bonyl oxygen in the next turn of the helix, indicating OHO hydrogen bonding. There are no unreasonably short distances between non-bonded atoms, provided R or R′ of each RR′R″ group is glycine. There are no large holes within the helix, although there appear to be suitable locations for some hydrogen-bonded water molecules, perhaps one per group of three residues.

Assuming[2] an average residue weight of 93 and close-packed helices 12.0 Å. apart, the computed density is 1.30 g./cc., or 1.38 if one molecule of bound water per three residues is assumed. The experimental *over-all* density of collagen has been reported as 1.35[2] and 1.41.[6]

The distribution of residues in the proposed structure will be discussed later.

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RECEIVED JUNE 22, 1954

THE BICHLORIDE ION[1]

Sir:

The epimerization of *l*-menthyl *l*-*p*-toluenesulfinate in nitrobenzene is third order with a first-order dependence on the ester, hydrogen chloride, and chloride ion added as tetraethylammonium chloride. Hydrogen chloride alone, which in nitrobenzene is un-ionized,[2,3] has no effect on the ester at concentrations below 0.01 *M*. As the concentration of one catalyst is held constant and that of the other is increased, a point is reached at which no further increase in the rate of epimerization is achieved since proportional amounts of catalyst are removed as bichloride ion. From the results, the equilibrium constant in nitrobenzene at 24.96 ± 0.03° for the formation of the bichloride ion

$$Cl^- + H{-}Cl \rightleftarrows HCl_2^-$$

has been calculated to be 5×10^2 $(m./l.)^{-1}$. Essentially the same value for this equilibrium constant has been obtained by the use of the benzene- and *p*-anisolesulfinates. Actually, continued addition of hydrogen chloride at constant chloride ion concentration does lead to a very slight increase in the rate. From this it has been possible to calculate an activity for the bichloride ion as chloride donor of one twentieth that of the free chloride ion.

That the bichloride ion exists in these solutions is also apparent from the fact that 0.659 m./l. of tetraethylammonium chloride dissolves in nitrobenzene which is 0.633 *M* in hydrogen chloride, although the normal chloride is only very slightly soluble in pure nitrobenzene. The vapor pressure of hydrogen chloride over the nitrobenzene is greatly diminished on addition of the salt.

The hydrogen chloride stretching frequency[4] at 2703 cm.$^{-1}$ completely disappears from its saturated solution in nitrobenzene on addition of tetraethylammonium chloride and is replaced by continuous absorption ranging from approximately 1667 to 730 cm.$^{-1}$ of sufficient intensity to mask most of the nitrobenzene absorption.

Isolation of tetraethyl- and tetramethylammonium bichloride from nitrobenzene has been accomplished by cooling or, preferably, by precipitation with ether or petroleum ether. The product, which recrystallized poorly, analyzed as 85–90% bichloride and 2–12% normal chloride. Passage of dry hydrogen chloride over the impure tetramethylammonium bichloride resulted in a product containing 98.46% tetramethylammonium bichloride (*Anal.* Calcd. for $C_4H_{13}NCl_2$: Cl, 48.55; HCl, 24.96. Found: Cl, 47.47; HCl, 24.58) with a chloride to proton ratio of 1.99/1.00.

The interaction of hydrogen chloride with chloride ion is also illustrated in the reported synthesis[5] of a liquid tetraethylammonium chloride trihydrochloride and of tetramethylammonium bichloride by the passage of hydrogen chloride over the quaternary salts at 0°. Further, the solvolytic behavior of hydrogen chloride on reactive organic chlorides[6] has led to the postulation[7] of the existence of the bichloride ion as a kinetic entity in solution. From our observations on the stability of the bichloride ion, we conclude, for reasons to be presented in detail in a later paper, that in certain of these solvolytic reactions the bichloride ion cannot be free but must exist in a tight ion pair with the organic cation.

(1) Sponsored by the Office of Naval Research.

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RECEIVED JUNE 14, 1954

TRANSPORT NUMBERS IN PURE FUSED SALTS[1]

Sir:

We believe we have devised the first practical method for measuring the transport numbers of the ions in pure fused salts. By means of a cell which is simple to construct and operate we have determined the transport numbers for molten lead chloride.

A Hittorf-type cell cannot be used for pure salts, since electrolysis causes a change in quantity, rather than concentration, of electrolyte in each compartment. This accumulation of salt is not observed, since it is free to flow back to the depleted compartment unless a restraining membrane is inserted.[2] This membrane must allow the ready passage of the ions carrying the current and, at the same time, resist the flow of the bulk of the liquid. We have found that by offering the liquid a much more accessible path by which to equalize the hy-

(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) S. Karpachev and S. Palguev, *Zhur. Fiz. Khim.*, **23**, 942 (1949).

drostatic pressure difference which develops we are afforded a ready means of measuring the accumulated salt.

The cell is constructed of Pyrex glass, and consists of two vertical compartments connected through two horizontal tubes, one above the other. The upper of these is a piece of 2.5-mm. capillary tubing. The lower contains the membrane which is to separate the compartments. For this purpose we have found fritted glass disks of "ultrafine" porosity to be the most suitable. The compartments themselves are large tubes near the bottom, which taper rapidly up to the level of the capillary. Above this point each side consists of uniform tubing of 6-mm. inside diameter flared sharply at the top to permit easy introduction of material. Through the bottom of each compartment is sealed a piece of tungsten wire.

In operation the electrodes consist of pools of molten lead which cover the tungsten wires. Above this the cell is filled with molten lead chloride in such a way that an air bubble is trapped in the capillary. The difference in levels which develops on electrolysis is most readily equalized by flow through the capillary, so that the displacement of the bubble provides an accurate measure of the volume changes occurring. The cell is most conveniently used as a null instrument by adding a weighed quantity of powdered $PbCl_2$ to one compartment and measuring the number of coulombs required to return the bubble to its original position.

Assuming the only current carrying species to be Pb^{++} and Cl^-, it can be shown readily that the transport number of the negative ion is given by the equation

$$t- \;=\; \frac{\pm\left(\dfrac{96{,}500\text{ wt. salt}}{\text{coulombs passed}}\right)+\left(2\text{ eq. wt. metal}\times\dfrac{\text{Density of salt}}{\text{Density of metal}}\right)}{2\text{ eq. wt. salt}}$$

the positive sign being used in this case since the bubble moves toward the cathode during electrolysis. Using the data of Lorenz, *et al.*,[3] and that of Pascal and Jouniaux[4] for the densities of lead chloride and lead, we find the value of *t*- at 565° to be 0.758 ± 0.014 (average deviation for 20 experiments). Substantially the same result was obtained using a plug of tightly packed asbestos as a membrane, but "fine" and "medium" porosity fritted disks permitted enough backflow to introduce appreciable errors.

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RECEIVED JUNE 30, 1954

AMINOETHYL DIARYLBORINATES; ISOLATION OF A STABLE UNSYMMETRICAL ORGANOBORON COMPOUND

Sir:

The development of the chemistry of the diarylborinic acids has been hampered seriously by the lack of adequate methods for their isolation and characterization. Several arylborinic acids have been reported, but in no case was the yield specified and in some cases considerable doubt exists about the identity of the compounds described.[1-4]

We recently observed that these compounds readily could be isolated and characterized as their aminoethyl esters. The acids were prepared by the reaction of two mole equivalents of the appropriate Grignard reagent with one mole equivalent of butylethylene borate or butyl borate, followed by hydrolysis with dilute hydrochloric acid. Diphenylborinic acid in the form of the butyl ester was separated from triphenylborine, another reaction product, by distillation and from butyl benzeneboronate by precipitation from ether with ammonia. The relatively unstable ammonia complex (m.p. 64–67°), isolated in 48% yield (based on the phenylmagnesium bromide), was then converted (80–90%) to aminoethyl diphenylborinate (m.p. 189–190°. Calcd. for $C_{14}H_{16}ONB$: B, 4.807; C, 74.70; H, 7.16; N, 6.23; neut. eq., 225. Found: B, 4.795, 4.807; C, 74.02; H, 7.11; N, 6.47; neut. eq., 225) by reaction with ethanolamine in an alcohol–water solution. In the case of aminoethyl di-α-naphthylborinate, it was convenient to precipitate the ester directly from a toluene solution of the reaction products without prior distillation and ammonia precipitation. Purification was accomplished in this case by reprecipitating the aminoethyl ester from alcohol and water, followed by recrystallization (yield based on butyl borate, 45%; m.p. 192–193.5°; calcd. for $C_{22}H_{20}ON_{13}$: B, 3.33; neut. eq., 325. Found: B, 3.30; 3.20; neut. eq., 328). Acid hydrolysis of these esters yielded the free diphenylborinic acid as an oil which did not crystallize, and the α-naphthylborinic acid as a solid, m.p. 105–106°; neut. eq., 290 (calcd. neut. eq., 282).

These techniques made possible the isolation of a stable, unsymmetrical diarylborinate. Of the previous attempts to isolate organoboron compounds with two different groups attached to the boron atom[5-8] success has been had only with the alkenylmethylborines.[8] Even these substances disproportionated slowly at room temperature. We isolated from a reaction of 0.049 mole of naphthylmagnesium bromide and 0.05 mole of butyl benzeneboronate in ether at −60°, 10.1 g. (75%) of aminoethyl phenyl-α-naphthylborinate (m.p. 228–229°; calcd. for $C_{18}H_{18}ONB$: B, 3.93; neut. eq., 275. Found: B, 3.93, 3.74; neut. eq., 275). This compound is stable and shows no sign of undergoing disproportionation under normal conditions. From degradation experiments with hydrogen peroxide, zinc chloride and bromine were isolated naphthol, naphthalene and bromobenzene (characterized by conversion to benzoic acid) and bromonaphthalene, respectively.

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