American Chemical Society

Second Central Regional Meeting

Columbus, Ohio
June 3-5, 1970
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COVER—The emblem of the American Chemical Society and the official centennial symbol of The Ohio State University.
PROCLAMATION
CHEMICAL WEEK
JUNE 3-7, 1970

WHEREAS, the Central Region of the American Chemical Society will meet in Columbus June 3-4-5, 1970; and

WHEREAS, the scheduled program to be presented at the Ballroom of Ohio State University has been correlated with the Centennial Year Anniversary of O.S.U.; and

WHEREAS, the meeting will feature a range of programs and exhibits designed to appeal to industrial and academic scientists and to teachers and students at several levels of academic development; and

WHEREAS, the program for Wednesday evening will include a panel of distinguished chemists and leaders of industry who will discuss environmental problems and the role of the Chemist and the Chemical Industry; and

WHEREAS, the Thursday and Friday programs will present over 200 technical papers and symposia topics and will feature in the Ballroom of the Ohio Union a chemical exposition conducted by approximately 50 exhibitors; and

WHEREAS, an attendance of over 1000 registrants is expected due to the fact that Columbus is the home of Battelle Institute, Chemical Abstract Services and Ohio State University. The program's inclusion of the two year College Conference and the Ohio Chapter of the American Institute of Chemists meeting will add substantially to the attendance.

BE IT FURTHER RESOLVED, that I, James A. Rhodes, Governor of the State of Ohio, in recognition of the academic standing and the professional achievements of this brilliant gathering of scientists, do hereby designate the week of June 3-7, 1970, as

CHEMICAL WEEK

in Ohio and I urge our citizens to avail themselves of the rare opportunity thus provided them to acquire a better understanding of the technical and industrial advancement of the State of Ohio.

IN WITNESS WHEREOF,
I have hereunto subscribed my name and caused the Great Seal of the State of Ohio to be affixed at Columbus, this 10th day of April, in the year of Our Lord, One Thousand Nine Hundred and Seventy.
Members of the American Chemical Society
Attending the 2nd Central Regional Meeting
The Ohio State University
Columbus, Ohio

Ladies and Gentlemen:

Welcome to The Ohio State University. The presence of your basic but relevant and forward-looking program on our campus is particularly apropos in this the Centennial Year of our University. We look to the next century with the intent that the prospects for mankind will be made brighter through more idealistic pursuit of the highest endeavors, more circumspect and understanding behavior in human relations at all levels and unrelenting progress by man in relating to his ever-expanding environment.

We are pleased to see increasing pertinent involvement of scientists and other professional groups in all aspects of their realms. It is heartening to know that dedicated specialists can at once find marked progress in the more profound and esoteric parts of their fields and in those areas where all of society needs their distinct capabilities in order to overcome compelling problems, some of which are either artifacts of past errors or have first come to light through growing knowledge. While the many excellent papers and symposia in your program generally testify to the continuing progress in that first area, your opening session on "The Responsibilities of Chemists in this Era of Social Change" and your symposium on "Environmental Chemistry" evidence the second.

Best wishes for a most successful and useful meeting.

Sincerely,

Novice G. Fawcett
President
2nd Central Regional Meeting

AMERICAN CHEMICAL SOCIETY

Columbus, Ohio
June 3, 1970

Fellow ACS Members and Guests
2nd Central Regional Meeting
American Chemical Society
Columbus, Ohio 43210

Greetings:

It is with pleasure that I welcome you to this the 2nd Central Regional Meeting of the American Chemical Society. We are immensely pleased that Governor Rhodes has seen fit to declare this Chemical Week in Ohio and we hope you feel thoroughly welcomed by him and by the Mayor of our City, M.E. Sensenbrenner. We also count it an especially happy situation that the Ohio State University has welcomed our meeting to their campus during their Centennial Year. To these our gracious hosts, we offer our most sincere thanks.

The pages of this program contain the technical program, abstracts of papers, a summary calendar, a schedule of special events, and a map of the exhibitors' area. Much additional information is presented in a special issue of the Chemical Record containing feature material relative to the professional and special event program. Certain materials have been included to aid you as a visitor to our city and the Ohio State University.

The personnel staffing our registration areas are well provided with information to serve you and a message center is available there. They can also put you in touch with our meeting headquarters.

Chemical Abstracts Service, Battelle Memorial Institute, Warren-Tweed Pharmaceuticals, Co., and the Ohio State University have been particularly generous in contributing their personnel, facilities, and services to the planning and implementing of this meeting. The essential support of those companies displaying exhibits at our meeting is equally well appreciated.

Finally, I wish to personally thank all those individuals who have devoted their thoughts, actions, time, and concerns to the minutiae that must be taken care of in order to hold such programs as the one we share this week. The Chemical Record has a few words to say about your Operating Committee and I hope you will read it.

Kindest regards.

Sincerely,

Daryle H. Busch
Chairman
GENERAL INFORMATION

• Registration—Registration and information desks at the Center for Tomorrow and the Ohio Union will be open from 6:00 p.m. to 10:00 p.m. on Wednesday, June 3. Desks will be maintained at both sites on Thursday from 8:00 a.m. to 5:00 p.m., on Friday from 8:00 a.m. to 7:30 p.m., and on Saturday from 8:00 a.m. to noon. Those who have preregistered may pick up packets at the Center for Tomorrow registration center.

Registration badges are required for admission to all sessions of the meeting. Exhibitors must register for special free badges.

• Fees—On-site registration fees are $10 for ACS and Two-year College Chemistry Conference members, $15 for nonmembers, $5 for students and high school teachers, $1 for wives. The fee for half-day registration is $5.

• Ladies Program—The Ladies Hospitality Room is located on the ground floor of the OSU University Law Building just south of the Ohio Union. A Ladies Lounge is also maintained at the Center for Tomorrow. (Inquire at desk). Events planned as part of the Ladies Program are: Thursday—bus tour of center city, conducted walking tour of German Village, tea at Swiss Club; Friday—luncheon at University Faculty Club.

• ACS Short Course—Registrants for the Short Course on the Interpretation of Infrared Spectra will convene Saturday morning at 9:00 in Room 1008 of Evans Laboratory.

SHUTTLE SERVICE

Wednesday, June 3
Continuous service to Ohio Union from Center for Tomorrow, Stouffer’s University Inn, and Olentangy Inn. 7:30-11:30 p.m.

Thursday, June 4
Service at ten-minute intervals between the Ohio Union and Center for Tomorrow. 8:00 a.m.-8:45 p.m. Service extended to include Stouffer’s University Inn. 8:00-9:15 a.m. and 4:40-5:30 p.m.

Additional route with continuous service between Center for Tomorrow, Stouffer’s University Inn, and Olentangy Inn. 8:00 a.m.-9:00 p.m.

Continuous service between Ohio Union and Battelle Memorial Institute for the ACS Board Reception. 5:30-6:30 p.m.

Friday, June 5
Service at ten-minute intervals between the Ohio Union and Center for Tomorrow. 8:00 a.m.-6:00 p.m. Service extended to include Stouffer’s University Inn. 8:00-9:15 a.m. and 4:40-5:00 p.m.

Additional route with continuous service between Center for Tomorrow, Stouffer’s University Inn, and Olentangy Inn. 8:00 a.m.-6:00 p.m.
SPECIAL EVENTS

Wednesday—Opening session at 8:00 p.m. in the OSU Law Auditorium will be a panel discussion on “Responsibilities of Chemists in our Environment of Social Change.” The distinguished panel will consist of Moderator Dr. Alfred B. Garrett, Professor of Chemistry at Ohio State and President of the National Science Teachers Association, and Panelists Dr. Milton Harris, Chairman of the ACS Board of Directors, Dr. Charles G. Overberger, Member of the ACS Board of Directors, and Chairman of the Department of Chemistry at the University of Michigan, and Dr. Byron Riegel, President of the ACS and Director of Research at C. D. Searle and Co.

Following the discussion, a free general mixer for registrants will be held in the South Terrace and Franklin Rooms of the Ohio Union until 11:00 p.m.

Thursday—Reception for the ACS Board of Directors will be held at Battelle Memorial Institute from 5:30-7:00 p.m. Tickets for registrants and guests are $2.50 and may be obtained at the registration desks at any time or at Battelle during the reception.

Tour buses leave for Ross Laboratories from Center for Tomorrow at 11:00 a.m., for Battelle Memorial Institute from Center for Tomorrow at 2:00 p.m., and for German Village from Ohio Union at 1:00 p.m. A tour of Chemical Abstracts Service will be conducted beginning at 1:00 p.m. Tickets for all tours may be obtained at the registration desks at any time.

Friday—The Ohio Chapter of the American Institute of Chemists, meeting concurrently with the CRM, will host a luncheon in the Ohio Union, Rooms A and B, at 12:15 p.m. Dr. Henry B. Hass, director of planning in research and engineering development for the M. W. Kellogg Company, will address the luncheon meeting on “Postponing Personal Obsolescence.” Luncheon tickets will be available at the registration desks until Thursday evening.

Tour buses leave for Ross Laboratories from Center for Tomorrow at 11:00 a.m., and for Anheuser-Busch Brewery from Center for Tomorrow at 12:30, 1:30, 2:30, and 3:30 p.m. A tour of Chemical Abstracts Service will be conducted beginning at 1:00 p.m. Tickets for all tours may be obtained at the registration desks at any time.

WORKSHOPs

I. Chemical Safety: “How Can We Get Teachers and Students to Practice Safety?” 8:00-9:30 P.M., Thursday, June 4th. No charge. Center for Tomorrow, Room 5

Sources of Information and Guidelines to Laboratory Safety
Normal V. Steere, 3M Company

Profit-Making Spur Student Interest in Laboratory Safety
John Bedenbaugh, University of Southern Mississippi

Incentives for the Chemical Technologist’s Commitment to Safety
Ernest W. Bowerman, Ohio State University

II. Chemical Education: “Innovations in Chemical Education” Jointly Sponsored by ACS Central Regional Meeting and the Two-year College

Chemistry Conference. 7:30-10:00 P.M., Friday, June 5th. 9:00 A.M.-noon, Saturday, June 6th. No charge. McPherson Laboratory, Room 100

Friday Evening
Opening of the Two-Year College Chemistry Conference
William T. Mooney, Jr., El Camino College and 2YC Chair
Opening Remarks on Media, Computers and Systems Analysis Techniques
Harrison Allison, The Marion Institute

New Teaching Aids or New Uses for Old Ones
Robert Barnard, Ohio State University
Constant Variation Techniques
Lawrence E. Strong, Earlham College

Computer Assisted Instruction
Robert C. Grantey, University of Illinois at Urbana

Saturday Morning
Opening Remarks
Ethelreda Laughlin, Cuyahoga Community College-Western Campus and Vice Chairman for Midwestern Region, 2YC

Advances in Curriculum and Laboratory in General Chemistry: A Panel Discussion
W. T. Lippincott, Ohio State University and Editor of the Journal of Chemical Education, Moderator

Larry Wilson, Ohio Wesleyan University
Clifford Hous, Ohio University
William T. Mooney, El Camino College
George Gilbert, Denison University

Future Trends in Chemistry For Non-Science Majors
Stuart E. Whitcomb, Earlham College

The State of Chemical Technology Education and Chem Tec
Kenneth Chapman, American Chemical Society


Speakers:
Henry Dombrowski—Ohio Bureau of Criminal Identification and Investigation
Claude Hadden—Dayton Police Department
John Klosterman—Ohio Bureau of Criminal Identification and Investigation
Lloyd Shupe—Columbus Police Department

IV. Local Section Officers: “Local Financing” 9:00 A.M.-noon, Saturday, June 6th. No charge. Evans Laboratory, Room 1001

Earl Klinefelter—American Chemical Society, Washington, D.C.
ANALYTICAL CHEMISTRY
FRIDAY

General.  L.K. Hiller, Presiding  Center for Tomorrow, Room 2-3

Time  Paper No.

9:15  1.  Computer Simulation of Rapid Repeated Injections, RRI, of Samples

9:35  2.  Ensemble Averaging in Gas Chromatography.  L.J. Lorence, R.A.
     Culp, L.B. Rogers.

9:55  3.  Improvements in the Gas Chromatographic Separation of the
     Enantiomers of Secondary Amine Derivatives.  J.A. Corbin and L.B.
     Rogers.

10:15  4.  Chemical Activity of Tobacco Smoke Condensate.  L.W. Michael,
     E. Menden, H.G. Petering.

     L.B. Anderson and M.L. Rose.

     Bohl, F.A. Koehler, Jr., and D.E. Sellers.

11:15  7.  Continuous Amperometric Measurement of I⁻Br⁻ and Alkaloids
     at a Tubular Carbon Electrode.  C.L. Olson, M.T. Henne, T.A.L.
     Gouda.

11:35  8.  A Fully Automated Method for the Estimation of the Concentration
     of Ca and Mg in Serum and Urine.  J.A. Lott and T.S. Herman.

11:50  9.  The Determination of Rhenium in Platinum-Rhenium-Alumina Catal-

BIOCHEMISTRY AND MEDICINAL CHEMISTRY
THURSDAY

General.  M.H. Klapper, Presiding  Center for Tomorrow, Room 6-7

9:15  10.  Infrared Studies of Some N-Methylacetamide Complexes.  N.C. Li
     and Y.H. Shaw.

     Rippon, A.G. Walton, J.L. Koenig.

9:55  12.  Interaction Between Human Alpha-1-Acid Glycoprotein and Steroid
     Hormones.  J. Kerkay and U. Westphal.

     Uchida and M.H. Klapper.


10:55  15.  Kinetic and Binding Studies of Liver Alcohol Dehydrogenase Ter-
     minal Complexes.  J.D. Shore.

11:15  16.  Effect of Buffer System on Carbonic Anhydrase Activity in the

11:35  17.  The Hydrolysis of N-Aryl Substituted Carbamyl Phosphate Mono-
     and Diastere.  C.M. Allen and J. Jamieson.

General. D. Cornwell, Presiding Center for Tomorrow, Room 6-7
3:00 22. The Biosynthesis of the Phosphomannan of Hansenula Capnula. H.S. Prihar and R.M. Mayer.

FRIDAY
Symposium on Protein Conformation and Solution Properties.
J.L. Oncley, Presiding Center for Tomorrow, Assembly Hall
10:30 29. The Molecular Structures of Horse Heart and Bonito Ferricytochromes C. R.E. Dickerson, D. Eisenberg, T. Takano, O. Battayj, and J. Varnum.
11:30 30. Functions and Conformation of the Cytochrome c Surface as Revealed by Immunological Reagents. E. Margoliash, M. Reichlin, L. Smith, H.C. Davies, and A. Nisenoff.

Symposium on Protein Conformation and Solution Properties.
J.L. Oncley, Presiding Center for Tomorrow, Assembly Hall
2:00 31. Conformation of Myoglobin in Solution. F.R.N. Gurdon.
4:30 34. Optical Rotatory Dispersion and Circular Dichroism Patterns as Indicators of Protein Conformation. D.W. Urry.

CHEMICAL EDUCATION
FRIDAY
Section A—General. V.I. Meeke, Presiding Center for Tomorrow, Room 6-7
10:30 38. Water Pollution Study as a Method for Teaching General and Analytical Chemistry. J.F. Corwin.
11:45 41. Large Scale Electronic Grading and Grade Storage for General Chemistry Courses. Q. VanWinkle, W.T. Lippincott, R.J. Beaton, A.E. Petrarese.

Section B—General. P. Glassoe, Presiding Center for Tomorrow, Room 8-9
9:55 44. Qualitative and Quantitative Analysis with Pure Salts. G.L. Gilbert.

Symposium on Chemistry Curricula in the 1970's.
G.L. Galloway, Presiding Ohio Union, Conference Theater
2:00 50. Introductory Remarks. G.L. Galloway.
2:55 52. Discussion
3:50 54. Discussion
4:05 55. Chemical Education in the Seventies. L.E. Strong.
CHEMISTRY AND ENVIRONMENT  
THURSDAY

Symposium on Environmental Chemistry. 
K.H. NancY, Presiding 
Ohio Union, East Ballroom

2:00 Introductory Remarks.
4:35 57. Chemistry and Environmental Toxicology. M.M. Luckens.

INORGANIC CHEMISTRY  
THURSDAY

General. N.V. Duffy, Presiding  
Center for Tomorrow, Room 8-9

9:55 60. Photochemistry of Aryl Isocyanide Metal Complexes. R.A. Bailey.
10:55 63. Transition Metals as Lewis Bases: Co(CO)₅ Adducts with Hg(II) and In(III). W.R. Robinson, H.L. Conder, and D.P. Schussler.
11:15 64. Lewis Base Properties of Platinum (0). T.R. Durkin and E.P. Schram.

General. M.F. Farona, Presiding  
Center for Tomorrow, Room 8-9

2:00 67. Crystalline Coordination Complexes of Copper(II) Salts with Alkanol-Substituted Ethylenediamines. D.N. Zimmerman and J.L. Hall.

FRIDAY

Symposium on Non-carbon Catenation.

J.P. Fackler, Jr., Presiding  
Ohio Union, Conference Theater

10:05 Discussion
10:10 77. Coordination Polymers. B.P. Block.
10:55 Discussion
11:00 78. Sheet Organosilicon Polymers. M. Kenney.
11:40 Discussion
12:30 Discussion

General. F.L. Urbach, Presiding  
Center for Tomorrow, Room 2-3

2:00 80. Asymmetric Induction in Inner-Sphere Redox Reactions. Sister M.J. DeChant.
3:00 83. The Stereochemistry of N,N'-Bis(3-isopropylallylic)cyclopentadienylcobalt(II) Complexes in Donor and Nondonor Solvents and in the Solid State. M. Harirhan and F.L. Urbach.
4:00 86. The Crystal and Molecular Structure of Bis(p-perthiocumate) Zinc(II). J.P. Fackler, Jr. and D.G. Fries.
ORGANIC CHEMISTRY
THURSDAY

Section A—General

B.L. Fox, Presiding
Ohio Union, East Ballroom

9:15 90. The Synthesis and Solvolysis of the Isomeric 1-Chloro-2,3-diphenyl-

9:35 91. The Rearrangement of Some 1-Phenylcycloalkylcarbinols in Strong

9:55 92. The Trapping of Cations in the Reaction of Benzhydryl Azide with

10:15 93. The Chemistry of the Four Epimeric 2-Hydroxybicycle[6.1.0]non-
anes. E.A. Williams, P.G. Gasman.

10:35 94. The Chemistry of Cyanothiouimidocarbonic Acid. Part II: Synthesis
of 3-Halo-1,2,4-thiadiazoles. L.S. Wittenbrook, G.L. Smith, R.J.
Timmons.


11:15 96. The Preparation and Properties of 7,7-Dimethyl-1,2,3,4-tetraphenyl-
7-alla-2,3-norbornadiene. R. Maruca.

11:35 97. A Metallation Study of 2- and 3-Benzylthiophenes. A.T. Jeffries,
D.W.H. MacDowell.

11:55 98. Cyclo-dimerization of Dienes by Iron Catalysts. N.A. Maily, H.R.
Menapace.

Section B—General

J. Kosier, Presiding
Ohio Union, Conference Theater

9:15 99. The Reaction of Olefin Oxides with Dimethylhydrazides: A New


9:55 101. Evidence Regarding the Stereochemistry of 5-[(Methoxycarbonyl-

10:15 102. Evidence for Ylide Intermediates from Pyrolyses of Betaine and

10:35 103. A Novel 1,3-Dipolar Addition Reaction of Pyridinium Carboxy-

10:55 104. The Role of Iodine Complexation in Iodine Isocyanate Addition

Downie.

11:35 106. Amino Acids with Two Centers of Asymmetry from Microbial Pepti-
ides. G.G. Marconi, M. Bodanszky.

W.J. McKillip.

FRIDAY

Symposium on Application of Resonance Spectroscopy to Organic Chemistry.
T.A. Evans, Presiding
Ohio Union East Ballroom

Grant.

10:05 Discussion


11:05 Discussion

11:15 119. New Experiments and Theory of Chemically Induced Nuclear Spin
Polarization. G.L. Closs, A.D. Trifunac, D.E. Paulson, and C.
Doubleday.

12:05 Discussion

Symposium on Application of Resonance Spectroscopy to Organic Chemistry.
T.A. Evans, Presiding
Ohio Union East Ballroom

2:00 120. Aliphatic Semidiones. Applications of E.S.R. Spectroscopy to Organic
Chemistry. G.A. Russell.

2:50 Discussion

3:00 121. Spin Density Distributions in Strained Ring Molecules. L.M. Stock.

3:50 Discussion

4:00 122. E.S.R. Studies of Alkyl Radicals in Solution. P.J. Krusic and J.K.
Kochi.

4:50 Discussion
PHYSICAL CHEMISTRY
THURSDAY

Symposium on Fast Reactions—Heterogeneous and Homogeneous Kinetics.
T. Kuwana, Presiding Center for Tomorrow, Assembly Hall

10:20 Discussion
11:40 Discussion

Symposium on Fast Reactions—Heterogeneous and Homogeneous Kinetics.
J. Stuehr, Presiding Center for Tomorrow, Assembly Hall

2:30  128. Participation by Water Molecules in Fast Proton-Transfer Reactions. J.C. Harris and E. Grunwald.
3:00 Discussion
3:45 Discussion — Break

FRIDAY

General. G.E. Owen, Jr., Presiding Center for Tomorrow, Room 6-7

3:00  133. The Wetting of Thin Films of Organoclay Complexes. R.J. Ruch, M. Shen.
3:20  134. Quenching Studies of the Norrish Type II Reaction in Esters. F.S. Wetack, G.R. Dennison.

4:00  136. Polynuclear Complex Formation in Solutions of Calcium, Ion and Ethane-1-hydroxy-1,1-diphosphonic Acid. II. Light Scattering, Sedimentation, Mobility, and Dialysis Measurements. B.H. Wiers.
5:00  139. The Reaction of Ozone with Nitrogen Dioxide: An Important Step in the Mechanism of Photochemical Smog. W.E. Wilson, Jr., A. Levy.

POLYMER CHEMISTRY
THURSDAY

Symposium on Polymer Surfaces.
T. Fort, Jr., Presiding Center for Tomorrow, Room 2-3

10:05 Discussion
10:15 142. The Structure of Polymers Absorbed at Solid-Liquid Interfaces. C. Thiers.
11:05 Discussion
12:05 Discussion

Symposium on Polymer Textures.
G.S.Y. Yeh, Presiding Center for Tomorrow, Room 2-3

2:00  144. Texture of Styrene-Butadiene Block Copolymers. E.B. Bradford.
2:40 Discussion
3:25 Discussion
3:30  15 Minute Break
4:25 Discussion
CHEMICAL EXPOSITION

Latest advances in equipment, instrumentation, publications, and services for scientific support are featured at the Exposition in the Ohio Union. The exhibits will be open from 9:30-11:00 a.m. on Wednesday, 8:30 a.m.-5:30 p.m. on Thursday, and 8:30 a.m.-3:00 p.m. on Friday. Admission is by the CRM registration badge. An Exposition Visitor's badge must be obtained at the registration desk by nonregistrants who wish to view the Exposition.

Participants in the Exposition are listed below. Representatives will be available to discuss their equipment and services. Numbers shown here are booth numbers and correspond to those on the map of the exhibition area on the next page.
A FULLY AUTOMATED METHOD FOR THE ESTIMATION OF THE CONCENTRATION OF Ca AND Mg IN SERUM AND URINE. John A. Lotz, Thomas S. Horan, Ohio State University, Department of Pathology, Columbus, Ohio 43210

The concentration of calcium and magnesium in serum and urine can be determined by atomic absorption spectrophotometry provided that the interferences caused by phosphate, sulfate, and proteins are overcome. The depressing effects of polyvalent anions was overcome by the addition of LaCl₃ and HCl. For serum, dilution with a LaCl₃/HCl solution and a subsequent aspiration into the burner was found to be unsatisfactory when many samples had to be examined for Ca and/or Mg. The serum proteins did not burn well and they were found to be found in the flame of a Perkin-Elmer 303 atomic absorption spectrophotometer fairly rapidly. An Automatic sampler, pump 1, and diluter were used to dilute the specimen and aspirate the Ca and Mg from the serum or urine. The dilutions were debubbling and fed directly into the burner. A strip-chart recorder was used to monitor the output of the automated system. The only manipulation required was loading the sampler with the specimens.


The recent introduction of rhenium into platinum-alumina catalysts used for reforming petroleum products has necessitated the accurate analysis of such materials for their rhenium content. A new procedure is described for this analysis. Rapid sample dissolution is accomplished using phosphoric acid, and optimum conditions for the analysis are presented in a recommended procedure. The very small spectral interference of platinum is compensated for by using the platinum standards. A nitrate reagent is used to dissolve the sample with aqueous nitric acid; the sample must subsequently be dissolved using perchloric acid.
The laser excited Raman spectrum of helical poly-L-proline with cis peptide bonds (form II) has been obtained. Comparison of this spectrum with the previously reported laser excited Raman spectrum of poly-L-proline II reveals a number of absorption bands which are sensitive to the conformation; some of these are also seen in the infrared spectrum - others are unique. The spectra in addition, it is noted that the relative intensities of certain bands are also sensitive to conformation. A preliminary spectrum obtained from the "collapsed" form of poly-L-proline precipitated from concentrated calcium chloride solution is also presented. Oligomers of proline are shown to favor the trans form in aqueous solution for D5=c and in dried solids for D5=n.

Interaction Between Human Alpha-1-Acid Glycoprotein and Steroid Hormones. Julius Kerkay, Ulrich Westphal, Euclid Clinic Foundation, 18599 Lakeshore Blvd., Cleveland, Ohio 44119.

The binding affinity of human alpha-1-acid glycoprotein (AAG) for a number of steroid hormones was determined by equilibrium dialysis at 4°C and 37°C. The number of binding sites and apparent association constants were determined according to Scatchard's procedure. The binding affinity of the steroids to AAG was found to follow the polarity rule in that the steroid with the least number of polar groups was bound most firmly. With the exception of estradiol which interacted at several binding sites, the other steroids tested associated with AAG at a single primary binding site. The AAG-progesterone interaction was studied further and was found to be inhibited by Et3+, Na+, K+, Cu2+, and Fe3+. The inhibition of complex formation by these metal ions was analyzed by Scatchard plots and interpreted as competitive for the progesterone-binding site. The glycoprotein could be protected from the action of the metal ions by EDTA. Moreover, the inhibitory effect of the metal ions was found to be reversible when EDTA was added to a maximally inhibited system. The inhibitory effect of these ions may indicate the involvement of disulfide groups.

On the mechanism of cooperative binding by hemoglobin. Hiroshi Uchida, Michael H. Kupper, Department of Chemistry, Ohio State University, Columbus, Ohio 43210.

Hemoglobin, bromide and nitrilotriacetic acid reversibly, and significantly to the iron of human methemoglobin A. The apparent affinity of bromide and iodide depend on the counter ion such that the affinity increases in the series NaCl > tetramethylammonium > tetraethylammonium > tetraethylammonium > sodium. The dissociation constants indicate that the sigmoidal binding curves of bromide and iodide are due to salt induced, protein conformation perturbation. Tetraethylammonium bromide promotes the binding of hemoglobin, a low spin complex, but inhibits binding of cyanate, a high spin complex. We conclude that structural perturbation induced by neutral salts results in a shift of the iron electronic configuration toward the low spin form, resulting in enhanced binding of bromide and iodide, ligands which form low spin complexes. Nitrate binds with site-site cooperativity. Properties of the binding curve will be presented. We propose that cooperative nitrite binding by methemoglobin is triggered by shift in the iron spin state.

A study of sodium ion binding to proteins. Gerald E. Clemen, Department of Chemistry, Kent State University, Kent, Ohio 44240.

The sodium ion binding to proteins was studied using a gel-filtration method employing Sephadex G-25 and radiotracer sodium 22. The proteins employed at various pH values and buffer solutions were bovine serum albumin, ferritin, lysozyme and g-globulin and a mixture of A and B. As expected, lysozyme did not show any sodium ion binding by this method at pH 5.5 while the sodium ion binding with g-globulin in the pH range 6.8-7.4 agreed quite well with data previously reported. The main emphasis of this work was to determine the sodium ion binding to proteins in the in vivo state. High sodium ion concentrations, sodium ions 2.4-6 molal, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ion concentration was 0.3 molal at pH 4.6. At comparable sodium ion concentrations, sodium ions (1.0) were employed with pH values near eight. These included tris(hydroxymethyl)methylammonium (tris), trichloroacetic acid, and veronal. Ethylenediaminetetraacetic acid (EDTA) or peptone was added to the receptor mixtures to a final concentration of 10-20% excess by weight of agent to carbonic anhydride. Carbonic anhydride catalyzed activity was measured in the veronal buffer. Addition of EDTA or peptone increased the carbonic anhydride catalyzed activity in the veronal buffer significantly above that found in either tris or trichloroacetic acid. Peptone or EDTA had no effect on the carbonic anhydride activity in either tris or trichloroacetic acid. This observed effect in veronal buffer could be blocked by equivalent amounts of divalent metal salts such as zinc or calcium. On the other hand, EDTA had no effect on the steroids reaction of carbonic anhydride using p-nitrophenyl acetate as the substrate, regardless of the buffer used. The significance of these findings will be discussed. (Supported in part by NSF grant GB 7044.)
The hydrolysis of carboxylate phosphate monoester in other acyl phosphate monoesters involves ester-bond fission. Acyl phosphate dimers undergo ester-bond fission, whereas carboxylate phosphate dimers undergo ester-bond fission with the elimination of inorganic phosphate. This work provides support for the hypothesis that the stable isomers are observed in the equilibrium experiments which indicated that the substitution of a single acyl group on the carboxylate phosphate nitrogen results in a mechanism for ester-bond fission which involves an ester-bond fission reaction. The first-order rate constants for the hydrolysis of the acyl phosphate monoester and dinitrophenyl acyl phosphate have been obtained at 37°C and ionic strength 0.6 over a pH range in which mono- and dimethane species predominate. The values of kobs for the hydrolysis of the dimethane species show more dependence on the electronic delocalization ability of S-substituents in the phenyl ring (p<0.62) than do the values of kobs for the monoacetyl group. Evidence for the absence of an isocyanate intermediate during the hydrolysis of 3-nitrophenyl carboxylate phosphate is discussed in studies using acetylene as a trapping agent.


Human lysozyme is similar to hen egg-white lysozyme in that it has a single histidine residue. However, these histidine residues occur at different sites in the respective enzymes, being his-13 in hen and his-78 in human. (J. A. Canfield, Brookhaven Symposium Biol., 21: 126 (1968)). The His-15 of hen lysozyme has been shown to be non-essential for enzyme activity by Hartley et al. (Biochemistry 8, 700 (1968)). When human lysozyme is treated with iodacetate at pH 6.5 for 18 hours, a chromatographically different modified enzyme results. Iodoacetate analysis indicates the loss of histidine and the formation of 3-carboxymethylhistidine in the modified enzyme. The modification occurs at the 1-3 times that of the native enzyme, indicating the essentiality of the single histidine residue for lysozyme activity. Preliminary results indicate that when human lysozyme is treated with a 60-100 excess of 3-carboxymethylhistidine, the molecular weight of the modified molecule is acetylated. Approximately 2 of the 5 lysine residues are simultaneously acetylated, and the acetylated enzyme has an activity which is from 3 to 5 times that of the native enzyme. When human lysozyme is treated with 0.5 N-hydroxysuccinimide for 6 days at pH 10.5, 4.8 of the 5 lysine residues are converted to homoserine. This modified lysozyme has 60% of the activity of the native enzyme against M. lysodeikticus at pH 7.4.

Synthesis and antistaphylococcal activity of N-α-(ω-nitroacetyl)-lysine. Abhra Purii, K. N. Yankasa, and E. S. Cook, Division of Chemistry and Biochemistry, Institutut Divi Thomas, Cincinnati, Ohio 45267.

It has been previously reported that a series of N-α-amino acids and their derivatives inhibit the growth of streptococci and staphylococci. The present work is concerned with the preparation of new compounds obtained from S. aureus infection. (K. Tanaka et al., Nat. Acids, 45, 1457 (1969)) and S. Purii et al. (Abstr. 13th National ACS Meeting, New York, 1969). The present investigation was undertaken to learn if N-α-aminoacetylylamine also have antistaphylococcal activity. N-Glycyllysine, N-seryllysine, N-lactyllysine, N-valeryllysine, N-α-(ω-nitroacetyl)-lysine, N-α-(ω-aminobutyryl)-lysine, N-α-(ω-nitrovaleryl)-lysine, and N-α-(ω-methylpropionyl)-lysine were synthesized through the coupling of each carboxylated amine with the bis-carboxyl group of N-(N-ε-aminoacetyl)-lysine ethylester dinitrophenylamide by the mixed carbodimide-carbodiimide method. The yields, melting points, and δ values on FPC and TLC will be presented. The antistaphylococcal activity of these N-α-aminoacetylylamine was demonstrated through their protective effect against staphylococcal infections in mice. A total of 5 mg of each sample was given in divided doses subcutaneously 3 times before and 4 hrs after the injection on S. aureus. While all of the dimedroxylic thyrophorins showed protective effect, the activity of N-α-(ω-nitroacetyl)-lysine was found to be the highest among the N-α-aminoacetylylamine and to be almost equivalent with that of N-ε-nitroacetyllysine. The antifibromyocytic property of these dimedroxylic thyrophorins will also be reported.

Studies on the purification of Aspergillus niger. Betty E. Klapner, Robert J. Bajer, Department of Chemistry, Ohio State University, 140 W. 18th Avenue, Columbus, Ohio 43210.

Aspergillus niger releases an extracellular protease into liquid shake culture during stationary phase of growth. Study of this protease has led to a simple two-step purification of the enzyme. Homogeneity was shown by acrylamide gel electrophoresis. Two experimental approaches were used. For the first, glucose-30°C (UL 0.1 m) was added after 60-72 hours growth, together with an unlabeled suspected precursor. Isoenzyme analysis, followed by purification by precipitation, gave results which were consistent with the values of kobs for the monomeric species (p<0.27). The effect of temperature and varying salt and buffer concentration on the values of kobs for the monomeric species is consistent with the values of kobs for the monomeric species of Aspergillus niger. Evidence for the absence of an isocyanate intermediate during the hydrolysis of 3-nitrophenyl carboxylate phosphate is discussed in studies using acetylene as a trapping agent.

Studies of the biosynthesis of pyridoxine. Richard A. Schroeder and Edward H. Frieden, Department of Chemistry, Kent State University, Kent, Ohio 44240.

Studies of the biosynthesis of pyridoxine have been undertaken using Lactobacillus casei. The organism was grown in a medium containing (1.5%) glucose and harvested at 6 days at 30°C. Pyridoxine (270 mgm) was isolated from the medium by chromatography on Dowex 50 and purified by recrystallization. Two experimental approaches were used. For the first, glucose-30°C (UL 0.1 m) was added after 60-72 hours growth, together with an unlabeled suspected precursor. Isoenzyme analysis, followed by purification by precipitation, gave results which were consistent with the values of kobs for the monomeric species (p<0.27). The effect of temperature and varying salt and buffer concentration on the values of kobs for the monomeric species is consistent with the values of kobs for the monomeric species of Aspergillus niger. Evidence for the absence of an isocyanate intermediate during the hydrolysis of 3-nitrophenyl carboxylate phosphate is discussed in studies using acetylene as a trapping agent.
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THE FRESHWATER Ecosystem: PERSPECTIVES ON LAKE ERIE. Paul L. Zabikoff, Academic Faculty of Biochemistry, The Ohio State University, Columbus, Ohio 43210

The relationships between limnological parameters, including phytoplankton, hydrology, currents, water mass movements, and temperature, are discussed in relation to the primary management programs of Lake Erie. Spring conditions, when phytoplankton blooms occur, are compared to those of late summer when blue-green algae blooms dominate. Under conditions favorable to blue-green algal growth, and assuming a generation time of 2 hours, a bloom should be observed macroscopically in 48-72 hours. In situ information is available to make a simple calculation for green algae.


PPCA (1966) "Lake Erie Environmental Summary, 1965-66."  
PPCA (1967) "Lake Erie Report: A Plan for Water Pollution Control!"

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CONFORMATIONS OF PROTEINS. John Lawrence, John L. Oley, Biological Research Division, Institute of Science and Technology, and Departments of Chemistry and of Biological Chemistry, University of Michigan, Ann Arbor, Michigan.

Data from high resolution X-ray analysis of crystallized globular protein structures has been obtained for almost twenty proteins since the classic work on the conformation of myoglobin. Although the α-helix appeared to be the most important element of myoglobin, there has been recently much contributed to our understanding of the conformation of ribonuclease, lysozyme, and hemoglobin in solution, and to the mode of action of these proteins.

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DETERMINATION OF PROTEIN STRUCTURE FROM X-RAY CRYSTALLOGRAPHIC STUDIES. M. J. Adams, S. G. Ford, R. Knecht, P. J. Lents, Jr., A. McPherson, Jr., M. G. Rossman, W. M. Schvitz, I. E. Smiley, Department of Biological Sciences, Purdue University, Lafayette, Indiana 47907.

The relationship of protein structure to function is revealed by crystallographic studies during the last decade. Cationic groups, with sophisticated subunit assemblies, will be discussed with particular reference to tetrameric, lactate dehydrogenase. It is anticipated that a high resolution (2.5 Å) map has been completed. The recent discovery of the protein in solution adds to this belief. There are also increasingly powerful computational methods which strengthen our belief that X-ray crystallographic studies yield conformational limits of minimum free energy in aqueous environments.

The structure of horse heart ferricytochrome c has been determined by x-ray diffraction analysis of 2.7 Å. The amino acid sequence of the protein has been elucidated to include 20 of the 104 amino acids, crystallized in the same space group, P41.

The home region in a crevice lined with hydrophobic side chains, with the iron atom coordinated to His 18 and Met 80. The evolutionary conserved region 70-85 forms the left side of the molecule and the home crevice. Two hydrophobic channels lead to the home from the surface of the molecule. The one on the left side of the molecule contains five aromatic side groups arranged roughly along the home group, including Tyr 74 and Trp 59. This channel in particular may be involved either with electron transfer or the transfer of energy excited electronic states.

The basic and acidic groups are strongly localized on the surface of two positive "patches", one next to each of the apparent channels, and one negative "patch" of acidic residues. The positive patch adjacent to the left channel (with the aromatic groups) includes Lys 72 and Lys 73, which have been implicated in binding to cytochrome oxidase.

The evolutionary history of the cytochromes and possible mechanisms of action will be discussed.


Following the determination of the tertiary structure of cytochrome c by Dickerson and collaborators (see preceding abstract) and the development of techniques for the isolation of antibody populations directed toward particular sites on the protein surface, it has become possible to employ antibodies to cytochrome c to identify the surface areas of the protein involved in binding to cytochrome oxidase. For example, Fab fragments of specifically purified rabbit anticytochrome c antibodies modify the reactions of human ferricytochrome c with beef cytochrome oxidase, as follows: 1) the initial rate constant is decreased, and 2) a fraction of the cytochrome c oxidase is oxidized at a very slow rate. This fraction is stoichiometric to about 1/4th the amount of antibody added and corresponds to one of the four populations present in the anticytochrome c antibody. It has also been shown that the antibody directed to the site of the cyan or red domains of the red cell membrane does not interfere with binding to cytochrome oxidase. The generalization of site-specific antibodies as probes of cytochrome c surface function and conformation will be considered.

31 CONFORMATION OF MYOGLOBIN IN SOLUTION. Frank R. Gurd, Department of Chemistry Indiana University, Bloomington, Indiana 47401.

The conformation of myoglobin in solution is being studied in three settings: first, with reference to the crystalline structure; second, by comparison of myoglobins from related species, with reference to the disorganized state obtained by treatment with cupric ion. Carboxymethylation with bromoacetate serves as a method of labeling the exposed cysteiny] residues that is applicable to both the crystalline and dissolved state. Carboxymethylation of sperm whale myoglobin shows very similar patterns of reactivity in both states, with one exception that indicates a conformational change. All myoglobins studied are similar with respect to the properties of the heme group as observed by absorption and EPR spectra and oxygen affinity. Indications in different species of the influence of structural variations on function are apparent from hydrogen exchange rates and the rate of reaction of cyanate with the terminal group. The rate of recovery of the native structure following disorganization by cupric ion also shows a qualitatively similar conformation. Similar studies were carried out on myoglobin, but with qualitative differences according to the particular amino acid sequence represented.


The structure of porcine 2 zinc insulin as obtained from an electron density map derived from an x-ray analysis at 2.6 Å will be described. The crystals contain six insulin monomers (MM 5624 and two zinc atoms per rhombohedral unit cell. The asymmetric unit contains two independent insulin monomers which have been shown to be related by a 2-fold screw axis. The insulin is composed of three dimers, each monomer is co-ordinated to a zinc atom on the 3-fold axis by the N1 histidine. A part of the A chain forms the B chain region within the dimer while the A chains are outside the hexamer. The structure will be discussed with particular reference to the exactness of the 2-fold axis and to any correlation with biological activity of insulin.


Proinsulin, a single chain precursor of insulin, has been identified in human and rat islet tissue and has been isolated from crystalline bovine, porcine, rat and human insulin preparations. The polypeptide is ordered: N1-b-chain-Arg-Arg-2-cysteine-Lys-2-Arg-2-A-chain-Gly-Gly. The major intermediate forms isolated from human insulin crystals have undergone cleavage at either end of the connecting segment with loss of the corresponding pair of basic residues. Our efforts to characterize the proteolytic enzyme responsible for this transformation will be described. Examination of pepines digests with the diagonal electrophoresis method of Brown and Hartley (Biochem. J., 101, 214, 1966) indicates that the disulfide bonds in proinsulin are identical with those in insulin. Methods have been developed for isolation of the C-peptide, which is retained within the A chain in the pancreas after cleavage from proinsulin. Structural studies of human, monkey, bovine and porcine C-peptides indicate that the region of the proinsulin molecule is more variable than the insulin portions. These variations in sequence are reflected in the failure of new somatotropins to the proinsulin region to exhibit significant interspecies cross-reaction. Immunological probes of proinsulin C-peptide conformation and its role in folding and correct disulfide bond orientation in proinsulin will be considered.

34 OPTICAL ROTATORY DISPERSION AND CIRCULAR DICHROISM PATTERNS AS INDICATIONS OF PROTEIN CONFORMATION. Dan W. Urba, Institute for Biomedical Research, American Medical Association/Endowment and Research Foundation, 535 E. Dearborn, Chicago, Illinois 60611.

Studies on L-glutamyl-gamma-glutamyl and L-glutamyl-gamma-glutamyl antibiotics have shown that molecules which do not have an α-helical disposition of peptide groups exhibit optical rotatory properties and configurational patterns which are characteristic of the α-helix. Furthermore, attempts to study particular systems such as membranes have revealed absorption, fluorescence, and circular dichroism that are characteristic of the α-helix. The interpretation of such spectra will necessarily be subject to the problem, noted above, of uniqueness of the patterns. The second application is the study of crystalline matrices in an approach to the crystallographic problem. Successful calculation of the crystal growth of the α-helix from the crystal symmetry would argue for invariance of the optical rotation properties on crystallization.
Although formal education is an absolute prerequisite to success in most cases, not everything learned is taught or learned in schools. It is our contention that the continuing education of chemists in industrial research laboratories should be a matter of vital interest to people in both the academic and industrial fields. Chemists who have maintained their sharpness and competence both broadly and in their own fields of specialization are in an excellent position for three reasons: first, they can better contribute to the advancement of chemistry as a science and secondly, they are in a better position to advance their own careers; and third, they can contribute more ably to the success of their company's efforts. We describe the features of a unique continuing education program in the chemical industry and delineate the problems encountered and how they were successfully solved. We also contend that some of the greatest teachers are those leaders who can successfully inspire and encourage others.


A report is presented of the results of the second year study of the undergraduate program in chemistry at Ohio Northern University in light of several basic foundation premises and how this faculty has applied the results of this study in establishing a curriculum for chemistry in the 1970's at ONU. Included among the basic foundation premises are the following: (1) Chemistry is an experimental science concerned primarily with the interactions of matter. Everything we are concerned with in this science has as a primary the understanding of these interactions, in order that predictions of material interactions can be made. (2) The classical lines particularly in advanced laboratory between analytical, inorganic, organic and physical chemistry have been too sharply drawn. (3) Too little attention has been paid to formal instruction in the use of the chemical literature and the writing and presentation of technical papers. (4) Too often beginning students have been exposed to a too mathematical and abstract approach to our science which has been uncovered to the extent of the reaction and discovery aspects of our science. (5) Science has something important to say to all who would be educated citizens in our modern society. Therefore the non-science student should not be considered a second class citizen and be given no science or be relegated to a separate course. Rather along with the science student he should partake of some introductory philosophy of science, become aware of the relationship between science and society, and at the same time gain a view of several of the basic principles and concepts important to all of scientific thought.


During the January Interim of 1970, a group of students at Muskingum College participated in a program entitled Fundamentals of Chemical Research. Participants were involved in the actual attack upon a research problem, phases of which included literature search, experimental work in the laboratory, and report and evaluation of results. Because the students were able to concentrate their efforts in one area and had extended periods of time available for uninterrupted laboratory and library work, they not only made significant progress toward many of their goals in a relatively short time, but also gained more realistic insights into what "it's like" to be involved in full-time research. The program format and an evaluation of strengths and weaknesses (including student comments) will be discussed.

WATER POLLUTION STUDY AS A METHOD FOR TEACHING GENERAL AND ANALYTICAL CHEMISTRY. James F. Cuneen, Antioch College, Chemistry Department, Yellow Springs, Ohio.

The belief that to be concerned about the destruction of our environment makes the understanding of and the chemical determination of the major pollutants in water a pressing need. Since General and Analytical Chemistry is basically the study of water solutions and the equilibrium involved, these topics are chosen for the direct connection of theoretical concepts to the environment. As presented, these concepts are usually examined in simple systems involving pure materials. The simple systems are, however, fraught with the design of the laboratory, the problems encountered, and the general implication on the environment. The pollutants will be presented.

COMPUTER INSTRUCTION AND USE IN UNDERGRADUATE CHEMISTRY COURSES. James H. Coleman, and Elizabeth B. Swiger, Fairmont State College, Fairmont, West Virginia 26554.

Computer instruction and use has been incorporated into the chemistry curriculum at Fairmont State College utilizing an IBM 1130 computer. The primary purpose of this program is (1) to stimulate student interest in computer technique, (2) to introduce the student to the FORTRAN IV language, and (3) to demonstrate the usefulness of the computer in working problems in chemistry. In the general chemistry laboratory simple computer programming problems are introduced to give the student an introductory knowledge of the operations of the computer, the basic elements of programming, a suitable programming language for this field, and the experience of having prepared the computer to work up data for a current experiment. Basic elements learned in this experience are requirements for input, simple calculations, called functions, simple looping, and the introduction of logical statements. An introductory FORTRAN IV program is introduced for the calculation of titration curves, standard deviations, etc. The student also uses stored programs which are called to work up data from specific experiments, and a subroutine which utilizes the printer to make data plots. More extensive use is made of stored programs in the physical chemistry course in which more sophisticated programming assignments are planned. This approach is designed to give the student an understanding and appreciation of the computer and the field of computer programming. Initial use of this approach has been very encouraging.

INSTRUCTION ON AUTOMATIC SEARCHING OF THE CHEMICAL LITERATURE. A. E. Petrako, Dept. of Computer and Information Science, R. J. Beaton, Dept. of Chemistry, V. R. Yagisawa, Ohio State University, Columbus, Ohio 43210.

With the advent of computer-produced publications such as those provided by Chemical Abstracts Service (CAS), the Institute for Scientific Information (ISI), and other information processing organizations, a variety of new services for searching magnetic tape versions of these publications are now available. However, while many institutions provide formal courses on how to search the chemical literature, replete with problems and exercises involving the use of traditional tools available in the library, few of them provide any exercises involving the use of the computerized services. In view of the fact that several of these services are now available at the Ohio State University, some by subscription and others on a trial basis, it seemed desirable to provide a formal course of instruction in the use of such services. The course we have been experimenting with, which is intended to complement another formal course covering the traditional methods of searching the chemical literature, includes instruction and exercises in phrasing queries (search profiles) which are automatically searched against appropriate data bases. The search results provide the student with the necessary feedback to evaluate both the adequacy of his query and the performance of the search system. At present, the course searches of data bases can be obtained from CAS. However, other data bases and on-line interactive systems will also be utilized as soon as the necessary resources are available.
42 THE DESIGN AND CONSTRUCTION OF AN ELECTRODE OF GENERAL UTILITY FOR SELECTIVE ION MEASUREMENTS. P. R. Ogil, Chemistry Department, Otterbein College, Westerville, Ohio 43081.

The price and individuality of commercially available selective ion electrodes restrict their use in mass for undergraduate laboratory experiments. However, the wide spread routine and research applications for these devices underline the desirability for their introduction into the student's laboratory experience. The motive for this work was the production of an inexpensive and reliable device to be used in the laboratory. The various steps leading to the development of the electrode will be outlined. The methods and materials of construction will be detailed. The adaptability of the electrode to a variety of selective ion measurements will be described. The versatility of the electrode is illustrated by the results obtained for fluoride and chloride ion measurements where the electrodes were solid silver chloride and solid silver fluoride, respectively. The fluoride ion measurements made with this electrode will be compared with those obtained by a commercial fluoride ion electrode.

43 BENZENE FLUORESCENCE STUDIES IN THE PHYSICAL CHEMISTRY LABORATORY. F. Sheldon Weissbach, Department of Chemistry, Hope College, Holland, Michigan 49428.

The study of excited electronic states is currently an active area of research. In particular, emission quenching studies in both the gas and liquid phases are being used to determine the involvement of singlet and triplet states in photochemical processes, the rates of intermolecular energy transfer and the relative energies of excited states. In order to familiarize our chemistry students with this type of research, we have included in our physical chemistry laboratory a study of the quenching of benzene fluorescence in the gas phase. By studying the effect of various added gases on the benzene fluorescence as a function of pressure we are able to introduce the student to such concepts as excited state energy levels, energy transfer and quenching cross-sections, and to the techniques involved in measuring fluorescence in the gas phase. Student response to this experiment has been gratifying and, as a result, we wish to describe it for others at this time.

44 QUALITATIVE AND QUANTITATIVE ANALYSIS WITH PURE SALTS.

By George L. Gilbert, Department of Chemistry, Denison University, Granville, Ohio.

The second semester freshman laboratory at Denison University encompasses the major exposure of students to topics such as qualitative and quantitative analysis as well as the illustrations of qualitative techniques. In keeping with the philosophy of involving students in the planning of laboratory work while maintaining an overall direction we have evolved the following program:

There are given several unknown, pure compounds and use qualitative analytical techniques to establish the identity of the species. Subsequent quantitative analyses using volumetric, gravimetric, spectrophotometric, and potassium permanganate methods are selected by the students and carried out. The evidence for the nature of the compounds is assembled in a final report.

45 A MULTILEVEL ORGANIC CHEMISTRY PROJECT. I. THE GENERAL CHEMISTRY LEVEL.

By Thomas M. Sultif and Lawrence B. Wick, Department of Chemistry, Ohio Wesleyan University, Delaware, Ohio 43015.

Chemical energy has stimulated the methods of inquiry used in chemistry are no exception. When the need for such experiences becomes evident at Ohio Wesleyan University, it was considered that appropriate project type experiences would be created. One project with multilevel possibilities has been tested in general chemistry. The results of these tests are herein reported. The chemical system chosen was aniline. This reaction is an inexpensive, well understood reaction that can be studied by many methods and at many depths. For the general chemistry experience the partial esterification of acetic or propionic acid with various combinations of methanol, ethanol, n-propyl alcohol, and iso-butanol was used. The reaction products were analyzed by gas chromatography and the data obtained was used to calculate the percentage conversions of the various alcohols. Physical properties of the reactants and products of the reactions were determined and compared. The relative percent conversions lead to discussions of chemical reactivity and equilibrium compositions. Further pursuit of the experiment's capabilities become the perogative of the student.

46 TEACHING X-RAY CRYSTALLOGRAPHY TO UNDERGRADUATE CHEMISTRY MAJORS.

Ralph M. Colling, Department of Chemistry, Eastern Michigan University, Ypsilanti, Michigan 48197.

Traditionally, X-ray crystallography has been taught as an elective graduate course, with only brief discussions of the X-ray powder method included in most undergraduate physical chemistry and instrumental analysis courses. This limited coverage was adequate when X-ray structure studies were done only by crystallographers specialists; however, with the aid of modern automated diffractometers many chemists now use X-ray methods. In addition to producing many more structure publications, this rapid growth in X-ray crystallography suggests that the modern chemistry curriculum should include thorough coverage of X-ray diffraction methods. Consequently, our X-ray Crystallography course which has a physical chemistry prerequisite is now offered to junior and senior chemistry majors as well as to graduate students. Topics covered in the course include: production of X-rays; symmetry, including both point groups and space groups; powder and single crystal X-ray techniques; and solving structures by Fourier methods. The course also includes laboratory experience with the powder method and the Weissenberg single crystal method, extensive use of computer programs for data reduction and simulation, and discussions of recent X-ray structure publications. To date, undergraduates have performed satisfactorily in the course, and several have gone on to graduate work involving X-ray crystallography.

47 IT'S A GAS, MAN. R. Battino and D. J. Karl, Department of Chemistry, W. S. University, Dayton, Ohio 45431.

"It's a Gas, Man," is a multimedia presentation which we use to introduce the topic of the gas laws to our general chemistry students. The presentation involves coordinated screening of a set of color slides with taped music and dialogue. This method of getting into a new subject elicits great interest from the students and whets their appetites for learning about the material which is treated casually, provocatively, irreverently and relevantly in the presentation. We hope that our presentation will serve as an illustration of an interest-getting way of presenting topics in general chemistry.
As we look for teaching analogies and models to illustrate or re-enforce chemical concepts, we often resort to outright black-box thinking in the form of mnemonic devices or systematized methods with a purpose well beyond their intended use. We often use these devices as a stepping Stone to understanding and become ends to themselves, especially if presented as "keys" to problem solving. Examples include temperature conversion formulas, "plug-in" (tabular) methods for finding the pH of a solution, special tricks for solving radical equations, and memorized colligative property relationships that make students vary of alternate presentations. The problem is further illustrated in a simple diagram developed by the author for correlating electron quantum numbers with atomic energy levels. In so far as it is presented as only a help in recalling and constructing energy level diagrams which, in turn, can be used to learn periodic table relationships, it is justified. But each such mnemonic device should be put in proper perspective, so that students do not become victims of "memory-ministry." This paper is an plea for continuous re-evaluation of "memory crutches" which may become handicaps to development of real understanding in chemistry.

A MECHANISM FOR ADDING RELEVANCE AND CURRENTNESS TO FRESHMAN CHEMISTRY, John J. Fortman, Dept. of Chemistry, Wright State Univerisity, Dayton, Ohio 45433.

The overused word on college campuses in 1969 was relevance. It seems well and good to relate the student's chemistry course to the modern world around him but attempts to do so often result in simply adding some topics of more current interest without relating them to anything. In an attempt to rectify this at Wright State all students in the introductory chemistry course for non-science majors have been required to read the monthly issues of "Chemistry" magazine in addition to their textbooks this year. This ACS publication, which is intended for high school and beginning college students, features several short articles plus fuller columns on current research news and interesting sidelights in science. The student is able to read how chemistry is applied in such areas as agriculture, archaeology, art, engineering, industry, medicine, pollution control, and space exploration. Chemistry is also humanized through biographical articles on such scientists as Benjamin Rush. The topics of many articles have fit neatly into the course outline.

Eight month subscriptions are sent to the department which distributes them in the labs. The cost is included in the student's lab manual fee.

The response from the students has been very gratifying. Their answers to test questions relating to the magazine are generally better than those on the text. Some students who discontinued the course requested to continue receiving the magazine. Many chemistry majors have sought the extra copies and next year the department plans to use it in the class as general chemistry for science majors as supplementary reading.

INTEGRATION OF BIOCHEMISTRY INTO THE UNDERGRADUATE CHEMISTRY CURRICULUM. E. H. Correa, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

The thesis will be developed that a principal failing in dealing with biochemistry in the undergraduate curriculum is isolation of pertinent subject matter from the core chemistry courses: general, organic, and physical chemistry. The student too frequently encounters even the most basic biochemical facts only in senior-level courses. These courses, in turn, suffer from the necessity of dealing with elementary physico-chemical and organismal matters which might well have been introduced in earlier courses without loss of time or content in such courses. Specific means of achieving integration of meaningful biochemical material into basic undergraduate courses and laboratory work will be detailed. General curriculum revisions related to the above will also be considered.

COMPUTERS IN TEACHING CHEMISTRY. Dr. Peter G. Lykes, IIT. Computation Center, 3201 S. Michigan Avenue, Chicago, Illinois 60616.

The Information Processing Machine (the computer) has penetrated all of chemistry. In addition to numerical calculations, it has enhanced and vitalized simulation, information storage and retrieval, data reduction, and automatic control. Accordingly, the training of the 'complete chemist' requires blending in all those computer-based techniques into the academic program. Additionally, the computer provides a pedagogical tool, particularly in graphics terminals as a lecture-aid, and large scale computer-assisted instruction in the near future. The problem of providing inexpensive comprehensive computer support to education is only now coming to be solved. With increasingly convenient access to major computer centers from remote terminals to facilitate broadcast use of sophisticated applications programs dealing with sophisticated solutions to modern chemical problems, it is clear the computer is fast becoming a channel of communication between the frontiers of knowledge and the classroom. A major problem facing chemistry education today is that many chemistry professors lack a basic understanding of what a computer system is, how it operates, and how it is impacting their particular area of interest in chemistry.

CHEMISTRY OF THE AQUATIC ENVIRONMENT. Werner Stumpp, Harvard University, Pierce Hall - MIT, Cambridge, Massachusetts 02138.

In order to obviate nature's complexity, simplified and manageable models (equilibrium models) are used to illustrate the principal regulatory factors that control the mineral composition of natural waters and in turn the composition of the atmosphere. Thermodynamic equilibrium models are shown to facilitate identification of the many variables and to establish chemical boundary conditions toward which aquatic environments must proceed, however slowly. Alternatively, the time-invariant condition of a chemical reaction system, which is open to its environment may frequently be the idealized counterpart of a natural water, which indeed is open and dynamic system with variable inputs and outputs of mass and energy. In natural waters organisms and their abiotic environments are interrelated and interdependent. The real world.

Stream pollution may be interpreted as a departure from a balance between photosynthetic activity, P, and respiratory activity, R. Stream pollution control consists not only of waste treatment; it is primarily necessary to attempt to establish an ecological balance desirable for man.

AIR POLLUTION CHEMISTRY, Jack G. Calvert and Kenneth Damron, Chemistry Department, The Ohio State University, Columbus, Ohio 43210.

A review is given of the basic chemistry involved in the polluted atmospheres. The role of various primary pollutants in the development of secondary pollutants is described. A computer kinetic analysis of the reactions has made it possible to rationalize the observed rates of secondary polluted formation and expected rates of pollutants removal processes.

The results are used to indicate areas of major uncertainty in our knowledge of the chemistry of the polluted atmosphere.

NEEDS FOR CHEMICAL RESEARCH IN SOLID WASTE MANAGEMENT PROGRAMS. Andrew W. Breidenbach, Environmental Control Administration, Cincinnati Laboratories, Cincinnati, Ohio 45213.

The requirement to recycle and re-use discarded solid materials generated from residences, industrial establishments and agricultural enterprises as well as solid residues resulting from air and water pollution control operations calls for research directed at improved effectiveness of degradability, improved conversion reactions as they apply to solid wastes in the natural environment as well as the modified environments of solid waste processing and disposal systems will require special efforts of the work already begun in this area are reviewed and the requirements for future information and technology discussed. The need for chemically related research and development associated with the problem of waste disposal is paramount.
The aqueous chemistry of aluminum was examined over wide ranges of concentration and pH. The solubility limits of aluminum hydroxide were determined by light absorption measurements and the effects of the type and concentration of anions present and the age of the Al(III) solutions on the X-ray diffraction patterns, pH boundaries of solubility, and molecular weight of the hydroxide precipitate were studied. Potentiometric studies were also run on the Al(III) solutions and the data were analysed using the SCOGS computer program for least squares adjustment to a non-linear equation to obtain equilibrium constants. The precipitates were colloidal at pH less than 7 in the presence of univalent anions up to about 6.01 only. Very small amounts of silica were required to destabilize the Al(III) sols. In the presence of phosphate, stable sols were found at both low and high pH. Apparently, polynuclear Al(III) species are formed at pH values lower than the precipitation limits, but only in relatively small concentrations. It was found that clays are destabilized by Al(III) solutions in these pH regions in which stable aluminum sols form.

This paper considers the role played by chemistry in the development of environmental toxicity. It presents an overview of the role of bioactive chemicals, forces, and processes in the overall problem of this relatively new and important discipline, as well as the initiation and mitigation of biologic damage. The effects of reproductive or continual subchronic toxic insult on the biotic and abiotic components of the ecosystem as well as on the response to massive exposure will be discussed. The role of the toxicologist, chemist, chemical engineer, and urban planner in the development of optimal environments will be emphasized.

In recent years a number of heterocyclic-boranes have been synthesized which have trivalent boron in the cage structure. This paper deals with the synthesis and characterization of heterocyclic-boranes containing nineteen atoms in the cage framework. Reaction of n-B_{19}H_{20} with CO(CO)_{5} in tetrahydrofuran at room temperature, followed by treatment with aqueous tetramethylammonium chloride, gave red (CH)_{2} n-[n-B_{19}H_{20}]. This was isolated in yield. In a similar manner (CH)_{2} n-[n-B_{19}H_{20}] was obtained as well. The compound was isolated in form red (CH)_{2} n-[n-B_{19}H_{20}] as purple (CH)_{2} n-[n-B_{19}H_{20}]. The elemental analyses and molecular weight data are consistent with the formulations given. The 320 MHz 1H NMR spectrum of CO(CO)_{5} is very different from that of n-B_{19}H_{20}. The increased complexity of the metal-borate spectrum is qualitatively what would be expected if one of the open faces of the n-B_{19}H_{20} - ion became bonded to the cobalt atom. Recently a series of transition metal complexes of B_{19}H_{20} has been characterized. From the similarities in structure of B_{19}H_{20} and n-B_{19}H_{20}, we propose that the metal-borate bonding in both n-B_{19}H_{20} and B_{19}H_{18} complexes is similar.

The bonding and properties of isocyanide and carbonyl complexes of ruthenium(II) have been studied. Joseph R. Crook and Randy K. Kehn, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

Ruthenium(II) complexes with the general formula Ru(CN)_{x}Cl_{2} have been synthesized for cases in which x = cyclohexyl, n-octyl, and n-phenyltolyl. Infrared data indicates that all four isocyanide complexes possess trans arrangement of the CN groups by contrast with corresponding iron(II) complexes in which the cis arrangement is more stable. Based on a comparison of the infrared frequencies of the ruthenium complexes with frequencies observed for other metal, qualitative conclusions regarding the extent of π bonding can be drawn. These conclusions suggest no unusual deviation from established patterns.

Attempts to generate mixed carbonyl/isocyanide ruthenium complexes have been unsuccessful under the observation that the isocyanides are significantly better ligands than carbon monoxide with reference to their ability to stabilize lower oxidation states of metals.
CRYSTALLINE COORDINATION COMPLEXES OF COPPER(II) SALTS WITH ALCOHOL-SUBSTITUTED ETHYNYLAMINES. Donald E. Zimmerman, James L. Hall, West Virginia University, Morgantown, W. Va. 26506

Crystallographic coordination compounds of perchlorate, nitrate, sulfite, and chloride salts of copper(II) with N-hydroxyethylmethylamine (HNETMA) and N-(2-hydroxypropyl)-ethylenediamine (HPEDMA) have been prepared and characterized by elemental analyses, by studies of electronic and vibrational spectra and by measurement of magnetic moments. The low-temperature diffusional resistance were determined in the visible region. These spectra were resolved into Gaussian components and were treated by a crystal field model to determine the type of coordination about the copper(II) ion. The infrared spectra were resolved to show the number of nitrite and halogen bonding oxygen atoms coordinated. These results showed that the perchlorate, nitrate, and sulfite ions were not coordinated and confirmed the presence of a Schiff base (SEH) in one compound. The magnetic moments were consistent with the results of the spectral studies. It is concluded that Cu(m)(HNETMA) and Cu(m)(HPEDMA) are six-coordinate, with the chloride ion being coordinated, the structure being a distorted octahedron; that Cu(m)(HNETMA)(Cl) and Cu(m)(HPEDMA)(Cl) are five-coordinate with square pyramidal structures; and that Cu(m)(HPEDMA) is a five-coordinate trigonal bipyramidal structure while Cu(m)(HNETMA) has an intermediate five-coordinate structure.

COPPIES OF N,N-DIALKYLTHIOCARBONATES LIGANDS. B. Jack McCormick and Benjamin P. Sturman, Department of Chemistry, West Virginia University, Morgantown, W. Va. 26506

While complexes of N,N-dialkylthiocarbamate ligands with a variety of metal ions have been known for many years, there is a surprising lack of work on N,N-dialkylthiocarbanote complexes (DThCO(2)R)O complexes. Six nickel(II) complexes of the type Ni(m)(DThCO(2)R) have been prepared in the present work: R = CH(2)CH(2), - CH(2)CH(2)CH(3), and - CH(2)CH(3); R = CH(2)CH(2)CH(2) and - CH(2)CH(3)CH(3). The nature of the R groups affects the stability of the complexes, as evidenced by the fact that it has not been possible to prepare complexes with bulky groups such as - CH(2)CH(3). infrared studies suggest that the ligands are chelated through oxygen and sulfur atoms, and a characteristic banding sequence has been found at 1950 cm(-1). Measured molecular weights of the complexes with R = CH(2)CH(2) and - CH(2)CH(3) are concentration dependent. The remaining four complexes are insoluble and unsuitable for molecular weight studies. These studies suggest that the compounds are polymers in the fluid state and that, for the soluble complexes, the degree of polymerization decreases with decreasing concentration. The complexes are paramagnetic and electronic spectral studies suggest that the nickel ions are 5 or 6 coordinate. Some possible structures will be discussed. The results of these studies with metal ions other than nickel(II) also will be discussed.

PROPERTIES OF TRANSITION METAL COMPLEXES WITH FLUORINATED PHOSPHINE LIGANDS. F. Gary Eiler and Devon W. Nash, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

A number of polydentate phosphorus and sulfur ligands, containing one or two 1,2,3,4-tetrafluorophenyl substituents, were readily synthesized from the lithium derivatives of diphenyl-1,2,3,4-tetrafluorophenylphophsine and 2,3,4,5-tetrafluorophenylphosphate. The nickel(II) complexes of the tridentate and bidentate ligands, A and B, are five-coordinate Ni(m)(A)(X) and Ni(m)(B)(X) species, respectively. Ligand C forms four-coordinate Ni(m)(A)(X) and six-coordinate Ni(m)(C)(X) complexes, rather than the five-coordinate examples.

One especially interesting result obtained with the phosphorus-sulfur ligand C is the tendency for facile s-desulfuration to produce coordination compounds of the corresponding phosphine-phosphorus ligands. The results obtained from optical, magnetic, and 19F NMR studies will be discussed with respect to a- and s-bonding by these ligands.
70 COBALT AND NICKEL COMPLEXES OF MIXED ARGININE-ANTIMONY AND ARGININE-PHENYLOXANETREATMENT LIGANDS: Gary Kordoski, Billy Cook, and Devon W. Meek, Department of Chemistry, The Ohio State University, Columbus, Ohio. 14210.

Several mixed polydentate ligands A, B, and C have been synthesized, and their cobalt and nickel complexes have been examined in some detail.

The 'tripod-like' tetradentate ligand A forms trigonal-bipyramidal nickel(II) complexes [Ni(A)] and cis-octahedral cobalt(III) complexes [Co(A)]Az. Ligands B and C readily form both four-coordinate NiC2 and five-coordinate [NiC3] complexes, depending on the preparative conditions. The spectral and magnetic data obtained for these complexes will be compared with those of similar polynuclear and polychelate ligands in order to evaluate the bonding properties of alkylamine ligands.

71 RHENIUM(III) AND (IV) CHLORIDES AND THEIR REACTIONS WITH CERTAIN NITROGEN AND PHOSPHONITE DONOR MOLECULES: B. A. Walton, Department of Chemistry, Purdue University, Lafayette, Indiana 47907.

The chlorides RbCl2 and Ra Cl2, both of which have structures containing strong metal-metal bonds, undergo redox reactions with certain nitrogen and phosphorus donor molecules. For instance, contrary to previous literature reports, RaCl2 does not react with pyridine to form the expected complex RaCl2Py, but instead the rhenium(II) species [ReCl2Py]+ is isolated. The redox reaction is characteristic of those which occur with many other nitrogen donors. The reduced species may be readily reoxidized to derivatives of RaCl2. Aqueous solutions of RaCl2 react with triphenylphosphine to give complex reaction mixtures, from which trans- RaCl2PPh3, [ReCl2PPh2], and RaCl2PPh3Cl can be isolated. A full three-dimensional X-ray analysis of the complex RaCl2PPh3Cl, C15 H13 Cl Ra, has been carried out and the results will be discussed. 8 This derivative is believed to be identical to that isolated previously by Bouchelle and Wilkinson (J. Chem. Soc., A, 993 (1967)) by a different route.

This study was carried out in collaboration with N.G. Drew and D.C. Tilley at the University of Reading, England.

72 COBALT COMPLEXES OF SOME SYNTHETIC MACROCYCLES AND THEIR DERIVATIVES CONTAINING COBALT-CARBON BONDS: Keith Farmery and Daryle H. Busch, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Several new macrocyclic ligands containing four nitrogen atoms as donors have recently been prepared in these and other laboratories. These may differ in chelate ring size, net charge, and the degree and type of unsaturation and electronic delocalization. These ligands are ideally suited for the study of the effects of ligand type on the formation and properties of alkyl-cobalt species. Such studies should lead to a greater understanding of the fundamental chemistry underlying derivatives of vitamin B12. The cobalt(II) derivatives are generally low-spin and five-coordinate, with electronic spectra which are best described in terms of a tetragonal ligand field model with a 4A1 ground state. Oxidative alkylation of the cobalt atom in the complexes has been achieved and the products are either monomethyl-, trans-dimethylcobalt complexes, or mixtures of these. The electronic spectra of the alkyl and normal acido-cobalt(II) complexes will be compared, and the stability of the Co-C species discussed in terms of the field strength of the planar macrocycle, and the nature of the ligating groups in these macrocycles.

73 IRON(III) COMPLEXES CONTAINING A TETRADENTATE MACROCYCLIC LIGAND DERIVED FROM ORTHO-AMINOBENZALDEHYDE: Vladimir Katovic and Daryl H. Busch, the Evans Chemical Laboratory, Ohio State University, Columbus, Ohio 43210.

Iron(III) complexes of the tetradentate macrocyclic ligand, tetrasodium[b.f,j.n][5,8-B]-tetraazacyclodecine (TAA), have been prepared by the template reaction of orthoaminobenzaldehyde with an iron salt. Two types of complexes were isolated and characterized: Dimeric Fe2(TAA)2O4(NO3)4ClO4, which contain the Fe-O-Fe bridging group and monomeric compounds Fe(TAA)BF4F3H2O, X = NO3 and ClO4. They were characterized by analysis, IR spectra, mass spectra, conductivity studies, molecular weight determination and magnetic susceptibility measurement over the temperature range 80-300 K. The presence of the Fe-O-Fe linkage in basal compounds was deduced on the basis of IR evidence and magnetic data. A new IR band at 810 cm-1 is assigned to the Fe-O-Fe antisymmetric stretch. The temperature dependence of the magnetic susceptibility shows an antiferromagnetic interaction in the dimer, while the monomeric compounds are low spin. The Fe-O-Fe linkage in these compounds is unusually difficult to cleave; only acidic fluoride media appear to cause cleavage. Fe(TAA)2Cl2O4ClO4 reacts with methoxy ions giving the neutral compound Fe(TAA)BF4F3H2O, where two methoxy ions are incorporated in the macrocycle forming a-aminocyclohexane linkages. Molecular weight determination confirms that the latter compound is dimeric.

74 SOME STEREOSELECTIVE ANOMALIES OF CERTAIN AMINO ACID OUTER-SPHERE COMPLEXES: D.C. Francis, Detroit Institute of Technology, Detroit, Michigan 48201.

When L-tryptophan was precipitated separately with the enantiomers of tri-ethylamino-phenylcobalt(III) ion it was observed that the outer-sphere complex formed with D-[Co(Trp)]+ differed from the complex formed with L-[Co(Trp)]+ in several important physical as well as chemical aspects. These included rates of formation, macroscopic appearance of crystals, temperature and light stability, chemical analysis and behavior, and optical spectra, including optical rotary dispersion and circular dichroic bands. The significance of the influence of the stereospecific nature of the amino acid on the metal ions on the behavior of the amino acid outer-sphere ligand and the analogy to physiological systems will be discussed.

75 AMIDE EXCHANGE (TRANSNITRINATION) IN Zn(II) ELLIPTIC BASE COMPLEX SYSTEMS: Bruce E. Leach and D.L. Leisinger, Chemistry Department, Ohio State University, Columbus, Ohio 43210.

Exchange of ethylamine in N,N-dimethylethylamine by glycinate, α-alanine and β-alanine in the presence of Zn(II) has been studied using stopped flow and pKα techniques. The reactions are direct and do not proceed through hydrolysis. Both proton and metal ion catalysed pathways were observed. The methyl substituent of α-alanine inhibits the rate of the proton catalysed path but has no effect on the rate of the Zn(II) path.

Amide exchange rates are faster by a factor of 1000 over the rates at which the amine reacts with salicylaldoxime to form the Schiff base. The rate laws and mechanisms for these reactions will be discussed.

76 TRANSITION METAL CLUSTER SYNTHESIS AND PROPERTIES: R.B. King, Department of Chemistry, University of Georgia, Athens, Georgia 30601.

A review of the known chemistry of compounds with transition metal clusters will be presented with examples drawn largely from the author's own work on polynuclear metal carbonyl derivatives. Compounds containing dinitrogen, tetraiodide, and oxo bridged metal clusters will be discussed. In the case of metal carbonyl chemistry compounds with transition metal clusters can often be prepared by decarboxylation of derivatives containing fewer metal atoms but a higher ratio of carbonyl groups per metal atom than in the desired products. The mass spectra of certain polynuclear metal carbonyl derivatives are of interest in exhibiting fragmentation to give unusual basic metal cluster ions, e.g. Co6+ from the mass spectrum of Co6(CO)13.
COORDINATION POLYMERS: B. P. Block. Pennwalt Corporation, 900 First Avenue, King of Prussia, Pa. 19406

Coordination polymers fall into several classes depending upon what part coordination polymers fall into the organometallic class in which non-carbon catalysis can exist in each class, whereas some are quite sparse for coordination polymers based on polymeric ligands. On the other hand there are numerous examples of non-carbon-catalyzed coordination polymers with relatively simple bridging ligands between coordination centers. Many of these polymers do not have properties like those of plastic organic polymers, but are more or less typical inorganic metal compounds. It is characteristic of this kind of compound that the evidence for its polymeric nature is primarily confined to the solid state. A few families of coordination polymers, such as the poly(metal phosphinates), do contain members which have solution properties suggesting that they retain polymeric structures when dissolved. These systems will be considered in detail in comparison with typical organic polymers, and the reasons for the differences in properties among the various coordination polymers involving non-carbon catalysis will be discussed. It will be necessary to exploit these polymers for specialized uses based on unique properties if they are to become of industrial importance.

SILICON CARBIDE POLYMERS. M. E. Kachur, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio, 44106.

Although planar inorganic polymers are well known and understood (e.g., graphite and boron nitride), little attention has been given to planar organic polymers. This is most likely attributable to the difficulties of synthesizing such polymers since an examination of their probable nature suggests that in many cases they ought to possess interesting and valuable combinations of properties. Ways of preparing sheet organosilicon polymers from sheet silicates have now been worked out. Studies of two such polymers (one derived from chrysotile and one from amorphite) using various techniques have provided specific information about these two polymers and considerable insight as to the nature of such polymers in general. Work done with the electron microscope has proved to be of particular value in these studies, especially when combined with analogous work carried out on the corresponding silicates.

Boron-Boron Nitride. Sheldon LI. Shore, Department of Chemistry, The Ohio State University, 232 West 19th Avenue, Columbus, Ohio 43210.

A number of boron-nitrogen systems from boron nitride through borates are discussed. Structural features, properties, relevancy of isoelectronic analogies with carbon systems, and synthesis procedures are considered.

ASYMMETRIC INDUCTION IN INNER-SPHERE REDOX REACTIONS. Sister M. J. DeChant, Department of Chemistry, Notre Dame College, Cleveland, Ohio 44122.

Measurements of asymmetric induction have been used as a probe to study the details of two inner-sphere redox reactions, specifically the interaction of non-bridging ligands. The oxidation of chromium(II) by d-cis-Chloroaminobenzylidenechelate(III) ion in aqueous ethylene-diamine, for example, yields 94% d-cis,trans-chloroamino-diamine-bridged products; the cis-isomer is leavocoratory at the medium D line. The reaction of d-cis-dichloroethyllenechelate(III) and d-cis-

REDOX ELECTROCHEMISTRY OF COBALT(II) COMPLEXES IN DOUGHNUTS AND IN THE SOLID STATE. M. Harbahan and M. L. Urbonas, Department of Chemistry Case Western Reserve University, Cleveland, Ohio 44106.

The homologous series of cobalt(II) complexes with N,N'-bis(3-isopropylallylamide) polyethyleneamines and (CH,)(N,N',N'-N,N '*N,N') is in aqueous solution and in the solid state. The spectral and magnetic properties of the n = 2 to 7 complexes indicate that in the solid state and in dichloromethane and pyridine solutions. The spectral and magnetic properties of the n = 2 to 7 complexes exhibited pseudo-tetrahedral spectra in the solid state and in nonpolar solvents. The trimethylamine derivative does not exhibit a characteristic pseudo-tetrahedral spectrum and it is postulated that these derivatives possess a strongly distorted tetrahedral geometry. All of these complexes are mononuclear in dichloromethane, but higher coordination numbers via intermolecular association. In pyridine, all of these complexes expand their coordination number, achieving pseudo-octahedral structures as deduced from spectral and magnetic measurements.

BONDING IN VANADIUM COMPLEXES. James A. Ryan, Henry A. Fustos, Department of Chemistry, University of Akron, Akron, Ohio 44324.

Selected literature ESR data for which intermolecular distances are known or can be approximated were found to encode computer programs to determine the various possibilities of optical assignments which are consistent with the ESR data. The program used, based on Do loops for the values of the four-spin transition, and, for each combination, it attempted to carry the calculation to charge self-consistency for the spin orbit coupling and the metal hyperfine splitting parameters. The results will be compared with charge self-consistent molecular orbital calculations of the Wolfstein-Heinrichs type.
85 ELECTRON PARAMAGNETIC RESONANCE OF TRANSITION METAL COMPLEXES IN LIQUID CRYSTAL SOLUTIONS. John F. Pachler, Jr., and James A. Smith, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Electron paramagnetic resonance spectral studies of a number of paramagnetic transition metal coordination compounds dissolved in nematic liquid crystals have been carried out. In addition to the spin orientations of the nematic phases in strong magnetic fields, certain anisotropic parameters can be obtained from analysis of anisotropic g tensors and hyperfine splitting tensors.

86 THE CRYSTAL AND MOLECULAR STRUCTURE OF BS(PS-PERSTILOCUANATO)ZINC(II). John F. Pachler, Jr. and David C. Fries, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

BS(PS-PERSTILOCUANATO)ZINC(II) is a member of the general class of sulfur-enriched dithio aromatic acid transition metal complexes. Crystals suitable for X-ray analysis were obtained by slow cooling of a solution in a 1:1 mixture of methanol and water. The crystals belong to the monoclinic system, space group P2_1/a, with unit cell constants a = 21.07 Å, b = 12.65 Å, and c = 8.95 Å. The calculated and measured densities indicate a Z of four. Diffraction data were collected and the structure determination will be accomplished using vector superposition techniques applied to the Patterson Function.

87 THE STRUCTURE AND ISO EXCHANGE PROPERTIES OF CERIUM(IV) PHOSPHATES. E.L. Hower, Abraham Clearfield, Department of Chemistry, University of Oklahoma, Norman, Oklahoma, 45701.

Cerium(IV) phosphates exist as gels in one of several crystalline forms, all of which exhibit ion exchange behavior. We have prepared a number of new crystalline cerium(IV) phosphates and found that all of the phases may be derived from each other by decreasing the pH or increasing the phosphorus-sodium ratio. The X-ray and neutron diffraction methods. The relationship between these exchangers and other metal(IV) phosphate ion exchangers will be briefly discussed.


Attention in materials research has been devoted to development of high purity materials. Metal alkoxides offer a unique approach for obtaining high purity metal oxides, and silicon, boron, beryllium and yttrium have been developed. Difficulty in obtaining chlorine-free oxides of these metals is overcome by using a modification of a previously unreported reaction. The epoxide, alcohol, and catalyst. Compared with the fluoroalkylated ligands, it is found that the fluoroalkylated chlorides have increased volatility and improved hydrolytic stability, making them more suitable for vapor deposition of the corresponding metal. Physical properties have been investigated and are related to the usefulness of the various complexes. The branched-chained fluoroalkylated chlorides may be modified easily to produce different properties and to extend their usefulness, as in fire extinguishing agents or anti-bacterial agents.

89 REACTION OF NaSnPO4 WITH CaO(PO3)2(OH)2: INVESTIGATION OF A POSSIBLE CARBONATION TIN(II) COMPOUND. Ronald W. Collins, U.S. Naval Medical Research Institute, Bethesda, Maryland 20014.

Although SnPO4 is generally accepted as a fluoride ion inhibitor, there is disagreement about the precise mechanism of this anti-oxidation agent. Some controversy exists regarding the extent to which the tin(II) ion contributes to this action. As part of a continuing effort to define the chemical role of tin(II) in caries inhibition, CaO(PO3)2(OH)2 has been studied. Calcium hydroxylapatite, the major constituent of bone and enamel. Numerous experiments covering a wide range of tin(II) concentration and temperature have been run at 25°C to 150°C and at various pH values. The products of these heterogeneous reactions, as identified by chemical analysis, X-ray diffraction, and IR, include CaSnO3, a hydroxy tin(II) oxide, and a tin(II) phosphate. The latter salt is also the major product of the reaction of SnPO4 with CaO(PO3)2(OH)2. Lack of any evidence for direct isomorphous substitution of tin(II) into the apatite lattice, coupled with the determined in vitro formation of the acid-insoluble tin(II) salt, suggests that similar in vivo deposition of tin(II) salts could be a contributing factor to the caries reduction in non-carious lesions.


The solvolysis of cyclopropyl halides proceeds by a concerted electrophilic process, and the stereochemistry of the ring-opening process may be predicted by orbital symmetry considerations as described by Woodward and Hoffmann. The synthesis and acetylation of the isomeric 1-chloro-2,3-diphenylcyclopropanes were undertaken in order to clarify the nature of the ring-opening process through investigation of the effect of stereochemistry. The synthesis of the isomers of 1-chloro-2,3-diphenylcyclopropane was accomplished by the addition of dichlorocarbene to cis- and trans-stilbenes. The stereochemical effects of the solvolysis of the cyclopropyl chlorides in aqueous dioxane and tetrahydrofuran were studied. A previous study [J. W. Kessinger and J. R. Finn, J. Amer. Chem. Soc., 79, 6681 (1967)] suggested the possibility of alternative reaction modes of ring-opening for cis- and trans-1-chloro-2,3-diphenylcyclopropanes. The stereochemical effects of the phenyl group as seen in the solvent effect of solvolysis will be considered in terms of the possible modes of ring-opening.

91 THE REARRANGEMENT OF SOME 4-PHENYL-1-CYCLOALKYLCARBONILS IN STRONG ACIDS. Arthur S. Kusner and Wei Han Wang, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115.

A number of y-phenyl-1-cycloalkylcarbonils have been prepared, I, II and III. When

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CH2
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I is placed in chlorosulfonic or fluorosulfonic acid at room temperature or below, a clean rearrangement to the corresponding indenyl cation (IV) is observed. An almost quantitative recovery of the corresponding indene is obtained when cation solutions of conditions. II rearranges to the cation V while the structure of the rearranged cation from III is not yet elucidated. The synthetic utility of these reactions will be discussed.

Alkyl nitrite reacts with alkylnitronium salts to produce alkylnitronium cations. Thus triphenylmethyl nitronium salt produces, quantitatively, triphenylmethyl tetrafluoroborate when reacted with nitrous acid in anhydrous acetone. The yield is approximately 90% on treatment with nitrosimonitrile, followed by addition of water, enzyme (95%). Benzaldehyde and benzohydrol are thought to be oxidized either by hydrogen and hydrogen yield or by the presence of water where the yield of carbonyl components remains essentially constant. Use of trialkylsilanes, such as dimethylamino, is common over the acetonitrile. Addition of the trapping reagent at different times after preparation of the benzyl nitronium then leads to product yields. The benzyl cation in acetonitrile solutions is viewed to exist in equilibrium with N-alkylated nitronium cations, as shown:

\[(\text{CH}_3)_2\text{CHCH}_2\text{Cl} + \text{CH}_3\text{C} = \text{NH} \rightarrow (\text{CH}_3)_2\text{CHCH}_2\text{N}=\text{C}=\text{NH}\]

Trapping of these nitronium cations is in competition with the rapid equilibrium transfer. The relative ability of various nucleophiles to trap the benzyl cation and N-alkylated nitrotrile cations in acetonitrile as well as various other nitrotrile solutions will be presented and discussed.

93 THE CHEMISTRY OF THE FOUR EPIMERIC 2-HYDROXYCHLORO[3,1-d]NAPHTALINES. Paul G. Gaenil, Elizabeth A. Williams, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

It has been suggested that trans-duralo a small ring to a cyclopropane should introduce a unique type of strain into the bond common to the two fused rings. As part of our studies of the effects of such 'twist' bonds we have prepared the two epimeric alcohols represented by I and the two epimeric alcohols represented by II: the systems represented by I and II are both functionalized in a manner suitable for the conversion of I into the corresponding cyclopropanone system. The ease of this fused trans system is as a part of a kinetic investigation of the cyclopropane ring in formation, the four epimers of 2-hydroxybenzaldehydes derived from I and II have been prepared. The details of this study will be presented.

94 THE CHEMISTRY OF CYANOMETHYLDICARBONIC ACID, PART II, SYNTHESIS OF 3-HALO-1,2,3,4-TETRAHYDRO-7,8-BENZACRIDINES. Robert Maruo, Department of Chemistry, Miami University, Oxford, Ohio 45056.

The title compound was prepared from diphenylacetylene and 1,1-dimethyl-2,5-diphenyl-1-1-2,4-cyclopanetidene at room temperature. The compound is very unstable and it undergoes depolymerization at 100°C, which appears to be two modes of decomposition. The above mentioned reaction proceeds by a Diels-Alder reaction which occurs and in addition the molecule eliminated methyl isocyanide, (CH₃)₂N⁺. When 1,2,3,4-tetraphenylbenzene. The elimination of silylbenzenes by 7-alkanobenzobenzenes has been reported. However, a reverse Diels-Alder reaction has not been observed for the other examples known. The title compound has the following interesting properties, in addition to its pyrolytic behavior. It is yellow apparently because of thionocyanate. At 42°C it dissolves in benzene to give solutions of its reverse Diels-Alder products while at 10°C in cyclohexane solution the compound appears to be more stable. Other specific fulerene properties have also been investigated and will be reported.

95 SOME "ACTIVE" SULFAURUS REACTIONS. T. C. Shields, A. N. Kurtz, Union Carbide Corporation, Chemicals and Plastics Division, Research and Development Department, South Charleston, W. Va. 25303.

Sulfur "activated" by ammonia is le presence of an amino has previously been shown to add across carbon-carbon double bonds. The reactions of this compound with amines have been studied. δ-δ-7,8-Diethynyl-2,5-diketocyclonaphthene (3) reacts with ammonia, sodium hydroxide, and secondary amines to give materials probably consisting of aminesulfonated products. Under similar benzaldehyde, N,N-dimethylbenzaldehyde and benzene were produced from sulfonamide results in 1,1,4-trimethyl-2,5-N,N-dimethylaminobenzene.

2-thi-4-acryloxy-3-one. Attempts to isolate the cyclic-sulfonamide by vacuum distillation also failed to yield N,N-dimethylaminobenzene. 454°C. The aspects of the scope of "active" sulfonation are discussed.


96 THE PREPARATION AND PROPERTIES OF 2,7-DIMETHYL-1,2,3,4-TETRAHYDRO-7,8-BENZACRIDINES. Robert Maruo, Department of Chemistry, Miami University, Oxford, Ohio 45056.

The title compound was prepared from diphenylacetylene and 1,1-dimethyl-2,5-diphenyl-1-1-2,4-cyclopanetidene at room temperature. The compound is very unstable and it undergoes depolymerization at 100°C, which appears to be two modes of decomposition. The above mentioned reaction proceeds by a Diels-Alder reaction which occurs and in addition the molecule eliminated methyl isocyanide, (CH₃)₂N⁺. When 1,2,3,4-tetraphenylbenzene. The elimination of silylbenzenes by 7-alkanobenzobenzenes has been reported. However, a reverse Diels-Alder reaction has not been observed for the other examples known. The title compound has the following interesting properties, in addition to its pyrolytic behavior. It is yellow apparently because of thionocyanate. At 42°C it dissolves in benzene to give solutions of its reverse Diels-Alder products while at 10°C in cyclohexane solution the compound appears to be more stable. Other specific fulerene properties have also been investigated and will be reported.

97 A MATURATION STUDY OF 2- AND 3-BENZYLTHIONATES. A. T. Jeffers and D. W. H. MacBee, Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506.

While metation of 1H-indenyl[2,1-b]thiophene and 2H-indenyl[3,2-b]thiophene with N-butyllithium followed by carbonylation yielded the corresponding bridgehead acids, similar metation of 2H-indenyl[2,1-b]thiophene gave much smaller amounts of bridgehead acid accompanied by substantial amounts of products which could be isolated in the thiono position. In order to ascertain if the presence of a deuterium bond between the benzene and thiophene ring was necessary for metation to occur at the benzene position, the analysis resulting from the removal of this bond, viz. 2- and 3-benzyllithiourea were prepared and their metation and carbonylation studied. Only 2-benzyllithiourea-2-carboxylic acid resulted from 2-benzyllithiourea. In the case of 3-benzyllithiourea, white metation at the methyl group occurred, a mixture consisting of predominantly 2-benzyllithiourea-2-carboxylic acid and minor amounts of 2-benzyllithiourea-2-carboxylic acid was produced. The mixture was separated by fractional crystallization, the compound with the similar spectral properties and by independent syntheses. A synthesis of 2H-thiophen-3-thienylacetic acid is described and the transformation of 2H-thiophen-3-thienylacetic acid to 2H-indenylthiophene, 2H-indenyl-2-carboxylic acid is described.

The 5-ketoester, 2, may be prepared as the Dieckmann product from the corresponding 2, 5-seco diester, 1, as in the cholestane series.

The chemical shift of the C-19 methyl singlet may be used to determine the configuration of the ester group. Comparison of 2 with the analogous A-norketone, 3, shows that the ester function is exerting little influence on the C-19 resonance, 4a = 4b = -0.04 ppm (CDCl3). Similarly, there is little difference in pyridine, nor is an appreciable solvent effect observed. The spectrum of the corresponding 2-hydroyxyster, 4, shows a small deshielding effect (CDCl3) and a moderate solvent effect in pyridine, being deshielded 0.20 ppm. This is consistent with a 4-or configuration for the OH group. Since OH has been shown to be trans to the C20Me function independently, the latter is assigned an configuration in 4 and in 2.

102 EVIDENCE FOR YLID INTERMEDIATES FROM PYRIMIDINES OF BETAINES AND PYRIDINE BETAINES IN 1 MASS SPECTROMETER. Rudolph A. Giese and D. L. Plahel, Kent State University, Kent, Ohio 44240.

Betaine 1 undergoes thermal rearrangement and pyrolysis when heated at temperatures above its melting point to give methyl dimethylaminoacetate, amines, carbon dioxide, and some water-soluble materials. These reactions have been studied by time-resolved mass spectrometry. Mechanistic pathways that have been proposed include rearrangement of ylides with loss of carbon dioxide to give the ylide, the ylide may function as a source of methylene in subsequent reactions with the substrate or the rearranged ester. Pyridine betaine, 2, and its 2-methyl derivative, 2, also undergo reactions analogous to the latter pathway for betaine. The ylides derived from these materials may also give trimers and ethylene polymers.

103 A NOVEL 1,3-DIPOLAR ADDITION REACTION OF PYRIDINIUM CARBETHOXYCYANOMETHYLIDE. James E. Douglas and Joseph M. Wesolosky, Department of Chemistry, Marshall University, Huntington, WV 25701.

Numerous pyridinium ylides 1 have been reported to react with dimethyl acetylene dicarboxylate 2 to yield indolines 4 via the intermediate dihydroindolines 3. We wish to report that pyridinium carbethoxycyanomethylide (X=CN, Y=CO$_2$Et) reacts with 2 to afford a quite different compound, namely, dimethyl ethyl 2-(3-pyridyl)acetate (5). Proof of structure of the product and a postulated mechanism of the transformation will be discussed.
THE ROLE OF IODINE COMPLEXATION IN IODINE ISOYANATE ADDITION REACTIONS. II. 
COMPETITIVE REACTIONS. Charles G. Seidelin, Department of Chemistry, Youngstown 
State University, Youngstown, Ohio, 44503

Previous studies have shown that the rate of addition of INO, generated 
in situ from silver cyanate and iodine, to cyclohexene in methylene chloride 
increases with increasing iodine concentration but decreases with increasing 
cyclohexene concentration. This unusual behavior has been ascribed to an 
alternate reaction pathway involving an iodine-alkene complex. This complex 
can react in several ways including a direct reaction with silver cyanate to 
form the vicinal iodocyclohexane product. Evidence supporting this route 
has been found in competitive reaction studies. 2-Chloro-1,5-cycloheptene 
reacts faster with silver cyanate in situ generated INO than does cyclohexene when 
run independent of each other. However, when mixtures of 2-Chloro-1,5-cycloheptene 
are run competitively with INO generated INO the cyclohexene reacts much faster that the 
2-Chloro-1,5-cycloheptene. The competitive reaction conditions favor iodine-alkene complexation. 
The enhanced reactivity of cyclohexene, compared to 2-Chloro-1,5-cycloheptene, in competitive 
reactions apparently arises because cyclohexene complexes more readily with 
iodine. Under these in situ competitive reaction conditions, the major reaction 
pathway appears to be the direct reaction of the iodine-alkene complex with 
silver cyanate.

THE PYROLIDYSIS OF SULFUR DIOXIDES. John R. Grunwell, Robert E. Maruca, 

The pyrolysis of diphenylsulfur dimide at 200° for 0.5 hours gave 
66% azobenzene. However, di-2-methyl-1-propylsulfur dimide, pyrolyzed at 
260° for 24 hours, gave azobenzene, ammonia, and hydrogen sulfide in 
addition to small amounts of carbon disulfide, 2-methyl-2-propanethiol, 
and 2,2,4,4-tetra-methyl-3-thiapentane. The mechanism of the latter 
reaction does not go through bis-azo-2-methyl-2-propane since this 
compound pyrolyzed to 2-methyl-2-propane and nitrogen. The 2-methyl-2 
propyl radical is also not an intermediate because this radical di 
proportionation to 2-methyl-2-propane and a trace of 2-methyl-2-propane.

The mass spectrum shows prominent peaks at m/e = 118 ([CH(S)2]-
C-NH-S-N=C), and m/e = 62 (HNS=NH), a fact, which tends to support a concerted 
intramolecular elimination mechanism.

AMINO ACIDS WITH TWO CENTERS OF ASYMMETRY FROM MICROBIAL PEPTIDES. Gary G. Marconi 
and Milos Bodansky, Department of Chemistry, Case Western Reserve University, 
Cleveland, Ohio 44106.

The stereochimistry of the diastereomeric amino acids N-methyl-L-threonine, 
N-methyl-L-allo-threonine, and N-stannomycine ([2-methylino-3 methyl hexahyrido 
pyrimidyl]-2-glycine) from the peptide antibiotic stannomycin, and N,N-diamino 
lactic acid from ammonium was studied. Optical rotatory dispersion and ir 
spectra were applied for the elucidation of the absolute configurations. 
The rule of semiplanarity (Bodansky and Perlman) will also be discussed.

THE SYNTHESIS OF THE DERIVATIVES OF 5-HYDROXYLINDOLES by David A. Galloway, M.D.
Macklin, Ashland Chemical Company, 10703 Lyndale Ave South, Bloomington, Minnesota 55437

Indoloinoedin-2 derivatives have found use as central nervous system repre 
sents and as bactericidal agents in the pharmaceutical industry. They are used in 
permeant protein gels and in adhesives for bonding reinforcing materials to rubber, 
and as adhesives in non-woven plylles. The following general method for their 
preparation was used successfully on a number of preparations in good overall yields:

1. Hydrolysis

2. Cyclization

3. Reduction

The convenience in boiling clylene favors the formation of cyclic ureas. Higher 
themolysis temperatures and longer times at themolysis temperatures favor the formation 
of polynitranes. & represents aromatic, heterocyclic, paratopic and olefins. Most of 
the enamides are crystalline compounds melting below the decompositoin point.

THE CONFORMATION OF SODIUM 4-PHENYL-BUTYRATE IN DEUTERIUM OXIDE. John P. Sebastian, Mila Tl, Department of 
Chemistry, Miami University, Oxford, Ohio 45056.

The conformation of sodium 4-phenyl-butyrate has been Investigated in deuterium oxide by nuclear magnetic resonance spectroscopy. 
The magnetic anisotropy arising from the phenyl ring was used as a conformational probe. Limiting conformational populations and 
the phenyl ring's influence on the chemical shifts of the α and ω 
protons were calculated by the methods of Johnson and Bovey. 
Comparison of the calculated shifts with the observed shifts allowed selection 
3. The conformation of sodium 4-phenyl-butyrate was found to exist in the anti form with respect to both the α - β 
and β-γ carbon-carbon bonds.

THE GENERATION OF NITROGEN IONS FROM DIAZALICYCLHYDROXYLAMINES. Paul B. Gaskin, 
George D. Hartman, Kokoli Shino, Department of Chemistry, The Ohio State University, 
Columbus, Ohio 43210.

The solvolytic generation of nitrogen ions (1) from N-chloramines (2) has 
attached considerable attention during the past few years. Various workers have shown 
that the nitrile ions, in addition to being of significant theoretical interest, are of 

R-NCl + C2H5OH → RN + + Cl-

Two extensive practical importance in the synthesis of unusual nitrogen-containing 
compounds. As part of our efforts to extend the scope of nitrogen ion chemistry, we 
have sought other precursors of 2. We now wish to report on the generation of nitro 
ion 3 from diazahexacycloses. A general procedure has been developed for the 
conversion of secondary amines into hydroxylamines via the initial addition of the 
secondary amine to ethyl cyanate to form the Michael adduct followed by reaction of 
the Michael adduct with periodate to give the N-oxide. Pyrolysis of the N-oxides gave 
the corresponding hydroxylamines. The hydroxylamines were treated with methyl 
chloride to produce the azides of the hydroxylamines which were subsequently reacted with 
phosphorus(V) chloride or with nitrilhydroxylamines to give the corresponding 
azides and nitriles, respectively. Under solvolytic conditions the hydroxyimine derivatives 
were converted to products via the formation of nitrenium ion intermediates. The details of this study will be presented.
Cyclopropane Geometry. II. Cyclopropane Structure Effects on Intramolecular Charge Transfer Phenomena.

R. C. L. Chn., Philip H. Howard, and George A. Lorenzo, Department of Chemistry, Syracuse University, Syracuse, New York 13210.

Ultraviolet spectra have been obtained of the twenty-six nitroaromatic systems formulated below. The geometry of a cyclopropyl group meta to a nitro group has a marked effect on donor-acceptor interaction between these two substituents. Spectral features of these compounds can be explained via ground state resonance structures. An analysis is offered in terms of existing theories of excited state donor-acceptor interactions.

III. The Photochemistry of 7-Carbomethoxy-3,4-Benzotropilidene. John S. Swenton, Denise Madigan, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

The photochemistry of 7-carbomethoxy-3,4-benzotropilidene (I) has been investigated. Irradiation of I in cyclohexane with a pyrex filter produces three products: 7-carbomethoxy-3,4-benzononacaradiene (II), 7-carbomethoxy-3-benzononacaradiene (III), and 6-carbomethoxy-3,4-benzononacaradiene (IV). Upon prolonged irradiation of the solution, (IV) becomes the major product. Photolysis of (III) produces (IV). The mechanism of the rearrangement and its implications for benzononacaradiene photochemistry will be discussed.

\[ \text{COOCH}_3 \]  
\[ \text{H} \]  
\[ \text{COOCH}_3 \]  
\[ \text{COOCH}_3 \]  

(II)  
(III)  
(IV)


The photolysis of a series of para substituted phenyl thiol acetates in cyclohexane at 2537 Å gives the corresponding diphenyl disulfide and methylphenyl sulfide. However, 1-cyclohexenylthiol acetate under the same conditions gives octahydrodibenzoethiophene. The latter reaction probably proceeds through di-1-cyclohexenyl disulfide. No photo-Fries rearrangement occurs. The rate of disappearance of ester is insensitive to substituent and solvent. A study of the absorption spectra as a function of substituent and solvent shows that intramolecular charge transfer involving the thiolacetate moiety as an acceptor is not important to the structure of the excited state.

113 Stereoechemically Controlled Fragmentations from Ester Triplet States.

James E. Cane, Department of Chemistry, University of Toledo, Toledo, Ohio 43606.

The possibility of concerted and stepwise pathways competing in the photolysis of olefins from carbonyl compounds was investigated. A suitable substituted ester, three- and cyclohex-3,4-dimethyl-2-pentene were prepared and shown to produce mixtures of cis and trans 2-methyl-2-pentene upon photolysis at conversions of less than 25%. Further sensitization and quenching studies showed the olefin products to isomerize under the reaction conditions concealing a completely stereospecific elimination. Stern-Volmer plots and the isomerization data suggested two unique triplet states participate in the stereospecific photocleavage and subsequent isomerization of the olefin products.

114 The Photochemistry of Hydrazones. Roger E. Rinkley, Department of Chemistry, Cleveland State University, Cleveland, Ohio, 44115.

The photochemistry of benzaldehyde phenylhydrazone, benzaldehyde diphenylhydrazone, benzophenone hydrazone, benzophenone phenylhydrazone, and benzophenone diphenylhydrazone have been investigated. The products formed from these irradiations indicate that hydrazones are capable of two types of reaction. First, the nitrogen-nitrogen bond of the hydrazone system may be cleaved in a process which results in the formation of an amine and an aldehyde (isolated in most cases as the corresponding aldehyde or ketone). In cases where the hydrazone is derived from an aldehyde this same reaction pathway also produces a nitrite. The second type of reaction, observed only for benzaldehyde phenylhydrazone and benzophenone hydrazone, is one which reduces the hydrazone system to a hydrocarbon; hence, this latter reaction type is a photochemical analogue of the Wolff-Kishner reduction. Possible mechanisms for these two reaction processes are proposed and discussed.

\[ \text{C}_6\text{H}_5\text{CHN}=\text{NH}-\text{C}_6\text{H}_5 \]  
\[ \text{H}_2 \]  
\[ \text{C}_6\text{H}_5\text{CHN}=\text{NH}-\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{CN} + \text{C}_6\text{H}_5\text{CH} = \text{C}_6\text{H}_5\text{CHO} \]

115 The Mercury ²P₃/₂-Photonsensitized Decomposition of Cyclopropane.

Ernest G. Spiitller, and George W. Klein, John Carroll University, University Heights, Ohio 44118.

The room temperature Hg(²P₃/₂)-photonsensitized decomposition of cyclopropane has been studied. The pressure dependence over the range 0.16-1700 torr was examined. Below 100 torr, the ethylene yield is larger than the propylene yield; above 100 torr, they are approximately equal. It is suggested that complete quenching occurs above 100 torr. A time-dependent study at 300 torr revealed that C₂H₂, C₂H₃, and C₃H₄ are linear with time up to 60 minutes. There is a very rapid decrease (0.7 to 0.3) in the C₂H₂/C₃H₄ ratio as oxygen is added to 10 torr of cyclopropane. A plateau is reached at about 0.17 torr oxygen. The following mechanism appears to be able to interpret the results rather well:

\[ \text{Hg}(²P₃/₂) + \text{C}_3\text{H}_₄ \]  
\[ \text{H} \]  
\[ \text{C}_3\text{H}_₄ \]  
\[ \text{H} = \text{C}_3\text{H}_₄ \]  

(1)  
(2)  
(3)  
(4)
THE PHOTOCHROMY OF 1,3-DIARYLBENZENE,
Stein, M. Rosen, David D. Rosen, and Milton Orchin, Dept. of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221.

The photocyclization of 1,3-diarylbenezene has been reported
to yield benzo[a]chrysene as the only product. Initial photo-
cyclization of diarylbenezene can yield either 2,3-diphenyl-
benzanthracene and 2,4-diphenylanthracene, or of which could yield the observed
phenanthrene. Detailed product analysis has
shown that in addition benzene[0]cyclopentadiene, dibenz[a]anthracene
(2,2-diphenylbenzanthracene) and 4-phenylbenzanthracene from 2,4-
yield data will be presented for 1,3-diarylbenezene and
4-phenylbenzanthracene along with a brief discussion of predicted r
reaction paths based on metal excited state free valence
and localization energies.

117 CARBON-13 MAGNETIC RESONANCE AND MOLECULAR STRUCTURE
David W. Drum, Dept. of Chem., University of Utah, Salt Lake City, Utah 84112.

Magnetic resonance studies of the carbon-13 isotope recently have been increasing
in both number and application. The results indicate that much of the potential for the
117 in molecular structure and molecular conformation, and examples of
these will be presented. As the carbon-13 isotope appears in nature only at a
1.1% abundance level, experimental techniques are critical in the detection of the
processes so important to the nuclear Overhauser effect which provides an important
signal enhancing feature whenever proton-decoupling methods are used.

118 EFFECT OF CHANGE ON CHEMICAL SHIFT.
Gideon Frankel and Yasushi Tsuchiya, Department of Chemistry, The Ohio State University, 140 W. 18th Avenue, Columbus, Ohio 43210.

The origin of the observed relationship of change to carbon-13 and proton chemical
shifts and of substituent contributions to chemical shifts will be shown to be both the theory of the chemical shift and the wave function in the
calculation can be derived by means of perturbation methods.

119 NEW EXPERIMENTS AND THEORY OF CHEMICALLY INDUCED NUCLEAR SPIN POLARIZATION

A theory of chemically induced nuclear spin polarization will be presented. This
theory explains the singlet-triplet mixing in radical pairs by hyperfine interactions
and g-shifts. Experiments in support of the theory will be presented.

120 ALIPHATIC SEMIDIONES. APPLICATIONS OF ELECTRON SPIN RESONANCE
Spectroscopy to Organic Chemistry, Glen A. Russell, Department of Chemistry, Iowa State University, Ames, Iowa 50010.

The semidine spin label from [N-0(0)](0)M has been introduced into
acyclic, monocyclic, and bicyclic compounds. By examination of the esr
spectrum of the spin label it has been possible to study
(a) semi-quinone in acyclic semidiones
(b) spin inversion in cyclophane semidiones half-chair conformation
(c) the preferred conformation of cyclophane semidiones
(d) molecular rearrangements in the bicyclo[3.1.0]hexane semidiones
(e) valence isomerization between monocyclic unsaturated semidiones and
(bicyclic semidiones)
(f) the delocalization of electron spin into the sigma framework
of an organic molecule.

121 SPIN DENSITY DISTRIBUTION IN STRAINED RING COMPOUNDS.
Leon M. Stock, Department of Chemistry, University of Chicago, Chicago, Illinois 60637.

The distribution of spin and electron density in bicyclic and tricyclic derivatives
of semidiones, semiquinones and aromatic nitrocompounds will be discussed.

122 ELECTRON SPIN RESONANCE STUDIES OF ALKYL RADICALS IN SOLUTION
Wilton, D. S. K., Central Research Laboratory, E. I. du Pont de Nemours Co.,
Wilmington, Delaware 19898.

A variety of free radicals are generated by direct photolysis of peroxides and
disulfides in static solutions. Structures and conformations of some interesting alkyl
radicals and the chemistry of alkyl radical pairs will be presented. The effect of
alkyl radicals substituted in the p-position with S, Se, and Te show unusual
behavior in preferred conformations in which the hetero-atom eclipses the p-orbital
of the radical center.

123 STATUS OF THEORY IN HETEROGENEOUS AND HOMOGENEOUS KINETICS.
R. A. Marcus, Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801.

Theoretical studies of reactions in solution and at electrodes have sometimes
focused on calculation of individual rate constants (heats, entropies and free energies
of activation A S, and sometimes on trends of the rate constants with thermodynamic
parameters, e.g., pH of Brønsted plots, E vs Tafel plots). Others

With this background in mind we explore the possibility of expressing A S as
A S = f 1 + (1 + A S 4/4A) 1/2

f is the work required to bring the catalyst together to form some separation distance
K. The last term in the expression is another (secondary) reorganization to form the
activated complex. A S 4 is the 'standard' free energy of reaction in the prere-
organizational term, the reorganization barrier when A S 4 = 0. A has certain convec
tional characteristics of a property. The implications of this equation for several topics in kinetics are noted--the
free energy plots. The equation can be derived from several rather different approx
imation models and is accurate calculations of potential energy surfaces will be noted.

124 PARALLEL HETEROGENEOUS ELECTROCHEMICAL REACTIONS. 
Richard W. H. Jones, Chemistry Department, Case Western Reserve University, 2177 Adelbert Road, Cleveland, Ohio 44106.

The kinetics of steady state electrochemical methods are generally restricted to
the study of heterogeneous kinetics with effective standard rate constants of 10^12
cm/sec or less because of mass transport limitations. A number of non-steady state
techniques, however, are available for rate constants of 10^7 cm/sec and in some
instances 10^10 cm/sec. These include step function methods (potential, current,
charge, pressure, corresponding c.e. and periodic perturbation methods, and
non-linear response methods (faradaic rectification and higher harmonics). The
range of conditions over which these methods are applicable, instrumentation, and
collection, associated with each will be reviewed briefly. Specific applications
will then be considered, including catalytic reactions (hydrogen electrode kinetics
under high exchange current density conditions), metal-metal ion couples (pure
metals and auranets), and various redox couples, with particular emphasis on faradaic
rectification and the pressure step perturbation methods.
125 HETEROGENEOUS ELECTRON TRANSFER RATES OF AROMATIC SPECIES IN APROTIC MEDIA

Donald E. Smith, Roying L. Hung, Barry J. Huebert, Kathryn R. Bullock and William E. Geiger, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

Electrolytic redox processes of aromatic or pseudo-aromatic molecules in aprotic solvents are characterized by an overwhelming prevalence of simple, rapid one-electron transfers. Correlation of rates of such processes with characteristics of molecular structure is a most promising approach to better characterizing the nature of heterogeneous electron transfer processes. Until recently, quantitative rate measurements have been discouraged by experimental problems induced by the high electron transfer rates encountered and the relatively low resistivity of the appropriate solvents. However, recent developments in methodology have minimized these and other problems sufficiently that experimental results are now being revealed at a reasonable rate.

Measurement techniques and problems will be identified and briefly discussed. Emphasis will be placed on examining recent experimental results in light of both qualitative molecular structure considerations and predictions of modern quantitative theories for heterogeneous redox processes.

126 ELECTRON AND PROTON TRANSFER KINETICS OF AROMATIC MOLECULES IOD IN POLAR SOLVENTS

Mark W. Dorfman, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

The pulse radiolysis method, which has proved effective as a fast reaction technique, has been used extensively to study reactions of aromatic radical anions and of aromatic cations in solution. In polar protic liquids such as the aliphatic alcohols, substrate-unsaturated compounds in solution form to the radical ions. Absolute rate constants may be obtained for the rate of electron transfer between the anion and a different aromatic compound in solution: \( A^- + B \rightarrow A^+ + B^- \). For some reactions, the dependence of the rate on the solvent and the dielectric properties of the solvent. For a single reaction, the effect of the solvent on the rate may be investigated. Equilibrium constants have also been determined for the proton transfer reaction: \( A^- + HO^+ \rightarrow A^+ + HO^- \). In two-component solvent systems, the dependence of the rate on the solvent is illustrated by the formation of the positive charge centre in the solvent. Rate constants for transfer to the aromatic solvent: \( A^- + B \rightarrow A^+ + B^- \) may be determined for several reactions.

127 FAST HETEROGENEOUS ELECTRON EXCHANGE STUDIED SPECTROELECTROCHEMICALLY

Nicholas A. Wingard, Theodore K. Kavanagh, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

For the homogeneous electron exchange reaction

\[ A + C \xlongright{28} k_{eb} B \xlongrightarrow{\text{b}} A + C \]

where \( A \) and \( C \) differ by one electron in oxidation states, a method of optically monitoring one of the species during electrochemical perturbation has been devised for determining kinetic rates. This spectroelectrochemical method is also applicable to studying cross electron transfer reactions:

\[ A_1 + B \xlongright{28} k_{eb} B_1 + A_2 \]

Bimolecular rates as high as \( 5 \times 10^6 \text{ M}^{-1} \text{s}^{-1} \) have been evaluated for several aromatic systems. The technique will be described and the results will be discussed.

128 PARTICIPATION OF WATER MOLECULES IN FAST PROTON-TRANSFER REACTIONS

Judith D. Harris, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Fast proton-transfer reactions between an acid and its conjugate base in aqueous solution proceed either with \( k_{H^+}^0 \) or without \( k_{H^+}^0 \) participation by water molecules:

\[ A + H_2O \xlongright{28} k_{H^+}^0 + B \rightarrow \text{products} \]

\[ A + H_2O \rightarrow k_{H^+}^0 + B + H_2O \]

We shall describe the measurement of the rate constants (when \( k_{H^+}^0 > 10^6 \text{ M}^{-1} \text{s}^{-1} \)) and the number of participating water molecules, by nuclear magnetic resonance techniques, the results and their implications. For reaction (2) we shall consider whether the rate-determining step is a dissociation step.

129 ENZYME CATALYSIS AND METABOLIC CONTROL

James G. Hanson, Department of Chemistry, Cornell University, Ithaca, New York 14853.

Fast reaction techniques (stopped flow, temperature jump, and stopped flow-temperature jump) have been used to study the mechanism of action of many enzymes. In the case of ribonuclease and caseinophosphatase, a number of unstable intermediates have been detected and detailed reaction mechanisms have been proposed. The general features of enzyme catalysis which have emerged from these and other studies are as follows: (1) the initial formation of the enzyme-substrate complex is close to diffusion controlled for most physiological substrates; (2) a common number of different enzyme-substrate complexes (or reactive intermediates) exist; (3) formation of enzyme-substrate complexes is very rapid and interconversion of reaction intermediates have been studied. The implication of these findings to the mechanism of enzyme catalysis will be discussed. The study of enzyme-substrate interactions accompanying substrate and feedback inhibitor binding. Details of the concerted conformational change of the substrate appear to be most consistent with the available data.

130 Comparative Homogeneous-Heterogeneous Pyrolyses Using a Wall-less Reactor

J. J. Glushar and Donald M. Kellie, Department of Chemistry, Kent State University, Kent, Ohio 44240; David A. Huschings and Kenneth Ohio, 44240.

The pyrolysis of neopentane using a wall-less reactor (J. Am. Chem. Soc., 91, 2215 (1969)) is a first order reaction with the activation energy equal to the bond dissociation energy. Under heterogeneous conditions (J. Phys. Chem., 73, 3167 (1969)) there is an alteration of the mechanism with a significant decrease in the activation energy. These studies have been extended to other hydrocarbons. Of particular interest are the pyrolyses of propene and methylnitropropane. The common products, methane, ethane, ethene, propene, allene, propyne, amine, and propyne. In the presence of a surface, the allene and propyne are believed present. However, the allene and propyne are present in relatively small amounts under heterogeneous conditions. In the presence of a surface, the allene and propyne are present. However, the allene and propyne are present.

Results have been obtained on the quenching of the Norrells Type II reaction from esters in the solution phase. The monolignone used is presumably quenching the triplet state of the esters and the resulting Stern-Volmer data provide an estimate of the lifet ime of the ester triplet state. The results indicate that the triplet lifetime is less than that for the aliphatic ketones. Moreover, the relative involvement of the singlet and triplet states in the Type II reaction is comparable to the ketones. Hence, if the rate constants for singlet and triplet Type II reaction are comparable for the esters, as is true for the aliphatic ketones, the rate of intersystem crossing must be greater for the esters. The splitting between the singlet and triplet states is greater for esters (as opposed to ketones), and, hence, the increased rate of intersystem crossing may have importance for a theoretical interpretation of the factors governing this radiationless process.


Turbidimetric and pH titrations have been used to study the complexation reactions between calcium ion and ether-1-hydroxy-1,1-dihydroxophosphate ion. The results are presented which indicate that polymeric complexes are formed resulting ultimately in the formation of a micelle-like or solid-like phase at concentrations of calcium ion above about 2 x 10^{-6} M. Previous investigators have reported stability constants for 1:1 and 2:1 (Ca-MEDP) species, as well as for a protonated complex, but have not made no mention of polymeric complexes. In this investigation, both potentiometric and turbidimetric experiments were carried out in the concentration of MEDP' caused a pronounced increase in the apparent stability constant (k) for the calcium complexes. The composition of the complexes has been deduced from changes in the pH titration curves in the presence of varying amounts of calcium ion, and from a pD/4 slope derived from the turbidimetric data. The log formation constant (ß) which best fits the experimental results was found to be (ß) = 11.7 ± 0.08, ß_2 = 18.78 ± 1.14, ß_3 = 29.0 ± 0.12, ß_4 = 48.73 ± 0.56, and k_0 = 9.5 x 10^{10}. These results are consistent with the formation of a series of complexes up to and including a 7:1 (Ca-MEDP) species and subsequently the clustering of these into very large aggregates. The formation of such large poly nuclear species is believed to be unprecedented for metal ions which, unlike calcium, form chiefly electrovalent bonds.

POLYNUCLEAR COMPLEX FORMATION IN SOLUTIONS OF CALCIUM ION AND ETHER-1-HYDROXY-1,1-DIHYDROXOPHOSPHITE ACID. II. LIGHT SCATTERING, SEDIMENTATION, MOBILITY, AND ANALYSIS MEASUREMENTS. Brandon H. Wiers, Miami Valley Laboratories, The Proctor & Gamble Company, Cincinnati 45229.

Light scattering, sedimentation, electrochromatic mobility, and dialysis measurements were performed on solutions containing calcium chloride, ether-1-hydroxy-1,1-dihydroxophosphate, and tetramethylammonium hydroxide. All measurements indicate the existence of high molecular weight species which, in 1.51 Ca^2+ : MEDP solutions, have weights of 10^6 g/mole or higher. From an estimated particle charge of Z = -16 ± 4 it is concluded that the Ca^2+ : MEDP mole ratio in the aggregates must be significantly greater than one but less than two, the ratio of stoichiometric equivalence. This confirms that the aggregates are highly polymeric soluble complexes or small Ca^2+ : MEDP micelles.
THE ABSORPTION SPECTRUM OF CS, 1650-1900Å. W. B. White, Jr., K. C. Myles, and C. N. N. Mathey, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Observation of the vacuum ultraviolet spectrum of CS in absorption has permitted us to identify and characterize three new electronic states for this molecule. The bands observed between 1750 and 1900Å are assigned to the transitions C-X, C-Y, and D-X. Each of the newly identified excited states is a Rydberg state which is strongly influenced by predissociation or other perturbations. The molecular constants and assignments of the perturbations will be discussed and compared to similar isoelectronic systems.

Acknowledgement. Grateful acknowledgement is made to Dr. W. B. White and associates, National Research Council, Ottawa, Canada, for their assistance in obtaining the data and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support during the course of the work.

The 196th Annual Meeting of the American Chemical Society, Chicago, Illinois.

138 THE SOLUBILITY OF A SERIES OF FLUORINE CONTAINING GASES IN SEVERAL NONPOLAR SOLVENTS. E. W. Kistner and R. C. Matt, Department of Chemistry, Wright State University, Dayton, Ohio 45431.

The solubility of CF3H and CF2H2 has been determined in the five nonpolar solvents benzene, carbon tetrachloride, cyclohexane, n-heptane, and n-octane; in addition, the solubility of CF3H and CF2H2 in n-hexane has been measured. All determinations were made in the temperature range 24°C to 36°C using a technique described in detail elsewhere. The results are given in terms of the Oswald coefficients and mole fractions of the solvents at 25°C and one atmosphere partial pressure. The solubility increases roughly tenfold for every 1°F in temperature. The results of others are also given. Combining our results with those of other authors, it turns out that the behavior of these gases deviates strongly from the normal pattern of relationships shown by other gases. The solubility increases roughly tenfold for every 1°F in temperature. The results of others are also given. Combining our results with those of other authors, it turns out that the behavior of these gases deviates strongly from the normal pattern of relationships shown by other gases.

139 THE REACTION OF OZONE WITH HYDROGEN DECIOR. AN IMPORTANT STEP IN THE NITROGEN CYCLE. E. C. Wilson, Jr., Arthur Levy, Battelle Memorial Institute, Columbus, Ohio 43201.

A photochemical smog mechanism will be presented which qualitatively accounts for the number of important aspects of the chemistry of urban atmospheres as studied in smog chambers. These are: (1) the disappearance and ultimate fate of NO2, (2) the accelerating influence of water vapor on certain rate parameters, (3) the solution in maximum oxidant concentration by water vapor, (4) the oxidation of SO2 by peroxy radicals, (5) the reduction in maximum oxidant by SO2. Experiments will be reported which demonstrate that (1) the reaction of NO and NO2 occurs at a sufficiently high rate to be important in air pollution, (2) the rate of this reaction is increased in the presence of water vapor, (3) SO2 reacts with a mixture of HO and NO2, but does not react with NO. Results of non-smoker runs which demonstrate the effects of NO and SO2 on reaction rates and product concentrations will be presented. The mechanism based on the notion that NO and HNO2 are the most important species in the atmosphere will be used to explain qualitatively the fate of the NO and the interaction of NO2 and HNO2 in photochemical smog: NO + O3 + HO + NO2 + HNO2 + HNO3 + H2O + HNO2 + NO + HO2 + NO2 + SO2 + H2O + NO3 + SO2 + HNO2 + HNO3.

140 AN X-RAY DIFFRACTOMETRIC ANALYSIS OF A MODIFIED NICKEL(II) COMPLEX. A SUBSTITUTED MACROCYCLIC LIGAND. L. M. Gooden, J. W. Mason, and F. W. Corfield, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Several isomers of 6,7,8,9,10-tetrasubstituted-1,4,5,6,7,8,9,10-octahydro-1,4-phenanthroline. The structure of a monosubstituted derivative of this molecule, which has the macrocyclic configuration, has been determined. All these isomers equilibrate to this structure in neutral basic solution. The presence of a macrocyclic compound is indicated in the x-ray diffraction pattern of the octahedral octahydro-1,4-phenanthroline complex. The cation is shown to have the structure 141.

141 THE SURFACE ENERGY OF POLYMERS. George L. Gaines, Jr., General Electric Rayden Center, Schenectady, New York 12302.

Recent measurements of the surface tension of polymer melts will be summarized. Estimates of surface energy based on wetting and other effects will also be described and compared with these direct experimental measurements. Various methods of altering the surface properties of polymers will be described.


The structure of an adsorbed polymer layer can vary greatly depending on the nature of adsorption due to the attractive forces between the polymer and the surface. The basic interactions between the polymer and the surface will be reviewed. The effect of the polymer conformation on the structure of adsorbed polymer layers will be discussed. The results obtained for a variety of adsorption conditions and surface coverage conditions will be presented. The effect of the polymer composition, conformation, and surface coverage conditions will be reviewed. The effect of the polymer composition, conformation, and surface coverage conditions will be reviewed. The effect of the polymer composition, conformation, and surface coverage conditions will be reviewed.

With the extension of the osmium tetroxide fixation and staining technique to diene containing copolymers, the electron microscope has been used extensively to observe polymer morphology. Some styrene-butadiene block copolymers display vivid color separations of cast films from nonselective solvents possess layered structures. However, the texture of the copolymer can be completely reversed by the proper use of selective solvents. Molecular alignment was observed in thin films dried from diene copolymer solutions, but the alignment was not observed when the same solutions were stained before the film was dried.

The alignment presumably was caused by the incompatibility of the two block segments and the narrow molecular weight distribution of the copolymer molecules. However, a striped pattern was observed in a cast film of a 40/60 styrene-butadiene copolymer which contained a sizable homopolymer contaminant (determined by gel permeation chromatography). The addition of polystyrene homopolymer destroys the pattern, but additional polybutadiene only produced homopolymeric islands in the striped pattern.

MORPHOLOGY AND CRYSTALLIZATION OF POLYCARBONATE. P. H. Neel, Case Western Reserve University, Cleveland, Ohio 44106.

Anomalous polycarbonate cast from solution or quenched from the melt consists of small (ca. 100Å) nodular regions of aligned chain segments. Annealing below Tg results in an increase in size of these regions and apparently related changes in physical properties. Annealing near Tg results in the growth of single crystals and lamellar structures. In contrast to models for normal polymer crystal growth, the polycarbonate crystallization appears to occur through the aggregation of the nodular structure followed by perfection of the lamellar structure. Strain induced crystallization results in the formation of small isometric crystals.

KINK BANDS AND RIBBING FROM THE DEFORMATION OF ORIENTED POLYETHYLENE. Richard B. Robertson, General Electric Research and Development Center, P. O. Box 12, Schenectady, N. Y. 12301.

We have been studying the shear deformation at room temperature of polyethylene that had previously been uniaxially oriented. Among the ways by which the oriented polyethylene can deform, which also include a further stretching of the fibrils and the splitting between the fibrils, is the formation of kink bands and ribbing. The kink bands form and grow with sharp boundaries and almost mirror-reflection of the fibrils about the boundary. Sharpness seems to result from the fibrils tending to collapse when bent more sharply than some critical angle of curvature. The reflection symmetry seems to result from the fibrils neither lengthening nor shortening, and thus not changing their cross-sectional area, when drawn into the kink band. At strain rates less than 1 min.−1 rather than form kink bands, oriented polyethylene tends to ribble by the fibrils becoming compressed into waves. The predominance of ribbing at low strain rates seems to result from a relaxation at low rates of the forces hindering inter fibril slip. Because the structure of the lamellar bundles existing within unoriented spherulites is similar to the oriented structure, especially after annealing, it is possible that ripples and kink bands or the equivalent may form in spherulites during necking, for example.

X-RAY LOW ANGLE SCATTERING FROM ORIENTED POLYMER FILMS. C. J. Heelfinger, E. L. Lippincott, Jr., R. J. du Pont de Nemours, Inc., Film Department, Circleville, Ohio.

X-ray low angle scattering is used to deduce the morphology of oriented polymer films and fibers. Generally, the structural models proposed to explain these patterns have been extrapolations of observations made with solution grown polymer single crystals or from highly crystalline bulk polymers. These models and explanations may not be applicable to oriented systems having only modest amounts of crystallinity or to those generated from precursor states that are grossly different. Poly(ethylene terephthalate) was chosen as a model polymer system for study. A systematic series of uniaxially and biaxially deformed films were produced from this polymer, made from the initially glassy or crystalline states. The low angle X-ray scattering patterns generated from these films were studied as a function of a) the sequence of deformation, b) the effect of the precursor structure, c) the effect of molecular orientation, and d) the direction of observation. Optical diffraction and model structures were used as an aid to the interpretation of the morphology produced. At least three different deformed states are developed upon deformation ranging in size from that of the unit cell (about 10Å) to large lamellar domains of about 300 × 2500Å. This structure is shown to be substantially different from that developed in a biaxially oriented polyethylene film.

SYNTHESIS, HOMO- AND COPOLYMERIZATION STUDIES OF 1,1,1-TRIMETHYL ACETYLACRYLAMIDE CHLORIDE (I) AND 1,1,1-TRIMETHYL METHACRYLAMIDE CHLORIDE (II). R. M. Coleman and R. E. Freis, Ashland Chemical Company, Bloomington, Minnesota 55420.

Monomers I and II were synthesized and shown to readily homo- and copolymerize with a variety of vinyl monomers to produce soluble polymers containing pendant

C₆H₅-CN  =  COOH(C₆H₅)₃Cl

1 R = H II R = CH₃

quaternary ammonium groups. The resultant polymers may be treated with base to produce the corresponding carboxylate with pendant amide groups (CH₃CN). Since molecules with amide residues suffer a carbon-nitrogen migration rapid reaction of polymers with the chromic salts of monomers I and II is the preferred method for preparing polymeric structures, which have an absorption at 3600 cm⁻¹ in the solid state but possess unique, reactive polymers. The reactivity ratios of each monomer (N) with styrene (N₁) were determined: Monomer I, N₁ = 0.56; Monomer II, N₁ = 0.63; N₁ = 0.51. The Alfrey-Price Q values were also calculated: Q₁ = 0.69, Q₂ = 0.64, and Q₁ = 0.61, respectively.


In the dithiocarbonate antibiotics, and carboxylate salts of metals are effective catalysts for the polymerization of olefin oxides (The Polymer Sci. B, 273 (1967)). To investigate the mechanism of initiation, the bulk polymerization at 25°C of 1,2,4-trimethylbenzene (ZMA) at monomer to ZMA molar ratio of 600:1 was studied by UV and IR spectroscopy. There is a rapid conversion of the sulfur-sulfur bond in the metal xanthate to a structure containing sulfur-carbon and oxygen-sulfur bonds, the

C₆H₅-C=O-S-Oh-CH₂-O-S-C₆H₅

latter acting as the site for the propagation step during polymerization. The xanthate ester moiety is subsequently converted to the oxygenated analogs, namely, O₂CI-thiocarbonate and dialkyl carbonate. These changes are independent of the propagation step. A change in the observed in the polymerization of tetenes oxides with zinc dithiobis-dithiocarbonate are similar, but much slower than in the case of ZMA. The presence of the carbonic acid ester moiety was also shown in the benzene-insoluble, catalytically active fraction isolated from the reaction product of propylene oxide and ZMA at a molar ratio of 80:1 or lower. This fraction also contained. iodo-sulfur.
Molecular weight distribution is known to affect the viscoelastic flow properties of linear amorphous polymers quite severely. Previous work has shown that among polymer samples having similar weight average molecular weights, \( M_w \), those with broad molecular weight distributions have more desirable flow characteristics, since their melt viscosities are less sensitive to thermal fluctuations and are lower at a given shear rate. These phenomena are most marked in samples having very low values of number weight, \( M_n \). A low value of \( M_n \) indicates the presence of a large low molecular weight fraction in the distribution, and, therefore, a large number of chain ends. The free volume introduced by chain ends is the most likely cause for the desirable characteristics observed. Evidence is presented which suggests that a broad molecular weight distribution should also enhance the glassy state impact strength of amorphous polymers by increasing the magnitude of molecular relaxation processes occurring below the glass transition; these relaxation processes can be measured by mechanical spectroscopy. An experimental program for investigating this problem and the results obtained to date are discussed.
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