

**Acknowledgment.**—We thank the National Institutes of Health, Grant AI-01425-09, for their generous support of this work.

DEPARTMENT OF CHEMISTRY  
POLYTECHNIC INSTITUTE OF BROOKLYN  
BROOKLYN, NEW YORK 11201

C. G. OVERBERGER  
W. H. DALY

RECEIVED JUNE 4, 1964

### Synthesis of Tetraisoamylammonium Tetraisoamylboride. A Reference Electrolyte for the Evaluation of Single Ion Conductivities

Sir:

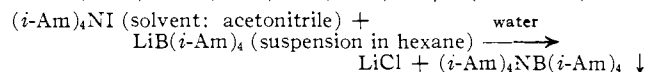
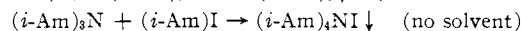
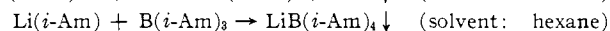
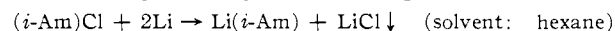
For the investigation of ion-solvent interactions, reliable values of single ion conductivities are invaluable. Ideally, precise transference number measurements are required for this purpose. However, in the majority of nonaqueous solvents serious experimental difficulties are encountered in such measurements, with the result that reliable transference numbers are available only for methanol, and, somewhat less reliably, for ethanol and nitromethane as solvents.<sup>1</sup> Consequently, for other solvents several investigators have estimated single ion conductivities indirectly, by assuming that in any given solvent the cation and anion of a salt such as tetrabutylammonium tetraphenylboride,  $\text{Bu}_4\text{NBPh}_4$ , or triisoamylbutylammonium tetraphenylboride,  $(i\text{-Am})_3\text{BuNBPh}_4$ ,<sup>2</sup> will have equal mobilities. This assumption is justified as a first approximation, because the cation and anion are of approximately equal crystallographic size, and because (classical) solvation may be expected to be small since the ions are large and reasonably symmetrical, and the single charge is fairly well shielded. Methanol is the only solvent for which the applicability of these salts has been tested so far on a reliable scale derived from directly measured transference numbers. It was found<sup>2</sup> that the limiting equivalent conductivity of  $\text{Ph}_4\text{B}^-$  in methanol is 8% lower than that of  $\text{Bu}_4\text{N}^+$  and agrees to within 1% with that of  $(i\text{-Am})_3\text{BuN}^+$ . On this basis Coplan and Fuoss recently have recommended the use of  $(i\text{-Am})_3\text{BuNBPh}_4$  as a reference electrolyte for the indirect estimation of single ion conductivities in other solvents. However, models show that the average (effective) crystallographic radius of  $\text{Ph}_4\text{B}^-$  is somewhat smaller than that of  $\text{Bu}_4\text{N}^+$  and considerably smaller (by ca. 10%) than that of  $(i\text{-Am})_3\text{BuN}^+$ . It is our opinion that although  $\text{Ph}_4\text{B}^-$  may be the best reference anion hitherto available, it is by no means ideal for this purpose. Some degree of classical solvation<sup>3</sup> may occur with this anion in polar (even in nonhydrogen-bonding) solvents, since the phenyl groups are somewhat polarizable. More important, in a hydrogen-bonding solvent, such as methanol, hydrogen bonding of the solvent to the phenyl groups is conceivable, of the type described by Schleyer, *et al.*<sup>4</sup> Such solvation could account for the fact that in methanol the mobility of  $\text{Ph}_4\text{B}^-$  is considerably lower than that of  $\text{Bu}_4\text{N}^+$ , despite its somewhat smaller

crystallographic radius. Specific solvation must of course be absent if an ion is to serve as a reference in a variety of solvents.

We have succeeded in synthesizing the salt tetraisoamylammonium tetraisoamylboride,  $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$ , and recommend it as a reference electrolyte for the evaluation of single ion conductivities. It has an advantage over previous salts used for this purpose in that its anion matches the cation closely in having virtually the same size, and particularly in that the anion should be much less susceptible to specific solvation effects than may be the case with  $\text{Ph}_4\text{B}^-$ . Furthermore, this salt is interesting *per se* in that it is an unusual boron compound. To our knowledge, no other tetraboride has been prepared with such large alkyl groups.

The applicability of this salt to the evaluation of single ion conductivities is now being tested in this laboratory by measuring its conductivity and those of an appropriate series of other salts in acetonitrile, acetone, and nitromethane. Preliminary results<sup>5</sup> obtained in nitromethane agree with known transference numbers<sup>1</sup> to better than 0.1%. We are also attempting to measure transference numbers directly in acetonitrile and acetone.

The synthesis of  $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$  is difficult, but it was accomplished by the following series of reactions



**Synthesis of Lithium Tetraisoamylboride.**—Isoamyl-lithium was prepared by a modification of the procedure given by Gilman, *et al.*,<sup>6</sup> for the preparation of similar compounds. The following changes were made in Gilman's procedure. (1) A magnetic stirrer and Dry Ice-acetone reflux condenser were used. (2) The reaction medium was hexane (Fisher Certified Reagent, dried over Drierite). The yield decreases in the order hexane, pentane, petroleum ether (b.p. 60–70°). (3) Filtration was conducted in an argon-filled drybox. The filtered solution (deep violet in color) was transferred in the drybox to a flask fitted with a serum cap and was then injected with triisoamylboron (Callery Chemical Co.). *Caution.* Triisoamylboron is air sensitive. Immediately upon injection, a dense white precipitate formed which could not be filtered without causing extensive decomposition. Consequently, the precipitate was stored under the supernatant liquid in a freezer until needed.

**Synthesis of Tetraisoamylammonium Tetraisoamylboride.**—Tetraisoamylammonium iodide was prepared by the method of Fuoss and Kraus.<sup>7</sup> It was repeatedly recrystallized from a 1:8 acetone-water mixture and dried *in vacuo* at 60°. A solution of this salt in pure, anhydrous acetonitrile<sup>8</sup> was added to the suspension of  $\text{LiB}(i\text{-Am})_4$  in hexane, with careful exclusion of air. The suspension dissolved. After stirring for 2 hr., the

(1) S. Blum and H. I. Schiff, *J. Phys. Chem.*, **67**, 1220 (1963).

(2) M. A. Coplan and R. M. Fuoss, *ibid.*, **68**, 1177 (1964).

(3) The decrease in the mobility of the ions caused by the relaxation effect induced by the motion of the ions in a polar medium need not be considered here, since the decrease presumably will be the same for the cation and anion of the reference electrolyte. This relaxation effect has been suggested by Fuoss and treated theoretically by R. H. Boyd and by R. Zwanzig [*J. Chem. Phys.*, **38**, 1603 (1963)].

(4) P. von R. Schleyer, D. S. Trefon, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).

(5) G. P. Cunningham, "Single Ion Conductivities in Acetonitrile and Nitromethane," Ph.D. Thesis, University of Pittsburgh, 1964.

(6) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(7) R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 21 (1933).

(8) J. F. Coetzee, G. P. Cunningham, D. K. McGuire, and G. R. Padmanabhan, *Anal. Chem.*, **34**, 1139 (1962).

solution was flooded with water. Large, flaky white crystals separated. The product was recrystallized eight times from a 1:8 acetone-water mixture, avoiding undue heating, and was then dried *in vacuo* at 60° for 8 hr. *Anal.* (by Alfred Bernhardt, Microanalytical Laboratories, Max Planck Institute, Mülheim, Germany, with values calculated for  $(i\text{-Am})_4\text{NB}(i\text{-Am})_4$  given in parentheses): C, 80.73 (80.88); H, 15.26 (14.94); N, 2.69 (2.36). The compound which had m.p. 181° dec. was nonhygroscopic and was readily

soluble in acetone, acetonitrile, and nitromethane, and only very slightly soluble in methanol.

**Acknowledgments.**—This work was supported by the National Science Foundation under Grant Number NSF GP-1479. We also wish to acknowledge the advice of Professor J. C. Carter of this department concerning the above synthesis.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF PITTSBURGH  
PITTSBURGH, PENNSYLVANIA 15213

J. F. COETZEE  
G. P. CUNNINGHAM

RECEIVED JUNE 15, 1964

## BOOK REVIEWS

**Technique of Inorganic Chemistry. Volume I.** Edited by HANS B. JONASSEN and ARNOLD WEISSBERGER. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 268 pp. 6.5 × 9.5 cm. Price, \$9.50.

The stated objective of this companion series to "Technique of Organic Chemistry" (Weissberger, Interscience) is "to present in a comprehensive manner the various techniques used specifically in inorganic chemistry and radiochemistry." Within the broad scope of this objective, Vol. I of "Technique of Inorganic Chemistry" succeeds admirably well. It contains six very well-written and thoroughly documented chapters. Brief statements of the contents of these chapters are given below.

"Determination of Formation Constants of Complexes" by Sture Fronaeus contains a short discussion of calculation techniques and a more lengthy consideration of experimental methods.

"Techniques with Nonaqueous Solvents" by Alexander I. Popov considers nonaqueous solvents with respect to selection of solvent, synthesis in a solvent, liquid-liquid extraction, and potentiometric and conductometric studies.

"Fused Salt Techniques" by John D. Corbett and Frederick R. Duke considers techniques with respect to apparatus, preparation and purification of materials, studies of equilibrium and dynamic properties, and spectroscopic and diffraction methods.

"Spectral Measurements in High Pressure Systems" by W. W. Robertson discusses windows, pressure-transmitting fluids, high pressures at high temperatures, and intensity measurements.

"The Use of Electric Discharges in Chemical Syntheses" by William L. Jolly discusses in detail electrode discharges, electrodeless discharges, arcs under liquids and solutions, and arcs in flowing gases.

"Differential Thermal Analysis" by W. Wendlandt considers instrumentation, factors affecting results, quantitative aspects of differential thermal analysis, and reaction kinetics and applications to chemical problems.

While the other chapters in Vol. I are restricted to relatively special topics which are either thoroughly discussed or documented, "Techniques with Nonaqueous Solvents" is general in nature, illustrating generalizations with a few selected examples. Unfortunately, by restricting the discussion to generalizations, techniques which are intimately related to specific solvent systems are not necessarily discussed and a vast body of information is ultimately ignored, in spite of Prof. Popov's extensive bibliography. In the opinion of this reviewer a more useful presentation would have been to devote an entire volume to nonaqueous solvents with perhaps an introductory chapter, such as Prof. Popov's, followed by more detailed discussions of techniques related to specific solvents.

This reviewer was surprised and disappointed to note that vacuum technology is not listed in the contents of the existing volumes (I, II, III) of this series. Hopefully a volume or at least a chapter will be devoted to this important topic in a future volume of the series.

The contents of Vol. I and III do not appear to have a coherent plan. Topics for each volume have been chosen, seemingly, at

random. Although Vol. II is devoted to "Nuclear Chemistry" exclusively, it is of interest to note that "Technique of Handling Highly Active Beta- and Gamma-Emitting Material" is presented in Vol. III. Considering the apparently haphazard arrangement of topics plus the relatively small size and high price of Vol. I, perhaps Vol. I and III should have been combined into a single volume, thereby minimizing the cost of the series.

THE OHIO STATE UNIVERSITY  
COLUMBUS 10, OHIO

SHELDON G. SHORE

**Oxidation Mechanisms. Applications to Organic Chemistry.**

By ROSS STEWART, University of British Columbia. W. A. Benjamin, Inc., 2465 Broadway, New York 25, N. Y. 1964. 179 pp. 16 × 23.5 cm. Price, \$7.50.

The oxidation of organic compounds has attracted the attention of countless chemists, resulting in a tremendously complex literature. Professor Stewart is to be commended for having picked and chosen well. After first defining what he means by oxidation, he goes on to describe equivalence in oxidation reactions and breaking of carbon-hydrogen and carbon-carbon bonds. Next, he discusses most of the better known oxidants for organic compounds. These include chromic acid, permanganate, and other transition metal derivatives, the so-called glycol-cleaving group, various nonmetallic oxides, including dimethyl sulfoxide, peroxides, and various miscellaneous agents such as quinones. He concludes with a chapter on "Biochemical Oxidation Mechanisms."

Each topic is considered carefully and completely from the standpoint of scope and reaction mechanism. It is impossible to completely satisfy everyone on such a broad field; the reviewer, for example, would have liked to see a more complete discussion of dimethyl sulfoxide oxidations and mention of oxidative coupling reactions, particularly oxidative polymerization of phenols. However, Prof. Stewart has in general done an excellent job in choosing and presenting his material.

He is to be particularly commended for his chapter on biochemical oxidations. It is an especially concise summary of this frequently confused area. The information is well presented, particularly for those who have some previous acquaintance with biological systems. For the general reader, however, an additional introductory paragraph explaining the interrelationship of the various biological oxidations would have been useful. Those without a modern biochemical background may regard the chapter as series of interesting but unrelated essays, although those who persist to the section on "Biochemical Machines" will be well rewarded.

The book is well written and easy to read. The format is pleasing and the text relatively free of misprints.

E. I. DU PONT DE NEMOURS AND CO., INC. T. W. CAMPBELL  
PIONEERING RESEARCH DIVISION  
EXPERIMENTAL STATION  
WILMINGTON, DELAWARE