

zyme mole ratio 10/1), yielding lysine, and to a lesser extent leucine, methionine, glutamic and aspartic acids, threonine, serine and glycine.

Denaturation was effected by 48 hours of exposure to HCl, pH 1, at 0°, followed by 24 hours of dialysis against HCl, pH 3.

The present results are compatible with the suggestion that activation of trypsinogen is accompanied by the splitting of a peptide from the amino end of the polypeptide chain⁵ but it remains to be seen whether in analogy with the activation of chymotrypsinogen to α -chymotrypsin,² a peptide is split from the carboxyl end of the chain as well. Further quantitative studies of these phenomena are in progress and will be published at a later time.

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

EARL W. DAVIE
HANS NEURATH

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IONIZATION OF ORGANOMETALLIC HALIDES

Sir:

Although trimethyltin iodide¹ and the triethyllead halides² have long been known to be soluble in water and to undergo metathetic reactions in aqueous solution, the rapid and complete hydrolysis of organosilicon halides³ precludes such reactions. The similar alcoholysis⁴ of organosilicon halides, and their related reaction with ammonia⁵ and amines⁶ prevent the use of these polar liquids as ionizing solvents.

For much the same reasons, the electrochemistry of organometallic compounds has been concerned chiefly with the electrolytic behavior of organomercury compounds in water,⁷ the conductivity of trimethyltin iodide in acetone, alcohols, and pyridine,⁸ and of Grignard reagents⁹ in ether and related solvents. The organosilicon halides exhibit no conductivity in ether.

We now find that a considerable number of methyl-, ethyl-, dodecyl-, octadecyl- and phenyl chlorosilanes are soluble in anhydrous dimethylformamide, and that such solutions are highly conducting. For example, dimethyldichlorosilane exhibits an equivalent conductance of 18 ohms⁻¹ at a concentration of 0.004 equivalent per liter, and 0.5 ohm⁻¹ at one equivalent per liter, both at 30°. The conductances of eleven organochlorosilanes are being studied, and from these and the colligative properties of the solutions the degrees of ionic dissociation are being sought. Preliminary results indicate that the dissociation constants are relatively small, in the range 10⁻² to 10⁻⁴.

The chemical significance of these results lies in the fact that the concentrations of organosilicon ions of the types R₃Si⁺, R₂Si⁺⁺, and RSi⁺⁺⁺ are

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(2) W. Klemm, FIAT Report of Inorganic Chemistry, Part II, p. 169 (1948).

(3) W. I. Patnode and D. F. Wilcock, *THIS JOURNAL*, **68**, 358 (1946).

(4) C. A. Burkhard, *J. Org. Chem.*, **15**, 106 (1950).

(5) R. O. Sauer and R. Hasek, *THIS JOURNAL*, **68**, 241 (1946).

(6) Y. N. Volnov and A. Reutt, *J. Gen. Chem. (U.S.S.R.)*, **10**, 1600 (1940).

(7) F. Hein and H. Meiningner, *Z. anorg. Chem.*, **145**, 95 (1925).

(8) C. A. Kraus and C. C. Callis, *THIS JOURNAL*, **45**, 2624 (1923).

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amply sufficient to permit ionic oxidation-reduction and metathetic reactions in dimethylformamide. Thus dichromate ion is reduced by dimethyldichlorosilane in this solvent to several lower oxidation states of chromium; ammonium thiocyanate undergoes metathetic reaction with the same chlorosilane to precipitate ammonium chloride; boric acid reacts to form a silicone polymer of the "bouncing putty" variety; phosphotungstic acid precipitates a dimethylsilyl phosphotungstate; *para*-nitrobenzoic acid dissolves in a solution of dimethyldichlorosilane in dimethylformamide, but not in the amide itself nor in a mixture of the amide with hydrogen chloride.

In similar vein, we have found that some organogermanium halides form conducting solutions in dimethylformamide and undergo ionic metatheses. While it may prove possible to employ concentrated hydrochloric acid as a dissociating solvent for organogermanium compounds because of an observable reversibility,¹⁰ the preparative utility of such a solvent is more limited. However, we have found that dimethyltin dichloride may readily be handled in acidic aqueous solution; it hydrolyzes in pure water only to the extent of 10.5% in 0.064 molal concentration at 25°. Cryoscopic measurements in water give a van't Hoff *i* factor of 2.60 at 0.1693 molal concentration, 2.69 at 0.1041 molal, and 2.86 at 0.0639 molal. The (CH₃)₂Sn⁺⁺ ions may be retained on a cation exchange resin and eluted with various acids. By elution and by metathesis we have prepared dimethyltin tungstate, molybdate, sulfide, oxalate, succinate, naphthionate, salicylate, phthalate, benzoate, ferricyanide, ferrocyanide, iodate, arsenate, vanadate, cyanate and antimonate. A report on the preparation, purification, and properties of these compounds is being prepared.

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(10) E. G. Rochow, *ibid.*, **70**, 1801 (1948).

MALLINCKRODT LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.

KURT GINGOLD
EUGENE G. ROCHOW
DIETMAR SEYFERTH
ALBERT C. SMITH, JR.
ROBERT WEST

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ISOTOPE EFFECTS IN THE IONIZATION OF ALKYL CHLOROSULFITES

Sir:

Examples occur frequently in the literature of marked changes in the rate of reactions which break bonds to hydrogen, when deuterium or tritium is substituted for this hydrogen. No appreciable effects have heretofore been observed when the reactant and product have all bonds to hydrogen intact. Such studies have in fact become a standard tool for the detection of bond-breaking in the rate determining steps of reactions.^{1,2} In an experiment designed to study by this technique the mechanism of the elimination reaction which ac-

(1) F. H. Westheimer and N. Nicolaidis, *THIS JOURNAL*, **71**, 25 (1949).

(2) L. Melander, *Arkiv för Kemi*, **2**, 211 (1950).