then the potassium was eluted with HCl and precipitated with tetraphenylborate for counting of the ^{42}K.

Neu[163] noted that tetraphenylborate forms diphenylborinic acid esters with hydroxyalkyl(aryl)amines and that this reaction offers a means for detection of tetraphenylborate.

E. Electroanalytical Methods

A variety of electroanalytical methods has been employed in the determinative step in analytical procedures using tetraphenylborate. Of these, potentiometry, coulometry, and amperometry have been the most popular. Geyer and Bormann[75] proposed a direct potentiometric determination of potassium using tetraphenylborate as the titrant. To carry out this determination an indicator electrode was developed, consisting of copper or silver plated on platinum and amalgamated with mercury. The method worked well on pure KCl solutions but was subject to errors in the presence of foreign ions. Below pH 2.5 the reagent decomposed, but in the pH range 2.5 to 10.2 the results were satisfactory.

Heyrovsky[100] carried out titrations of aromatic boron compounds with mercuric nitrate and perchlorate in 0.1M acetate solution. The endpoints were detected potentiometrically by using a mercury-coated platinum electrode as the indicator electrode and an SCE as the reference electrode, or amperometrically with a dropping mercury electrode and an SCE. Tetraphenylborate and other borates were determined in this way. Compounds which contain more than one phenyl group were found to react in two stages and to yield two separate potential jumps. The reverse titration of Hg^{++} with tetraphenylborate was also found to be possible. A continuation of this study[101] gave information on the roles of the intermediates formed and their effects on the polarograms and titrations. The effects of bromide, iodide, thiocyanate, and acetone were studied. The method was found to be suitable for the determination of potassium, thallium(I), silver, and certain protonated nitrogen compounds.

Geyer and Frank[77] proposed a glass electrode as the indicator electrode in the direct titration of potassium with calcium tetraphenylborate. The electrode (whose composition was 62% SiO_2, 33% Na_2O, and 5% Al_2O_3) is sensitive to sodium and potassium, slightly sensitive to cesium, and almost insensitive to calcium, magnesium, and lithium. At pH 7.1 this electrode can follow the precipitation of $KBPh_4$ with a $Ca(BPh_4)_2$ reagent solution.

Havir[91] developed a method for the microdetermination for potassium, rubidium, and cesium with tetraphenylborate by indirect potentiometric titration. The cation was precipitated by tetraphenylborate, the precipitate was filtered and dissolved in acetone, and the solution was titrated potentiometrically with silver nitrate. Bluemel[23] reported an industrial control method for the determination of K_2O. The potassium was precipitated by an excess of tetraphenylborate and filtered off, and the excess reagent was titrated with an 0.002N solution of thallium(I) using potentiometric end-point detection.

Levins and Ikeda[133] developed a direct potentiometric titration for polyethyleneglycols and their derivatives, using tetraphenylborate as the titrant in the presence of barium ion. These compounds, which formed insoluble complexes with tetraphenylborate when barium is present, permitted both titrimetric and gravimetric determinations and reacted stoichiometrically in the molecular weight range of 600 to 4000. The precipitate formed contained 2 moles of tetraphenylborate and 10.4 ± 0.2 moles of ethylene oxide for each mole of barium. The electrode system consisted of a silver indicator electrode and a calomel or silver-silver chloride reference electrode with a suitable salt bridge. Well-defined titration curves were obtained, although the slopes in the vicinity of the inflection points were very small, typically about 2mV/0.01 ml.

Seher[210] developed a volumetric method for nonionic surfactants in which the glycol derivative was precipitated with tetraphenylborate as a complex containing barium. The precipitate was dissolved in dimethylformamide and decomposed in a mercuration procedure using 0.5M $Hg(NO_3)_2$. The excess Hg^{++} was then titrated with NH_4CNS using Fe^{+++} as the indicator.

Amperometric titrations have been successfully applied to a number of analytical systems which make use of tetraphenylborate as a precipitant. The tetraphenylborate anion does not yield a reduction wave at the dropping mercury electrode. However, it does yield anodic waves. The anodic waves are the basis for the amperometric methods. Three reviews of the literature of this area have been made by Stock.[221-223]

Smith and co-workers[218] developed an amperometric method for end-point detection in the direct titration of potassium with tetraphenylborate. In aqueous solution the tetraphenylborate ion gives two anodic voltammetric waves at the graphite electrode. These waves form a basis for the direct titrimetric determination of potassium. The authors say that the method is simple and rapid, and that it eliminates the need to filter, wash, and redissolve the precipitate as in the indirect titration procedures. The method is relatively free from interferences and tolerates large amounts of chloride and other commonly encountered anions. It was successfully applied to several refractory and silicate samples.

Turner and Elving[237] studied the electrooxidation of tetraphenylborate at a pyrolytic graphite electrode and suggested the following reaction sequence to explain the two waves observed:

$$B(C_6H_5)_4^- \longrightarrow B(C_6H_5)_2^+ + (C_6H_5)_2 + 2e^-$$

$$B(C_6H_5)_2^+ + H_2O \longrightarrow B(C_6H_5)_2OH + H^+$$

The second wave, which is less well-defined than the first, represents a 2-electron process which involves the oxidation of diphenylborinic acid:

$$B(C_6H_5)_2OH + 2\,H_2O \longrightarrow B(OH)_3 + (C_6H_5)_2 + 2H^+ + 2e^-.$$

Grubitsch[83] reported a method for the rapid determination of potassium in cement that used amperometric end-point detection. In a sample containing 40μg of potassium, the potassium can be determined by precipitating $KBPh_4$, dissolving this in 50ml of acetone, and titrating with 0.0005N silver nitrate. His results for cement samples compare favorably with the flame photometric and chloroplatinate methods.

Florea[64] determined acridine and certain of its derivatives by conductometric titrations of 0.01M solutions of their salts with 0.01M tetraphenylborate. The precipitates were recovered, their thermal properties were studied, and their absorption spectra recorded. Ebel[58] studied the conductometric and oscillometric titrations, with 0.05N sodium tetraphenylborate, of alkaloids dissolved in dilute acetic acid, using two Pt wire electrodes. Rondeau and co-workers[192] determined potassium in the 0.01 to 0.02M range by the precipitation of $KBPh_4$ and the back titration of the excess tetraphenylborate with KCl. The end-point was detected by thermometric methods.

Phaf[178] reported a rapid and simple titrimetric method for the determination of alkaloids and potassium by means of tetraphenylborate, using a "reversed dead-stop" end-point detection technique. The sample was precipitated with tetraphenylborate, and the precipitate was dissolved in acetone and titrated with 0.1N $AgNO_3$ to the end-point. Two identical silver electrodes were used, and a potential of 25 mV was applied across them. The method gave satisfactory results with potassium, morphine, papaverine, and reserpine.

Havir and Krivanek[93] used an isotope dilution procedure for the analysis of potassium, rubidium, and cesium. These ions were precipitated as their tetraphenylborate salts, and the precipitate was dissolved in acetone and titrated with $AgNO_3$ solution labeled with ^{110}Ag. The $AgBPh_4$ was filtered and the activity of the filtrate measured with a Geiger-Muller counter.

Coulometric titrations of tetraphenylborate have received considerable attention. In common with many other analytical methods based on tetraphenylborate, these are subject to limitations because of the inherent lack of stability of the tetraphenylborate anion, which can be decomposed by both proton and radical attack.[145,147] These methods electrically generate the silver ion which, in turn, reacts with tetraphenylborate to form $AgBPh_4$.

Suzuki[224] titrated sodium tetraphenylborate (9 to 36 mg) with Ag(I) electrically generated at 10 to 30 mA in a 0.5M solution of $NaNO_3$ in 60% acetone containing 0.02M acetic acid. The end-point can be located either potentiometrically or amperometrically. Potassium (1 to 4 mg) was precipitated as $KBPh_4$, and the precipitate was dissolved in acetone and then subjected to coulometric titration.

Patriarche and Lingane[174,175] also studied the potentiometric coulometric titration of tetraphenylborate ion with electrogenerated silver ion in aqueous acetone solutions. They found the reaction to be stoichiometrically exact in a neutral aqueous acetone medium containing 35 to 50% by volume of acetone with 0.4M sodium nitrate as the supporting electrolyte. They avoided the decomposition of tetraphenylborate by dissolving the wet precipitate in acetone. The method gave good results with potassium, rubidium, and cesium. These authors also applied similar coulometric procedures to the determination of alkaloids and salts of organic bases after precipitation as the tetraphenylborates. Patriarche[173] described coulometric titrations of alkaloids, nitrogenous organic bases, and quaternary ammonium salts, using electrolytically generated silver(I). The bases were precipitated with BPh_4^- and the precipitate dissolved in acetone and titrated coulometrically, using standard techniques. For 21 compounds the mean error was ± 0.1 mg for 1 to 10 mg base. The method was not successful with sparteine.

Moody and co-workers[151] also applied the coulometric titration of tetraphenylborate ion with electrogenerated silver ion to the determination of potassium and polyethylene glycols. The sample was separated as the tetraphenylborate salt, which was then dissolved in the generating electrolyte (40% acetone) and titrated amperometrically. Samples of 0.1 to 4/μeq of sodium tetraphenylborate were determined with a precision of 1%. The overall accuracy ranged from -7 to -3% for samples containing 1-4/μeq of potassium. Artificial serum samples, because of protein interference, gave discordant results. The method developed for polyethyleneglycols in the molecular weight range 600 to 4000 gave errors of less than 5% when reasonable care was exercised.

In a study of plastic electrodes specific for organic ions, Higuchi and co-workers,[103] using a PVC-amide indicating electrode and a 0.01M solution of sodium tetraphenylborate as the reagent, developed titrimetric procedures for benadryl•HCl and dextromethorphan•HBr.

F. Tetraphenylborate Salts of Other Complex Ions

Tetraphenylborate has found wide usage in the field of preparative inorganic chemistry as a reagent for making crystalline derivatives of a variety of complexes. The negatively substituted, and hence more stable, tetraarylborates suggest themselves as interesting possibilities for this purpose.[38,146,147,152,240]

Headly and co-workers[94] prepared a series of complexes of the formula [MX(Qas)]R, where Qas is (o-$Me_2AsC_6H_4)_3As$; X and R can be tetraphenylborate as well as other ligands; and M is Pt, Pd, or Ni. All these complexes are five-coordinate species, are diamagnetic, and behave as 1:1 electrolytes. Visible and UV spectra were recorded and a ligand-field interpretation of them was given. Hartley and co-workers[88] used the quadridentate ligand tris(o-diphenylphosphinophenyl)phosphine to form Co(II) complexes of the type [CoX(QP)]Y, where X = Cl, Br, and I; Y = BPh^{-4} or ClO_4; and QP = the ligand. Razuvaev and co-workers[186] studied the acid cleavage of bis(ethylbenzene)chromium tetraphenylborate and dicumenechromium tetraphenylborate and the products formed. A pyrolysis of bis(ethylbenzene)chromium tetraphenylborate yielded a brown paramagnetic solid tetraphenylborate which ignited on contact with the air.

In a study of the reactions of metal carbonyls, Hieber and Freyer[102] synthesized the complex

$[Co(CO)_3 \cdot 2I]\ [BPH_4].$

Tsutsui and Zeiss,[235] in a study of π complexes of the transition metals, formed interesting complexes with manganese and chromium:

$[(C_6Me_6)_2Mn]\ [BPh_4]$ and $[(C_6Me_6)_2Cr]\ [BPh_4].$

Das and Kitching,[49] in a study of the coordination chemistry of tin, prepared a number of complexes of types $[(CH_3)_2SnL_4]^{++}\cdot 2\ BPh_4$, where L = DMSO, DMF, and DMA; and $[(CH_3)_3SnL_2]\ BPh_4^-$, where L = H_2O, DMSO, DMF, and DMA. These compounds are:

Tetrakis(dimethylsulfoxide)dimethyltin(IV)bis (tetraphenylborate)

Tetrakis(dimethylformamide)dimethyltin(IV) (tetraphenylborate)

Tetrakis(dimethylacetamide)dimethyltin(IV) bis (tetraphenylborate)

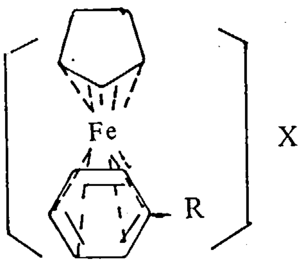
Bis(dimethylacetamide)trimethyltin(IV)tetraphenylborate

Bis(dimethylsulfoxide)trimethyltin(IV)tetraphenylborate

Bis(dimethylformamide)trimethyltin(IV)tetraphenylborate

Diaquotrimethyltin(IV)tetraphenylborate.

Nesmeyanov and co-workers[161] studied the mobility of the halogen on the benzene ring of the complex chlorobenzene-cyclopentadienyl iron



where R = Cl and X = BPh_4. The chlorine was removed and replaced via treatment with various bases. Five of the ten compounds so produced were isolated as their tetraphenylborate salts.

Fischer and co-workers[60] prepared $Fe(C_6H_3Me_3)_2{}^{++}\cdot 2BPh_4$ in a study of K-edge absorption spectra.

Nolte and Gafner[167] described the preparation, the nmr spectrum, and the molecular structure of the neutral compound $Rh[P(OMe)_3]BPh_4$. This compound is the first recognized example of the coordination of the tetraphenylborate anion to a transition metal through an arene ring. The addition of $NaBPh_4$ to $(C_8H_{12}RhCl)_2$ and an excess of $P(OMe)_3$ in methanol gave an ionic derivative $\langle Rh[P(OM)_3]_5\rangle$ BPh_4 which decomposed in air to yield deep yellow monoclinic crystals of the neutral compound. Schrock and Osborn[202] prepared several complexes of tetraphenylborate with Rh(I) and Ir(I) in which tetraphenylborate coordinates to the metal via π bonded interaction. These compounds are:

Rh(norbornadiene)BPh_4
Rh(1,3-butadiene)BPh_4
Rh(2,3-dimethyl-1,3-butadiene)BPh_4
Rh(1,3-cyclohexadiene)BPh_4
Rh(1,5-hexadiene)BPh_4
Rh(1,5-cyclooctadiene)BPh_4
Rh(1,3,5,7-cyclooctatetraene)BPh_4
Rh(ethylene)$_2$ BPh_4
Ir(1,5-cyclooctadiene)BPh_4
Ir(1,5-hexadiene)BPh_4.

These authors consider the phenyl ring to be slightly puckered (ca 6°) into a boat form, the bonding to involve an interaction using all sixπ electrons of the phenyl ring, and the metal to achieve an inert gas configuration. They predict that tetraphenylborate, which is forming complexes analogous to those of the cyclopentadienyl anion, should have an extensive coordination chemistry.

Other platinum metal tetraphenylborate complexes were prepared by Fischer and Zahn[61] in a study of the chemistry of cyclopentadienylrhodium and cyclopentadienyliridium. The complexes prepared were $[Rh(C_5H_5)_2]BPh_4$ and $[Ir(C_5H_5)_2]BPh_4$. Farago and co-workers[59] prepared tetraphenylborate and perchlorate salts of the nickel(II) complexes of ethylenediamine and determined their visible and infrared spectra, electrolytic conductances, and magnetic susceptibilities. These results permitted establishment of the structure of the nickel(II) complexes.

A patent[271] covering the preparation of tetraphenylborates of arene chromium complexes reports the preparation of a red diphenylchromium, an orange benzene-diphenylchromium, and a bisbenzenechromium tetraphenylborate. Hein and Reinert[95] reported the preparation of the yellow crystalline $(C_6H_5)_2CrPBh_4$ in a study of the reactions of bis-biphenylchromium. Sacco and Freni[196] prepared the interesting gold compound $[(p\text{-}CH_3C_6H_4NC)_4Au]BPh_4$, which is a white solid.

G. Solid Organic Derivatives

In a wide variety of stuides, tetraphenylborate has been used to make solid derivatives useful in the characterization of certain functionalities and compounds. This use is exemplified in the following studies of compounds of pharmacological interest: "Tetrahydrofuran (muscarine) Derivatives,"[272] "Stereochemicstry of the Tropane Alkaloids•XII. The Total Synthesis of Scopolamine,"[54] "Pharmacologically Interesting Amino Ethers,"[191] and "The Alkaloids from Lobelia Syphilitica."[234] In some preparative and theoretical studies, Wittig formed derivatives in such diverse chemical systems as "Ylides of the N,N-dimethylpyrrolidinium System"[263] and "Lithium Diethylamide as Hydride Donro"[264] Other studies reporting tetraphenylborate derivatives are "Tetrakis(dimethylamino) Ethylene•V. The Reaction of Tetrakis(diamino)Ethylene with Lewis Acids,"[254a] "2,2-Dialkyltriazinium Salts,"[78] "Rearrangements of Quaternary Allylammonium Salts,"[96] "Oxidation Products of Thiocarboxylic Acid Amides•IV. Oxidation Products of Secondary and Tertiary Thioamides,"[246] and "New Tropylium Salts. Polarography of the Tropylium Ion."[244]

V. ANALYTICAL APPLICATIONS OF OTHER TETRAARYLBORATES AND RELATED COMPOUNDS

The first tetraarylborate, tetraphenylborate, was introduced into analytical chemistry in the years 1949-1959. As outlined in a preceding section, this compound, as the lithium or sodium salt, was recommended for the precipitation of potassium, rubidium, cesium, protonated basic nitrogen, and quaternary ammonium compounds. However, the reagent has limited stability in aqueous solution. This fact prompted several workers to investigate the possibilities of preparing a similar molecule that would be more stable.

Wittig and Raff[258] synthesized sodium triphenylcyanoborate (Caesignost) and found it to be more stable than tetraphenylborate. They noted that it is less susceptible to acid decomposition and participates less easily in the mercuration reaction than sodium tetraphenylborate. Although Wendlandt[252, 253] found in thermogravimetric studies that sodium, rubidium, cesium, and thallium(I) triphenylcyanoborates do not have better thermal stabilities than the corresponding tetraphenylborates, the triphenylcyanoborates of organic basic nitrogen compounds are more stable than corresponding tetraphenylborate salts.[86,204 252] The reactions of sodium triphenylcyanoborate with metal ions were studied by Havir,[92] especially by electrometric methods. He found that cesium, silver, copper(I), and thallium(I) all give precipitates and that rubidium coprecipitates badly with the cesium salt. The reagent was successfully used in detecting and determining small amounts of cesium. The potassium ion was not precipitated. It was several years later, in 1968, when Bauman[10] reported that sodium triphenylcyanoborate quantitatively separates cesium from potassium. A radioactive tracer technique was used to develop the analytical procedure, with expectations of applying the method to separations of radioactive cesium. Cesium analyses were performed on samples ranging from 20 to 50mg with standard deviations of 1.40 mg and 2.24 mg, respectively, and a maximum coefficient of variation of 7.1%. The precipitation of cesium in the presence of up to 200 mg of potassium was satisfactory if the digestion time was limited to 30 minutes. Sodium triphenylcyanoborate underwent a decomposition similar to the decomposition of sodium tetraphenylborate, but its decomposition has not yet been explained. Bauman reported that in periods varying from a few hours to several weeks the salt solution becomes turbid and a progressively strong phenolic odor develops. Data characteristic of the determination of cesium in the presence of potassium are summarized in Table 8.

As reported in an earlier section, Wittig and Herwig[259] prepared the lithium salts of tetrakis(*p*-methylphenyl)borate, tetrakis(*m*-methylphenyl)borate, and tetrakis(*o*-methylphenyl)borate. They did not report the analytical properties of these salts. However, they synthesized the sodium salts of tris(*p*-methylphenyl)cyanoborate, tris(*m*-methylphenyl)cyanoborate, and tris(*o*-methylphenyl)cyanoborate. They investigated the analytical potential of sodium tris(*p*-methylphenyl)cyanoborate and found that it readily forms a heavy precipitate with cesium. With rubidium, the precipitate forms slowly. Cadmium forms a slight precipitate, while copper and silver form flaky precipitates. Calcium, barium, strontium, ammonium, zinc, iron(III), cobalt, nickel, and manganese apparently give no precipitates.

In that same year, Nesmeianov and his coworkers[162] reported the preparation of potassium tetrakis(*p*-methylphenyl)borate, but four years passed before Sazonova and Leonov[198] prepared the sodium salt and also suggested lithium tetrakis(*p*-methylphenyl)borate as a possible reagent for sodium. Murphy[157] prepared the mixed magnesium-sodium salt of tetrakis(*p*-methylphenyl)borate and found it to be less stable than sodium tetraphenylborate when evaluating it as an analytical reagent for potassium.

Sodium tetraphenylethynylborate reported by Kruerke[130] gave crystalline precipitates of undetermined compositions with ammonium, potassium, iron(II), calcium, and aluminum. In the same year, Kruerke[131] reported magnesium di-tetrakis (phenylethynyl)borate. No formal analytical studies have been reported for this unique anion, however.

In 1957, Sazonova and co-workers[199] reported preparing potassium tetrakis(*p*-methoxyphenyl)borate but did not discuss its stability. Humecki[109] prepared the mixed magnesium-sodium salt and evaluated it as a possible potassium reagent. The highly electrondonating methoxy group in the para-phenyl ring position apparently increases the instability of the reagent in

TABLE 8

Precipitation of Cesium in the Presence of Large Quantities of Potassium Using Sodium Triphenylcyanoborate

Cesium taken. mg	KCl added, g	Cesium Found, %		Potassium coprecipitated, %
		Gamma spectrometry	Gravimetric	
20	0	98.8	98.3	
20	5	59.6	59.4	
20	10	59.4	59.4	

aqueous solutions. He was not able to obtain meaningful analytical results. Vandeberg,[239] using a proton scavenger and "in situ" reaction, prepared sodium tetrakis(*p*-methoxyphenyl)borate in good yields. He noted a high degree of selectivity for the cesium ion but a lack of stability in aqueous solution.

The highly fluorinated lithium tetrakis(pentafluorophenyl)borate salt reported by Massey and Park[144] gave a potassium precipitate seemingly too soluble for analytical applications. No report was made on the activity of the anion toward other cations. The authors pointed out that this highly fluorinated compound attacks glass containers.

Holzapfel and Richter[104] made the lithium and sodium salts of tetrakis(*p*-biphenylyl)borate anion, but did not report their solubilities or mention the selectivity of this anion for other cations. Vandeberg[239] isolated lithium tetrakis(*p*-biphenylyl)-borate in low yields and made a preliminary study of its properties as a gravimetric reagent. The lithium salt was insoluble in water but soluble in methanol, ethanol, propanol, or acetone. A solution of the compound in ethanol was tested as a precipitant for the alkali metal cations and with cesium yielded an insoluble precipitate. Efforts to develop analytical procedures using this anion in non-aqueous systems are being pursued.

Sodium tetrakis(*p*-chlorophenyl)borate was synthesized and independently reported by three research teams.[22,38,106] However, it was Cassaretto and co-workers[38] who evaluated it as an analytical reagent for potassium. Their results are summarized in the following table.

TABLE 9

Results of Quantitative Tests for Potassium Ion Using Sodium Tetrakis(*p*-Chlorophenyl)Borate

K^+ taken (mg)	K^+ found (mg)
47.6	45.6
47.6	44.9
47.6	44.9
47.6	45.1
20.0	19.7
20.0	19.5
20.0	19.6
21.4	21.0
21.4	21.0

The thermal stability of the potassium salt was examined by drying at 110°C in an air oven. After the initial constant weight was established (usually in about 30 min), no further weight loss occurred during a 1 to 3-hr drying period. The authors reported that potassium tetrakis(*p*-chlorophenyl)-borate appears to be more crystalline in character, to flocculate more readily and settle more rapidly, and to be generally easier to handle than potassium tetraphenylborate, but it has the disadvantage of being more soluble than potassium tetraphenylborate. The tetrakis(*p*-chlorophenyl)borate anion forms heavy precipitates with potassium, ammonium, rubidium, and cesium, while barium, calcium, copper, nickel, cadmium, and cobalt give no precipitates. The compound was found useful as a reagent for the formation of derivatives of quaternary ammonium and protonated basic nitrogen compounds. Representative derivatives and their melting points are listed in Table 10. Other derivatives are also possible as indicated by the precipitates formed with 1-phenylethylamine, N-ethylamine, dibenzylamine, atropine, hexamethylenetetraamine, 1,6-diaminohexane, glycine, and tetrabutylammonium chloride.

TABLE 10

Some Basic Nitrogen Compounds Forming Salts With Tetrakis(*p*-Chlorophenyl)Borate Anion

		% Nitrogen	
Material Tested	M.P. (°C)	Calculated	Found
Benzidine	173-176	4.24	4.43
n-Butylamine	117-118	2.63	2.52
Brucine	148-149	3.29	3.24
Quinine	146-151	3.58	2.79

Sodium tetrakis(*p*-fluorophenyl)borate was independently described by Holzapfel and co-workers[106] and Moore and co-workers.[152] The latter authors investigated the analytical properties of sodium tetrakis(*p*-fluorophenyl)borate and indicated that its anion was remarkably selective for cesium. They based their conclusions on the data shown in Tables 11, 12, and 13. Previously, it had not been possible to separate cesium from rubidium satisfactorily be precipitation techniques. The extent of the coprecipitation of potassium and rubidium is shown in Tables 12 and 13.

TABLE 11

Recovery of Cesium From Pure Cesium Solutions Using Sodium Tetrakis(*p*-Fluorophenyl)Borate

Cs taken (mg)	Cs found (mg)	% Recovery
65.3	64.5	98.8
65.3	64.3	98.5
32.7	32.5	99.4
32.7	32.2	98.5
32.7	32.2	98.5
32.5	32.0	98.5
32.5	31.9	98.2
32.5	31.9	98.2
32.5	31.8	97.8
16.3	16.0	98.2
16.3	16.2	99.4
16.2	16.0	98.8
16.2	15.9	98.1

TABLE 12

Recovery Of Cesium In The Presence of Potassium Using Sodium Tetrakis(*p*-Fluorophenyl)Borate

Cs taken (mg)	K taken (mg)	Cs found (mg) (gravimetric)	K found (mg)	Corrected result for Cs (mg)
32.5	11.9	32.0	0.02	32.0
32.5	11.9	32.0	0.02	32.0
32.5	23.8	32.0	0.04	31.9
32.5	23.8	31.9	0.03	31.8
32.5	23.8	31.8	–	–
32.5	23.8	31.8	--	
32.7	23.8	32.3	–	
32.5	35.7	32.2	0.06	32.0
32.5	35.7	32.1	0.04	32.0

TABLE 13

Recovery Of Cesium In The Presence Of Rubidium Using Sodium Tetrakis(*p*-Fluorophenyl)Borate

Cs taken (mg)	Rb taken (mg)	Cs found (mg) (gravimetric)	Rb found (mg)	Corrected Result for Cs (mg)
32.5	2.8	32.3	0.22	32.0
32.5	2.8	32.3	0.20	32.0
32.5	8.5	33.2	0.63	32.3
32.5	8.5	33.2	0.71	32.2
32.5	14.1	33.8	1.25	32.0
32.5	14.1	33.7	1.13	32.1
32.5	14.1	33.8	–	–

The authors noted that cesium tetrakis(*p*-fluorphenyl)borate separates as a white crystalline compound with good analytical characteristics. It is easily separated by filtration and it achieves constant weight rapidly at 110°C. Prolonged heating (18 hours) causes no further weight loss or signs of decomposition. In addition to cesium, the anion forms precipitates with silver, thallium(I), and rubidium but not with potassium or ammonium.

McLafferty[137] also tested the reagent as a precipitant for quaternary ammonium ions and other ions containing a protonated basic nitrogen atom. The following compounds gave precipitates: quinidine, cinchonine, di-n-heptylamine, tetrabutylammonium iodide, *p*-bromoaniline, aniline, brucine, and quinine.

Vandeberg and co-workers[240] continued the study of substituent effects on the stability and selectivity of tetraarylborates. Two new tetraarylborate compounds, sodium tetrakis(*p*-trifluoromethylphenyl)borate and sodium tetrakis(*m*-fluorophenyl)borate, were prepared, and their analytical properties were investigated.

In a qualitative test of the tetrakis(*p*-trifluoromethylphenyl)borate reagent, potassium, ammonium, silver, and thallium(I) gave heavy precipitates; rubidium and cesium yielded slight precipitates; and copper(II), nickel, cobalt, calcium, barium, and magnesium gave no precipitates. This reagent was tested as a precipitant for quaternary ammonium and for the protonated forms of compounds containing basic nitrogen atoms. Results are summarized in Table 14.

TABLE 14

Some Basic Nitrogen Compounds Forming Salts With Tetrakis(*p*-Trifluoromethylphenyl)Borate Anion

Material Tested	M.P.(°C)	% Nitrogen Found	% Nitrogen Calc.
Tetrabutylammonium iodide	145-6	1.70	1.68
N-Butylamine	107-9	2.38	2.10
Benzidine	188-191	2.27	2.05
	not sharp	di-substituted salt	
Ethylamine	121-3	2.17	2.20
N-Ethylaniline	113-4	1.94	1.96
β-Alanine	>300	2.20	2.06
Ammonium hydroxide	185-6	2.29	2.30

In addition, quinidine, cinchonine, quinine, and 1-phenylethylamine gave heavy precipitates. This compound appears to be much superior to tetraphenylborate as a derivatizing reagent for some nitrogen compounds. Its principal advantage is that it yields highly pure derivatives, having sharp melting points and compositions agreeing well with the theoretical ones.

The reagent proved to have a high sensitivity for potassium, as summarized in Table 15.

For a comparison, the authors used several other tetraarylborates in a similar series of tests. The results are summarized in Table 16.

In their study of the properties of sodium tetrakis(*m*-fluorophenyl)borate, the authors found that this reagent gives heavy precipitation with cesium, silver, and thallium(I); medium precipitation with rubidium; and slight precipitation with potassium and ammonium. Table 17 summarizes a test of the sensitivity of the reagent as a precipitant for cesium as well as a series of similar tests with sodium tetraphenylborate, sodium tetrakis(*p*-fluorophenyl)borate, sodium tetrakis(*p*-chlorophenyl)borate, and sodium(*p*-trifluoromethylphenyl)borate.

The results of gravimetric tests using sodium tetrakis(*m*-fluorophenyl)borate to determine the recovery of cesium from pure cesium solutions are summarized in Table 18.

Several representative quaternary ammonium compounds and compounds containing a protonated basic nitrogen atom were precipitated with the tetrakis(*m*-fluorophenyl)borate anion. Some of the precipitates were isolated, recrystallized, and

TABLE 15

Recovery Of Potassium From Pure Potassium Solutions With Tetrakis(*p*-Tri- fluoromethylphenyl)Borate Anion

K taken(mg)	K found(mg)	% Recovery	K taken(mg)	K found(mg)	% Recovery
20.38	20.30	99.6	4.98	4.80	96.4
20.38	20.28	99.5	4.98	4.87	97.8
12.46	12.29	98.6	4.98	4.92	98.8
12.46	12.31	98.8	4.98	4.91	98.6
12.46	12.49	100.2	4.98	4.89	98.2
12.46	12.40	99.5		$\sigma = \pm 0.05$	
12.46	12.34	99.0			
12.46	12.31	98.8			
	$\sigma = \pm 0.08^a$				

[a] σ=standard deviation.

TABLE 16

Comparative Sensitivities Of Some Tetraarylborates as Precipitants for Potassium

K taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4p\text{-}F)_4$	$NaB(C_6H_4p\text{-}Cl)_4$	$NaB(C_6H_4m\text{-}F)_4$	$NaB(C_6H_4p\text{-}CF_3)_4$
2.0	None	Heavy, immediate	Heavy, immediate	Heavy, immediate	Heavy, immediate
0.2	None	Heavy, immediate	Heavy, immediate	Slight, slow	Heavy, immediate
0.1	None	Medium, Immediate	Medium, immediate	None	Heavy, immediate
0.05	None	Medium, slow	Medium, immediate	None	Heavy, immediate
0.02	None	Slight, slow	Slight, immediate	None	Medium, slow
0.01		Trace, slow	Slight, immediate	–	Medium, slow
0 005		None	Trace, slow	–	Slight, slow
0.002		None	None		Trace, slow

TABLE 17

Comparative Sensitivities Of Some Tetraarylborates As Precipitants For Cesium

Cs taken (mg/ml)	$NaB(C_6H_5)_4$	$NaB(C_6H_4p\text{-}F)_4$	$NaB(C_6H_4p\text{-}Cl)_4$	$NaB(C_6H_4m\text{-}F)_4$	$NaB(C_6H_4p\text{-}CF_3)_4$
2.0	Heavy, immediate	Heavy, immediate	Heavy, immediate	Heavy, immediate	Medium, immediate
0.2	Heavy, immediate	Medium, immediate	Heavy, immediate	Heavy, immediate	Slight, immediate
0.1		Slight, slow		Heavy, immediate	Trace, immediate
0.05		Trace, slow		Medium, immediate	Trace, immediate
0.02	Light, immediate	None	Slight, immediate	Slight, immediate	Trace, immediate
0.01	Slight, immediate	None	Slight, immediate	Trace, immediate	None
0.005	Trace, immediate	None	Slight, immediate	Trace, immediate	None
0.002	None	None	None	None	None
		None			

TABLE 18

Recovery of Cesium from Pure Cesium Solutions Using Sodium Tetrakis(*m*-Fluorophenyl)Borate

Cs taken(mg)	Cs found(mg)	% Recovery	Cs taken(mg)	Cs found(mg)	% Recovery
70.52	70.50	100.0	23.51	23.48	99.9
70.52	69.79	99.0	23.51	23.38	99.4
			23.51	23.28	99.0
47.02	46.99	99.9		$\sigma = \pm 0.09$	
47.02	46.94	99.8			
47.02	46.92	99.8	9.40	9.26	98.5
47.02	46.97	99.9	9.40	9.23	98.2
47.02	46.99	99.9	9.40	9.36	99.6
	$\sigma = \pm 0.03$		9.40	9.33	99.3
			9.40	9.43	100.3
23.51	23.33	99.2	9.40	9.46	100.6
23.51	23.26	98.9		$\sigma = \pm 0.09$	
23.51	23.46	99.8			

analyzed for nitrogen, and their melting points were determined. The results are given in Table 19. In addition, the anion forms heavy precipitates with N-butylamine, benzidine, N-ethylaniline, quinidine, and quinine.

This study also showed that potassium and cesium can be gravimetrically determined with either tetrakis(*p*-trifluoromethylphenyl)borate or tetrakis(*m*-fluorophenyl)borate. The precipitates separate as white crystalline compounds with desirable analytical properties. Sodium tetrakis(*p*-trifluoromethylphenyl)borate sodium tetrakis(*m*-fluorophenyl)borate appear to offer possibilities as reagents for use in quantitative analysis where interferences from coprecipitation are absent. Aqueous solutions of these reagents at pH 8 proved to be stable and very active when tested over a period of six months.

A 3,5-disubstituted tetraarylborate, lithium tetrakis(3,5-di-trifluoromethylphenyl)borate, was

TABLE 19

Some Basic Nitrogen Compounds Forming Salts with Tetrakis(*m*-Fluorophenyl)Borate Anion

Material Tested	M.P. (°C)	% Nitrogen Found	% Nitrogen Calc.
Trimethylamine	150-1	3.12	3.10
Tetrabutylammonium iodide	176-7	2.13	2.21
Brucine	141-2	3.64	3.55
Ethylamine	134-5	3.18	3.20
1-Phenylethylamine	122-3	2.86	2.73

cesium ion. The anion did not satisfactorily precipitate any of the above cations.

Meisters and co-workers[146] prepared and investigated the reagent properties of sodium tetrakis(*m*-trifluoromethylphenyl)borate. A dilute solution of the reagent gave heavy precipitates with cesium, thallium(I), and silver. Rubidium formed a precipitate only after a large excess of reagent was added. No precipitates formed with copper(II), cobalt, nickel, calcium, magnesium, barium, lithium, and potassium. This information indicated the possibility of using sodium tetrakis(*m*-trifluoromethylphenyl)borate as a selective reagent for cesium, especially for precipitating cesium in the presence of rubidium and potassium. Subsequent testing confirmed this possibility, and the results are summarized in Table 20. The extents of coprecipitation of foreign ions in the cesium precipitate were checked using flame photometry. Neither rubidium nor potassium was detected in the cesium precipitates, within the limits of detection of flame photometry (about 2 ppm). Results of these analyses are summarized in Tables 21 and 22.

TABLE 20

Recovery Of Cesium From Pure Cesium Solutions Using Sodium Tetrakis(*m*-Trifluoromethylphenyl)Borate

Cs taken (mg)	Cs found (mg)	% Recovery
24.78	24.39	98.4
24.78	24.34	98.2
24 78	24.32	98.1
24.78	24.37	98.3
24.78	24.59	99.2
24.78	24.56	99.1
	$\sigma = \pm 0.12$	
9.91	9.38	94.6
9.91	9 14	92.2
9.91	9.34	94.3
9.91	9 16	92.4
9.91	9.25	93.3
9.91	9 30	93.8
	$\sigma = \pm 0.10$	

In aqueous solution at pH 8, the reagent remained clear and colorless and was still effective in precipitating cesium after standing for four months. In acid media, it is comparable in stability to the other tetraarylborates which have strongly electronegative substituents in the para and meta positions on the benzene rings. The reagent proved unsuitable for precipitating protonated amines and basic nitrogen compounds under investigation.

VI. EXTRACTIVE SEPARATIONS USING TETRAPHENYLBORATE

Interest has been shown in the use of tetraphenylborate in separation procedures which do

TABLE 21

Recovery of Cesium in the Presence of Rubidium Using Sodium Tetrakis(*m*-Trifluoromethylphenyl)Borate

Cs taken(mg)	Rb taken(mg)	Rb found(mg)	Cs found(mg)	%Cs recovery
24.95	24.99	0.00	24.20	97.0
24.95	24.99	0.00	24.48	98.1
24.95	24.99	0.00	24.65	98.8
24.95	24.99	0.00	24.90	99.8
24.95	24.99	0.00	24.45	98.0
24.95	24.99	0.00	24 25	97.2
			$\sigma = \pm 0.26$	

TABLE 22

Recovery of Cesium in the Presence of Potassium Using Sodium Tetrakis(*m*-Trifluoromethylphenyl)Borate

Cs taken(mg)	K taken(mg)	K found(mg)	Cs found(mg)	% Cs recovery
24.95	30.00	0.00	24.61	98.6
24.95	30.00	0.00	24.52	98.3

not depend on the formation and collection of a precipitate. In the field of reactor technology there have been several publications describing the extraction of tetraphenylborate salts from nuclear wastes. A U. S. patent has been issued to McKenzie and Scholz[136] on a process for the recovery of cesium from waste liquids obtained in the processing of nitric acid solutions of neutron-irradiated uranium. Adding a solution of sodium tetraphenylborate, in a water-immiscible solvent, to an aqueous solution containing cesium led to the separation of an organic phase containing cesium tetraphenylborate. Krtil and co-workers[128] extracted cesium tetraphenylborate from aqueous solution by means of nitrobenzene. They investigated the effects of sodium, ammonium, iron(III), and pH on the system. Nitrobenzene proved to be the best of a number of organic solvents tested. Schonfeld and co-workers[201] found that sodium tetraphenylborate in combination with an aminopolycarboxylic acid gave a promising Cs enrichment in a process designed for the removal of cesium, strontium, and rare earth cations from dilute aqueous solutions by adsorption on foam surfaces.

Haruyama and Ashizawa[89] extracted trace amounts of the tetraphenylborate salts of cesium and francium into benzene or a 1:1 mixture of benzene and methylisobutylketone. The aqueous solution was at pH 5 and contained 0.003 to 0.1M $NaBPh_4$. Means for preventing emulsification of the organic layer and for avoiding interferences by potassium were described. Sekine and Dyrssen[211] studied the extraction of sodium and small quantities of potassium, rubidium, and cesium from aqueous solutions containing sodium tetraphenylborate, sodium perchlorate, and perchloric acid. Of the solvents studied (nitromethane, nitroethane, nitrobenzene, methylisobutylketone, and tributyl phosphate), nitromethane gives the highest distribution ratio (org/aq) for perchlorate, and nitrobenzene gives the highest distribution ratio and separation factor for the tetraphenylborates. By assuming that the tetraphenylborates are fully dissociated in both phases, most of the distribution data can be explained. The equilibrium constants and distribution ratios increase in the order sodium $<$ potassium $<$ rubidium $<$ cesium. Collins,[43] in the analysis of oil-field waters, extracted the tetraphenylborates of rubidium and cesium into nitromethane and determined the metals by flame photometry.

Beyermann[15] extracted the tetraphenylborate salts of biogenic amines and alkaloids into ethyl ether from aqueous solutions at pH 2 to 3. Hauptmann and Winter[90] developed a method for the thin-layer chromatographic separation of mixtures containing adrenalin and noradrenalin tetraphenylborates. The use of the tetraphenylborate reagent avoids the conversion of the compounds into the free amine, which always results in a loss of yield. Standard techniques were employed for the elution, the development of the spot, and the measurement of its optical density.

DeMumbrum[53] reported the rapid conversion of micas to vermiculite by extraction of the potassium by BPh_4^-. Changes in basal spacings were followed by x-ray diffraction. The laboratory procedure simulates the geologic and soil phenomenon of mica weathering. The relative x-ray diffraction intensities of the micas and vermiculites were reported as measures of the degree of potassium removal and the conversion of mica to vermiculite.

VII. ECONOMICS OF THE TETRAARYLBORATES

Economic considerations have stimulated some of the research on the tetraarylborates. Sodium tetraphenylborate has been used in the manufacture of alkaloids;[205] the alkaloid is precipitated as the tetraphenylborate salt, which is then dissolved in acetone and the alkaloid recovered by ion exchange. The process also permits the recovery of the precipitant. Patents have also been issued on uses, reactions, and compounds in this area. The earliest of these was granted to Wittig and Raff[260] for a process for the production of tetraphenylborate. A patent[136] has been issued on an extraction process for recovering ^{137}Cs, a long-life fission product obtained from neutron-irradiated uranium. The sodium tetraphenylborate is dissolved in a water-immiscible organic solvent and the resulting solution used to extract the aqueous solution containing the ^{137}Cs. The organic phase is concentrated and the cesium recovered. A patent[22] has been granted on reactions of boron halides and tetrasubstituted boron compounds. Several tetraarylborates are cited in this patent, but in some cases their existence is not substantiated.

Two patents[56,247] concern the tetraarylborates as biological toxicants, where they seem to offer possibilities as herbicides, fungicides, and bacteriocides. One patent[153] envisions certain tetraarylborates as useful reagents in the process of production of pure cesium for use as a propellant in the ion propulsion engine of space vehicles.

A patent[30] has been issued to Buechl for the separation of vitamin B_{12} from aqueous solution. The cobalamin is precipitated from a weakly acid solution using the BPh_4^-, $CNBPh_3^-$, or preferably $(tolyl)_3BC\overline{N}$ anion. The precipitate is separated and dissolved in a solvent such as acetone or acetonitrile from which the vitamin can be obtained.

Sato and Otsu[197] in a study of vinyl polymerization which was initiated with amine acyl/peroxide and tertiary amine/acid anhydride, isolated N-benzoyloxytriethylammonium tetraphenylborate, N-benzoyloxytrimethylammonium, and N-toluyloxytrimethylammonium tetraphenylborates. All of these salts showed activity in the polymerization of methyl methacrylate.

VIII. MEDICAL AND BIOLOGICAL USAGE OF THE TETRAARYLBORATES

It is not surprising to find interest in the tetraarylborates in areas other than analytical methodology. The reactions investigated by the analytical chemists appear to be responsible for these diverse interests. Stanbury and Wicken[219] reported enzyme inhibition by tetraphenylborate in their studies on plasma membrane preparations from calf thyroids, observing that tetraphenylborate inhibited the Mg^{++} dependent ATPase activity. It was non-specific in its action and inhibited several other enzymes.

Recently, some of the negatively substituted tetraarylborates have been found to have biological activity.[28] Table 23 summarizes preliminary information on biological activity.

The "+" designation in the table indicates a level of biological activity sufficient to warrant further study beyond the initial screening, while the "-" notation indicates no activity or a level adjudged to be of no interest. The compounds were tested against a variety of gram-positive and gram-negative bacteria as well as certain fungi. The results are summarized in the chemotherapy column. Parisitology tests were carried out against helminth eggs and/or larvae and for anti-coccidial activity in chicks.

Harris and Leone[87] noted that sodium tetraphenylborate causes extensive in vivo changes in mouse liver cells when used as a dispersing agent in tissue culture studies.

Patents have been issued on tetraarylborates as long-lasting biological toxicants, and it has been suggested that they be used as additives to gasoline to control the growth of biological material in gasoline storage tanks, and also as additives to paint, wood, spray, and dust preparations to inhibit the growth of fungi and bacteria. Herbicidal effects have been noted on test plots contain-

TABLE 23

Biological Activity of Some Tetraarylborates

	Parasitology in vivo	Parasitology in vitro	Chemotherapy
Tetraarylborate	+	-	+
Sodium Tetrakis(p-chlorophenyl)borate[38]	+	-	+
Sodium Tetrakis(p fluorophenyl)borate[152]	-	+	+
Sodium Tetrakis(m-fluorophenyl)borate[240]	-	-	+
Sodium Tetrakis(a,a,a-trifluoro-p-tolyl)borate[240]	-	-	+
Sodium Tetrakis(*a,a,a*-trifluoro-m-tolyl)borate[146]	+	-	+

ing such plants as oats, flax, cucumbers, field peas, mustard, beans, and sugar beets. The compounds claimed are the polymeric salts of the general formula $[(RNH_2^+)(BPh_4^-)]_n$, where R is a divalent radical;[56] and $[Ar_3B\text{-}L\text{-}Ar_3]^= 2Na^+$, where Ar is an arene substituent containing 6 to 12 annular carbon atoms, and L is an arylene substituent.[247] There are compounds in this area which appear to warrant investigation as analytical reagents.

Nesterov[159] used $NaBPh_4$ to bind and thus localize potassium in a mostly osmotically inactive state in the wing of the honey bee. This procedure permits examination of the wing muscle fibrils by interference microscopy and evaluation of the potassium in single elements of myofibril sarcomeres. Nigrovic[165] followed the retention of radiocesium given orally or injected into rats. He noted the effects of various compounds on the cesium retention. Tetraphenylborate given orally was found to decrease the cesium retention.

IX. CONCLUSION

The field of tetraarylborate chemistry has advanced significantly since the introduction of tetraphenylborate. The present review has attempted to sample the areas of growth and to indicate the potential analytical chemical usage of the newer developments rather than to devote its major effort to critically reviewing the many useful, but rather straightforward, applications that have been developed based on tetraphenylborate.

The decade 1960-1970 saw a continued high level of interest in the properties of sodium tetraphenylborate as a reagent. Gravimetric and volumetric procedures were developed for potassium, rubidium, cesium, and certain "onium" compounds in a wide variety of chemical systems. The volumetric methods vary from direct titrations to multi-step back-titrations of the desired cations. End-point detection in these procedures is an interesting exercise in the analytical chemist's art, with virtually all standard methods of end-point detection being employed. The use of the tetraarylborates, especially tetraphenylborate, as derivative-forming reagents has found wide application. Solid derivatives with acceptable melting points are formed with a wide range of "onium" compounds and cationic transition metal complexes.

A number of studies devote themselves to the chemistry of the tetraarylborate anions and especially to that of tetraphenylborate. These studies include non-aqueous solution chemistry; electrochemical oxidation of tetraphenylborate; structural investigations by nmr, infrared, and Raman spectroscopies; thermal decompositions of the salts; and a few structural determinations by x-ray methods.

Improved methods have been developed for the synthesis of tetraphenylborate. A number of new tetraarylborates have been synthesized and screened for reagent possibilities. Some of these are superior to tetraphenylborate in resistance to acid attack and in selectivity for the larger cations.

Tetraarylborate chemistry is indeed an area rich in research possibilities.

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