

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.

Assuming² 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 1.35² and 1.41.⁶

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

(6) C. D. Pomeroy and R. G. Mitton, *J. Soc. Leather Trades Chemists*, **35**, 360 (1951).

RESEARCH LABORATORIES
EASTMAN KODAK CO.
ROCHESTER 4, N. Y.

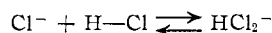
MAURICE L. HUGGINS

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THE BICHLORIDE ION¹

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



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*-anisolesulfates. 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 frequency⁴ at 2703 cm.⁻¹ completely disappears from its saturated solution in nitrobenzene on addition of tetra-

(1) Sponsored by the Office of Naval Research.

(2) M. Hlasko and E. Michalski, *Roczniki Chem.*, **6**, 534 (1926); *Chem. Zentr.*, **98**, I, 2803 (1927).

(3) D. M. Murray-Rust, H. J. Hadow and H. Hartley, *J. Chem. Soc.*, 215 (1931).

(4) W. Gordy and P. C. Martin, *J. Chem. Phys.*, **7**, 60 (1939).

ethylammonium 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 C₄H₁₃NCl₂: 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 synthesis⁵ 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 chlorides⁶ has led to the postulation⁷ 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.

(5) F. Kaufler and E. Kunz, *Ber.*, **42**, 385, 2482 (1909).

(6) H. Meerwein and K. van Emster, *Ber.*, **55**, 2500 (1922); P. D. Bartlett and I. Pöckel, *THIS JOURNAL*, **60**, 1585 (1938); see also H. Hart and F. A. Cassis, *ibid.*, **76**, 1634 (1954); R. Leimu and P. Salomaa, *Acta Chem. Scand.*, **1**, 353 (1947); K. H. Meyer, *Ber.*, **41**, 2568 (1908).

(7) P. D. Bartlett, "Organic Chemistry, An Advanced Treatise," Vol. III, Henry Gilman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 66.

DEPARTMENT OF CHEMISTRY HARRY F. HERBRANDSON
RENSSELAER POLYTECHNIC INST.

TROY, NEW YORK RICHARD T. DICKERSON, JR.
JULIUS WEINSTEIN

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TRANSPORT NUMBERS IN PURE FUSED SALTS¹

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. Karpacher and S. Palguer, *Zhur. Fiz. Khim.*, **23**, 942 (1949).