

CHEMISTRY

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ABSTRACTS

Synthesis and Purification of Phthalocyaninogermanium (II). C. L. THRALL and R. D. JOYNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The reaction of phenyl germanium hydride with metal-free phthalocyanine to apparently give phthalocyaninogermanium (II) was described by Stover and Joyner in Volume 78, *Proceedings of the Indiana Academy of Science*. Analytical data were not then conclusive. The synthesis of this compound by the reaction of sodium borohydride with dichlorophthalocyaninogermanium (IV) was described. The phthalocyaninogermanium (II) compound was also purified and analyzed. Chemical studies show this compound to be relatively inert, particularly when it is compared with the corresponding tin compound.

The Contribution of Lattice Defects to the Heat Capacity of Crystalline Materials. J. H. MEISER, Department of Chemistry, Ball State University, Muncie, Indiana 47306; J. E. DAVISON, and G. W. LAWLESS, Research Institute, University of Dayton, Dayton, Ohio 45409.—A detailed consideration of the contribution of the formation and migration of lattice defects to the heat capacity of a series of metals was made. This series includes Ag, Al, Au, Cu, Li, Na, Pb, Pt, and W. We showed that the exponential-like upward trend of the C_p versus temperature curve, as observed for the above metals near their melting point, can be ascribed to the presence of lattice defects. The preceding development also includes a brief background describing the main contributors to metallic heat capacities: harmonic and anharmonic lattice vibrations and the electronic contribution.

Further Studies of a Cyanamide Complex of Iron (II). F. J. HOLLER and R. D. JOYNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—A pentacyanocyanamide complex of iron (II) appears to exist as a dimer in aqueous solution. The complex is readily formed in basic solutions of sodium pentacyanoaquoferrate (II) and cyanamide. Separation of the pure complex from the reactants was accomplished by eluting the solution with water from a Sephadex® column. Most experiments with the light sensitive complex must be conducted in the dark. Spectrophotometric and polarographic studies were used to indicate the composition of the complex.

Integration of a Time-Sharing Computer into the Chemistry Curriculum. PHILIP A. KINSEY, Department of Chemistry, University of Evansville, Evansville, Indiana 47704.—A time-sharing on-line com-

puting system adds an extra dimension to computer use and resolves some of the difficulties that prevent effective student use of the computer. Three levels of usage were described. First, in a simulation mode the student can have a sense of discovery with no knowledge of programming necessary. Acid-base titration curves were drawn for equal pH intervals. The trajectory of a molecule in a Lennard Jones 6-12 potential was demonstrated for various impact parameters and energies. Second, single concept movies were filmed showing the changes in population in rotational levels and the effect on the vibrational rotational IR spectrum as the temperature was changed. Third, the student was furnished with a selection of numerical analysis programs to curve fit, integrate, and to solve differential equations. The student then wrote his own problem solution incorporating these programs. The solution to one dimensional Schroedinger equation for various models along with other examples were presented.

Thermolysis and Photolysis of Some 1-Pyrazoline-3,4-dicarboxylic Anhydrides. TERRY L. KRUGER and JOHN SHARP, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—In a series of experiments comparing the modes of decomposition of some cyclic azo compounds the emphasis has so far been on 1-pyrazolines. The facile 1,3-dipolar addition of diazomethane to the appropriate cyclic anhydrides has yielded 1-pyrazoline-3,4-dicarboxylic anhydride and the 4-methyl analog. These compounds are decomposed by light and heat and isomerized by acid or base. Study results of the thermolysis and photolysis of these labile materials were presented. These reactions proceed with the evolution of nitrogen and some carbon dioxide. Major isolable products are citraconic anhydride and dimethylmaleic anhydride, respectively. Some evidence was presented which supports the proposal that $[2 + 4 + 2]$ retroaddition was competing in the thermal process. A quick treatment of $[2 + 4 + 2]$ cycloreversion from the consideration of the Woodward-Hoffmann rules for conservation of orbital symmetry was included. The 75 electron volt mass spectrum of the parent compound is perhaps best explained by analogy with the proposed concerted retroaddition.

Photochemistry of Conjugated Dinitrones. M. L. DRUELINGER and S. R. LAMMERT, Department of Chemistry, Indiana State University, Terre Haute 47809.—The irradiation of N,N'-disubstituted dinitrones was studied. When the nitrogen substituents are tertiary alkyl groups, at least four products were identified. They are formed sequentially and involve ring closure to the strained oxazirane system followed by rearrangement to amides. The structures were assigned on the basis of spectral data and independent syntheses. Results of studies on an N,N'-diaryl system were also noted. Mechanistic aspects of these reactions were discussed.

Preparation and Decomposition of N-Alkyl-N-aryloxyamines. TERRY L. KRUGER and STEPHEN L. HARTZELL, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Eugen Bamberger first prepared and studied many substituted hydroxylamine compounds, but

the actual mechanistic pathway for the acid-catalyzed rearrangement observed by him has not been extensively studied. To explain the observations, a variety of mechanisms have been proposed but none agrees completely with the experimental facts.

This research first involved the development of a convenient synthetic route for obtaining the desired hydroxylamines. Secondly, the synthesis required the preparation and identification of several previously unreported compounds. Finally, a mechanism of the acid-catalyzed hydroxylamine rearrangement was suggested to explain our results.

For preparing the N, N'-disubstituted hydroxylamines, the Cope elimination was chosen as the synthetic pathway. Since an olefin was ejected from the amine oxide, the reaction rate is conveniently measured. It was found that hydrated amine oxides and various μ -substituents affected the reaction rate significantly.

The Effect of Vitamin-E Deficiency and Dietary Histidine on Serum Aldolase and Transaminase, and Tissue Phosphatase Activity. JOSEPHINE SHANGKUAN and L. C. SMITH, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.—Vitamin-E deficiency has caused rabbits to excrete 1-methyl-histidine in large amounts. Appearance of this amino acid generally precedes that of creatine making it one of the earliest detectable symptoms of nutritional muscular dystrophy. The loss of large amounts of 1-methyl-histidine might itself produce secondary effects such as a significant drain on the body's reserve of the essential amino acid histidine. This, in itself, might effect the activity of several enzymes. It seemed desirable to determine what effect, if any, the dystrophic condition as well as dietary histidine would have on enzymic activity of tissue other than muscle. Our studies describe the alkaline phosphatase activity in liver and kidney as well as serum aldolase and transaminase of normal and Vitamin-E deficient rabbits. Also the influence of dietary histidine on these enzymes was reported.

Kinetic versus Thermodynamic Control: An Organic Chemistry Experiment. L. A. MCGREW and T. L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Very few current laboratory manuals include experiments designed to illustrate reaction systems in which a competition exists between two processes, one favored by the rate of the process, the other by product stability. The base-catalyzed polymerization of aromatic isocyanates have yielded a kinetically-controlled or a thermodynamically-controlled product under conditions which can easily be adapted to a laboratory situation. Materials needed, technique to be used, and results to be expected were discussed.