CHEMISTRY

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JOSEPH R. SIEFKER, Indiana State University, was elected Chairman for 1970

ABSTRACTS

Determination of the Hydrolysis Constant of the Stannous Ion by an Electromotive Force Method. LUSAN G. ONG and EUGENE SCHWARTZ, DePauw University.—The formal hydrolysis constant

$$K = \frac{[SnOH+][H+]}{Sn^{2+}}$$

for the hydrolysis reaction

$$Sn^{2+} + H_{2}O = SnOH^{+} + H^{+}$$

was obtained at 25° C and at an ionic strength of unity by an electromotive force method employing the concentration cell

$$\frac{\text{Sn(Hg)}}{\text{Sn(ClO}_{4})_{2}(0.020\text{M})} / \frac{\text{HClO}_{4}(\text{XF})}{\text{Sn(ClO}_{4})_{2}(0.020\text{F})} / \frac{\text{HClO}_{4}(\text{XF})}{\text{NaClO}_{4}(1.0\text{-XM})} / (\text{Hg})\text{Sn}$$

in which x was varied from 0.04 to 0.96. The liquid junction potentials for the above cell were obtained from voltages of the cell

Ag, AgCl/HCl (1.0M)
$$/$$
 HCl(XM) $/$ AgCl, Ag
NaCl(1.0-XM) $/$

The hydrolysis constant of the stannous ion was found to be $1.5\pm~0.5 imes~10^{-2}$.

The Infrared Spectra of Coordination Compounds. JAMES NOWAK, ROBERT WILLIAMS and JAMES GEORGE, DePauw University.—The infrared spectra of $[Co(NH_3)_5Cl]Cl_2$, $[Co(ND_3)_5Cl]Cl_2$, $[Cr(NH_3)_5Cl]Cl_2$ and a series of related compounds containing ions of the form $[M(NH_3)_5X]^{p+}$ (where M = Co(III) or Cr(III) and $X = H_2O$, F⁻, Cl⁻, Br⁻ NO₂⁻, SCN⁻ and $CO_3^{2^-}$) have been obtained. The spectra of these compounds are very similar to those of other metal-ammonia systems which have been more extensively studied. The absorptions arising from the vibrations of the coordinated ammonia molecules occur in the regions: 31,500 cm⁻¹; 1,600-1,650⁻¹; 1,300-1,350 cm⁻¹; and 800-850 cm⁻¹. The metal-ammonia stretching frequencies are near 500 cm⁻¹. The coordinated polyatomic ligands could, in all cases studied, be distinguished from their ionic counterparts.

pH Dependent Isotope Effects on the Flavin Enzyme L-Amino Acid Oxidase. ROBERT L. VANETTEN and DAVID S. PAGE, Purdue University.— The effects of changes in pH and of deuterium substitution upon the kinetic parameters of the reaction of L-amino acid oxidase with L-leucine have been examined. The Michaelis-Menten parameter K_m was measured for the L-amino acid oxidase—L-leucine system as a function of pH in H₂O at 25, 30 and 35° C in the pH range 5.5 to 9.5. Treatment of the data according to Dixon's rules yields pK values for a group situated in the active center (i.e., in the ES complex) and for a group in the free enzyme. The temperature dependence of these pK values allows the calculation of an enthalpy of ionization of 7-8 kcal/mole for this ionizable group. This value together with the observed pK values lead to the conclusion that a histidyl group is involved in the catalytic interaction between enzyme and substrate. Studies of the pK dependence of the system in D₂O at 25° C reveals substantial D₂O solvent isotope effect. particularly at lower pD values. A major part of this D₂O effect is attributable to effects upon the ionization constant of one or more catalytically active groups. Such an interpretation is consistent with the observed shift of 0.7 units in the pK value of the catalytically important group described previously, as well as the changed pKa of free imidazole in $D_{2}O$. When DL-[a-2H]leucine is employed as a substrate there is observed a strikingly pH dependent kinetic isotope effect, with a value of $k_{\rm H}/k_{\rm D}$ of 4.0 being observed at pH values less than 6.5, but approaching 1.0 at pH values above 8.5. Stopped-flow experiments have been conducted to locate the particular steps in the action mechanism which are affected by deuterium substitution.

A Kinetic Study of the Decarboxylation of Duroic Acid in Sulfuric Acid Solutions. JOHN T. SNOW and GERALD R. BAKKER, Earlham College. —The decarboxylation of diortho-substituted benzoic acids in strong mineral acids has long been known and is of some synthetic use, but the mechanism of the reaction is not well understood. Kinetic data are presented on the decarboxylation of duroic acid in various concentrations of sulfuric acid and at several different temperatures. The reaction is first order in duroic acid, but the rate dependence on sulfuric acid concentration allows no simple interpretation. Several possible mechanisms are presented.

Kinetic data were obtained by measuring evolved carbon dioxide. The development of the gasometric technique is discussed and a comparison is made of the gasometric method and the infrared and ultraviolet spectrophotometric methods of analysis.

Molecular Complexes of Bromine and Various Substituted Carbostyrils and their Hydrolysis Products. DONALD J. COOK, DePauw University.— A number of 1:1 molecular compounds between bromine and various carbostyrils have been prepared. These compounds are fairly stable at room temperature and are inert in nonpolar solvents. However, in the presence of water, hydroxide ion, or pyridine, the molecular compound is destroyed resulting in the substitution of a bromine on the three or six position of the carbostyril. Identification of the substituted bromine carbostyrils was made by infrared studies and by independent synthesis of the compound by known methods. The position of the bonded bromine molecule on the carbostyril is not known but some studies with the nuclear magnetic resonance have been initiated to determine the structure.

The molecular compounds have also been shown to be brominating agents for alkenes and ketones.