# ABSTRACTS OF DOCTORAL DISSERTATIONS
## 1952

## THE PURIFICATION OF ALKALINE PHOSPHATASE FROM CALF INTESTINAL MUCOSA: A PHYSICO-CHEMICAL CHARACTERIZATION

Alden R. Adams, Chemistry

Alkaline phosphatase from calf intestinal mucosa has been purified by a simple procedure and its activity as a function of pH, substrate concentration and temperature has been determined.

The Michaelis constant and isoelectric point for the purified enzyme have been found to be 0.0012 moles/liter and pH 4.0 respectively. The activation energy of the enzyme-catalyzed hydrolysis of sodium beta-glycerophosphate has been found to be 7,200 calories/mole when magnesium and alanine were used as activators. The temperature coefficient for the 27.0-37.0 degree C. increment has been evaluated as 1.61.

The ultraviolet absorption spectra have been obtained for solutions of alkaline phosphatase and maximum absorption has been shown to be in the neighborhood of 2800 Angstrom units.

Equilibrium data suggest that the function of alkaline phosphatase *in vivo* is as a hydrolytic and not synthetic enzyme.

Sedimentation constants from ultracentrifuge data have been listed.

## RADIOACTIVELY TAGGED 2, 6–DIAMINOPURINE AND RELATED STUDIES

Lewis Pearson Albro, Chemistry

The preparation of adenine tagged in the eight position with $C^{14}$ by a new variation of the method of Clark and Kalakar has been performed and the desired product was obtained in 78% yield based on the radioactive carbon used.

The preparation of 2, 6-diaminopurine tagged in the eight position with $C^{14}$ has been performed and the desired product was obtained in 79% yield based on the radioactive carbon used.

A series of biological experiments was performed to determine whether or not any interaction existed between these two compounds when they were administered simultaneously to rats. Unfortunately the methods used for the determination of the results of these experiments led to completely anomalous results and no conclusions could be reached.

## KINETICS OF ISOPROPYLBENZENE DEALKYLATION OVER SILICA-ALUMINA CATALYSTS

Edward R. Boedeker, Chemistry

A kinetic study of the dealkylation of isopropylbenzene over a series of silica-alumina cracking catalysts was carried out for the purpose of studying the relationships which exist between the acidities of the catalysts and the reaction rate constants and activation energies for the catalytic dealkylation of isopropylbenzene.

The catalysts used in the present study were commercial synthetic silica-alumina cracking catalysts. Kinetic measurements were made at 371° C. and 427° C.

It was found for all of the catalysts studied that the reaction was first order with respect to the concentration of isopropylbenzene in the gas phase and also was first order with respect to the amount of catalyst used. Furthermore, at a given temperature level, the first order reaction rate constant is a linear function of the acidity of the catalyst.

The activation energy required for the catalytic dealkylation of isopropylbenzene decreases as the catalyst acidity increases and appears to be approaching a minimum limiting value of 12-13 Kcal./mole.

From these results it is concluded that silica-alumina catalysts possess different numbers of active acid sites and the activities of the acid sites are not uniform but vary from site to site.

## POLAROGRAPHIC PHENOL FORMALDEHYDE KINETIC STUDIES

Martin Gerson Chasanov, Chemistry

The half wave potential for the reduction of formaldehyde at the dropping mercury electrode was determined versus both the mercury pool and the saturated calomel electrode. Calibration curves for the polarographic reduction of formaldehyde were determined at 5°, 15°, and 25° C. using 0.05 M. lithium hydroxide as supporting electrolyte, and at 25° C. using 0.05 M. lithium hydroxide plus 0.125 M. lithium choride as supporting electrolyte. The results obtained agreed excellently with those reported in the literature.

Prepared mixtures of formaldehyde and phenol were allowed to react, and the disappearance of formaldehyde was followed by polarographic analysis. Determinations of the reaction velocity constant, k, were made over the pH range 11.2 to 12.3. In this range and at the above temperatures the reaction was found to obey first order kinetics with respect to formaldehyde. Plots of log k versus pH showed a negative slope, indicating acid catalysis. Apparent activation energies were determined from the kinetic data, and they were found to vary with pH; a plot of $\Delta E_a$ versus pH gave a straight line with negative slope.

At 25° C. determinations at a pH of 11.7 and 12.3 were made in which ionic strength was varied from 0.05 to 0.175; a plot of log k versus the square root of ionic strength gave a pair of straight lines with negative slopes.

A possible reaction mechanism amenable to the experimental observations was proposed.

## PERMANGANATE OXIDATION OF CIS AND TRANS-DIHYDRO-ALPHA-TERPINEOL

Ralph P. Chesluk, Chemistry

The oxidation of cis-dihydro-alpha-terpineol and trans-dihydro alpha-terpineol by alkaline potassium permanganate has been performed. The products obtained from the oxidations were identical

but the quantity was different. In order to obtain satisfaction in this explanation, two of the resulting products were prepared and oxidized under identical conditions. The time required to discolor the permanganate by cisterpin hydrate indicates it had no part in contributing to the high yield of oxalic acid obtained from the oxidation of the dihydro-alpha terpineols.

Mechanisms for the oxidation of the dihydro-alpha-terpineols to cis-terpin hydrate and trans-terpin are discussed, as well as the mechanisms for the oxidation of the dihydro-alpha-terpineols and of the terpins to oxalic acid, acetic acid, and carbon dioxide.

## THE OXIDATION OF BORNYL–P–TOLYLCARBINOL AND SOME RELATED TERPENE STUDIES

Lester Samuel Cohen, Chemistry

A new terpene-aromatic alcohol, bornyl-p-tolylcarbinol has been synthesized and oxidized with chromic anhydride in acetic acid. The products of the oxidation were isolated and identified. It is theorized that they indicate the existence of a positive oxygen intermediate which attracts the pair of electrons binding the bornyl group to the carbinol carbon. The action results in the bornyl group's becoming increasingly positive in nature. The increase in positive character increases interaction with the solvent which is drawn in on the side opposite to that where the electrons are being withdrawn by the oxygen. Thus the products are protonated isobornyl acetate, which expels its proton, and p-tolualdehyde. The aldehyde is unstable under the oxidative character of the chromic acid and is oxidized to p-toluic acid.

The rehydration studies on cis and trans 1:8 terpin by W. A. Mosher have been confirmed and a quantitative determination of the products of the dehydration of cis and trans 1:4 terpinene has been accomplished.

The two isomeric cineoles (1:4 and 1:8) have been ignited and theories postulated for the higher heat of combustion obtained from the 1:4 cineole.

## A FUNDAMENTAL STUDY OF THE OXIDATIVE DEGRARATION OF POLYVINAL FORMAL

Leonard Harry Cutler, Chemistry

Polyvinyl formal undergoes serious changes on aging. This research was made to study the oxidative degradation of polyvinyl formal at high temperatures to develop basic data in order to predict the rate of deterioration at or near room temperature.

Kinetic studies showed that the rate of oxygen uptake followed half order kinetics with an apparent energy of activation of 3 kilocalories. The evolution of products followed first order kinetics with an apparent energy of activation of 15.6 kilocalories.

The kinetic data and the products of the degradation are interpreted on the basis of a free radical, peroxide, chain mechanism.

The films were found to have a powerful affinity for solvent and required long periods of heating in a vacuum oven at 110° C. for final solvent removal.

## A DIAZO–COUPLING REACTION AS THE BASIS FOR THE COLORIMETRIC ESTIMATION OF THYMINE IN HYDROLYSATES OF DESOXYPENTOSENUCLEIC ACIDS

Eugene D. Day, Chemistry

An improved colorimetric method for the quantitative estimation of thymine in hydrolysates of extracted and unextracted desoxypentosenucleic acids has been developed. The method is based upon the coupling reaction between thymine and p-diazobenzene sulfonic acid in carbonate solution and upon the subsequent production of red color by the addition of sodium hydroxide.

Evidence has been presented to support a newly proposed mechanism for the diazo-coupling and color-development reactions. The coupling reaction has been shown to be oxygen-catalyzed; the development of red color, to be pH-dependent.

A procedure has been developed (1) for the isolation of the pyrimidine fraction from hydrolysates of extracted and unextracted desoxypentosenucleic acids and (2) for the subsequent colorimetric estimations of thymine in this fraction. A method for the determination of the total desoxypentosenucleic acid content of nuclei which is based upon this procedure has also been developed.

An increase in the desoxypentosenucleic acid content of the liver nuclei of rats administered alloxan and of rats mantained on protein-free diets has been found. An accompanying change in the structure of the desoxypentosenucleic acids from these nuclei has also been found. Support is thereby given to the theory that desoxypentosenucleic acid is not a nuclear constant under certain abnormal conditions.

## CHROMIC ACID OXIDATION OF LEVO-3-METHYL-3-PHENYL-2-PENTANOL

Susan Duckworth, Chemistry

1. *Levo*-3-methyl-3-phenyl-2-pentanol was synthesized and subjected to chromic acid oxidation. The cleavage product, 2-phenyl-2-tubanol, which was obtained in 15% yield, was shown to have undergone complete racemization. The significance of this evidence with regard to the cleavage and the subsequent nucleophilic attack was discussed in relation to $SN_1$ and $SN_2$ reaction mechanisms.

2. The conditions for the Hofman reaction of *dextro*-1-methyl-1-phenyl-butanamide were investigated. Apparent racemization occurred during the rearrangement and hydrolysis to 2-phenyl-2-aminobutane. A possible explanation for the racemization was discussed.

3. In the course of the work the following new compounds were synthesized: 3-methyl-3-ethyl-2-hexanol, 2-methoxy-2-phenylbutane, 1-methyl-1-phenylbutanoic acid, 1-methyl-1-phenylbutanoyl choride, 3-methyl-3-phenyl-2-pentanone, 3-methyl-3-phenyl-2-pentanol, 1-methyl-1-phenylbutanamide, and 2-phenyl-2-aminobutane.

## THE EFFECTS OF SOLVENTS AND LITHIUM BROMIDE IN THE REACTION OF BUTYLLITHIUM WITH BENZONITRILE

Peter Fotis, Jr., Chemistry

An investigation of the effect of various solvents and of lithium bromide in the reaction of n-butyllithium has been carried out. The products obtained from the reaction of n-butyllithium and benzonitrile in ethyl ether in the presence of lithium bromide were valeroprenone (79% of the theoretical) and 2, 4, 6-triphenyl-2-n-butyl-1, 2-dihydro-1, 3, 5-triazine (15% of the theoretical). In the absence of lithium bromide the yields were 43% and 50% respectively.

A systematic investigation of the same reaction has been carried out in the solvents n-pentane, ethyl ether, tetrahydrofuran, dioxane, dimethylaniline and N-ethylmorpholine. In the presence of lithium bromide the yield of valerophenone varied from 40% to 79%, depending on the basicity of the solvent and the solubility of the lithium bromide. In the absence of lithium bromide the yield of valerophenone decreased with increasing coordinating power of the solvent; at the same time the rate of the reaction decreased very markedly. This is similar to the effect of basic solvents in the Grignard reaction. An attempt to measure the reaction rate in ethyl ether was unsuccessful because the reaction was too fast, being 95% complete in seven minutes.

## FURTHER CHROMIC ACID OXIDATIONS

Dennis L. Funck, Chemistry

Di-t-butylcarbinol was oxidized by chromic acid in glacial acetic acid to give only 1.5 to 2.5% t-butlyalcohol, along with the corresponding ketone.

t-Butylanisylcarbinol when oxidized with chromic acid glacial acetic acid, gives 34.8% cleavage products. When the oxidation is run in 55.5% acetic acid the amount of cleavage is decreased. The

presence of manganous ion seems to have little effect upon the amount of cleavage which occurs.

The tertiary alcohol, methyl-t-butylanisylcarbinol, oxdizes at room temperature to give p-methoxyacetophenone. When the oxidations are carried out in 55.6% acetic acid and at 58-60°, trace amounts of pinacolone are obtained. The pinacolone is thought to be formed by an external nucleophilic displacement, while the major product, p-methoxyacetophenone, is produced by an internal displacement by a pair of electrons.

Methylanisylcarbinol is oxidized by chromic acid in glacial acetic acid to p-methoxyacetophenone in fair yields.

2, 2-Dimethyl-1-indanol gives 90-95% yields of the ketone when oxidized with chromic acid in glacial acetic acid.

The oxidation of dimethylanisylcarbinol in the presence of sodium acetate gives a high boiling fraction which when hydrolyzed yields p-methoxyphenol. This fraction is probably the product obtained by an external nucleophilic displacement which causes a carbon to oxygen rearrangement.

The suggestion has been advanced that N. G. P. (neighboring group participation) is a prerequisite for cleavage to occur in the chromic acid oxidation of secondary alcohols.

## HIGHLY POLYMERIZED LIVER RIBONUCLEIC ACID: PHYSICO-CHEMICAL STUDIES AND CYTOPLASMIC LOCALIZATION

Edward L. Grinnan, Chemistry

A procedure is described for the isolation of highly polymerized ribonucleic acid (RNA) from the cytoplasm of rat and calf liver. The procedure is carried out at a nearly neutral pH and involves the precipitation of a nucleic acid-protein complex from a cytoplasmic extract, heat denaturation of the protein for two minutes at 100°, and removal of the protein by shaking with chloroform-butanol.

The molecular weight of RNA isolated by this procedure is in the order of 300,000 as determined by sedimentation and viscosity data. Physico-chemical data are presented for a number of prepa-

rations. The isolation procedure shows a moderately high degree of reproducibility. Sedimentation velocity constants average 9.2 with a range of 8.1 to 10.3; the RNA is somewhat polydisperse in the ultracentrifuge. Solutions of high polymer RNA exhibit anomalous viscosity and moderate streaming birefringence; viscosity data indicate that the RNA is a polyelectrolyte.

Several modifications of the original method are presented, including one which yields RNA that forms solutions of extremely high viscosity.

RNA was depolymerized or disaggregated by x-radiation, chemically generated free radicals, and sonic vibration.

Cytoplasmic fractionation by differential centrifugation of the cytoplasmic extract was carried out on several preparations; three fractions were obtained: mitochondria, microsomes, and supernatant. Nearly all the high polymer cytoplasmic RNA was recovered from the microsome fraction; only traces of RNA were found in the supernatant after sedimentation of the microsomes for one hour at 100,000 x g. in a 0.25 M sucrose medium. The average sedimentation constant of the RNA from isolated microsomes was about 30 per cent lower than that of RNA obtained directly from the cytoplasmic extract. This lower sedimentation constant indicated a molecular weight of about 150,000, and was probably caused by some enzymatic degradation during fractionation. RNA was isolated from large and small microsomes obtained by modifications of the fractionation procedure; no consistent difference was noted in the sedimentation constants of the RNA from the two types of microsomes.

RNA could not be isolated from mitochondria by means of the guanidine hydrochloride procedure, but data are given on several preparations of mitochondrial RNA isolated by a more drastic procedure. Sedimentation constants indicate a molecular weight of about 50,000.

# HYDROGEN EXCHANGE IN THE HETEROGENEOUS SYSTEM CRACKING CATALYST, WATER, ISOBUTANE–1–d

S. G. Hindin, Chemistry

This paper deals with the kinetics of hydrogen exchange in the heterogeneous system, cracking catalyst, water and isobutane. The reaction is followed by labeling a primary hydrogen of the hydrocarbon with deuterium and determining the gaseous products using the mass spectrometer. This work was undertaken to learn more about the nature of the original catalyst-hydrocarbon complex which must be formed if hydrocarbon molecules are to react with such oxide catalysts.

The effect of each of the variables on the initial rates of reaction was investigated by holding two of them constant, and varying the third. The results obtained are as follows:

1. Exchange involves all hydrogen of the catalyst structure in addition to the hydrogen of the added water.

2. The reaction is first order with respect to hydrocarbon over the entire range of concentrations studied, from $9 \times 10^{-6}$ to $9 \times 10^{-4}$ moles.

3. The reaction is first order with respect to water up to an amount of water equal to about 0.3 weight per cent, based on catalyst weight; this value corresponds to complete coverage of all active sites of the catalyst. Increasing the amounts of water beyond this leads to a change in the nature of the effect produced, in that the reaction then becomes negative second order with respect to water. This is due to poisoning of the active sites by water.

4. The reaction is approximately negative first order with respect to catalyst, until such catalyst-water ratio is reached as corresponds to complete coverage of the active sites of the catalyst. For amounts of catalyst such that there is more water than required for complete coverage of sites, increasing the amount of catalyst causes the initial rate to vary as the second power of the catalyst weight.

5. The reaction requires an apparent activation energy of $9.6 \pm 2.0$ Kcal.

Analysis of the kinetic data indicates that the reaction proceeds via a Langmuir-Hinshelwood type of mechanism, in which water and hydrocarbon are sorbed side by side on neighboring catalyst sites. The number of active sites on the catalyst, as calculated from these data, leads to a value in good agreement with that obtained by other investigators using different techinques of measurement.

## THE MECHANISMS OF LEAD TETRAACETATE OXIDATIONS

Clifton L. Kehr, Chemistry

In the oxidation of organic acids with lead tetraacetate, formic acid yielded 95% carbon dioxide. Triphenylacetic acid gave 95% carbon dioxide and 95% triphenylcarbinol. Pivalic acid gave carbon dioxide (79%), butene-1 (4%), isobutene (38%), *tert.*-butyl acetate (3%), and *tert.*-butyl trimethylacetate (3%). Isobutyric acid gave carbon dioxide (67%), propane (24%), propene (9%), *α*-isobutyroxyisobutyric acid (9%) and isopropyl isobutyrate (4%). Isovaleric acid gave carbon dioxide (75%), isobutane (12%), isobutene (less than 1%), n-butane (10%), butene-1 (4%), butene-2 (7%) and *sec.*-butyl isovalerate (9%).

A new reaction involving the action of lead tetraacetate in acetic acid on organic esters was discovered. n-Propyl acetate yielded propylidene diacetate (25%), carbon dioxide (53.5%) and an inflammable gas (presumably methane). Isopropyl acetate gave carbon dioxide (44.7%) and acetic anhydride (19.1%). n-Butyl-n-butyrate yielded carbon dioxide (44.1%), 1-acetoxy-1-butyroxy butane (11.6%) and a triply esterified compound (12.8%) which was probably 1-acetoxy-1-butyroxy-2-acetoxy butane.

Several monohydroxy alcohols were oxidized in acetic acid solution. Ethanol yielded 74.5% acetaldehyde. Phenylmethylcarbinol gave 88.2% acetophenone. Pinacolyl alcohol gave acetaldehyde (11.6%), isobutene (15.1%, *tert.*-butyl acetate (20.1%) and pinacolone (1.7%). Di-tert.-butylcarbinol gave 28.6% trimethylacetaldehyde.

Sodium alkoxides (solid) added to a solution of lead tetraacetate caused decomposition of the oxidizing agent to carbon dioxide and lead acetate.

For the above reactions, ionic mechanisms were postulated.

## DIFFUSION IN A TERNARY GAS SYSTEM: APPLICATION TO GAS SEPARATION BY EXTRACTIVE DIFFUSION

John Judson Keyes, Jr., Chemical Engineering

The Maxwell–Stefan differential equations for diffusion of three gaseous components are derived, and integrated for the case of axial diffusion in a cylinder. The following steady-state cases are treated:

A. Diffusion of two gases through a third which is stagnant.

B. Simultaneous diffusion of all three components.

1. General case
2. Simplifications
   a. Two components approach infinite dilution in the mixture.
   b. Ratio of diffusion rates of two of the components is great.

The theoretical development is applied to the enrichment of binary gas mixtures by extraction with counter flowing vapor, which preferentially retards the heavier component, and permits the lighter one to pass.

Extensive experimental measurements were made with and without countercurrent flow of vapor. Average deviation of $a$ from theory is 3% for the first case, 10% for the second.

Using methanol as extractive agent, 98.5% pure $H_2$ product is obtained from 45% $H_2 - N_2$ feed. This is considerably better enrichment than reported by Maier[1] in experiments with mass diffusion through porous membranes.

Design curves based upon the simplified equations (B. 2 b. in

[1] Maier, G. G., U. S. Bur. of Mines Bull. 431, "Mechanical Concentration of Gases" (1940).

above outline) are presented, and applied to the solution of an illustrative example.

Proposals for scale-up to large capacity are given, including a sketch of a suggested production unit. Improvement in over-all performance by addition of an unpacked stripping section is discussed.

Application of the theory to separation of $He^3 - He^4$ and $A^{36} - A^{40}$ is made, with emphasis on the utility of the simplified equations for the early and final stages of the cascade. By employing sufficiently high vapor rate, enrichments equivalent to fifteen or twenty gaseous effusion stages are possible with a single extraction column.

It is concluded that countercurrent gaseous extraction is particularly applicable to separations where product purity is the prime consideration; e. g., enrichment of very dilute isotope mixtures.

## THE CATALYTIC VAPOR PHASE DEHYDROGENATION OF SECONDARY AND TERTIARY ALCOHOLS

Donald Bixby Lake, Chemistry

The catalytic vapor phase dehydrogenation of pinacolyl alcohol and tert. butyl alcohol over copper at 350° C. was studied. It was found, in the case of pinacolyl alcohol, that dehydrogenation predominated to the extent of 84% while tert. butyl alcohol did not react except to give 14% isobutylene which was attributed to hydrolytic pyrolysis.

A similar study was made over chromia catalysts at 400° C. using the following compounds: pinacolyl alcohol, butanol-2, methyl isopropyl carbinol, methyl cyclopropyl carbinol, methyl cyclopentyl carbinol, dimethyl isopropyl carbinol, methyl ethyl t-butyl carbinol, dimethyl neopentyl carbinol and 2, 2, 4-trimethylpentane. Both an acidic and basic catalyst was used.

It was found that basic chromia preferentially catalyzed dehydrogenation and tertiary alcohol cleavage while acidic chromia catalyzed, equally, dehydration and dehydrogenation and caused no cleavage.

Chromic acid oxidation of methyl ethyl t-butyl carbinol yielded 50% pinacolone.

Basic concepts and current theories of heterogeneous catalytic reactions were discussed. Ionic reaction mechanisms were proposed to explain observed results.

## GLYCYL DERIVATIVES OF AMINOBARBITURIC ACIDS

Donald J. Lyman, Chemistry

The purpose of this research was to prepare conjugated peptides in which the conjugate is an aminobarbituric acid derivative. It was considered desirable to synthesize these conjugated peptides in order to study their physiological behavior, which includes their effect on enzymatic synthesis.

Three new intermediates were synthesized in the preparation of the amino derivatives of barbituric acid. They were: diethyl chloromethylethylmalonate; 5-chloromethyl-5-ethylbarbituric acid; and 5-aminomethyl-5-ethylbarbituric acid.

Six new compounds were prepared in the synthesis of the glycyl derivatives of the aminobarbituric acids. They were: 5-(chloroacetyl) amino-5-ethylbarbituric acid; 5-(chloroacetyl)-aminomethyl-5-ethylbarbituric acid; 5-(chloroacetyl)-$\beta$-aminoethyl-5-ethylbarbituric acid; 5-ethyl-5-glycylaminobarbituric acid; 5-ethyl-5-glycylaminomethylbarituric acid; and 5-ethyl-5-(glycyl)-$\beta$-aminoethylbarbituric acid.

The acetyl derivatives of the glycylaminobarbituric acids were synthesized.

## THE VAPOR PHASE DEHYDRATION OF CERTAIN ISOMERIC HEXANOLS OVER ALUMINUM OXIDE

Louis Emil Mattison, Chemistry

A systematic investigation of the effect of temperature upon the dehydration of the isomeric hexanols, 3, 3-dimethylbutanol-1, 3, 3-dimethylbutanol-2, 2, 3-dimethylbutanol-1 and 2, 3-dimethylbutanol-2 has been carried out in the temperature range of 250° to 425° C. over aluminum oxide of pH = 10. The data indicate a linear increase in olefin formation with temperature as long as there is unreacted alcohol. Once the dehydration reaction is complete, there is no further change in the ratio of products formed with increased temperature. It was observed that under these imposed experimetal conditions, the rate of formation of *t*-butylethylene is the fastest and the rate of formation of tetramethylethylene is the slowest reaction taking place.

A systematic investigation of the effect of temperature upon the dehydration of pinacolyl alcohol (3, 3-dimethylbutanol-2) over aluminum oxide, pH = 5.4, was completed. The data indicate that beyond 300° C. the principal conversion is the isomerization of *t*-butylethylene into unsym-methylisopropylethylene and tetramethylethylene. The reaction products appear to be those of dehydration and isomerization.

A study of the acidity of aluminum oxide using pinacolyl alcohol showed the importance of pH in determining the course of the reaction.

## ALDEHYDE OXIDATIONS AND RELATED STUDIES

Donald Merle Preiss, Chemistry

The chromic acid oxidation of aldehydes in the presence of primary alcohols and ethers was studied. The related compound δ-hydroxyvaleraldehyde (I), which exists almost entirely in the cyclic hemiacetal form, was synthesized and oxidized under similar

conditions. The oxidation of isovaleraldehyde (II) in the presence of diisopropyl ether (III) yielded 20% isopropyl isovalerate. When II was oxidized in the presence of isobutanol (IV), a 24% yield of isobutyl isovalerate (V) and 9% of isobutyl isobutyrate (VI) was obtained. Propionaldehyde (VII), when oxidized in the presence of III and IV, yielded 34% isobutyl propionate and 6% of VI. (I) on oxidation gave a 70% yield δ-n-valerolactone. There was no evidence for the presence of levulinic aldehyde or acid among the products in the last case.

A kinetic study indicated that the rates of oxidation were in the following order: I > a mixture of II and IV > 2-pentanol > II or IV. Also, the rates of oxidation of II, IV, and a mixture of II and III were equal.

The conclusions drawn from the experimental results were (1) an acyl carbonium ion is conceivably capable of being generated by the action of $CrO_3$ on an aldehyde, but that (2) the intermediate in the oxidation of a primary alcohol or aldehyde-alcohol mixture is probably a hemiacetal.

Three new compounds were synthesized. They were (1) 5.6,6-trimethyl-heptene-1-ol-5, (2) 4,5,5-trimethyl-4-hydroxy-n- caproaldehyde (1-hydroxy-4-methyl-4-*tert*-butyl-tetrahydrofuran), and (3) 4,5,5-trimethyl-δ-caprolactone.

A study of the oxidation with lead tetraacetate of triphenyl methane indicated that a triphenylmethyl carbonium ion was an intermediate. This was formed by the action of a methyl carbonium ion produced in the decomposition of lead tetraacetate. Acenaphtheme on oxidation with $Pb(OAc)_4$ yields 80% acenaphthenyl acetate and no $CO_2$ or methane. A tentative mechanism was proposed, which involves the formation of a lead-carbon bond.

## THE SYNTHESIS AND DEHYDRATION OF SOME ALCOHOLS CONTAINING A PHENYL GROUP

Donald Max Simons, Chemistry

Three new alcohols, 3,3-dimethyl-2-phenyl-1-butanol, 3,4-dimethyl-4-phenyl-2-pentanol and *trans*-2-(phenylisopropyl)-cyclohexanol, have been prepared. The first two were dehydrated.

Ozonization of the olefins produced by dehydrating 3, 3-dimethyl-2-phenyl-1-butanol gave acetaldehyde, acetone, methyl isopropyl ketone, phenylacetone and benzaldehyde. The acetaldehyde may be explained by assuming 1, 3-rearrangement of a methyl group during dehydration and the remaining products are accounted for by two 1, 2-rearrangements followed by partial isomerization of the double bond.

Ozonization of the olefins produced by dehydration of 3, 4-dimethyl-4-phenyl-2-pentanol gave acetaldehyde, 3-methyl-3-phenyl-2-butanone and a small amount of acetophenone. The first two products arise from the normal dehydration product, 3, 4-dimethyl-4-phenyl-2-pentene. Evidence indicates that the acetophenone arises from an olefin produced by 1, 3-rearrangement of either a methyl or phenyl group.

It has also been found that organic acids are oxidized by chromium trioxide. It is postulated that the acetophenone produced by chromic acid oxidation of the olefins produced by dehydration of 4-methyl-4-phenyl-2-pentanol arises from oxidation of 4-methyl-4-phenyl-2-pentene to dimethylphenylacetic acid followed by oxidation of the dimethylphenylacetic acid. A mechanism is advanced.

## HEAT TRANSFER AND FLUID FRICTION DURING FLOW THROUGH BAFFLED SHELL AND TUBE HEAT EXCHANGERS

Frederick W. Sullivan, Chemical Engineering

This dissertation presents the results of a study of heat transfer and fluid friction in the shell side of baffled shell-and-tube heat exchangers. The work was undertaken as part of a comprehensive program in progress at the University of Delaware. The purpose of this investigation was to determine the effect of leakage through the annular holes between the tubes and a baffle on the performance of heat exchangers.

In the experimental work heat transfer and fluid friction measurements were made on a heat exchanger with a single baffle. This exchanger was used so that the experimental results could be

readily analyzed. It was found that pressure drop through the experimental exchanger could be predicted by properly combining the results of tests on fluid friction during flow through unbaffled tube banks and on leakage through the annular orifices formed by tubes and a baffle.

Flow of fluid through multi-baffle shell and tube heat exchangers has been analyzed on the basis of the results of the experimental work. This analysis has been reduced to a series of graphs which should prove useful in predicting pressure drop in commercial heat exchangers.

## A SPECTROPHOTOMETRIC STUDY OF LOCAL FLAME RADIATION

Frederick Welty, Chemical Engineering

The spatial distribution of infrared, visible, and ultraviolet radiation intensity in the neighborhood of the primary burning zone of three representative butane-air flames has been extensively investigated. Each flame was maintained between the quartz windows of an enclosed burner so that the flame front was flat and could be viewed edgewise by a spectrophotometer. The aperture of the light gathering optical system was sufficiently narrowed so that radiation was received from only a very thin cross-section of flame. The burner was then moved past the instrument so that radiation intensity as a function of distance from the burning zone — i. e. a physical traverse — was obtained.

Near infrared radiation at three water band peaks was used to measure the temperature and water vapor concentration. Physical traverses at the three wavelengths then gave these quantities in relation to distance from the flame front. The time required for complete combustion could thus be obtained.

The intensity of radiation at visible and ultraviolet wavelengths representative of CH, CC, OH, CHO and background continuum was also studied as a function of distance from the burning zone. The absolute peak intensity within the burning zone, the initial strong rate of decay behind the burning zone, and the characteristics of the more gradual continuation of the decay curves were deter-

mined. The range of radiation intensity for a given emitter from the burning zone to a point 30 mm. beyond was found to vary from 500-fold for OH to 500,000-fold for CH. The inital rate of decay of background radiation was the slowest of all the emitters, with OH next in order; correlation of intensity with distance for the former indicated a 1.5 order mechanism for the decay of the intermediate responsible for the radiation, while for OH a second-order reaction was indicated. The decay rate of CH, CC, and CHO was shown to be extremely rapid immediately behind the burning zone and about the same for each emitter. Beyond the burning zone CHO radiation could not be detected and the survival of CC and CH radiation was found to be strongly dependent on the initial gas mixture composition. The decay curves of all the radiators tended to assume a logarithmic (first-order reaction) decay form at 10-20 mm. from the flame front.

## OXIDATIVE STUDIES OF SOME SECONDARY ALCOHOLS

Rudolph S. Wilsher, Chemistry

The oxidative effect of ceric sulfate on benzpinacolyl alcohol was studied. Addition of the alcohol in a warm acetic acid solution to a slurry of ceric sulfate in acetic acid resulted in 15.5% normal oxidation to the ketone, 30.4% triphenyl carbinol, 27.4% benzaldehyde, and 37.9% tetraphenylethylene. When the alcohol was added to the reaction flask before warming, oxidation yields improved at the expense of dehydration to 55.70% beta-benzopinacolone, 37.75% triphenyl carbinol, 30.20% benzaldehyde and 2.74% tetraphenylethylene. These oxidations were carried out in the 60-65 degree temperature range.

A study of the comparative ease of oxidation between pinacolyl and benzpinacolyl alcohol employing manganese triacetate as the oxidant was made. Benzpinacolyl alcohol was cleaved in the highest yields obtained to date. 89.8% triphenyl carbinol and 95.2% benzaldehyde were recovered along with 6.6% tetraphenylethylene and 1.0% betabenzopinacolone. On the other hand, pinacolyl alcohol gave rise to 12.54% dehydration products, 2.80% acetaldehyde and 3.66% *t*-butyl acetate as cleavage products, 3.41% pinacolone, and 38.1% pinacolyl acetate.

Treatment of benzpinacolyl alcohol with glacial acetic acid at reflux temperature for 24 hours resulted in nearly quantitative dehydration to tetraphenylethylene.

Benzpinacolyl alcohol was treated with benzoyl peroxide, a free radical producer, with no effect.

Studies with manganese triacetate reveal that it does not attack the double bond of tetraphenylethylene. Furthermore, it apparently does not attack ethers or benzene. However, refluxing acetic acid reduces it to the divalent state. The only decomposition product uncovered from the latter was carbon dioxide to the extent of 20%.