

CHEMISTRY

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ABSTRACTS

Computer-Assisted Nitrate Analysis System Using a Nitrate Ion Selective Electrode and an Apple II Plus Microcomputer. STANLEY, L. BURDEN, DOUGLAS W. TAYLOR, CHRISTOPHER L. MYER and MARK A. NUSSBAUM, Department of Chemistry, Taylor University, Upland, Indiana 46989.—Software has been developed and hardware configured to enable an Apple II Plus microcomputer to control the acquisition, reduction and display of data from a nitrate ion selective electrode. The computer samples potential readings from the electrode, determines when electrode-solution equilibrium is reached, and stores the equilibrium potential reading. Measurements from standard solutions are plotted in color on a television set using high resolution color graphics to display a calibration curve. A cubic fit to the standards is made and also displayed in a different color passing through the calibration points. The cubic fit allows measurements to be conveniently made in the lower concentration (1-2ppm) non-linear region of the calibration curve as well as on the linear region. Potential readings from unknowns are acquired in a similar fashion, the cubic equation is solved by the Newton-Raphson iterative method and the concentration is printed on the television. Hard copy output of all data, calibration curve plot, fitted equation, and unknown concentrations is available using a Paper Tiger 460 printer. The precision and accuracy of the system is equal to manually acquired and plotted data but the time required for the analysis is significantly decreased.

The Occurrence of Certain Toxic Organics in the Nature and Their Degradation. ROBERT H. L. HOWE, and ROBERTA C. HOWE, West Lafayette, Indiana 47906.—The occurrence of phenols, pyridines, and cyanides in the nature, unrelated to industrial processes, is discussed. Their degradation by natural processes is presented.

The Hydrolysis of Bovine Insulin A-chain by Guanidine-stable Chymoelastase in the Presence of Denaturant. KATHERINE J. JORDAN and ERIC R. JOHNSON, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Guanidine-stable chymoelastase, a denaturant-stable protease isolated from Pronase, was found to catalyze the hydrolysis of bovine insulin A-chain (glycyl chain) in the presence and absence of 6.0 M guanidinium chloride. In the presence of this denaturant, an average of two peptide bonds per insulin A-chain molecule was hydrolyzed by the stable protease. However, only one peptide bond per insulin A-chain molecule, on the average, was cleaved by this enzyme in the absence of guanidinium chloride. The appearance of an additional cleavage site on the insulin A-chain molecules in the presence of denaturant indicates that the guanidinium chloride unfolds the peptide substrate, rendering internal cleavage sites accessible to the stable protease. Thus guanidine-stable chymoelastase can be used in con-

junction with the denaturing properties of guanidinium chloride for the cleavage of proteolysis-resistant polypeptides and proteins.

Phosphorus Ligand Size Effects Upon Reactions with $W(CO)_4$ (pyridine)₂. CONSTANCE A. KIESLER and JOHN A. MOSBO, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The steric effects of phosphorous ligands (L and L') upon the *cis-trans* distributions of $W(CO)_4LL'$ products were studied for the reactions of $W(CO)_4$ (pyridine)₂ with L and L'. When L = L', the sterically dissimilar ligands methyl (diphenyl)-, ethyl(diphenyl)-, isopropyl (diphenyl)-, and tert-butyl (diphenyl)- phosphine were chosen because of their comparable electronic properties. Through integration of 31-phosphorus NMR spectra, it was observed that an increase in ligand size brought about a decrease in *cis:trans* product ratio. Also investigated were the reactions of L' with $W(CO)_4$ (PPh₂Et) (pyridine) which provided $W(CO)_4$ (PPh₂Et) L' products. The resulting *cis:trans* ratios were discussed in terms of proposed reaction mechanisms and ligand sizes as defined by cone angles.

Asymptotic Expansions of the Eigenvalues of Burrau Molecules. PAUL C. MCKINNEY, Department of Chemistry, Wabash College, Crawfordsville, Indiana 47933.—Two nuclei and an electron bind together to form a Burrau molecule. The Schrodinger equation for these simple molecules has the advantage that it can be separated into three ordinary differential equations. One of the equations can be solved with elementary functions and it generates the quantum number for the z-component of the angular momentum, m. The two remaining equations, which have the same general form,

$$\frac{d}{dx} \left[(1-X^2) \frac{dP(x)}{dx} \right] + \left[\frac{-m^2}{(1-X^2)} + 2abx - a^2(1-X^2) + t \right] P(x) = 0,$$

where a and b are molecular parameters, t is the eigenvalue, and m is an integer, may be investigated with infinite power or functional series. Unfortunately, these series are divergent in general, but they do provide asymptotic descriptions of the eigenvalues and eigenfunctions. It is possible to determine asymptotic expansions for t when the molecular parameters, a and b, both small, or one is small and the other is large, or when both are large. The results of these expansions are presented as an aid for numerical calculation of the eigenvalues.

The Synthesis of β -lactams Using a Photochemical Reaction. LAURA L. NELSON and LYNN R. SOUSA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Recently we discovered a photochemical reaction of 1, 1-dioxo-2-aryl-4-thiazolidinones that produces 2-azetidiones in reasonably good yield. 2-Azetidione rings (β -lactams) are a crucial element in the structures of β -lactam antibiotics such as penicillin and cephalosporin. With this in mind we set out to use this photochemical β -lactam synthesis to make a simple compound with potential antibiotic activity: 1-acetic acid-4-furyl-3-(methoxycarbonylhydroxymethyl)-2-azetidione.

The sequence of synthetic steps begins with a one-pot reaction to produce 2-furyl-4-thiazolidinone from thioglycolic acid, ammonium carbonate, and furfural. The nitrogen was then alkylated with the requisite functional group (methyl chloroacetate was used). The next step, oxidation to 1,1-dioxo-2-furyl-3-(methylacetate)-4-thiazolidinone, proved difficult. Finally, a procedure using $KMnO_4$ produced the desired product. Problems in separation and analysis will be discussed. Condensation of the active methylene with methyl pyruvate will yield the thiazolidinone

with the proper functionality targeted for biological activity. Work on the final photochemical SO₂ expulsion to produce the desired β -lactam will also be discussed.

The ¹⁸O-Isotope Effect in NMR Spectroscopy: A Method for Simultaneously Following Kinetics and Establishing the Site of Bond Cleavage During the Hydrolysis of Phosphate Monoesters. JEAN E. PARENTE, JOHN M. RISLEY and ROBERT L. VAN ETEN, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907.—An upfield shift in the ¹³C-NMR signals of various organic compounds upon replacement of ¹⁶O by ¹⁸O has been shown to occur in ¹³C-NMR spectroscopy [Risley, J. M. and Van Etten, R. L. (1979) *J. Amer. Chem. Soc.* 101, 252-253]. A similar observation of an upfield shift has been described for the ³¹P-NMR signal of inorganic phosphate [Cohn, M. and Hu, A. (1978) *Proc. Natl. Acad. Sci. USA* 75, 200-203]. These ¹⁸O-isotope effects have great utility in studies of reaction mechanisms. The ability to measure the isotopic content of substrates and products, simultaneously, as a function of time, provides distinct advantages over previously-used discontinuous methods of analysis such as mass spectroscopy, where the compound(s) of interest often require isolation and derivatization before analysis. In particular, the NMR techniques are very useful for studying enzymatic (and non-enzymatic) reactions of phosphate esters. We have examined the hydrolysis of [α -¹³C, ¹⁸O] benzyl phosphate catalyzed by homogeneous human prostatic acid phosphatase, making use of the ¹⁸O-isotope effect in ¹³C-NMR. It is demonstrated that the application of the ¹⁸O-isotope effect in NMR spectroscopy affords a convenient, non-destructive method of analysis for following kinetics and for determining the position of bond cleavage during such enzyme-catalyzed hydrolysis reactions.

An Improved Qualitative Test for Acetate Ion. ROBERT E. VAN ATTA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Qualitative tests for acetate ion rarely appear in general chemistry laboratory assignments, owing to the unreliable nature of existing tests for the ion. A modified version of the basic ferric acetate test has been developed which has yielded an average accuracy of about 90% in the hands of inexperienced analysts. The test involves the formation of the characteristic brown basic ferric acetate when the warm unknown solution, previously treated to remove interfering cations and anions, is added to concentrated ferric nitrate reagent and the color produced compared with that obtained with a similarly treated blank test solution. Certain cations, sulfide, iodide, and some oxygenated anions interfere; simple procedures for preliminary removal of these interfering ions are also described.

Apple Computer Simulations Used in Teaching Chemical Instrumentation. JOHN F. ZIMMERMAN, Department of Chemistry, Wabash College, Crawfordsville, Indiana 47933.—The advent of "low cost" personal computer systems with graphics capability makes it possible, via simulation, to bring "real" instrumentation into the classroom. Computer simulations provide the ability to generate controlled presentations of time-dependent phenomena. This capability has been combined with computer text, color graphics and sound to produce lecture demonstrations in two areas, chromatography and the interaction of electromagnetic radiation and matter.