ABSTRACTS OF DOCTORAL DISSERTATIONS
1955

ANNULAR ORIFICE COEFFICIENTS WITH APPLICATION TO HEAT EXCHANGER DESIGN

Kenneth J. Bell, Chemical Engineering

Coefficients for the annular orifice formed between a circular disc and a cylindrical shell of slightly greater diameter are reported for several orifices having diameter ratios between 0.95 and 0.996 and orifice length-to-width ratios from 0.118 to 33.3. Data are given over an orifice Reynolds number range from 1.5 to 25,000 for concentric and tangent orientations of the disc. Theoretical and semi-empirical equations are developed to predict the coefficients over the range tested and permit extrapolation.

Using the measured coefficients, two methods are presented for calculation of the effect of baffle leakage on baffled shell- and-tube heat exchanger performance. The first method is an empirical correlation of previously reported exchanger data; the second involves evaluating the various leakage streams and their effect on exchanger characteristics.

THE METABOLISM OF FROG SPERM

Gerald S. Bernstein, Chemistry

Some of the metabolic properties of *Rana pipiens* and *R. clamitans* sperm have been studied. The motility of sperm from both species was reversibly inhibited at low oxygen tensions (alkaline pyrogallol chamber) and by $10^{-3}M$ and $10^{-2}M$ HCN. Added glucose did not prevent the inhibition of motility by lack of oxygen or by cyanide.

The average amount of oxygen consumed by unwashed *R. clamitans* sperm during eight hours of incubation at $20.5°C$. was 1.2 l. $O_2/10^7$ cells/8 hrs. Added glucose or fructose did not affect the oxygen consumption of intact sperm, but fructose increased the

oxygen consumption of the sperm when they were mechanically disrupted; this suggests that the sperm contain enzymes capable of oxidizing fructose but that the intact cells are relatively impermeable to the sugar.

There are several available substances that may be used as substrates by frog sperm. *R. clamitans* and *R. pipiens* sperm contain about 2.3×10^{-8} gm. of lipid phosphorus per cell. Suspensions of unwashed *R. clamitans* sperm contain 3 gm. of reducing sugar per 10^7 sperm cells. At least 84% of this is extracellular sugar. Paper chromatographic analyses showed that only one reducing sugar is present; this is an aldohexose (reddish-brown color with *p*-anisidine hydrochloride) and was identified as glucose by its position on the chromatograms.

These data indicate that frog sperm derive energy for motility from aerobic metabolism, possibly involving the oxidation of phospholipids or glucose.

A NEW ALKYLATION MECHANISM

Howard S. Brady, Chemistry

Evidence has been found for a new alkylation mechanism in which R^+ reacts with HR', in the presence of an electrophilic catalyst, to give H^+ and $R-R'$. R^+ represents a carbonium ion. HR' is a saturated aliphatic hydrocarbon containing hydrogen activated by its location in the group $CH-C = C$. Coupling has thus occurred via an ionic rather than a free radical mechanism.

The ionic nature of the oxidation of organic compounds by chromic oxide has been further confirmed.

A new compound, bis(p-phenylbenzhydryl) ether, has been prepared in 70% yield.

THE EFFECT OF COBALTOUS 2-ETHYL HEXOATE ON THE DECOMPOSITION OF TETRALIN HYDROPEROXIDE

Kenneth Roberts Carle, Chemistry

A thorough study has been made of the kinetics of the free-radical, cobalt-octoate catalyzed decomposition of tetralin hydroperoxide in xylene. The k values for the first order kinetics decrease as the hydroperoxide concentration is increased, indicating that products of the reaction act as retarders of the decomposition. Water and α-tetralone were found to decrease the rate of decomposition, while α-tetralol increased the rate slightly. The reaction is second order with respect to the catalyst concentration.

The heat of activation determined from the k values at four different temperatures is 17.4 k cal./mole.

In cyclohexane the reaction shows second order kinetics, while in toluene, xylene, benzene, and carbon tetrachloride the kinetics fit both first and second order initially, but is first order finally. The rates become progressively slower from cyclohexane to carbon tetrachloride, where the reaction stops entirely before reaching 100% completion.

The per cent of ketone formed during the reaction was found to be independent of the catalyst concentration and temperature, directly proportional to the tetralin hydroperoxide concentration and only slightly affected by the solvent and the products of the reaction.

APPLICATIONS OF THE HAMMETT EQUATION TO CHROMIC ACID REACTIONS AND RELATED STUDIES

Peter Schuyler Francis, Chemistry

Several applications of the Hammett equation have been made to reactions involving chromic acid oxidation of secondary alcohols under greatly varying conditions. Rho constants were determined for the following: (a) the reaction of α-phenylethanols with

chromic anhydride in 30% acetic acid-70% water ($\rho = -1.01$), (b) the same reaction in anhydrous 40% pyridine-60% benzene ($\rho = -0.37$), (c) the same reaction in anhydrous benzene without acid or base catalysis ($\rho = -0.52$), (d) the equilibrium between substituted di 2-phenyl-2-propyl chromate esters and α-(p-chlorophenyl)ethanol ($\rho = 0.91$).

The equilibration of borneol, isoborneol and cis and trans 2-methylcyclohexanol under treatment with sodium tertiary butoxide and fluorenone was studied to determine the equilibrium compositions of the isomeric pairs. In both cases equilibrium was found to lie toward the alcohol least likely to be formed in a Meerwein-Pondorff reduction of the corresponding ketone.

A short kinetic study of triphenylmethane oxidation by chromic acid was undertaken to determine the effects of chloride ion, hydrogen ion and substitution of deuterium for the oxidizable hydrogen. The rate of oxidation of deuterotriphenylmethane was approximately one-half of the rate of the non-deuterated hydrocarbon. When chloride ion was present in solution, the reaction was second-order to hydrogen ion and first-order to chloride ion. In the absence of chloride ion the reaction became first-order to hydrogen ion. Triphenyl carbinol was found to be oxidized by chromic acid rather rapidly in the absence of chloride ion but was inert to oxidation when the solution contained chloride ion.

The rates of esterification of some monocyclic and bicyclic secondary alcohols with acetic anhydride were studied. It was hoped that some correlation between the relative rates of esterification and oxidation could be found for these alcohols.

SELECTIVE SOLVENTS FOR USE IN PARAFFIN-OLEFIN SEPARATIONS

John A. Gorton, Chemical Engineering

Hydrocarbons of differing chemical nature but of nearly equal vapor pressure are separated with difficulty by simple fractional distillation. The ease of separation may be improved by distillation in the presence of a selective solvent. Simple theoretical considerations based on the regular solution theory of Hildebrand indicate that, in general, the effectiveness of a solvent for promoting a high

relative volatility of a given hydrocarbon pair increases with the difference in the value of the cohesive energy density for the solvent and the corresponding values for the solutes. However, a large difference in cohesive energy density also promotes low miscibility between the hydrocarbons and the solvent.

This study presents measurements of the activity coefficients for n-pentane and l-pentene, at infinite dilution in numerous solvents, to show the effectiveness of the solvents for promoting the relative volatility of a typical paraffin-olefin pair of hydrocarbons. The results show that with the exception of alcohols and other strongly hydrogen-bonded compounds, the solvents with values of cohesive energy density above one hundred and thirty-five calories per milliliter are quite selective for the paraffin-olefin separation. Among the good solvents were: dimethyl sulfolane, propylene carbonate, dimethyl formamide, nitromethane, acetonitrile, and acetonyl acetone.

Although a preliminary choice of solvents for a given separation can be made from cohesive energy density and solubility considerations, final choice of a solvent would be made by considering other factors as well, such as ease of recovery of solvent, stability, toxicity, and so forth.

THE ADDITION OF BROMIDE TO THE DOUBLE BOND OF BICYCLO [2,2.1] HEPTENE-2 AND ITS DERIVATIVES

Lloyd Kaplan, Chemistry

The structures previously assigned to the dibromoanhydrides prepared by the addition of bromine to the double bond of endo- and exo-3, 6-methylene-1, 2, 3, 6-tetrahydro-cis-phthalic anhydride have been checked by dipole moment measurements. The dibromoanhydride obtained from endo-3, 6-methylene-1-2, 3, 6-tetrahydro-cis-phthalic anhydride has been assigned a new structure; exo-cis-4, 5-dibro-endo-3, 6-methylenehexahydro-cis-phthalic anhydride. This structural assignment was based upon the results of the chemical degredation of the molecule as well as the data obtained from dipole moment measurements.

A third dibromoanhydride in this series was found to have a

dipole moment which was in agreement with only one structure; 4-*endo*-7-*cis*-dibromo-*exo*-3, 6-methylenehexahydro-cis-pathalic anhydride. However this structure was not in accord with the recently reported results of the resolution of the dibasic acid obtained from this anhydride.

Various mixtures of three dibromonorcamphanes were obtained upon brominating bicyclo[2.2.1]heptene-2 under varied reaction conditions. In carbon tetrachloride or carbon tetrachloride containing one equivalent of pyridine, 2-*exo*-7-cis-dibromonorcamphane and trans1, 3-dibromonorcamphane were formed. Using pyridine as the reaction medium, led to the formation of 1-*exo*-6-*endo*-dibromonorcamphane together with 2-*exo*-7-cis-dibromonorcamphane.

The structural assignments given to these dibromides were based upon the dipole moments of these compounds as well as the results of a structure proof involving the conversion of the dibromides to known derivatives of norcamphane.

The stability of the dibromonorcamphanes in the presence of electrophilic catalysts as well as their formation from 3-bromonortricyclene and hydrogen bromide was also studied.

Mechanisms, which are consistent with the previously observed carbon skeleton rearrangements occurring in this system, have been proposed for the formation and isomerization of the dibromonorcamphanes.

THE VIBRATIONAL STRUCTURE AND THERMODYNAMIC PROPERTIES OF DIMETHYL PHOSPHINE

Bernard Katlafsky, Chemistry

Assuming a pyramidal structure with the phosphorus atom at the apex and the two methyl groups and the single hydrogen atom at the corners of the base, a structure corresponding to symmetry species C_s, the twenty-four characteristic modes of vibration of dimethyl phosphine were calculated on the basis of a valence force model by an approximation method. Assignments were made to all the experimentally observed infrared and Raman bands. The moments of inertia calculated from the geometric structure were: $I_x = 131.9$, $I_y = 22.3$ and $I_z = 154.2 \times 10^{-40}$ g cm². Assuming ideal gas behavior, the entropy of the gas at 1 atmosphere pressure and

298.1° K was calculated to be 67.68 cal./deg. mole, and the heat capacity at atmosphere pressure was evaluated over the temperature range of 300 to 1500° K.

NEAR INFRARED SPECTRA OF THE BORON HYDRIDES AND RELATED TOPICS

Eugene Jack Levy, Chemistry

A complete assignment for the observed overtone and combination bands of liquid diborane is presented. The assignment is in agreement with the D_2H or non-planar bridge model and trends to support this structure.

Pentaborane was treated in an analogous manner using the tentative fundamental assignments of Hrostowski and Pimental. The observed near infrared bands were consistent with the infrared active overtones and combinations predicted for a C_{4v} symmetry.

The near infrared spectrum of decaborane was obtained in concentrated solutions at long path lengths. The third overtone of the B-H stretching mode was identified and a quantitative study made of the changes in intensity of the first overtone of the Boron-Hydrogen stretching mode with changes in concentration.

The near infrared spectra of ethylene (liq.), trimethylborine (liq.), and dimethylphosphine (liq.) were obtained and the observed bands tabulated.

THE EFFECT OF OXYGEN ON METHYL VINYL KETONE AND METHYL ISOPROPENYL KETONE IN THE PRESENCE OF FREE RADICALS

Oscar A. Pickett, Jr., Chemistry

The effect of oxygen on methyl vinyl ketone in the presence of free radicals has been studied under constant temperature-constant pressure conditions. As expected, the polymerization of methyl vinyl ketone to high molecular weight polymers was completely inhibited and oxygen was absorbed.

Kinetic studies were made in aqueous systems using potassium

persulfate as an initiator. The rates of disappearance of oxygen and of monomer were followed during the reaction to determine the effect of varying either the monomer or initiator concentration while holding the other constant. The following rate expressions have been calculated:

$$-\frac{dO_2}{dt} = k\,(MVK)^{0.7\pm0.1}\,(K_2S_2O_8)^{0.4\pm0.1}$$

$$-\frac{dM}{dt} = k\,(MVK)^{1.0\pm0.2}\,(K_2S_2O_8)^{0.5\pm0.1}$$

The amount of oxygen absorbed in the reaction is quite insufficient for the amount of monomer used and on this basis it is postulated that dimeric methyl vinyl ketone is formed. There is also corroborative evidence for this assumption. Attempts to prepare a polymeric peroxide of methyl vinyl ketone failed.

Reaction products isolated and identified were carbon monoxide, carbon dioxide, formic acid, and formaldehyde.

Methyl isopropenyl ketone was subjected briefly to analogous reaction procedures. The polymerization to high polymers was completely inhibited and oxygen was absorbed in even greater amounts than in the case of methyl vinyl ketone.

The methyl isopropenyl ketone gave a polymeric peroxide, which was characterized by analysis, molecular weight determination, and qualitative tests for peroxides. The molecular weight was approximately that of a trimer.

A comparison of monomers which have been studied in the presence of oxygen indicates that the peroxide is more stable if there are electron-releasing groups attached to the number two carbon atom of the vinyl group.

REACTION OF OXYGEN WITH METHACRYLONITRILE AND ACRYLONITRILE

Sterling F. Strause, Chemistry

The reaction of oxygen with acrylonitrile in aqueous solution in the presence of potassium persulfate has been investigated. Glyceronitrile was identified definitively as a major product, and a mechanism has been proposed to account for the formation of the other

products from the polymeric peroxide of acrylonitrile through the intermediary glyceronitrile.

The polymeric peroxide of methacrylonitrile, having a peroxide content of at least 21% and a minimum molecular weight of 1400, was prepared by the action of oxygen on the monomer. This reaction was accelerated by ultraviolet radiation. It was found that the peroxide could be analyzed iodometrically by the use of sodium iodide in acetic anhydride. The resulting values for peroxide content showed excellent correlation with the quantitative yields obtained in thermal decompositions. The peroxide was reduced smoothly with zinc and acetic acid to yield the cyanohydrin of acetol.

Decomposition reactions in alcohols and other solvents were investigated, and the products were determined qualitatively and quantitatively. Pyruvonitrile and formaldehyde were found as primary decomposition products, but varying amounts of reductive-cleavage products also were obtained.

The results of these investigations have been correlated with other work in the same field.

SUURFACE PHENOMENA RELATED TO THE BORON HYDRIDES

Harold S. Veloric, Chemistry

The adsorption, desorption, and decomposition of diborane and pentaborane on various solid surfaces has been investigated. The adsorption isotherms, isobars and isosters were obtained for several more active adsorbents. The temperature was varied from— 100° C to 80° C in the pressure range of one tenth to one atmosphere. The calculated isosteric heats of adsorption indicate that physical adsorption is taking place. Infra-red analysis of the gaseous phase indicate that no decomposition occurs at room temperature or below.

REACTION RATES IN ENCLOSED TURBULENT FLAMES

Hermann Eugene von Rosenberg Chemical Engineering

A method is developed for calculating the volumetric rate of generation of a given species of mass for turbulent flames and in particular for turbulent flames burning in a two-dimensional duct. This method is based on the differential equation for the conservation of the species of mass about a differential volume. Since this equation is not amenable to solution for turbulent flames, the rate of generation is obtained by numerically differentiating the experimental data as required and substituting these partial derivatives into the differential equation. In order to check the validity and applicability of this method, it is applied to a stoichiometric propane-air flame with an approach stream velocity of 60 feet per second which is burning in a small, experimental ram-jet type of combustor and is stabilized by a bluff-body flameholder. Averages of the point values of the rates of generation calculated by this method for this flame were found to agree with average rates of generation in incremental lengths of the combustor which were obtained by application of a mass balance for the species of mass over this incremental length. Most of the results obtained in this application could be explained by postulating that the turbulent flame zone is an inhomogeneous mixture of unburned and burned gases on a scale larger than the laminar flame thickness.

KINETICS OF SOLVOLYSIS OF SOME ORGANIC HALIDES

William R. Watt, Chemistry

Rates of solvolysis of some organic halides in mixed aqueous organic solvents have been measured. The halides used were tertiary butyl chloride, benzhydryl chloride, and benzyl chloride. Solvents used were aqueous ethanol, dioxane and acetone containing varying amounts of water from 10% to 80% H_2O. Studies were made at different temperatures to permit calculation of activation energies.

The general shape of the plot of the logarithm of the solvolytic

rate constant versus mole fraction water in the solvolytic media has been determined. It is found to contain regions of near-linearity. In these regions, the heat of activation is nearly constant, showing little change with changes in solvolytic media.

A MECHANISTIC STUDY OF THE HYDROLYSIS OF t-BUTYLCHLORIDE

William C. Wilson, Chemistry

A new method for following the rates of rapid solvolytic reactions has been developed and mathematical equations pertinent to the method derived. The method has been tried and found to yield reproductible results that are in good agreement with values obtained by other methods.

Using the new method, data for the rates of solvolysis of tertbutylchloride in aqueous solutions of methanol, ethanol and acetone have been obtained in regions of high water concentration previously inaccessible because of the rapidity of the reaction.

Various equations predicting the effects of varying the solvent medium have been examined and their merit discussed. A refined method for calculation of activation energies assuming an ionic transition state was tried and found to give results which agree well with the experimental values. The method is found applicable in predicting the effect of changing solvent composition on the reaction rate over a limited range of high aqueous concentrations.

Two deuterium substituted t-butylchlorides were prepared, (d-6 and d-9). Their solvolytic rates were determined at various temperatures in a number of aqueous solvents. The results have been discussed in terms of the ionic intermediate hypothesis and the manner of dependence of the activation energy on the solvating ability of the solvent further established.

THE PREPARATION OF HIGHLY BRANCHED TERTIARY ALCOHOLS AND RELATED STUDIES

Harry W. Wolfe, Jr., Chemistry

A series of highly branched tertiary alcohols has been prepared in yields ranging from 48 to 95%. That this synthesis was possible was due to the technique of adding a highly branched ketone to an alkyllithium at a temperature of — 72° C.

The alcohols isolated from this method were tert-amyl-n-butyl-isobutylcarbinol, b.p.$_{9mm}$ 114°, n_D^{20} 1.4515, d^{20} 0.8530; tert-amyl-n-propylisobutylcarbinol, b.p.$_{10mm}$ 110°, n_D^{20} 1.4538, d^{20} 0.8598; tert-amylisopropylisobutylcarbinol, b.p.$_{10mm}$ 108°, n_D^{20} 1.4550, d^{20} 0.8648; di-tert-butyl-n-propylcarbinol, b.p.$_{9mm}$ 106°, n_D^{20} 1.4578, d^{20} 0.8668; di-tert-butylisobutylcarbinol b.p.$_{10mm}$ 104°, n_D^{20} 1.4578, d^{20} 0.8668; tert-amyl-tert-butyl-n-butylcarbinol, b.p.$_{10mm}$ 126°, n_D^{20} 1.4624, d^{20} 0.8734; tert-amyl-tert-butylisobutylcarbinol, b.p.$_{10mm}$ 119°, n_D^{20} 1.4654, d^{20} 0.8794.

All attempts to prepare an acetate ester of tert-amyl-diisobutyl-carbinol resulted in either dehydration or no reaction, depending on the presence of pyridine.

The formation and thermal decomposition of the xanthate ester of tert-amyl-n-propylisobutylcarbinol gave an 11% yield of olefin which was not identified. The balance of the yield was represented by unreacted alcohol.

The reaction of phosphorous trichloride and tert-amyldiisobutyl-carbinol in the presence of quinoline and chlorobenzene gave a 72% yield of an olefin, b.p. 205-6°, n_D^{20} 1.4441, d^{20} 0.7857. From the ozonolysis of this unsaturated hydrocarbon, isobutyraldehyde and tert-amylisobutyl ketone were isolated.

The dehydration of tert-amyl-n-propylisobutylcarbinol with B-naphthalenesulfonic acid gave a quantitative yield of an olefin mixture with a boiling point range of 25 degrees at atmospheric pressure. From the ozonolysis of an aliquot portion, two normal dehydration products with an accountable yield of 90% was observed in a ratio of 2: 1. The respective components were n-propionaldehyde, tert-amylisobutyl ketone, isobutyraldehyde and tert-amyl-n-propyl ketone. Traces of acetaldehyde and methylethyl

ketone were found, thus indicating that intramolecular rearrangement had taken place.

PURE NUCLEAR QUADRUPOLE SPECTRA AND CHEMICAL BONDING IN THE GROUP Vb TRIHALIDES.

Frederick Oliver Wooten, Chemistry

Equations are derived relating nuclear quadrupole couplings to properties of the chemical bond. The agreement of calculated quadrupole couplings with experiment is within fifteen per cent in all cases for the group Vb trihalides. This variation is less than the estimated probable error due to dipole interactions with neighboring molecules. The agreement is achieved with a consistent variation in bond properties. The anomalous variation in the nuclear quadrupole couplings of arsenic in the trihalides is shown to be consistent with a regular variation in bond properties and need not be due to a change in crystal structure. A new interpretation of the asymmetry parameter for iodine in the tri-iodides is proposed.