

CHEMISTRY

Chairman: L. A. MCGREW, Ball State University

JOHN W. MCFARLAND, DePauw University, was elected chairman for 1969

ABSTRACTS

X-Ray Diffraction Study of Aqueous Thallium (III) Chloride. RICHARD M. LAWRENCE, Ball State University.—The radial distribution function of 2.5 M aqueous thallium (III) chloride having a mole ratio of chloride ion to thallium ion of 4.3 was calculated from x-ray diffraction data. The radial distribution function is consistent with the existence of the tetrachlorothallate (III) ion as the dominate ionic species in the solution. There is evidence that the shape of the $TlCl_4$ -ion is that of a distorted tetrahedron with each chloride ion being at about 95° from two others and about 127° from a third. The distortion in the complex ion is qualitatively attributed to solvent stabilization effects. There is no evidence for thallium-ion—water-molecule contact in the proposed model of the tetrachlorothallate (III) ion.

Studies of a Cyanamide Complex of Iron(II). F. J. HOLLER and R. D. JOYNER, Ball State University.—A number of possible ways that the cyanamide unit could coordinate with a metal are suggested. These possibilities include simple ionic and molecular complexes as well as bridge structures. A pentacyano-cyanamide complex of iron(II) has been referred to in analytical studies of cyanamide, but no previous studies have been concerned with its actual preparation. Optimum conditions for the formation of this complex have now been determined. Additional studies have been made concerning the isolation and purification of the complex.

Phthalocyaninogermanium(II) and Other Phthalocyaninogermanium Compounds. R. L. STOVER and R. D. JOYNER, Ball State University.—Reactions of germanium compounds of the form R_nGeCl_{4-n} (R = phenyl, n -butyl, hydrogen; n = 0, 1, 2, 3, 4) with metal free phthalocyanine, sodium phthalocyanine, and diiminoisindoline are described. Apparently phthalocyaninogermanium compounds are not formed from compounds of the type R_nGeCl_{4-n} where $n > 1$. The reaction of phenyl germanium hydride with metal-free phthalocyanine to apparently give phthalocyaninogermanium(II) is described.

A Kinetic Study of the Reaction of Phenyl Isocyanate with Water. LEROY A. MCGREW and STEPHEN C. ROBLING, Ball State University.—The rate of the reaction of phenyl isocyanate with water in acetone solution was followed by measuring the rate of carbon dioxide evolution. In the presence of excess water the reaction was found to be first order with respect to isocyanate concentration. The pseudo-first order rate constant was found to be $5.5 \times 10^{-3} \text{ sec}^{-1}$. The reaction was found to be catalyzed by tertiary amine bases. Primary amines suppressed the normal decomposition by reacting with the isocyanate in a fast step to produce

N,N-diphenylurea. This urea was also observed to be the only product of the normal reaction with water. The experimentally determined rate law was shown to be consistent with a proposed mechanism.

Organonitrile Complexes of Rhenium (I) and Manganese (I). BRUCE N. STORHOFF, Ball State University, and J. R. DOYLE, the University of Iowa.—Bromopentacarbonylrhenium(I) reacts with acetonitrile, propionitrile, acrylonitrile and benzonitrile to yield complexes of the stoichiometry $\text{Re}(\text{CO})_5(\text{RCN})_2\text{Br}$. Bromopentacarbonylmanganese(I) reacts, in an analogous manner, with acetonitrile and benzonitrile to yield the tricarbonyl complexes $\text{Mn}(\text{CO})_5(\text{RCN})_2\text{Br}$. The infrared spectra of the complexes suggest octahedral structures with the two nitriles *cis* to each other and *cis* to the bromine.

Bromopentacarbonylmanganese(I) reacts with acrylonitrile and propionitrile to yield complexes of the stoichiometry $\text{Mn}(\text{CO})_5(\text{RCN})\text{Br}$ which are suggested to be halogen bridged dimers on the basis of molecular weight and infrared studies. *Di-μ*-bromooctacarbonyldirhenium(I) reacts with acetonitrile to yield *cis*- $\text{Re}(\text{CO})_4(\text{CH}_3\text{CN})\text{Br}$.

Infrared studies indicate that for each complex the organonitriles are attached to the metals through the pair of electrons associated with the nitrogen. Molecular weight studies and nuclear magnetic resonance studies of the tricarbonyl complexes, $\text{M}(\text{CO})_5(\text{CN})_2\text{Br}$, indicate that they dissociate in chloroform solution but not in dimethylsulfoxide solution.

Replacement reactions indicate that the nitriles of all the manganese(I) and rhenium(I) complexes can be replaced by pyridine and suggest that olefins do not replace the nitriles.

Use of Computers in Undergraduate Physical Chemistry. RICHARD F. COPELAND, Ball State University.—Computers can be very valuable tools for the student of physical chemistry, but for most students the junior or senior year course in undergraduate physical chemistry is not the time to begin to learn computer programming. The best results should be obtained by a program integrating the use of computers into chemistry courses beginning with the freshman course in general chemistry. Instruction at the freshman level may be in either a special course, or, preferably, incorporated into the general chemistry laboratory sequence. Analysis of data using library programs is a very useful asset, but emphasis should be on the student's use of programming to solve his individual problems. Simulation of complex chemical systems involving large numbers of variables can be a valuable tool in instruction.

Synthesis and Properties of [2.2.2]Bicyclooctyl Enamines. A. G. COOK and T. A. HECHT, Valparaiso University.—Some [2.2.2]bicyclooctyl enamines have been synthesized and some of their properties investigated. The ultraviolet spectra of some of them seems to be indicative of some homoconjugation.

Reduction of Selected Enamines with Lithium Aluminum Hydride. A. G. COOK and D. J. SCHULTZ, Valparaiso University.—It has been observed that certain enamines possess structural features which make them susceptible to reduction by lithium aluminum hydride. These features will be discussed.