FREE ENERGY OF DISSOCIATION OF AMINE HYDROCHLORIDES AT 25° FROM CELL MEASUREMENTS[1]

Sir:

The standard free energy of the reaction

$$RNH_3Cl(s) = RNH_2(g) + HCl(g)$$

is a criterion of base strength. It is given by

$$-\Delta F^\circ = RT \ln P_{RNH_2}P_{HCl} \qquad (1)$$

The two pressures can be obtained from the electromotive force of the cell

$$H_2(g),\ RNH_2(m = x),\ RNH_3Cl(s),\ AgCl,\ Ag \qquad (A)$$

With water as solvent the silver chloride electrode is attacked, but if alcohol be used this difficulty is avoided. The value of E^0_g, for the cell

$$H_{2(g)},\ HCl(g),\ AgCl(s)\ Ag \qquad (B)$$

is $E^0 = -0.1509$.[2] From this and the electromotive force of cell A the fugacity of the hydrogen chloride can be calculated.

The partial pressure of the amine can be obtained by passing the exit hydrogen through dilute sulfuric acid, then through activated alumina. The total increase in weight together with the amount of amine (as determined by microtitration) carried over by a measured volume of hydrogen, allow the calculation of the necessary mole fractions to calculate the partial pressure (fugacity) of amine. The methylammonium chloride system has been studied.

In the first measurements, in which the alcohol was purified by distilling 95% alcohol over lime followed by final drying with magnesium and iodine and storing under nitrogen, the electromotive force stayed constant for about one hour and then started to fall. Seven values of ΔF^0 at 298.16°K., with a variation of the amine molality from 0.17 to 0.45, varied between 23,204 and 23,229 cal. The most probable value, calculated using the value of $\Delta H^0_{298.16}$,[3] together with the entropies of methylammonium chloride[3] and methylamine calculated from the spectroscopic data[4] is 22,867 ± 54 cal. The difference is well outside any reasonable error and was at first taken to indicate a possible zero point entropy of $R \ln 2$ in methylammonium chloride.[5] However, as a test of thermodynamic consistency, measurements were made of cell A at several temperatures between 0 and 40°, and it was found that the discrepancy was traceable to aldehydes (or other reducible material) in the alcohol. These reduce silver chloride and produce a local excess of chloride ion, thereby making the HCl partial pressure and hence ΔF^0 appear higher. Finally all alcohol was distilled from ethyl phthalate, sodium and silver nitrate and stored under nitrogen. Excess silver chloride was always placed on the silver side of the cell and the cells were made to come to equilibrium from the high side, as well as the low, by electrolysis. The value of ΔF^0 at 298.16°K. was finally found to be 22,831 ± 12 cal. The value of $\Delta H^0_{298.16}$ obtained from the temperature coefficient agreed with the measured ΔH^{013} within 30 cal. The close agreement with the calorimetric free energy indicates no randomness in methylammonium chloride.

As a matter of interest the corresponding ΔF^0 at 298.16 for the dissociation of ammonium chloride is 21,860 cal.,[6] which is 1000 cal. lower than that for the methyl substituted derivative. The effect of the methyl group in increasing the basicity of the amine is thus not as great by this criterion as from base strength measurements in aqueous solution which correspond to a 1800 cal. difference.

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(1) Contract N60nr-269 T.O. III of the Office of Naval Research.

(2) J. G. Aston and F. L. Gittler, to be published.

(3) John G. Aston and Charles W. Ziemer, *ibid.*, **68**, 1405 (1946).

(4) J. G. Aston and Paul J. Doty, *J. Chem. Phys.*, **8**, 743 (1940).

(5) J. G. Aston, *Faraday Society Discussions*, No. 10, 119 (1951).

(6) C. C. Stephenson, *J. Chem. Phys.*, **12**, 319 (1944).

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POLYPEPTIDES. I. THE SYNTHESIS AND THE MOLECULAR WEIGHT OF HIGH MOLECULAR WEIGHT POLYGLUTAMIC ACIDS AND ESTERS[1]

Sir:

We wish to report the synthesis of a number of polypeptides of very high molecular weight (>100,000) and the determination of their molecular weights.[2] γ-Benzyl-L-glutamate is treated with an excess of phosgene in tetrahydrofuran solution at 60° to yield γ-benzyl-N-carboxy-L-glutamate anhydride, which is crystallized from ethyl acetate until the melting point is 93–94° (dec.) and the chloride content is less than 0.02% (Volhard method). γ-Methyl-N-carboxy-L-glutamate anhydride, m.p. 96–97° (dec.) is also prepared from the methyl ester[3] by treatment with phosgene.

The reproducible attainment of high molecular weight polymers depends upon the purity of the anhydride and particularly upon the elimination of traces of amino acids which may act as initiators, or traces of halogen acids or phosgene which neutralize the added initiator. The polymerization is carried out at 25° by shaking a 3% solution of the anhydride in dry dioxane or a mixture of dioxane–tetrahydrofuran using sufficient initiator to neutralize the halide and to initiate to the desired molecular weight. The preferred initiator is sodium hydroxide in methanol. Polymerizations are essentially complete in four hours, as indicated by titration of the residual anhydride.[4]

Polymers prepared from γ-benzyl-L-glutamate (BG) are particularly interesting because of their relatively high solubility in organic solvents and because removal of the benzyl groups by phosphonium iodide[3] provides polymers of L-glutamic acid (GA) which are water soluble, as the partial sodium salts, at *p*H's >4. We also find that some of the methyl groups of copolymers containing γ-methyl glutamate (MG) are removed by phosphonium io-

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(1) Supported by the Office of the Surgeon General, Department of the Army.

(2) See for example (a) E. Katchalski, in *Advances in Protein Chemistry*, VI, 123 (1951); (b) R. R. Becker and M. A. Stahmann, THIS JOURNAL, **74**, 38 (1952).

(3) W. E. Hanby, S. G. Waley and J. Watson, *J. Chem. Soc.*, 3239 (1950).

(4) A. Berger, M. Sela and E. Katchalski, *Anal. Chem.*, **25**, 1554 (1953).