



American
Chemical
Society

Second Central Regional Meeting

Columbus, Ohio

June 3-5, 1970





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CONTENTS

	<i>page</i>
Greetings	5
General Information	9
Shuttle Service	9
Special Events	10
Workshops	10
Program Outline	12
Program	13
Abstracts	23
Directory of Exhibitors	69
Exhibition Area	70
Author Index	71

COVER—The emblem of the American Chemical Society and the official centennial symbol of The Ohio State University.

STATE OF OHIO
Executive Department

OFFICE OF THE GOVERNOR

Columbus

P R O C L A M A T I O N

C H E M I C A L W E E K

JUNE 1-7, 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 30 exhibitors; and

WHEREAS, an attendance of over 1200 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.

NOW, THEREFORE, I, James A. Rhodes, Governor of the State of Ohio, in recognition of the academic standing and the professional achievements of this brilliant assemblage of scientists, do hereby designate the week of June 1-7, 1970, as

C H E M I C A L W E E K

in Ohio and I alert 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
16th day of April, in the year
of Our Lord, One Thousand
Nine Hundred and Seventy.

James A. Rhodes
GOVERNOR





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,

A handwritten signature in cursive script that reads "Novice G. Fawcett".

Novice G. Fawcett
President



2nd Central Regional Meeting
AMERICAN CHEMICAL SOCIETY

Columbus, Ohio
June 3, 1970

June 3, 4, 5, 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. Sensesbrenner. 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-Teed 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,
Darryle H. Busch
Darryle 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, \$13 for nonmembers, \$5 for students and high school teachers, \$1 for wives. The fee for half-day registration is \$3.
- **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. 5:30-8:30 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 4:40-6:00 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 Chemistry Safely?" 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 Spurs 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 2YC₃ Chairman

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. Grandey, University of Illinois at Urbana

Saturday Morning

Opening Remarks

Ethelreda Laughlin, Cuyahoga Community College-Western Campus and Vice Chairman for Midwestern Region, 2YC₃

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 Houk, 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

III. Forensic Chemistry: "What Part Does Science Play in Modern Law Enforcement?" 8:30 A.M.-noon, Saturday, June 6th. No charge. Center for Tomorrow, Room 2-3

Speakers:

Henry Dombrowski—Ohio Bureau of Criminal Identification and Investigation

Claude Hazen—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 Klinfelter—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 in Gas Chromatography. D. Macnaughtan, Jr. and L.B. Rogers.
- 9:35 2. Ensemble Averaging in Gas Chromatography. L.J. Lorenz, 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.
- 10:35 5. Potential and Current Control at Multiple Working Electrodes. L.B. Anderson and M.L. Rose.
- 10:55 6. Determination of Arsenic by Controlled-Potential Coulometry. D.R. Bohl, F.A. Kochler, Jr., 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. Gonda.
- 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.
- 11:55 9. The Determination of Rhenium in Platinum-Rhenium-Alumina Catalysts. L.A. Knecht and R. Northcraft.

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.
 - 9:35 11. Raman Spectroscopy of Proline Oligomers and Poly-L-Proline. W.B. 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.
 - 10:15 13. On the Mechanism of Cooperative Binding by Methemoglobin. H. Uchida and M.H. Klapper.
 - 10:35 14. A Study of Sodium Ion Binding to Proteins. G.E. Clement.
 - 10:55 15. Kinetic and Binding Studies of Liver Alcohol Dehydrogenase Ternary Complexes. J.D. Shore.
 - 11:15 16. Effect of Buffer System on Carbonic Anhydrase Activity in the Presence of EDTA or Peptone. J.E. Sell and H.G. Petering.
 - 11:35 17. The Hydrolysis of N-Aryl Substituted Carbamyl Phosphate Mono- and Dianions. C.M. Allen and J. Jamieson.

2nd CENTRAL REGIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY — TECHNICAL PROGRAM

	Thursday morning 9:15	Thursday afternoon 2:00	Friday morning 9:15	Friday afternoon 2:00
ANALYTICAL CHEMISTRY			General papers — Center for Tomorrow, Room 2-3	
BIOCHEMISTRY AND MEDICINAL CHEMISTRY	General papers — Center for Tomorrow, Room 6-7	General papers — Center for Tomorrow, Room 6-7	Symposium on Protein Conformation and Solution Properties — Center for Tomorrow, Assembly Hall	Symposium on Protein Conformation and Solution Properties — Center for Tomorrow, Assembly Hall
CHEMICAL EDUCATION			General papers — Section A — Center for Tomorrow, Room 6-7 ----- General papers — Section B — Center for Tomorrow, Room 8-9	Symposium on Chemistry Curricula in the 1970's — Ohio Union, Conference Theater
CHEMISTRY AND ENVIRONMENT		Symposium on Environmental Chemistry — Ohio Union, East Ballroom		
INORGANIC CHEMISTRY	General papers — Center for Tomorrow, Room 8-9	General papers — Center for Tomorrow, Room 8-9	Symposium on Non-carbon Catenaion — Ohio Union, Conference Theater	General papers — Center for Tomorrow, Room 2-3
ORGANIC CHEMISTRY	General papers — Section A — Ohio Union, East Ballroom ----- General papers — Section B — Ohio Union, Conference Theater	General papers — Ohio Union, Conference Theater	Symposium on Application of Resonance Spectroscopy to Organic Chemistry — Ohio Union, East Ballroom	Symposium on Application of Resonance Spectroscopy to Organic Chemistry — Ohio Union, East Ballroom
PHYSICAL CHEMISTRY	Symposium on Fast Reactions — Heterogeneous and Homogeneous Kinetics — Center for Tomorrow, Assembly Hall	Symposium on Fast Reactions — Heterogeneous and Homogeneous Kinetics — Center for Tomorrow, Assembly Hall		General papers — Center for Tomorrow, Room 6-7
POLYMER CHEMISTRY	Symposium on Polymer Surfaces — Center for Tomorrow, Room 2-3	Symposium on Polymer Textures — Center for Tomorrow, Room 2-3		General papers — Center for Tomorrow, Room 8-9

- 11:55 18. The Chemical Modification of Amino Acid Side Chains of Human Lysozyme and the Effect on Enzymatic Activity. C.L. Borders, E. McDonald, R. Fawcett, T. Limbird.
- General.** D. CORNWELL, Presiding *Center for Tomorrow, Room 6-7*
- 2:00 19. Synthesis and Antistaphylococcal Activity of N α - (w-Aminoacyl)-Lysines. A. Fujii, K. Tanaka, E.S. Cook.
- 2:20 20. Studies on the Proteases of *Aspergillus Oryzae*. B.F. Klapper, D.M. Jameson, R.M. Mayer.
- 2:40 21. Studies on the Biosynthesis of Pyridoxine. R.A. Schroer and E.H. Frieden.
- 3:00 22. The Biosynthesis of the Phosphomannan of *Hansenula Capsulata*. H.S. Prihar and R.M. Mayer.
- 3:20 23. Ultrastructure of Beef Heart Mitochondria: Effects of Adenosine Diphosphate on Morphology. N.E. Weber and P.V. Blair.
- 3:40 24. The Effects of Abnormal Urinary Metabolites of Phenylketonuria on Brain Nucleotide Phosphohydrolases. L. Bartolomeo and G. Rendina.
- 4:00 25. Cervical Dysplasia Experimentally Induced by Barium Salts. W.C. Gillchrist, J.E. Ayre, J.M. LeGuerrier.
- 4:20 26. The Fresh Water Ecosystem: Perspectives on Lake Erie. P.L. Zubkoff.

FRIDAY

Symposium on Protein Conformation and Solution Properties.

- J.L. ONCLEY, Presiding *Center for Tomorrow, Assembly Hall*
- 9:15 27. Conformations of Proteins. J.L. Oncley.
- 9:45 28. Determination of Protein Structure from X-Ray Crystallographic Studies. M.J. Adams, G.C. Ford, R. Koekoek, P.J. Lentz, Jr., A. McPherson, Jr., M.G. Rossman, R.W. Schevitz, and I.E. Smiley.
- 10:30 29. The Molecular Structures of Horse Heart and Bonito Ferricytochromes C. R.E. Dickerson, D. Eisenberg, T. Takano, O. Battjaj, and J. Varnum.
- 11:30 30. Functions and Conformation of the Cytochrome *c* Surface as Revealed by Immunochemical Reagents. E. Margoliash, M. Reichlin, L. Smith, H.C. Davies, and A. Nisonoff.

Symposium on Protein Conformation and Solution Properties.

- J.L. ONCLEY, Presiding *Center for Tomorrow, Assembly Hall*
- 2:00 31. Conformation of Myoglobins in Solution. F.R.N. Gurd.
- 3:00 32. The Structure of Rhombohedral Zinc Insulin. M.J. Adams, T.L. Blundell, E.J. Dodson, G.G. Dodson, D.C. Hodgkin, and M. Vijayan.
- 3:45 33. Studies on Proinsulin and Related Polypeptides. P.E. Oyer, A.H. Rubenstein, C. Nolan, C. Birdwell, F. Melani, W. Kemmler, and D.F. Steiner.
- 4:30 34. Optical Rotatory Dispersion and Circular Dichroism Patterns as Indications of Protein Conformation. D.W. Urry.

CHEMICAL EDUCATION

FRIDAY

Section A—General. V.I. MEEK, Presiding *Center for Tomorrow, Room 6-7*

- 9:15 35. Chemical Education: Are We Ready for Tomorrow? W.E. Hanford and R.E. Maizell.
- 9:40 36. Curriculum '70 ONU. D.J. Bettinger, W.E. Godwin, H.L. Haight, B.L. Hawbecker, T.D. Putnam and D.L. Wilhelm.
- 10:05 37. Research in the January Term. R.G. Landolt.
- 10:30 38. Water Pollution Study as a Method for Teaching General and Analytical Chemistry. J.F. Corwin.
- 10:55 39. Computer Instruction and Use in Undergraduate Chemistry Courses. J.E. Coleman and E.D. Swiger.
- 11:20 40. Instruction on Automatic Searching of the Chemical Literature. A.E. Petrarca, Ronald J. Beaton, Virginia E. Yagello.
- 11:45 41. Large Scale Electronic Grading and Grade Storage for General Chemistry Courses. Q. VanWinkle, W.T. Lippincott, R.J. Beaton, A.E. Petrarca.

Section B—General. P. GLASSOE, Presiding *Center for Tomorrow, Room 8-9*

- 9:15 42. The Design and Construction of an Electrode of General Utility for Selective Ion Measurements. P.R. Ogle
- 9:35 43. Benzene Fluorescence Studies in the Physical Chemistry Laboratory. F.S. Wettack.
- 9:55 44. Qualitative and Quantitative Analysis with Pure Salts. G.L. Gilbert.
- 10:15 45. A Multilevel Organic Chemistry Project. I. The General Chemistry Level. T.M. Sutliff and L.B. Wick.
- 10:35 46. Teaching X-ray Crystallography to Undergraduate Chemistry Majors. R.W. Collins.
- 10:55 47. "It's a Gas, Man." R. Battino and D.J. Karl.
- 11:15 48. "Gimmickry-Mimicry." G.O. Larson.
- 11:35 49. A Mechanism for Adding Relevance and Currentness to Freshman Chemistry. J.J. Fortman.

Symposium on Chemistry Curricula in the 1970's.

- G.L. GALLOWAY, Presiding *Ohio Union, Conference Theater*
- 2:00 Introductory Remarks. G.L. Galloway.
- 2:15 50. Integration of Biochemistry into the Undergraduate Chemistry Curriculum. E.H. Cordes.
- 2:55 Discussion
- 3:10 51. Computers in Teaching Chemistry. P.G. Lykos.
- 3:50 Discussion
- 4:05 52. Chemical Education in the Seventies. L.E. Strong.

CHEMISTRY AND ENVIRONMENT

THURSDAY

Symposium on Environmental Chemistry.

- K.H. MANCY, Presiding
Ohio Union, East Ballroom
- 2:00 Introductory Remarks.
- 2:10 Chemistry of the Aquatic Environment. W. Stumm.
- 2:50 Air Pollution Chemistry. J.G. Calvert and K. Demerjian.
- 3:30 Needs for Chemical Research in Solid Waste Management Programs. A.W. Breidenbach.
- 4:10 Chemistry of Aluminum(III) in Coagulation Processes. P.L. Hayden and A.J. Rubin.
- 4:35 Chemistry and Environmental Toxicology. M.M. Luckens.

INORGANIC CHEMISTRY

THURSDAY

- General. N.V. DUFFY, Presiding
Center for Tomorrow, Room 8-9
- 9:15 Transition Metal Complexes of $B_{10}H_{20}^{2-}$. R.L. Sneath and L.J. Todd.
- 9:35 Bonding and Properties of Isocyanide and Carbonyl Complexes of Ruthenium(III). J.R. Crook and R.E. Keith.
- 9:55 Photochemistry of Aryl Isocyanide Metal Complexes. R.A. Bailey.
- 10:15 Mass Spectra of Substituted Group VIB Metal Carbonyls. S.T. Bond, N.V. Duffy, V.M. Kothari.
- 10:35 Mass Spectra of Platinum(II) Metal Carbonyls. K.L. Klassen and N.V. Duffy.
- 10:55 Transition Metals as Lewis Bases: $Co(CO)_4^-$ Adducts with Hg(II) and In(III). W.R. Robinson, H.L. Conder, D.P. Schussler.
- 11:15 Lewis Base Properties of Platinum(0). T.R. Durkin and E.P. Schram.
- 11:35 Constrained Phosphite Ester Complexes of Cyclopentadienyliron Carbonyl Halides and Dihalogenotetracarbonyliron(II) Compounds. W.E. Stancilift and D.G. Hendrickler.
- 11:55 Some Aluminum-Nitrogen Polymers Containing Aluminum-Halogen Bonds. K. Gosling and A.L. Bhuiyan.
- General. M.F. FARONA, Presiding
Center for Tomorrow, Room 8-9
- 2:00 Crystalline Coordination Complexes of Copper(II) Salts with Alkanol-Substituted Ethylenediamines. D.N. Zimmerman and J.L. Hall.
- 2:20 Complexes of N,N-Dialkylthiocarbamate Ligands. B.J. McCormick and B.P. Stormer.

- 2:40 Properties of Transition Metal Complexes with Fluorinated Phosphine Ligands. P.G. Eller and D.W. Meek.
- 3:00 Cobalt and Nickel Complexes of Mixed Arsenic-Antimony and Arsenic-Phosphorus Polydentate Ligands. G. Kordosky, B. Cook, D.W. Meek.
- 3:20 Rhodium(III) and (IV) Chlorides and Their Reactions with Certain Nitrogen and Phosphorus Donor Molecules. R.A. Walton.
- 3:40 Cobalt Complexes of Some Synthetic Macrocycles and Their Derivatives Containing Cobalt-Carbon Bonds. K. Farmer and D.H. Busch.
- 4:00 Iron(III) Complexes Containing a Tetradentate Macrocyclic Ligand Derived from Ortho-Aminobenzaldehyde. V. Katovic and D.H. Busch.
- 4:20 Some Stereospecific Anomalies of Certain Amino Acid Outer-Sphere Complexes. D.E. Francis.
- 4:40 Amine Exchange (Transamination) in Zn(II) Schiff Base Complex Systems. B.E. Leach and D.L. Leussing.

FRIDAY

Symposium on Non-carbon Catenation.

- J.P. FACKLER, JR., Presiding
Ohio Union, Conference Theater
- 9:15 Introductory Remarks. J.P. Fackler, Jr.
- 9:20 Transition Metal Cluster Synthesis and Properties. R.B. King.
- 10:05 Discussion
- 10:10 Coordination Polymers. B.P. Block.
- 10:55 Discussion
- 11:00 Sheet Organosilicon Polymers. M. Kenney.
- 11:40 Discussion
- 11:45 Boron-Nitrogen Systems. S.G. Shore.
- 12:30 Discussion
- General. F.L. URBACH, Presiding
Center for Tomorrow, Room 2-3
- 2:00 Asymmetric Induction in Inner-Sphere Redox Reactions. Sister M.J. DeChant.
- 2:20 Reductions of Carboxylatocobalt(III) Complexes with Copper(I). S.A. Kazmi and E.S. Gould.
- 2:40 Optical Activity of β -Diketone Complexes of Cobalt(III). L.J. Boucher.
- 3:00 The Stereochemistry of N,N'-Bis(3-isopropylsilylidene) Polymethylenediaminocobalt(II) Complexes in Donor and Nondonor Solvents and in the Solid State. M. Hariharan and F.L. Urbach.
- 3:20 Bonding in Vanadyl Complexes. J.A. Ryan and H.A. Kuska.
- 3:40 Electron Paramagnetic Resonance of Transition Metal Complexes in Liquid Crystal Solutions. J.P. Fackler, Jr. and J.A. Smith.
- 4:00 The Crystal and Molecular Structure of Bis(p-Perthiocumato) Zinc(II). J.P. Fackler, Jr. and D.C. Fries.

- 4:20 87. The Structure and Ion Exchange Properties of Cerium(IV) Phosphates. R.G. Herman and A. Clearfield.
- 4:40 88. The Synthesis of Fluorinated Alkoxides. R.L. Hough and K.W. Nordquest.
- 5:00 89. Reaction of NaSn_2F_6 with $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: Investigation of a Possible Cariostatic Tin(II) Compound. R.W. Collins and J.M. Terris.

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-diphenylcyclopropanes. J.W. Hauser, J.T. Uchic.
- 9:35 91. The Rearrangement of Some α -Phenylethylcarbinols in Strong Acids. A.S. Kushner, P.H. Wang, Herman G. Richey, Jr.
- 9:55 92. The Trapping of Cations in the Reaction of Benzhydryl Azide with Nitrosonium Salts in Acetonitrile. M.P. Doyle, W. Wierenga.
- 10:15 93. The Chemistry of the Four Epimeric 2-Hydroxybicyclo[6.1.0]nonanes. E.A. Williams, P.G. Gassman.
- 10:35 94. The Chemistry of Cyanodithioimidicarbonic Acid. Part II. Synthesis of 3-Halo-1,2,4-thiadiazoles. L.S. Wittenbrook, G.L. Smith, R.J. Timmons.
- 10:55 95. Some "Active" Sulfuration Reactions. T.C. Shields, A.N. Kurtz.
- 11:15 96. The Preparation and Properties of 7,7-Dimethyl-1,2,3,4-tetrahydro-7-sila-2,5-norbornadiene. R. Maruca.
- 11:35 97. A Metalation 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. Maly, H.R. Menapace.

- Section B—General.** J. Koser, Presiding *Ohio Union, Conference Theater*
- 9:15 99. The Reaction of Olefin Oxides with Dimethylhydrazides: A New Synthesis of Aminimides. E.A. Sedor, R.A. Grimm, R.E. Freis.
- 9:35 100. Reactions of Isocyanide with Acetylenes. T.R. Oakes, D. Donovan.
- 9:55 101. Evidence Regarding the Stereochemistry of 3 α -Methoxycarbonyl-5 α -A-norcholestan-2-one. J.L. Pyle, B.V. Paranjape.
- 10:15 102. Evidence for Ylide Intermediates from Pyrolyses of Betaine and Pyridine Betaine in a Mass Spectrometer. R.A. Champa, D.L. Fisher.
- 10:35 103. A Novel 1,3-Dipolar Addition Reaction of Pyridinium Carbethoxycyanomethylide. J.E. Douglass, J.M. Wesolosky.
- 10:55 104. The Role of Iodine Complexation in Iodine Isocyanate Addition Reaction. II. Competitive Reactions. C.G. Gebelein.
- 11:15 105. The Pyrolysis of Sulfur Diimides. J.R. Grunwell, R.E. Maruca, J.L. Downie.
- 11:35 106. Amino Acids with Two Centers of Asymmetry from Microbial Peptides. G.G. Marconi, M. Bodanszky.
- 11:55 107. A New Synthesis for the Derivatives of Imidazolidinone-2. D. Aelony, W.J. McKillop.

General. R. Binkley, Presiding *Ohio Union, Conference Theater*

- 2:00 108. The Conformation of Sodium 4-Phenylbutyrate in Deuterium Oxide. J.F. Sebastian, M. Ti.
- 2:20 109. The Generation of Nitrenium Ions from Dialkylhydroxylamines. P.G. Gassman, G.D. Hartman, K. Shudo.
- 2:40 110. Cyclopropyl Aromatic Chemistry. II. Cyclopropane Geometry Effects on Intramolecular Charge Transfer Phenomena. R.C. Hahn, P.H. Howard, G.A. Lorenzo.
- 3:00 111. The Photochemistry of 7-Carbomethoxy-3,4-Benzotropolidene. J.S. Swenton, D. Madigan.
- 3:20 112. The Photochemistry of Enethiol Esters. J.R. Grunwell, S.I. Hanhan.
- 3:40 113. Stereochemically Concerted Fragmentations from Ester Triplet States. J.E. Gano.
- 4:00 114. The Photochemistry of Hydrazones. R.W. Binkley.
- 4:20 115. The Mercury (^{199}Pb)-Photosensitized Decomposition of Cyclopropane. E.G. Spittler, G.W. Klein.
- 4:40 116. The Photochemistry of 1,3-Distyrylbenzene. S. Horgan, D.D. Morgan, M. Orchin.

FRIDAY

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

- 9:15 117. Carbon-13 Magnetic Resonance and Molecular Structure. D.M. Grant.
- 10:05 Discussion
- 10:15 118. Effect of Charge on Chemical Shift. G. Fraenkel and T. Tokuhiro.
- 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*

- 9:15 123. Status of Theory in Heterogeneous and Homogeneous Kinetics. R. Marcus.
- 9:50 124. Fast Heterogeneous Electrochemical Reactions. E. Yeager.
10:20 Discussion
- 10:40 125. Heterogeneous Electron Transfer Rates of Aromatic Species in Aprotic Media. D.E. Smith, H.L. Hung, B.J. Huebert, K.R. Bullock, and W.E. Geiger.
- 11:10 126. Electron and Proton Transfer Kinetics of Aromatic Molecule Ions in Polar Solvents. L.M. Dorfman.
- 11:40 Discussion

Symposium on Fast Reactions—Heterogeneous and Homogeneous Kinetics.

J. STUEHR, Presiding *Center for Tomorrow, Assembly Hall*

- 2:00 127. Fast Homogeneous Electron Exchange Studied Spectroelectrochemically. N. Winograd and T. Kuwana.
- 2:30 128. Participation by Water Molecules in Fast Proton-Transfer Reactions. J.C. Harris and E. Grunwald.
3:00 Discussion
- 3:15 129. Enzyme Catalysis and Metabolic Control. G.G. Hammes.
- 3:45 Discussion — Break
- 3:55 Panel Discussion on Frontiers in Fast Kinetics.

FRIDAY

General. G.E. OWEN, JR., Presiding *Center for Tomorrow, Room 6-7*

- 2:00 130. Comparative Homogeneous-Heterogeneous Pyrolyses Using a Wall-less Reactor. J.E. Taylor, D.A. Kulich, D.A. Hutchings, K.J. Frech.
- 2:20 131. A Model for Nematic Mesophase Transitions. J.T.S. Andrews.
- 2:40 132. Viscosity of Molten Alkali Tetrafluoroborates. R. DeWitt, L.J. Wittenberg.
- 3:00 133. The Wetting of Thin Films of Organo-Clay Complexes. R.J. Ruch, M. Shen.
- 3:20 134. Quenching Studies of the Norrish Type II Reaction in Esters. F.S. Wettack, G.R. Dennison.
- 3:40 135. Polynuclear Complex Formation in Solutions of Calcium Ion and Ethane-1-Hydroxy-1, 1-Diphosphonic Acid. R.J. Grabenstetter, W.A. Cilley.

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.

4:20

137. The Absorption Spectrum of CF₄, 1650-1900A. W.P. White, Jr., K.C. Casleton, C.W. Mathews.

4:40

138. The Solubility of a Series of Fluorine Containing Gases in Several Nonpolar Solvents. E. Wilhelm, R. Battino.

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.

5:20

140. An X-ray Conformational Analysis of a Nickel(II) Complex of a Substituted Macrocyclic Ligand. V.L. Goedken, G.J. Gainsford, P.W.R. Corfield.

POLYMER CHEMISTRY

THURSDAY

Symposium on Polymer Surfaces.

T. FORT, JR., Presiding *Center for Tomorrow, Room 2-3*

- 9:15 141. The Surface Energy of Polymers. G.L. Gaines, Jr.
- 10:05 Discussion
- 10:15 142. The Structure of Polymers Adsorbed at Solid-Liquid Interfaces. C. Thies.
- 11:05 Discussion
- 11:15 143. The Effect of Surface Interactions on the Polymerization of Ordered Monomers. J.B. Lando.
- 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
- 2:45 145. Morphology and Crystallization of Polycarbonate. P.H. Geil.
- 3:25 Discussion
- 3:30 15 Minute Break
- 3:45 146. Kink Bands and Rippling from the Deformation of Oriented Polyethylene. R.E. Robertson.
- 4:25 Discussion
- 4:30 147. X-Ray Low Angle Scattering from Oriented Polymer Films. C.J. Heffelfinger and E.J. Lippert, Jr.

FRIDAY

- General. C.J. HEFFELFINGER, Presiding *Center for Tomorrow, Room 8-9*
- 2:00 Introductory Remarks. C.J. Heffelfinger.
- 2:05 148. Synthesis, Homo- and Copolymerization Studies of 1,1,1-Trimethyl Acrylylhydrazinium Chloride (I) and 1,1,1-Trimethyl Methacrylylhydrazinium Chloride (II). B.M. Culbertson and R.E. Freis.
- 2:30 149. Polymerization of Olefin Oxides with Zinc n-Butyl Xanthate and Zinc Dimethyl-Dithiocarbamate Catalysts: Mechanism of Initiation. J. Lal, E.F. Devlin.
- 3:00 150. The Influence of Molecular Weight Distribution on Relaxation Processes in Amorphous High Polymers. R.P. Chartoff.

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 p.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.

1 COMPUTER SIMULATION OF RAPID REPEATED INJECTIONS, RRI, OF SAMPLES IN GAS CHROMATOGRAPHY. Donald MacNaughtan, Jr. and L. B. Rogers, Department of Chemistry, Purdue University, Lafayette, Indiana 47907

A computer simulation study has been carried out to determine the results of rapidly and repeatedly injecting samples into a gas chromatographic system at intervals shorter than the base width of the resulting peaks. Certain rules have been found which allow one to overlap the chromatograms and still discern each individual peak of interest; resulting in a more continuous method of monitoring a process stream. It has also been discovered that overlapping of sample by this method can result in the "deconvolution" of two peaks under certain conditions.

2 ENSEMBLE AVERAGING IN GAS CHROMATOGRAPHY. L. J. Lorens, R. A. Culp, and L. B. Rogers Department of Chemistry, Purdue University, Lafayette, Indiana 47907

A high-precision gas chromatograph has been applied to the analysis of trace gases using the technique of ensemble averaging. Repetitive samples were run and digital data were recorded on punched paper tape for subsequent off-line computer analysis. Gases in the concentration range which produce a signal-to-noise ratio of unity were readily determined.

In order to check for quantitative accuracy of the sensing program simulation studies were performed. Mathematically generated Gaussian peaks of known height and standard deviation were then detected using derivative techniques. The peak areas resulting from this program were compared to the true calculated areas of the Gaussians. Further studies were performed to determine the effect of the summation of small peaks by comparison with large single peaks of equivalent height.

3 IMPROVEMENTS IN THE GAS CHROMATOGRAPHIC SEPARATION OF THE ENANTIOMERS OF SECONDARY AMINE DERIVATIVES. James A. Corbin and L. B. Rogers, Department of Chemistry, Purdue University, Lafayette, Indiana 47907

A systematic study has been made of the variables in the gas chromatographic separation of enantiomeric secondary amine derivatives using the urside of L-valine isopropyl ester. Although α , the ratio of the corrected retention times, was not very temperature sensitive for the liquid phase, it increased markedly when the stationary phase solidified. α was also significantly larger for the pentanorpropionyl derivative relative to the corresponding trifluoroacetyl derivative. The solid could be used satisfactorily over a wide range of sample sizes, but α was sensitive to polar contaminants. Water and alcohol were far worse than methylene chloride while n-pentane had relatively little effect.

4 CHEMICAL ACTIVITY OF TOBACCO SMOKE CONDENSATE. L. W. Michael, E. Menden, and H. G. Peterling, Department of Environmental Health, University of Cincinnati, College of Medicine, Cincinnati, Ohio 45219.

A comparison of the alkylative, reductive and copper binding activity of tobacco smoke condensate (TSC) has been conducted to provide chemical probes for variation in the reported biological activity of TSC. Alkylating activity was determined using the method of Stedman and Miller (Chem. & Ind. (London), 618 (1967)) and the reducing activity was determined using the method reported by Hagopian (Environ. Sci. & Tech., 6: 567 (1969)). Copper binding activity was determined by our own partition method. TSC was collected either on Cambridge filters or in acetone traps cooled in an ice bath. Representative noncommercial cigarettes (Research Cigarettes, University of Kentucky) were used in this study. Variation in the activity of TSC as shown by these chemical probes was observed to be a function of the specific activity of the sample rather than a function of the mode of collection. Since alkylating, reducing and metal binding agents are known to interact with biological systems, the chemical probes delineated here provide a means of specifying the activity of fractions of TSC and of correlating this activity with biological interactions. (This work was supported by a grant from the American Medical Association Research Fund and by Public Health Service Grant ES-00159)

5 POTENTIAL AND CURRENT CONTROL AT MULTIPLE WORKING ELECTRODES. L. B. Anderson and M. L. Rose, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210

General methods have been developed for controlling electrode potential and/or current in electrochemical systems employing multiple working electrodes. Specific applications of the circuit designs investigated are to be found in ring-disc, flowing-solution, thin-layer methods, and in dummy-cell techniques.

An instrument has been constructed with the capability of n-electrode potential or current control. Its design is modular in order to allow for open-ended variation of the number of working electrodes without modification of the basic instrument. A programmable switching matrix allows synthesis of electrochemical experiments involving as many as eight successive control steps.

6 DETERMINATION OF ARSENIC BY CONTROLLED-POTENTIAL COULOMETRY. Donald R. Bohl, Francis A. Koehler, Jr., and Douglas E. Sellers, Monsanto Research Corporation, Mound Laboratory, *Miamisburg, Ohio 45342.

A controlled-potential coulometric procedure [W. M. MacNevin and B. B. Baker, *Anal. Chem.* 24, 986 (1952)] has been extended for use in the determination of microgram quantities of arsenic. The arsenic is determined by coulometric oxidation of arsenic(III) to arsenic(V) at a platinum electrode. Improved sensitivity and accuracy were obtained by using a small titration cell in conjunction with an electronic solid-state, controlled-potential coulometer. Results for arsenic(III) determinations at the 120-360 µg level had an average error of +0.19% and a relative standard deviation of ±0.22%. The maximum sensitivity of the procedure for quantitative arsenic(III) determinations has been evaluated. The controlled-potential coulometric procedure for the determination of arsenic(III) compares favorably to constant-current coulometric procedures.

*Operated for the U.S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

7 CONTINUOUS AMPEROMETRIC MEASUREMENT OF I⁻, Br⁻, AND ALKALOIDS AT A TUBULAR CARBON ELECTRODE. Carter L. Olson, Mary Tachdjian Henne, and Tayseer A. L. Gouda, College of Pharmacy, The Ohio State University, Columbus, Ohio 43210

A simple method was developed for continuously measuring Br⁻ and I⁻ concentration in the region of 1 to 100 x 10⁻⁶ molar at a tubular electrode. A solution containing Br⁻ or I⁻ is pumped through one flow line and caused to mix with a AgNO₃ reagent flowing through a reagent flow line. The Ag⁺ is measured amperometrically at a tubular carbon or platinum electrode. The current decrease in Ag⁺ reduction is correlated to the concentration of I⁻ or Br⁻ in the sample stream. Both sample and reagent stream are continuously degassed removing oxygen from the solution. In a similar manner several alkaloids were measured by their reaction with silicotungstic acid where the current changes for the silicotungstic acid reduction were correlated with alkaloid concentration.

A FULLY AUTOMATED METHOD FOR THE ESTIMATION OF THE CONCENTRATION OF CA AND MG IN SERUM AND URINE. John A. LotL, Thomas S. Herman, 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 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 clog the three-slot burner of the Perkin-Elmer 303 atomic absorption spectrophotometer fairly rapidly. An Auto-Analyzer sampler, pump I, and dialyzer were used to dilute the specimens and dialyze the Ca and Mg from the serum or urine. The dialyzer was debubbled and fed directly to the burner. A strip-chart recorder was used to monitor the output to give a fully automated system. The only manipulation that was required was loading the sampler wheel with the specimens.

9 THE DETERMINATION OF RHENIUM IN PLATINUM-RHENIUM-ALUMINA CATALYSTS. L. A. Knecht and Robert Northcraft, Marietta College, Marietta, Ohio 45750 and American Cyanamid Co., Willow Island, W. Virginia 26190.

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 (0.3 to 0.8% Re). This paper outlines a differential spectrophotometric method for such an analysis, adapted from that of Meloche et. al. [*Anal. Chem.*, 29, 527 (1957)]. It makes use of the color produced when an acidic perchlorate solution is treated with alpha-furildioxime and stannous chloride. This method is compared with the better known thiocyanate method, which was found unsuitable 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 by including platinum in the standards. Nitrate is a serious interference and must be absent. If sample dissolution requires treatment with aqua regia - to dissolve reduced (metallic) platinum - nitrate must subsequently be destroyed using formic acid.

10 INFRARED STUDIES OF SOME N-METHYLACETAMIDE COMPLEXES. Norman C. Li, Y.H. Shav, Dept. of Chemistry, Duquesne University, Pittsburgh, Pa. 15219

Hydrogen bonding of N-methylacetamide (NMA) with dimethylsulfoxide (DMSO) and N,N-dimethylacetamide (DMA) in carbon tetrachloride and CCl₄/CHCl₃ mixed solvent was studied by a near-infrared method, which consists of measuring the effects of various concentrations of DMSO or DMA on the molar absorptivity of 0.061 NMA at 6800 cm⁻¹, corresponding to the first overtone of the uncomplexed NH stretching vibration. The association constants for the formation of 1:1 NMA-DMSO and NMA-DMA complexes in CCl₄ are 12 and 10 l/mole, respectively, at 25°. In order to obtain association constant for the formation of NMA-DMSO in CCl₄/CHCl₃ mixed solvent, it is necessary to have data on association constants of CHCl₃-DMSO complexes in CCl₄, and we have obtained these by determining the effects of various concentrations of DMSO on the proton magnetic resonance frequency of 0.05N CHCl₃ in CCl₄. The association constants for the formation of NMA-DMSO and NMA-DMA in CCl₄/CHCl₃ mixed solvent are slightly higher than in CCl₄, presumably due to hydrogen bonding between OH and C=O in NMA. NMA was chosen as the simplest molecule containing the peptide amide group and hence can be regarded as a structural unit of the polypeptide chain. Our results show that DMSO and DMA are effective in disrupting the interamide bonds, by acting as hydrogen acceptors to the NH group.

RAMAN SPECTROSCOPY OF PROLINE OLIGOMERS AND POLY-L-PROLINE.

W. B. Rippon, A. G. Walton, J. L. Koenig, Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106.

The laser excited Raman spectrum of helical poly-L-proline with *cis* peptide bonds (form I) 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 spectra -- others, however, appear to be unique to the Raman spectra. In addition, it is noted that the relative intensities of certain bands are also sensitive to conformation. A preliminary spectra obtained from the "collapsed" form of poly-L-proline precipitated from concentrated calcium chloride solution is also presented. Oligomers of proline are shown to favour the trans form in aqueous solution for $DP > 3$ and in dried solids for $DP > 4$.

Interaction Between Human Alpha-1-Acid Glycoprotein and Steroid Hormones.

Julius Kerker, 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 40 and 37°. 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-steroid interaction was studied further and was found to be inhibited by Hg^{++} , Ag^+ , Cu^+ , and Fe^{++} . 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 METHHEMOGLOBIN.

Hiroshi Uchida, Michael H. Klepper, Department of Chemistry, Ohio State University, Columbus, Ohio 43210

Iodide, bromide and nitrite bind reversibly, and sigmoidally 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 $Na^+ < tetramethylammonium < tetraethylammonium < tetrabutylammonium$. Competitive binding experiments indicate that the sigmoidal binding curves of bromide and iodide are due to salt induced, protein conformation perturbation. Tetrapropylammonium bromide promotes the binding of imidazole, a low spin complexer, but inhibits binding of cyanate, a high spin complexer. 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. Nitrite 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.

14 A STUDY OF SODIUM ION BINDING TO PROTEINS.

Gerald E. Clement, Department of Chemistry, Kenyon College, Gambier, Ohio 43022

The sodium ion binding to proteins was studied using a gel-filtration method employing coarse Sephadex G-25 and radioactive sodium 22. The proteins employed at various pH values and buffer solutions were pepsinogen, pepsin, lysozyme and β -lactoglobulin A and a mixture of A & B. As expected lysozyme did not show any sodium ion binding by this method at pH 5.5 while the sodium ion binding with β -lactoglobulin in the pH range 6-8.8 agreed quite well with data previously reported. The main emphasis of this work was to determine the sodium ion binding to pepsin in the acid pH range. At high sodium ion concentrations, pepsin binds 2.4 moles of sodium/mole of protein at pH 3.6 and 5.0 moles sodium at pH 4.6. At comparable sodium ion concentrations pepsinogen at pH 6.75 binds ca 3 times as much sodium as pepsin. The advantages and disadvantages of employing the gel-filtration method for ion binding studies will be discussed. Finally, the sodium ion binding data for pepsin will be used in the analysis of the titration curve of pepsin in the pH range 2-6 by modifying the Z value (charge on the protein at any pH) in the Linderström Lang equation.

KINETIC AND BINDING STUDIES OF LIVER ALCOHOL DEHYDROGENASE TERNARY COMPLEXES.

Joseph D. Shore, Edsel B. Ford Institute, Henry Ford Hospital, Detroit, Michigan 48202.

The binding of pyrazole to binary complexes of LADH, NAD and NAD analogs and the binding of isobutyramide to binary complexes of LADH, NADH and NADH analogs was studied. The dissociation constants of pyrazole from the binary complexes were 0.14, .10 and 1.2 μM for complexes in which the coenzyme was NAD, hypoxanthine adenine dinucleotide (NHD) and 3-acetyl pyridine adenine dinucleotide (APAD) respectively. Stopped-flow kinetic studies indicated that the higher dissociation constant of pyrazole from LADH-APAD was due to a much slower pyrazole "on" velocity. The dissociation constants of isobutyramide from ternary complexes consisting of LADH, NADH or APADH, and isobutyramide were all in the range 180 - 200 μM . The results of this study indicate that either the amide group of NAD is required for ternary complex formation with pyrazole or the conformation of LADH-APAD complex is different from that of LADH-NAD, and that there is apparently no interaction in part NADH and isobutyramide in the ternary complex formed with LADH. (Supported in part by NSF grant GB 7174).

16 EFFECT OF BUFFER SYSTEM ON CARBONIC ANHYDRASE ACTIVITY IN THE PRESENCE OF EDTA OR PEPTONE.

J. E. Sell and H. G. Petering, Depts. of Biological Chemistry and Environmental Health, College of Medicine, University of Cincinnati, Cincinnati, Ohio 45219.

The hydration of carbon dioxide which is catalyzed by carbonic anhydrase was monitored by the colorimetric method of Wilbur and Anderson (*J. Biol. Chem.*, 176, 147, 1948). Buffers (0.025 M, pH 8.2) were employed with pK_a values near eight. These included tris(hydroxymethyl)amino-methane (Tris), triethanolamine, and veronal. Ethylenediamine tetraacetate (EDTA) or peptone were added to the reaction mixture up to 40-fold excess by weight of agent to carbonic anhydrase. Carbonic anhydrase catalyzed activity was slowest in the veronal buffer. Addition of EDTA or peptone increased the carbonic anhydrase catalyzed activity in the veronal buffer significantly above that found in either Tris or triethanolamine. Peptone or EDTA had no effect on the carbonic anhydrase activity in either Tris or triethanolamine. This observed effect in veronal buffer with EDTA could be blocked by equivalent amounts of divalent metal salts such as zinc or cadmium. On the other hand EDTA had no effect on the esterase reaction of carbonic anhydrase using p-nitrophenylacetate as the substrate, regardless of the buffer used. The significance of these findings will be discussed. (Supported by USPH ES-00159)

STUDIES ON THE PROTEASES OF *ASPERGILLUS ORYZAE*, Betty F. Klapper, David M. Jameson, Robert M. Mayer, Department of Chemistry, Ohio State University, 140 W. 18th Avenue, Columbus, Ohio 43210

Aspergillus oryzae 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. Studies of this purified enzyme has shown it to be inhibited by diisopropylfluorophosphate and to have esterase activity. Intracellular proteases have also been studied in an attempt to determine their relationship to the purified exoprotease. The specific activity of the intracellular protease increases in stationary phase at the same time that extracellular protease is detected in the medium. The mechanism controlling release of the protease into the medium and the possible activation of an intracellular precursor have also been studied.

21 STUDIES OF THE BIOSYNTHESIS OF PYRIDOXINE. Richard A. Schroer and Edward H. Frieden, Department of Chemistry, Kent State University, Kent, Ohio 44240.

Studies of the biosynthesis of pyridoxine have been undertaken using *Saccharomyces fragilis*. The organism was grown in a glucose containing (1-5%) medium and harvested after 6 days at 30°. Pyridoxine (270 μ M) was isolated from the medium by chromatography on Dowex 50 and purified by recrystallization. Two experimental approaches were used. For the first, glucose- 14 C (UL, 0.1 mCi) was added after 60-72 hours growth, together with an unlabeled suspected precursor. Involvement of the precursor in the biosynthesis of pyridoxine would presumably be reflected in reduction of the incorporation of glucose carbons in pyridoxine. Experiments of this nature have shown that aspartic acid + glycylaldehyde, and pyridoxine itself reduced glucose incorporation, but that asparagine, glutamic acid and serine were without effect. Addition of 4-deoxy pyridoxine resulted in increased labeling by glucose. The other approach used labeled compounds other than glucose. These experiments have shown that 14 C-aspartate (UL) and 14 C-acetate (C- α) would label pyridoxine, while 14 C-methionine was not incorporated to any measurable extent. 14 C-formate did not label under comparable conditions, but was incorporated to a significant extent when 4-deoxy pyridoxine was added along with the label.

22

THE BIOSYNTHESIS OF THE PHOSPHOMANNAN OF *HANSENULA CAPSULATA* Harbajan S.

Prihar and Robert M. Mayer, The Ohio State University, Columbus, Ohio 43210

Studies have been carried out on the cell-free formation of the phosphomannan of *Hansenula capsulata* NRRL-Y-1842, in which the phosphoryl residues are present as phosphomonoesters linking the reducing carbon of one repeating unit to the non-reducing end of the next. Evidence has been obtained that indicate that both mannose and phosphate are derived from guanosine-5'-diphosphate mannose (GDPM). Utilizing GDPM labeled with mannose- 14 C it has been possible to demonstrate that the product formed has a structure similar to that of the native polysaccharide. The product is susceptible to hydrolysis catalyzed by an enzyme specific for the degradation of phosphomannans. In addition, the products of mild acid hydrolysis appear to correspond to the product formed from the native polymer under the same conditions; the primary product being a phosphomonoester of a mannosyl disaccharide. In addition, the product formed in reaction mixtures which contained β -P $_2$ -GDPM also yielded the same disaccharide phosphate after mild acid hydrolysis. The incorporation of both mannosyl and phosphoryl residues are dependent upon the addition of Mg $^{++}$ and ATP. Other nucleotide triphosphates can be substituted for ATP, however, the rate of mannose incorporation is decreased. The incorporation into the product is inhibited by GMP, GDP, and GTP to the same extent at equal concentrations of the nucleotides. (Supported by NSF Grant GB-7854, and USPHS, NIH Grant AI-0884-01.)

17 THE HYDROLYSIS OF N-ARYL SUBSTITUTED CARBAMYL PHOSPHATE MONO- AND DIANIONS.

Charles M. Allen, Jr., and Jane Jamieson, Department of Biochemistry, College of Medicine University of Florida, Gainesville, Fla. 32601.

The hydrolysis of carbamyl phosphate monoanion like other acyl phosphate monoanions proceeds via P-O bond fission. Acyl phosphate dianions undergo P-O bond fission, whereas carbamyl phosphate dianion undergoes C-O bond fission with the elimination of inorganic phosphate. The results of this work support and give additional evidence for preliminary experiments which indicated that the substitution of a single aryl group on the carbamyl phosphate nitrogen results in a mechanism for dianion hydrolysis which involves P-O bond fission. Pseudo first order rate constants for the hydrolysis of phenyl, o-ethoxyphenyl and p-nitrophenyl carbamyl phosphate have been obtained at 37° and ionic strength 0.6 over a pH range in which mono- and dianionic species predominate. The values of k_{obs} for the hydrolysis of the dianionic species show more dependence on the electron delocalizing ability of p-substituents in the phenyl ring (p=0.62) than do the values of k_{obs} for the monoanionic species (p=0.27). The effect of temperature and varying salt and buffer concentrations on the values of k_{obs} are consistent with the mechanisms proposed for other acyl phosphate mono- and dianions. Evidence for the absence of an isocyanate intermediate during the hydrolysis of p-nitrophenyl carbamyl phosphate dianion is provided by studies using azide as a trapping agent.

18 THE CHEMICAL MODIFICATION OF AMINO ACID SIDE CHAINS OF HUMAN LYSOZYME

AND THE EFFECT ON ENZYMIC ACTIVITY. C. L. Borders, Jr., E. McDonald, R. Fawcett, and T. Limbird, Department of Chemistry, The College of Wooster, Wooster, Ohio 44691.

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-15 in hen and his-78 in human. [R.E. Canfield, Brookhaven Symposium Biol. 21, 136 (1968)] The his-15 of hen lysozyme has been shown to be non-essential for enzyme activity by Rafferty, et al. [Biochemistry 8, 700 (1968)]. When human lysozyme is treated with iodoacetic acid at pH 6.5 for 18 hours, a chromatographically different modified enzyme results. Amino acid analysis indicates the total loss of histidine and the formation of 3-carboxymethylhistidine in the modified enzyme. The activity of the modified enzyme is 1-2 times that of the native enzyme, indicating the non-essentiality of the single histidine for activity. Preliminary results indicate that when human lysozyme is treated with a 60-molar excess of N-acetyl-midazole at pH 7.5, only one tyrosine residue out of a total of six in the 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 M o-methylisourea for 6 days at pH 10.5, 4-8 of the 5 lysine residues are converted to homoarginine. This modified lysozyme has 60% of the activity of the native enzyme against *M. lysodeikticus* at pH 7.5.

19

SYNTHESIS AND ANTISTAPHYLOCOCCIC ACTIVITY OF N $^{\epsilon}$ -(β -AMINOACYL)-LYSINES.

Akira Fujii, Kinji Tanaka, and Elton S. Cook, Division of Chemistry and Biochemistry, Institutum Divi Thomae, Cincinnati, Ohio 45206

It has been previously reported that a series of β -amino acids and their histidine dipeptides protected mice from death by *Staphylococcus aureus* infections (K. Tanaka et al, Appl. Microbiol., 16, 1457 (1968) and A. Fujii et al, Abstr. 158th National ACS Meeting, New York, 1969). The present investigation was undertaken to learn if β -aminoacyllysines also have antistaphylococic activity. N-Glycyllysine, N $^{\epsilon}$ -(β -alaninyl)-lysine, N $^{\epsilon}$ -(β -aminobutyryl)-lysine, N $^{\epsilon}$ -(β -aminovaleryl)-lysine, and N $^{\epsilon}$ -(β -aminocaproyl)-lysine were synthesized through condensation of each carboxenzylo-amino acid with N $^{\epsilon}$ -carboxenzylo-L-lysine ethyl ester ditoluensulfonate by the Mixed Carboxylic-Carbonic Acid Anhydride Method. The yields, melting points, and R_f values on PPC and TLC will be presented. The antistaphylococic activity of these β -aminoacyllysines was demonstrated through their protective effect against staphylococcal infections in mice. A total 5 mg of each sample was given in equally divided doses subcutaneously 2 hrs before and 4 hrs after the injection of *Staphylococcus aureus*. While all of these dipeptides showed protective effects, the activity of N $^{\epsilon}$ -(β -alaninyl)-lysine was found to be highest among the β -aminoacyllysines and to be almost equivalent with that of β -aminobutyrylhistidine. The antibiolytic property of these dipeptides will also be reported.

23 ULTRASTRUCTURE OF BEEF HEART MITOCHONDRIA—EFFECTS OF ADENOSINE DIPHOSPHATE ON MORPHOLOGY. Nicholas E. Weber, Paul V. Blair, Department of Biochemistry, Indiana Univ., School of Medicine, Indianapolis, Indiana 46202

Mitochondria will assume a distinct morphological arrangement upon the addition of substrate and adenosine diphosphate and when inorganic phosphate is added, the cristae membrane remains essentially unchanged from its previous condensed appearance. This observation indicates that the gross morphological changes in mitochondria described by Green, et al. Arch. Biochem. Biophys. 125, 681, (1968) and Hackenbrock Proc. Natl. Acad. Sci. U.S. 61, 598 (1968) during the state II to III transition need not specifically reflect energy transducing conformational changes that almost surely exist at the molecular level during these processes. In addition, the level of adenosine diphosphate required to promote a considerable change in mitochondrial morphology is in the range of 1.0 to 1.5 μ moles per gram of mitochondrial protein. Inorganic phosphate which helps promote the energized-twisted configuration Green, et al., 1968 had its effect in the 100 to 500 μ moles per gram range. These observations along with others involving nucleotide specificity and atracyloside sensitivity lead us to speculate that the specific ultrastructural arrangement generated by adenosine diphosphate may be due to stoichiometric binding of adenosine diphosphate and extrusion of small molecules from the matrix of the inner membrane. It is difficult to accommodate the tripartite unit structure in the highly condensed inner mitochondrial membrane (110-120 angstroms) under the influence of adenosine diphosphate. Thus, other alternatives are considered for the functional membrane structure.

24

24 THE EFFECTS OF ABNORMAL URINARY METABOLITES OF PHENYLKETONURIA ON BRAIN NUCLEOTIDE PHOSPHORYLASES. Luke Bartolomeo, George Rendina, Bowling Green State University, Bowling Green, Ohio 43402

The abnormal urinary metabolites associated with phenylketonuria (PKU) have been studied for effects on brain nucleotide phosphorylases (Afpases). These are Mg^{++} , Na^+ , and K^+ dependent multi-enzymes found in mitochondria (Mc), microsomes (Ms), and other cell fragments (Cf) of ruptured neurons. Using an automated assay procedure for determining Pi release, it was found that five of the fifteen abnormal metabolites tested inhibited the Afpases very selectively. Phenylethylamine inhibited the Na^+ -stimulated activity in all three fractions, but only inhibited the Mg^{++} -stimulated activation of the Mc enzyme. Indolylpyruvic and p-hydroxyphenylpyruvic acids inhibited the Mg^{++} -stimulated activity in all three subcellular fractions, in this case the Ms enzyme was the least sensitive to these metabolites. Indole strongly inhibited the Mg^{++} activation of all three fractions while N-phenylacetylglutamine was the only metabolite to inhibit the Na^+ - K^+ -interacting activation of Ms and Cf phosphorylases. These studies not only indicated the possibility of interference of brain function by the abnormal metabolites but also provided additional evidence that the nucleotide phosphorylases behave as a multi-enzyme system within each of the subcellular particles studied.

25 CERVICAL DYSPLASIA EXPERIMENTALLY INDUCED BY BARIUM SALTS.

W.G. Galleher, J.E. Ayre, and J.M. Ledwiler

Barium ions have been found to induce cervical dysplastic positive cells to cancer cells in a period of days as compared to years in the normal nonbarium induced sequence of events. Barium ions form varying degrees of insoluble compounds with oxyanions found in biological cells. One important biological oxyanion is phosphate in its many ester forms, including the nucleic acids and coenzymes. Barium forms insoluble compounds with phosphate. Pulmonary experimental cancer can be provoked by inhaled beryllium compounds. The toxicity of beryllium is well known. One big difference in solution chemistry between beryllium and barium is their behavior toward phosphate anions. Beryllium phosphate is soluble in aqueous solution whereas barium phosphate is not. The normally nonbiologically associated alkaline earth elements provide a novel tool to study the induction and differentiating process involved in the establishment of cancer cells. The opportunity to study rate controlled reversible mechanisms of the preneoplastic halocell and to isolate the first irreversible steps in the barium modified differentiation process leading to cancer cells is available on a custom synthesis basis. This barium concentration control method in conjunction with chemical solvents such as DMSO, known to assist ions and molecules through the membranes, offers an approach to oncologists that is otherwise not available. The approach offered is many fold, (1) the study of the time sequence of events condensed into laboratory manageable periods, (2) the ability to predict for a five to seven year time period whether the patient does or does not have cancer cells and (3) the ability to differentiate between inherited and infectious (viral) cancer.

THE FRESH WATER ECOSYSTEM: PERSPECTIVES ON LAKE ERIE. Paul L. Zubkoff, Academic Faculty of Biochemistry, The Ohio State University, Columbus, Ohio 43210

The relationships between limnological parameters, including morphometry, hydrology, currents, water mass movements, and temperature, will be discussed in relation to the periodic "algal bloom" phenomena of Lake Erie. Spring conditions, when green algal blooms occur, are compared to those of late summer when blue-green algal blooms predominate. Under conditions favorable to blue-green algal growth, and assuming a generation time of 8 hours, a bloom should be observed macroscopically in 48-72 hours. Insufficient information is available to make a similar calculation for green algae. Casper, V.L. (1965) "A Phytoplankton Bloom In Western Lake Erie", p29, Pub. No. 13, Great Lakes Research Division, U. Mich.

FWPCA (1968) "Lake Erie Environmental Summary, 1963-4"

FWPCA (1968) "Lake Erie Report: A Plan for Water Pollution Control"

Zubkoff, P.L. (1969) "The Fresh Water Ecosystem: A Model", W 31, 158th Meeting, Am. Chem. Soc., Sept., N.Y.

27 CONFORMATIONS OF PROTEINS. J. Lawrence Oncley, Biophysics 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 crystalline globular protein structures has been obtained for almost twenty proteins since the classic work on sperm whale myoglobin. Although the α -helix appeared to be the most important element of myoglobin structure, the β -structure, pleated sheet, and $\alpha 2^+$, 310^- and π -helices have appeared in other studies. But much of the peptide chain often consists of "fixed but disordered structures" (Schellman and Schellman), and we now believe that secondary and tertiary structure depends upon side-chain hydrogen bonding and hydrophobic-, dipole-dipole- and π -interactions to a larger extent than upon peptide hydrogen bonds.

Questions concerning the structural similarities of protein molecules in crystals and in aqueous solutions must be answered by study of "short-range properties" (Kauzmann). Studies using chemical and immunochemical properties, optical rotatory dispersion and circular dichroism will be discussed in this symposium. Nuclear magnetic resonance has recently contributed much to our understanding of the conformation of ribonuclease, lysozyme and hemoglobin in solution, and to the mode of action of these proteins.

It now appears that the extended peptide chain, without covalent disulfide bonds, is capable of finding a conformation of minimum free energy which leads to the formation of specific disulfide cross-links and the three-dimensional conformation seen in crystals. The recent discovery of the proinsulin molecule adds to this belief. There are also increasingly powerful computation methods which strengthen our belief that X-ray crystallographic studies yield conformations of minimum free energy in aqueous environments.

28 DETERMINATION OF PROTEIN STRUCTURE FROM X-RAY CRYSTALLOGRAPHIC

STUDIES. M. J. Adams, G. C. Ford, R. Koekoek, P. J. Lentz, Jr., A. McPherson, Jr., M. G. Rossmann, R. W. Schevitz, I. E. Smiley, Department of Biological Sciences, Purdue University, Lafayette, Indiana 47907.

The relationship of protein structure to specific function, as revealed by crystallographic studies during the last decade, culminating with sophisticated subunit assemblies, will be discussed with particular reference to tetrameric lactate dehydrogenase. It is anticipated that a high resolution (2.8 Å) map of LDH will have been analyzed early in 1970. In addition there is now available, at lower resolution, an electron density map of the binary complex of enzyme with coenzyme as well as a map of the abortive ternary complex of enzyme, coenzyme, and product. These results should reveal the precise mechanism of catalytic action, specificity, and any possible subunit interactions.

29 THE MOLECULAR STRUCTURES OF HORSE HEART AND BONITO FERRICYTOCHROMES C. Richard E. Dickerson, David Eisenberg, Tsunehiro Takano, Olga Batfay, and Joan Varnum. Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California, 91109.

The structure of horse heart ferricytochrome c has been determined by x-ray diffraction methods to a resolution of 2.7 Å. The analysis is currently being extended to bonito ferricytochrome c, which, although it differs from horse by 20 of the 104 amino acids, crystallizes in the same space group, P₄.

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

30

FUNCTIONS AND CONFORMATION OF THE CYTOCHROME c SURFACE AS REVEALED BY IMMUNOCHEMICAL REAGENTS. E. Merzollasch, M. Reichlin, Lucile Smith, Helen C. Davies and A. Nisonoff, Dept. Molecular Biol., Abbott Labs., North Chicago, Ill., Depts. Med. and Biochem., State Univ. N. Y. at Buffalo, N. Y., Dept. Biochem., Dartmouth Med. Sch., Hanover, N. H., Dept. Microbiol., Univ. Penna. Med. Sch., Philadelphia, Penna., and Dept. Biochem., Univ. Ill. Med Sch., Chicago, Ill.

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 towards 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 its various functions. For example, Fab fragments of specifically purified rabbit antihuman cytochrome c antibodies modify the reactions of human fericytochrome c with beef cytochrome oxidase, as follows: 1) the initial rate constant is decreased, and 2) a fraction of the cytochrome c 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 antihuman cytochrome c antibody. It has also been shown that the antibody directed to the site of isoleucyl residue 58 on the 'back' of the protein does not interfere with binding to cytochrome oxidase. The generalized usage of site-specific antibodies as probes of cytochrome c surface functions and conformation will be considered.

31

CONFORMATION OF MYOGLOBINS IN SOLUTION. Frank E. M. Gurd, Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

The conformation of myoglobins in solution is being studied in three settings: first, with reference to the crystalline structures; second, by comparison of myoglobins from related species; third, with reference to the disorganized state obtained by treatment with cupric ion. Carboxymethylation with bromoacetate serves as a method of assessing reactivity of histidyl residues that is applicable to both the crystalline and dissolved states. Carboxymethylation of sperm whale myoglobin shows very similar patterns of reactivity in both states, with one exception that indicates a conformational difference. All myoglobins studied are similar with respect to the properties of the heme group as observed by absorbance and NMR spectra and oxygen affinity. Indications in different species of the influence of structural variations farther removed from the heme are apparent from hydrogen ion titration and the rate of reaction of cyanate with the terminal α -amino group. The rate of recovery of the native structure following disorganization by cupric ions again shows a qualitatively similar pattern for all the myoglobins studied but with quantitative differences according to the particular amino acid sequences represented.

32 THE STRUCTURE OF RHOMBOHEDRAL ZINC INSULIN. M. J. Adams, T. L. Blundell, E. J. Dodson, G. G. Dodson, D. C. Hodgkin, M. Vijayan, Chemical Crystallography Laboratory, South Parks Road, Oxford, England

The structure of porcine 2 zinc insulin as obtained from an electron density map derived from an x-ray analysis at 2.8 Å will be described. The crystals contain six insulin monomers (MW 5870) 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 non-crystallographic 2-fold axis. The hexamer, with 32 symmetry, is composed of three dimers, each monomer is co-ordinated to a zinc atom on the 3-fold axis by the B10 histidine. A part of the B chain forms the contact region within the dimer while the A chains are on the outside of 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.

33

STUDIES ON PROINSULIN AND RELATED POLYPEPTIDES. Philip E. Oyer, Arthur H. Rubenstein, Chris Nolan*, Charles Birdwell, Franco Melani, Wolfgang Kemmler, and Donald E. Steiner. Departments of Biochemistry and Medicine, University of Chicago, 947 E. 58th St., Chicago, Illinois, 60637, and *Abbott Laboratories, North Chicago, Illinois.

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: NH₂-B-chain-Arg-Arg-C-peptide-Lys-Arg-A-chain-COOH. The major intermediate forms isolated from bovine 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 system responsible for this transformation will be described. Examination of pepsin 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 islet cells in the pancreas after cleavage from proinsulin. Structural studies of human, monkey, bovine and porcine C-peptides indicate that this region of the proinsulin molecule is more variable than the insulin portions. These variations in sequence are reflected in the failure of most antisera to the connecting region to exhibit significant intraspecies 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. Den W. Urry, Institute for Biomedical Research, American Medical Association/Education and Research Foundation, 535 N. Dearborn, Chicago, Illinois 60610

Studies on L-5-methyl pyrrolid-2-one, gramicidin S, and other cyclic polypeptide antibiotics have shown that molecules which do not have an α -helical disposition of peptide groups may exhibit optical rotation patterns which resemble those known to be characteristic of the α -helix. Furthermore, attempts to study particulate systems such as membranes have revealed absorption flattening and light scattering distortions of a form which cause the α -helix circular dichroism (CD) pattern to simulate, in the extreme case, the CD pattern of β -structures. Successful calculation of the distorted spectra give rise to two interesting applications. One is the opportunity to obtain the optical rotatory dispersion pattern of an interface, i.e. of the molecules comprising the solution-membrane interface. 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 crystal suspensions in an approach to the crystal-solution problem. Successful calculation of the crystal suspension CD spectrum from the solution spectrum would argue for invariance of the optical rotation properties on crystallization.

35 CHEMICAL EDUCATION: ARE WE READY FOR TOMORROW? William E. Hanford and Robert E. Maizell, Olin Corporation, New Haven, Conn.

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 technology; secondly, they are in a better position to advance their own careers; and third, they can contribute more ably to the success of their companies' 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.

36 CURRICULUM '70 OSU Donald J. Bettinger, *J.S. Godwin, H.L. Haight, B.L. Hawbecker, T.D. Fritman and D.L. McInelm, Department of Chemistry, Ohio Northern University, Ada, Ohio 45810

A report is presented of the results of a two 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 OSU. 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 end 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 often 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 too early to a too mathematical and abstract approach to our science and have been underexposed to the excitement 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 more 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.

37

RESEARCH IN THE JANUARY TERM. Robert George Landolt, Department of Chemistry, Muskingum College, New Concord, Ohio 43762.

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 data. Because students were able to concentrate their efforts in one area and had extended periods of time available for uninterrupted library and laboratory work, they not only made significant progress toward many of their goals in a relatively short time, but also gained more realistic insight 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. Corwin, Antioch College, Chemistry Department, Yellow Springs, Ohio 45387

The belated drive toward being concerned about the destruction of our environment makes the understanding of and the chemical determination of the major pollutants in water a most pressing need. Since General and Analytical Chemistry is primarily the study of water solutions and the equilibria involved, these are ideal places for the direct connection of theoretical concepts to the environment. As presently presented, these concepts are usually examined in simple systems involving pure materials. The simple systems are scarcely ever found when one attempts to apply classroom theory to actual situations. In this presentation the author will outline an already tested program which makes water pollution studies a definite part of General and Analytical Chemistry courses. The subject matter of the usual general chemistry will be directly connected to chemical theory. The results of a pollution study which is germane to an environmental problem will be presented.

39 COMPUTER INSTRUCTION AND USE IN UNDERGRADUATE CHEMISTRY COURSES. James E. Coleman, and Elizabeth D. 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 techniques, (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 students an introductory knowledge of the operation of the computer, the basic elements of programming, a suitable programming language for this field, and the experience of having programmed 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 output. In analytical chemistry DO loops and arrays are introduced for the computation of titration curves, standard deviations, etc. The student also uses stored programs which are called to work up data from specific experiments, and a routine 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 application of computers to the field of chemistry and not intended to replace the more conventional course in computer programming. Initial use of this approach has been very encouraging.

40 INSTRUCTION ON AUTOMATIC SEARCHING OF THE CHEMICAL LITERATURE. A. E. Petrarca, Dept. of Computer and Information Science, R. J. Beaton, Dept. of Chemistry, and V. E. Yagello, Chemistry Library, The 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), CCM Information Services, 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 newer automated 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 is geared to batch-mode searching of data bases available from CAS. However, other data bases and on-line interactive systems will also be utilized as soon as the necessary resources are available.

LARGE SCALE ELECTRONIC GRADING AND GRADE STORAGE FOR GENERAL CHEMISTRY COURSES.

Q. Van Winkle, W. T. Lippincott, R. J. Beaton, Department of Chemistry, Ohio State University, Columbus, Ohio 43210, A. E. Petrarca, Department of Computer and Information Science, Ohio State University, Columbus, Ohio 43210.

Electronic Grading and Grade Storage (EGGS) is a series of computer programs specifically written for the maintenance of the grade records of students enrolled in General Chemistry courses in the Department of Chemistry at The Ohio State University. A procedure for converting the data into computer compatible form was selected which was simple and reliable but which did not require special programming efforts. A series of options allows selection of several report forms including alphabetical lists of the course and the laboratory groups, nameless listings to provide feedback to the students, and descending grade order lists. If the system operator elects not to mark the options, a series of default options are used. Although a generalized grading formula capable of handling many grading schemes was built into the system, any arbitrary formula can be easily added to the program and selected for a given course. Output also includes statistical analysis of examination results. Facilities are available for handling special cases such as withdrawn students or graduating seniors.

42

THE DESIGN AND CONSTRUCTION OF AN ELECTRODE OF GENERAL UTILITY FOR SELECTIVE ION MEASUREMENTS. P. R. Ogle, Chemistry Department, Otterbein College, Westerville, Ohio 43081.

The price and individuality of commercially available selective ion electrodes restricts their use en masse 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 versatile selective electrode. The various steps leading to the development of the electrode will be outlined. The method 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 chloride and fluoride ion measurements where the detectors used are solid silver chloride and doped lanthanum 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 Wetzack, Department of Chemistry, Hope College, Holland, Michigan 49423.

The study of excited electronic states is currently an active area of chemical 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 developing quantitative techniques. In keeping with the intent of involving students in the planning of laboratory work while maintaining an overall direction we have evolved the following program:

Students 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 potentiometric techniques selected by the students are 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. Sutliff and Lawrence B. Wick, Department of Chemistry, Ohio Wesleyan University-Delaware, Ohio 43015

Chemical experiences stressing the methods of inquiry used in chemistry are unavailable. When the need for such experiences became evident at Ohio Wesleyan University, it was decided 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 esterification. This reaction is an inexpensive, well understood reaction that can be studied by many methods and to many depths. For the general chemistry experience the partial esterification of acetic or propionic acid with various combinations of methanol, ethanol, n-propanol and n-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 mixtures of products 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 prerogative of the student.

46 TEACHING X-RAY CRYSTALLOGRAPHY TO UNDERGRADUATE CHEMISTRY MAJORS.

Ronald W. Collins, Department of Chemistry, Eastern Michigan Univ., 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 crystallography 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 of 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 do 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 gimmicks in the form of mnemonic ditties or diagrams. Many serve their purpose well, but some tend to get in the way of real understanding and become ends to themselves, especially if presented as "keys" to problem solving. Examples include temperature conversion formulas, "plug in" (tabular) methods for solving gas law problems, special tricks for balancing redox equations, memorized colligative property relationships that make students wary 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, its use is justified. But each such mnemonic device should be put in proper perspective, so that students do not become victims of "gimmickry-mimickry". This paper is a plea for continuous re-evaluation of "memory crutches" which may become handicaps to development of real understanding in chemistry.

49 A MECHANISM FOR ADDING RELEVANCE AND CURRENTNESS TO FRESHMAN CHEMISTRY, John J. Fortman, Dept. of Chemistry, Wright State University, Dayton, Ohio 45431.

The overused word on college campuses in 1969 was relevance. It seems well and good to try 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 texts this year. This ACS publication, which is intended for high school and beginning college students, features several short articles plus capsular notes on current research news and interesting insights 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 ideally into the course outline.

Eight month subscriptions are sent bulk 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 are requested to continue receiving the magazines. Many chemistry majors have sought the extra copies and next year the department plans to use it in the class in general chemistry for science majors as supplementary reading.

INTEGRATION OF BIOCHEMISTRY INTO THE UNDERGRADUATE CHEMISTRY CURRICULUM. E. H. Cordes, Department of Chemistry, Indiana University, Bloomington, Indiana 47401.

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- and organochemical matters that 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 course and laboratory work will be detailed. General curricular revisions related to the above will also be considered.

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 now, 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 Stumm, Harvard University, Pierce Hall - 123, 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 an open and dynamic system with variable inputs and outputs of mass and energy. In natural waters organisms and their abiotic environments are interrelated and interact upon each other.

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 Demerjian, 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 to help rationalize the observed rates of secondary polluted formation and expected rates of pollutant removal processes.

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

55 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 ease of degradability. Improving the rate of degradative 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. Examples 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.

CHEMISTRY OF ALUMINUM(III) IN COAGULATION PROCESSES.
Philip L. Hayden, Alan J. Rubin, Water Resources Center, Ohio State University, 1791 Neil Ave., Columbus, Ohio 43210

The aqueous chemistry of aluminum was examined over wide ranges of concentration and pH. The solubility limits of aluminum hydroxide were determined by light scattering 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 analyzed using the SCOGS computer program for least squares adjustment to a non-linear equation to obtain equilibrium constants. The precipitates were colloidal stable at pH less than 7 in the presence of univalent anions up to about 0.01 molar. Only very small amounts of sulfate were required to destabilize the Al(III) sols. In the presence of phosphate, stable sols were formed 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 restabilized by Al(III) solutions in those pH regions in which stable aluminum sols form.

CHEMISTRY AND ENVIRONMENTAL TOXICOLOGY. Mark M. Luckens, College of Pharmacy, University of Kentucky Medical Center, University of Kentucky, Lexington, Kentucky 40506.

This paper will consider the part played by chemistry in the development of environmental toxicology. It will present an overview of the role of bioactive chemicals, forces and processes in the overall problems of this relatively new and important discipline; as well as the initiation and mitigation of biologic damage. The effects of repetitive or continual sublethal toxic insult on the biotic and abiotic components of the ecosystem as well as 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.

TRANSITION METAL COMPLEXES OF $B_10H_{12}^{2-}$. R.L. Sneeth and L.J. Todd, Department of Chemistry, Indiana University, Bloomington, Indiana, 47401.

In recent years a large number of heteroatom-boranes have been synthesized which have twelve or less atoms in the cage structure. This paper deals with the syntheses and characterization of heteroatom-boranes containing nineteen atoms in the cage framework. Reaction of $n-B_10H_{12}^{2-}$ with $Co_2(CO)_8$ in tetrahydrofuran at room temperature, followed by treatment with aqueous tetramethylammonium chloride, gave red $(CH_3)_4N[(n-B_10H_{12}O)]$ in moderate yield. In a similar manner $(\phi_3P)_2NiCl_2$ or $(\phi_2PCH_2CH_2)_2P_2NiCl_2$ and $n-B_10H_{12}^{2-}$ reacted to form red $(\phi_3P)_2Ni(n-B_10H_{12}O)$ or purple $(\phi_2PCH_2CH_2)_2P_2Ni(n-B_10H_{12}O)$ respectively. Elemental analyses and molecular weight data are consistent with the formulations given. The 32 MHz ^{11}B nmr spectrum of $(CO)_3Co(n-B_10H_{12}O)$ is similar to that of $n-B_10H_{12}^{2-}$. The increased complexity of the metal-borane spectrum is qualitatively what would be expected if one of the open faces of the $n-B_10H_{12}^{2-}$ ion became bonded to the cobalt atom. Recently a series of transition metal complexes of $B_{10}H_{12}^{2-}$ have been characterized. From the similarities in structure of $B_{10}H_{14}$ and $n-B_{10}H_{12}^{2-}$, we propose that the metal-borane bonding in both the $n-B_{10}H_{12}^{2-}$ and $B_{10}H_{12}^{2-}$ complexes is similar.

59 BONDING AND PROPERTIES OF ISOCYANIDE AND CARBONYL COMPLEXES OF RUTHENIUM(II).

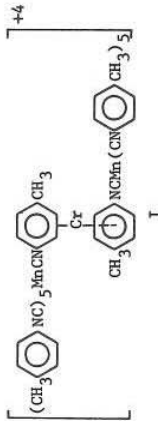
Joseph R. Crook and Randy E. Keith, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115

Ruthenium(II) complexes with the general formula $Ru(CNR)_4Cl_2$ have been synthesized for cases in which R = cyclohexyl, tert-butyl, allyl, and ortho-tolyl. Infrared data indicate that all four isocyanide complexes possess trans arrangement of the chloride groups by contrast with corresponding iron(II) complexes in which the cis arrangement is more stable. Based on a comparison of the infrared N-C stretching frequencies of the ruthenium complexes with frequencies observed for other metals, qualitative conclusions regarding the extent of pi bonding can be drawn. These conclusions suggest no unusual deviation from established patterns.

Attempts to generate mixed carbonyl/isocyanide ruthenium complexes have been unsuccessful underscoring the observation that the isocyanides are significantly better ligands than carbon monoxide with reference to their ability to stabilize lower oxidation states of metals.

60 PHOTOCHEMISTRY OF ARYL ISOCYANIDE METAL COMPLEXES. Rodney A. Bailey, Department of Chemistry, The Cleveland State University, Cleveland, Ohio 44115.

The photochemical reaction between hexa(p-tolyl isocyanide)manganese(I) nitrate and chromium hexacarbonyl has been carried out with 3500A irradiation in CCl_4 under an atmosphere of oxygen. During a 2-3 hr reaction time, a dark blue-violet precipitate was formed. This material was filtered under nitrogen and rinsed several times with CCl_4 and 5% CH_3NO_2 in CCl_4 to free it of starting materials. The resulting solid was extremely moisture sensitive but was stable for extended periods of time at -20 under nitrogen. Decomposition in aqueous acetonitrile followed by extraction with CH_2Cl_2 gave back the starting manganese complex in the organic phase and left a chromium salt in the aqueous phase. Elemental analyses indicated the presence of Mn, Cr, Cl, and O in addition to C, H, and N, with rather substantial amounts of both Cl and O being present. A structure incorporating a chromium "sandwich" complex (I) is proposed. The location and type (molecular, atomic, or peroxide) of oxygen in the complex is still undetermined.



MASS SPECTRA OF SUBSTITUTED GROUP VIB METAL CARBONYLS. S. Thomas Bond, Norman V. Duffly, and Vipin N. Kothari, Department of Chemistry, Kent State University, Kent, Ohio, 44240

The mass spectra of $M(CO)_5L$ have been examined in detail (M=Cr, Mo, or W; L= $P\phi_3$, $As\phi_3$, or pyridine) with an AEI MS-12 Mass Spectrometer. The most abundant metal containing fragment in each spectrum was M_L although, in general, all possible fragments of the types $M(CO)_L$ and $M(CO)$ (n=0-5) were observed. In every case, the fragment $M(CO)_{n-1}L^+$ was more abundant than the corresponding $M(CO)_n$ fragment. The dissociation of CO preferentially to L is explained on the basis "hard and soft" acid-base theory. Numerous metastable ions have been observed and are consistent with the stepwise dissociation of CO from the molecular ion. The mass spectra of the substituted Cr carbonyls are quite different from the corresponding Mo and W derivatives. The Cr derivatives are more subject to thermal decomposition than are the corresponding Mo and W compounds. The mass spectrum of $Cr(CO)_5P\phi_3$ at $110^\circ C$ and $140^\circ C$ are quite different, the spectrum at $140^\circ C$ being dominated by the peaks Cr and $P\phi_3$.

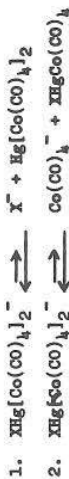
62 MASS SPECTRA OF PLATINUM(II) METAL CARBONYLS. Kenneth L. Klassen,

Norman V. Duffly, Department of Chemistry, Kent State University, Kent, Ohio, 44240

Dichlorocarbonyltri-n-tolylphosphineplatinum(II) and dichlorocarbonyltriphenylphosphineplatinum(II) have been prepared and characterized. The CO stretching frequency of the former complex is 2110 cm^{-1} , 12 cm^{-1} greater than that of the latter. The mass spectra of these two complexes have been compared, indicating characteristic loss of CO from the molecular ion with the expected fragmentation pattern for a metal carbonyl. Fragments, both singly and doubly charged, containing coordinated CO, confirm the proposed mononuclear molecular formula. Recent experiments with other substituted phosphines, including the corresponding ortho- and para- tolylphosphines will also be discussed.

63 TRANSITION METALS AS LEWIS BASES: $\text{Co}(\text{CO})_4^-$ ADDUCTS WITH $\text{Hg}(\text{II})$ AND $\text{In}(\text{III})$. William R. Robinson, Harold L. Conder, and David P. Schussler, Department of Chemistry, Purdue University, Lafayette, Ind. 47907

Air sensitive solutions of trigonal planar $\text{Hg}[\text{Co}(\text{CO})_4]_2$ and tetrahedral $\text{In}[\text{Co}(\text{CO})_4]_4$ can be prepared by reaction of $\text{Co}(\text{CO})_4^-$ in CH_2Cl_2 with $\text{Hg}(\text{Co}(\text{CO})_4)_2$ or $\text{In}[\text{Co}(\text{CO})_4]_3$, respectively. Brown solids, stable for short periods in air, can be isolated by addition of large cations. The i.r. spectra of these compounds as solids exhibit two strong CO stretching frequencies which are consistent with a single negative charge delocalized over 3 (or 4) $\text{Co}(\text{CO})_4^-$ units. In solution, the i.r. spectra indicate limited dissociation into $\text{Co}(\text{CO})_4^-$ and either $\text{Hg}[\text{Co}(\text{CO})_4]_2$ or $\text{In}[\text{Co}(\text{CO})_4]_3$; the extent of dissociation being dependent upon the solvent. With halides and pseudohalides, species of the type $\text{X}[\text{Hg}[\text{Co}(\text{CO})_4]_2^-]$ and $\text{X}[\text{In}[\text{Co}(\text{CO})_4]_3^-]$ can be isolated. The i.r. spectra of these ions are similar to that of $\text{Hg}[\text{Co}(\text{CO})_4]_2^-$ in the solid state, although the solution behavior is more complex. In CH_2Cl_2 , tetrahydrofuran and acetonitrile, the halo species exhibit equilibrium 1, while in dimethylformamide and dimethylsulfoxide, equilibrium 2 is observed:



64 LEWIS BASE PROPERTIES OF PLATINUM(O). T. R. Durkin and E. P. Schram, Ohio State University, Department of Chemistry, Columbus, Ohio 43210.

Treatment of $\text{Pt}[\text{C}_6\text{H}_5]_2$ with BCl_3 , SiF_4 , or $[\text{Al}(\text{CH}_3)_3]_2$ affords species tentatively characterized as Lewis acid-base adducts. Boron trichloride affords 1:1 and 1:2 adducts, whereas SiF_4 results in only a 1:1 adduct. The reaction product with $[\text{Al}(\text{CH}_3)_3]_2$ affords the first reported example of a molecular paramagnetic platinum complex, $g = 1.99$. Discussion will include characterization of the adducts, Lewis acid displacement reactions with pyridine and I_2 , and the results of an esr study of the platinum complex.

65 CONSTRAINED PHOSPHITE ESTER COMPLEXES OF CYCLOHEXADIENYLIRON DICARBONYL HALIDES AND DIHALOGENOTETRACARBONYLIRON(II) COMPOUNDS; William E. Stencliff and David G. Hendricker, Clippinger Labs, Department of Chemistry, Ohio University, Athens, Ohio 45701

The brown, air-stable $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{LX}$, where L = the constrained phosphite ester $\text{P}(\text{OCH}_2)_2\text{CR}$ (R = CH_3 , C_2H_5 , C_6H_5), or X = Cl, Br or I, have been synthesized and were characterized by elemental analysis and infrared spectroscopy. The strong single band observed in the carbonyl stretching region for these complexes was evidence that they are neutral and not ionic compounds. The order in the position of the carbonyl stretching frequency varied as expected ($\text{Cl} > \text{Br} > \text{I}$) from electronegativity considerations. The CO band appeared at higher wave numbers for the constrained phosphite ester complexes than for compounds where L = phosphines or trialkyl phosphites. The CO band position is independent of the nature of R for $\text{P}(\text{OCH}_2)_2\text{CR}$ complexes. Compounds of the type $\text{Fe}(\text{CO})_3\text{LX}_2$ and $\text{Fe}(\text{CO})_2\text{L}_2\text{X}_2$ have also been prepared and characterized. The infrared spectra of $\text{Fe}(\text{CO})_3\text{LBr}_2$ complexes suggest a cis-cis CO arrangement while a cis-trans CO arrangement is implied for the $\text{Fe}(\text{CO})_3\text{Li}_2$ compounds. For both the mono- and tri-substituted halides, the CO stretching frequencies followed the same trends as noted for the $\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{LX}$ compounds.

66 SOME ALUMINUM-NITROGEN POLYMERS CONTAINING ALUMINUM-HALOGEN BONDS. Keith Gosling, A. L. Bhuiyan, Department of Chemistry, West Virginia University, Morgantown, West Virginia, 26506

In order to study the electronic effects which may play an important role in controlling the extent of polymerization of some aluminum-nitrogen systems, compounds have been prepared which contain electron withdrawing halogen atoms attached to aluminum. Starting either from the reaction $\text{Et}_2(\text{X})\text{Al} + \text{NHR}_2 \rightarrow \text{Et}_2(\text{X})\text{Al:NR}_2$ or $\text{Et}_3\text{Al} + \text{R}_2\text{NH}_2\text{X} \rightarrow \text{Et}_2(\text{X})\text{Al:NR}_2 + \text{EtH}$ (X = F, Br, I; R = H , alkyl), successive thermal decomposition reactions involving loss of ethane from the above initial products, have led to the isolation of compounds of the type $(\text{Et}(\text{X})\text{Al:NR}_2)_n$ and $(\text{X-Al-N})_n$. The degree of polymerization observed will be discussed in terms of steric, electronic and entropy effects in these systems. Infrared, n.m.r. and mass spectrometric data will be cited and suggestions made concerning the probable molecular structure of these compounds.

67 CRYSTALLINE COORDINATION COMPLEXES OF COPPER(II) SALTS WITH ALKANOL-SUBSTITUTED ETHYLENEDIAMINES. Donald N. Zimmerman, James L. Hall, West Virginia University, Morgantown, W. Va. 26506

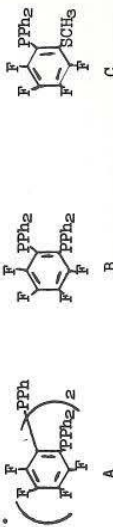
Crystalline coordination compounds of perchlorate, nitrate, sulfate and chloro salts of copper(II) with N-hydroxyethylthylenediamine (hm), N-(2-hydroxypropyl)-ethylenediamine (hpn) have been prepared and characterized by elemental analyses, by studies of electronic and vibrational spectra and by measurement of magnetic moments. The low-temperature diffuse reflectance spectra 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 used to show the number of amine nitrogen and alcoholic oxygen atoms coordinated. These results showed that the perchlorate, nitrate and sulfate ions were not coordinated and confirmed the presence of a Schiff base (HSB) in one compound. The magnetic moments were consistent with the results of the spectral studies. It is concluded that $\text{Cu}(\text{hm})_2\text{Cl}_2$ and $\text{Cu}(\text{hpn})_2\text{Cl}_2$ are six-coordinate, with the chloride ions being coordinated, the structure being a distorted octahedron; that $\text{Cu}(\text{hm})_2(\text{ClO}_4)_2$, $\text{Cu}(\text{hpn})_2(\text{ClO}_4)_2$, and $\text{Cu}(\text{HSB})(\text{NO}_3)_2$ are five-coordinate with square pyramidal structures; and that $\text{Cu}(\text{hpn})_2\text{SO}_4$ has a five-coordinate trigonal bipyramidal structure while $\text{Cu}(\text{hm})_2\text{SO}_4$ has an intermediate five-coordinate structure.

68 COMPLEXES OF N,N-DIALKYLTHIOCARBAMATE LIGANDS. B. Jack McCormick and Benjamin P. Stormer, 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-dialkylthiocarbamate (OSCNR_2) complexes. Six nickel(II) complexes of the type $\text{Ni}(\text{OSCNR}_2)_2$ have been prepared in the present work with: $\text{R}_1\text{-R}_2 = \text{CH}_3$, C_2H_5 , $\text{N-C}_3\text{H}_7$, and $\text{N-C}_4\text{H}_9$; $\text{R}_1\text{-R}_2 = -\text{CH}_2(\text{CH}_2)_2\text{CH}_2-$ and $-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-$. The nature of the R groups exerts a critical influence on the stability of the complexes, as evidenced by the fact that it has not been possible to prepare complexes with bulky groups such as $\text{i-C}_3\text{H}_7$. Infrared studies suggest that the ligands are chelated through oxygen and sulfur atoms, and a characteristic C—N stretching frequency has been found at ca. 1540 cm^{-1} . Measured molecular weights of the compounds with $\text{R}_1\text{-R}_2 = \text{N-C}_3\text{H}_7-$ and $\text{N-C}_4\text{H}_9-$ are concentration dependent. The remaining four complexes are insoluble and unsuitable for molecular weight studies. These results suggest that the compounds are polymeric in the solid 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 studies with metal ions other than nickel(II) also will be discussed.

69 PROPERTIES OF TRANSITION METAL COMPLEXES WITH FLUORINATED PHOSPHINE LIGANDS, P. Gary Eller and Devon W. Meek, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

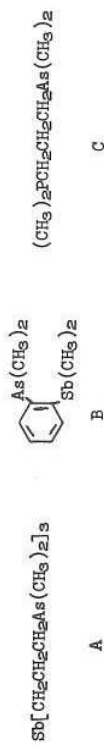
A number of polydentate phosphorus and sulfur ligands, containing one or two 1,2,3,4-tetrafluorophenyl connecting groups, were readily synthesized from the lithium derivatives of diphenyl(g-bromotetrafluorophenyl)phosphine and 2,3,4,5-tetrafluorothioanisole. The nickel(II) complexes of the tridentate and bidentate ligands, A and B, are five-coordinate $\text{Ni}(\text{A})\text{X}_2$ and $[\text{Ni}(\text{B})_2\text{X}]^+$ species, respectively. Ligand C forms four-coordinate $\text{Ni}(\text{C})\text{X}_2$ and six-coordinate $\text{Ni}(\text{C})_2\text{X}_2$ complexes, rather than the five-coordinate examples.



One especially interesting result obtained with the phosphorus-sulfur ligand C is the tendency for facile S-demethylation to produce coordination compounds of the corresponding phosphine-mercaptide ligand. The results obtained from spectral, magnetic, and 100 MHz NMR studies will be discussed with respect to σ - and π -bonding by these fluorinated ligands.

70 COBALT AND NICKEL COMPLEXES OF MIXED ARSENIC-ANTIMONY AND ARSENIC-PHOSPHORUS POLYDENTATE LIGANDS, Gary Kordosky, Billy Cook, and Devon W. Meek, Department of Chemistry, The Ohio State University, Columbus, Ohio, 43210.

The new 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 $[\text{Ni}(\text{A})\text{X}]^+$, and cis-octahedral cobalt(III) complexes $[\text{Co}(\text{A})\text{X}_2]^+$. Ligands B and C readily form both four-coordinate NiX_2 and five-coordinate $[\text{NiL}_2\text{X}]^+$ complexes, depending on the preparative conditions. The spectral and magnetic data obtained for these complexes will be compared with those of similar polyarsine and polyphosphine ligands in order to evaluate the bonding properties of alkylantimony ligands.

71 RHEMIUM(III) AND (IV) CHLORIDES AND THEIR REACTIONS WITH CERTAIN NITROGEN AND PHOSPHORUS DONOR MOLECULES. R. A. Walton, Department of Chemistry, Purdue University, Lafayette, Indiana 47907.

The chlorides $\beta\text{-ReCl}_4$ and Re_2Cl_9 , 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, Re_2Cl_9 does not react with pyridine to form the expected complex $\text{Re}_2\text{Cl}_9\text{Py}_2$, but instead the rhodium(II) species $[\text{ReCl}_2\text{Py}_4]$ is isolated. This redox reaction is characteristic of those which occur with many other nitrogen donors. The reduced species may be readily reoxidized to derivatives of Re_2Cl_9 . Acetonitrile solutions of $\beta\text{-ReCl}_4$ react with triphenylphosphine to give complex reaction mixtures, from which trans- $\text{ReCl}_2(\text{PPh}_3)_2$, $[\text{ReCl}_2(\text{PPh}_3)_2]$ and $\text{ReCl}_2(\text{PPh}_3)_3$ can be isolated. A full three-dimensional X-ray analysis of the complex $\text{ReCl}_2(\text{PPh}_3)_3$ has now been carried out and the results will be discussed.* This derivative is believed to be identical to that isolated previously by Rouchias and Wilkinson (J. Chem. Soc., A, 993 (1967)) by a different route.

* This study was carried out in collaboration with H.G.B. Drew and D.G. Tisley 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, Ohio State University, Columbus, Ohio

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 electron 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 2A_1 ground state. Oxidative alkylation of the cobalt atom in the complexes has been achieved and the products are either monoalkyl-, trans-dialkylcobalt complexes, or mixtures of these. The electronic spectra of the alkyl and normal acido-cobalt(III) 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-AMINOENZALDEHYDE. Vladimir Katovic and Daryle H. Busch, the Evans Chemical Laboratory, Ohio State University, Columbus, Ohio

Iron(III) complexes of the tetradentate macrocyclic ligand, tetrabenzob[5,9,9,9]tetraazacyclohexadecene (TAAB), have been prepared by the template reaction of ortho-aminobenzaldehyde with an iron salt. Two types of compounds were isolated and characterized: Dimeric $\text{Fe}_2(\text{TAAB})_2\text{OX}_4 \cdot 4\text{H}_2\text{O}$, $\text{X} = \text{NO}_3^-$ and ClO_4^- , which contain the Fe-O-Fe bridging group and monomeric compounds $\text{Fe}(\text{TAAB})\text{FX}_2 \cdot 2\text{H}_2\text{O}$, $\text{X} = \text{NO}_3^-$ and ClO_4^- . 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 binuclear 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. $\text{Fe}_2(\text{TAAB})_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ reacts with methoxy ions giving the neutral compound $\text{Fe}_2(\text{TAAB})_2 + 2\text{OCH}_3^-$ where two methoxy ions are incorporated in the macrocycle forming α -aminoether linkages. Molecular weight determination confirms that the latter compound is dimeric.

74 SOME STEREOSPECIFIC ANOMALIES OF CERTAIN AMINO ACID OUTER-SPHERE COMPLEXES. Dawn E. Francis, Detroit Institute of Technology, Detroit, Michigan 48201.

When L-tryptophan was precipitated separately with the enantiomers of tris-ethyl-enediaminecobalt(III) ion it was observed that the outer-sphere complex formed with D- $[\text{Co}(\text{en})_3]^{+3}$ differed from the complex formed with L- $[\text{Co}(\text{en})_3]^{+3}$ in several important physical as well as chemical aspects. These included rates of formation, macro appearance of crystals, temperature and light stability, chemical analysis and behavior and optical spectra, including optical rotatory dispersion and circular dichroic bands.

The significance of the influence of the stereospecific nitrogen atoms of the inner-sphere metal ion complex on the noted behavior of the amino acid outer-sphere ligand and the analogy to physiological systems will be discussed.

75 AMINE EXCHANGE (TRANSIMINATION) IN $\text{Zn}(\text{II})$ SCHIFF BASE COMPLEX SYSTEMS. Bruce E. Leach and D.L. Leussing, Chemistry Department, Ohio State University, Columbus, Ohio 43210

Exchange of ethylamine in N-salicylideneethylamine by glycinate, α -alaninate and β -alaninate in the presence of $\text{Zn}(\text{II})$ has been studied using stopped flow and pH-stat techniques. The reactions are direct and do not proceed through hydrolysis. Both proton and metal ion catalyzed paths were observed. The methyl substituent of α -alanine inhibits the rate of the proton catalyzed path but has no effect on the rate of the $\text{Zn}(\text{II})$ path.

Amine exchange rates are faster by a factor of 1000 over the rates at which the amines react with salicylaldehyde to form the Schiff bases. 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 with triangular, tetrahedral, and octahedral metal clusters can often be prepared by decarbonylation of derivatives containing fewer metal atoms but a higher ratio of carbonyl groups per metal atom than in the desired product. The mass spectra of certain polynuclear metal carbonyl derivatives are of interest in exhibiting fragmentation to give unusual bare metal cluster ions, e.g. Co_4^+ from the mass spectrum of $\text{Co}_4(\text{CO})_{12}$.

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 plays in the repeat unit of the polymer. Although in principle non-carbon catenation can exist in each class, examples are quite sparse for coordination polymers based on polymeric ligands. On the other hand there are numerous examples of non-carbon-catenated 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 catenation 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.

78 SHEET ORGANOSILICON POLYMERS. M. E. Kenney, 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 fromrophyllite) using various techniques have provided specific information about these two polymers and considerable insight as to the nature of sheet 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.

79

BORON-NITROGEN SYSTEMS. Sheldon G. Shore, Department of Chemistry, The Ohio State University, 140 West 18th Avenue, Columbus, Ohio 43210.

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

80

ASYMMETRIC INDUCTION IN INNER-SPHERE REDOX REACTIONS. Sister M. J. DeChant, Department of Chemistry, Notre Dame College, Cleveland, Ohio 44121.

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-chloroaminobis(ethylenediamine)cobalt(III) ion in aqueous ethylenediamine solution yields 94% *trans*-chloroquoibus(ethylenediamine)chromium(III) ion and 6% *cis*-isomer as the major chromium-containing products; the *cis*-isomer is levorotatory at the sodium D line. The reaction of *d*-cis- α -dichlorotriethylenetetraamincobalt(III) and *l*-*cis*- α -dichlorotriethylenetetraamincobalt(III) with Cr(II) ion in aqueous triethylenetetraamine medium yields the *l*-*cis*-chloroquoitriethylenetetraamincromium(III) and the *d*-*cis*-chloroquoitriethylenetetraamincromium(III) ion, respectively. The high degree of asymmetric induction suggested by optical rotation measurements indicates that reaction rates are dependent on very subtle structural differences.

81

REDUCTIONS OF CARBOXYLATO-COBALT(III) COMPLEXES WITH COPPER(I). Syed Arif Kazmi & Edwin S. Gould, Chemistry Department, Kent State University, Kent, Ohio 44240.

Comparisons of rates of reduction of various carboxylato-pentamminecobalt(III) complexes with copper(I) disclose a number of trends similar to those observed with chromium(II) reductions, indicating that the Cu(I) reductions occur through a carboxylato-bridge mechanism. There are, however, some differences in detail. Both the 2- and 4-carboxylatopyridine complexes are reduced much more rapidly than benzoato complexes, and their rate laws exhibit very large inverse-acid terms, suggesting electron transfer through the pyridine ring. With the salicylato complex, only the inverse-acid route is observed, indicating complete predominance of a chelating path. Rapid reductions of the *o*- and *p*-nitrobenzoato complexes point to remote attack involving the nitro groups. Aliphatic carboxylato complexes are reduced about ten times as rapidly as benzoato derivatives; and, in contrast to Cr(II) reductions, no accelerating action due to α -OH or α -SR groups is observed.

82 OPTICAL ACTIVITY OF β -DIKETONE COMPLEXES OF COBALT(III). L. J. Boucher, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pa. 15213

Complexes of the type $[\text{Co en}^2\text{dik}]_2^{2+}$ (dik = acetylacetonate, propionylacetonate, trifluoroacetylacetonate, ethylacetoacetate and ethylacetoacetate) and $[\text{Co acac}_2\text{L}_2]$ (L_2 = ethylenediamine and 2 ammonia) have been resolved and the absorption, O.R.D. and C.D. spectra determined. Substituent related shifts of the maxima are observed in the spectra for the visible and ultraviolet regions. On the basis of the visible C.D. spectra, the (+)546 isomers of all the complexes are assigned the $\Delta(\text{C}_2)$ absolute configuration. Complexes of the first type show C.D. spectra with a single broad unresolved maximum at each of the two octahedral cobalt(III) bands in the visible. Complexes of the second type show components of opposite sign at the first band and a single absorption at the second band. Both kinds of materials show an intense C.D. maximum at the metal-ligand charge transfer band in the near u.v. Complexes of the first type show an intense C.D. maxima at the next charge transfer band, while complexes of the second type show an intense maximum of opposite sign in this region. Neither type of materials shows a C.D. maximum at the high energy ligand absorption in the ultraviolet. Assignments of the electronic structure and transitions of β -diketone complexes of cobalt(III) will be discussed in light of the absorption and C.D. spectra.

83 THE STEREOCHEMISTRY OF N,N'-BIS(3-ISOPROPYLSALICYLIDENE) POLYMETHYLENE-DIAMINOCOBALT(II) COMPLEXES IN DONOR AND NONDONOR SOLVENTS AND IN THE SOLID STATE. M. Hariharan and F.L. Urbach, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

The homologous series of cobalt(II) complexes with N,N'-bis(3-isopropylsalicylidene) polymethylenediamine ligands, $\text{HO}(\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3\text{CH}=\text{N}(\text{CH}_2)_n\text{N}=\text{CH}(\text{C}_6\text{H}_3)_2\text{OH}$, where $n = 2-7$, has been prepared and characterized in the solid state and in dichloromethane and pyridine solutions. The spectral and magnetic properties of the $n = 2$ derivative indicate that it is a low-spin planar complex in the solid state and in dichloromethane. The higher homologs are all high-spin and the $n = 4-7$ complexes exhibit pseudo-tetrahedral spectra in the solid state and in non-donor solvents. The trimethylene derivative does not exhibit a characteristic pseudo-tetrahedral spectrum and it is postulated that this derivative possesses a strongly distorted tetrahedral geometry. All of the complexes are monomeric in dichloromethane ruling out higher coordination numbers via intermolecular association. In pyridine, all of the complexes expand their coordination number, achieving pseudo-octahedral structures as deduced from spectral and magnetic measurements.

84 BONDING IN VANADYL COMPLEXES. James A. Ryan, Henry A. Kuska, Department of Chemistry, University of Akron, Akron, Ohio 44304.

Selected literature ESR data for which internuclear distances are known or could be approximated were fed to a computer program to determine the various possibilities of optical assignments which are consistent with the ESR data. The program used nested Do loops for the values of the four optical transitions; 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 Wolfsberg-Heilmholz type.

85 ELECTRON PARAMAGNETIC RESONANCE OF TRANSITION METAL COMPLEXES IN LIQUID CRYSTAL SOLUTIONS. John P. Fackler, 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. Because of orientational ordering of nematic phases in strong magnetic fields, certain anisotropic terms in the spin expression are not completely averaged to zero. Additional information about various molecular parameters can be obtained from analysis of anisotropic g tensors and hyperfine splitting tensors.

86 THE CRYSTAL AND MOLECULAR STRUCTURE OF BIS(p-PERTHIOCUMATO)ZINC(II). John P. Fackler, Jr. and David C. Fries, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Bis(p-perthiocumato)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 from a chloroform-methanol solution of the complex. The crystals belong to the orthorhombic system, space group $Ima2$ or $Imma$, with unit cell constants $a = 21.07$ Å, $b = 13.66$ Å, and $c = 8.05$ Å. The calculated and measured densities indicate a Z of four. Diffractometric data will be collected and the structure solution will be accomplished using vector superposition techniques applied to the Patterson function.

87 THE STRUCTURE AND ION EXCHANGE PROPERTIES OF CERIUM(IV) PHOSPHATES. R.G. Herman, Abraham Clearfield, Department of Chemistry, Ohio University, Athens, Ohio, 45704.

Cerium(IV) phosphates exist as gels or 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 shown that all of the phases may be derived from each other by decreasing or increasing the phosphorus-cerium ratio. The structures of these phases were deduced by a combination of X-ray and ion-exchange methods. The relationship between these exchangers and other metal(IV)phosphate ion exchangers will be briefly discussed.

88 THE SYNTHESIS OF FLUORINATED ALKOXIDES, Ralph L. Hough, Elm W. Nordquest, Hough Laboratory, 708 Rice Street, Springfield, Ohio 45505
Attention in materials research has been devoted to development of high purity materials. Metal alkoxides offer one approach for obtaining the respective metal oxides in high purity. The synthesis of fluorinated alkoxides of zirconium, thorium, silicon, aluminum, boron, beryllium and yttrium have been developed. Difficulty in obtaining chloride-free oxides of thorium and other metals can now be overcome by using a modification of a previously unsuccessful reaction of the metal, alcohol, and catalyst. Compared with the unfluorinated ligands, it is found that these fluorinated alkoxides (primarily the hexafluoro-isopropoxides) have increased volatility and improved hydrolytic stability, making them more suitable for vapor deposition of the corresponding oxide. Basic physical properties have been investigated and are related to the usefulness of the respective compounds. The branched chained fluorinated alkoxides may be modified easily to produce different properties and to expand their usefulness, as in fire extinguishing agents or anti-bacterial agents.

89 REACTION OF $MgSn_2F_5$ WITH $Ca_{10}(PO_4)_6(OH)_2$: INVESTIGATION OF A POSSIBLE CARIOSTATIC TIN(II) COMPOUND. Ronald W. Collins, James M. Ferris, Department of Chemistry, Eastern Michigan Univ., Ypsilanti, Michigan, 48197.

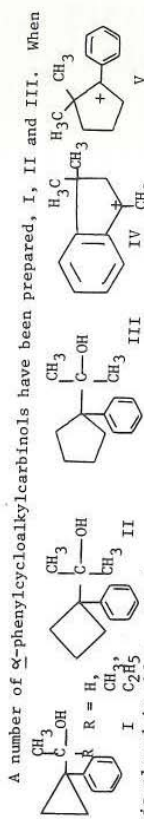
Although it is generally accepted that fluoride ion inhibits dental cariogenic action, there is disagreement about the chemical mechanism of this anti-preventive agent, some controversy exists regarding the extent to which the tin(II) ion contributes to this action. As part of a continuing effort to define the chemical role of tin(II) in carries inhibition, the reaction of $MgSn_2F_5$ with $Ca_{10}(PO_4)_6(OH)_2$ has been studied. Calcium hydroxylapatite, $Ca_{10}(PO_4)_6(OH)_2$, is the major constituent (95% by weight) of human dental enamel. Numerous experiments covering a wide range of tin(II) concentration have been run at 37° to approximate physiologic temperature and also at 100°. The products of these aqueous heterogeneous reactions, and also identified by chemical analysis, X-ray diffraction, and IR, include CaF_2 , a hydrous tin(II) oxide, and a basic tin(II) salt with the empirical formula, $Sn_4(PO_4)_2(OH)_2 \cdot 2H_2O$. This latter salt is also the major product of the reaction of SnF_2 with $Ca_{10}(PO_4)_6(OH)_2$. Lack of any evidence for direct isomorphous substitution of tin(II) into the apatite lattice, coupled with the demonstrated in vitro formation of the acid-insoluble tin(II) salt, $Sn_4(PO_4)_2(OH)_2 \cdot 2H_2O$, suggests that similar in vivo deposition of this basic salt could be a contributing factor to the cariostatic nature of tin(II).

90 THE SYNTHESIS AND SOLVOLYSIS OF THE ISOMERIC 1-CHLORO-2,3-DIPHENYLCYCLOPROPANES, Jack W. Hausser, John T. Uchic, Department of Chemistry, Duquesne University, Pittsburgh, Pa., 15219.

The solvolysis of cyclopropyl halides proceeds by a concerted electrocyclic process to afford ring-opened allylic products. The stereochemistry of the ring-opening process may be predicted by orbital symmetry considerations as suggested by Woodward and Hoffmann. The synthesis and acetoysis of the isomeric 1-chloro-2,3-diphenylcyclopropanes were undertaken in order to clarify the nature of the ring-opening process through an investigation of the effect of phenyl substitution.

The synthesis of the isomers of 1-chloro-2,3-diphenylcyclopropane was accomplished by the addition of dichlorocarbene to *cis* and *trans*-stilbene followed by partial reduction by controlled potential electrolysis. The solvolysis of the cyclopropyl chlorides in acetic acid at temperatures up to 120°C proceeds with expected ring-opening giving α -phenyl cinnamyl acetate. A previous study [J. W. Hausser and N. J. Pinkowski, J. Amer. Chem. Soc., 89, 6981 (1967)] suggested the possibility of alternate disrotatory modes of ring-opening for *cis*- and *trans*-1-chloro-2-phenylcyclopropane. The steric and electronic effects of the phenyl group as seen in the relative rates of solvolysis will be considered in terms of the possible modes of ring-opening.

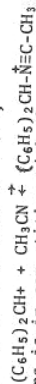
91 THE REARRANGEMENT OF SOME α -PHENYLCYCLOALKYL CARBINOLS IN STRONG ACIDS. Arthur S. Kushner and Pei Hsun Wang, Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115; Herman G. Richey, Jr., Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802



A number of α -phenylcycloalkylcarbinols have been prepared, I, II and III. When I is placed in chlorosulfonic or fluoro-sulfonic acid at room temperature or -78°, 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 I are quenched in base. II and III are also observed to rearrange under these acidic 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.

92 THE TRAPPING OF CATIONS IN THE REACTION OF BENZHYDRYL AZIDE WITH NITROSONIUM SALTS IN ACETONITRILE. Michael P. Doyle, Wendell Wierenga, Department of Chemistry, Hope College, Holland, Mich. 49423.

Alkyl azides react with nitrosonium salts to produce alkyl cations. Thus triphenylmethyl azide produces, quantitatively, triphenylmethyl tetrafluoroborate when reacted with nitrosonium tetrafluoroborate. Solutions of benzhydryl azide in anhydrous acetonitrile at 10°C upon treatment with nitrosonium salts, followed by addition of water, yield benzhydryl (25%), N-(diphenylmethyl)-acetamide (55%), benzaldehyde (5%), and benzophenone (15%). Benzaldehyde and benzophenone are thought to arise by phenyl and hydrogen migrations to electron deficient nitrogen. When methanol is added in place of water the yield of benzhydryl methyl ether is approximately the same as that of the acetamide; the effective in hydride transfer to carbonium ions, as trapping agents produces a predominance of diphenylmethane over the acetamide. Addition of the trapping reagents at different times after commencement of the benzhydryl azide - NOBF₄ reaction produces no change in product yields. The benzhydryl cation in acetonitrile solutions is viewed to exist in equilibrium with N-alkylated acetonitrile as shown,



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

93 THE CHEMISTRY OF THE FOUR EPIMERIC 2-HYDROXYBICYCLO[6.1.0]NONANES. Paul G. Gassman, Elizabeth A. Williams, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

It has been suggested that trans-fusing 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 systems containing such "twist bent" bonds we have prepared the two epimeric alcohols represented by **1** and **2** and the two epimeric alcohols represented by **3**. The



systems represented by **1** and **2** are both functionalized in a suitable manner for the conversion of **1** and **2** into the corresponding cyclopropylcarbonyl cations. The ease of carbonyl ion formation should reflect the inherent strain of the cyclopropyl ring in these fused-ring systems. As part of a kinetic investigation of the ease of cation formation, the four epimeric p-nitrobenzoates derived from **1** and **2** have been prepared. The details of this study will be discussed.

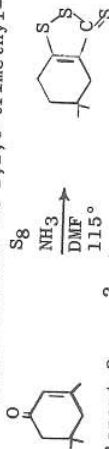
94 THE CHEMISTRY OF CYANODITHIOIMIDOCARBONIC ACID. PART II. SYNTHESIS OF 3-HALO-1,2,4-THIAZAZOLES. Lawrence S. Wittenbrock, Gary L. Smith, and R. Jerome Timmons, Chemical Research, O. M. Scott and Sons Co., Marysville, Ohio 43040

Reaction of dipotassium cyanodithioimidocarbonate (I) with one molar equivalent of methyl iodide has been shown to proceed stepwise to afford exclusively potassium S-methylcyanodithioimidocarbonate [R. J. Timmons and L. S. Wittenbrock, J. Org. Chem., **32**, 1566 (1967)]. This reaction has now been extended to include a variety of monoalkyl derivatives (II). Attempts to monoalkylate I failed, and evidence is presented to indicate that competitive N-substitution occurs. Halogenating agents (eg. SO₂Cl₂, Cl₂, Br₂) effect an oxidative cyclization of II to give the titled compounds (III, X=Cl, Br), a new class of 1,2,4-thiazazoles, in yields which ranged from 60-90%. The scope of this reaction was investigated and found to be general for every case where II could be prepared. The chemistry of III was also investigated. To illustrate, oxidation of the sulfur atom at the 5-position with one and two molar equivalents of oxidizing agent afforded sulfonides and sulfones, respectively. The 3-halo substituent proved to be generally inert to nucleophilic displacement; a phenomenon also observed by other workers. Attempted alpha-chlorination of an alkyl sulfide was unsuccessful.



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

Sulfur "activated" by ammonia in the presence of an amide has previously been shown to add across norbornene double bonds.¹ Extensions of this system have been studied. Δ^{1,5}-7-Dimethyl-2,3-dithiabicyclo[4.3.0.1,5]nonen-4-thione was synthesized from isophorone probably proceeding through a non-oxidative sulfuration of a dienamene intermediate. Under similar conditions N,N-dimethylbenzothioamide and benzoic acid were prepared from benzaldehyde. N,N-Dimethylisobutenyl amine when treated with sulfur followed by methylisocyanate results in 1,1,4-trimethyl-5-N,N-dimethylamino-



2-thia-4-azocyclopent-3-one.² Attempts to isolate the enamine-sulfur intermediate by vacuum distillation led to isolation of N,N-dimethylamino-isobutyrothioamide in 44% yield. Aspects of the scope of "active" sulfuration are discussed.

I. T. C. Shields, A. N. Kurtz, J. Am. Chem. Soc., **91** 5415 (1969).
2. K. Ley, R. Nast, *Angew. Chem. Internat. Edit.*, **4** 519 (1965).

96 THE PREPARATION AND PROPERTIES OF 7,7-DIMETHYL-1,2,3,4-TETRAPHENYLSIL-7-SILA-2,5-NORBORNADIENE. Robert Maruca, Department of Chemistry, Miami University, Oxford Ohio. 45056.

The title compound was prepared from diphenyl acetylene and 1,1-dimethyl-2,5-diphenyl-1-sila-2,4-cyclopentadiene at room temperature. The compound is fairly unstable as it will undergo a reverse Diels-Alder reaction at 65°. When pyrolysed at 300° there appears to be two modes of decomposition. The above mentioned reverse Diels-Alder reaction occurs and in addition the molecule eliminated dimethylsilylene, (CH₃)₂Si, giving 1,2,3,4-tetraphenylbenzene. The elimination of silylenes by 7-silanorbornadienes 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 its chromism. At 42° it dissolves in benzene to give solutions of its reverse Diels-Alder products while at 18° in cyclohexane solution the compound appears to be more stable. Other physical and chemical properties have also been investigated and will be reported.

97 A METALATION STUDY OF 2- AND 3-BENZYLTHIOPHENES

A. T. Jeffries and D. W. H. Macdowell, Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506.

While metalation of 8H-indeno[2,1-b]thiophene and 4H-indeno[2,2-b]thiophene with n-butyllithium followed by carbonation yielded only the corresponding bridgehead acids, similar metalation of 8H-indeno[2,2-c]thiophene gave much smaller amounts of bridgehead acid accompanied by substantial amounts of products resulting from metalation on the thiophene ring [J. Org. Chem., **35**, 0000 (1970)]. In order to ascertain if the presence of a direct link between the benzene and thiophene rings was necessary for metalation to occur at the methylene position, the analogs resulting from the removal of this bond, viz. 2- and 3-benzylthiophene were prepared and their metalation and carbonylation studied. Only 5-benzylthiophene-2-carboxylic acid resulted from 2-benzylthiophene. In the case of 3-benzylthiophene, while no metalation at the methylene group occurred, a mixture consisting of predominantly 4-benzylthiophene-2-carboxylic acid and minor amounts of 3-benzylthiophene-2-carboxylic acid was produced. The mixture was separated by fractional crystallization and the components were characterized by their spectral properties and by independent syntheses. A synthesis of phenyl-3-thienylsulfonic acid is described and the transformation of α-hydroxyphenyl-3-thienylsulfonic acid to 4H-indenothiothiophene[2,2-b]thiophene-4-carboxylic acid is described.

98 CYCLO-DIMERIZATION OF DIENES BY IRON CATALYSTS. N. A. Maly and H. R. Menapace, Research Division, The Goodyear Tire & Rubber Co., Akron, Ohio 44316

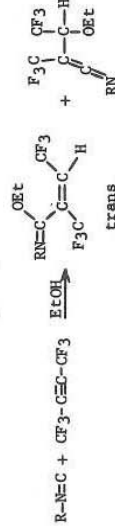
The cyclo-dimerization of dienes by nickel catalysts is well known and has been the commercial method for producing C₈ and C₁₂ ring systems. However, only sparse results have been reported for such catalysis by iron. Yanamoto et al. [J. Am. Chem. Soc. 87, 4652 (1965)] reported butadiene conversion of 73% and 33% yield to 1,5-cyclooctadiene in 4 hours using a ferric acetylacetonate, bipyriddy, triethylaluminum catalyst system. After discovering significant temperature and solvent effects, we obtained 95-98% conversion in 4 minutes with 79% yield to 1,5-cyclooctadiene. Consideration of Wilke's work with nickel [Wilke et al., Angew. Chem. Int. Ed., 2, 105-115 (1963)], led us to believe that the spatial environment around the metal atom could control both the extent and direction of dimerization. Experiments indicated the desirability of the basic structure R=N-C(R')-C(R'')-R as a ligating group. Suitable substitution of R adjacent to N should then have substantial effects on stereochemistry, and appropriate substitution elsewhere in R could change the liganey of the nitrogen atoms by electronic effects. Many Schiff bases were prepared, in which R was a substituted phenyl ring and R' was hydrogen or methyl. Results showed steric effects to predominate. Thus the ligand glyoxal bis-2,6-dimethylanil, iron octanoate, and triethylaluminum gave conversions of 75 to 90%, with 91-95% of converted butadiene forming 1,5-cyclooctadiene. Other dienes studied were piperylene and isoprene.

99 THE REACTION OF OLEFIN OXIDES WITH DIMETHYLHYDRAZIDES: A NEW SYNTHESIS OF AMINIMIDES, Edward A. Sedor, Robert A. Grimm, Richard E. Freis, Ashland Chemical Company, 10701 Lyndale Ave South, Bloomington, Minnesota 55420

The preparation of dialkylammonium-N-acyl ylides (aminimides) has been known for some time. Alkylation of dialkyl hydrazides followed by basic removal of the labile proton is the reported synthetic route [R. L. Himman, J. Amer. Chem. Soc. 76, 2918 (1954)]. Recently McKillop reported the direct preparation from acyl esters and trialkylhydrazinium salts [Can. J. Chem. 45, 2619 (1967)]. Slagel also reported the preparation of dialkyl-2-hydroxy alkyl aminimides by the reaction of acyl ester, dimethyl hydrazine and epoxides [J. Org. Chem. 33, 1374 (1968)]. Our work was the result of further mechanistic studies on the Slagel synthesis. The intention of the work was to determine the intermediate or intermediates in the reaction. A possible intermediate is the 1,1-dimethyl-2-acyl hydrazine which could react with the epoxide. The dimethyl hydrazides are known to react with alkyl halides to form the quaternary hydrazides. Epoxides could well react in the same manner, however, now resulting in the formation of the aminimide, not the quaternary hydrazide. The aminimide was formed, but this reaction sequence was discounted as being a major contributor. Reasons for the conclusion will be presented. Also, the synthetic results, indicating the generality of the reaction, will be reported.

100 REACTIONS OF ISOCYANIDE WITH ACETYLENES. Thomas R. Oakes and Daniel Donovan, Cleveland State University, Cleveland, Ohio 44115

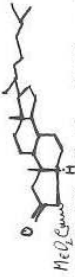
Isocyanides have been shown to react with a number of activated (electron deficient) acetylenes to produce a wide variety of products depending upon the structure of the acetylene. The best yields and most easily interpreted results are obtained with perfluorobutene-2. The nature of the intermediates in these reactions has been inferred from substituent studies and from trapping experiments. The use of alcohols as trapping agents results in a stereospecific reaction of isocyanide and alcohol with the acetylene.



NMR studies using model compounds indicates that a trans addition to the acetylene predominates.

101 EVIDENCE REGARDING THE STEREOCHEMISTRY OF 3 α -METHOXYCARBONYL-5 α -A-NORCHOLESTAN-2-ONE. James L. Pyle, B.V. Paranjape, Department of Chemistry Miami University, Oxford, Ohio, 45056.

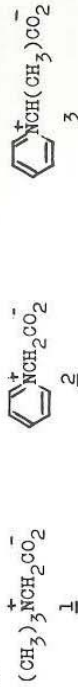
The 8-ketoester, **2**, may be prepared as the Dieckmann product from the corresponding 2,3-seca diester, **1**, as in the cholestane series.



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, $\delta - \delta_3 = +0.04$ ppm (CDCl₃). Similarly there is little difference in pyridine, nor is an appreciable solvent effect observed. The spectrum of the corresponding 2-hydroxyester, **4**, shows a small deshielding effect (CDCl₃) and a moderate solvent effect in pyridine, being deshielded .20 ppm. This is consistent with a β -conformation for the OH group. Since OH has been shown to be trans to the CO₂Me function independently, the latter is assigned an α configuration in **4** and in **2**.

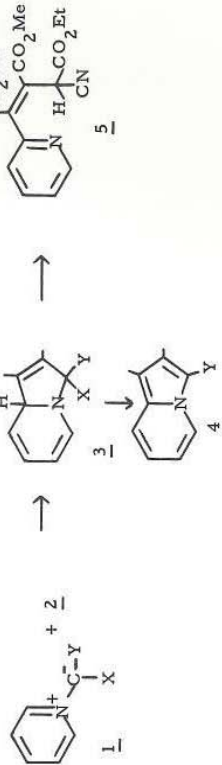
102 EVIDENCE FOR YLIDE INTERMEDIATES FROM PYROLYSES OF BETAINE AND PYRIDINE BETAINE IN A MASS SPECTROMETER. Rudolph A. Champa and D. L. Fishel, Kent State University, Kent, Ohio 44240.

Betaine, **1**, undergoes thermal rearrangement and pyrolysis when heated at temperatures above its melting point to give methyl dimethylaminoacetate, amines, carbon dioxide and amorphous water-soluble materials. These reactions have been studied by time-resolved mass spectrometry. Mechanistic pathways that are indicated include rearrangement via S_Ni displacement and parallel loss of carbon dioxide to give the ylide. The ylide may function as a source of methylene during subsequent reactions with the substrate or the rearranged ester. Pyridine betaine, **2**, and its 2-methyl derivative, **3**, also undergo reactions analogous to the latter pathway for betaine. The ylide derived from these materials may also give telomers and methylene polymers.



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

Numerous pyridinium ylides (**1**) have been reported to react with dimethyl acetylenedicarboxylate (**2**) to yield indolizines (**4**) via the intermediate dihydroindolizines (**3**). We wish to report that pyridinium carbethoxycyanomethylide (X=CN, Y=CO₂Et) reacts with **2** to afford a quite different compound, namely, dimethyl ethyl γ -cyano- α -(2-pyridyl)acetate (**5**). Proof of structure of the product and a postulated mechanism of the transformation will be discussed.

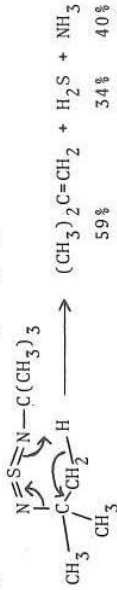


104 THE ROLE OF IODINE COMPLEXATION IN IODINE ISOCYANATE ADDITION REACTIONS. II. COMPETITIVE REACTIONS. Charles G. Bebelin, Department of Chemistry, Youngstown State University, Youngstown, Ohio, 44503

Previous studies have shown that the rate of addition of INCO, 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 behaviour 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 iodoisocyanate product. Evidence supporting this route has been found in competitive reaction studies. E-3-hexene reacts faster with in situ generated INCO than does cyclohexene when run independent of each other. However, when mixtures of E-3-hexene and cyclohexene are run competitively with in situ generated INCO the cyclohexene reacts much faster than the E-3-hexene. The competitive reaction conditions favor iodine-alkene complexation. The enhanced reactivity of cyclohexene, compared to E-3-hexene, 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.

105 THE PYROLYSIS OF SULFUR DIIMIDES. John R. Grunwell, Robert E. Maruca, Jack L. Downie, Miami University Chem. Dept., Oxford, Ohio, 45056.

The pyrolysis of diphenylsulfur diimide at 200° for 0.5 hours gave 66% azobenzene. However, di-2-methyl-2-propylsulfur diimide, pyrolyzed at 265° for 24 hours, gave isobutene, 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 proceed 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 disproportionates to 2-methyl-2-propane and a trace of 2-methyl-2-propene.



The mass spectrum shows prominent peaks at $m/e = 118$ $((\text{CH}_3)_3\text{C-NH-S=N}^+)$ and $m/e = 62$ (HN=S-NH^+) , a fact, which tends to support a concerted intramolecular elimination mechanism.

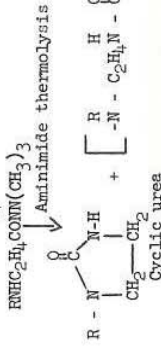
106 AMINO ACIDS WITH TWO CENTERS OF ASYMMETRY FROM MICROBIAL PEPTIDES. Gary G. Marconi and Miklos Bodanszky, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

The stereochemistry of the diasymmetric amino acids N-methyl-L-threonine, N-methyl-L-allothreonine, and stendomycidine [(2-methylimino-5-methyl hexahydro-pyrimidyl)-4-glycine] from the peptide antibiotic stendomycin, and α, β -diaminobutyric acid from amphotycin was studied. Optical rotatory dispersion and nmr spectra were applied for the elucidation of the absolute configurations. The rule of α -epimerization (Bodanszky and Perlman*) will also be discussed.

*M. Bodanszky and D. Perlman, Nature, 218, 291-292 (1968).

107 A NEW SYNTHESIS FOR THE DERIVATIVES OF DIMAZOLIDINONE-2. David Aelroy, V.J. McKillip Ashland Chemical Company, 10701 Lyndale Ave South, Bloomington, Minnesota 55420

Imidazolidinone-2 derivatives have found use as central nervous system depressants and as bactericidal agents in the pharmaceutical industry. They are used in permanent press garments and in adhesives for binding reinforcing materials to rubber, and as adhesives in non-woven fabrics. The following general method for their preparation was used successfully on a number of preparations in good overall yields:



Thermolysis in boiling xylene favors the formation of cyclic ureas. Higher thermolysis temperatures and longer times at thermolysis temperatures favor the formation of polyureas. R represents aromatic, heterocyclic, paraffinic and olefinic groups. Most of the aminimides are crystalline compounds melting below the decomposition point.

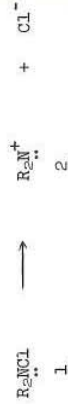
108

THE CONFORMATION OF SODIUM 4-PHENYLBUTYRATE IN DEUTERIUM OXIDE. John F. Sebastian, Mila Ti, Department of Chemistry, Miami University, Oxford, Ohio 45056

The conformation of sodium 4-phenylbutyrate 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 conformers were chosen as models and the phenyl ring's influence on the chemical shifts of the α - and β -proton resonances was calculated by the method of Johnson and Bovey. Comparison of the calculated shifts with the observed shifts allowed selection of the preferred conformer. The conformation of sodium 4-phenylbutyrate was found to exist in the anti form with respect to both the α - and β -Y carbon-carbon bonds.

109 THE GENERATION OF NITRENIUM IONS FROM DIALKYLHYDROXYLAMINES. Paul G. Gassman, George D. Hartman, Koichi Shudo, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

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

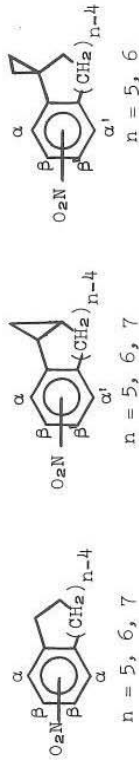


extensive practical importance in the synthesis of unusual nitrogen-containing compounds. As part of our efforts to extend the scope of nitrenium ion chemistry, we have sought other precursors of 2. We now wish to report on the generation of nitrenium ions from dialkylhydroxyamines. A general procedure has been developed for the conversion of secondary amines into hydroxyamines via the initial addition of the secondary amine to ethyl acrylate to form the Michael adduct followed by reaction of the Michael adduct with peracid to give the N-oxide. Pyrolysis of the N-oxides gave the corresponding dialkylhydroxyamines. The hydroxyamines were treated with methyl lithium to produce the anions of the hydroxyamines which were subsequently reacted with p-toluenesulfonyl chloride or with p-nitrobenzoyl chloride to give the corresponding tosylates and p-nitrobenzoates, respectively. Under solvolytic conditions the hydroxyamine derivatives were converted to products via the formation of nitrenium ion intermediates. The details of this study will be presented.

110 CYCLOPROPYL AROMATIC CHEMISTRY. II. CYCLOPROPANE GEOMETRY EFFECTS ON INTRAMOLECULAR CHARGE TRANSFER PHENOMENA.

Roger C. Hahn, Phillip H. Howard, and George A. Lorenzo, Department of Chemistry, Syracuse University, Syracuse, New York 13210.

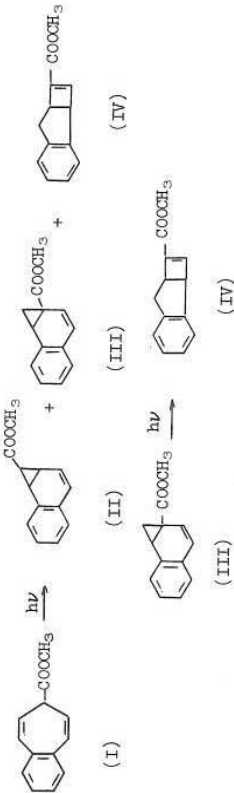
Ultraviolet spectra have been obtained of the twenty-six nitroaromatic systems formulated below. The geometry of a cyclopropyl group meta



to a nitro group has a marked effect on donor-acceptor interaction between these two substituents. Spectral features of these compounds cannot be explained via ground state resonance structures. An analysis is offered in terms of existing theories of excited state donor-acceptor interactions.

111 THE PHOTOCHEMISTRY OF 7-CARBOMETHOXY-5,4-BENZOTROPILIDENE. John S. Swenton, Denise Madigan, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

The photochemistry of 7-carbomethoxy-5,4-benzotropilidene (I) has been investigated. Irradiation of I in cyclohexane using a pyrex filter produces three products: 7-carbomethoxy-2,3-benzonorcaradiene (II), 6-carbomethoxy-2,3-benzonorcaradiene (III), and 6-carbomethoxy-2,3-benzocyclo[4,2,0]-6-heptene (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 benzonorcaradiene photochemistry will be discussed.



112 THE PHOTOCHEMISTRY OF ENETHIOL ESTERS. John R. Grunwell, Saliba I. Hanhan, Miami University, Chem. Dept., Oxford, Ohio, 45056.

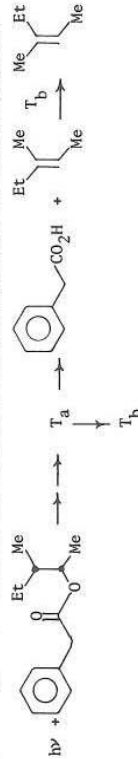
The photolysis of a series of para substituted phenyl thiol acetates in cyclohexane at 2537Å gives the corresponding diphenyl disulfide and methyphenyl sulfide. However, 1-cyclohexenylthiol acetate under the same conditions gives octahydrodibenzothioephene. The latter reaction



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.

STEREOCHEMICALLY CONCERNED FRAGMENTATIONS FROM ESTER TRIPLET STATES. James E. Gano, Department of Chemistry, University of Toledo, Toledo, Ohio 43606

The possibility of concerted and stepwise pathways competing in the photoelimination of olefins from carbonyl compounds was investigated. Suitably substituted esters, threo- and erythro-1,2-dimethylbutyl phenylacetate were prepared and shown to produce mixtures of cis and trans-3-methyl-2-pentene upon photolysis at conversions of less than 2%. Further sensitization and quenching studies however 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 photoelimination and subsequent isomerization of the olefin products.



114 THE PHOTOCHEMISTRY OF HYDRAZONES, Roger W. Binkley, Department of Chemistry, Cleveland State University, Cleveland, Ohio, 44115.

The photochemistry of benzaldehyde phenylhydrazone, benzaldehyde diphenylhydrazone, benzophenone hydrazone, benzophenone phenylhydrazone, and benzophenone diphenylhydrazones 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 imine (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 nitrile. 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.



115 THE MERCURY (¹P₁)-PHOTOSENSITIZED DECOMPOSITION OF CYCLOPROPANE. Ernest G. Spittler, and George W. Klein, John Carroll University, University Heights, Ohio 44118.

The room temperature Hg(¹P₁)-photosensitized decomposition of cyclopropane has been studied. The pressure dependence over the range 0.06-1700 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 200 torr revealed that C₂H₄, C₃H₆, C₂H₂ and C₂H₆ are linear with time up to 40 minutes. There is a very rapid decrease (6.4 to 0.2) in the CH₄/C₂H₄ ratio as oxygen is added to 10 torr of cyclopropane. A plateau is reached at about 0.17% oxygen. The following mechanism appears to be able to interpret the results rather well;



116 THE PHOTOCHEMISTRY OF 1,3-DISTYRYLBENZENE.
Steven Horzan, David D. Morzan, and Milton Orchin, Dept. of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221.

The photocyclization of 1,3-distyrylbenzene has been reported to yield benzo(c)chrysenes as the only product. Initial photo-cyclization of distyrylbenzene can yield either 2-styrylphenanthrene or 4-styrylphenanthrene either of which could yield the observed product in a second photocyclization. Detailed product analysis has shown that in addition to benzo(c)chrysenes, dibenz(a,j)anthracene (from 2-styrylphenanthrene) and 4-phenylpyrene (from 4-styrylphenanthrene) are also formed. Product distribution and quantum yield data will be presented for 1,3-distyrylbenzene, and 2- and 4-styrylphenanthrene along with a brief discussion of predicted reaction paths based on Hückel excited state free valence indices and localization energies.

117 CARBON-13 MAGNETIC RESONANCE AND MOLECULAR STRUCTURE
David M. Grant, 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 very high potential for the technique in studies of 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 resonance. These methods will be reviewed along with basic information on relaxation processes so important to the nuclear Overhauser effect which provides an important signal enhancing feature whenever proton-decoupling methods are utilized.

118 EFFECT OF CHARGE ON CHEMICAL SHIFT. Gideon Fraenkel and Tadashi Tokuhiro, Department of Chemistry, The Ohio State University, 140 W. 18th Avenue, Columbus, Ohio 43210

The origin of the observed relationship of charge to carbon-13 and proton chemical shifts and of substituent contributions to chemical shifts will be discussed. It will be shown that both the theory of the chemical shift and the wavefunction used in the calculations can be derived by means of perturbation methods.

119 NEW EXPERIMENTS AND THEORY OF CHEMICALLY INDUCED NUCLEAR SPIN POLARIZATION.
G. L. Closs, A. D. Trifunac, D. E. Paulson, C. Doubleday, The University of Chicago, Department of Chemistry, 5747 South Ellis Avenue, Chicago, Illinois 60637.

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

120 ALIPHATIC SEMIDIIONES. APPLICATIONS OF ELECTRON SPIN RESONANCE SPECTROSCOPY TO ORGANIC CHEMISTRY, Glen A. Russell, Department of Chemistry, Iowa State University, Ames, Iowa 50010.

The semidione spin label (R-C(O)=C(O)R) 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) cis-trans equilibria in acyclic semidiones
- (b) ring inversion in cyclohexane semidione half-chair conformation
- (c) the preferred conformation of cycloheptane semidione
- (d) molecular rearrangements in the bicyclo[3.1.0]hexane semidione
- (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 semiquinones, semifurazones and aromatic nitrocompounds will be discussed.

122 ELECTRON SPIN RESONANCE STUDIES OF ALKYL RADICALS IN SOLUTION
Paul J. Krusic, Central Research Department, E. I. du Pont de Nemours Co., Wilmington, Delaware, 19898 and Jay K. Kochi, Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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 ESR spectra of alkyl radicals substituted in the β -position with S, Si, Ge and Sn show unusual temperature dependences. These radicals are not symmetrically bridged but exist 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 ΔF^\ddagger) and sometimes on trends of the rate constants with thermodynamic parameters, e.g., pK's (Bronsted plots), E's (Tafel plots), and others.

With this background in mind we explore the possibility of expressing ΔF^\ddagger as

$$\Delta F^\ddagger = w^r + (1 + \Delta F_{R_0}^{\ddagger})^2 \lambda$$

w^r is the work required to bring the reactants together to some typical separation distance R. The last term in the equation is another (subsequent) reorganizational one to form the activated complex. $\Delta F_{R_0}^{\ddagger}$ is the "standard" free energy of reaction in the prevailing medium at the separation distance R (it equals $\Delta F_{R_0}^{\ddagger} + wP_{-w}^r$). λ is an intrinsic reorganizational term, the reorganizational barrier when $\Delta F_{R_0}^{\ddagger} = 0$. λ has certain convenient approximately additive properties.

The implications of this equation for several topics in kinetics are noted--they include, among others, relations between rate constants, and calculations of slopes of free energy plots. The equation can be derived from several rather different approximations [cf. R. A. Marcus, J. Phys. Chem. 72, 891 (1968)]. The relationship of the models to accurate calculations of potential energy surfaces will be noted.

124

FAST HETEROGENEOUS ELECTROCHEMICAL REACTIONS, Ernest Yeager, Chemistry Department, Case Western Reserve University, 2074 Adelbert Road, Cleveland, Ohio 44106.

Conventional steady state electrochemical methods are generally restricted to the study of heterogeneous kinetics with effective standard rate constants of 10⁻² cm/sec or less because of mass transport limitations. A number of non-steady state techniques, however, are available for rate constants of 10³ cm/sec and in some instances 10⁴ cm/sec. These include step function methods (potential, current, charge, pressure), corresponding a.c. 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 complication, 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 amalgams), 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, Hying 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 represents 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 high resistivity of 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.

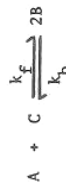
Measurement techniques and problems will be identified and briefly discussed. Emphasis will be placed on examining recent experimental results in light of both qualitative molecular structure considerations and predictions of modern quantitative theories for heterogeneous redox processes.

126 ELECTRON AND PROTON TRANSFER KINETICS OF AROMATIC MOLECULE IONS IN POLAR SOLVENTS. Leon M. Dorfman, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

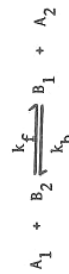
The pulse radiolysis method, which has proved effective as a fast reaction technique, has been used extensively to study reactions of aromatic radical anions and of aromatic cations in solution. In polar protic liquids such as the aliphatic alcohols, subjected to a microsecond pulse of electrons, the electron is solvated and attaches to aromatic compounds in solution to form the radical anions. Absolute rate constants may then be obtained for the rates of electron transfer between the anion and a different, unchanged aromatic compound in solution: $A_1 + A_2 = A_1 + A_2$ (1). Values of k_1 for some fourteen pairs have been examined with regard to the dependence upon the standard free energy of the reaction and the dielectric properties of the solvent. For a single solvent, the dependence of k_1 upon ΔF_0 , D_s and D_{op} is in accord with Marcus theory. Solvent effects are now being investigated. Equilibrium constants have also been obtained for two pairs. Rate constants have been obtained for the proton transfer reaction: $A^- + ROH = AH + RO^-$ (2). In two-component solvent systems, values of k_2 exhibit a profound dependence upon the nature and composition of the solvent. Increase and decrease in the values for k_2 may be discussed in terms of structure making and structure breaking in the solvent. In halogenated hydrocarbons containing aromatic solutes, the solvated electron is localized by attachment to form halide ion, and the aromatic cation is formed by charge transfer to the positive charge centre in the solvent. Rate constants have been determined for the electron transfer to the aromatic cation: $A_1 + A_2 = A_1 + A_2$ (3). The general kinetics involved in the study of all these reactions will be discussed.

127 FAST HOMOGENEOUS ELECTRON EXCHANGE STUDIED SPECTROELECTROCHEMICALLY. Nicholas Winograd and Theodore Kuwana, Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

For the homogeneous electron exchange reaction



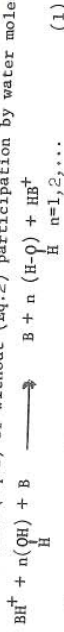
where A, B and C differs by one electron in oxidation states, a method of optically monitoring one of the species during electrochemical perturbation has been devised for determining kinetic rates. This spectroelectrochemical method is also applicable to study cross electron transfer reactions.



Bimolecular rates as high as $5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ have been evaluated for several aromatic systems. The technique will be described and the results will be discussed.

128 PARTICIPATION BY WATER MOLECULES IN FAST PROTON-TRANSFER REACTIONS. Judith C. Harris and Ernest Grunwald, Department of Chemistry, Brandeis University, Waltham, Ma. 02154.

Fast proton-transfer reactions between an acid and its conjugate base in aqueous solution proceed either with (Eq. 1) or without (Eq. 2) participation by water molecules.



We shall describe the measurement of the rate constants (when $k_2 > 10^6 \text{ sec}^{-1} \text{ M}^{-1}$), and of the number of participating water molecules, by nuclear magnetic resonance techniques. We shall examine the effects of substrate-structure, deuterium isotope effects, and the reaction mechanism. For reaction (2) we shall consider whether the rate-determining step is a desolvation step.

129

ENZYME CATALYSIS AND METABOLIC CONTROL. Gordon G. Hammes, Department of Chemistry, Cornell University, Ithaca, New York 14850.

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 cases of ribonuclease and aspartate aminotransferase a large number of reaction 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 large number of different enzyme-substrate complexes (or reaction intermediates) exist; and (3) conformational changes (isomerizations involving noncovalent changes) are prevalent in enzymatic processes. The dynamics of enzyme-substrate complex formation, conformational changes and interconversion of reaction intermediates have been studied. The implication of these findings to the mechanism of enzyme catalysis will be discussed. The kinetic studies of the enzyme aspartate transcarbamylase indicate that in this case control is mediated through rapid conformational changes associated with changes in subunit interactions accompanying substrate and feedback inhibitor binding. Details of the underlying molecular mechanism can be obtained with fast reaction techniques. A concerted conformational change of the subunits appears to be most consistent with available data.

130

Comparative Homogeneous-Heterogeneous Pyrolyses Using a Wall-less Reactor. Jay E. Taylor and Donald M. Kulich, Department of Chemistry, Kent State University, Kent Ohio 44240; David A. Hutchings and Kenneth J. Frech, Research Division, The Goodyear Tire and Rubber Co., Akron, Ohio, 44316.

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 methylpropene. The common products, methane, ethane, ethene, propene, allene and propyne plus smaller amounts of other products form in varying amounts under homogeneous conditions. In the presence of a surface, the allene and propyne are almost completely absent. In each case the homogeneous activation energy roughly equals the bond dissociation energy of the allylic C-H bond. The initial reaction appears, therefore, to be a dissociation of the C-H bond followed by reactions of the resultant radicals.

A series of other hydrocarbons are now under examination.

131 A MODEL FOR NEMATIC MESOPHASE TRANSITIONS. John T. S. Andrews, Liquid Crystal Institute, Kent State University, Kent, Ohio 44240

The positional theory of melting developed by Leonard-Jones and Devonshire [Proc. Roy. Soc. A169, 317 (1939)] has been extended by Pople and Karasz [J. Phys. Chem. Solids 18, 28 (1961)] so as to allow for molecular orientation. This model leads to the appearance of a phase which is structurally similar to the nematic mesophase and permits the calculation of the thermodynamic parameters of the associated thermal transitions. This study presents the results of these calculations and correlates them with available experimental results; it was supported, in part, by the THEMIS project monitored by AFOSR.

132

VISCOSITY OF MOLTEN ALKALI TETRAFLUOROBORATES. Robert DeWitt and L. J. Wittenberg, Mound Laboratory, Monsanto Research Corporation, Miamisburg, Ohio.

The viscosities of molten NaBF_4 and KBF_4 have been measured in a torsionally oscillating, sealed-cup, viscometer. The logarithm of the viscosity varied linearly with the reciprocal temperature over the temperature range investigated. For NaBF_4 , the viscosity decreased from 2.66 cP at the melting point (407°C) to 1.63 cP at 520°C; while for KBF_4 , the viscosity decreased from 1.41 cP at the melting point (570°C) to 1.03 cP at 680°C. The precision of the viscosity measurements was estimated to be within $\pm 5\%$. The viscosity data were rationalized on the basis of the crystalline structure of the solids and the free volume concept of viscous flow. Both NaBF_4 and KBF_4 undergo polymorphic modifications in the solid state at high temperatures resulting in more symmetrical structures than exist at low temperatures. The molar volumes of solid NaBF_4 and KBF_4 at their melting points were estimated from viscosity and molar volume data for the liquids at their melting points. Moreover, the characteristic frequencies of vibration of some simple molten salts calculated from viscosity data were found to compare favorably with those calculated from elastic constant measurements of the solids.

Sponsored by U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

133

THE WETTING OF THIN FILMS OF ORGAWO-CLAY COMPLEXES
Richard J. Ruch, Ming-shing Shen, Department of Chemistry,
Kent State University, Kent, Ohio, 44240

Contact angles of water were measured on thin films of organo-bentonite complexes prepared from Wyoming Bentonite and the hydrochlorides of decyl-, dodecyl-, tetradecyl-, hexadecyl-, and octadecylamine. The clay complexes were dispersed in a 80% benzene-20% propanol medium. The thin films were formed on a platinum substrate by evaporation of the benzene-propanol dispersions, by adsorption from these dispersions, and by the Langmuir-Blodgett technique with the aid of a film balance. The largest advancing angles were obtained for the evaporated films. Maximum advancing angles for the adsorbed films and the Langmuir-Blodgett films varied from 2-6° less than for the evaporated films. Advancing angles on Langmuir-Blodgett films were very low unless the films were dried in an oven prior to measurements. Receding angles were in the range of 25-40° and were less reproducible than the advancing angles. Advancing contact angle behavior is fit by a contact angle equation for a composite surface. The variation between the various types of films is discussed in terms of spreading pressures and a heterogeneous surface model.

QUENCHING STUDIES OF THE NORRISH TYPE II REACTION IN ESTERS. Gary R. Dennison, F. Sheldon Wettsack, Department of Chemistry, Hope College, Holland, Michigan 49423.

Results have been obtained on the quenching of the Norrish Type II reaction from esters in the solution phase. The monolefins used are presumably quenching the triplet state of the ester and the resulting Stern-Volmer data provide an estimate of the lifetime of the ester triplet state. The results indicate that the triplet lifetime is less than that for the aliphatic ketones. However, 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 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.

135 POLYNUCLEAR COMPLEX FORMATION IN SOLUTIONS OF CALCIUM ION AND ETHANE-1,1-DIPHOSPHONIC ACID. R. J. Grabenstetter and W. A. Cilley, Miami Valley Laboratories, The Procter & Gamble Company, Cincinnati, Ohio 45239.

Turbidimetric and pH titrations have been used to study the complexation reactions between calcium ion and ethane-1-hydroxy-1,1-diphosphonic acid (H_2HEDP) at 25° and pH 11.0 in 0.1 M tetramethylammonium chloride. Evidence is presented which indicates that polynuclear complexes are formed resulting ultimately in the formation of a micelle- or solid-like phase at concentrations of calcium ion above about 2×10^{-6} M. Previous investigators have reported stability constants for 1:1 and 2:1 (Ca:HEDP) species, as well as for a protonated complex, but have made no mention of polynuclear complexes. In this investigation during both potentiometric and turbidimetric experiments, an increase in the concentration of HEDP caused a pronounced increase in the apparent stability constant(s) for the calcium complex(es). 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 p,q diagram derived from the turbidimetric data. The log formation constants (overall) which best fit the experimental results were found, through the use of Sillén's computer program Letagopryid, to be $\beta_1, 1 = 5.52 \pm 0.08$, $\beta_2, 3 = 18.78 \pm 1.4$; $\beta_4, 3 = 29.0 \pm 0.12$, $\beta_7, 4 = 48.23 \pm 0.44$, and $K_0 =$ (aggregation constant) $= 4.6 \pm 0.9$. These results are consistent with the formation of a series of complexes up to and including a 7:4 (Ca:HEDP) species and subsequently the clustering of these into very large aggregates. The formation of such large polynuclear species is believed to be unprecedented for metal ions which, like calcium, form chiefly electrovalent bonds.

136

POLYNUCLEAR COMPLEX FORMATION IN SOLUTIONS OF CALCIUM ION AND ETHANE-1,1-DIPHOSPHONIC ACID. II. LIGHT SCATTERING, SEDIMENTATION, MOBILITY, AND DIALYSIS MEASUREMENTS. Brandon H. Wiers, Miami Valley Laboratories, The Procter & Gamble Company, 45239.

Light scattering, sedimentation, electrophoretic mobility, and dialysis measurements were performed on solutions containing calcium chloride, ethane-1-hydroxy-1,1-diphosphonic acid, and tetramethylammonium hydroxide. All measurements indicate the existence of high molecular weight aggregates which, in 1.5:1 Ca^{2+} :HEDP solutions, have weights of 104 gm/mole or higher. From an estimated particle charge of $Z = -16 \pm 4$ it is concluded that the Ca^{2+} :HEDP 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 polynucleated soluble complexes or small Ca^{2+} -HEDP micelles.

THE ABSORPTION SPECTRUM OF CF, 1650-1900Å. W. P. White, Jr., K. C. Casleton*, and C. Weidon Mathews, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.

Observation of the vacuum ultraviolet spectrum of CF in absorption has permitted us to identify and characterize three new electronic states for this molecule. The bands observed between 1670 and 1900Å are assigned to the transitions $C^2\Sigma - X^2\Sigma$, $D(\pi) - X^2\Sigma$, and $E^2\Sigma - X^2\Sigma$. Each of the newly identified excited states is a Rydberg state which is strongly influenced by predissociation or other perturbations. The molecular constants and nature of the perturbations will be discussed and compared to similar isoelectronic systems.

Acknowledgement. Grateful acknowledgement is made to Dr. A. E. Douglas 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 analysis of the data.

*NSF-URP Participant at The Ohio State University, Summer 1969. Present address: Department of Chemistry, Southern Illinois University, Carbondale, Illinois.

138 THE SOLUBILITY OF A SERIES OF FLUORINE CONTAINING GASES IN SEVERAL NONPOLAR SOLVENTS. Emmerich Wilhelm and Rubin Battino, Department of Chemistry, Wright State University, Dayton, Ohio 45431.

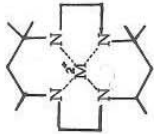
The solubility of CF_3Cl and CF_2Cl_2 has been determined in the five nonpolar solvents benzene, carbon tetrachloride, cyclohexane, n-hexane, and n-octane; in addition, the solubility of CF_4 and of SF_6 in n-octane has been measured. All determinations were made in the temperature range 24°C to 36°C using a technique described in detail elsewhere. The results are given in terms of the Ostwald coefficient and mole fractions at 25°C and one atmosphere partial pressure. The entropies of solution are also given. Combining our results with those of other authors, it turns out, that the behavior of these gases deviates strongly from the pattern of relationships shown by other gases. The solubility increases roughly ten times for every F (in CF_4) substituted by a Cl. Nearly all the above gases show a marked negative temperature dependence of the solubility, i.e., it decreases with increasing temperature. The significance of the results is discussed in terms of the Regular Solution Theory and of some current semi-empirical correlations.

139 THE REACTION OF OZONE WITH NITROGEN DIOXIDE: AN IMPORTANT STEP IN THE MECHANISM OF PHOTOCHEMICAL SMOG. *M. E. Wilson, Jr., Arthur Levy, Battelle Memorial Institute, Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201.

A photochemical smog mechanism will be presented which qualitatively accounts for a number of important aspects of the chemistry of urban atmospheres as studied in smog chambers. These are: (1) the disappearance and ultimate fate of NO_2 , (2) the accelerating influence of water vapor on certain rate parameters, (3) the reduction in maximum oxidant concentration by water vapor, (4) the oxidation of SO_2 in photochemical smog, (5) the reduction in maximum oxidant by SO_2 . Experiments will be reported which demonstrate that (1) the reaction of O_3 and NO_2 occurs at a sufficient rate to be important in air pollution, (2) the rate of this reaction is increased in the presence of water vapor, (3) SO_2 reacts with a mixture of O_3 and NO_2 but does not react with O_3 or NO_2 alone. Results of smog-chamber runs which demonstrate the effects of H_2O and SO_2 on reaction rates and product concentrations will be presented. A mechanism based on the following reactions will be used to explain qualitatively the fate of NO_2 and the interaction of SO_2 and H_2O in photochemical smog: $NO_2 + O_3 \rightarrow NO_3 + O_2$, $NO_3 + NO_2 \rightarrow N_2O_5$, $N_2O_5 + H_2O \rightarrow 2HNO_3$, $N_2O_5 + SO_2 \rightarrow 2NO_2 + SO_3$, and $SO_3 + H_2O \rightarrow H_2SO_4$.

* Supported in part by Public Health Service Grant No. APO0828 from the National Air Pollution Control Administration and in part by the American Petroleum Institute.

140 AN X-RAY CONFORMATIONAL ANALYSIS OF A NICKEL(II) COMPLEX OF A SUBSTITUTED MACRO-CYCLIC LIGAND. V. L. Goedken, G. J. Gainsford, and P. W. R. Corfield, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.



Several isomers of 5,7,7',12,14-hexamethyl-1,4,8,11-tetraazacyclo-tetradecane nickel(II) perchlorate have been isolated (L. G. Warner, D. H. Busch, Coordination Chemistry (1969)). The structure of a bromide derivative, with two asymmetric carbon atoms having the meso configuration has been determined. All other meso isomers equilibrate to this structure in neutral solution. The yellow diamagnetic compound $[Ni(C_6H_5SeM_4)]Br_2 \cdot 2H_2O$ crystallizes in the orthorhombic space group Fdd_2 with cell constants $a = 60.35$, $b = 19.82$, $c = 7.975$, and $Z = 16$. The R factor based on 1945 diffractometer recorded reflections is .08. The cation has the structure labelled m-1,4-1 in the above reference. Both of the six-membered chelate rings have chair conformations and are on the same side of the plane of the four nitrogen atoms. The two five-membered chelate rings have k and k' conformations which forces the six-membered rings to be dissimilar. The ethylenediamine residues are staggered. The water molecules are hydrogen-bonded to the bromide ions and one water molecule lies 2.8Å from the nickel atom in an axial position.

141 THE SURFACE ENERGY OF POLYMERS. George L. Gaines, Jr., General Electric R&D 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.

142

THE STRUCTURE OF POLYMERS ADSORBED AT SOLID-LIQUID INTERFACES. Curt Thies, Materials Research Dept., The National Cash Register Co., Dayton, Ohio 45409.

The structure of an adsorbed polymer layer can vary greatly due to the multiple adsorbing sites distributed along polymer chains. Although adsorption isotherms provide valuable information about polymer adsorption phenomena, they do not give a direct measure of adsorbed polymer structure. One means of shedding more light on such structures is to use infrared spectroscopy to determine ρ , the average fraction of polymer segments attached directly to a solid adsorbent. By determining values of ρ under a variety of adsorption conditions, one gains valuable insight into the structure of adsorbed polymer layers. This presentation will deal with the experimental procedure for determining values of ρ , and point out the limitations of the technique. Results obtained for a number of polymers under a variety of agitation and surface coverage conditions will be reviewed. The effect that copolymer composition, stereoregularity, and various nonpolymeric additives have upon adsorbed structure also will be surveyed. Competitive adsorption effects in systems that contain two chemically different polymers will be discussed. Efforts will be made to stress the broad applicability and value of infrared spectroscopy in studies of a number of polymer adsorption systems.

143

THE EFFECT OF SURFACE INTERACTIONS ON THE POLYMERIZATION OF ORDERED MONOMERS. Jerome B. Lando, Case Western Reserve University, Cleveland, Ohio 44106

The epitaxial or oriented crystallization of ϵ -aminocaproic acid and hexamethylenediammonium adipate on graphite-like fibers has been observed. These reaction under a variety of conditions, yielding Nylon 6 and Nylon 66, respectively. Under identical conditions, after epitaxial crystallization on the graphite-like fibers, much more rapid topotactic reactions occur, yielding the cyclic trimer of specific interactions between the carbon fiber surface and these crystalline monomers must change the course of these solid state reactions. Crystallographic studies of the structure of the reactants, products and the substrate have yielded information concerning these interactions. Apparently, the monomer crystallizes on the carbon fibers so as to maximize the interaction between the polar groups on the monomer and the polar groups on the surface edges of the graphite-like crystallites. A second area of investigation of surface influences on the polymerization of ordered monomers has involved the formation of condensed monomolecular films of monomers such as vinyl stearate on water. The polymerization of these monolayers is being investigated. In addition the reaction of vinyl stearate multilayers prepared from monolayers by the Blodgett technique has been followed by means of infrared spectroscopy.

147 X-RAY LOW ANGLE SCATTERING FROM ORIENTED POLYMER FILMS,
C. J. Hefeffinger, E. L. Libbert, Jr., E. I. du Pont de Nemours, Inc.
Film Department, Circleville, Ohio

Low angle X-ray scattering is used to deduce the morphology of oriented polymeric 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 broadly 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 sized domains are developed upon deformation ranging in size from that of the unit cell (about 10\AA) to large laminar domains of about $300 \times 250\text{\AA}$. This structure is shown to be substantially different from that developed in a biaxially oriented polyethylene film.

148 SYNTHESIS, HOMO-AND COPOLYMERIZATION STUDIES OF 1,1,1-TRIMETHYLACRYLYLHYDRAZINIUM CHLORIDE (I) AND 1,1,1-TRIMETHYL METHACRYLYLHYDRAZINIUM CHLORIDE (II). B.M. Culbertson and R.E. Freis, Ashland Chemical Company, Bloomington, Minnesota 55120

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 quaternary ammonium groups. The resultant polymers may be treated with base to provide "reactive polymers" with pendant amidimide residues - $\text{CONH}(\text{CH}_2)_3$. Since molecules with amidimide residues suffer a carbon-nitrogen migration reaction on thermolysis (W.J. McKillop, L.M. Clemens, and R. Haugland, Can. J. Chem., **45** 2613 (1967)), the aforesaid polymers may be thermolyzed in solution or in the solid phase to produce unique, "reactive polymers" with pendant secondary and tertiary NCO groups. The work demonstrates that monomers such as I and II are highly useful for preparing new, unique "reactive polymers." The reactivity ratios of each monomer (M_1) with styrene (M_2) were determined: Monomer I, $r_1 = 0.46$, $r_2 = 0.56$; Monomer II, $r_1 = 0.23$, $r_2 = 0.51$. The Alfrey-Price Q and e -values were also calculated: $Q = 0.69$, $e = 0.34$ and $Q = 0.61$, $e = 0.66$, respectively.

149 POLYMERIZATION OF OLEFIN OXIDES WITH ZINC n-BUTYL XANTHATE AND ZINC DITHIOCARBAMATE CATALYSTS: MECHANISM OF INITIATION. Joginder Lal, Edward F. Devlin, The Goodyear Tire & Rubber Company, Research Division, Akron, Ohio 44316

Xanthates and dithiocarbamates of metals are effective as catalysts for the polymerization of olefin oxides (J. Polym. Sci. B, **5**, 793 (1967)). To investigate the mechanism of initiation, the bulk polymerization at 50°C of 1,2-butene oxide with zinc n-butyl xanthate (ZBX) at monomer to ZBX molar ratio of 600:1 was studied by UV and IR spectroscopy. There is a rapid conversion of the sulfur-zinc bond in the metal xanthate to a structure $\text{C}_4\text{H}_9\text{-O-S-O-CH}_2\text{-CH-O-Zn-}$ containing sulfur-carbon and oxygen-zinc bonds, the latter acting as the site of the propagation step during polymerization. The xanthate ester moiety is subsequently converted to the oxygenated analogs, namely, O,O-dialkyl thiocarbonate and dialkyl carbonate. These changes are independent of the propagation step. The changes observed in the polymerization of butene oxide with zinc dimethyl-dithiocarbamate are similar, but much slower than in the case of ZBX. The presence of the carbonate ester moiety was also shown in the benzene-insoluble, catalytically active fraction isolated from the reaction product of propylene oxide and ZBX at a molar ratio of 8:1 or lower. This fraction also contained ionic sulfur.

144 TEXTURE OF STYRENE-BUTADIENE BLOCK COPOLYMERS. E. B. Bradford, Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640.

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 colors and ultrathin sections 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 dilute copolymer solutions, but the alignment was not observed when the same solutions were stained before the film was dried.

The layering 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 polybutadiene homopolymer contaminant (determined by gel permeation chromatography). The addition of polystyrene homopolymer destroyed the pattern, but additional polybutadiene only produced homopolymeric islands in the striped pattern.

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

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

146 KINK BANDS AND RIPPLING FROM THE DEFORMATION OF ORIENTED POLYETHYLENE. Richard E. Robertson, General Electric Research and Development Center, P. O. Box #8, 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, are the formation of kink bands and rippling. The kink bands form and even grow with sharp boundaries and almost mirror-reflection of the fibrils about the boundaries. The sharpness seems to result from the fibrils tending to collapse when bent more sharply than some critical radius 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 ripple by the fibrils becoming compressed into waves. The predominance of rippling at low strain rates seems to result from a relaxation at low rates of the forces hindering interfibril 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.

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.

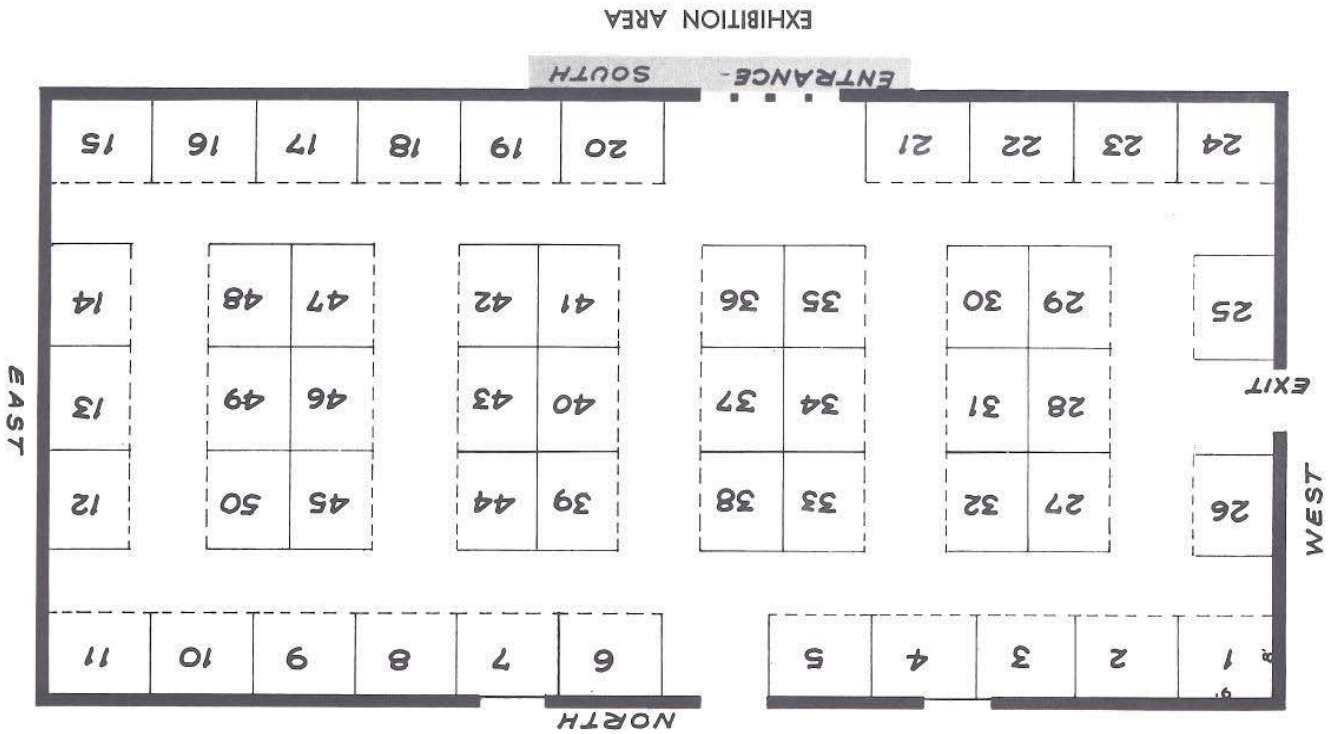
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AUTHOR INDEX

Numbers indicate abstract numbers, not pages

- | | |
|--|---|
| <p>Adams, M. J., 28, 32
 Aclony, D., 107
 Allen, C. M., Jr., 17
 Anderson, L. B., 5
 Andrews, J. T. S., 131
 Ayre, J. E., 25
 Bailey, R. A., 60
 Bartolomeo, L., 24
 Battfay, O., 29
 Battino, R., 138, 47
 Beaton, R. J., 41, 40
 Bettinger, D. J., 36
 Bhuiyan, A. L., 66
 Binkley, R. W., 114
 Birdwell, C., 33
 Blair, P. V., 23
 Block, B. P., 77
 Blundell, T. L., 32
 Bodanszky, M., 106
 Bohl, D. R., 6
 Bond, S. T., 61
 Borders, C. L., Jr., 18
 Boucher, L. J., 82
 Bradford, E. B., 144
 Breidenbach, A. W., 55
 Bullock, K. R., 125
 Busch, D. H., 72, 73
 Calvert, J. G., 54
 Casleton, K. C., 137
 Champa, R. A., 102
 Chartoff, R. P., 150
 Cilley, W. A., 135
 Clearfield, A., 87
 Clement, G. E., 14
 Closs, G. L., 119
 Coleman, J. E., 39
 Collins, R. W., 46, 89
 Conder, H. L., 63
 Cook, B., 70
 Cook, E. S., 19
 Corbin, J. A., 3
 Cordes, E. H., 50
 Corfield, P. W. R., 140
 Corwin, J. F., 38
 Crook, J. R., 59</p> | <p>Culbertson, B. M., 148
 Culp, R. A., 2
 Davies, H. C., 30
 DeChant, Sister M. J., 80
 Demerjian, K. L., 54
 Dennison, G. R., 134
 Devlin, E. F., 149
 DeWitt, R., 132
 Dickerson, R. E., 29
 Dodson, E. J., 32
 Dodson, G. G., 32
 Donovan, D., 100
 Dorfman, L. M., 126
 Doubleday, C., 119
 Douglass, J. E., 103
 Downie, J. L., 105
 Doyle, M. P., 92
 Duffy, N. V., 61, 62
 Durkin, T. R., 64
 Eisenberg, D., 29
 Eller, P. G., 69
 Fackler, J. P., Jr., 85, 86
 Farmery, K., 72
 Fawcett, R., 18
 Fishel, D. L., 102
 Ford, G. C., 28
 Fortman, J. J., 49
 Fraenkel, G., 118
 Francis, D. E., 74
 Frech, K. J., 130
 Fries, D. C., 86
 Freis, R. E., 99, 148
 Frieden, E. H., 21
 Fujii, A., 19
 Gaines, G. L., Jr., 141
 Gainsford, G. J., 140
 Gano, J. E., 113
 Gassman, P. G., 93, 109
 Gebelein, C. G., 104
 Geiger, W. E., 125
 Geil, P. H., 145
 Gilbert, G. L., 44
 Gillchrist, W. C., 25
 Godwin, W. E., 36
 Goedken, V. L., 140</p> |
|--|---|



- Gosling, K., 66
 Gouda, A. L., 7
 Gould, E. S., 81
 Grabenstetter, R. J., 135
 Grant, D. M., 117
 Grimm, R. A., 99
 Grunwald, E., 128
 Grunwell, J. R., 105, 112
 Gurd, F. R. N., 31
 Hahn, R. C., 110
 Haight, H. L., 36
 Hall, J. L., 67
 Hammes, G. G., 129
 Hanford, W. E., 35
 HanHan, S. I., 112
 Hariharan, M., 83
 Harris, J. C., 128
 Hartman, G. D., 109
 Hausser, J. W., 90
 Hawbecker, B. L., 36
 Hayden, P. L., 56
 Heffelfinger, C. J., 147
 Hendricker, D. G., 65
 Henne, M. T., 7
 Herman, R. G., 87
 Herman, T. S., 8
 Hodgkin, D. C., 32
 Horgan, S., 116
 Hough, R. L., 88
 Howard, P. H., 110
 Huebert, B. J., 125
 Hung, H. L., 125
 Hutchings, D. A., 130
 Jameson, D. M., 20
 Jamieson, J., 17
 Jeffries, A. T., 97
 Karl, D. J., 47
 Katovic, V., 73
 Kazmi, S. A., 81
 Keith, R. E., 59
 Kemmler, W., 33
 Kenney, M. E., 78
 Kerkey, J., 12
 King, R. B., 76
 Klapper, B. F., 20
 Klapper, M. H., 13
 Klassen, K., 62
 Klein, G. W., 115
 Knecht, L. A., 9
 Kochi, J. K., 122
 Koehler, F. A., Jr., 6
 Koekoek, K., 28
 Koenig, J. L., 11
 Kordosky, G., 70
 Kothari, V. N., 61
 Krusic, P. J., 122
 Kulich, D. A., 130
 Kurtz, A. N., 95
 Kushner, A. S., 91
 Kuska, H. A., 84
 Kuwana, T., 127
 Lal, J., 149
 Lando, J. B., 143
 Landolt, R. G., 37
 Larson, G. O., 48
 Leach, B. E., 75
 LeGuerrier, J. M., 25
 Lentz, P. J., Jr., 28
 Leussing, D. L., 75
 Levy, A., 139
 Li, N. C., 10
 Limbird, T., 18
 Lippert, E. L., 147
 Lippincott, W. T., 41
 Lorenz, L. J., 2
 Lorenzo, G. A., 110
 Lott, J. A., 8
 Luckens, M. M., 57
 Lykos, P. G., 51
 Madigan, D., 111
 Maizell, R. E., 35
 Maly, N. A., 98
 Marconi, G. G., 106
 Marcus, R. A., 123
 Margoliash, E., 30
 Maruca, R. E., 96, 105
 Mathews, C. W., 137
 Mayer, R. M., 20, 22
 McCormick, B. J., 68
 McDonald, E., 18
 MacDowell, D. W. H., 97
 McKillip, W. J., 107
 Macnaughtan, D., Jr., 1
 McPherson, A., Jr., 28
 Meek, D. W., 69, 70
 Melani, F., 33
 Menapace, H. R., 98
 Menden, E., 4
 Michael, L. W., 4
 Morgan, D., 116
 Nisonoff, A., 30
 Nolan, C., 33
 Nordquest, K. W., 88
 Northcraft, R., 9
 Oakes, T. R., 100
 Ogle, P. R., 42
 Olson, C. L., 7
 Oncley, J. L., 27
 Orchin, M., 116
 Oyer, P. E., 33
 Paranjape, B. V., 101
 Paulson, D. E., 119
 Petering, H. G., 4, 16
 Petrarca, A. E., 40, 41
 Prihar, H. S., 22
 Putnam, T. D., 36
 Pyle, J. L., 101
 Reichlin, M., 30
 Rendina, G., 24
 Richey, H. G., Jr., 91
 Rippon, W. B., 11
 Robertson, R. E., 146
 Robinson, W. R., 63
 Rogers, L. B., 1, 2, 3
 Rose, M. L., 5
 Rossmann, M. G., 28
 Rubenstein, H., 33
 Rubin, A. J., 56
 Ruch, R. J., 133
 Russell, G. A., 120
 Ryan, J. A., 84
 Schevitz, R. W., 28
 Schram, E. P., 64
 Schroer, R. A., 21
 Schussler, D. P., 63
 Sebastian, J. F., 108
 Sedor, E. A., 99
 Sell, J. E., 16
 Sellers, D. E., 6
 Shaw, Y. H., 10
 Shen, M., 133
 Shields, T. C., 95
 Shore, J. D., 15
 Shore, S. G., 79
 Shudo, K., 109
 Smiley, I. E., 28
 Smith, D. E., 125
 Smith, G. L., 94
 Smith, J. A., 85
 Smith, L., 30
 Sneath, R. L., 58
 Spittler, E. G., 115
 Stanclift, W. E., 65
 Steiner, D. F., 33
 Stock, L. M., 121
 Stormer, B. P., 68
 Stumm, W., 53
 Sutliff, T. M., 45
 Swenton, J. S., 111
 Swiger, E. D., 39
 Takano, T., 29
 Tanaka, K., 19
 Taylor, J. E., 130
 Terris, J. M., 89
 Thies, C., 142
 Ti, M., 108
 Timmons, R. J., 94
 Todd, L. J., 58
 Tokuiro, T., 118
 Trifunac, A. D., 119
 Uchic, J. T., 90
 Uchida, H., 13
 Urbach, F. L., 83
 Urry, D. W., 34
 Van Winkle, Q., 41
 Varnum, J., 29
 Vijayan, M., 32
 Walton, A. G., 11
 Walton, R. A., 71
 Wang, P. H., 91
 Weber, N. E., 23
 Wesolosky, J. M., 103
 Westphal, U., 12
 Wettack, F. S., 43, 134
 White, W. P., Jr., 137
 Wick, L. B., 45
 Wierenga, W., 92
 Wiers, B. H., 136
 Wilhelm, D. L., 36
 Wilhelm, E., 138
 Williams, E. A., 93
 Wilson, W. E., Jr., 139
 Winograd, N., 127
 Wittenberg, L. J., 132
 Wittenbrook, L. S., 94
 Yagello, V. E., 40
 Yeager, E., 124
 Zimmerman, D. N., 67
 Zubkoff, P. L., 26

