

## ABSTRACTS OF DOCTORAL DISSERTATIONS

1953

### REACTION, FLOW, AND RADIATION IN ENCLOSED, PILOT-STABILIZED FLAMES AT LOW PRESSURE AND HIGH VELOCITIES

David H. Archer, Chemical Engineering

It is the purpose of this investigation to study flames at conditions which approximate those in the combustion chambers of jet aircraft at high altitudes. Research has been conducted upon flames burning within a cylindrical, water-cooled combustion chamber with an inner diameter of  $3\frac{1}{8}$  inches. Combustion is initiated, and the flame is maintained burning stably within the combustor by a small stoichiometric  $H_2 - O_2$  pilot flame in the axis of the chamber. The pressure is held constant at 0.20 atmosphere; but the composition, velocity, and turbulence level of the combustible gases entering the chamber have been studied as variables affecting the combustion processes. The composition of the combustibles has been varied from 1.0 to 4.2%  $C_4H_{10}$  in air; the stoichiometric  $C_4H_{10}$ -air mixture contains 3.13%  $C_4H_{10}$ . The cold stream velocity has been varied from 10 to 115 ft./sec.; and the fraction of turbulence has been varied by the use of screens from 0.006 to 0.070.

The objects of study were the following: (1) the stability of the pilot flame; (2) the ignition of the main stream by the pilot; (3) the turbulent burning velocity of the main flame; (4) the burning zone thickness; (5) the chemical reaction time; (6) the progress of the chemical reaction throughout the combustion chamber; (7) flow velocities in the chamber.

## LINEAR POLYURETHANS AND THEIR ALKALI STABILITY

George William Bartels, Jr., Chemistry

Ten new polyurethans have been prepared from the reaction of methylene-bis (4-phenyl isocyanate), 1,6-hexamethylene diisocyanate, and m-tolylene diisocyanate with various diols and diphenols.

The polyurethans were all relatively brittle in nature. The majority exhibited the tendency to form films and fibers. None of the polymers prepared was rubbery in nature. Viscosity studies indicated that relatively high molecular weights were obtained.

The alkaline stability of polyurethans has been found to be very dependent on the structure of the polymers. Those prepared from aliphatic diols were very stable under alkaline conditions while those prepared from diphenols were extremely susceptible to alkaline hydrolysis. The alkaline stability was not affected by the nature of the diisocyanate.

The hydrolysis of the polyurethans was followed by studies of weight recovery, viscosity, and infrared absorption, and by quantitative separation and identification of the hydrolysis products. The formation of polyurea during hydrolysis has been discovered and a mode of reaction postulated which involves a free diamine intermediate. This hypothesis has been verified by showing that the proposed diamine intermediate could attack the urethan linkage to give the polyurea.

## 2,2-DIALKYL-3,5-THIAMORPHOLINEDIONES

John Beeh Bicking, Chemistry

A series of 2,2-dialkyl-3,5-thiamorpholinediones has been synthesized including the compounds 2,2-dimethyl-, 2,2-diethyl-, 2,2-dipropyl-, 2,2-dibutyl-, 2-butyl-2-ethyl-, 2-thyl-2-phenyl-, and 2,2-diphenyl-3,5-thiamorpholinedione. These compounds contain the group  $\text{RRC-CO-NH-CO-}$  which is present in a number of clinically useful hypnotics, sedatives, and anticonvulsants, and were thus thought to be of pharmacological interest. Tests have shown

that the compounds, with the exception of 2,2-diphenyl-3,5-thiamorpholinedione, have significant hypnotic activity in mice.

The 2,2-dialkyl-3,5-thiamorpholinediones were prepared by the pyrolysis of the amides or the ammonium salts of the corresponding  $\alpha$ ,  $\alpha$ -dialkylthiodiacetic acids. A method for the preparation of only  $\alpha$ ,  $\alpha$ -diphenylthiodiacetic had been described previously. The other acids or their amides were prepared most efficiently by the basic hydrolysis of the 5,5-dialkyl-2-imino-4-thiazolidones, and the subsequent reaction of the crude hydrolysates with either bromoacetic acid or chloroacetamide.

$\alpha$ ,  $\alpha$ -Dimethyl,  $\alpha$ ,  $\alpha$ -diethyl-, and  $\alpha$ ,  $\alpha$ -dipropylthiodiacetic acid were also prepared by an alternate, less efficient, procedure. The ethyl  $\alpha$ -bromodialkylacetates were treated with ethyl thioglycolate in the presence of sodium ethoxide to give the diethyl  $\alpha$ ,  $\alpha$ -dialkylthiodiacetates. These esters were hydrolyzed in basic solution to give the  $\alpha$ ,  $\alpha$ -dialkylthiodiacetic acids. The overall yields of the acids obtained by this procedure were low, decreasing with increasing size of the alkyl substituents.

## THE PREPARATION OF HIGHLY BRANCHED SECONDARY ALCOHOLS

Donald Rockey Bradley, Chemistry

The preparation of 2-methyl-1,3-diphenyl-2-pentene-1-one was achieved by the self-condensation of propiophenone in the presence of anhydrous aluminum chloride. In the reaction of this unsaturated ketone with methylmagnesium iodide, no 1-4 addition was observed.

*Tert*-amyl lithium and cyclohexene oxide failed to react in either anhydrous diethyl ether or *n*-pentane as reaction media.

The reaction of di-*tert*-butyl cadmium and methyl- $\alpha$ -chloroisobutyl ketone yielded 20% crude ketonic product when carried out at  $-70^{\circ}\text{C}$ . This product when reduced and purified was shown to consist of a mixture of aldol condensation products. No coupling reaction between the di-*tert*-butyl cadmium and the methyl- $\alpha$ -chloroisobutyl ketone was observed.

*Tert*-butyl lithium and  $\alpha$ -bromoisovaleric acid did not react

either in anhydrous diethyl ether at  $-70^{\circ}\text{C}$ . or in refluxing *n*-pentane as reaction media.

*Tert*-butylmagnesium chloride and isobutyryl chloride reacted to yield 2,2,4-trimethyl-3-pentanone in the presence of metallic copper as catalyst.

## FORCES ACTING IN FLOWING BEDS OF SOLIDS

John Watson Delaplaine, Chemical Engineering

The purpose of this investigation was to determine the internal and external forces or stresses acting in consolidated beds of solids flowing downward in vessels of constant cross section, to show the stress relationships and to determine the characteristics of flowing beds. The general relationships developed are valid for tube diameter to particle ratios greater than 20 and are independent of solids velocity. Equations are presented for calculation of the vertical, radial and shear stresses as a function of fractional radius, bed height, pipe diameter, bulk density, and coefficient of friction of solids on the pipe wall. The experimental data are consistent with theoretical equations developed in this report. Both are used to explain the characteristics of solids flow. In the central portion of the bed all normal stresses and solids properties are constant and particles flow in a rod-like manner. Rotational shear occurs in the outer 25 percent of the bed because of an unbalance of moments, giving rise to a large radial stress gradient and a small velocity gradient near the wall. The contribution of this investigation is to establish laws of solids flow on a fundamental basis.

## HEAT TRANSFER BY FREE CONVECTION TO FLUIDS CONTAINED IN VERTICAL TUBES

Charles Vernon Foster, Chemical Engineering

Heat transfer by free convection to water and two oils contained in vertical tubes has been studied. Temperature profiles at several levels across a diameter of the tube have been determined. The object of this study was the determination of the factors affecting heat transfer by free convection to liquids contained in heated

vertical tubes, closed at the bottom and opening at the top into a large chamber that contained a cooling coil.

Experiments were conducted with brass tubes, one foot in length, with inside diameters of  $\frac{1}{2}$ ,  $\frac{3}{4}$ , 1 and 3 inches. Heat fluxes varied from 230 to 13,300 Btu/(hr.) (sq. ft.). The average temperature drop across the liquid film varied from 9.1 to 171.3 degrees F.

The results were correlated for the three smaller tubes with an equation involving two dimensionless heat-transfer groups: the Grashof number and the Prandtl number. The results for the 3-inch diameter tube followed the theoretical equation derived by Eckert and Jackson for a flat plate.

Temperature profiles for turbulent flow conditions were similar to those found in fixed bed reactors. Turbulent flow conditions were noted in the three smaller tubes at high values of the product of the Grashof and Prandtl numbers. The temperature drop between the inside wall and the fluid at the centerline of the tube decreased from the top to the bottom of the tube. A temperature difference, averaged over the height of the tube, was correlated with the product of the Grashof and Prandtl numbers. This gave a correct value of the average temperature difference for design purposes.

## FLUID FLOW PHENOMENA IN NATURAL CIRCULATION VERTICAL TUBE BOILERS

Girard Edward Golden, Chemical Engineering

This research was initiated in order to gain a knowledge of the phenomena associated with the flow of boiling fluids in tubes. Two 6 ft. heat transfer tubes, 0.75 in. I.D. and 1.00 in. I.D., respectively, were fabricated from brass. The fluids in the tubes, methanol, cyclohexane, benzene, n-pentane and n-heptane, were vaporized by heat transfer oil which passed through an annular space formed by the tube and a  $2\frac{1}{2}$  in. I.D. brass pipe.

Friction factors were calculated assuming homogeneous flow and plotted vs. the average gas phase Reynolds number. With the aid of a dimensionless group it was possible to correlate all the friction factor data obtained in this research. A flow pattern has been proposed for vertical tube boilers operating between 0-100%



quality. At the low range of qualities the flow type is homogeneous while at high ranges it is annular. Between these extremes is a transitional region which is difficult to characterize.

## THE SYNTHESIS OF 5,5-DIALKYLHEXAHYDRO-2-PYRIMIDONES

Richard H. Hall, Chemistry

The 5,5-diethylhexahydro-2-pyrimidone previously made in this laboratory has been tested for pharmacological activity by the Eli Lilly Co. The anticonvulsant properties of this substance made it desirable to prepare a series of 5,5-dialkylhexahydro-2-pyrimidones.

The only known method of forming the 5,5-dialkylhexahydro-2-pyrimidone involves a condensation with the corresponding 2,2-dialkyl-1,3-propanediamine. In this case the condensation was accomplished with ethyl carbonate. The synthesis of the 2,2-dialkyl-1,3-propanediamines was the key to the solution of the problem.

There was only one practical method of preparing these diamines. This difficulty may be ascribed to the character of the neopentyl system. It was found that the reduction of the 2,2-dialkyl-1,3-dinitropropane was the best synthetic route to the diamines. The synthesis of the dinitro compound was carried out by the condensation of a ketone with nitromethane in the presence of a secondary amine.

The following compounds have been made as a part of this work: 2,2-Dimethyl-1,3-dinitropropane; 2-Ethyl-2-methyl-1,3-dinitropropane; 2-Isobutyl-2-methyl-1,3-dinitropropane; 2-*n*-Amyl-2-methyl-1,3-dinitropropane; 2-*n*-Butyl-2-ethyl-1,3-dinitropropane; 2,2-Di-*n*-propyl-1,3-dinitropropane; 2,2-Dimethyl-1,3-propanediamine; 2-Ethyl-2-methyl-1,3-propanediamine; 2-Isobutyl-2-methyl-1,3-propanediamine; 2-*n*-Amyl-2-methyl-1,3-propanediamine; 2-*n*-Butyl-2-ethyl-1,3-propanediamine; 2,2-Di-*n*-propyl-1,3-propanediamine; 5,5-Dimethylhexahydro-2-pyrimidone; 5-Ethyl-5-methylhexahydro-2-pyrimidone; 5-Isobutyl-5-methylhexahydro-2-pyrimidone; 5-*n*-Amyl-5-methylhexahydro-2-pyrimidone; 5-*n*-Butyl-5-ethylhexahydro-2-pyrimidone; 5,5-Di-*n*-propylhexahydro-2-pyrimidone; 4-Methylhexahydro-2-pyrimidone.

STUDIES ON THE PHOSPHOMONOESTERASES OF  
HAPLOID AND DIPLOID *HABROBRACON*

Earl B. Herr, Jr., Chemistry

The present investigation deals with the characterization of the phosphomonoesterases in the parasitic wasp *Habrobracon* and with the determination of phosphatase activity during development.

Activity—pH curves were plotted for seven phosphate esters. These showed that alkaline phosphatase was present in small amounts while acid phosphatase exhibited relatively high activity. For various substrates the calculated value of the Michaelis constant and the pH optimum were correlated with the corresponding pK value. It was apparent that the more basic the substrate the lower the pH optimum and the higher the affinity constant. Rate curves of 3'- and 5'-adenylic acid mixtures indicated that a single enzyme is involved as the dephosphorylating agent.

During the pupal stages of development there is a decrease in phosphatase activity with age for haploid males and diploid females. Females, upon emergence from the cocoon, show a marked increase in acid phosphatase activity. There is a continued increase throughout the adult stage. When they emerge, males show a less marked increase than do females, and the enzyme activity remains constant with age. This difference is due to sex rather than to ploidy. The difference in phosphatase activity between male and female adults was observed when  $\beta$ -glycerophosphate and 5'-adenylic acid were used as substrates, but not when 3'-adenylic acid, uridylic acid, cytidylic acid and guanylic acid were used as substrates. For none of the substrates used was a sex difference observed during the pupal stage. These data point to a difference between males and females during the adult stage.

## MASS TRANSFER IN A WETTED-WALL COLUMN

Eric Ronald Kent, Chemical Engineering

A wetted-wall column, six feet long by 1.063 inches inside diameter, was operated adiabatically and as a partial condenser, using mixtures of ethylene dichloride and toluene. The effect of

concentration, fluid velocities, and amount of reflux on the rate of mass-transfer was investigated in the adiabatic case. In an expansion of the transfer unit concept to the case of partial condensation, new theoretical equations have been derived relating the transfer unit to liquid and gas film resistances, concentration, column height, and amount of condensation. Experimentally, point conditions prevailing inside the column during partial condensation and the overall effect of the amount of condensation on the number of transfer units were determined.

The liquid film mass transfer coefficients of the adiabatic column and the partial condenser are related by a theoretical equation, and a procedure for the design of partial condensers is outlined.

## FLUCTUATIONS OF RADIATION, TEMPERATURE AND ABSORPTIVITY IN TURBULENT DIFFUSION FLAMES

John B. Lyon, Chemical Engineering

A detailed knowledge of the average temperature and radiation distribution in turbulent flames, as well as point temperature and radiation fluctuations with time, is necessary for a full interpretation of nearly all phases of flame research and its application.

For this study, a new type of instantaneous (0.1 millisecc. resolution) absorption-emission pyrometer was built and tested for following the fluctuations of temperature, absorptivity and radiation intensity from turbulent luminous (soot-bearing) diffusion flames. Acetylene two-dimensional and jet flames were mainly studied. Some measurements were made with butane and butane-air flames.

Interchange of the recording equipment permitted the direct determination of the root-mean-square of the radiation fluctuations, the average radiation level, and the average absorptivity and temperature. Another modification of the recording equipment permitted the determination of the "power spectrum" of the radiation fluctuations.

From the instantaneous measurements, probability distributions were determined and interpreted. Also from these data, a coupling of the average temperature and the average absorptivity was



found to exist. In analogy to percent turbulence of velocity, values of the root-mean-square of the radiation fluctuations divided by the average level of the radiation have been given and are termed "the percent turbulence of radiation." This quantity is held to be a measure of the turbulence state in the flame. Power spectra have been measured and compared with a simple mathematical model.

## SPECTROPHOTOMETRIC KINETIC STUDIES OF THE CLAISEN-SCHMIDT CONDENSATION

Alonzo L. Mantz, Chemistry

The Claisen-Schmidt type of condensation between acetophenone and benzaldehyde and two substituted benzaldehydes in the presence of a basic catalyst has been studied spectrophotometrically. The medium in which the reaction was investigated was a 90% by weight ethanol solution. The catalyst was 0.10 N. potassium hydroxide.

The spectrophotometric method was particularly adapted to the study since the wavelength of maximum absorption of the product was considerably far removed from that of the reactants. The rate of formation of the product was used to follow the extent of the reaction with time.

The specific rate constants were calculated at 15° C., 25° C., and 35° C. By use of the Arrhenius equation the energy of activation was found to be approximately 12,000 cal./mol. in each reaction.

By varying the molar ratios of the reactants, the condensation was shown to be a second-order reaction; and by varying the concentration of the catalytic ions the condensation was proven to be base-catalyzed. The effect of substituted groups on the benzene ring of benzaldehyde has been studied. A primary salt effect was realized by introducing various amounts of lithium chloride to the reaction mixture, lithium hydroxide being used as the catalyst.

## QUANTITATIVE STUDIES IN THE ANHYDROUS HYDROGEN FLUORIDE SYSTEM

Albert Gregory Morris, Chemistry

1) This dissertation reports a detailed investigation of the salt-forming reaction of acids and bases in the anhydrous hydrogen fluoride system.

2) The existence of certain basic salts, previously described in the author's M.S. thesis, was confirmed and their formation explained on the basis of the weakness of the acid and the weakness of the base. In the case of tellurium, selenium, and iodine it has definitely been shown that basic salts are formed in the presence of excess acid and are, therefore, not due to a deficiency of acid.

3) The previous investigation of bifluorides has been extended. Bifluorides were obtained with strontium ( $\text{SrF}_2 \cdot 2\text{HF}$ ) but not with calcium or zinc.

4) The reaction between chlorine trifluoride and water was been investigated. The products are hydrofluoric, hypochlorous and hydrochloric acids, chlorine, oxygen and oxygen difluoride.

5) An all-Teflon refrigerated apparatus was designed and constructed for handling liquid hydrogen fluoride solutions.

6) A system for handling and metering (by visual observation) liquid or gaseous hydrogen fluoride, etc., was developed.

7) Previous work found in a search of the literature was correlated into a unified theory of acid-base reactions in anhydrous hydrogen fluoride.

## KINETICS OF GAS-LIQUID REACTIONS: SIMULTANEOUS ABSORPTION AND CHEMICAL REACTION

Robert H. Perry, Chemical Engineering

This dissertation had two main objects: (1) utilization of a high speed electronic digital computer to solve for the first time the differential equations describing the rate of absorption of a solute material from a gas phase by a liquid; and (2) an experimental investigation of the rates of absorption of carbon dioxide by aqueous

solutions of potassium hydroxide in an effort to verify in part the mathematical results mentioned in (1).

By the theory developed, it was found that certain dimensionless variables, such as the ratio of reactants and a variable involving the specific rate constant, initial liquid reactant concentration, and time of phase contact could be used to correlate all of the computed values of the liquid film absorption coefficient, expressed as a fraction of the coefficient that would be realized without reaction.

The results of the experimental work qualitatively confirmed many of the conclusions of the mathematical analyses, one of the main ones being the unique dependence of liquid mass transfer coefficient on the absorption driving force when second-order reactions of finite speed occurred. Quantitative agreement with the mathematics was poor; in all cases the mass transfer rate was lower than had been predicted.

This discrepancy is explained in terms of interfacial resistance, the mathematics having assumed thermodynamic equilibrium between gaseous  $\text{CO}_2$  and dissolved but unreacted  $\text{CO}_2$  at the liquid-gas interface. The magnitude of the interfacial resistance, while of the order of magnitude predicted by recent theory, was found to be a complex function of gas and liquid compositions. It is concluded that interfacial resistance is likely to be important for other similar systems, in which a slightly soluble gas is dissolved under conditions such that the diffusional resistance that is usually present is destroyed by chemical reaction of diffusing molecules.

## THE DIPOLE MOMENTS OF THE METHYL-PHENYL SUBSTITUTED MONOSILANES IN HYDROCARBON SOLVENTS

Robert Crowell Robbins, Chemistry

The polarization of trimethylphenylsilane, dimethyldiphenylsilane and methyltriphenylsilane was investigated in the series of normal hydrocarbon solvents, n-hexane through n-nonane. Any solvent effect on the polarization at infinite dilution was not sufficiently large to show a measurable trend.

This series of substituted monosilanes, because of their small polarities and large range of molecular weights, clearly showed the

failure of a distortion polarization as a direct function of the molar refraction. The apparent dipole moments based on this distortion polarization increased regularly with molecular weight.

The distortion polarization was treated as an additive and a constitutive property, and was also related to the refraction. The dipole moments obtained were 0.31, 0.36, 0.28 D for trimethyl, dimethyl, and monomethyl derivatives respectively. However, as the gross error was approximately  $\pm 0.05$  D the polarities of the three compounds must be considered equal.

The tetraphenylsilane-benzene system exhibited a large departure from the normal behavior of nonpolar liquid systems. A dipole moment of 1.7 D at 25° C. and 1.0 D at 50° C. for tetraphenylsilane was observed. This temperature dependence is probably indicative of an unusually strong solvent-solute interaction.

#### PINACOL-PINACOLONE REARRANGEMENTS INVOLVED IN THE ACTION OF ZINC-ACETYL CHLORIDE ON AROMATIC KETONES

Frank P. Romano, Chemistry

Benzophenone, p-phenylbenzophenone, p-methylbenzophenone, phenyl- $\alpha$ -naphthyl ketone, and fluorenone undergo transformation to corresponding pinacolones when placed in contact with zinc and acetyl chloride in diethyl ether solution.

The beta (ketone) form of the pinacolone occurs nearly exclusively over the alpha (epoxide) form in all cases, the quantity of acyl halide used affecting solely the yield and not the type of product. Paal had claimed that a mole per mole ratio of acyl halide to ketone produced the alpha form, while larger quantities of acetyl chloride produced the beta form.

The mechanism tentatively assigned to this conversion of ketones to pinacolone involves the formation of transient intermediate benzopinacol diacetate. Zinc subhalide free radical ( $\text{Zn Cl}_2$ ), arising from the first reaction between zinc metal and acetyl chloride, attacks the carbonyl oxygen of benzophenone to form the chloro zinc aroketyl ( $\text{O}_2\text{COZnCl}$ ) free radical, which dimerizes to chloro-zinc pinacolate ( $\text{O}_4(\text{CO})_2(\text{ZnCl})_2$ ). This reacts with acetyl chloride

to form benzopinacol diacetate. Zinc chloride, arising from the reaction of zinc subhalide free radical with acetyl chloride, attacks benzopinacol diacetate immediately at basic (oxygen) sites of the acetoxy-groups with subsequent removal of the latter. The tertiary carbonium ion thus formed stabilizes itself by the Whitmore mechanism; namely, phenyl group migration followed by expulsion of acetyl positive fragment ( $\text{CH}_3\text{C}=\text{O}$ ) and ketonization, to give the product, beta benzopinacolone.

Conversion of diethyl ether solvent to ethyl acetate indicates that the former is being attacked by the acetyl chloride-zinc chloride complex formed as the result of Friedel-Crafts reaction between the acyl halide and metal halide.

#### A QUANTITATIVE CHEMICAL AND CHROMATOGRAPHIC STUDY OF CHANGES OCCURRING IN AMINO ACIDS AND OTHER NITROGENOUS CONSTITUENTS IN ETIOLATED SOYBEAN SEEDLINGS

Martin M. Sackoff, Chemistry

This investigation was undertaken to study in greater detail the changes occurring in various nitrogen components, particularly the amino acids, in the cotyledons and embryonic axes of soybean seeds and seedlings during different growth periods.

Soybeans were grown at constant temperature in the dark for periods of one, three, and six days. At zero time and at the end of each growth period the seeds were separated into cotyledons and embryonic axes. Each was fractionated and analyzed for insoluble proteins, soluble proteins, and an aqueous extract containing peptides and free amino acids. Chemical nitrogen analyses were made on each of the isolated fractions.

Protein and peptide nitrogen fractions were hydrolyzed, and each of eleven amino acids determined by quantitative paper chromatography. Chromatograms were also made on the aqueous extract before hydrolysis.

Rapid, significant metabolic changes in growing and storage parts, usually in the opposite direction, were observed. The classic protein degradation and regeneration theory and the dynamic aspects of protein metabolism were confirmed.



It was found that asparagine seems to serve as a detoxifying agent. The changes observed in glutamic and aspartic acids suggest that transamination is a metabolic pathway for the interconversion of these acids. The changes in the percent of arginine nitrogen are spectacular.

## A STUDY OF THE CHARACTERISTICS OF OPEN TURBULENT FLAMES BURNING FROM TUBES

Leon B. Shore, Chemical Engineering

Data are presented for the variation of the turbulent burning velocity for flames burning from 0.4 inch, 1 inch, and 1.5 inch tubes. Velocity in the tube has been varied from 160 cm./sec. to 1,500 cm./sec.; screens have been placed in the tube to vary the percent turbulence; butane and methane mixed with air have been used as fuels.

The burning velocities obtained have been analyzed with regard to relative values of turbulence in the flame fronts as shown by instantaneous schlieren photographs. It is shown that rich butane-air flames are more turbulent than lean butane-air flames.

Chemical analysis data have been taken with a water cooled probe. From these data flame widths have been calculated which show that rich butane flames have a narrower combustion zone than lean butane flames.

Theoretical explanations have been advanced for the data obtained in this work.

## THE OXIDATION OF TETRAPHENYLETHYLENE WITH CHROMIC ACID AND RELATED STUDIES

Frederick Williams Steffgen, Chemistry

The oxidation of tetraphenylethylene has been studied in detail under various conditions of solvent composition, of temperature, and of reaction time. Procedures for working up reaction products to give material balances of 84 to 97% have been given. The results of these studies have been utilized to compare ionic and

free radical mechanisms, each of which could explain the products found.

An obvious need for modifying the very successful Hickinbottom theory for the oxidation of olefins has been presented. The concept of epoxide formation as the first stable oxidation product has been contradicted by the experimental evidence presented. It has been shown that the three products, tetraphenylethylene oxide, benzophenone, and the carbonate ester of benzopinacol, were each the first stable oxidation products formed under anhydrous oxidation conditions.

Three new compounds have been isolated from the oxidation reactions. They are: the cyclic carbonate ester of benzopinacol, the cyclic carbonate ester of 4, 4', 4'', 4'''-tetrabromobenzopinacol and epoxy-tetrakis-(4-bromophenyl)ethane. The structural proof of these compounds is complete.

The oxidation of cyclohexene has been investigated in the light of epoxide formation as a primary stable product. Results of this work show that cyclohexene oxide is too unstable in the reaction mixture to remain in more than trace amounts.

The polymerization and dehydration of *tert*-amyl alcohol with 75% sulfuric acid was performed to obtain 3, 4, 5, 5-tetramethyl-2-hexene and 3, 5, 5-trimethyl-2-heptene. These products could not be obtained free from impurities and were therefore not used in oxidation reactions.

## A STUDY OF HEAT TRANSFER TO ORGANIC LIQUIDS IN NATURAL CIRCULATION VERTICAL TUBE BOILERS

Robert Talty, Chemical Engineering

A study of heat transfer to cyclohexane, methanol, benzene, pentane, and heptane was carried out in two single short-tube natural-circulation vertical boilers. Two oil-jacketed brass tubes, 0.75 in. I.D.  $\times$  6 ft., and 1.0 in. I.D.  $\times$  6.5 ft., were used as test sections. Test fluid stream temperatures were measured at 6 in. intervals along the length of each test section. Point heat transfer coefficients and the amount of vaporization along the test sections were calculated.

The results of the investigation are as follows:

(1) In short-tube boilers the transfer of heat occurs simultaneously by two processes: convection and nucleate boiling. An analysis is presented which accounts for both processes.

(2) There is an upper and a lower limit of vaporization consistent with stable operation in a natural-circulation vertical boiler. The minimum and maximum exit vapor quantities for stable operation are a strong function of the specific volume of the vapor.

(3) A small amount of vapor (approximately 5% of the total exit vapor quantity) is formed in the preheating section of a boiler.

## A STUDY OF SABINENE AND ITS DERIVATIVES

John H. Taylor, Chemistry

The sabinene used in this investigation was obtained from oil of savin by fraction distillation. Five different methods of separation were tried in order to improve the yield and purity of the product. Thermal hydrolysis with alcoholic potassium hydroxide, steam distillation, and fractionation under diminished pressure gave the best results. Sabinene (19-22%) and sabinol (10-14%), each having a high degree of purity, were obtained.

The hydrocarbon and some of its derivatives were hydrogenated with Raney nickel, palladium-black and platinum-black in order to study the products formed. Raney nickel and palladium-black gave five membered saturated and unsaturated monocyclic ring products under controlled conditions; while platinum-black gave preferentially a six-membered bicyclic ring product. These results validated the results and observations obtained by previous investigators.

N-bromsuccinimation of sabinene and its unsaturated hydrogenation product gave two new bromides: sabina bromide and 1,2-dimethyl-3-isopropylcyclopentenyl bromide.

Oxidation of sabinene by ozonization and potassium permanganate yielded sabina ketone. Three new ketols were formed by the reaction of sabina ketone and the Grignard reagent: propylsabina ketol, butylsabina ketol, and amylsabina ketol.

## A STUDY OF CARBOXYHYDROXAMIC ACIDS AND THEIR BENZOYL DERIVATIVES

William Charles Undeutsch, Chemistry

Several new benzoylhydroxamic acids have been prepared and characterized: DL-erythro-3-carboxy-2-methylbutyro-, DL-threo-3-carboxy-2-methylbutyro- and 4-carboxybutyro-(benzoylhydroxamic) acid. These were obtained from the disodium salts of the corresponding unbenzoylated hydroxamic acids. In the case of one substance, 4-carboxybutyrohydroxamic acid, the free hydroxamic acid was isolated and identified. In addition, the disodium salt of 2-carboxy-2-phenylacetoxyhydroxamic acid was prepared and characterized.

In aqueous medium, the Lossen rearrangement of 3-carboxypropiono-(benzoylhydroxamic) acid gave  $\beta$ -alanine, of 4-carboxybutyro-(benzoylhydroxamic) acid, 4-aminobutyric acid, and of DL-threo-3-carboxy-2-methylbutyro-(benzoylhydroxamic) acid, an amino acid and dibenzoylhydroxylamine. The aqueous rearrangement of DL-erythro-3-carboxy-2-methylbutyro-(benzoylhydroxamic) acid gave material resembling a polypeptide. Rearrangement of 4-carboxybutyro-(benzoylhydroxamic) acid in boiling toluene afforded a small amount of infusible material and a monomeric substance. DL-erythro-3-carboxy-2-methylbutyro-(benzoylhydroxamic) acid, when rearranged in toluene, gave polypeptide-like material.

## A KINETIC STUDY OF THE CORROSION OF CADMIUM IN HYDROCHLORIC ACID

Henry David Weaver, Chemistry

The rate of reaction with hydrochloric acid was studied for cadmium electroplated on brass, dipped on brass and molded. The effect of annealing the sample, the effect of rate of stirring, and the effect of gassing the solution with nitrogen were studied. By using annealed samples of molded cadmium, and stirring them at 1200 R. P. M., the rate constant was determined with 0.0050, 0.010,

and 0.020 molal HCl, at 15.0°, 25.0°, and 35.0° centigrade. It varied from 9.8 to 15.5 molality of cadmium ions per square centimeter per second times  $10^{-7}$ .

The activation energy was determined for the three concentrations of acid used. It was between 0.5 to 5.0 kilocalories per mole.

The reaction was of zero-order, and the rate controlling step seems to be the diffusion of cadmium ions through the film of hydrogen gas which surrounds the cadmium sample.

## THE EFFECT OF METAL SALTS ON THE DECOMPOSITION OF TETRALIN HYDROPEROXIDE

Donald Edward Weiman, Chemistry

The investigation of the effect of metal salts on the decomposition of tetralin hydroperoxide has shown that the decomposition rate depends on the concentration of peroxide as well as on the amount of metal salt present. Curves which describe the rates of decomposition are usually "S-shaped," indicating an autocatalytic reaction. The rate expression which described these curves failed, however, to yield constant  $K$  values when the concentration of peroxide was varied to any great extent.

Comparisons between the rates of oxygen evolution and the rates of peroxide decomposition showed that if the amount of oxygen liberated at any time was subtracted from the amount of peroxide remaining at that time a straight line resulted. These comparisons indicated the occurrence of two simultaneous reactions, one of which was zero order and the other autocatalytic.

Coördination of the metal salt by the peroxide is suggested as the criterion for a metal salt to be effective in catalyzing the peroxide decomposition.

The preparation, purification, properties, and analyses of lead II hexahydrobenzoate, lead II 2-ethylhexoate, manganous II hexahydrobenzoate and manganese II  $\beta$ -cyclohexyl propionate are incidentally described.



## SOME DERIVATIVES OF AMINOTHIAZOLECARBOXYLIC ACIDS

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Ethyl-2-bromoacetamidothiazole-4-carboxylate, 2-chloroacetamidothiazole-4-carboxamide, and ethyl-2-bromoacetamidothiazole-5-carboxylate were prepared in an attempt to replace the halogens with the aid of ammonia to give the corresponding ethyl glycylaminothiazolecarboxylate or glycylaminothiazolecarboxamide. In all cases the haloacetyl group was cleaved. With alcoholic ammonia ethyl-2-bromoacetamidothiazole-4-carboxylate gave ethyl-2-aminothiazole-4-carboxylate and 2-aminothiazole-4-carboxamide. With ammonium hydroxide ethyl-2-bromoacetamidothiazole-4-carboxylate gave only 2-aminothiazole-4-carboxamide. Ammonium hydroxide with 2-chloroacetamidothiazole-4-carboxamide gave 2-aminothiazole-4-carboxamide. The reaction of alcoholic ammonia on ethyl-2-bromoacetamidothiazole-5-carboxylate gave ethyl-2-aminothiazole-5-carboxylate.

Ethyl-2-bromoacetamidothiazole-4-carboxylate was condensed with thiourea and aniline in ethyl alcohol to give ethyl-2-(4-(2-aminothiazolyl))-aminothiazole-4-carboxylate, and ethyl-2-phenylaminothiazole-4-carboxylate, respectively. Ethyl-2-phenylaminothiazole-4-carboxylate was amidated to give 2-phenylaminothiazole-4-carboxamide. Similarly 2-chloroacetamidothiazole-4-carboxamide and 5-chloroacetamidothiazole-2-carboxamide were condensed with thiourea to give 2-(4-(2-aminothiazolyl))-aminothiazole-4-carboxamide and 5-(4-(2-aminothiazolyl))-aminothiazole-2-carboxamide. The above compounds were prepared for pharmacological testing.