A POLAROGRAPHIC STUDY OF α- AND β-ANGELICALACTONE

by

Vance Kirkland
A.B., William Jewell College, 1941
A.M., University of Kansas, 1943

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Advisory Committee:

C. A. VanderWerf
Chairman

C. A. Reynolds
associate chairman

R. Taft

R C Mills

Ernest Griswold

Ray Q. Brewster
Chairman, Dept. of Chemistry

September, 1948

I wish to express my appreciation to the American Chemical Society for the predoctoral fellowship held for two years which has made possible the work in this thesis.

A POLAROGRAPHIC STUDY OF α- AND β-ANGELICALACTONE

Table of Contents

I. PURPOSE 1

II. HISTORY 1

Unsaturated Lactones 1

Olefinic Peroxides 4

Analytical Methods for Peroxides 23

Polarography 26

Polarography of Peroxides 31

III. EXPERIMENTAL 34

Materials and Preparations 34

Apparatus 43

Figure I, Polarographic Cell 45

Figure II, Oxygen Uptake Apparatus 53

Procedure 55

Method of Handling Data 64

Determination of m 66

Diffusion Coefficient of Oxygen 66

Reversibility of Reduction Waves and the Number of Electrons Involved 67

Oxygen Uptake of the Angelicalactones 69

IV. RESULTS 71

Calibration of Capillaries, Determination of m 71

Determination of the Diffusion Coefficient of Oxygen at 0°C. 73

Determination of the Diffusion Coefficient of Oxygen at 25°C. 76

Half Wave Potential of α-Angelicalactone Peroxide: Effect of Concentration, pH and Media 79

Reversibility of the Reduction of α-Angelicalactone Peroxide and the Number of Electrons Involved 81

Oxygen Uptake of α-Angelicalactone at 25°C. 82

Oxygen Uptake of α-Angelicalactone at 0°C. 87

Kinetics of Oxygen Uptake of α-Angelicalactone 95

Half Wave Potential of β-Angelicalactone Peroxide: Effect of Concentration 100

β-Angelicalactone Peroxide: Reversibility and the Number of Electrons Involved in the Reduction 103

Oxygen Uptake of β-Angelicalactone at 25°C. 104

Oxygen Uptake of β-Angelicalactone at 0°C. 108

Kinetics of Oxygen Uptake of β-Angelicalactone 113

Reduction of α- and β-Angelicalactone 114

Reduction of Levulinic Acid and 2,3-Dihydroxy Valerolactone 119

Index of Refraction of α- and β-Angelicalactone 120

V. DISCUSSION OF THE RESULTS 121

Diffusion Coefficient of Oxygen 121
Half Wave Potential of α-Angelicalactone and Reversibility of Reduction 122
Half Wave Potential of β-Angelicalactone and Reversibility of Reduction 125
Reduction of α- and β-Angelicalactone 126
Oxygen Uptake of α-Angelicalactone 128
Figure 3, Polarogram of α-Angelicalactone Solution 131
Oxygen Uptake of β-Angelicalactone 134
Figure 4, Polarogram of β-Angelicalactone Solution 135
Kinetics of Oxygen Uptake of α- and β-Angelicalactone 138
Polarographic Reduction of Levulinic Acid and 2,3-Dihydroxy Valerolactone 139
Postulated Mechanism of Formation of the Peroxide of α- and β-Angelicalactone 140
Index of Refraction of α- and β-Angelicalactone 143
VI. SUGGESTION FOR FUTURE WORK 144
VII. SUMMARY 147
BIBLIOGRAPHY 150

I. PURPOSE

As originally projected, the present work was to consist of a polarographic investigation of the reduction of unsaturated lactones. The behavior of those $\Delta^{\beta\gamma}$-lactones which are catalytically hydrogenated to saturated acids without the appearance of the saturated lactone was singled out for special study; it was hoped that the polarographic method might make possible an unequivocal proof of whether this was a one or two step reduction. On the other hand, other unsaturated lactones are catalytically hydrogenated first to the saturated lactone and the polarograph was expected to show this as a one step reduction.

During the course of the work, the spontaneous formation of a compound between an unsaturated lactone and oxygen was detected. This compound is presumably a peroxide. The direction of this problem then changed to study the oxygen uptake of the unsaturated lactone. It was hoped that, by means of the polarograph and a newly designed polarographic cell, a new method for the quantitative analysis of such olefinic peroxides and some new knowledge concerning their structure and character might be found.

II. HISTORY

Unsaturated Lactones

α-angelicalactone ($\Delta^{\beta\gamma}$) and β-angelicalactone ($\Delta^{\alpha\beta}$) were first reported by Wolff in 1885 (1), later in the same

year by Thorne (2) and still later (1901) by Thiele, Tischbein and Lossow (3). Their preparation consisted essentially in refluxing levulinic acid with acetic anhydride to obtain the α-lactone. The β-lactone was prepared by rearrangement of the α-lactone by catalysis with a tertiary amine such as triethyl amine.

Cavallito and Haskell (105) have shown that alkalies break the lactone ring of α-angelicalacctone with simultaneous loss of the double bond, converting the lactone to a keto acid. Since this double bond seems to be necessary for the antibiotic acctivity of certain compounds containing an unsaturated lactone, alkalies destroy such activity. Also, the mercapto groups of certain compounds such as cystein are generally thought to add across the double bond of unsaturated lactone although no such addition compounds have been isolated. The resulting lactones may then react with an amino group. Such postulated reactions may be of significance as a mode of action of unsaturated lactone antibiotics with sulfhydryl and possible amino groups of enzyme proteins. Mendez (106) has shown that α- and β-angelicalactones produce systolic standstill of the isolated frog heart. Action is shown to be due to the formation of peroxides in the solutions of the lactones; these peroxides are resistant to catalase, but not to peroxidases. Tertiary butyl hydroperoxide causes the same effect, but is not effected by peroxidases.

This systolic standstill is preceded by an increased amplitude of contraction and then diminished relaxation of the ventricle (107).

These lactones are closely related in structure to the strophanthidin group of cardiac aglucones; i.e., digitalis glucosides such as digitoxigenin and gitoxigenin (104), which are also $\Delta^{\beta\gamma}$- unsaturated-γ-lactones. Poist, Blout, Uhle and Elderfield (111) believe that the most outstanding of digitalis-strophanthus group of cardiac aglucones is an unsaturated lactone such as butenolide $\Delta^{\alpha\beta}$ with a cyclopentanophenanthrene joined at the β-position.

The hydrogenation of these unsaturated lactones is interesting. Jacobs and Scott (4) found that the α-angelicalactones catalytically hydrogenates easily with the absorption of two moles of hydrogen to give valeric acid. No saturated lactone could be detected, even when the hydrogenation was only partially completed. On the other hand, β-angelicalactone takes up one mole of hydrogen at the double bond to form γ-valeric lactone. If the reduction is continued without interruption, valeric acid is obtained. But once stopped at the lactone stage, reduction to valeric acid is difficult. The hydrogenation of several isomeric lactone pairs of this type has been investigated by Jacobs and Scott (4)(5) and Mannich and Butz (6). LaForge and Smith (7) investigated the hydrogenation of rotenone, Borsche and Peitzsch (8) investigated the catalytic reduct-

ion of methysticin to tetrahydro methysticin, and Jacobs and Gustus (9) investigated the catalytic reduction of anhydro -γ-isogetongenic methyl ester and γ-digito analdiacid mono methyl ester. In general, lactones in which the γ -or δ- C-atom carries a lactone bond and a double bond reduce to the saturated acid apparently in one step. Other unsaturated lactones hydrogenate in two steps. Jacobs and Scott (4) conclude that, if a substance containing a lactone group and a double bond is promptly hydrogenated to a saturated acid without a break at the one mole stage, then the lactone is that of an enolized keto-acid. Exceptions to this are compounds which have a conjugated double bond and unsaturated lactones substituted in β- and γ-positions.

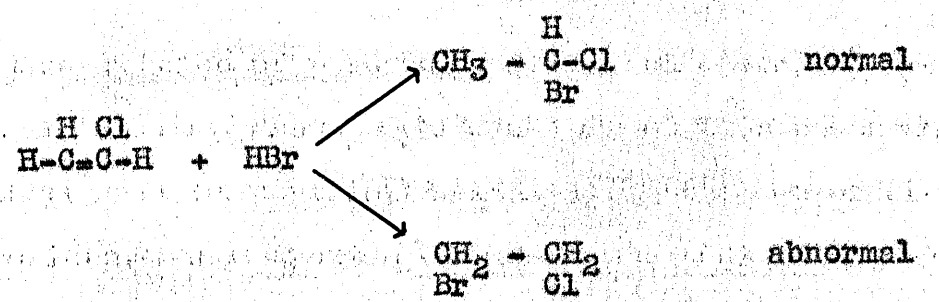
Related to these facts are the findings of Packenforff (10) that levulinic acid, the starting product for the preparation of α-angelicalactone, is catalytically hydrogenated to γ-valerolactones containing only traces of valeric acid.

Olefinic Peroxides

Markownikoff's Rule states that a halogen hydride adds to a double bond with the halogen bonding to the C-atom carrying the smaller number of hydrogen atoms or larger number of alkyl groups. Since the formulation of this rule, Kharasch and co-workers have shown that it holds in the absence of peroxides (and oxygen), but it is reversed

in the presence of peroxides. Kharasch and his co-workers have done a great amount of work on this addendum with subsequent contributions to the knowledge of olefinic peroxides. The peroxide effect on the addition of halogen acids to olefins is limited to the addition of hydrogen bromide since hydrogen iodide and hydrogen chloride add only one way -- the so called normal addition. Hydrogen chloride adds normally to trimethyl ethylene (11), to trichloro methyl ethylene (12), to vinyl chloride when catalysed by ferric chloride (13), to butadiene by 1,2- and 1,4- addition (14), to 2-halo propenes in the presence of ferric chloride (15), and to trichloro ethylene (16). Hydrogen iodide reduces trichloroethylene, but does not add (16); it does, however, add normally to trimethyl ethylene (11), vinyl chloride (13), propylene, butene-1, 4,4-dimethyl pentene-1, and allyl bromide (17), and to propene, 1-bromopropene and allyl chloride (18). This is explained by the fact that hydrogen iodide reduces the peroxides to give free iodine, which is known to catalyze the normal addition (17)(13)(18). Anhydrous hydrogen flouride adds normally in good yields to ethylene, propylene, cyclopropane, cyclohexene (19).

Hydrogen bromide adds according to Markownikoff's Rule in the absence of peroxides and oxygen. In the presence of peroxides, either added or naturally occuring, however, hydrogen bromide adds abnormally, as shown for vinyl chloride (13):



Apparently, some olefins do not form peroxides spontaneously in the presence of oxygen, since it is necessary to add a peroxide such as benzoyl peroxide and ascaridole in order to bring about the abnormal addition. The olefins which do not form peroxides spontaneously include 2-bromo propene, 2-chloro propene (compare with 1-halo propenes) (15), trichloro ethylene (16)(36), trimethyl ethylene (11) (35), isobutylene (29), pentene-1 (30), undecenoic acid (24), methyl acetylene (33), propene (34), butene-1 (26), styrene (35), and higher olefins such as nonene-1, tridecene-1, undecene-1, pentadecene-1, heptadecene-1, nondecene-1, 4-phenyl butene-1, and 6-phenyl hexene-1 (21). Some olefins, however, form peroxides spontaneously as shown by the fact that hydorgen bromide adds abnormally in the absence of externally added peroxides and the normal reaction can be obtained only by conducting the reaction in a vacuum, by distillation of olefin before use, and by the use of anti-oxidants such as diphenyl amine, hydroquinone, and thiocresonl. Included in this group of olefins are allyl bromide (22), 1-chloro- and 1-bromopropene (compare with 2-halo propenes above)(15), vinyl chloride (13), 4,4-dimethylpentene-1 (23)(25), phenyl and butyl acetylene (28),

vinyl bromide (37), undecylenic acid (38), butyne-2 (20), the peroxides of which are sometimes difficult to remove, and trichloromethylethylene (12) which forms peroxides so easily that the peroxide catalysed addition is the only one obtained with hydrogen bromide, although hydrogen chloride adds normally. Butadiene has been reported to form explosive peroxides under pressure (27), and possibly there is enough spontaneous peroxide formation to cause abnormal addition of the second mole of hydrogen bromide, the first mole of hydrogen bromide being unaffected by peroxides (31)(39). It should be remembered that these peroxides are present in small amounts; 0.05 mole of ascaridole or benzoyl peroxide is generally sufficient to cause abnormal addition of hydrogen bromide. The same criterion is used for stating whether olefins form peroxides spontaneously.

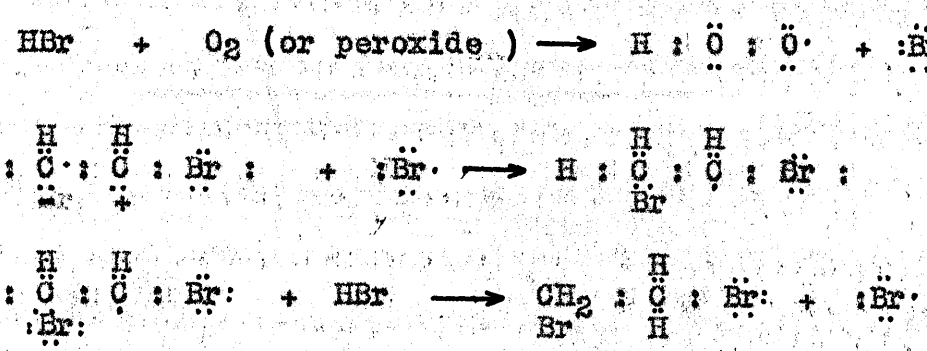
Considerable discussion concerning the effect of solvents on the addition of hydrogen bromide to olefins, both normal and abnormal has appeared in the literature. Kharasch, however, maintains the effect of a solvent is on the peroxide itself and that peroxides are the main factor determining the direction of addition (41)(22)(20)(26)(29)(30)(32)(35)(37). Sherrill, Mayer and Walter (42) and Linstead and Rydon (44) believe the solvent controls the direction of addition, Ingold and Smith (43) believe the internal pressure of the solvent affects the addition. In a series of solvents whose dielectric constants ranged from 1.83 to 80, by controlling the peroxide content, Kharasch and Potts (32)

were able to obtain both normal and abnormal addition although the rates varied. The solvent may affect peroxide conditions from one solvent to another with the same olefin. Michael and Weiner (11) working with trimethyl ethylene reported normal addition of hydrogen bromide in acetone, pentane, carbon disulphide and ethyl acetate, and abnormal addition in "pure" ether, acetic acid and methyl alcohol. On the other hand, Sherrill, Mayer, and Walter (42) observed abnormal addition in carbon tetrachloride, hexane, and acetic acid under dry conditions. Kharasch and Hannum (13) report acetic acid, nitrobenzene and mesitylene have a slight antioxidant effect. Lucas, Dillon and Young (45) obtained only normal addition of hydrogen bromide to 1-butene distilled into acetic acid. Kharasch, Hinckley, and Gladstone (30) found that pentene-1 (no spontaneous peroxide) adds hydrogen bromide normally in acetic acid solution even if ascaridole is added, although this may be due to separation of layers. In propionic acid solution, they were able to get some abnormal addition with the normal addition predominating. Ashton and Smith (24) obtained evidence with undecenoic acid and hydrogen bromide that the solvent effect is on the formation of peroxides. In ligroin or hexane using commercial samples of olefin and in the presence of air, they observed abnormal addition. In the absence of air, addition was normal although the solutions were sensitive to peroxide formation. By purifying the unsaturated acid, they were

able to obtain solutions in these solvents that were insensitive to oxygen, i.e., the addition was normal. With benzene or toluene as solvents, however, the purest undecenoic acid is sensitive to oxygen. Any water in the system causes the solutions to be susceptible to peroxide formation. O'Conner, Baldinger, Vogt and Hennion (46) working on the addition of hydrogen bromide and hydrogen chloride to cyclohexene and hexene-3, showed that the rate of reaction decreases with increasing tendency of halogen hydride to coordinate with a donor atom of the solvent. Thus, there is no connection between rate and dielectric constant; the reaction is fast, in anhydrous benzene (D, 2.27), but slow in dioxane (D, 2.10), since dioxane has two donor atoms.

An inert solvent does slow up the normal reaction by dilution and in some cases where the normal reaction is rapid, the abnormal reaction may be favored by diluting with such a solvent, because the abnormal reaction is a chain mechanism unaffected by dilution. Such a case is that of the addition of hydrogen bromide to butyne-2 (20). The normal reaction is nearly complete in two hours at 0°C. Although the abnormal reaction is not eliminated, it becomes more prominent upon dilution with an inert solvent such as pentane. Another example of this dilution effect is the case of styrene (35). In absence of a solvent, hydrogen bromide adds rapidly by normal addition; a maximum yield of 7% of the abnormal addition is obtainable

in the presence of peroxides. However, in a dilute solution of styrene in pentane, a 80% yield of the abnormal product, β-phenyl ethyl bromide, may be obtained, in the presence of peroxides. The fact that dilution slows the normal addition and does not affect the abnormal addition is taken by Kharasch (15) to mean that the normal addition is an ionic reaction while abnormal addition is a free-radical reaction with a chain mechanism, proposed as follows:



The difference between normal and abnormal addition therefore is the difference between the reaction of a bromide ion and a bromine atom. The peroxide acts as an initiator.

Free radicals, formed from peroxides or other sources, may also start or terminate a styrene polymerization chain (48). By employing p-bromo benzoyl peroxide and chloroacetyl peroxide, Price, Kell and Krebs (49) have shown that the peroxide used to initiate a polymerization chain appears as a part of the polymer. In the polymerization of indene, which is similar to styrene, using p- and o-chloro benzoyl peroxide as catalyst, Breitenbach and Bremer (96) also found the catalyst residues in the polymer. Bartlett and Altschul

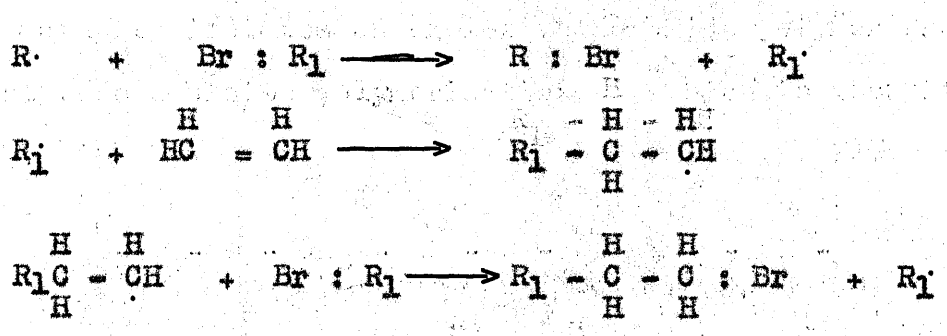
(97) found that in the polymerization of allyl acetate using benzoyl peroxide as catalyst, the benzoyl group is taken into the polymer as the end group. Kolthoff and Dale (50) have studied the emulsion polymerization of styrene with a persulfate catalyst. This catalyst produces free radicals to start the chain mechanism (51), but in the presence of oxygen there is an induction period during which no polymerization takes place. This is explained by a reaction between oxygen and the free radicals from the persulfate and styrene mix to form peroxides. When the oxygen is used up, then the peroxides act as catalysts for the polymerization. Bovey and Kolthoff (52) have actually isolated an explosive peroxide polymer from the styrene emulsion polymerization mix which is thought to be:

$$(- O - O - CH_2 - \underset{\phi}{CH} - O - O - CH_2 - \underset{\phi}{CH} -)_n$$

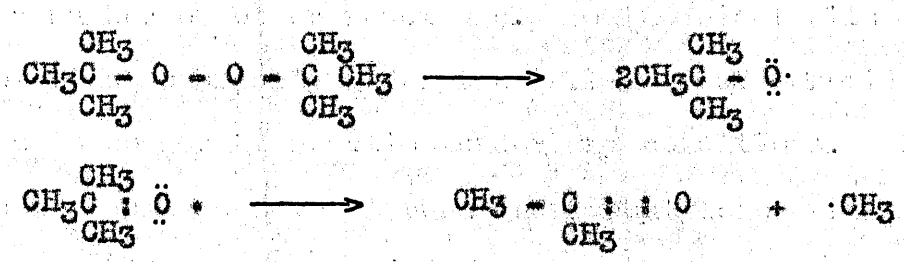
Peroxides can be used as catalysts in several polymerization reactions, such as polymerization of olefins with sulfur dioxide (53)(54) and vinyl acetate (55).

Peroxides, either natural or added, are also catalysts for a number of other reactions. Sodium bisulphite adds to olefins abnormally under the influence of peroxides (56); there is no normal reaction under any conditions. Thioglycolic acid adds to styrene and isobutylene abnormally when peroxide catalysed (57); there is no normal reaction.

Mercaptans add abnormally to olefins when peroxide catalysed, normally when suflur catalysed (62). An old sample of cyclohexene shows strong peroxide properties and reacts with sulfuryl chloride to add a molecule of chlorine at the double bond (58), while freshly distilled cyclohexene under antioxidant conditions does not react. Allyl chloride shows similar behavior, α-bromo carboxylic ester adds to olefins under peroxide conditions (59). Trihalomethanes and carbon tetrabromide add to olefins in the presence of peroxides (60)(61). In the last several reactions mentioned, the reaction is started by decomposition of the peroxide forming a free radical as:

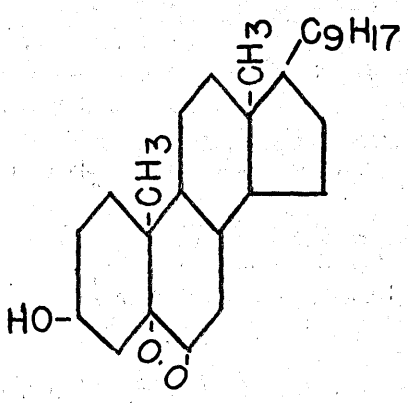


As mentioned above, the peroxide initiated the free radical chain by decomposing into free radicals itself. Rust, Senbold and Vaughan (63) have represented the decomposition of a tertiary alkyl peroxide as:

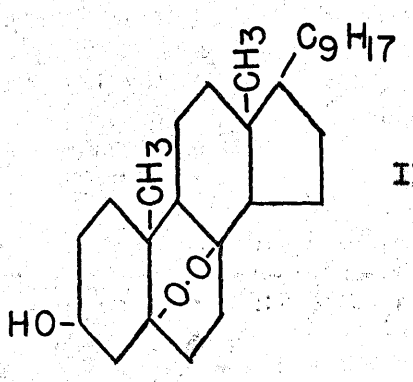


George and Walsh (64) postulated the first break as occuring between the oxygen atom followed by splitting at the weakest bond of the α-C atom other than the C-O bond. The free radical thus produced then initiates the reaction in question.

A peroxide of octahydroanthracene has been isolated by Hock and Lang (99) by shaking with oxygen until uptake had stopped. In this case, illumination with an incandescent or mercury vapor lamp caused decomposition. Windaus (100) obtained a peroxide of ergosterol and proposed the structure I below, while Fieser (101) proposed the structure II below:



I

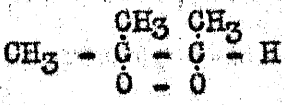


II

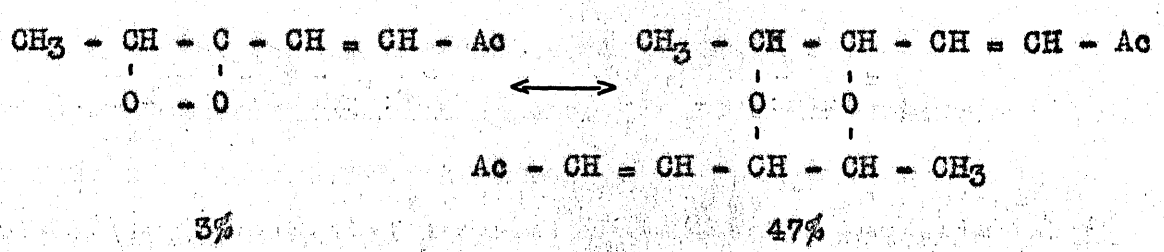
Triebs (102) found that the methyl ester of eleostearic acid is immediately dimerised to a peroxide by molecular oxygen. Without a solvent, this dimeric peroxide is formed of two moles of oxygen and two acid chains, while in acetone solution, only a monomeric peroxide is formed, since it would precipitate dimeric or larger. Methyl ricinenate in acetone absorbs more than two atoms of oxygen per mole of ester in the same way. Franke and Jerchel (103) showed that oleic, linolenic and ricinoleic acids absorb oxygen,

and the results indicate that once formed, the peroxides then decompose to α-hydroxy ketones.

Thomson (65) shook trimethyl ethylene with air and found that it gave a strong peroxide test with potassium iodide. After allowing to set overnight, a precipitate of iodoform was formed. He believed the structure of the peroxide was a cyclic one as:



A similar structure is given by Albers and Schmidt (66) to the peroxide formed by $CH_3(CH{=}CH)_2{-}Ac$ when exposed to the air. In this case, the peroxide values closely follow the oxygen uptake. There is an apparent equilibrium here between a monomeric and dimeric peroxide as:



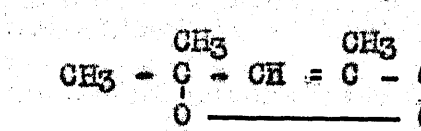
3% 47%

Machu in his book "Wasserstoff peroxyd und die Perverbindungen", reports the work of several authors on peroxides. For example, Engler (67) found that trimethyl ethylene, hexylene, styrol, cyclopentodien and allyl compounds take up oxygen to give a peroxide reaction. The peroxide thus formed can decompose with the formation of further oxidation products. The structure of these peroxides is similar to the monomeric cyclic structure above. Engler and Frankenstein (68) reported

that fulvene, methyl phenyl fulvene and methyl ethyl fulvene form an explosive, colorless diperoxide. Standinger (69) reported diphenyl ethylene forms an amorphous, white, weakly explosive and highly polymerised peroxide on exposure to light and oxygen. This peroxide quantitatively decomposes to benzophenone and formaldehyde when heated.

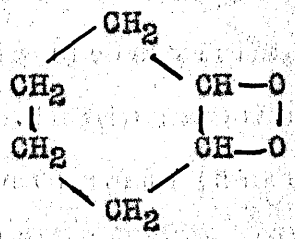
Young, Vogt, and Nieuwland (40)(28) have reported the allyl and phenyl acetylenes, either mono or di substituted, form peroxides. Butyl acetylene was allowed to form a peroxide for several weeks and then warmed to decompose the peroxide. From the viscous lachrymatory liquid obtained, they were able to isolate valeric acid which indicated a cyclic structure of the type given above.

Jacquemain (70), when he experienced difficulty in obtaining a bitertiary diol derivative of acetone alcohol, studied the oxygen uptake of 2,4-dimethyl,-1,3-pentadiene. The speed of this reaction depends upon the temerature and density of illumination in ultraviolet light; the reaction is autocatalytic and is poorly influenced by pressure. In darkness, there is no oxygen uptake while in ultraviolet light, there is a 50% oxygen uptake based on one mole oxygen per mole of diene at 40°C. The incompleteness of oxygen uptake is explained by postulation of a dissociable compound. The peroxide is explosive and could not be purified by distillation; the author gives the following formula:



or a dimer of this compound.

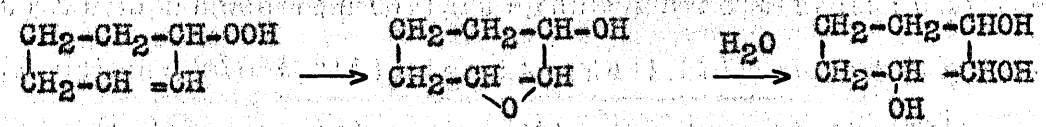
Zelinskij and Borissow (71) described a peroxide of cyclohexene and gave it a cyclic structure as:



Hock (72) in a brief review, describes the preparation, properties of pure peroxides. He includes a peroxide of tetralin and cyclohexene which was obtained in 18% yield in a purity of 97%, M. P. ca 50°. On the basis of its decomposition with H_2SO_4 and sodium hydroxide, he attributes both an open and cyclic form of oxygen attachment. Criegee, Pilz and Flygare (73) prepared the same cyclohexene peroxide by shaking cyclohexene in a quartz flask at 35° in the light of a mercury lamp for only 24 hours (Hock took 200 hours), in order to improve the purity. It was further purified by distillation at 0.3 mm., but even the best product was not absolutely pure because of rapid polymerization. They were able to prepare peroxides of cyclopentene and 1-methyl cyclohexene. α-pinene, camphene, and 1-heptene absorb oxygen too slowly to isolate a peroxide; 1-ethoxy cyclohexene takes up oxygen rapidly, but the peroxide decomposes too rapidly to be isolated. Criegee, et. al., gave the formula for this peroxide as:

The reasons for such a formula are based partly on work of Hock (74);

1. Acids give a mixture of triols, whose formation is explained best by hydration of the oxide formed by oxygen migration of the above peroxide as:

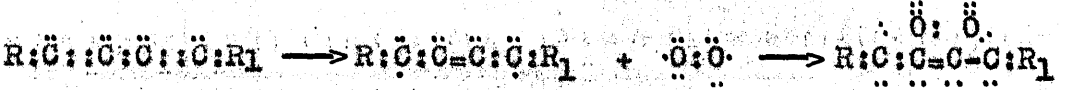


2. Concentrated alkalies give 2-cyclohexanol (reduction product) and a mixture of acids (oxidation products) in which the α-hydroxy acid predominates; 3. It adds smoothly two atoms of bromine; 4. It contains active hydrogen evolving 90% of the theoretical amount of methane based on above formula, with CH_3MgI; 5. It reacts with lead tetraacetate vigorously in the cold with evolution of heat and liberation of oxygen, a reaction given only by a hydroperoxide; 6. The molecular refractions agree better for a hydroperoxide structure than for another. Hock, in a later paper (74), agrees with the hydroperoxide structure.

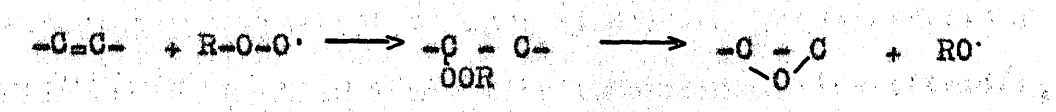
In England, Farmer has done extensive work on the structure of these peroxides and the mechanism of auto oxidation of olefins, and some of his ideas and statements are in order here. In auto oxidation, there is little doubt as to the formation of peroxide groups as the first stage, although only a small amount of the peroxides may remain at the end (75). Much of the earlier literature on the subject follows the Engler-Both idea that the peroxide

formed is the cyclic form given above. But this view cannot be maintained, because the disappearance of unsaturation rarely keeps pace with the incorporation of oxygen, although it is lessened due to secondary reaction and in all unconjugated olefinic systems examined by Farmer, the oxygen appears to enter at the methylenic carbon in the α-position to the double bond and forms hydroperoxides. Absorption is promoted by sunlight or ultra violet light and by numerous chemical catalysts. The hydroperoxides are comparatively unstable and easily decompose at elevated temperature, by prolonged illumination and in the presence of certain chemical catalysts such as iron salts. Several have been isolated, i.e., hydroperoxides of cyclohexene, 1-methyl cyclohexene, 1,2-dimethyl cyclohexene, and methyl oleate can be obtained by fractional distillation at reduced pressure. Experiments have indicated that inductive effects have an important effect in facilitating reaction and locating the point of reaction i.e, α-methylenic substitution resembles side chain substitution rather than nuclear substitution, one would expect the mechanism to be a free radical type rather than an ionic reaction. Also there is no reason why an electrophilic reagent such as oxygen should attack the α-C when there is a higher electron density at the double bond. The C-H bond has a low resonance energy and according to Waters (76), this increases symetrical or free-radical separation, which should be greatest in a media of

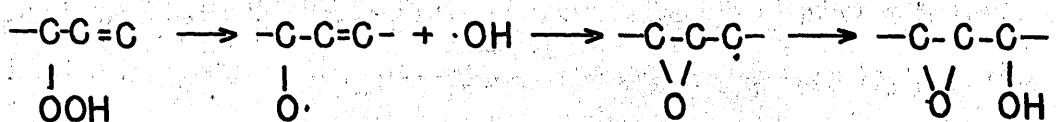
low dielectric constant. Certain cyclic dienes, not open chain, can add oxygen terminally, but probably owing to the paramagnetic character of oxygen and easily assumed free radical phase of the diene, the addition is free radical and not ionic.



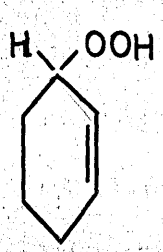
The addition depends on the ability of the ethylenic compound to form the radical form and the ease with which oxygen can form two simultaneous bonds. Thus it is not easily accomplished. Olefins which contain no α-methylene group as as. diphenyl ethylene give polymeric peroxides (77). The principal secondary reaction, which accounts for the decomposition of peroxides shortly after they are formed, is the conversion of the -OOH to -OH with the oxidation of an adjacent double bond or some remote double bond, even a double bond in another molecule, often with the formation of free radicals as:



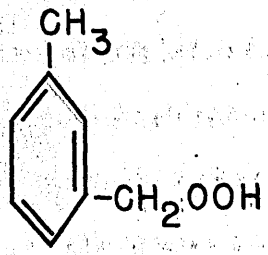
Perhaps a better scheme is similar to that of Hock (74) for cyclohexene peroxide in the presence of acids:



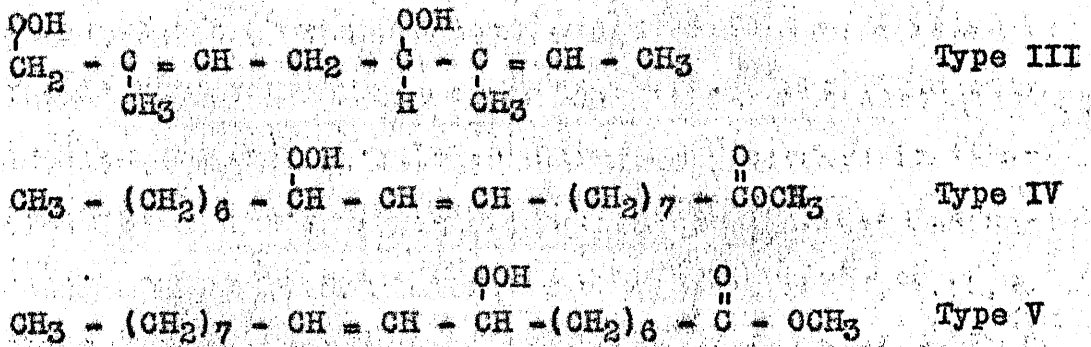
Farmer has classified these olefinic peroxides on the basis of α-methylenic reactivity (78):



Type I



Type II



Type III

Type IV

Type V

Type I includes the hydroperoxides of cyclohexene (79)(80) (73), 1,2--dimethyl cyclohexene (80) and tetralin (73). Type II includes the hydroperoxides of m- and p-Xylene (81), cymene (82), tert. butyl hydroperoxide (83) and other aliphatic hydroperoxides (98), phenyl, dimethyl methane, and diphenyl methane (84), and toluene (benqopropylene)(85). Type III includes the unstable mono and dihydroperoxides of dihydromyrcene which is the example given (86). Type IV is represented by rubber and polyisoprene (87); type V, by oleic acid (88). In all these hydroperoxides the original double bonds remain intact except when secondary decomposition takes place involving the utilization of active

oxygen for attack at unsaturated centers. This decomposition proceeds side by side with peroxidation and it is often almost impossible to arrest, making nearly impossible the isolation of pure hydroperoxides. This applies to mono-olefins. In cases of cyclic-comjugated dienes such as terpinene, 2,4-cholestadiene, ergosterol, dehydroergosterol, anthracene, and rubrene, terminal addition of molecular oxygen seems possible, as mentioned above (89). Groll, Hearne, et. al. (90), Stewart, et. al., (91) and Deanesly (92) have shown that α-methylenic substitution partly or wholly replaces double bond addition.

As mentioned above, Farmer (88) stated that photochemical auto-oxidation of methyl oleate takes place at 35° to give a hydroperoxide group alpha to the double bond. However, Morrell (93) wrote that the peroxide may be formed at the double bond and rearranges into a ketal. Atherton and Hilditch (94) studied the auto-oxidation of this compound and found that the iodine number decreased (formula of Farmer would show no decrease), but not so much as it would if the bound oxygen were held completely at the double bond. They then oxidised the peroxide formed at 20°C. with powdered $KMnO_4$ in acetone according to the directions of Armstrong and Hilditch (95) and separated the products by distillation to obtain four acids, two mono basic and two dibasic. Suberic and nonoic acid were obtained for the hydroperoxide group at C_8 and azelaic

and octoic acids were obtained for the hydroperoxide group at C_{11}, but the results are inconclusive as to the relative amounts of each. If the same procedure was carried out at 120°C., the product was mostly azelaic acid, with some suberic acid. This indicates complete absence of hydroperoxide groups at C_8 or C_{11}, oxidation takes place exclusively at the double bond followed by secondary oxidation at other points since the yields were low. The oxidation at 120° is very rapid compared to that at 20°. The results at 20° give another proof of the structure of olefinic peroxides as given by Farmer.

$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$	Oleic Acid
$HOOC-(CH_2)_7-COOH$	Azelaic Acid
$HOOC-(CH_2)_8-COOH$	Suberic Acid
$CH_3-(CH_2)_6-COOH$	Caprylic Acid(Octoic)
$CH_3-(CH_2)_7-COOH$	Pelargonic Acid(Nonoic)

Peroxides are of interest in the petroleum industry. Undoubtedly most of the work along these lines has not been published and the usual practice is the adding of antioxidants to gasolines and oils which react with and remove the peroxides. However, a few publications may be mentioned here. Peroxides are formed as intermediate products of the oxidation of petroleum products (108). The formation of peroxides is considerably accelerated by light, especially ultra-violet, storage under nitrogen is not completely effective since it does not remove dissolved air, which is sufficient for peroxide formation (109). The susceptibility

to peroxide formation varies with the origin of the gasoline. Generally, a decrease in octane number by peroxides is found only when the product is stored in small containers due to the unfavorable ratio of surface to quantity, and the octane number of synthetic fuels can be largely restored by removal of peroxides. By separating lubricating oil in a Fenske column, Denison (110) showed that alkyl naphtholenes are resistant to oxygen absorption, but naphenes are susceptible. Peroxides are a fundamental part of the chain reaction of oxidation of lubricating oils; the concentration seems to determine the rate of oxidation. Sulfur compounds act as inhibitors to oxidation and seem to be the agents responsible for the stability of straight mineral lubricating oil, although too much sulfur causes the formation of deleterious products by oxidation. Organic peroxides determine the rate of corrosion of bearing metals by converting the metal to oxides which dissolve by reaction with acids developed during oxidations.

Analytical Methods for Peroxides

Many methods of analysis for peroxides are to be found in the literature, both qualitative and quantit ative. Hock and Schrader (112) give a method for determining peroxides in motor fuel which consists of adding excess stannous chloride to the fuel in a carbon dioxide atmosphere. The excess stannous chloride is titrated with ferric chloride with indigo carmine as an indicator in carbon dioxide atmosphere.

Although the results are low, the authors believe the method is better than the iron carbonyl or titanium trichloride methods, which they also investigated.

Perhaps the most widely used method of detection of peroxides involves the use of potassium iodide. The reaction proceeds with the liberation of iodine. The iodine may be titrated with a standard solution of sodium thiosulphate (113). Marks and Morrel (114) titrated excess iodine in acetic acid solution for the determination of peroxides in linseed oil. Paschke and Wheeler (115) found that at least an hour is necessary for complete reaction of potassium iodide and peroxides of unsaturated fat esters, especially for high peroxides values. Nokumura (116) showed that determination of peroxides of soybean oil by the potassium iodide method gives different values depending on the kind of solvents used and the presence of acid constituents. Yamada (117) found that the method of determining peroxides by liberation of iodine from potassium iodide gives false values when the peroxide is an unsaturated compound. Some of the iodine is added at the double bond and the amount absorbed is dependent on the concentration of iodine, since the addition of iodine to a double bond is an equilibrium reaction. The addition of iodine to the double bond of an unsaturated peroxide following the liberation of iodine from potassium iodide was also noticed in the present work. Panyatin and Gindin (118) described a method of measuring peroxides with potassium iodide in

the presence of olefins by treating the sample with excess potassium iodide in alcohol in the presence of sulfuric acid. After reaction with the peroxide, the excess potassium iodide is extracted with water, oxidised with ferric alum and the liberated iodine titrated with standard thiosulphate solution. They say this method is applicable to the determination of peroxides in gasoline.

Kempf (119) has reported a qualitative test for peroxides. A precipitate of as little as 0.001 mg lead sulfide on gelatine paper or unglased white porcelain is bleached by 0.0005 mg hydrogen peroxide or other peroxides by oxidation to lead sulphate. Pratesi and Celeghini (120) reported that 2,5-bis-(2,3-dimethyl-N-pyrrol)-3,6-dibromo hydroquinone (colorless) is oxidized to an intense blue quinone in organic solvents by peroxides and they have used this test to detect peroxides.

Arakawa (121) reported the determination of peroxides by means of milk peroxidase. Poggi (122) decomposed carboxy peroxides with sulfuric acid and determined both oxygen and carbon dioxide in the exolved gas to get two determinations simultanously from the same sample. Gutmann (123) reported sodium arsenite reacts with quadravalent bound oxygen (peroxides), sulfur (persulfides and polysulfides) and quinquivalent nitrogen in azo compounds. Rupp and Siebler (124) treated peroxides with arsenic trioxide and titrated the excess with potassium bromate solution to measure the peroxides. They say these solutions are more

stable than the thiosulphate and iodine solutions generally used. Kienstedt (125) described the reactions of peroxides with mercury, copper and iron carbonyl and the use of the latter in measuring peroxides. Calo and Muntoni (126) recommend titanous sulphate for the determination of peroxides. D'Este (127) described a gasometric method for the determination of peroxides depending on the oxidation of hydrazine to nitrogen. Young, Vogt and Nieuwland (28)(128) described a method for the determination of peroxides based on the oxidation of ferrous sulphate in the presence of ammonium thiocyanate in absolute methyl alcohol. Rostovtseva (129) detected peroxides by adding isotinsulfonic acid and back titrating the excess with potassium permanganate. Müller and Brenneis (130) believe potassium permanganate solution is suitable to titrate hydrogen peroxide, but ferrous sulphate, stannous chloride, chromic acid, and perchloric acid are not suitable.

Polarography

The polarographic method for analysis was invented several years ago by Jaroslav Heyrovsky and shortly afterward, Heyrovsky and Shikato invented the polarograph (131), an automatic irstrument which records dropping electrode current-voltage curves, called polarograms. The development of this method is largely due to Heyrovsky up to the present time and he published many articles, mostly in Czechoslovakian journals. Because of the difficulty of

translating these works in foreign journals, polarography has developed slowly in this country. However, a book on Polarography was written and published in 1941 by Kolthoff and Lingane (132) in this country. The following short discussion of the application of this instrument is taken largely from this book.

The polarographic method is based on the interpretation of current-voltage curves obtained by electrolysing solutions of reducible substances with one electrode consisting of mercury falling dropwise from a very fine bore capillary tube. Electrolysis is the flow of electric current between the solution and the electrodes and the magnitude of the current is a measure of the rate of electrode reactions. Reduction occurs at the cathode, oxidation at the anode. A polarogram is the curve obtained when the applied EMF is plotted against current between the desired potentials. No reduction takes place until the decomposition potential is reached. Then, as the decomposition potential is exceeded, continued electrolysis occurs with resulting reduction at the cathode which is usually the dropping mercury electrode. But, as the EMF is increased, the current approaches a limiting value and generally becomes nearly constant. Under optimum conditions and with all other factors constant, the limiting current is directly proportional to the concentration of the reducible substance and is the basis for quantitative polarographic analysis. During electrolysis, discharge at the cathode

depletes the concentration of substances close to the mercury drop and this loss is compensated for by a diffusion of the reducible substance toward the mercury drop from the bulk of the solution. The rate of diffusion depends on the difference in concentration in the bulk of the solution and the solution in the immediate vicinity of the mercury drop, as well as the nature of the reducible substance. As the EMF is further increased, the concentration of reducible substance near the mercury drop becomes very small because it is electrolysed as soon as it arrives and the difference in concentration becomes equal to the concentration in the bulk of the solution, which is constant. Thus, the amount of substance discharging and hence the current becomes constant from this point, and practically independent of increasing EMF. With an excess of an indifferent electrolyte present in the solution, the limiting current is determined by the rate of diffusion and is called the diffusion current. In order to attain a limiting current, it is necessary that one electrode be very small and the concentration not too large. A condition of concentration polarization is attained. The platinum microy electrode has often been used. Since the mercury drop is constantly changing size, there is actually a current fluctuation between a maximum and a minimum. But if a galvanometer of relatively long period (ca 15 sec.) is used, the observed oscillations are not large and an average current may be measured within 1-2% (that is for the instrument used in

this work, in other instruments, precision is greater than 1%). The average current is independent of time of electrolysis due to the fact that a fresh surface is constantly being formed and each drop is duplicated by its successor. The half-wave potential is characteristic of the electroreducible substance present, i.e., the potential of the dropping mercury electrode against an external reference electrode (in this work, a saturated calomel electrode was used) at that point in the current voltage curve at which the current is one half the limiting value. Whereas the decomposition potential varies with concentration, the half wave potential, $E_{\frac{1}{2}}$, is independent of concentration providing the composition of the solution with respect to foreign salts remains the same and is independent of the particular capillary used and of its drop time within limits. Thus, both a quantitative and qualitative analysis may be obtained from the waves of a single polarogram. A typical polarogram obtained in this work will be found on page 131.

In the field of inorganic chemistry, the polarographic method has been applied to the determination of practically all the common metals and other reducible ions. The method is particularly suited to the determination of traces of materials and several applications of this kind have been made. Oxygen in solution (dissolved, not reacted) gives a well defined wave and this fact has been used in this work extensively. A large variety of organic substances are

reducible at the dropping mercury electrode and give well defined waves. These include aldehydes, ketones, unsaturated acids, nitro and nitroso compounds, azo and diazo compounds, quinones and certain peroxides. Compounds which contain a conjugated double bond are reducible at the dropping electrode, whereas compounds with a single ethylene linkage apparently are not reducible. Organic polarography is more complicated than inorganic because of the variety of unknown side reactions and has not been as extensively applied to organic work, but future use is promising.

Although the polarograph is often spoken of as an analytical instrument, it may be used for other purposes also. For example, Whitnack (142) followed the course of polymerization in a maleic anhydride and styrene or maleic anhydride and vinyl acetate. Maleic anhydride and maleic acid contain conjugated systems and they both give well defined waves on the polarograph. Since neither of the other substances present give polarographic waves, a polarogram of the system shows the amount of maleic anhydride or acid not polymerized. Bovey and Kolthoff (52) used the polarograph to show the amount of poly styrene peroxide present in the polymerization mix of styrene. They also used the polarograph to identify the decomposition products of the peroxide as benzaldehyde and formaldehyde. By means of the Ilkovic equation, the number of electrons involved in the polarographic reduction may be determined if the reduction is reversible and sometimes it can be determined if the

reduction is irreversible. This often gives valuable information as to the reaction of the electroreducible compound in other reactions.

Polarography of Peroxides

Little work has been reported on the application of the polarograph to organic peroxides and no reference to the polarography of olefinic peroxides has been found. It will be seen later in this thesis that this work deals with olefinic peroxides and this is the first work on the subject.

Kolthoff and Lingane write of only a little work on peroxides with the polarograph (132). However, they do state that organic hydroperoxides give waves that are very flat and drawn out. For example, methyl and ethyl hydroperoxides in dilute acid medium start at -0.25 volt and hardly show a region of constant diffusion current, since hydrogen dischargestarts just when the diffusion current is reached (ca -1.7 volt vs. SCE). Apparently, the pH has little effect on the"reduction potentials", which should not be confused with the half wave potential. The "reduction potential" is the potential at the beginning of the wave, measured by empirical methods. These peroxides decompose in alkaline media, in 0.1 N lithium chloride, the diffusion current is proportional to the concentration of the peroxide.

Polarograms for hydrogen peroxide, methyl hydroperoxide, ethyl hydroperoxide and diethyl peroxide have been reported

by Dobrinskaya and Neiman (134)(135) and by Shtern and Pollyak (133). These authors report their method for determining these peroxides in the presence of formaldehyde and acetaldehyde. These authors do not agree however on the reduction potentials. Bovey and Kolthoff (52) reported that polarograms of the polystyrene peroxide they isolated from the emulsion polymerization of styrene in the presence of oxygen are very similar to those of Shtern and Pollyak (133) for diethyl peroxide. These polarograms were run in a solution of ammonium acetate in a benzene-alcohol-water mixture. The polarogram of diethyl peroxide is long and drawn out.

Vitek (136) ran polarograms on solutions containing dissolved air and reported that oxygen gives two reduction waves. This method permits the determination of oxygen, hydrogen peroxide, and peroxides in solution and in a gas after bubling it through a suitable liquid. Petering and Daniels (137) reported the use of the polarograph for the determination of dissolved oxygen in biological substances. This work consisted in the measurement of the current at two different voltages and relating the difference in current to the oxygen content. Ingols (138) reported the use of the dropping mercury electrode at constant voltage for the determination of oxygen in sewage. Beecher, Followsbee, Murphy and Craig (139) diagramed a cell in which biological substances such as lymph could be placed out of contact with air and polarograms made on as little as one milliliter

of substance. The latest and most complete work of the polarography of oxygen is that of Kolthoff and Miller (140). Of the two waves obtained, neither is reversible, but the first wave with $E_{\frac{1}{2}}$ below -0.1 volt can be used for oxygen determinations while the second wave with $E_{\frac{1}{2}}$ at about -0.9 volt has a low slope and is difficult to work with. They give the reductions as:

First wave	$O_2 + 2H^+ + 2e \longrightarrow H_2O_2$
Second wave	$H_2O_2 + 2e \longrightarrow 2OH^-$

A polarographic study of pentenoic acids has been made by Zambotti (141). He reported that there appears to be no polarographic difference in the properties of the double bond in the α-, β-, or τ-positions in the pentenoic acids. The difference in the biological activity must be referred to the influence of enzymes and not to substrate.

III. EXPERIMENTAL

Materials and Preparations

1. Levulinic acid:

Some of the levulinic acid, technical grade, was purchased from the Pfanstiehl Chemical Company, Waukegan, Ill.

Some of the levulinic acid was prepared according to Organic Synthesis, Col. Vol. I, page 335. About 500 grams of cane sugar, 250 ml. of concentrated hydrochloric acid and one liter of water were mixed in a two liter flask and heated on a steam bath for twenty four hours. The mixture was filtered and the carbonaceous material washed with 300 ml. of water. The filtrates were combined and evaporated to dryness on a steam bath in a stream of air. The black residue was powdered and extracted with 500 ml. of ether for 6-8 hours. The ether was then removed by distillation and the levulinic acid distilled under reduced pressure. About 80 grams of product boiling at 135-140/10 mm was obtained.

For polarograms of levulinic acid, the acid used was distilled at reduced pressure. The acid, (b.p. 100-102°/3 mm) was crystallised by cooling in a stream of cold tap water. It melted at 30-31°.

2. α-Angelicalactone:

This lactone was first prepared by Wolff (1), but the procedure of Thiele, Tischbein and Lossow (3) was used because it gives better yields.

Levulinic acid, (11.6 grams, 0.1 mole) and 20.4 grams of acetic anhydride (0.2 mole) were mixed with one milliliter of acetyl chloride in a 100 ml. flask joined to a 4 inch claisin arm by means of a ground glass joint. The pressure in the system was lowered to 200-230 mm and the flask warmed slowly to about 130° by means of a heating bath. Acetic acid, b.p. 80°/200 mm, distilled off first, then acetic anhydride, b.p. 105°/200 mm. The vapor temperature rose slowly to about 105° and then dropped off. The distillate receiver was changed and the heating bath temperature was slowly increased. Material was collected up to about 160° C. This required about 6-8 hours. The acetyl levulinic acid first formed decomposed during this distillation and the lactone came over slowly. Thiele, et. al., suggest fractionation of this last fraction, but in this work, a fractionation was found unnecessary. The last portion distilling from the acetic acid-levulinic acid mixture was poured into three times its volume of ether and carefully washed three times with potassium carbonate solution made by dissolving 50 grams potassium carbonate in 100 grams water. For the first washing, a large excess of the potassium carbonate solution was used because the ether solution contained considerable acetic acid and acetic anhydride which had to be neutralised. There was considerable foaming. After washing, the ether solution was carefully separated from the water solution and dried over drierite. Then the ether was distilled off and 4.9-6.4

grams (50-65%) of α-angelicalactone, b.p. 58-59°/15 mm, was obtained. The ether solution had to be distilled within 24 hours of the time it was put over drierite. If left longer over drierite, the yield was low, possibly due to polymerization.

3. β-Angelicalactone:

The β-angelicalactone was prepared from α-angelicalactone according to the method of Thiele, Tischbein and Lossow (3).

α-Angelicalactone (39 grams) was mixed with 1 ml. triethyl amine and warmed on a steam bath for 3 hours. After cooling, an equal volume of ether was added and the mixture washed twice with 1 molar sulfuric acid saturated with sodium sulfate. The ether solution was then washed twice with a concentrated potassium carbonate solution made as described for the preparation of α-angelicalactone. The ether solution was then carefully separated from the water solution and dried over drierite for 24 hours. The ether was then removed and the β-angelicalactone distilled at reduced pressure. About 13.5-17.5 grams (35-45%) of product boiling at 88-90°/16 mm was obtained. Some tar was left in the flask. The amount of tar increased and the yield decreases if the ether solution was left drying over drierite more than 24 hours. A few drops of α-angelicalactone distilled before the β-angelicalactone started distilling.

At one time, triethyl amine was not available and an attempt to substitute tri-n-butyl amine as the isomerization base was made. When the above procedure was followed, a large forerun, b.p. 56-75°/10 mm, was obtained. The forerun and the main fraction separated into two layers. The upper layer nearly completely redistilled at 94-95°/16 mm; the lower layer again gave a large forerun from 65-84°/15 mm. Since the boiling point of tri-n-butyl amine at 10 mm is 90°, these distillations indicate that this amine was incompletely removed by the dilute acid washing. Since there is only 7-8°C difference in the boiling points of the amine and the lactone, separation by distillation was difficult when n-butyl amine was used. However, the triethyl amine can be easily separated by distillation because its boiling point is only 89° at atmospheric pressure.

At another time, an attempt was made to purify the β-angelicalactone by fractionation through a four foot column packed with glass helices and having an efficiency of about 20 theoretical plates. In this case, a large forerun of α-angelicalactone was obtained and most of the material distilled at 76-78°C at 10 mm pressure. When the distillation was changed to total reflux, the vapor temperature dropped to the boiling point of the α-angelicalactone and only slowly raised when distillate was collected at a reflux to take off ratio of 10 to 1. In the previous preparations, the β-lactone had been distilled through a 4-6

inch claisin distilling arm and the boiling points agree with that of Thiele, et. al. This indicates considerable conversion of the β-lactone to the α-lactone by prolonging heating such as that occuring in the fractionating column.

Wolff (1) stated that the β-lactone, as prepared above, contained some of the α-lactone. Anwers (143) measured the refractive indices and other physical properties of these lactones and found that the β-lactone always showed low refractive and dispersive properties when prepared according to Thiele. For the preparation of β-angelicalactone free from the α-lactone, the method of Wolff was adopted. This procedure utilises the property of the α-lactone to be completely hydrolysed by warm water in 3 hours, while the β-lactone is only slightly hydrolysed.

β-Angelicalactone (9 grams, b.p. 65-71/12 mm) as prepared above was heated on a steam bath with 30 grams of water for four hours (the lactone dissolves). The solution was then cooled and neutralised to litmus with a small amount of calcium carbonate. The solution was then extracted five times with an equal volume of ether, the ether extracts combined and dried over anhydrous sodium sulphate for twenty four hours. The ether was then removed and the lactone distilled under reduced pressure to give 4.5-5.5 grams (50-60%) of product, b.p. 81-81.5°/10 mm. The ether extractions of the water solution was easier and took half as much ether as above if the water solution was first saturated with potassium carbonate, but when this is done, the yield was lower and

more tar was left in the distilling flask. Refluxing the water solution of the lactone by means of a Glascol heater instead of only heating on a steam bath gave the same results with a possible small decrease in the yield. No α-angelicalactone was detected during the distillation.

β-Angelicalactone, (15 g.), purified by heating with water as given above, was further purified by dissolving in 60 ml. water and heated on a steam bath for twelve hours and then separated by the same procedure as above. The yield of product boiling at 81-83°/10.5 mm. was 8 grams. (53%)

4. 2,3-Dihydroxy Valerolactone

This compound was prepared by oxidation of β-angelicalactone with potassium permanganate after the method of Thiele, et. al. (3). The α-angelicalactone does not yield a hydroxy compound by the same procedure.

β-Angelicalactone (9.8 grams, 0.1 mole) was dissolved in water in a minimum amount of water. The solution was cooled to 0°C. in an ice bath. Then an equimolar amount of potassium permanganate and magnesium sulphate in enough water to make the added solution 5% in potassium permanganate was slowly added. This solution was made by dissolving 10.5 grams potassium permanganate and 8 grams magnesium sulphate in 200 ml. water. The oxidation is exothermic and the permanganate solution should be added slowly enough that the temperature can be kept near zero. When the addition was completed, the mixture was set aside for five minutes. Then the solution was warmed to 50° for a few minutes and the manganous dioxide filtered off. The filtrate was acidified

with sulfuric acid to the end point of methyl orange (solution turns from brown to yellow) and the solution evaporated to dryness at reduced pressure. The brown residue remaining was shaken loose and extracted several times with warm ether, the mixture being filtered through a fritted disk filter after each extraction. The ether filtrates were combined and evaporated in a stream of air. The solid so obtained was further dried on a clay plate. The yield of product melting at 95-98°C. was 1 gram (7.5%). Exactly 0.3 gram of this crude product was dissolved by warming in 2 ml. of ethyl acetate and then chilled in an attempted recrystallization after the method of Thiele, et. al. The material, however, did not precipitate, even after the solution had been stored in the dry ice chest overnight. It was necessary to evaporate the solution in a stream of air. When about three-fourths had evaporated, a mush was obtained and dried on a clay plate. The white crystals melted at 99-100°C.

Purification by sublimation was unsuccessful. At 2 mm. pressure, a white powder, which melts at 175-179° and boils at 180-183°, sublimes at 90° C.

4. Buffer solutions:

A series of buffer solutions were made according to Clark and Lubs and given by Kolthoff and Laitinen (144), page 32-37. The weights of solids given are those dissolved in a liter of solution and the pH was measured by a Beckman pH meter.

NaOH	1.91	grams	0.048 moles
$KHC_4H_4O_4$	20.4		0.10
		molarity	0.148
		pH	4.84
NaOH	3.64	grams	0.091 moles
$KHC_4H_4O_4$	20.4		0.10
		molarity	0.191
		pH	5.44
NaOH	4.74		0.059
KH_2PO_4	27.2		0.10
		molarity	0.159
		pH	6.94
NaOH	3.74		0.094
KH_2PO_4	13.6		0.10
		molarity	0.194
		pH	8.04
NaOH	1.70		0.043
KCl	7.40		0.10
H_3BO_3	6.20		0.10
		molarity	0.243
		pH	8.78
NaOH	3.31		0.083
KCl	7.40		0.10
H_3BO_3	6.20		0.10
		molarity	0.283
		pH	9.52-9.88

5. Tetramethyl ammonium bromide:

The tetramethyl ammonium bromide was obtained from Eastman Kodak Company. It was necessary to recrystalize the salt several times to remove impurities sufficiently so that the salt could be used as a polarographic electrolyte. Several references for recrystalization of this salt were found (132), but no procedures were given. The following procedure was adopted.

The impure salt (20 grams) was dissolved by warming in 20 grams of distilled water and filtered through a heated filter. Then 40 ml. of ethyl alcohol (95%) was added slowly with vigorous stirring and the mix chilled in an ice bath. After complete crystalization, the salt was filtered and dried in a vacuum desicator on a clay plate. The salt may be recrystalized again without drying completely. The crystals above were filtered on a vacuum filter and dissolved in two thirds their weight of water. To precipitate, alcohol equal to twice the weight of crystals was added. The yield is 40-50%, but the remainder of the salt may be recovered by evaporating the filtrate to dryness. This salt cannot be left on the clay plate to dry for long periods of time. If left for more than twenty four hours, impurities are formed in the salt which interfere with polarography.

6. Saturated calomel electrode:

Several calomel electrodes were made, but the most

useful model, prepared according to the directions of Kolthoff and Laitinen (144), page 84-85, is shown in Figure I, page 45.

Triple distilled mercury was added in the bottom of the cell until it covered the platinum sealed through glass electrode. On top of the mercury was placed a layer of paste made by grinding mercury and mercurous chloride together in a mortar. Then a saturated solution of potassium chloride was added till the end of the connecting tube was covered. The connecting tube had been previously filled with agar and saturated potassium chloride solution and allowed to solidify in the connecting tube. The agar for the connecting tube or bridge was prepared by warming 30 grams of potassium chloride, 3 grams of agar and 100 ml. of water until the solids were completely dissolved. After the bridge was filled, the agar was stoppered and set aside. The next time agar was needed, it was warmed until it melted and used as before.

Apparatus

In this work, a Heyrovsky Model XII polarograph built by the E. H. Sargent and Company was used. This instrument automatically records the current voltage curves on photographic paper. The curves are obtained by developing the paper by the usual photographic procedures. A typical polarogram obtained in this work is shown in Figure III.

A polarographic cell was designed and built of pyrex

glass so that it could be connected with a gas burrette and the oxygen uptake correlated with the polarographic diffusion current. A drawing of the cell is shown in Figure I, page 45.

The essential features of this cell are an inlet at the bottom for introducing mercury, a capillary outlet at the top of the cell for introducing solution and oxygen, and two electrode leads into the solution contained by the cell. One electrode is a tube sealed with a ring seal through the side of the cell, ending with a fritted disk in the solution. When the fritted disk is backed up with agar saturated with potassium chloride, no solution passes through the disk. A saturated solution of potassium chloride was poured over the agar above the fritted disk and the agar bridge of the saturated calomel half cell dipped into the saturated potassium chloride solution. For the dropping mercury electrode, a 12 mm. I. D. tube was sealed through the top of the cell by means of a ring seal. The lower end of this tube is a 12/15 standard taper ground glass female joint with ground surface on the inside, that is, the joint is reversed as compared to normal ground glass joints. The capillary shield is essentially a 12/30 male ground glass joint cut off near the joint and with a 8 mm. I. D. tube sealed on the smaller end which leads down into the solution. At the lower end of this capillary shield is a female ground glass joint with the ground surface on the inside, approximately 5/20 standard taper size. The dropping

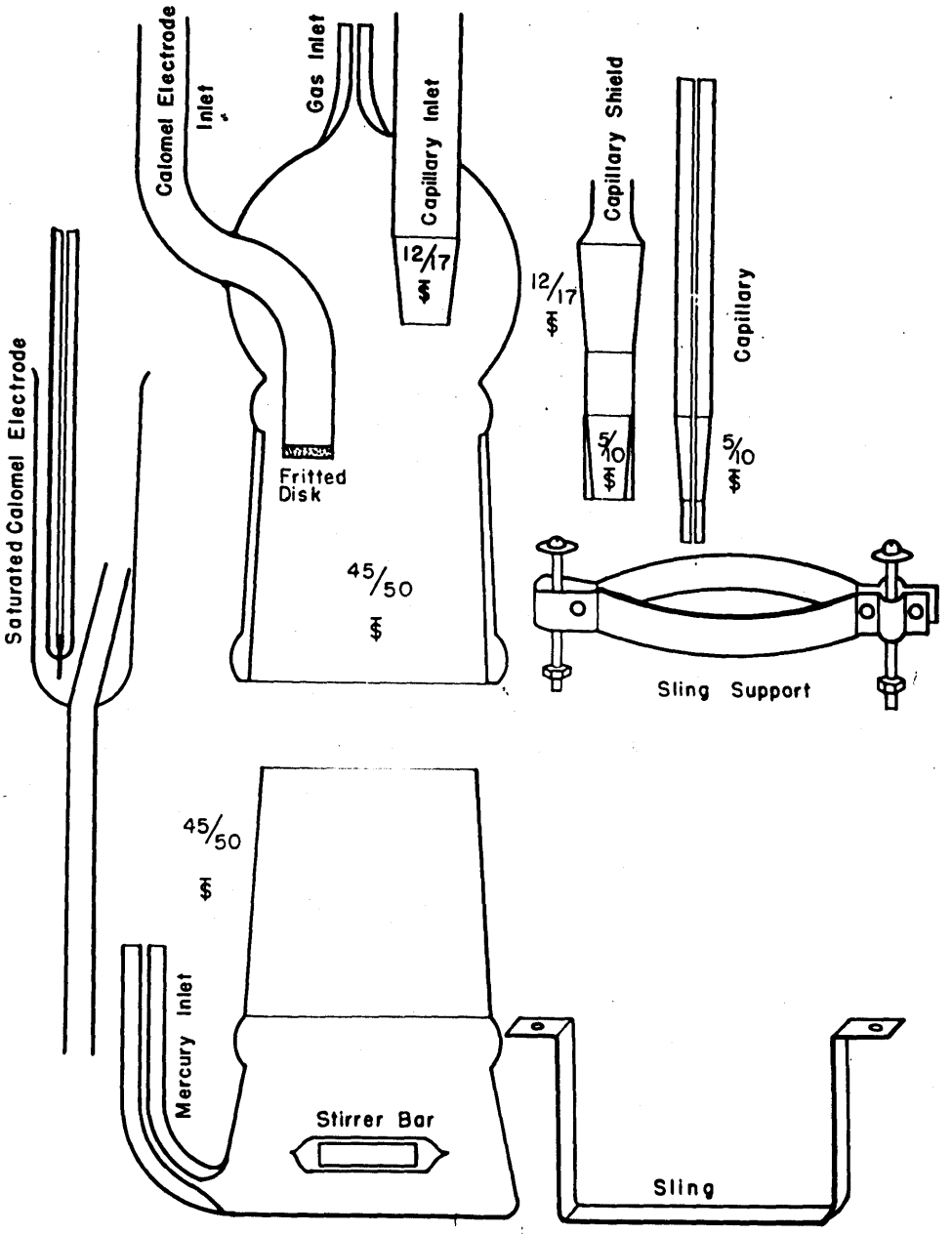


Figure 1. Oxygen Uptake — Diffusion Current Cell

mercury electrode capillary is 6 mm. I. D. marine capillary tubing, 0.05 mm. I. D., and is available commercially. It has a taper ground on the end approximately 5/20 standard taper so that it fits the joint at the lower end of the capillary shield and protrudes through the capillary shield and past the end from 3 to 10 mm. The ground glass joint on the end of the capillary and the joint at the lower end of the capillary shield were made by the author and the method of grinding them will be discussed later in this thesis. Both electrodes are made to just make contact with the liquid solution and not extend far enough so that they will be hit by a stirrer bar. The stirrer bar is a glass enclosed magnetic bar floating on the surface of the mercury which was made to stir the solution by means of a magnetic stirrer placed below the cell and a copper temperature bath. The top part of the cell contains the two electrodes and the oxygen inlet and is made of a female 45/50 standard taper joint. The lower part of the cell contains the mercury inlet and is made of a male 45/50 joint with a flattened bottom as shown by Figure I, page 45. Since the cell was completely filled with mercury at times and became heavy, it was necessary to construct a sling of thin copper stripping to hold the cell together. A copper strip 2 mm. thick and 8 mm. wide was bent around the joint of the upper part of the cell so that it caught on the lip of the lower end of the female joint. This strip was bent with a loop on one side of the cell and the two ends on the other side of the cell at right

angle to the cell. The strip was tightened around the cell with bolts and nuts through the right angle loop and through the ends protruding at right angle to the cell. The right angle loop and the ends at right angle to the cell serve as support for the copper sling passing under the bottom of the cell. This sling was copper stripping, 0.5 mm. thick and 6 mm. wide, and flexible. The ends were soldered to short right angle bends of the heavier copper stripping mentioned above which have holes drilled through the center of the part of the bend parallel to the bottom of the cell. Small bolts through these holes and through the supports on the top part of the cell were screwed through small nuts to hold the sling firmly to the supports on the upper part of the cell and thus hold the two parts of the cell together.

It is believed this work is the first time a dropping mercury capillary with a ground joint has been used. The advice of Mr. Fred Rustenbach, glassblower for the University of Kansas, concerning the grinding of these joints is fully appreciated. On end of a soft iron rod, 6 mm. diameter, was tapered on a machine lathe to make a mandel. This tapered end has the taper to be ground into the glass and if the iron rod has a standard taper, the joint will be standard taper. In this work, the mandel was a fraction of a millimeter different from standard taper and the joints did not quite fit a standard taper joint. The end of an 8 mm. I. D. pyrex tube was heated in an oxygen torch to thicken the walls and shrink the walls of the tube at the end. It was heated in such a

way that a taper was formed on the inside of the tube. The end of the tube was shrunk smoothly for about 2 cm. of the end of the tube until the inside diameter at the end was about 1-2 mm. tapering up to the original diameter of the tube about 2-3 cm. from the end. The mandel was attached to a stirrer motor with the mandel hanging downward. Then the glass tube, prepared above and cooled, was slipped over the mandel so that the mandel taper was touching the glass taper on the inside of the tube. A mush of 200 mesh carborundum and water was fed into the glass tube so that it worked between the mandel and glass and ran out the bottom into a receiver placed there for that purpose. The stirrer motor was started and with the carborundum mush being constantly fed into the grinding surface, the glass tube was pushed gently upward against the mandel. When the grind was shaped to a smooth taper, the 200 mesh carborundum was removed and 400 mesh carborundum used to complete the joint. The finer carborundum formed a smoother surface on the joint. The grinding was continued until the smaller end of the joint at the end of the tube was about 2½-3 mm. in diameter (inside). This finished joint can now be cut the proper length and sealed onto a 12/30 joint to make the capillary shield. The mandel can be used to make 15-20 joints before it must be reshaped.

The commercially available marine capillary tubing used for the dropping mercury electrode was not of pyrex glass, but it could be ground to a desired taper in the

same way as pyrex glass. The ends of a section of this tubing about 15-18 cm. long were heated in a flame until they were completely sealed. This was necessary so that carborundum would not work into the capillary while grinding and clog it. A grinding tool was made from a strip of tin 10 cm. long, as wide as the taper of the mandel is long and about 0.3 mm. to 0.4 mm. thick. The tin was selected so that it is thick enough to hold its shape as long as possible and still is thin enough to be shaped easily. It was shaped by wrapping around the tapered end of the mandel and drawn tight by squeezing the ends together in a vise. The jaws of the vise were placed on the tin close to the mandel. When properly shaped the inside of the tin taper will have the same taper as that of the mandel. The ends of the tin were bent outward slightly so as to form a trough. Then the marine capillary tubing, sealed off and cooled, was connected to a stirrer motor so that the tubing was horizontal. The tin grinding tool was held on the end of the capillary tubing and a mush of 200 mesh carborundum and water fed into the trough of the grinding tool. The stirrer motor was started and with the carborundum mush being constantly fed to the grinding surfaces, the tin tool was pushed gently over the end of the capillary tubing. When the taper was smoothly shaped and the capillary tubing was starting to protrude through the tin tool, the 200 mesh carborundum was replaced with 400 mesh carborundum to give a smooth surface. The grinding was continued until the capillary

protruded through the tin tool at least 1 cm. or farther; thus the capillary will protrude through the capillary shield at least 1 cm. Until the capillary is needed, it is best kept as it is, i.e., the ends sealed, so that no foreign material will work into the capillary and clog it. When the capillary is to be used, the ends were cut off so that the tubing was of the desired lenghth. The capillary was ground down until it protruded through the capillary shield at least 1 cm. so that it was sufficiently long to be cut off easily and given a square end. If the end at the capillary from which the drops fall is not square, the formation of the drops will be irregular. It should be cut so that 2-3 mm protrude through and below the capillary shield into the solution.

The burrette used at the beginning of this work was a 50 ml. pyrex gas burrette graduated every 0.1 ml. which can be found in any glass catalogue. It was enclosed in a glass jacket along with an auxiliary pyrex tube of approximately the same diameter as the burrette, but extending several centimeters above the burrette. At the bottom, the auxiliary tube and the burrette were connected to the same mercury reservoir through an F shaped adapter by means of short pieces of tygon tubing. The jacket was fitted at the bottom with an inlet and at the top with an outlet so that water could be passed through the jacket around the burrette to maintain constant temperature. A thermometer was wired to the auxiliary tube so that the temperature of

the water and hence of the gas burrette could be read. The auxiliary tube was included to facilitate reading of the burrette. By adjusting the leveling bulb reservoir of mercury so that the level of mercury in the burrette, auxiliary tube, and leveling bulb were the same, the volume of gas is read from the burrette was known to be that volume at the atmospheric pressure of that moment. The burrette described above was difficult to read to the nearest 0.01 ml., and since the oxygen absorbed in some runs was small, a burrette was built that could be read easier and more accurately. The lower part was tubing (not pyrex) with a diameter about half that of the 50 ml. burrette described above and graduated for 10 ml., every 0.05 ml. Above this was a bulb of about 80 ml. capacity. This burrette was fitted with a water jacket, auxiliary tube and thermometer in the same way as the 50 ml. burrette. The burrette was joined to 2 mm. capillary tubing at the top by means of tygon tubing. This capillary tubing led to a 2 mm. 3-way stop cock which could be turned either to connect the burrette to the polarographic cell or to an oxygen reservoir. This reservoir consisted of a large beaker containing water. A gas bottle upside down in the water trapped several hundred milliliters of oxygen over water. The capillary from the apparatus led into this oxygen sample so that oxygen could be drawn into the burrette as needed by displacement by water. From this stopcock, 2mm. capillary tubing led to another 3-way stopcock of the

same size. This stopcock was connected to the 2 mm. capillary tubing on top of the polarographic cell by means of tygon tubing. The stopcock was arranged so that the polarographic cell would be connected either with the burrette or with a funnel. The solutions to be put into the polarographic cell were pipetted into this funnel and drawn into the cell by withdrawal of mercury from the bottom of the cell. A drawing of the entire apparatus is shown in Figure II, page 53.

The burrette and connecting capillary tubing including the filling funnel were permanently set up. When necessary, the mercury in the burrette was withdrawn and cleaned. The connecting capillary tubing was generally washed and dried at the same time. However, after each run, the polarographic cell was disconnected at the tygon connection just above the cell, dismantled, cleaned and dried. When setting up the apparatus preparatory to making a run, the upper part of the cell was connected with tygon and the tygon wired to insure the absence of leaks. The clamp was placed around the upper part of the cell and tightened. The dropping mercury electrode was joined to a reservoir of mercury which could be raised or lowered so that mercury passing through the capillary was under the pressure of the desired head of mercury. The ground glass taper of the capillary was greased with a silicone grease. This grease was used because it is insoluble in nearly all organic compounds except saturated cyclic hydrocarbons; cyclohexane was used for

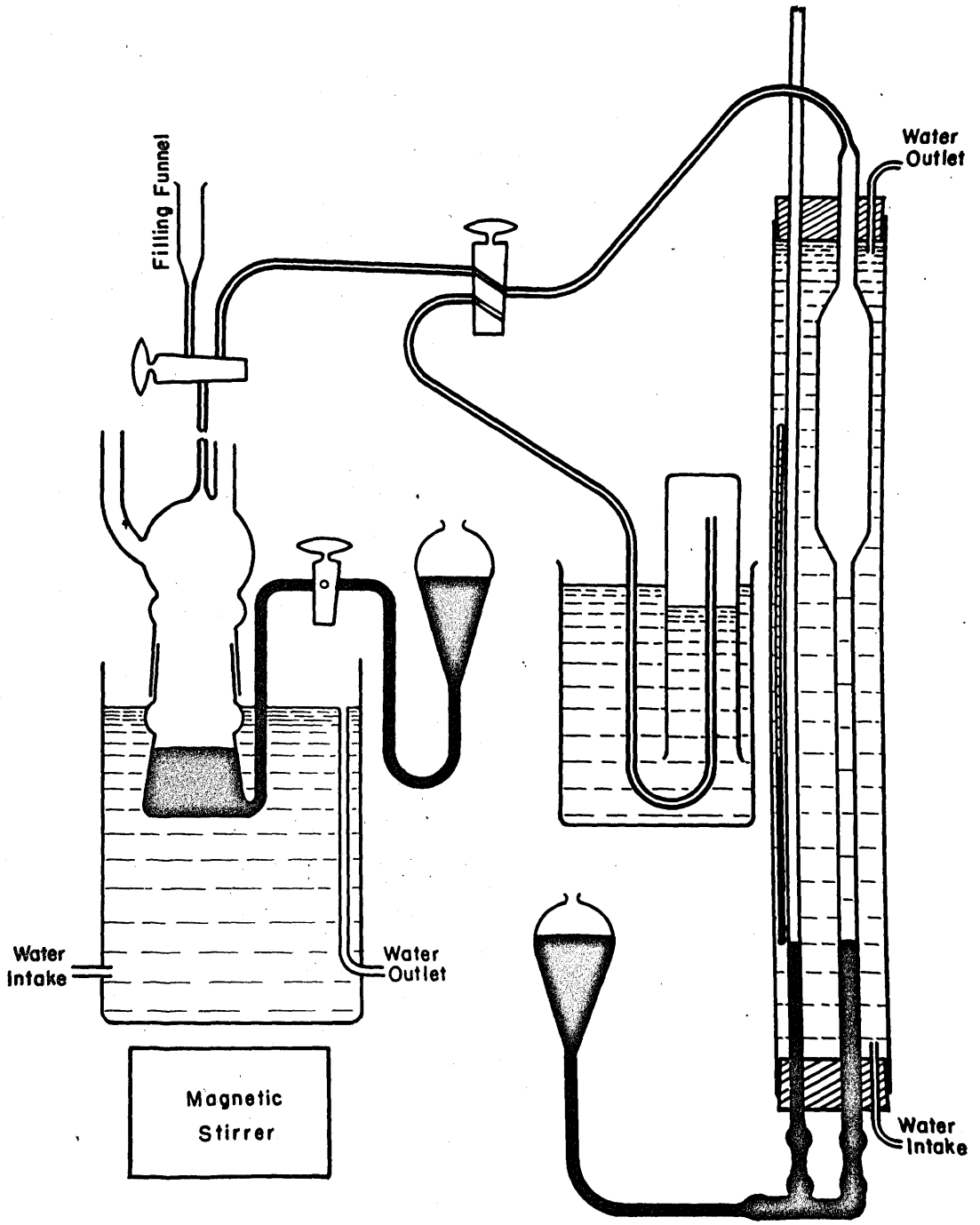


Figure 2. Oxygen Uptake Apparatus

cleaning the ground joints and apparatus after using. The capillary shield was slipped over the capillary and twisted a few times until the ground glass joint was firmly seated. Care was taken to prevent any of the silicone grease from getting on the end of the capillary, since this causes the dropping mercury electrode to operate improperly. Next, the joint on the capillary shield was greased with the silicone grease, and tne shield and capillary lowered into the ground glass joint in the top of the cell. It likewise was twisted a few turns until the joint was firmly seated. The magnetic stirrer bar was placed in the lower part of the cell and the large connecting ground joint on it thoroughly lubricated with the silicone grease mentioned above. This was raised into place in the upper part of the cell, twisted a few times to seat the joint, and the copper sling put into position and the connecting bolts tightened. Although there was some fear of tightening this sling enough to break the cell, no cells were broken, and the sling was tightened more than enough to hold the lower part of the cell in place when the weight of nearly 200 ml. of mercury was bearing on it. The mercury reservoir was connected to the inlet at the bottom of the polarographic cell and the copper water bath raised around the cell until the cell was completely covered with the water flowing through the bath. The dropping mercury electrode should be covered with some liquid in the cell as soon as possible, since it has a tendency to dry out and clog. The polarographic cell was not set up

until just before use for this reason.

The copper water bath was fitted with inlet and outlet tubes and water was circulated through the bath and around the cell so as to maintain the cell at constant temperature, that is, the temperature of the circulating water. The magnetic stirrer was clamped in place just below the water bath and touching the bath. It must be as close as possible to the stirrer bar or it may not turn the bar. The bath must be of a non-magnetic material.

For making polarograms without any gas measurements, small jars of about 50 ml. capacity were used. These were fitted with the correct size rubber stoppers in which four holes were bored. One hole for the dropping mercury electrode, one for the agar bridge of the saturated calomel electrode and one hole for a nitrogen tube. This nitrogen tube extends below the surface of the solution and it was used to remove oxygen from the solution by bubbling nitrogen through the solution.

Procedure

For polarograms of the organic compounds without measuring oxygen uptake, the compound was distilled from a semi-micro claisin flask. For the runs in which the oxygen uptake was measured, the substances were distilled from the same flask in an atmosphere of nitrogen. The system was flushed three times with nitrogen by evacuating, letting nitrogen into the system and evacuating again. In addition, nitrogen

was bubbled through a drawn out capillary in the liquid in the still pot during the distillation. Although the distillations were conducted at a pressure of about 10 mm., the flow of nitrogen was regulated so as to maintain reduced pressure and have nitrogen passing through the system. The distillate was left in a nitrogen atmosphere until ready for use. Then the compound was transferred as quickly as possible to the reaction cell to keep contact with atmospheric oxygen at a minimum. To make sure that all oxygen and peroxides were absent, the lactones were distilled twice as described above, the middle fraction being collected each time.

It was necessary that oxygen be absent from the solvent at the start of the run also, since when saturated, the solvent contains more than half the oxygen for the uptake during the run. Bubbling with nitrogen was not sufficient, since then the solvent was saturated with nitrogen and when the solutions was stirred in the presence of oxygen, some of the nitrogen escaped into the oxygen causing a false measurement of the oxygen uptake (uptake more than observed). It was found that heating the solvent to boiling and cooling to room temperature immediately before using eliminated most of the oxygen (and other gases) from the solvent. The solvent was not boiled since boiling for a few minutes causes a change in pH of some of the buffer solutions. The solvents contained considerable oxygen within one half hour after heating and cooling, so they could be

used only as described.

The procedure for starting a run whereby oxygen uptake of the organic compound was correlated with diffusion current was relatively simple. Mercury was run into the cell through the inlet at the bottom of the cell. The air in the cell was extruded through the filling funnel. When the stopcock just above the cell was turned in this direction, the cell was shut off from the gas burrette. When the cell was completely filled with mercury and about a milliliter was in the filling funnel, the mercury flow was stopped by means of a stopcock between the mercury reservoir and the cell. Then the compound being studied was dropped into the filling funnel. Withdrawal of mercury from the cell was started immediately by lowering the reservoir and opening the stopcock. At the same time, the solution in which the organic compound was to be dissolved was pipetted into the filling funnel, a few milliliters at a time. Thus, the organic compound was completely washed into the cell with the solvent. When all the solvent (buffer solution) had been pipetted into the filling funnel and the level of the liquid had lowered into the capillary tube connecting the filling funnel and the polarographic cell, the flow of mercury was stopped by shutting the stopcock between the mercury reservoir and the polarographic cell. With care, the solution can be introduced into the cell without letting any gas into the cell. If the volume of solution has been properly chosen, the magnetic stirrer may now be

started and run without hitting the electrodes dipping into the solution. At the same time, no pressure develops in the cell as a result of mercury entering the cell through the dropping mercury electrode and only a very small surface of solution is exposed to atmospheric oxygen. The magnetic stirrer was run until the organic compound was completely dissolved in the solvent and the temperature of the solution came to equilibrium at the temperature of the water bath. While the solution was reaching equilibrium, a sample of oxygen was drawn into the burrette and after it had reached the temperature of the water jacket, the initial volume was read from the burrette and recorded. When the solution in the polarographic cell had reached temperature and solution equilibrium, the magnetic stirrer was shut off and the initial polarogram made. Then with the stopcocks appropriately adjusted, the oxygen in the burrette was transferred into the polarographic cell by raising the mercury reservoir connected to the burrette and lowering the reservoir connected to the polarographic cell. When sufficient oxygen had entered the cell, the mercury flow out of the polarographic cell was stopped and the mercury level in the burrette adjusted until pressure in the system was equal to that of the atmosphere. The solution was then stirred for a short time, usually five or ten minutes and then the oxygen was returned to the burrette by reversing the above precedure. In this work, the level of the solution was raised to the stopcock just above the polarographic cell and stopped there.

Thus, the oxygen volume was measured under the same conditions as initially measured. Then the magnetic stirrer was shut off and another polarogram made on the solution. While the polarograph was running, the oxygen volume was determined and recorded. By continuing this process, a series of polarograms were obtained with the corresponding oxygen absorption. All of the oxygen absorbed was not reacted with the organic compound. The amount of oxygen dissolved in the solution unreacted was determined from each polarogram along with the diffusion current of the organic compound, since dissolved oxygen gives a well defined polarographic wave at a different applied potential.

The diffusion coefficient of oxygen at 0°C was determined by the same procedure described above except that no lactone was present. The oxygen uptake, i.e., the oxygen dissolved in the solvent, was correlated with the diffusion current at -0.4 v. vs SCE applied potential. Oxygen gives a polarographic wave starting at 0 volt applied potential and at -0.4 volt, the limiting value of the diffusion current had been reached and the wave leveled off.

After determination of the diffusion coefficient of oxygen at 0°C, the diffusion coefficient at 25° was determined from that at the lower temperature easily by a comparison of the diffusion currents at 0° and 25° of a solution containing the same concentration of oxygen. This was done by completely filling the cell in an ice bath with a sample of solvent containing oxygen dissolved in it. No gases were

present and the only contact between solvent and air was in the capillary tubing above the cell. After determination of the diffusion current, the cell and contents were warmed to 25°C while the solvent was allowed to expand into the filling cup. When temperature equilibrium was attained, the diffusion current was again determined. A simple calculation with these diffusion currents gives the diffusion coefficient at 25° based on that at 0°C.

For making polarograms of solutions without measuring the oxygen uptake, 25 ml. of solution was introduced into the previously described jars. The dropping mercury electrode, calomel electrode, and the nitrogen tube were placed in position through the rubber stopper and the solution bubbled with dry nitrogen from which all oxygen was removed. After about 10 minutes, or after all oxygen was removed from solution, bubbling was discontinued by shutting off the nitrogen or by raising the nitrogen tube until the nitrogen entered the cell above the solution but not through the solution. Any agitation of the solution interferes with the operation of the dropping mercury electrode.

For the work at 25°, water at this temperature was passed through the jacket around the burrette and through the bath surrounding the cell, all connected in series. The temperature of this water was controlled to within half a degree of 25°; a half degree change in temperature change causes a change in the diffusion current less than 1%. The diffusion currents can be measured from the polarograms

with an accuracy of no greater than 1%, so this precision of temperature control is sufficient for the polarograms. As can be shown later in this work, the measurement of diffusion currents were less precise than the other measurements. Better precision was attained with the volume measurements, since the exact temperature of the gas burrette was read at the same time as the volume.

For the work at 0°, the bath around the polarographic cell was disconnected from the burrette and packed with ice and water. By keeping the cell well packed in ice, a temperature of 0° was assured within a range of about 0.2°C. However, the polarograms can still be read with an accuracy of only about 1%, so the precision of temperature control was greater than necessary. Water passing through the burrette jacket was tap water which passed through a copper coil immersed in an ice bath before passing through the burrette jacket. Large quantities of ice were needed to keep the copper coil well chilled and the water temperature in the burrette jacket was not zero, but in the range of 4-6°C. However, by reading the temperature at the same time as the burrette, the precision of volume measurement was better than the precision of diffusion current measurement. The oxygen was left in the burrette several minutes on several occasions and no change in volume was noted. Therefore, either the temperature of the oxygen changed rapidly to that of the burrette or the temperature of the oxygen stayed within this range even when in the polarographic

cell immersed in ice and water.

For many of the calculations, the mass of mercury falling from the dropping mercury electrode per second was needed. This constant, designated by m, was measured in milligrams per second. This constant is independent of the medium in which the mercury drops are formed, but varies with the pressure head of mercury on the capillary. To determine m, the dropping mercury electrode was put in distilled water and the head adjusted to the level which was to be used. Then a micro funnel was placed in the water below the capillary and the mercury drops collected for a period of time as measured with a stop watch. The micro funnel was connected to a weighing bottle so that when sufficient mercury was collected, it could be sucked into the weighing bottle. The mercury was carefully washed with water, then with acetone, and finally dried and weighed on an analytical balance. By a simple calculation with the weight of mercury and the time during which it was collected, the constant, m, was obtained. This constant was used as the two thirds power, so the precision necessary was easily obtained by the procedure outlined.

The polarograph was calibrated several times at frequent intervals. This was necessary because of the tendency of the calibration of this instrument to vary. The instrument was calibrated by connecting a known resistance across the electrical leads and making a polarogram at the appropriate setting of the current sensitivity selector after marking

the voltage on the sensitive paper at several places. Then from the voltage and the resistance, the current was simply calculated. The distance on the graph for this amperage was measured on the polarogram and a simple calculation gave the current per millimeter. On the polarograms from which a diffusion current is determined, the height of the wave was measured in millimeters and by multiplication by the appropriate current sensitivity, the current in micro-amperes was obtained.

The time for a drop of mercury to form and fall off the capillary is an important factor in many of the calculations. It is designated by t and is given in seconds. It was determined for each polarogram at that voltage for which the calculations involving t were to be made. It varies both with the medium and the applied E.M.F. and thus cannot be determined previous to the polarogram as can be done with m. A stop watch is convenient to measure t, since it is used only to the one sixth power and high precision is not necessary. To make this measurement, the drops falling from the capillary in solution were watched when possible. When the capillary could not be seen, as was the case when the cell was immersed in ice, the falling and forming of mercury drops were observed by watching the visual scale of the polarograph.

Method of Handling Data

The diffusion currents were measured from the polarograms in the usual manner. During an oxygen uptake determination, the residual current could not be determined for each polarogram. At the low applied potentials at which oxygen was measured, -0.4 volt, the residual current was usually less than experimental error and measurements of the diffusion currents of oxygen were usually measured from the zero line of the polarogram. The zero line was marked on the sensitive paper before making the polarogram. The residual current at -0.4 volt was measured in a few cases from a sample of buffer solution left over after removal of the amount required for the determination. Thus, it was measured on a sample of solvent which had had the same treatment (heating to boiling temperature) as that used but had no lactone dissolved in it. The last remaining oxygen was removed by bubbling nitrogen through the sample.

The diffusion currents of the peroxide were measured by means of a series of drawn lines. A line was extended past the half wave potential of the peroxide and through the average of the diffusion currents preceeding the peroxide wave, i.e., through the average of the limiting current wave due to oxygen. A second line was drawn through the average of the peroxide limiting diffusion current and past the half wave potential. A third line was drawn

through the average of the wave itself. At the point where this last line intersected the line extension from the oxygen wave, a line was drawn at constant current, i.e., parallel to the zero line of the polarogram. This line served as a base line from which to measure the diffusion current. Another line was drawn parallel to this base line and through the point of intersection of the lines through the wave and through the average peroxide diffusion current. The distance from this line to the base line is a measure of the diffusion current. Essentially, the diffusion current is measured at the half wave potential. This distance was measured in millimeters; multiplication by the appropriate current sensitivity gives the diffusion current in micro amperes.

An equation for the diffusion current was first obtained by Ilkovic as:

$$i_d = 605\ n\ D^{\frac{1}{2}}\ c\ m^{2/3} t^{1/6}$$

where

i_d is the diffusion current, in micro-amperes

n is the number of faradays of electricity required per mole of the electrode reaction

D is the diffusion coefficient constant of the reducible substance, in the units $cm.^2 sec.^{-1}$

C is the concentration of the reducible substance in millimoles per liter

m is the rate of flow of mercury from the dropping mercury electrode, measured in milligrams per second

t is the drop time, measured in seconds

This equation is used throughout the calculations.

Determination of m

The constant m was experimentally determined at 25°C as previously described, but the value at 25°C must be corrected for temperature change when used for the calculations at 0°C. This was done by means of an equation given by Kolthoff and Lingane (132), page 75:

$$m_0 = m_{25} - \Delta T(0.0036)$$

and at 0°C;

$$m_0 = (m_{25} - 0.09) \text{ mg sec}^{-1}$$

Diffusion Coefficient of Oxygen

From the runs for the determination of this constant at 0°C, there were obtained diffusion currents and corresponding oxygen absorption in boric acid buffer solution, pH 9.6. These were graphed. Since oxygen could not be completely removed from the solvent, the straight line so obtained does not pass through the origin. The curve was corrected for the oxygen originally present by drawing a straight line through the origin and parallel to the experimental curve. From this corrected curve, corresponding values of diffusion current and oxygen absorption (concentration) were obtained and substituted in the Ilkovic equation. The value of n is known to be 2 and m and t were determined before add during the run. Thus, the only unknown is D, the diffusion coefficient, which is then easily calculated.

In the Ilkovic equation, temperature changes affect i_d, m, t, and D. Thus at 0° and 25°:

$$i_d^0 = 605\ n\ c\ m_0^{2/3} t_0^{1/6} D_0^{\frac{1}{2}}$$

$$i_d^{25} = 605\ n\ c\ m_{25}^{2/3} t_{25}^{1/6} D_{25}^{\frac{1}{2}}$$

When applied to the same electro-reducible substance at the same concentration at the two temperatures, one equation may be divided by the other to give:

$$\frac{i_d^0}{i_d^{25}} = \frac{m_0^{2/3}\ t_0^{1/6}\ D_0^{\frac{1}{2}}}{m_{25}^{2/3}\ t_{25}^{1/6}\ D_{25}^{\frac{1}{2}}}$$

This equation was used to determine the diffusion coefficient of oxygen at 25° from the diffusion coefficient at ice temperature.

Reversibility of Reduction Waves and Number of Electrons Involved

The potential of the dropping mercury electrode for a reversible reduction is given by:

$$E_{d.e.} = E^o - \frac{RT}{nF_y} \ln \frac{C_{red} f_{red}}{C_{ox} f_{ox}}$$

where:

$E_{d.e.}$ is the potential of the dropping mercury electrode

E^o is the standard oxidation-reduction potential of the system

R is the gas constant

T is the absolute temperature

n is the number of faradays of electricity involved

in the reduction of one mole of substance or the number of electrons involved in the reduction

F_y is the Faraday

C_{red} is the concentration of the reductant

f_{red} is the activity coefficient of the reductant

f_{ox} is the activity coefficient of the oxidant

C_{ox} is the concentration of the oxidant

Assuming that the concentration of reductant is negligible or zero, it can be readily derived that:

$$E_{d.e.} = E_{\frac{1}{2}}' - \frac{0.0591}{n} \log \frac{i}{i_d - i} \text{ at } 25^oC$$

where:

$E_{\frac{1}{2}}'$ is the half wave potential

n is the number of electrons involved in the reduction

i is the current at any point on the wave, corresponding to $E_{d.e.}$

i_d is the diffusion current

From this equation, it can be seen that a graph of $E_{d.e.}$ vs. $\log \frac{i}{i_d - i}$ should be a straight line and have a slope of $\frac{0.0591}{n}$. From this, the value of n can be determined. If the reaction is reversible, the value of n so obtained will be a whole rational integer. If the reaction is irreversible, the curve may still be a straight line, but the value of n will not be a whole rational number. At 0°C, the last equation is:

$$E_{d.e.} = E_{\frac{1}{2}}' - \frac{0.0542}{n} \log \frac{i}{i_d - i}$$

Oxygen Uptake of Angelicalactones

Diffusion currents for a given oxygen uptake for these lactones was determined as previously described and graphed. For some of these points, however, the total decrease in oxygen volume was not the amount of oxygen reacted with the lactones. The concentration of oxygen dissolved and unreacted was calculated from the diffusion currents of oxygen at -0.4 volt, by means of the Ilkovic equation. From the concentration of oxygen (millimoles per liter) and the total volume of solution, the volume of oxygen dissolved and unreacted was calculated by means of the equation:

$$V_d = C \frac{V_s}{1000} 22.4$$

where:

V_d is the volume of oxygen dissolved and unreacted, at standard conditions

C is the concentration of oxygen, in millimoles per liter

V_s is the volume of solution in the particular run

22.4 is the volume of 1 millimole of oxygen at standard conditions, in milliliters

The volumes of oxygen as measured from the gas burrette were corrected to standard conditions by means of the well known gas equation:

$$V_2 = V_1 \frac{P_1 T_2}{P_2 T_1}$$

The total decrease of volume of oxygen was then determined

for any point by subtracting the volume of oxygen at that point from the initial volume.

The volume of oxygen reacted with the lactone was obtained by subtracting V_d, the volume of oxygen dissolved and unreacted, from the total volume decrease as:

$$V_r = \Delta V_b - V_d$$

where:

V_r is the volume of oxygen reacted with the lactone, measured in ml. at standard conditions

V_b is the total decrease of oxygen volume, measured in ml. at standard conditions

V_d is the volume of oxygen dissolved and unreacted

The volume of oxygen reacted with lactone as calculated above may be graphed against diffusion current, but the graphs so obtained are intercomparable only if the amount of lactone used in each run is the same. In order that the different oxygen uptake runs might be comparable, the millimoles of oxygen reacted with lactone per liter solution was calculated for each point by means of the equation:

$$L = \frac{V_r \ 1000}{22.4 \ V_s}$$

where:

L is the millimoles oxygen reacted per liter solution

V_r is the volume of oxygen reacted with the lactone

22.4 is the volume in ml. at standard conditions of one millimole oxygen

V_s is the volume of solution used in the particular run.

IV. RESULTS

Calibration of Capillaries, Determinations of m

Since dropping mercury capillaries clog easily and must be discarded, several capillaries were used in this work. The value of m for each capillary used is as follows:

capillary	pressure head in cm. mercury	weight mercury in grams	time in min.	m in mg./sec.
1	43	0.4325	3	2.40
		0.7194	5	2.40
			average	2.40
S	40.6	0.8059	5	2.69
		0.8110	5	2.70
			average	2.69
S-1	69.0	0.3187	5	1.06
		0.3863	6	1.07
			average	1.06
S-2	47.0	0.4484	9	0.830
		0.3263	$6\frac{1}{2}$	0.837

capillary	pressure head in cm. percury	weight merucry in grams	time in min.	m in mg./sec.
			average	0.836
S-3(1)	47.5	0.4045	8	0.843
		0.3541	7	0.843
			average	0.843
S-3(2)	69.8	0.6692	9	1.24
		0.3739	5	1.25
			average	1.25
S-3(3)	69.8	0.4112	6	1.14
		0.5552	8	1.16
			average	1.15
S-4(1)	68.9	0.3063	4	1.28
		0.7616	10	1.27
			average	1.28
S-4(2)	68.9	0.8484	12	1.18
		0.4262	6	1.18
			average	1.18

Determinations of Diffusion Coefficient of Oxygen at 0°C

Determination #1

pH was 9.65, H_3BO_3-KCl-NaOH solution — av. t was 6.39 sec.

volume of the solution was 100 ml. — m was 1.16 mg./sec.

capillary was S-3(2) — $m^{2/3}t^{1/6}$ was 1.50

number	corrected volume of oxygen in ml.	ΔV in ml.	i_d at -0.4 volt in micro-amps.	drop time in sec.
1.	84.70	0	1.08	6.3
2.	84.50	0.20	1.285	6.4
3.	84.28	0.42	1.755	6.4
4.	84.12	0.58	2.16	6.4
5.	83.90	0.80	2.57	---
6.	83.84	0.86	3.01	6.2
7.	83.62	1.08	3.57	6.5
8.	83.34	1.36	4.04	6.4
9.	83.28	1.42	4.55	---
10.	83.08	1.62	4.93	6.4

number	corrected volume of oxygen in ml.	ΔV in ml.	i_d at -0.4 volt in micro-amps.	drop time in sec.
11.	83.04	1.66	5.06	6.2
12.	82.92	1.78	5.30	---
13.	82.82	1.88	5.50	6.2
14.	82.68	2.02	5.79	6.5
15.	82.66	2.04	6.19	6.2

Determination #2

pH wa 9.66, H_3BO_3-KCl-NaOH solution

volume of solution was 100 ml.

capillary was S-3(2)

av. t was 6.4 sec.

m was 1.16 mg/sec.

$m^{2/3} t^{1/6}$ was 1.51

number	corrected volume of oxygen in ml.	ΔV in ml.	i_d at -0.4 volt in micro-amps.	drop time in sec.
1.	84.82	0	0.401	6.3
2.	83.96	0.86	1.22	6.4
3.	83.90	0.92	1.74	6.4
4.	83.74	1.08	2.22	6.4

number	corrected volume of oxygen in ml.	ΔV in ml.	i_d at -0.4 volt in micro-amps.	drop time in sec.
5.	83.56	1.26	2.39	6.4
6.	83.46	1.36	2.55	6.4
7.	83.36	1.46	3.09	6.4
8.	83.20	1.62	3.30	6.3
9.	83.06	1.76	3.49	6.4
10.	83.02	1.80	3.76	6.4
11.	82.90	1.92	4.11	6.4
12.	82.80	2.02	4.40	6.6
13.	82.68	2.14	4.79	6.2
14.	82.62	2.20	4.87	6.5
15.	82.22	2.60	5.76	6.4
16.	82.16	2.66	6.19	6.4
17.	82.02	2.80	6.55	6.5

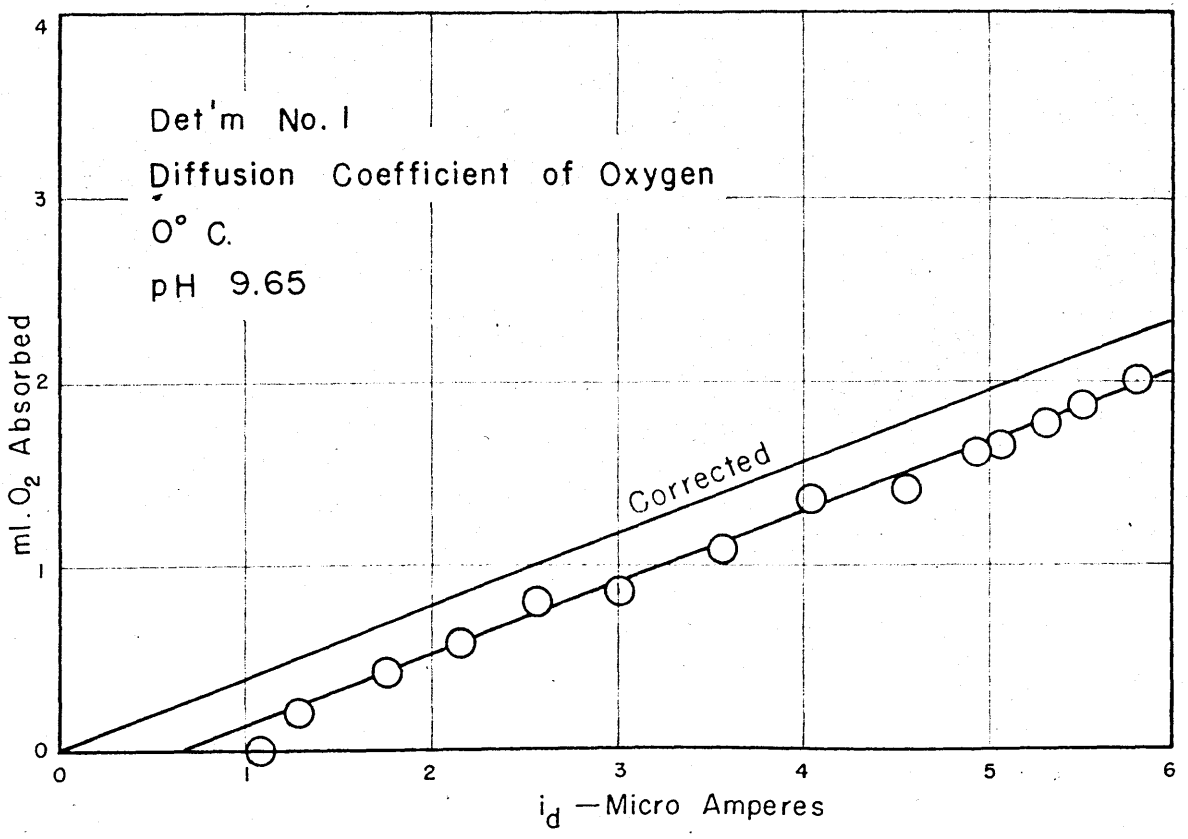
These results are shown in graphical form on page 77. The diffusion coefficient from two points on the corrected curve of each determination is given in the following table:

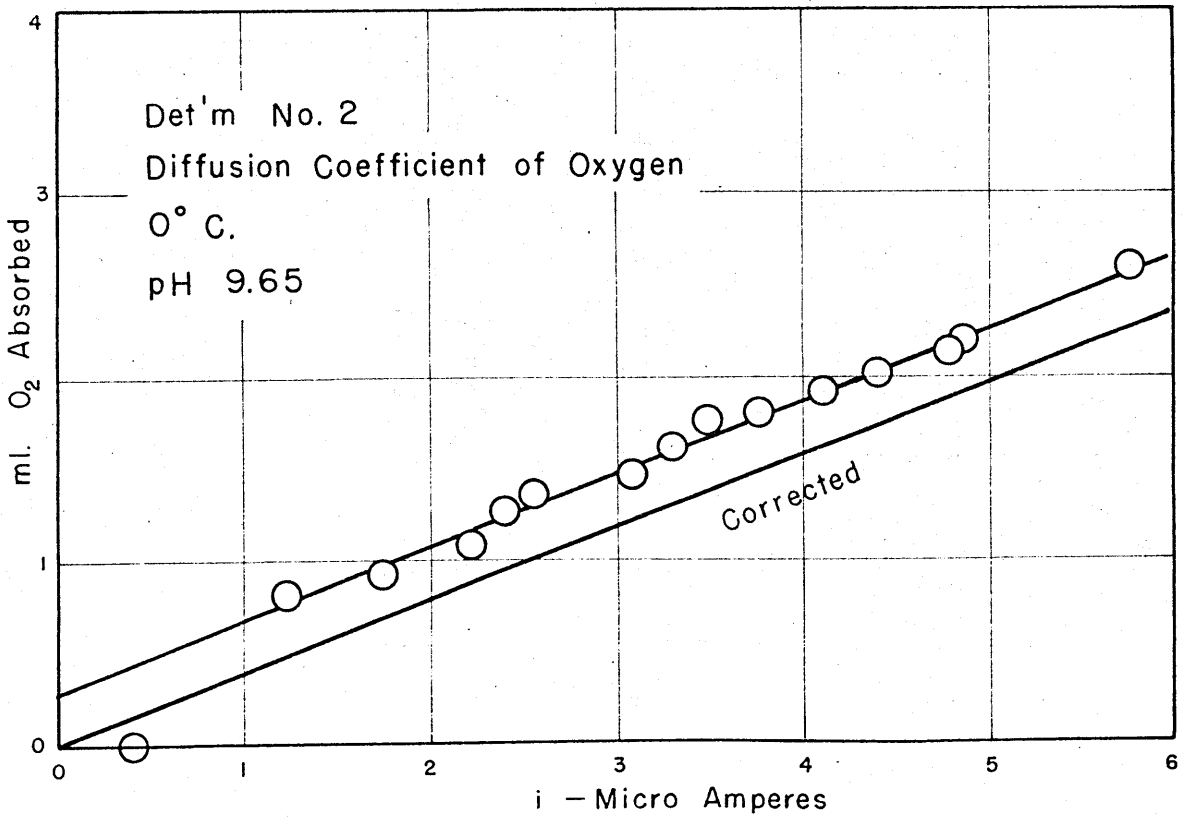
determination	ml. oxygen absorbed	concentration oxygen molar	corrected i_d in micro-amps	D
1	1	0.446	2.55	9.87×10^{-6}
	2	0.893	5.11	9.89×10^{-6}
2	1	0.446	2.54	9.78×10^{-6}
	2	0.893	5.08	9.76×10^{-6}
			average	9.83×10^{-6}
			tolerance	$\pm 0.08 \times 10^{-6}$

Determination of the Diffusion Coefficient of Oxygen at 25°

The diffusion coefficient of oxygen at 25° was determined as previously described, by comparison of the diffusion currents at 25° and 0° of solutions with the same concentration of oxygen.

number	at 0°C			at 25°C			Diffusion coeff. at 25°C
	i_d in mm.	m in mg./sec.	t in sec.	i_d in mm.	m in mg./sec.	t in sec.	
1.	57.5	1.09	6.4	95.0	1.18	5.83	2.49×10^{-5}
2.	57.5	1.09	6.4	94.5	1.18	5.83	2.46×10^{-5}
					average		2.48×10^{-5}
					tolerance		$\pm 0.08 \times 10^{-5}$


Det'm No. I
Diffusion Coefficient of Oxygen
0° C.
pH 9.65
Corrected
ml. O_2 Absorbed
i_d —Micro Amperes
0
1
2
3
4
5
6


Det'm No. 2
Diffusion Coefficient of Oxygen
0° C.
pH 9.65
Corrected
ml. O_2 Absorbed
i — Micro Amperes
0
1
2
3
4
5
6

Half Wave Potential of α-Angelicalactone Peroxide: Effect of Concentration, pH and Media

No.	pH	Lactone Concentration in molarity	$m^{2/3}t^{1/6}$ at -1.5v in mg./sec.	i_d in micro amps.	$E_{\frac{1}{2}}$ vs. SCE in volts	Capillary	Media
1.	9.50	0.00510	2.21	1.91	-1.32	1	H_3BO_3-KCl-NaOH
2.	9.50	0.00721	2.21	2.08	-1.32	1	"
3.	9.50	0.00906	2.21	2.66	-1.32	1	"
4.	9.50	0.0115	2.21	2.63	-1.32	1	"
5.	9.50	0.0140	2.21	2.41	-1.31	1	"
6.	9.50	0.0193	2.21	3.38	-1.32	1	"
7.	9.52	0.0196	2.21	4.28	-1.31	1	"
8.	9.52	0.0371	2.21	5.54	-1.31	1	"
9.	9.50	0.0607	2.19	1.40	-1.32	1	"
10.	9.65	0.0294	1.42	4.64	-1.31	S-4(2)	" , at 0°C
11.	9.65	0.0294	1.42	5.11	-1.30	S-4(2)	" , at 0°C
12.	9.65	0.0294	1.42	6.48	-1.31	S-4(2)	" , at 0°C
13.	9.65	0.0294	1.42	6.94	-1.32	S-4(2)	" , at 0°C

No.	pH	Lactone Concentration in molarity	$m^{2/3}t^{1/6}$ at -1.5v in mg./sec.	i_d in micro amps.	$E_{\frac{1}{2}}$ vs. SCE in volts	Capillary	Media
14.	9.65	0.0294	1.42	7.77	-1.32	S-4(2)	H_3BO_3-KCl-NaOH, at 0°C
15.	8.04	0.0110	2.12	0.864	-1.35	1	NaOH-KH_2PO_4
16.	8.78	0.0109	2.21	1.80	-1.32	1	H_3BO_3-KCl-NaOH
17.	9.50	0.0112	2.21	2.30	-1.31	1	"
18.	8.04	0.00420	2.21	0.54	-1.32	1	KH_2PO_4-NaOH
19.	8.04	0.00724	2.21	0.76	-1.32	1	"
20.	8.04	0.0132	2.21	0.90	-1.33	1	"
21.	8.04	0.01808	2.21	0.90	-1.33	1	"
22.	9.52	0.00890	2.19	1.25	-1.27	1	Glycine-NaCl-NaOH
23.	9.52	0.00898	2.19	1.21	-1.27	1	"
24.	10.06	0.00869	2.21	0.95	-1.27	1	"
25.	11.10	0.00907	2.19	0.846	-1.27	1	"
26.	8.80	0.00914	2.21	ca 1.12	ca -1.43	1	1:1 mix of cellosolve & NaOH-KH_2PO_4 of pH 8.04
				ca 1.04	ca -1.57	1	

No.	pH	Lactone Concentration in molarity	$m^{2/3}t^{1/6}$ at -1.5v in mg./sec.	i_d in micro amps.	$E_{\frac{1}{2}}$ vs. SCE in volts	Capillary	Media
27.	9.10	0.00898	2.21	ca 0.71	ca -1.39	1	1:1 mix of alcohol and
				ca 0.50	ca -1.60	1	$NaOH-KH_2PO_4$ of pH 8.04
28.	?	0.00748	2.17	ca 1.46	ca -1.60	1	0.1 M $(CH_3)_4NBr$
29.	?	0.00718	2.19	ca 2.57	ca -1.57	1	"
30.	?	0.00588	2.21	ca 0.56	ca -1.57	1	"
31.	?	0.01314	2.19	ca 1.54	ca -1.58	1	"
32.	?	0.02041	2.17	ca 2.91	ca -1.60	1	"

α-Angelicalactone Peroxide, Reversibility and the Number of Electrons Involved in the Polarographic Reduction

$E_{d.e.}$ in volts	i_d in micro-amps.	i in micro-amps.	$\log \frac{i}{i_d - i}$
1.274	3.74	0.98	-0.4497
1.292	3.74	1.49	-0.1790
1.303	3.74	1.84	-0.0140
1.315	3.74	2.16	0.1358
1.333	3.74	2.69	0.4086

These results are graphed on page 64.

slope of the line = 14.15

n = 0.767

Oxygen Uptake of α-Angelicalactone at 25°C

Run # 1, 25°C

pH was 9.60, H_3BO_3-KCl-NaOH solution

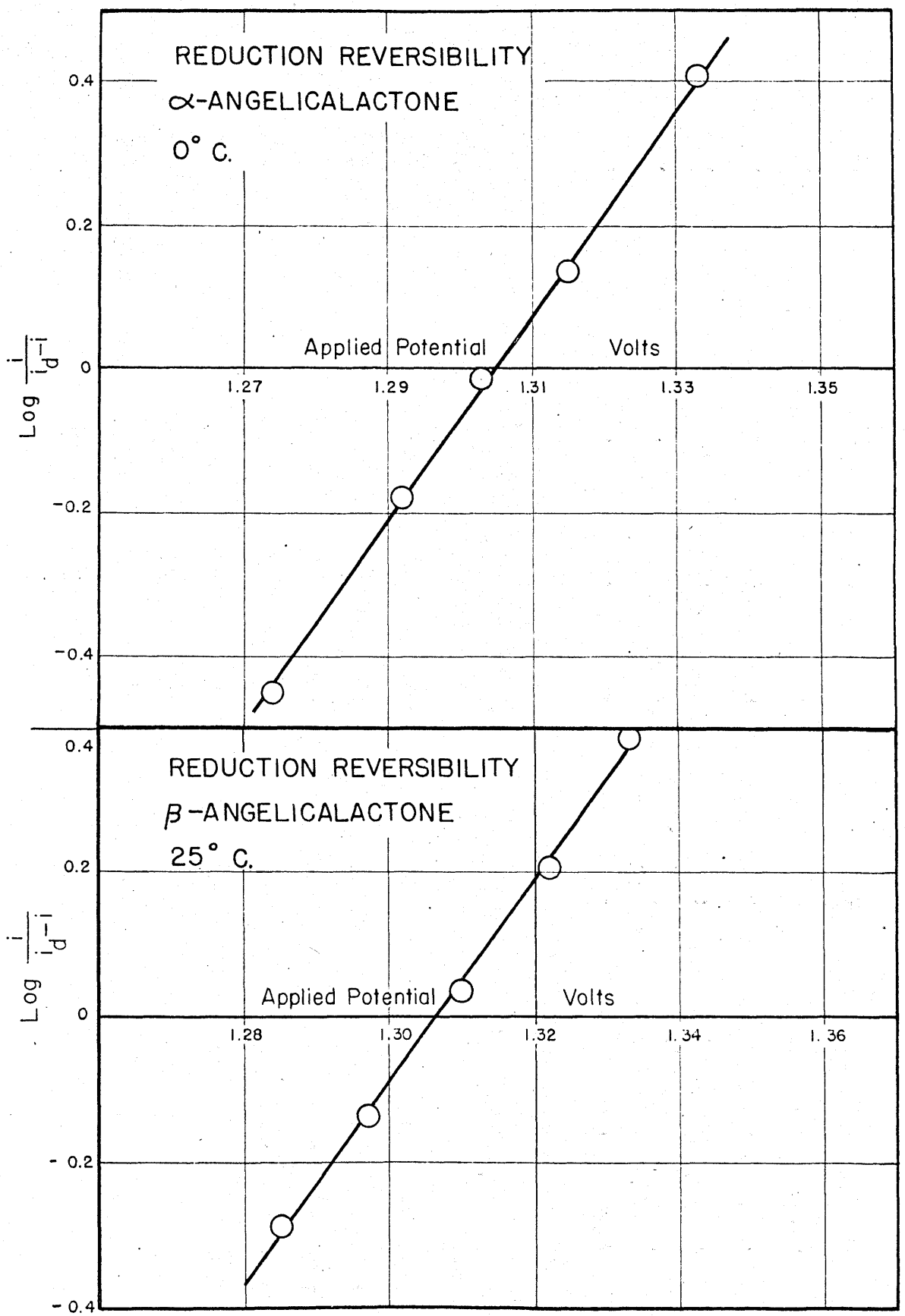
concentration lactone was 0.03117 molar.

Weight lactone was 0.3273 grams/125 ml. solution

capillary was S-1

$m^{2/3}t^{1/6}$ is 1.402 at -0.4 v

No.	i_d at -0.4 volt in micro-amps.	oxygen concentration m mole/ liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.601	b 0
2.	0.04	0.005	0.82	0.80	0.987	0.255
3.	0.04	0.005	1.23	1.21	1.395	0.385
4.	0.04	0.005	1.66	1.64	1.82	0.521
5.	0.04	0.005	1.88	1.86	2.04	0.592
6.	0.08	0.010	2.21	2.18	2.36	0.693
7.	0.11	0.013	2.41	2.37	2.53	0.754


REDUCTION REVERSIBILITY
α-ANGELICALACTONE
0° C.
0.4
0.2
0
-0.2
-0.4
Log $\frac{i}{i_d - i}$
Applied Potential
Volts
1.27
1.29
1.31
1.33
1.35
REDUCTION REVERSIBILITY
β-ANGELICALACTONE
25° C.
0.4
0.2
0
- 0.2
- 0.4
Log $\frac{i}{i_d - i}$
Applied Potential
Volts
1.28
1.30
1.32
1.34
1.36

No.	i_d -0.4 volt in micro-amps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
8.	0.21	0.025	2.61	2.52	2.81	0.803
9.	0.69	0.080	2.91	2.66	2.87	0.848
10.	1.16	0.136	3.11	2.68	2.75	0.852
11.	1.67	0.196	3.30	2.68	2.75	0.852
12.	2.23	0.263	3.48	2.65	2.66	0.844
13.	2.57	0.302	3.68	2.73	2.71	0.869
14.	3.13	0.367	3.86	2.71	2.91	0.863

* These volumes are at 25°C and 740 mm. pressure, one millimole oxygen is 25.1 ml.

These results are graphed on page -89-.

Run #2, 25°C

pH was 9.60, H_3BO_3-KCl-NaOH solution

concentration of the lactone was 0.03117 molar

weight lactone was 0.3273 grams/125 ml. solution

capillary was S-1

$m^{2/3}t^{1/6}$ was 1.402 at -0.4 volt

No.	i_d at -0.4 volt in micro-amps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.835	0
2.	0.04	0.005	0.47	0.45	1.35	0.142
3.	0.04	0.005	0.62	0.60	1.48	0.188
4.	0.04	0.005	0.84	0.82	1.80	0.258
5.	0.04	0.005	1.02	1.00	2.10	0.315
6.	0.06	0.007	1.12	1.10	2.38	0.346
7.	0.11	0.013	1.32	1.28	2.65	0.404
8.	1.31	0.154	1.99	1.50	3.05	0.473
9.	2.95	0.347	2.59	1.48	3.05	0.466
10.	4.35	0.510	3.17	1.55	3.01	0.489

* These volumes are at 25°C and 730 mm., one millimol oxygen is 25.45 ml. These results are graphed on page 89.

Run #3, 25°C

pH was 9.60, H_3BO_3-KCl-NaOH solution concentration lactone was 0.02865

weight lactone was 0.3510 grams per 125 ml. solution capillary was S-1

$m^{2/3}t^{1/6}$ was 1.402 at -0.4 volt

No.	i_d at -0.4 volt in micro-amps.	oxygen concentration m mole/ liter	V_0^* in ml.	V_f^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.858	0
2.	0	0	0.41	0.41	1.115	0.146
3.	0.04	0.005	0.69	0.68	1.500	0.243
4.	0.06	0.007	1.03	1.01	1.800	0.361
5.	0.06	0.007	1.18	1.16	2.25	0.415
6.	0.11	0.013	1.34	1.30	2.40	0.465
7.	0.11	0.013	1.60	1.56	2.66	0.559
8.	0.26	0.030	1.77	1.69	2.98	0.604
9.	2.77	0.266	2.61	1.86	2.96	0.665
10.	5.67	0.665	3.71	1.85	2.96	0.661

* These volumes are at standard conditions.

These results are graphed on page 90.

Run #4, 25°C

pH was 9.60, H_3BO_3-KCl-NaOH solution

concentration of lactone was 0.02471 molar

weight of lactone was 0.3027 grams per 125 ml. soln.

capillary was S-2

$m^{2/3}t^{1/6}$ was 1.27 at -0.4 volt

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.708	0
2.	0	0	0.67	0.67	1.42	0.239
3.	0.06	0.008	0.96	0.94	1.67	0.336
4.	0.06	0.008	1.27	1.25	2.12	0.446
5.	0.02	0.003	1.41	1.40	2.23	0.500
6.	0.09	0.011	1.68	1.65	2.46	0.590
7.	9.28	1.185	5.38	2.06	2.88	0.739

* These volumes are at standard conditions.

These results are graphed on page 90.

The corrected curves for the preceeding four runs, #1, #2, #3, and #4 are graphed together on page 91.

Oxygen Uptake of α-Angelicalactone at 0°C

Run #5, 0°C

pH was 9.65, H_3BO_3-KCl-NaOH solution

concentration of lactone was 0.02145 molar

Weight of lactone was 0.2102 grams per 100 ml. solution

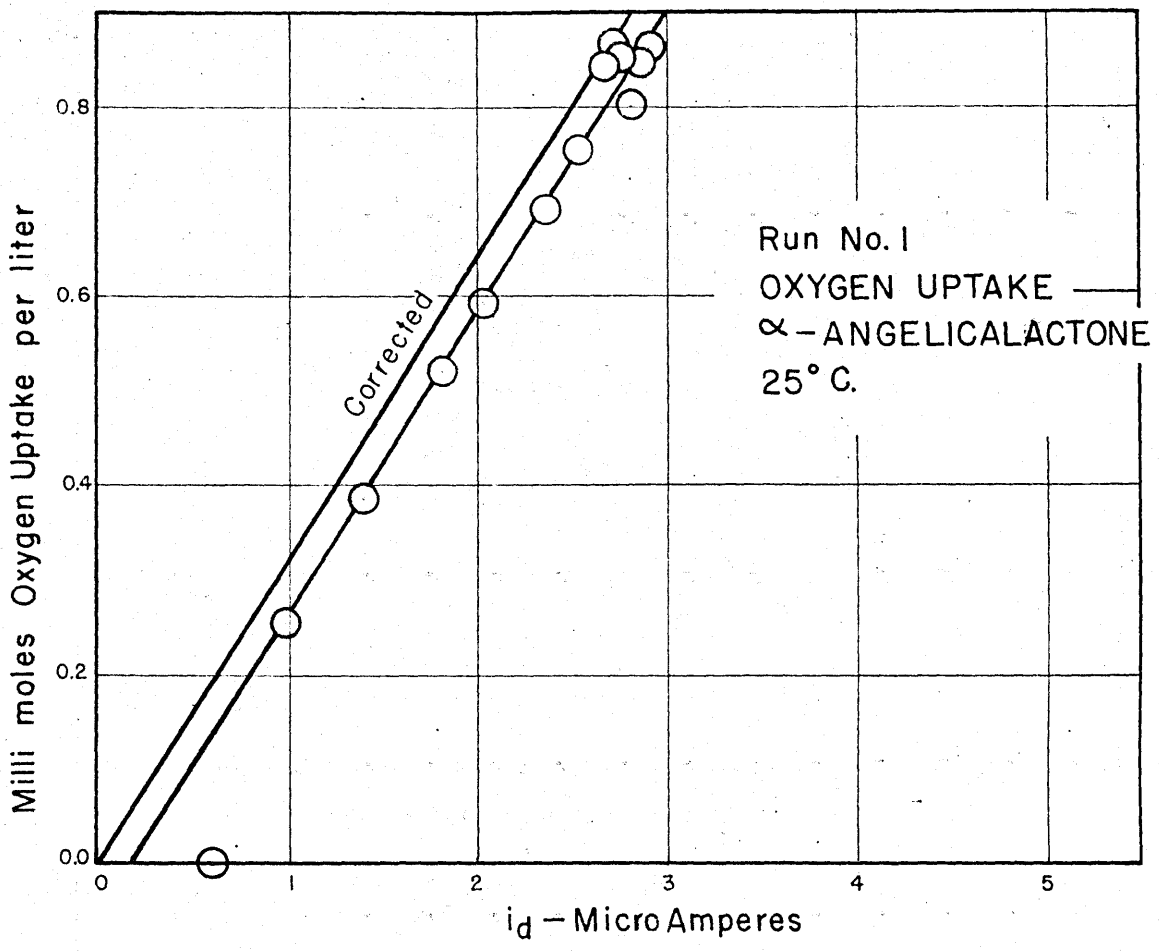
capillary was S-4 (1)

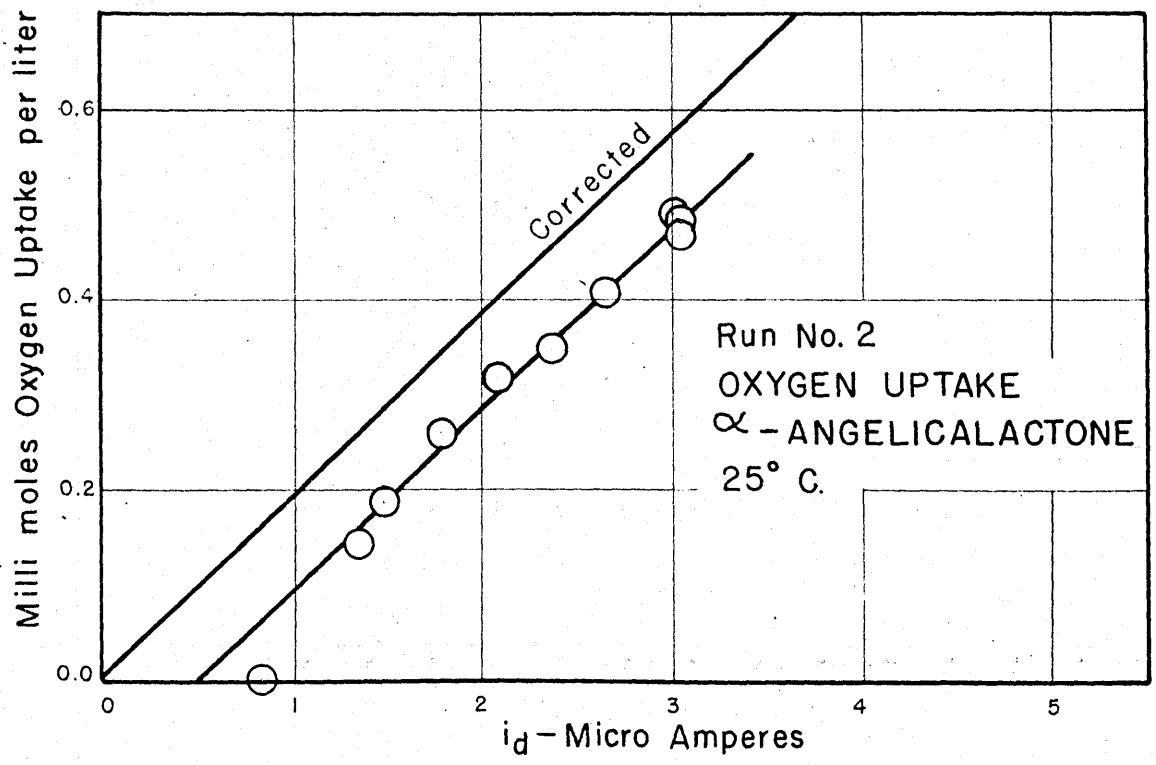
$m^{2/3}t^{1/6}$ was 1.51 at -0.4 volt

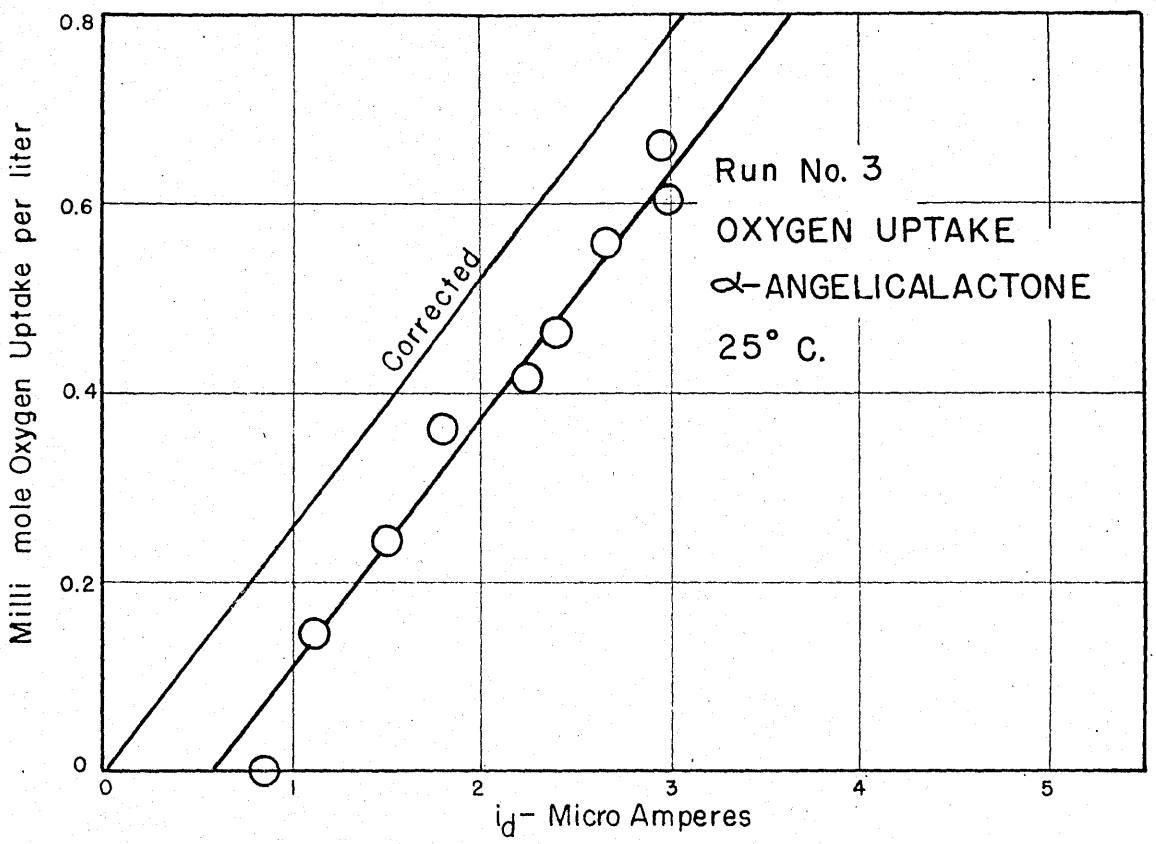
$m^{2/3}t^{1/6}$ was 1.32 at -1.4 volt

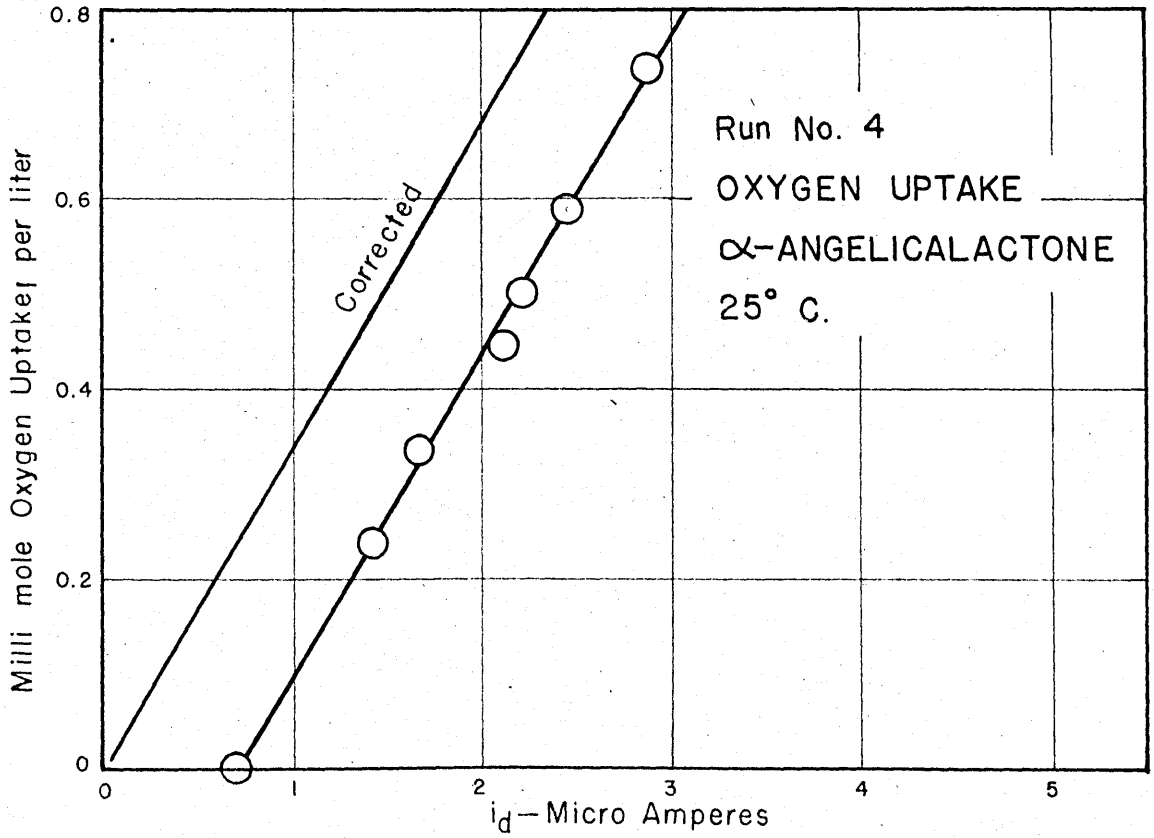
No.	i_d at -0.4 volt in micro-amps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.508	0
2.	0	0	0.24	0.24	0.697	0.107
3.	0	0	0.20	0.20	0.780	0.0892
4.	0	0	0.52	0.52	1.14	0.232
5.	0	0	0.52	0.52	1.26	0.232
6.	0	0	1.08	1.08	1.66	0.482
7.	0	0	1.26	1.26	1.77	0.562
8.	0	0	1.34	1.34	1.94	0.599
9.	0	0	1.54	1.54	2.28	0.688
10.	0	0	1.54	1.54	2.28	0.688
11.	n0	0	1.64	1.64	2.47	0.761
12.	0	0	2.00	2.00	2.66	0.893
13.	0	0	2.08	2.08	2.91	0.930

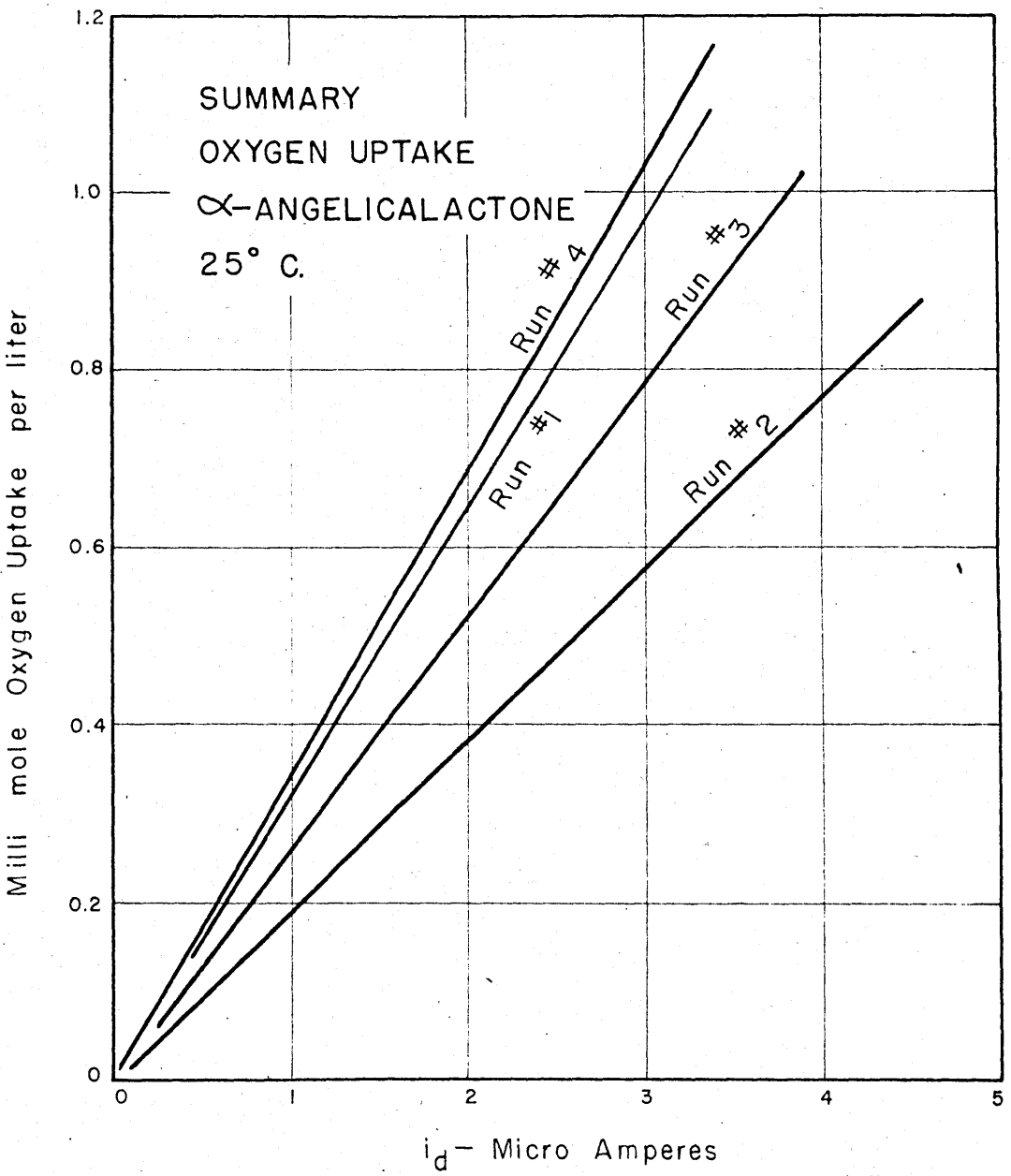
* These volumes are at standard conditions. These results are graphed on page 96.


Milli moles Oxygen Uptake per liter
0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
5
i_d – Micro Amperes
Corrected
Run No. 1
OXYGEN UPTAKE
α – ANGELICALACTONE
25° C.


Milli moles Oxygen Uptake per liter
0.0
0.2
0.4
0.6
0
1
2
3
4
5
i_d – Micro Amperes
Corrected
Run No. 2
OXYGEN UPTAKE
α – ANGELICALACTONE
25° C.


Milli mole Oxygen Uptake per liter
0.8
0.6
0.4
0.2
0
Corrected
Run No. 3
OXYGEN UPTAKE
α-ANGELICALACTONE
25° C.
0
1
2
3
4
5
i_d – Micro Amperes


Milli mole Oxygen Uptake per liter
0.8
0.6
0.4
0.2
0
Corrected
Run No. 4
OXYGEN UPTAKE
α-ANGELICALACTONE
25° C.
0
1
2
3
4
5
i_d – Micro Amperes


SUMMARY
OXYGEN UPTAKE
∝-ANGELICALACTONE
25° C.
Run #4
Run #3
Run #1
Run #2
1.2
1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
4
5
Milli mole Oxygen Uptake per liter
i_d – Micro Amperes

Run #6, 0°C

pH was 9.65, H_3BO_3-KCl-NaOH solution

Concentration of lactone was 0.02356 molar

weight of lactone was 0.2309 per 100 ml. soln.

capillary was S-4 (1)

$m^{2/3}t^{1/6}$ was 1.50 at -0.4 volt

$m^{2/3}t^{1/6}$ was 1.43 at -1.5 volt

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.508	0
2.	0	0	0.32	0.32	1.015	0.143
3.	0	0	0.78	0.78	1.458	0.349
4.	0	0	1.27	1.27	1.665	0.568
5.	0	0	1.58	1.58	2.06	0.708
6.	0	0	2.02	2.02	2.45	0.901
7.	0	0	2.50	2.50	2.74	1.119
8.	0	0	2.82	2.82	3.12	1.260
9.	0.084	0.0151	3.16	3.13	3.41	1.398
10.	0.084	0.0151	3.35	3.32	3.44	1.480
11.	0.190	0.0343	3.74	3.66	3.77	1.64

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
12.	0.190	0.0343	4.00	3.92	4.43	1.75
13.	1.46	0.264	5.54	4.95	5.19	2.21
14.	1.92	0.346	5.76	4.99	5.19	2.23
15.	2.51	0.452	6.00	4.99	5.36	2.23
16.	3.53	0.637	7.26	5.84	5.91	2.60
17.	4.00	0.720	7.48	5.87	5.81	2.61
18.	4.95	0.891	7.68	5.69	5.90	2.54
19.	5.69	1.022	7.90	5.61	5.79	2.50

* These volumes at standard conditions. These results are graphed on page 97.

Run #7, 0°C.

pH was 9.65, H_3BO_3-KCl-NaOH solution

concentration of lactone was 0.02942 molar

weight of lactone was 0.2883 grams per 100 ml. solution

capillary was S-4 (2)

$m^{2/3}t^{1/6}$ was 1.42 at -0.4 volt

$m^{2/3}t^{1/6}$ was 1.36 at -1.5 volt

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.426	0
2.	0	0	0.48	0.48	0.896	0.215
3.	0	0	0.76	0.76	1.255	0.340
4.	0	0	0.94	0.94	1.515	0.420
5.	0	0	1.18	1.18	1.812	0.528
6.	0	0	1.42	1.42	2.045	0.635
7.	0	0	1.80	1.80	2.470	0.805
8.	0	0	1.99	1.99	2.750	0.890
9.	0	0	2.78	2.78	3.37	1.24
10.	0	0	3.28	3.28	3.90	1.47
11.	0	0	3.78	3.78	4.51	1.69
12.	0	0	3.94	3.94	4.64	1.76
13.	0	0	4.14	4.14	4.85	1.85
14.	0	0	4.42	4.42	4.94	1.98
15.	0.213	0.0395	4.58	4.49	4.94	2.00
16.	0.256	0.0475	5.68	5.57	6.48	2.48

No.	i_d at -0.4 volt in microamps.	oxygen concentration m. mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.52 volt in microamps.	L millimole oxygen reacted per liter
17.	0.426	0.0790	5.92	5.74	6.64	2.57
18.	0.468	0.0869	6.34	6.15	6.82	2.75
19.	0.724	0.1341	6.74	6.44	6.94	2.88
20.	0.938	0.174	7.18	6.79	7.32	3.03
21.	0.639	0.118	7.18	6.92	7.50	3.10
22.	4.05	0.750	8.45	6.77	7.77	3.02
23.	4.89	0.908	8.62	6.59	7.45	2.94

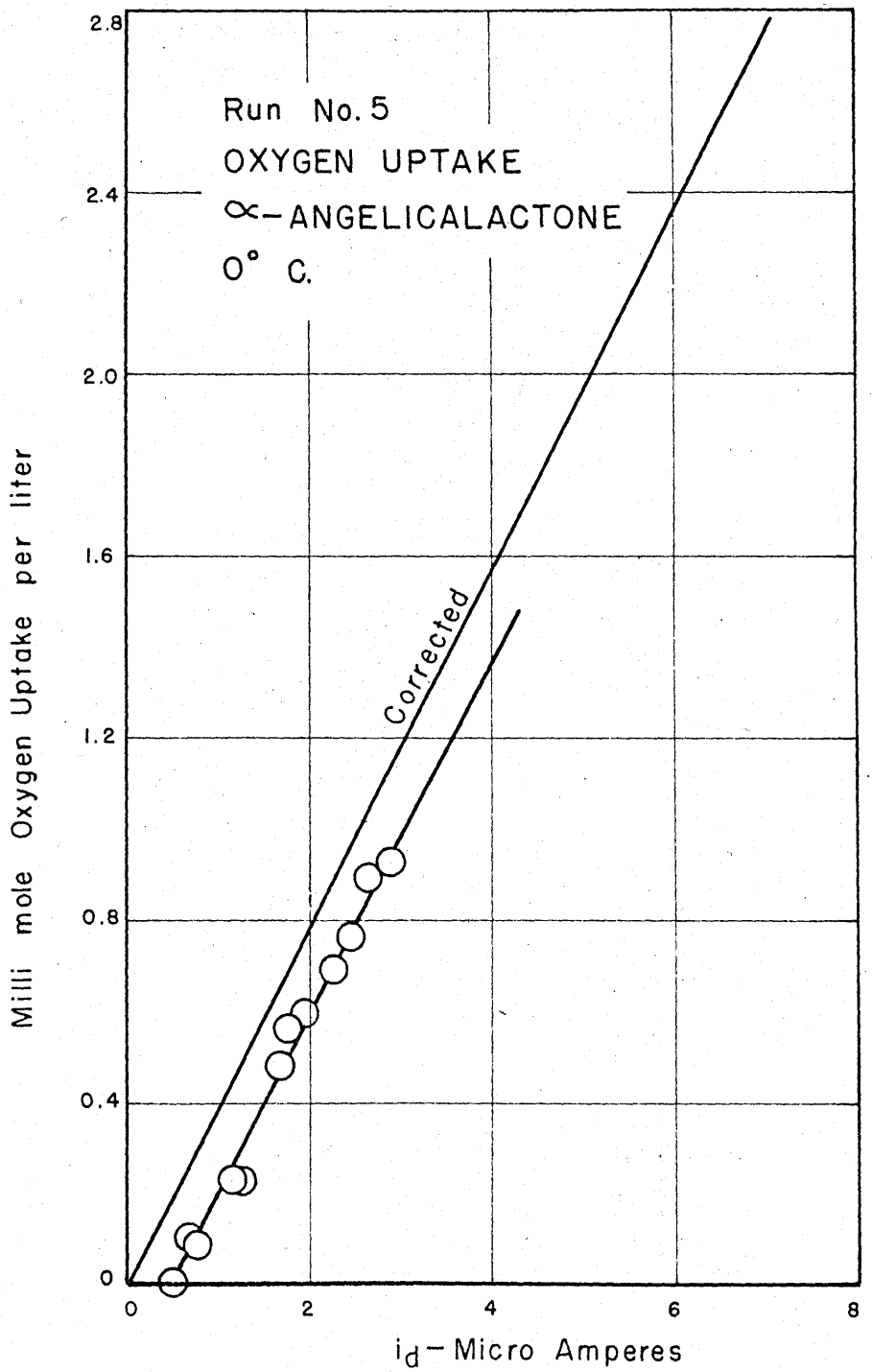
* These volumes are at standard conditions. These results are graphed on page 98.

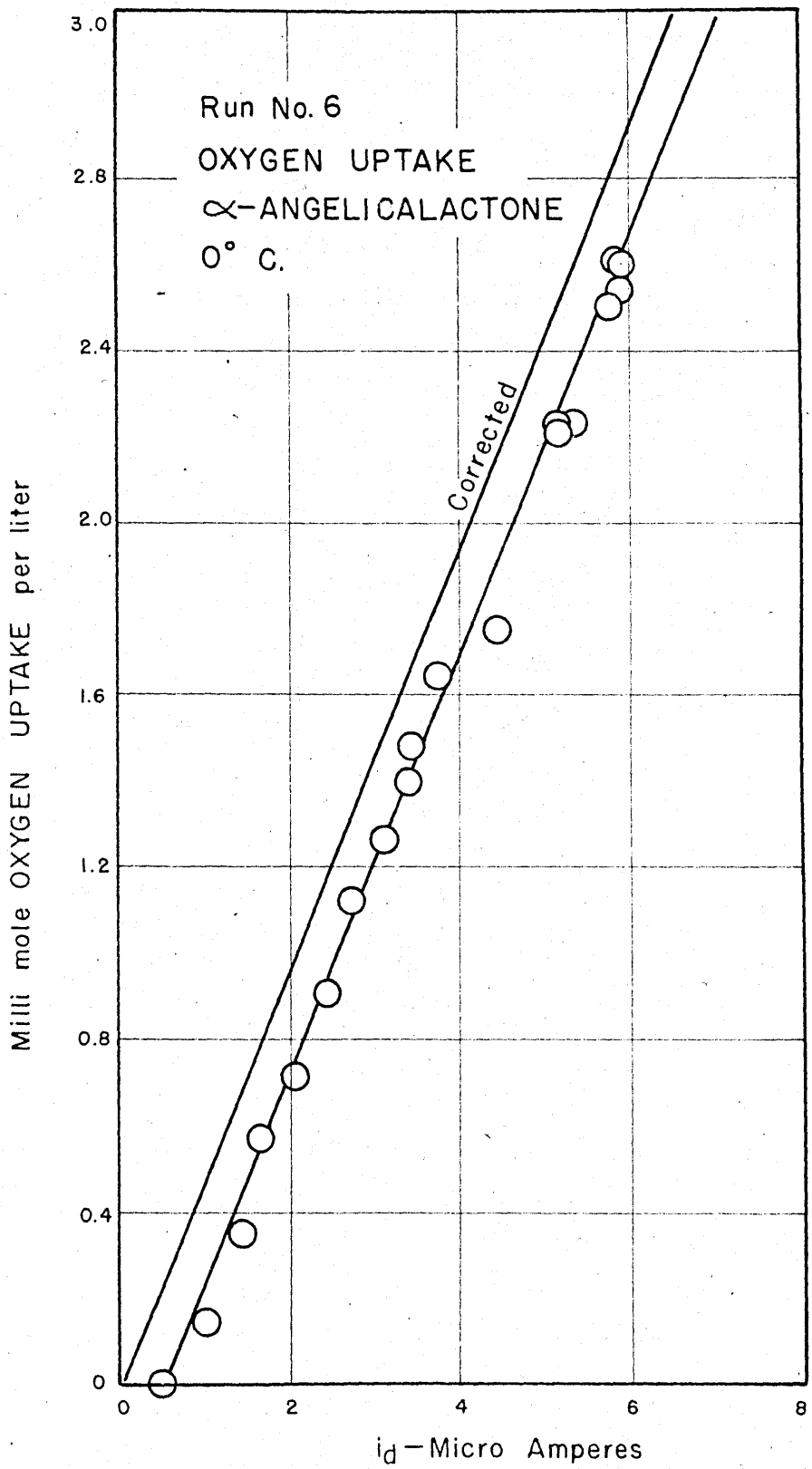
The corrected curves for runs #5, #6, and #7 are graphed together on page 99.

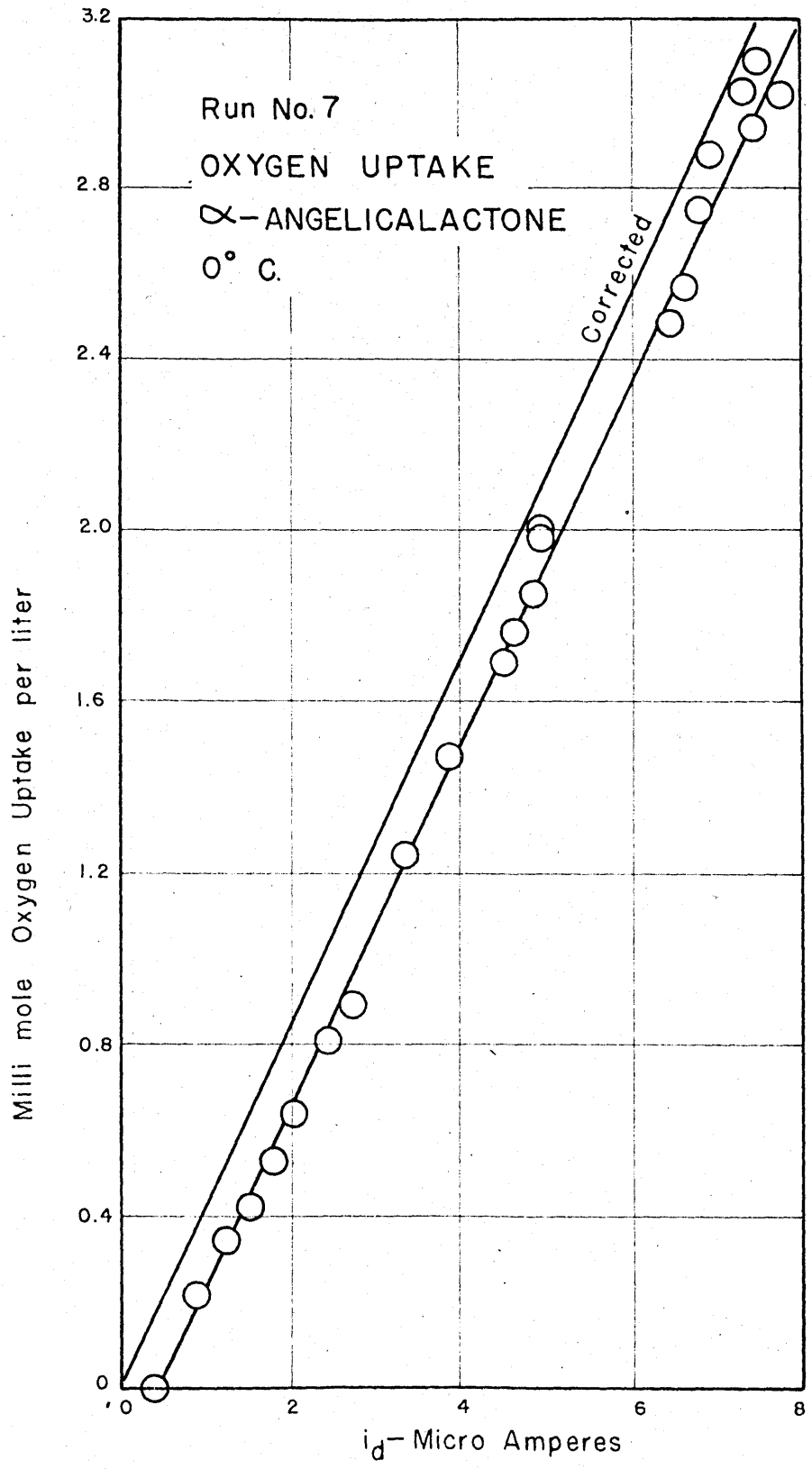
Kinetics of Oxygen Uptake of α-Angelicalactone

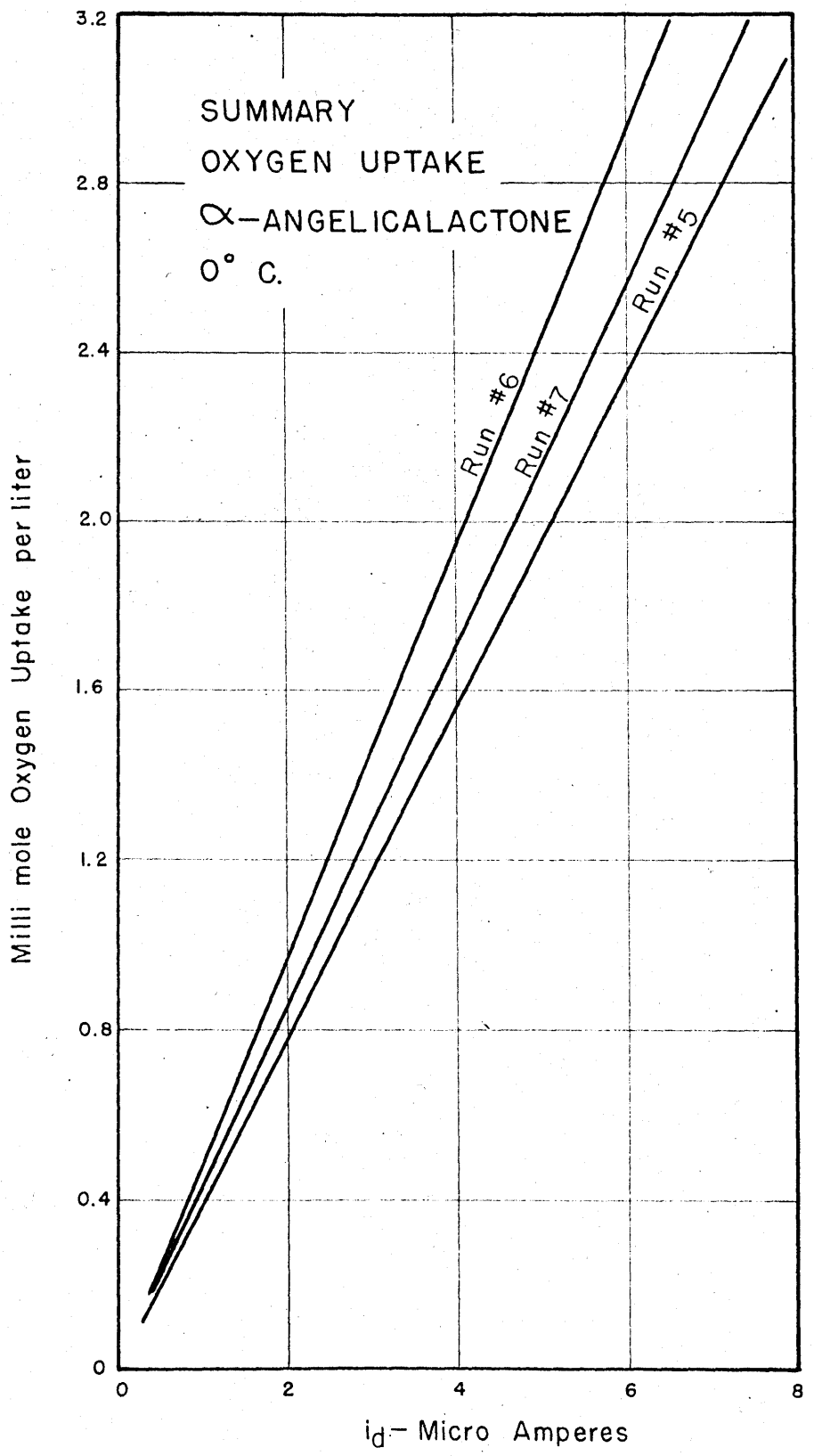
The kinetics data for one run at 25°C are taken from the run labeled #4 in this thesis.

time in min.	L (millimol oxygen per liter solution)	time in min.	L(millimol oxygen per liter solution)	time in min.	L (millimol oxygen per liter solution)
0	0	23	0.446	33	0.590
10	0.239	28	0.500	16 hr 55 min	0.739
15	0.336				


Run No. 5
OXYGEN UPTAKE
∝-ANGELICALACTONE
0° C.
Corrected
Milli mole Oxygen Uptake per liter
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
i_d - Micro Amperes


Run No. 6
OXYGEN UPTAKE
α-ANGELICALACTONE
0° C.
Corrected
Milli mole OXYGEN UPTAKE per liter
3.0
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
i_d – Micro Amperes


Run No. 7
OXYGEN UPTAKE
α-ANGELICALACTONE
0° C.
Corrected
Milli mole Oxygen Uptake per liter
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
i_d – Micro Amperes


SUMMARY
OXYGEN UPTAKE
α—ANGELICALACTONE
0° C.
Run #6
Run #7
Run #5
Milli mole Oxygen Uptake per liter
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
i_d — Micro Amperes

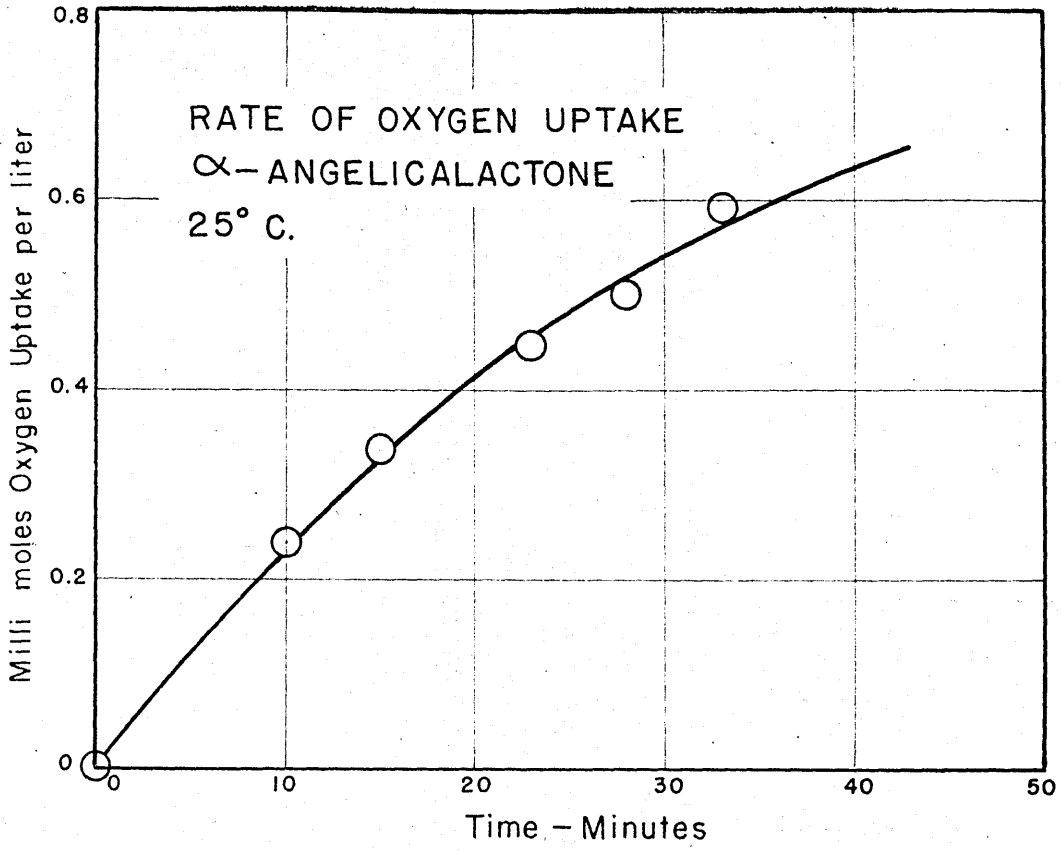
The kinetics data for one run at 0°C are taken from the run labeled #7 in this thesis.

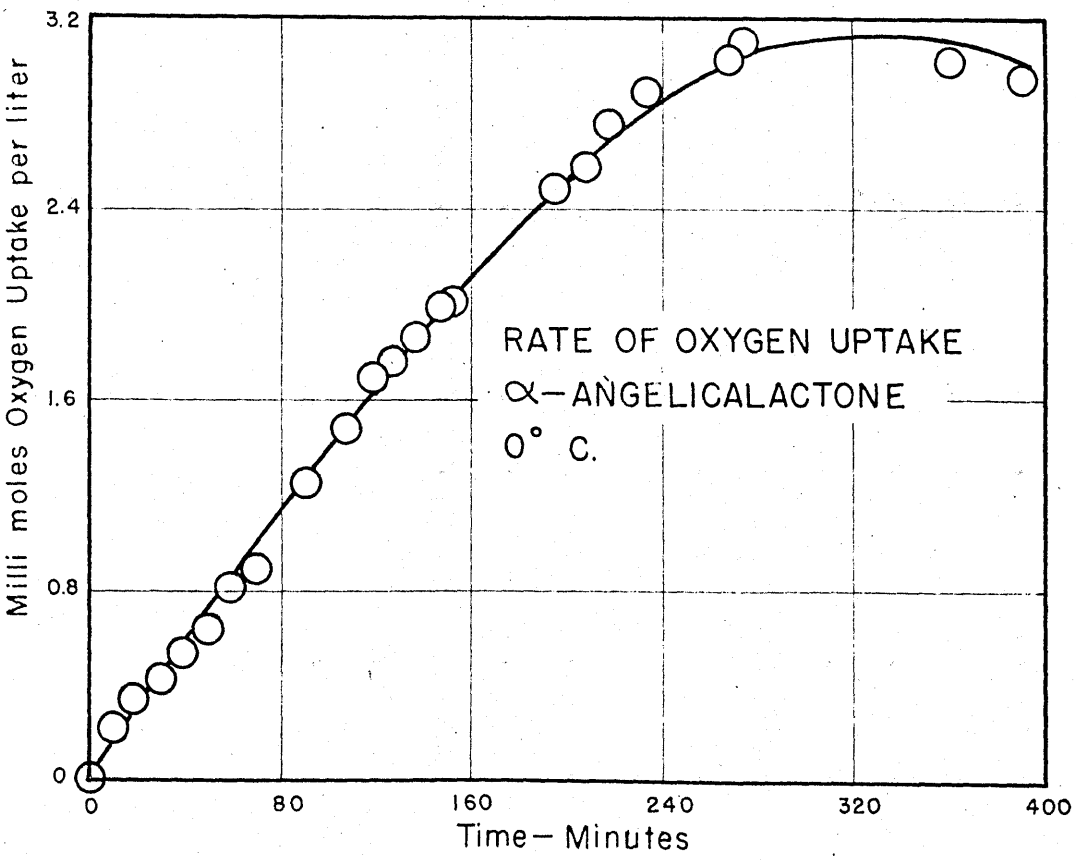
time in min.	L (millimol oxygen per liter solution)	Time in min.	L (millimol oxygen per liter solution
0	0	137	1.85
10	0.215	147	1.98
20	0.340	152	2.00
30	0.420	195	2.48
40	0.528	208	2.57
50	0.635	218	2.75
60	0.895	233	2.88
70	0.890	268	3.03
90	1.24	274	3.10
107	1.47	361	3.02
119	1.69	391	2.94
127	1.76		

These results are graphed on page 102.

Half Wave Potential of β-Angelicalactone Peroxide: Effect of Concentration.

No.	pH	Lactone Concentration in molarity	$m^{2/3}t^{1/6}$ at -1.5v in mg./sec.	i_d in micro amps.	$E_{\frac{1}{2}}$ vs. SCE in volts	Capillary	Media
1.	9.65	0.0173	1.46	0.347	-1.32	S-3(2)	H_3BO_3-KCl-NaOH
2.	9.65	0.0282	1.46	0.469	-1.33	S-3(2)	"
3.	9.65	0.0092	1.46	0.510	-1.32	S-3(2)	"
4.	9.65	0.0393	1.46	0.612	-1.33	S-3(2)	"
5.	9.65	0.0191	1.46	1.02	-1.33	S-3(2)	"
6.	9.52	0.0091	2.21	1.08	-1.31	1	"
7.	9.65	0.0440	1.46	1.22	-1.33	S-3(2)	"
8.	9.65	0.0276	1.46	1.39	-1.31	S-3(2)	"
9.	9.65	0.0370	1.46	1.92	-1.32	S-3(2)	"
10.	9.65	0.0211	1.48	2.35	-1.31	S-3(2)	"
11.	9.65	0.0211	1.48	3.01	-1.32	S-3(2)	"
12.	9.65	0.0211	1.48	4.28	-1.35	S-3(2)	"
13.	9.65	0.0211	1.48	5.79	-1.32	S-3(2)	"
14.	9.65	0.0211	1.48	6.23	-1.33	S-3(2)	"
15.	9.65	0.0211	1.48	7.75	-1.32	S-3(2)	"


RATE OF OXYGEN UPTAKE
α-ANGELICALACTONE
25° C.
Milli moles Oxygen Uptake per liter
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
Time - Minutes


RATE OF OXYGEN UPTAKE
α-ANGELICALACTONE
0° C.
Milli moles Oxygen Uptake per liter
3.2
2.4
1.6
0.8
0
0
80
160
240
320
400
Time - Minutes

No.	pH	Lactone concentration in molarity	$m^{2/3}t^{1/6}$ at -1.5 v in mg./sec.	i_d in micro amps.	$E_{\frac{1}{2}}$ vs. SCE in volts	Capillary	Media
16.	9.65	0.0211	1.48	8.98	-1.33	S-3(2)	H_3BO_3-KCl-NaOH
17.	9.65	0.0211	1.48	11.10	-1.32	S-3(2)	"
18.	8.78	0.00971	2.21	0.61	-1.31	1	"
19.	8.04	0.00951	2.21	0.18	ca -1.32	1	KH_2PO_4-NaOH

β-Angelicalactone Peroxide: Reversibility and the Number of Electrons Involved in Reduction

The following results are from a polarogram obtained in one of the oxygen uptake runs at 25°C.

E_{de} in volts	i_d in microamps	i in microamps.	$\log \frac{i}{i_d - i}$
-1.285	7.53	2.56	-0.2882
-1.297	7.53	3.18	-0.1362
-1.310	7.53	3.91	0.0335
-1.322	7.53	4.64	0.2056
-1.333	7.53	5.33	0.3843

These results are graphed on page 83.

slope of the curve is 14.0 n is 0.827

Oxygen Uptake of β-Angelicalactone at 25°C

Run #8, 25°C

pH was 9.65, H_3BO_3-KCl-NaOH solution Capillary was S-3 (2)

concentration of lactone was 0.02461 molar $m^{2/3}t^{1/6}$ was 1.54 at -0.4 volt

weight of lactone was 0.3015 grams per 125 ml. solution

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.755	0
2.	0.897	0.094	0.37	0.07	1.37	0.0279
3.	1.322	0.139	0.79	0.35	1.59	0.139
4.	1.425	0.150	0.87	0.40	1.75	0.159
5.	1.63	0.171	1.02	0.48	1.95	0.191
6.	1.875	0.197	1.19	0.57	2.08	0.226
7.	2.04	0.214	1.37	0.70	2.36	0.278
8.	2.20	0.231	1.59	0.86	2.65	0.342
9.	2.77	0.291	2.07	1.15	2.94	0.458

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
10.	2.76	0.290	2.22	1.31	3.26	0.522
11.	3.06	0.322	2.49	1.48	3.36	0.590
12.	3.46	0.364	2.95	1.81	3.67	0.720
13.	3.46	0.364	3.17	2.03	3.76	0.808
14.	4.29	0.450	3.47	2.05	4.18	0.815
15.	5.40	0.568	4.17	2.39	4.39	0.950
16.	9.68	1.015	9.59	6.41	9.79	2.55

* These volumes calculated at 25°C and 740 mm. pressure.

These results are graphed on page 109.

Run #9, 25°C

pH was 9.65, H_3BO_3-KCl-NaOH solution

concentration of lactone was 0.02271 molar

weight of lactone was 0.2226 grams per 100 ml. solution

capillary was S-3 (2)

$m^{2/3}t^{1/6}$ was 1.54 at -0.4 volt $m^{2/3}t^{1/6}$ was 1.46 at -1.5 volt

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0	0	0	0	0.734	0
2.	0.798	0.084	0.30	0.11	1.22	0.0491
3.	1.16	0.122	0.44	0.17	1.47	0.0760
4.	1.59	0.167	0.50	0.13	1.71	0.0581
5.	2.36	0.248	0.96	0.40	1.99	0.179
6.	2.77	0.291	1.16	0.51	2.16	0.228
7.	2.85	0.300	1.24	0.57	2.48	0.255
8.	3.05	0.321	2.04	1.32	4.12	0.590
9.	3.34	0.351	2.42	1.63	4.23	0.730
10.	3.91	0.412	2.50	1.58	4.64	0.708
11.	4.12	0.433	2.77	1.80	4.60	0.804
12.	4.89	0.513	3.27	2.12	5.30	0.950
13.	5.50	0.579	3.50	2.20	5.50	0.983
14.	5.70	0.600	3.64	2.30	5.50	1.026
15.	5.60	0.589	3.82	2.50	5.90	1.118
16.	0.915	0.096	3.97	3.75	8.35	1.67
17.	3.46	0.364	4.74	3.92	8.35	1.75

* These volumes calculated at standard conditions. These results are graphed on page 109.

Run #10, 25°C

pH was 9.65, H_3BO_3-KCl-NaOH solution — capillary was S-3 (2)

concentration of lactone was 0.02108 molar — $m^{2/3}t^{1/6}$ was 1.48 at -1.5 volt

weight of lactone was 0.2066 grams per 100 ml. soln. — $m^{2/3}t^{1/6}$ was 1.56 at -0.4 volt

No.	i_d -0.4 volt in microamps.	oxygen concentration m mole/liter	V_o^* in ml.	V_r^* in ml.	i_d at -1.32 volt in micro amps.	L millimole oxygen reacted per liter
1.	0.245	0.0254	0	-0.06	0.838	-0.0268
2.	1.43	0.148	0.48	0.15	1.14	0.0670
3.	2.12	0.219	0.52	0.03	1.10	0.0134
4.	0.511	0.053	0.64	0.52	2.35	0.232
5.	3.26	0.338	1.80	1.04	3.34	0.465
6.	3.59	0.371	2.28	1.45	4.48	0.649
7.	0.326	0.034	2.60	2.52	5.79	1.127
8.	2.36	0.245	3.03	2.48	6.02	1.110
9.	3.09	0.320	3.25	2.53	6.23	1.131

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_0^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen per liter solution
10.	0.571	0.059	3.32	3.19	7.53	1.425
11.9	1.324	0.138	3.58	3.27	7.75	1.461
12.	3.46	0.359	4.07	3.27	7.85	1.461
13.	4.28	0.443	4.38	3.39	7.53	1.518
14.	7.44	0.770	5.50	3.78	8.79	1.690

* These volumes are calculated at standard conditions.

These results are graphed on page 110.

The corrected curves of run #8, #9 and #10 are summarized on a graph on page 111.

Oxygen Uptake of β-Angelicalactone at 0°C

Run #11, 0°C

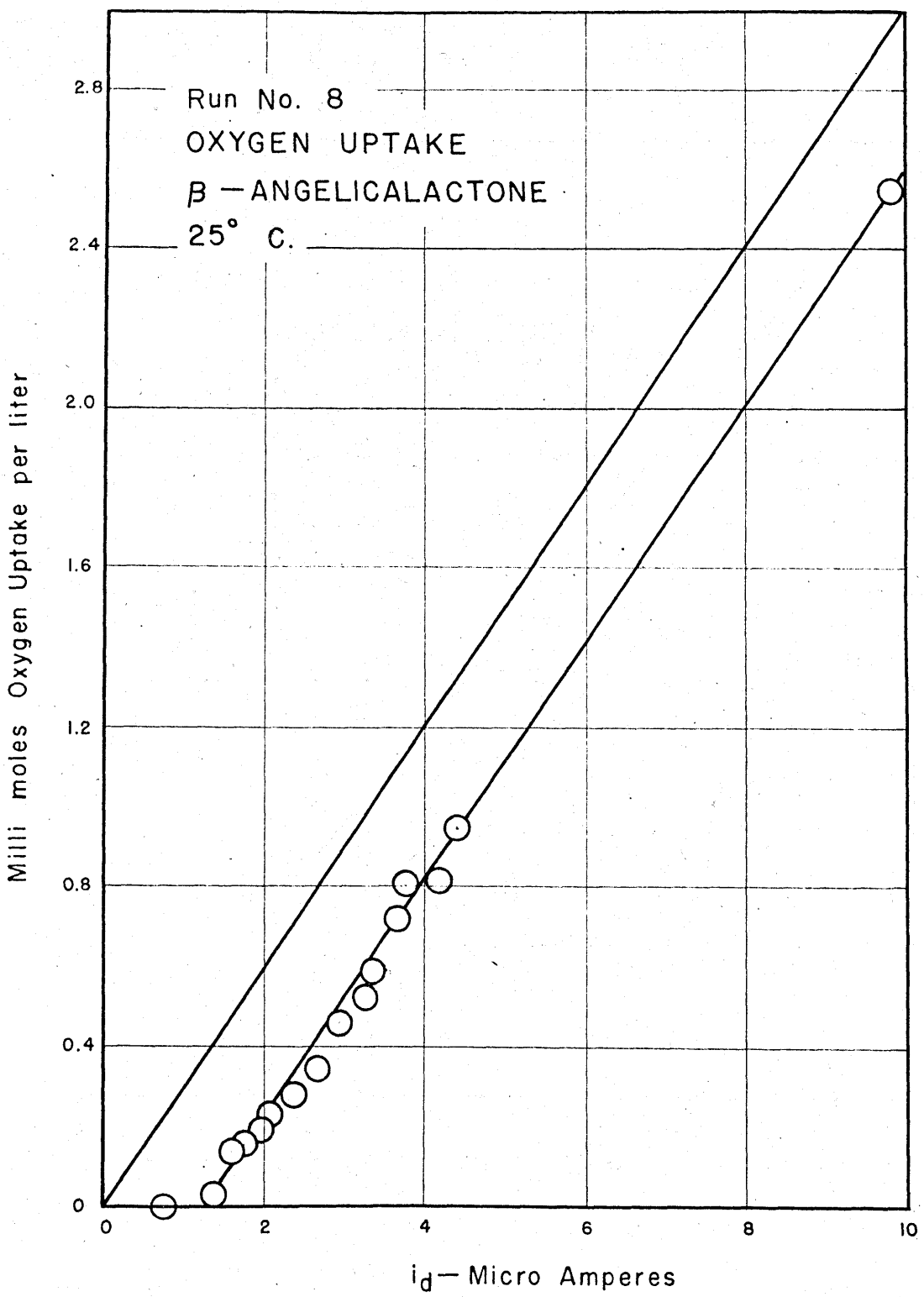
pH was 9.65, H_3BO_3-KCl-NaOH solution

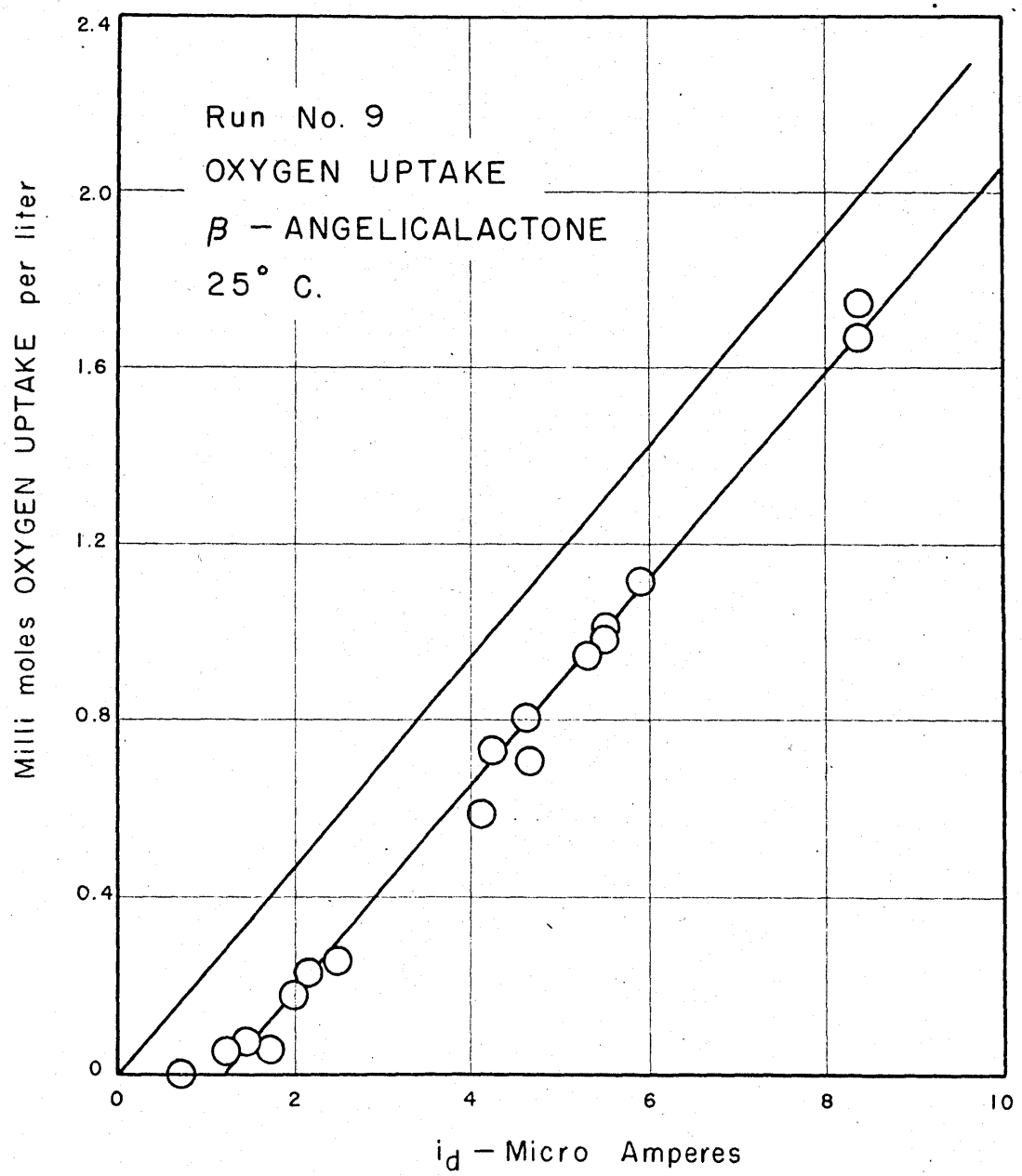
concentration of lactone was 0.02079 molar

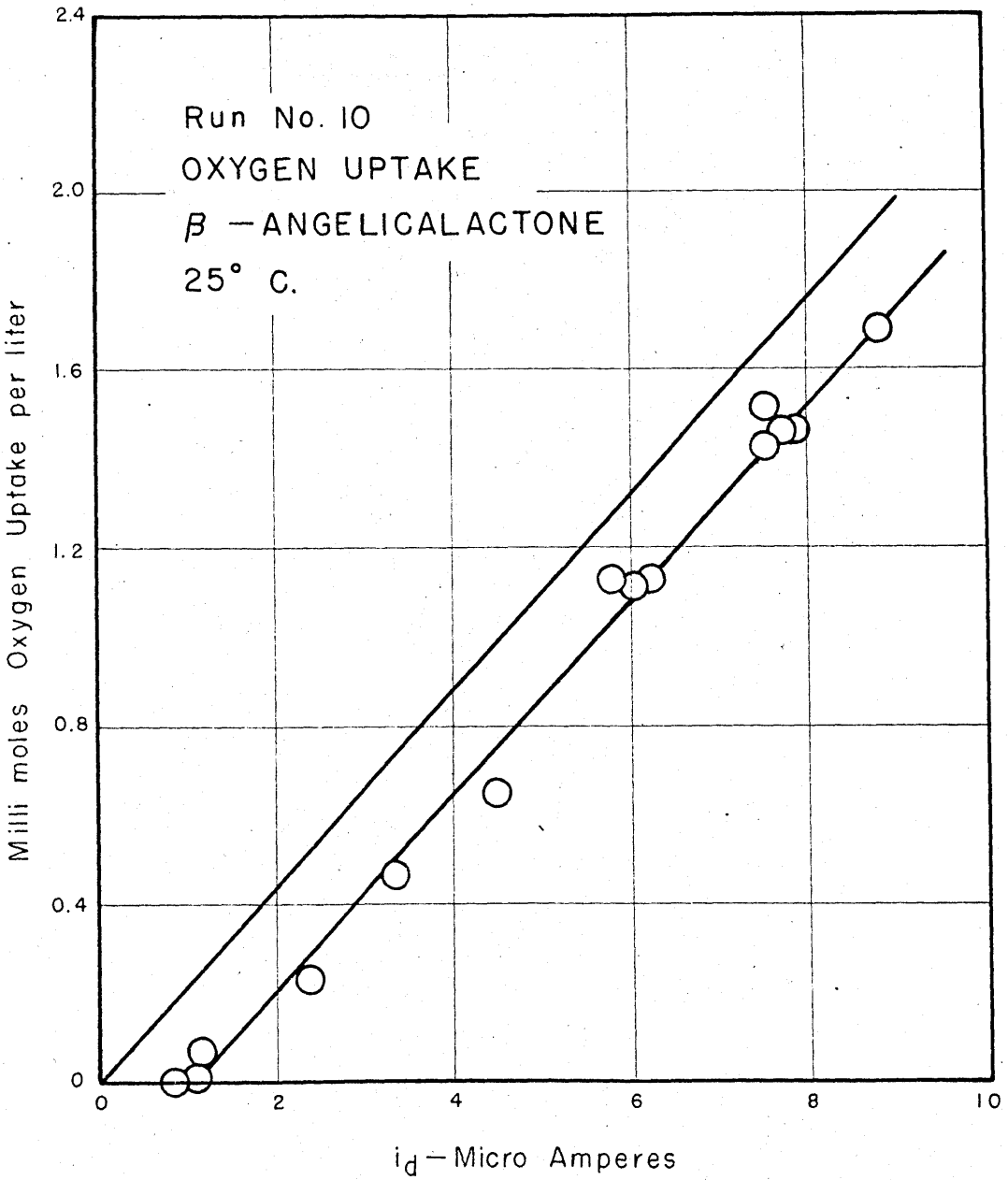
weight of the lactone was 0.2037 grams per 100 ml. solution

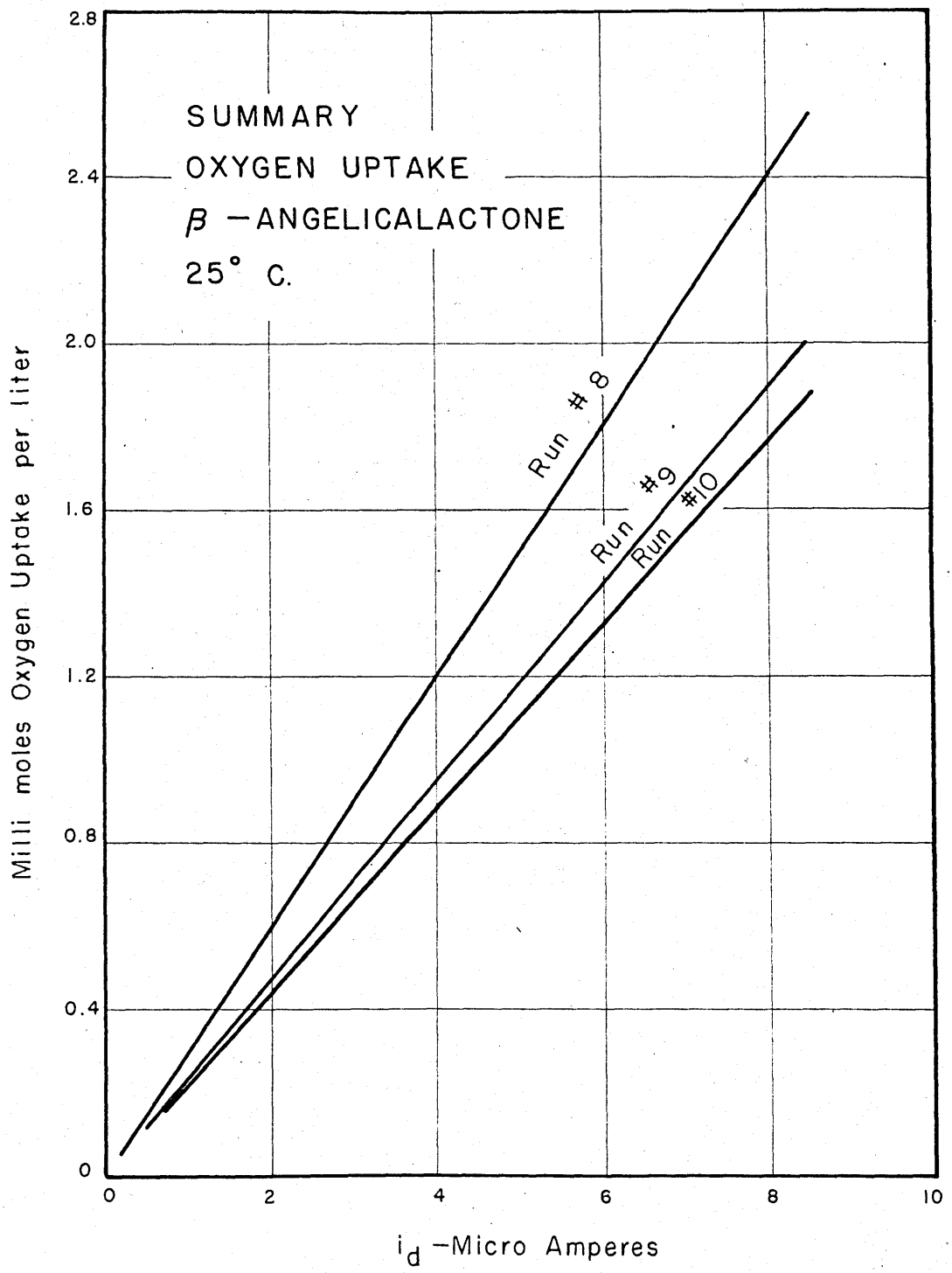
capillary was S-3 (3)

$m^{2/3}t^{1/6}$ was 1.42 at -0.4 volt


Run No. 8
OXYGEN UPTAKE
β — ANGELICALACTONE
25° C.
Milli moles Oxygen Uptake per liter
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
i_d — Micro Amperes


Run No. 9
OXYGEN UPTAKE
β – ANGELICALACTONE
25° C.
Milli moles OXYGEN UPTAKE per liter
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
i_d – Micro Amperes


Run No. 10
OXYGEN UPTAKE
β —ANGELICALACTONE
25° C.
Milli moles Oxygen Uptake per liter
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
i_d — Micro Amperes


SUMMARY
OXYGEN UPTAKE
β —ANGELICALACTONE
25° C.
Run #8
Run #9
Run #10
Milli moles Oxygen Uptake per liter
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0
0
2
4
6
8
10
i_d —Micro Amperes

No.	i_d at -0.4 volt in microamps.	oxygen concentration m mole/liter	V_b^* in ml.	V_r^* in ml.	i_d at -1.32 volt in microamps.	L millimole oxygen reacted per liter
1.	0.126	0.0233	0	-0.05	0.231	-0.0224
2.	0.581	0.1075	0.12	-0.12	0.337	-0.0538
3.	0.971	0.180	0.34	-0.06	0.401	-0.0268
4.	1.71	0.316	0.70	-0.01	0.529	-0.0045
5.	2.91	0.538	1.28	0.08	0.780	0.0358
6.	2.99	0.552	1.32	0.08	0.353	0.0358
7.	2.66	0.492	1.62	0.52	1.14	0.232
8.	3.75	0.693	2.06	0.51	1.01	0.228
9.	3.41	0.630	2.34	0.93	1.39	0.416
10.	2.00	0.370	2.24	1.41	1.96	0.631
11.	1.85	0.342	2.02	1.25	1.90	0.560

* These volumes are calculated at standard conditions.

These results are graphed on page 115.

Kinetics of Oxygen Uptake of β-Angelicalactone.

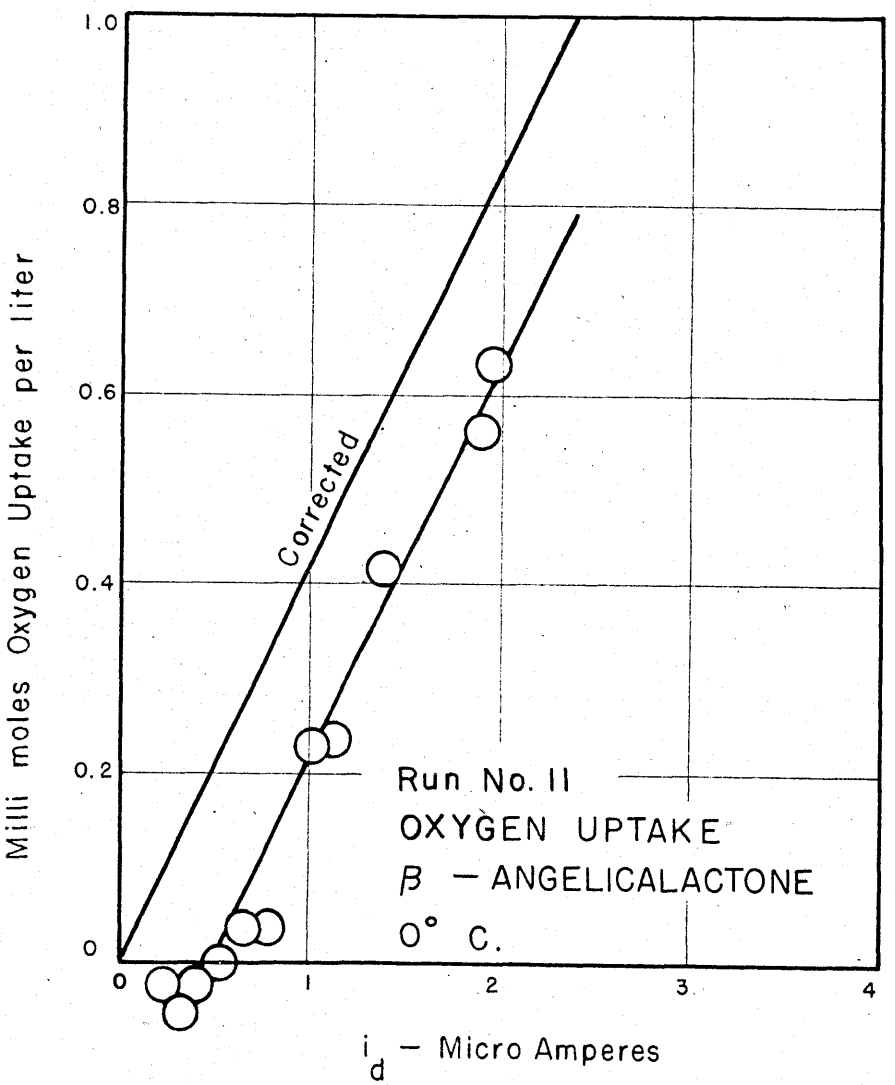
The kinetics data for one run at 25°C are taken from the run labeled #8 in this thesis.

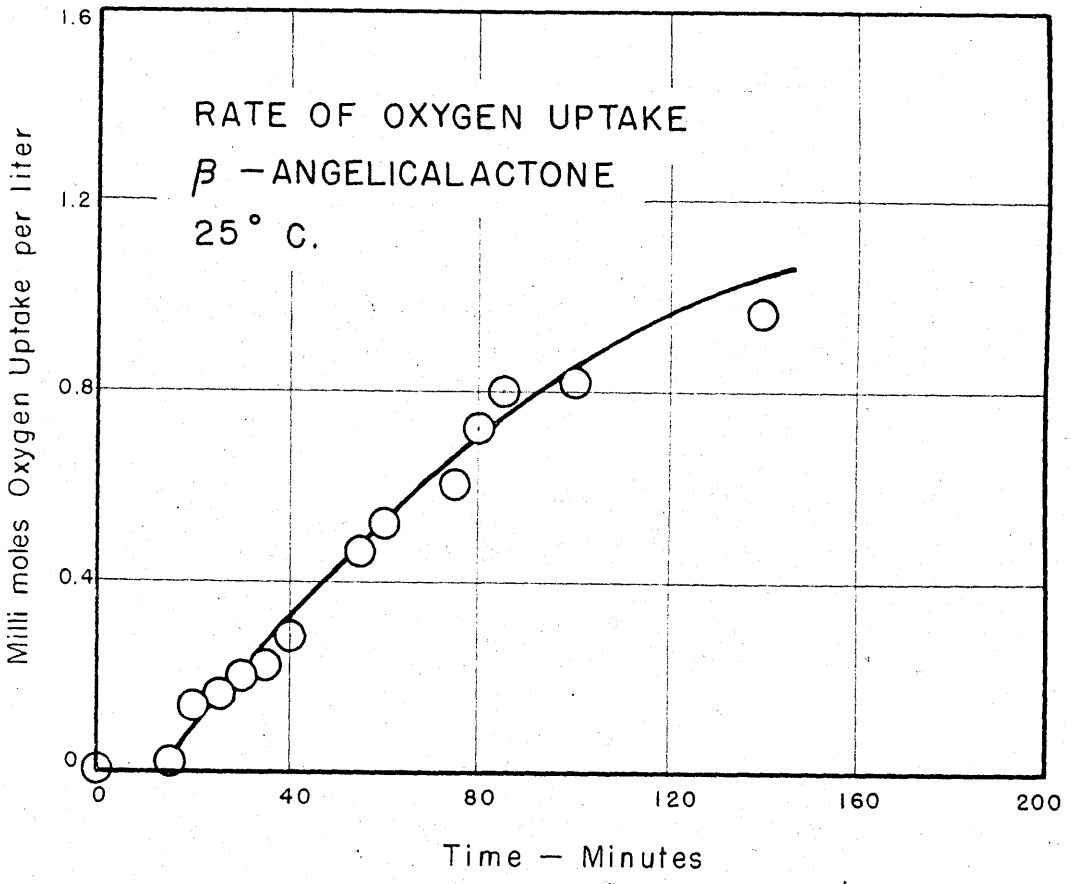
time in min.	L (millimol oxygen reacted per liter)	time in min.	L (millimol oxygen reacted per liter)	time in min.	L (millimol oxygen reacted per l)
0	0	35	0.236	75	0.590
15	0.0279	40	0.278	80	0.720
20	0.139	45	0.342	85	0.808
25	0.159	55	0.458	100	0.815
30	0.191	60	0.522	140	0.950

Reduction of α- and β-Angelicalactone

α-Angelicalactone

No.	Media	Lactone Concentration molarity	$E_{\frac{1}{2}}$ vs SCE in volts	i_d in microamps.	Capillary	$m^{2/3}t^{1/6}$
1.	0.1M $(CH_3)_4NBr$	0.00857	no wave		1	2.17 at -1.5 volt
2.	"	0.00755	no wave		1	2.17 at -1.5 volt
3.	"	0.00748	no wave		1	2.17 at -1.5 volt
4.	"	0.01302	no wave		S-3 (2)	1.34 at -2.0 volt
5.	"	0.02363	no wave		S-3 (2)	1.35 at -2.0 volt


1.0
0.8
0.6
0.4
0.2
0
0
1
2
3
4
Milli moles Oxygen Uptake per liter
Corrected
Run No. II
OXYGEN UPTAKE
β — ANGELICALACTONE
0° C.
i_d — Micro Amperes


RATE OF OXYGEN UPTAKE
β —ANGELICALACTONE
25° C.
Milli moles Oxygen Uptake per liter
1.6
1.2
0.8
0.4
0
0
40
80
120
160
200
Time — Minutes

β-Angelicalactone

No.	Media	Lactone Concentration molarity	$E_{\frac{1}{2}}$ vs SCE in volts	i_d in microamps.	Capillary	$m^{2/3}t^{1/6}$
1.	0.2 M $(CH_3)_4NBr$	0.00991	ca -1.88	ca 31	1	2.19 at -1.5 v
			ca -1.99	ca 18		
2.	0.1 M $(CH_3)_4NBr$	0.00873	ca -1.89	ca 20	1	2.17 at -1.5 v
			ca -1.97	ca 15		
3.	"	0.00890	ca -1.89	ca 29	1	2.19 at -1.5 v
			ca -1.98	ca 14		
4.	"	0.01082	ca -1.89	ca 35	1	2.19 at -1.5 v
			ca -2.00	ca 21		
5.	"	0.00869	ca -1.88	ca 28	1	2.17 at -1.5 v
			ca -1.97	ca 13		
6.	"	0.00971	ca -1.88	ca 36	1	2.19 at -1.5 v
			ca -2.00	ca 19		
7.	"	0.001049	ca -1.88	ca 27	1	2.17 at -1.5 v
			ca -1.97	ca 15		

No.	Media	Lactone Concentration molarity	$E_{\frac{1}{2}}$ vs SCE in volts	i_d in microamps.	Capillary	$m^{2/3}t^{1/6}$
8.	0.1 M $(CH_3)_4NBr$	0.01090	ca -1.88	ca 32	1	2.19 at -1.5 v
			ca -1.97	ca 19		
9.	"	0.01298	ca -1.88	ca 35	1	2.17 at -1.5 v
			ca -2.00	ca 21		
10.	"	0.00971	ca -1.88	ca 30	1	2.19 at -1.5 v
			ca -1.98	ca 13		
11.	"	0.00947	ca -1.88	ca 29	S-3 (2)	1.36 at -2.0 v
			ca -1.99	ca 11		
12.	"	0.01992	ca -1.88	ca 47	S-3 (2)	1.37 at -2.0 v
			ca -2.02	ca 28		
13.	H_3BO_3-KCl-NaOH pH 9.52	0.00918	ca -1.87	ca 35 maximum	1	2.21 at -1.5 v
14.	H_3BO_3-KCl-NaOH pH 9.66	0.00878	ca -1.90	ca 41 maximum	1	2.28 at -1.5 v
15.	H_3BO_3-KCl-NaOH pH 9.66 1 drop 1% gel.	0.00878	ca-1.91	ca 26 no max.	1	2.21 at -1.5 v

No.	Media	Lactone Concentration molarity	$E_{\frac{1}{2}}$ vs SCE in volts	i_d in microamps.	Capillary	$m^{2/3}t^{1/6}$
16.	H_3BO_3-KCl-NaOH pH 9.66	0.00906	ca -1.89	ca 38 maximum	1	2.17 at -1.5 v
17.	H_3BO_3-KCl-NaOH pH 9.66 2 drops 1% gel./ 25 ml. sol.	0.00906	ca -1.89	ca 37 no max.	1	2.15 at -1.5 v

Reduction of Levulinic Acid and 2,3-Dihydroxy Valerolactone

Levulinic Acid

No.	pH	Acid Concentration molarity	$E_{\frac{1}{2}}$ vs SCE in volts	i_d in microamps.	Capillary	$m^{2/3}t^{1/6}$	Media
1.	4.84	0.00873	no wave		1	2.26 at -1.5 volt	$KHC_4H_4O_4$-NaOH
2.	5.44	0.01078	no wave		1	2.26 at -1.5 volt	"
3.	6.94	0.01006	no wave		1	2.17 at -1.5 volt	KH_2PO_4-NaOH
4.	8.04	0.01073	no wave		1	2.17 at -1.5 volt	"
5.	8.78	0.01082	no wave		1	2.17 at -1.5 volt	H_3BO_3-KCl-NaOH
6.	9.50	0.01016	no wave		1	2.17 at -1.5 volt	"

2,3-Dihydroxy Valerolactone

	9.66	0.00673	no wave		1	2.17 at -1.5 volt	H_3BO_3-KCl-NaOH

Index of Refraction of α- and β-Angelicalactone

lactone	temperature	n_D^{25}
α-lactone	25.0 ± 0.1°C	1.4457 ± 0.0002
β-lactone	25.0 ± 0.1°C	1.4532 ± 0.0002

V. DISCUSSION OF RESULTS

Diffusion Coefficient of Oxygen

The value of the diffusion coefficient of oxygen as obtained at 25°C in this work, 2.48×10^{-5} cm.^{2} sec.$^{-1}$ $\pm$ 0.08×10^{-5} (cf page 76) is in agreement with that obtained by Kolthoff and Miller (140). Their value was 2.6×10^{-5} cm.^{2}sec.$^{-1}$ in 0.1 M potassium nitrate. It has been shown by Kolthoff and Lingane (132) that diffusion coefficients decrease with increasing concentration for electrolyte solutions but the decrease of diffusion coefficient with increasing concentration is not observed for uncharged substances. The total molarity in the buffer solutions composed of H_3BO_3-KCl-NaOH, pH 9.6, used in this work is 0.283. The fact that the concentration of electrolytes present in these solutions is therefore nearly three times that in the solutions of Kolthoff and Miller may explain the lower diffusion coefficients.

The value of 9.83×10^{-6} cm.^{2} sec.$^{-1}$ for the diffusion coefficient at 0°C is the first value of the diffusion coefficient of oxygen at this temperature to be found in the literature (cf page 76). Since this constant was used to determine that at 25°C, the value of the constant at the lower temperature is as accurate as that at the higher temperature. The average change of the diffusion coefficient per degree over the range 0° to 25° is 0.06×10^{-5} cm.^{2} sec.$^{-1}$ deg.$^{-1}$.

The experimental curves for two oxygen uptake determinations for the boric acid buffer solution at 0°C are graphed on page 77. It can be seen that the first point of each of these determinations is below the line through the remainder of the points. Although the oxygen in these determinations was cooled for at least one half hour before measurement of the volume for these first points, it is probable that temperature equilibrium was not attained in these samples of oxygen until after this first volume was measured and the oxygen was kept in the reaction cell several minutes. Thus, if the oxygen samples were cooled even as little as one degree to 0°C between the first and second point, the decrease in volume of oxygen for the second point was less than observed. However, the slope of the curve obtained is unaffected by this error, which is eliminated by drawing the curves parallel to the experimental curves and through the origin. The first points are included because it is at these points that the initial volumes were measured from which the volume decrease was calculated.

From the corrected curves, at the highest diffusion current obtained (saturated solution), the oxygen is 1.08 x 10^{-3} molar in determination # 1 and 1.14 x 10^{-3} molar in determination # 2.

Half Wave Potential of α-Angelicalactone Peroxide and Reversibility of Reduction

The graph of log $\frac{i}{i_d - i}$ vs. applied potential is a straight line (cf. page 83) for the peroxide of α-angelicalactone. However from the slope of this line, the value of n is 0.77. This is an ambiguous value for the number of electrons involved in the reduction. Therefore, this reduction is irreversible, and nothing can be said concerning the number of electrons involved in the reduction.

A polarographic wave was obtained for α-angelicalactone solutions at $E_{\frac{1}{2}}$ of -1.32 ± 0.02 volts vs SCE. in a basic solution in the pH range 8.04 to 9.65 and in the absence of organic solvents. This pH range was obtained with phosphate and borate buffer solutions. Therefore, these salts have no effect on the $E_{\frac{1}{2}}$. In neutral and acid solutions, no polarographic wave was obtained. Examination of the table of polarograms of α-angelicalactone on page 79 shows no variation of the $E_{\frac{1}{2}}$ in the lactone concentration range 0.00420 molar to 0.0607 molar. However, as will be seen in a later paragraph, the substance being reduced is a peroxide rather than the lactone. Since the diffusion current is proportional to the concentration of the peroxide, the range of diffusion currents over which $E_{\frac{1}{2}}$ is constant is a better estimate of the range of concentration over which $E_{\frac{1}{2}}$ is constant. In this case, the $E_{\frac{1}{2}}$ does not vary in the i_d range from 0.54 ua to 7.77 ua.

When alcohol is present in the solution, at pH of 9.10, there are two waves in the polarogram (cf. #27, page 81), $E_{\frac{1}{2}}$ -1.39v and -1.60 volt vs S.C.E. These waves are close

together and difficult to measure. The half wave potentials are probably accurate to ± 0.05 volt vs. S.C.E. When purified cellosolve is present in the solution at pH 8.80, two waves are again obtained (cf. # 26, page 80), $E_{\frac{1}{2}}$ -1.43 and -1.57 vs. S.C.E. These waves are even closer together than those in the presence of alcohol and the accuracy of these half wave potentials is probably ± 0.10 volt vs. S.C.E. The effect of these solvents could stand further investigation.

In glycine buffer solutions, the $E_{\frac{1}{2}}$ of the peroxide of α-angelicalactone is shifted to -1.27 ± 0.02 vs. S.C.E. This indicates some reaction between glycine and α-angelicalactone peroxide, the nature of which is unknown. The glycine buffer solutions were not used in further studies.

In tetramethyl ammonium bromide solutions, the peroxide $E_{\frac{1}{2}}$ is shifted to -1.58 ± 0.02 volts vs. S.C.E. This is the expected results in these strongly basic solutions. Hydrogen is probably involved in the reduction and the affect of a strong base is to decrease the hydronium ion concentration, thus changing the $E_{\frac{1}{2}}$ to more negative values.

Examination of the table of results on page 79 shows that there is no correlation between lactone concentration and diffusion currents and there should be some correlation if the reduction were that of the lactone. A sample of the lactone was distilled in a nitrogen atmosphere and dissolved in some buffer solution (pH of 9.6) which had been degassed by bubbling with nitrogen. A polarogram of this solution had practically no

wave at $E_{\frac{1}{2}}$ of -1.32 volt. Therefore, the reduction wave is due to the reduction of a peroxide. The fact that the oxygen uptake of this compound was measured further bears out the idea of spontaneous formation of a compound of the lactone and oxygen. The reason for the formation of peroxides in basic solution and the absence of peroxide in acid solutions will be discussed later.

Half Wave Potential of β-Angelicalactone Peroxide and Reversibility of Reduction

A graph of log $\frac{i}{i_d - i}$ vs applied potential is also a straight line for the β-angelicalactone peroxide (cf. page 83). From the slope of the curve, the value of n is 0.83. This is an ambiguous value for the number of electrons involved in the reduction of the peroxide. Therefore, this reduction is also irreversible.

A polarographic wave was obtained for β-angelicalactones solutions at $E_{\frac{1}{2}}$ of -1.32 ± 0.02 volt vs S.C.E. in the pH range 8.04 to 9.66. Examination of the table of polarograms of β-angelicalactone on pages 101 and 103 shows there is no variation in this $E_{\frac{1}{2}}$ over a lactone concentration range 0.0091 molar to 0.044 molar. Since the i_d is proportional to the peroxide concentration, the range of concentration of the reducible substances is given by the i_d range but not by the lactone concentration range. As seen from the table, the $E_{\frac{1}{2}}$ is constant over the i_d range of 0.18 ua to 11.10 ua. The conclusions reached concerning

the effect of pH, media and concentration on the $E_{\frac{1}{2}}$ of α-angelicalactone peroxide are also true for the β-angelicalactone peroxide. When this lactone is distilled in nitrogen, the wave at $E_{\frac{1}{2}}$ of -1.32 is virtually absent.

Reduction of α- and β-Angelicalactone

α-Angelicalactone does not reduce at the dropping mercury electrode in the pH range from 4.84 to 9.66 in the buffer solutions used in this work. The only wave present in the polarograms of these solutions is that of the peroxide in solutions with pH greater than 8.

β-Angelicalactone does reduce in the buffer solution, pH 9.6. The results are given on page 118. The $E_{\frac{1}{2}}$ is -1.89 ± 0.03 vs S.C.E. This wave is very close to the hydrogen wave (-1.95 v) and therefore the measurements on this wave are difficult. The measured diffusion currents are given on pages 118 and 119, but it is doubtful if an accuracy as great as 10% was attained. This wave shows a maximum. The maximum is eliminated by one drop of 1% gelatin solution per 25 ml. of the lactone solution.

In order to study the reduction of these lactones, solutions were made with tetramethyl ammonium bromide. These solutions are very basic and the pH of the solutions was not measured. However, the solutions were made accurately to the concentrations given by means of an analytical balance and volumetric flasks. In these strongly basic solutions, the hydrogen ion concentration is reduced to

such a degree that a hydrogen wave on the polarograms is not formed until an applied potential greater than -2.5 volts vs. S.C.E. is reached (the hydrogen wave for the buffer solutions starts at about -1.95 v at pH 9.5). It was hoped that the reduction wave for the lactones could thus be obtained at applied potentials greater than -1.9 volt.

As mentioned previously, difficulty was encountered in the purification of the tetramethyl ammonium bromide. After several recrystalizations one impurity remained. It had a $E_{\frac{1}{2}}$ of -2.15 vs S.C.E. This is probably an alkali metal such as sodium ($E_{\frac{1}{2}}$ -2.11) or potassium ($E_{\frac{1}{2}}$ -2.13 v).

The data for the reduction of α-angelicalactone in tetramethyl ammonium bromide solution is given on page 114. There is no reduction of α-angelicalactone in tetramethyl ammonium solutions at applied potentials up to -2.5 volts.

The data for the reduction of β-angelicalactone in tetramethyl ammonium bromide solution is given on pages 117 and 118. There are two reduction waves for β-angelicalactone solutions. The $E_{\frac{1}{2}}$ are -1.88 volts and -1.99 volt vs. S.C.E. This first wave was obtained in the buffered solutions. There is no shift of $E_{\frac{1}{2}}$ in tetramethyl ammonium bromide solutions. These waves are very close together and the waves merge together. Since measurements are difficult, the accuracy of the above half wave potentials are probably no betterthan ± 0.03 volt vs. S.C.E. The diffusion currents of the reductions are given on pages

117 and 118, but since the waves are run together, it is doubtful if an accuracy as great as 10% was attained on these measurements. There appears to be a rough proportionality between diffusion current and concentration. The diffusion currents are of the right order of magnitude for the concentrations of lactone in these solutions.

From this work, no conclusions can be drawn regarding the number of steps in the catalytic hydrogen reduction of α-angelicalactone. The reduction of β-angelicalactone in tetramethyl ammonium is a two step reduction. Therefore, the polarographic reduction is similar to the catalytic hydrogen reduction, since β-angelicalactone is hydrogenated first to the saturated lactone and then to the saturated acid by a two step process. Since the two reduction waves on a polarogram are so close together, it is impossible to make measurements accurate enough to determine the number of electrons involved in the reduction or to determine the reversibility. Although the wave at $E_{\frac{1}{2}}$ of -1.89 volt in the buffer solutions shows a maximum unless gelatin is added, the waves in the tetramethyl ammonium bromide solutions apparently do not show a maximum.

Oxygen Uptake of α-Angelicalactone.

A graph of millimoles oxygen per liter of solution reacted with α-angelicalactone vs i_d gives a straight line. The results of four such runs at 25°C are graphed on pages 89 and 90. The curves are corrected as previously described.

by drawing a line parallal to the experimental curve and through the origin. This was necessary since it was impossible to completely remove oxygen from the solution before starting the run.

In the first three runs the first points are below the experimental curve. When the lactone and buffer solutions were put into the cell, the lactone was put in first and washed into the cell with the buffer solution. Since the lactone does not dissolve rapidly, it is possible that the solution became layered with the higher concentration at the bottom next to the mercury. The solutions were mixed by means of a magnetic stirrer, but when the solutions were mixed, the cell contained no gas, i.e., the stirrer bar is further from the magnetic stirrer than when oxygen is in the cell. Putting oxygen in the cell lowers the level of mercury closer to the magnetic stirrer. Formation of layers of different concentration is thought to be the cause of the divergence of the first point because the run was started as soon as thought possible after mixing the solutions, to reduce the possibility of oxygen getting into solution.

In these runs at 25°C, it could be seen from the polarograms that oxygen was absent from solution for most of the range of peroxide concentration over which these runs were made. Even the small amount of dissolved oxygen known to be present initially was shown to be absent. This means that the lactone reacted with the oxygen as fast as it

dissolved in solution. Thus the reaction is a liquid phase reaction. When the concentration of the peroxide approached the limiting concentration, the reaction between oxygen and lactone slowed and stopped. Thus, although the oxygen volume continued to decrease, the decrease was due to the process of saturating the solution with oxygen. No further reaction took place as shown by nearly constant values of the peroxide diffusion current. This caused a grouping of points as shown in run #1. If the peroxide is assumed to be that formed by reaction of one mole of oxygen with one mole of lactone to give one mole of peroxide, then the fraction of lactone converted to peroxide may be calculated from the point on the corrected curves corresponding to the diffusion current of the last experimental point and the original lactone concentration. In run #1, conversion was 3.0%, in run #2, conversion was 1.9%, in run #3 conversion was 2.7%, and in run #4, conversion was 4.0%. These conversion fractions correspond to concentrations of peroxide (same assumption as above) of 9.4×10^{-4} molar in run #1, 5.8×10^{-4} in run #2, 7.8×10^{-4} molar in run #3 and 9.8×10^{-4} in run #4. A typical polarogram of a solution of α-angelicalactone is given in Figure 3, page 131.

The corrected curves are graphed together on page 91. It can be seen that the slopes of these lines are variable. It is known that this unsaturated lactone polymerizes readily. When it is distilled, there is always some polymerised tar

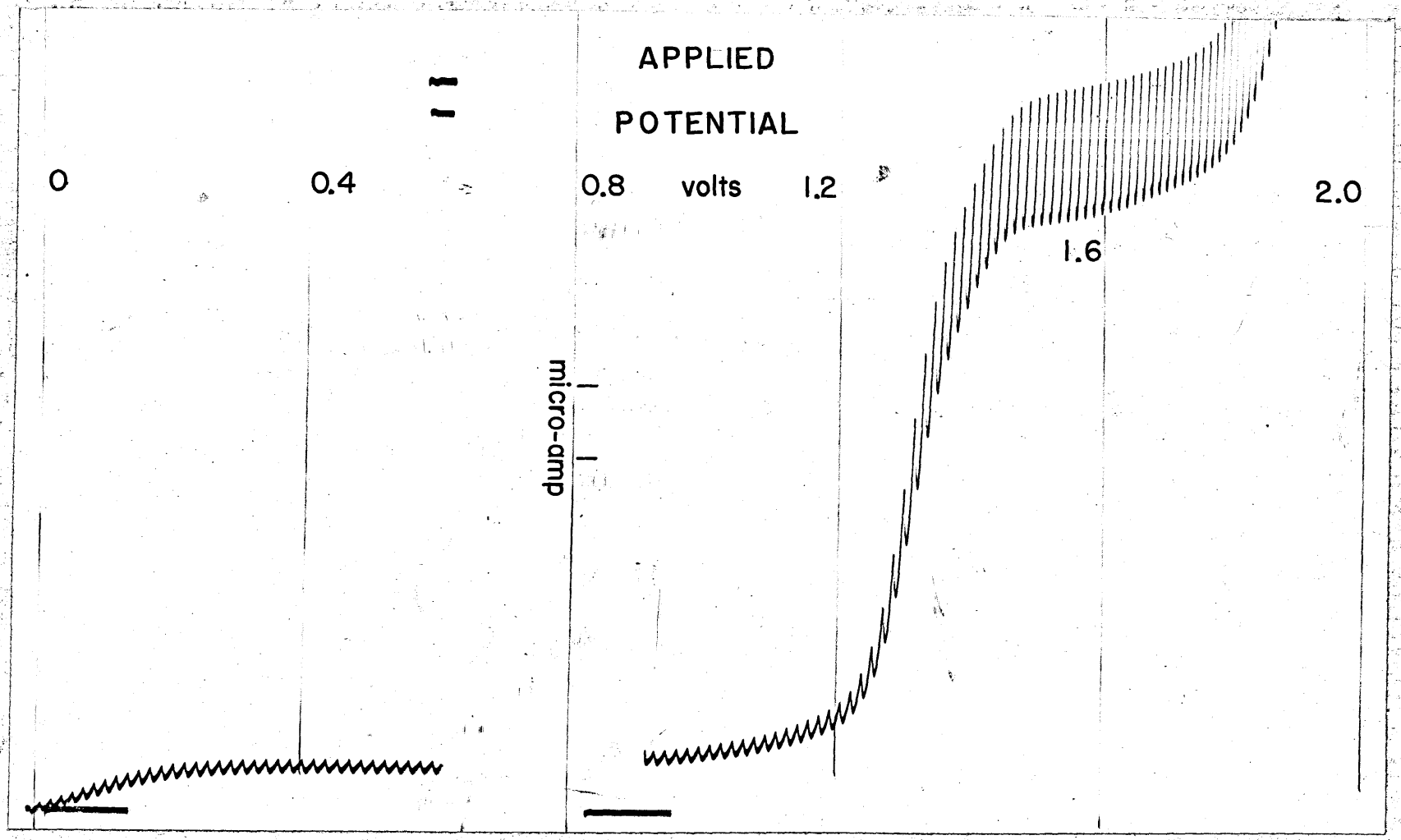


Fig. 3. Polarogram of α-Angelicalactone. Oxygen at 0.4 volt, peroxide at -1.32 volt.

remaining in the still pot. If the peroxide of α-angelicalactone were involved in a polymerization, the effect would be that obtained here. That is because most of the factors affecting this polymerization are unknown and little effort could be made to control polymerization. Polymerization will not affedt the diffusion current; it is a true indication of the peroxide content. Polymerization will cause the experimental oxygen uptake to be greater than the uncombined peroxide content as indicated by the diffusion current, although all the oxygen uptake was involved in peroxide formation initially. It is thought that polymerization is taking place in these solutions of α-angelicalactone.

It is known that the temperature coefficient of polymerization is large as compared to the temperature coefficient of many other reactions. If this is the case here, then decreasing the temperature might decrease the polymerization without affecting the oxygen uptake of α-angelicalactone appreciable. The results of three oxygen uptake determinations at 0°C are graphed on pages 96, 97 and 98. In run #5, page 96, it appears as if the limiting concentration (millimoles oxygen per liter) is no greater than at 25°C. This is not the case, however, since it can be seen on pages 97 and 98, runs #6 and #7, that the limiting concentration of peroxide at 0°C is several times greater than at 25°C. Run #5 was discontinued before the limiting concentration of peroxide was reached because of a clogged

dropping mercury electrode capillary. Assuming the reaction to be the additon of one mole oxygen to one mole lactone to give one mole of peroxide, the fraction of conversion can be calculated by the same method as above for the work at 25°C. Thus, for run #6, conversion was 12.1%; for run #7, conversion was 11.2%. This corresponds to a concentration of peroxide in run #6 of 2.86×10^{-3} molar and in run #7, a concentration of 3.30×10^{-3} molar. The actual concentrations were less than the values given due to the polymerization of some of the peroxide. Although, the oxygen uptake is slower at 0°C, than at 25°C, the reaction is fast enough that no oxygen is dissolved and unreacted in solution until the concentration of peroxide approaches the limiting concentration. The reaction then, must be a liquid phase reaction.

The corrected curves are graphed together on page 99. Again, the slopes are variable, but the slopes do not vary as much as at 25°C (cf. page 91). Therefore, the polymerization of the α-angelicalactone peroxide is reduced but not eliminated by decreasing the reaction temperature from 25° to 0°.

As mentioned above, the rate determining process seems to be the process of dissolving oxygen in solution so that it will be accessible to the lactone for reaction. But the rate at which oxygen dissolves will be dependent on the stirring. In this work a magnetic stirrer bar and a magnetic stirrer were used. With this method of mixing, the

agitation of the solution is variable for different runs and to a certain extent during a run. Therefore, even though the rate of polymerization is constant at 0°, the experimental lines have different slopes.

Oxygen Uptake of β-Angelicalactone

This lactone reacts with oxygen in the same was as α-angelicalactone and the oxygen uptake was measured in the same way. The results of three oxygen uptake determinations at 25°C are graphed on pages 109, 110 and 111. At the maximum i_d obtained and from the corrected curves, it may be calculated that conversion to peroxide is 12.0% in run #8, 8.8% in run #9 and 9.2% in run #10. This corresponds to concentrations of peroxide of 2.95×10^{-3} molar in run #8, 1.99×10^{-3} molar in run #9 and 1.94×10^{-3} molar in run #10. These values of concentration of peroxide are deceptive. The actual concentrations were less than these values, due to polymerization of some of the peroxide.

A typical polarogram of β-angelicalactone solution is given in Figure IV, page 135. The oxygen uptake of β-angelicalactone at 25°C is slower than α-angelicalactone at either of the temperatures studied. Oxygen is dissolved in these solutions as shown by even the earlier polarograms. The oxygen was not reacted with the lactone as fast as it dissolved. After the solution was stirred with oxygen for a period of time, considerable excess of oxygen was dissolved in solution as shown by the polarogram.

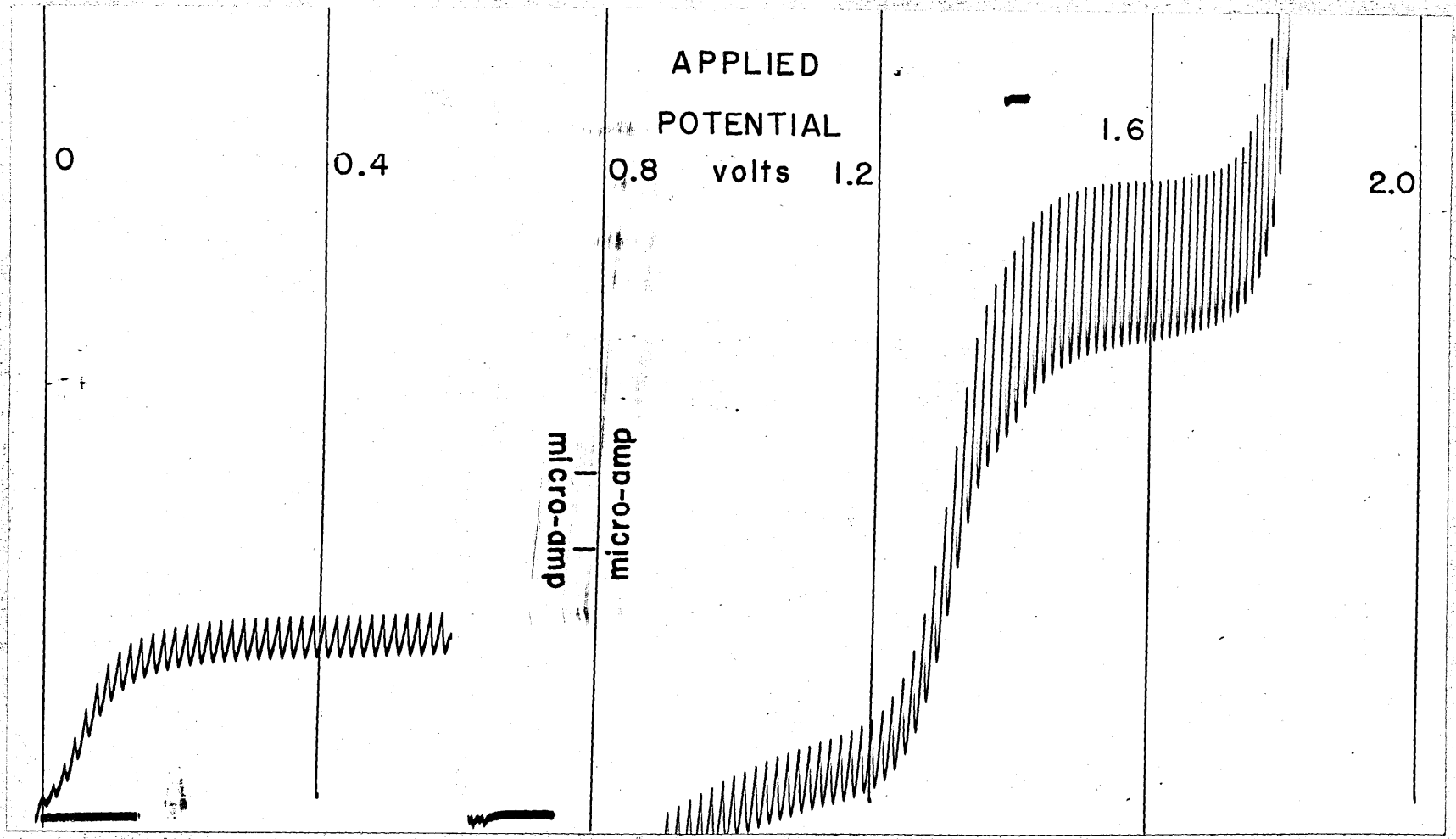


Fig. 4. Polarogram of β-Angelicalactone. Oxygen at 0.4 volt, peroxide at -1.32 volt.

However, if the solution was left for a period of time with the only contact between solution and oxygen in the 2 mm. capillary tubing, no more oxygen dissolved and the oxygen already in the solution decreased. At the same time, the concentration of the peroxide increased as shown by the polarograms. There are three examples of the phenomenon just discussed in run #10, points 4 and 5, points 7 and 8 and point 11 and 12. The reaction is a liquid phase reaction and from the preceeding discussion it may be concluded that the rate determining process for this reaction is not the dissolving of oxygen as in the case of α-angelicalactone. Instead, the rate determining step here is the reaction of lactone and oxygen.

The corrected curves are graphed together on page 112. The slopes of the lines vary with the different runs. However, the range of the slopes is not as great as the range of slopes for α-angelicalactone at 25° (cf. page 91) and greater than the range of slopes for α-angelicalactone at 0° (cf. page 99). The same results would be obtained if polymerization were taking place in the β-angelicalactone solutions at different rates for each run. It is known that β-angelicalactone polymerizes readily. When this lactone is distilled, there is always some light colored tar left in the still pot. If the peroxide forms a polymer, the result would be as shown here, the observed peroxide concentration as shown by the diffusion current

less than the total peroxide formed per liter as shown by the oxygen uptake. It is believed polymerization is taking place here. The factors affecting the polymerization are unknown and therefore uncontrolable. This is believed to be the reason for the different rates of polymerization in the separate runs.

At 0°, β-angelicalactone reacts with oxygen very slowly and only to a small extent. One oxygen uptake determination was made at 0° on β-angelicalactone and is graphed on page 113. It is seen that several negative values for oxygen uptake were obtained at the start of the run. This is due to the oxygen dissolved in the buffer solution incompletely removed at the start of the run. Since the dissolved oxygen reacts with the lactone slowly, most of the oxygen originally dissolved and unreacted is still unreacted with the lactone at the time of the first few polarograms. The decrease in volume of the oxygen was less than the volume of oxygen dissolved in solution. In the calculations, the volume of oxygen dissolved in solution (unreacted) was subtracted from the decrease in volume of oxygen and in these cases, a negative value resulted. The maximum conversion here is 3.9% if the assumption is made that one mole oxygen reacts with one mole lactone to give one mole peroxide. This corresponds to a concentration of 8.2×10^{-4} molar. The same (approximate) concentration of peroxide was reached in the case of α-angelicalactone at 0° in about an hour reaction

time. In this run with β-angelicalactone this concentration was reached only after 5 to 6 hours. Therefore the study of the oxygen uptake at 0° of β-angelicalactone was discontinued.

Since β-angelicalactone is prepared from α-angelicalactone, it was at first thought that the polarographic wave at $E_{\frac{1}{2}}$ of -1.32 might be due to impurities. However, repeated purifications of the β-lactone as discussed in the section on preparations failed to give some lactone which would not give this wave when dissolved. Therefore, the peroxide is formed from the β-lactone.

Kinetics of Oxygen Uptake of α- and β-Angelicalactone

It was not originally planned to make kinetics study of the oxygen uptake of these lactones and consequently, no special precautions were taken to insure very accurate time measurements. However, the oxygen uptake vs time is graphed on page 102 for α-angelicalactone and page 116 for β-angelicalactone. As a comparison, 0.6 millimole oxygen per liter solution is reacted with α-angelicalactone at 25° in thirty three minutes, with α-angelicalactone at 0° in forty four minutes, with β-angelicalactone at 25° in sixty seven minutes and with β-angelicalactone at 0° in several hours. The kinetics data for β-angelicalactone at 0° are inaccurate and no smooth curve could be drawn through the points. Therefore, the curve is not included in this thesis.

In the preceeding discussion, it was mentioned that a maximum concentration of peroxide attained was about 10%. The range of concentration from 0 to 10% is too small to determine the order of reaction. Both a graph of concentration of lactone vs. time and log concentration vs. time are nearly straight lines over the short range of concentrations of peroxide obtained here. However, the oxygen uptake of these lactones appears to be a first order reaction.

Polarographic Reduction of Levulinic Acid and 2,3-Dihydroxy Valerolactone

Since α-angelicalactone is prepared from levulinic acid, impurities of levulinic acid might be present in both lactones. This impurity would be present also, if any hydrolysis of the lactone took place. The polarograms were made on levulinic acid in the same buffer solutions as used for the polarograms of α- and β-angelicalactone. The results are given on page 119. There is no polarographic reduction of levulinic acid in the pH range 4.84 to 9.50. This verifies the work of Schwaer (145) who found that levulinic acid is non-reducible at the dropping mercury electrode.

Oxidation of β-angelicalactone gives a dihydroxy compound. Some of this dihydroxy compound, 2,3-dihydroxy valerolactone, was prepared as given in the section on preparations and polarograms made of solutions of it. The solvent was the same buffer solution used in the oxygen uptake

determination. The results are on page 119. There is no polarographic reduction at a pH of 9.66.

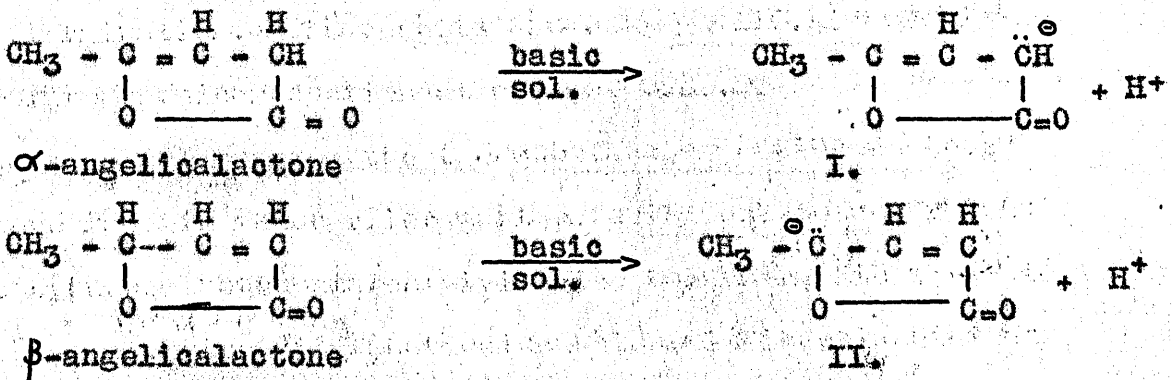
Polarograms of the two substances mentioned above were made in the earlier part of this work to determine if they were the substance giving the polarographic wave at $E_{\frac{1}{2}}$ -1.32. From the above discussion, it is evident that they are not the reducible substance and the formation of peroxide of unsaturated lactones is further substantiated.

Postulated Mechanism of Formation of the Peroxide of α- and β-Angelicalactone

The half wave potentials of the peroxides of α- and β-angelicalactones have been found to be the same, namely, -1.32 volt vs. S.C.E. As mentioned in the section on History in this thesis, the half wave potential is qualitatively characteristic of the compound being reduced. Therefore, barring an unlikely coincidence, the reducible peroxide formed from α-angelicalactone is identical with the reducible peroxide formed from β-angelicalactone.

The peroxide of these lactones is absent in solutions with pH less than 8. The mechanism of formation of the peroxide must then take into account the formation of peroxides only in basic solutions and the formation of the same peroxide from α- and β-angelicalactone.

The first step in the formation of these peroxides is thought to be the removal of a hydrogen ion from the lactone as:



α-angelicalactone

I.

β-angelicalactone

II.

This is an ionic reaction. The ions formed are bases and in an acid solution (or neutral), neutralization takes place with a resulting concentration of ion very low or zero. Rather, it should be stated that in an acid or neutral solution, the hydrogen ion is not removed. However, if the solution is more basic than these ions, the hydrogen ions will be removed. For these lactones, a solution with pH 8 or greater is sufficiently basic that the hydrogen ions are removed.

On examination of the ions formed as above, it is seen that these ions have a free electron pair conjugated with a double bond. These structures can therefore resonate. Further examination of these ions show that structures I and II are resonance forms of the same ion as:

I.

II.

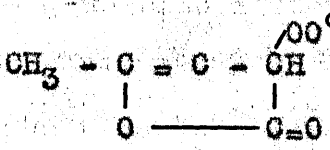
It cannot be this ion which is reduced at the dropping mercury electrode, because if this were the case, there

would be no correlation between oxygen uptake and diffusion current. Reaction with oxygen will be such as to form the peroxide with the lowest energy of formation. Therefore, the peroxide formed is the same regardless of which lactone is the source of the ion.

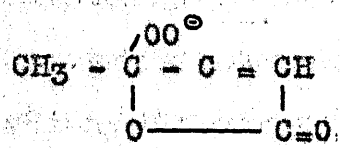
It was found that β-angelicalactone formed the peroxide slower than α-angelicalactone. If the rate determining step is the reaction of the ion with oxygen, the rate of peroxide formation would be the same for solutions of α-angelicalactone and β-angelicalactone. Since the rate of peroxide formation is not the same for the two lactone, it must be the removal of hydrogen ion which is the rate determining step. This is in complete agreement with the modern ideas of resonance. Examination of the structure of β-angelicalactone shows that it is a conjugated molecule with resonance between the carbon to carbon double bond and the carbonyl group. On the other hand, α-angelicalactone is not conjugated and therefore would be expected to be a stronger acid. By loss of a hydrogen ion, α-angelicalactone changes from a non-resonating molecule to a resonating ion whereas the β-angelicalactone is a resonating molecule and changes to a resonating ion. Therefore, the increase in stability in going from a molecule to the resonating ion is greater for the α-angelicalactone and the speed of removal of the hydrogen ion is greater.

Which ion reacts with oxygen to give the reducible

peroxide is not as readily apparent as the formation of these ions. However, by examination of ions I and II above, it is seen that whichever ion is attacked by the oxygen, the resulting hydroperoxide is a conjugating molecule and is therefore stabilized by resonance.



I.



II.

If the attack by oxygen is on structure I, the hydroperoxide group will be next to the carbonyl group. This grouping is probably less stable than that formed by the attack of the oxygen on structure II and the conjugation is not continuous. In the case of structure II, the hydroperoxide group is removed several carbon atoms from the carbonyl group and conjugation is continuous. Modern electronic theory indicates structure II as more likely. In general, the thermodynamics of the reaction of the oxygen with this type of ion are unknown and no definite conclusions can be drawn as to the structure of the hydroperoxide formed.

Since the rate determing step is the removal of hydrogen ion, the peroxide formation is a first order reaction. This was indicated by the kinetics data, but the kinetics data is too incomplete for a definate conclusion.

Index of Refraction of α- and β-Angelicalactone

Anwers (143) reported the refractive indices of these lactones compared to several different wave lenghths. However, this constant compared to the D line of sodium was not found in his work nor elsewhere in the literature. In this work, the refractive indice was measured with an Abbe refractometor. The results are given on page 120. For α-angelicalactone, n_D^{25} is 1.4457, for β-angelicalactone, n_D^{25} is 1.4532. The probable error is ± 0.0002.

VI. SUGGESTIONS FOR FUTURE WORK

A In the operation of the reaction cell, the only difficulty encountered was frequent clogging of the dropping mercury capillary. Since the capillary could be cleaned with cyclohexane but not with dilute nitric acid, the clogging is probably caused by the silicone grease used on the ground glass joint. When putting the cell together, considerable care was exercised to keep the grease off the end of the capillary. Therefore, it is believed this grease has a tendency to creep. A grease that will not creep and also will not dissolve organic compounds would improve the operation of the cell designed in this work.

A graph of time vs oxygen uptake in this work gave a smoother continuous curve than a graph of time vs diffusion current. This indicates the polarographic measurements are less accurate than the volume measurements. The use of a manual polarograph would be more accurate but would be very tedious and it would be nearly impossible to make

polarograms as rapidly as was necessary to obtain the oxygen uptake determinations in this work. The Model XII Heyrovsky polarograph used in this work gives polarograms that can be measured to within 1-2%. The only other recording polarograph on the market today known to this author to give more accurate polarograms is the Model XXI Heyrovsky polarograph, manufactured by the E. H. Sargent Company, the same company that manufactures the Model XII.

The oxygen volume measurements can be more accurately made by a temperature control more precise than that in this work. It is believed a circulating water system with automatic temperature control would afford more precise temperature control. A circulating system was not available for this work and the temperature control was mostly manual.

The total oxygen volume decrease in this work was never greater than 15-20 ml. and often was as small as 5 ml. If the total volume decrease were larger, in the range 20-30 ml. or larger, the oxygen measurements would be more accurate. This could be accomplished by making the determinations using larger volumes of solutions. The volume of solution is somewhat restricted with the present reaction cell, but a cell can be designed without difficulty to contain larger volumes of solutions.

For future work, a study similar to the present one on other unsaturated lactones is in order. A study of the

reduction of the unsaturated lactone itself will furnish more information by which the hydrogenation phenomenon, previously discussed, might be explained. A study of oxygen uptake of unsaturated lactones will furnish additional information regarding the structure of the peroxides and the mechanism of formation.

The order of reaction of this peroxide formation will furnish more information regarding the mechanism of formation. Although, in the present work, a sufficiently wide range of concentration to do this was not obtained, other peroxide formation might do so. For example, cyclohexene peroxide seems to be more stable than the present peroxide and an oxygen uptake study of cyclohexene will probably afford data from which the order of reaction can be determined.

From the work of Kharasch and co-workers discussed in an earlier section titled History, it was shown indirectly that several olefins spontaneously form peroxides. It would be interesting to determine if these peroxides are detectable with the polarograph. If they are, this instrument could be used to verify the work of Kharasch by direct methods.

In his publications, Kharasch and co-workers frequently mention the use of anti-oxidants (cf. History). It is possible that the polarograph might be used to clarify the effect of these antioxidants; that is, it may be possible to determine if the effect of antioxidants is to prevent

the formation of peroxides or to inhibit the polymerization even in the presence of peroxides. The present theory concerning the action of antioxidants is that they take up oxygen faster than the olefin. This phenomenon may perhaps be verified by use of the polarograph.

It is also possible that future work will suggest refinements of the present method used to determine the peroxide content of olefins which will make possible considerable increase in the accuracy of 10-15% obtained in this work.

VII. SUMMARY

1. The reduction of α- and β-angelicalactones at the dropping mercury electrode has been studied. It was found that α-angelicalactone does not reduce. β-angelicalactone reduces by a two step process. The waves are too close together for accurate analysis of the waves, $E_{\frac{1}{2}}$ -1.88 v and -1.99 v vs. S.C.E. This agrees with the two step reduction by hydrogen of β-angelicalactone. No conclusions can be made regarding the hydrogenation of α-angelicalactone to give the saturated acid by a one step process without the appearance of the saturated lactone.

2. It has been shown that α- and β-angelicalactones spontaneously form peroxides in the presence of oxygen that reduce at the dropping mercury electrode. The reduction is irreversible. In as much as the $E_{\frac{1}{2}}$ is -1.32 vs S.C.E. in both cases, the peroxide of α-angelicalactone

is very likely the same peroxide as that formed by β-angelicalactone.

In a strongly basic solution, such as a 0.1 M solution of tetramethyl ammonium bromide, the $E_{\frac{1}{2}}$ of the peroxide is shifted to more negative values, $E_{\frac{1}{2}}$ -1.58v vs. S.C.E. Glycine in solution shifts the $E_{\frac{1}{2}}$ to more positive values, to -1.27v vs. S.C.E., possibly due to a reaction of glycine with the lactone or peroxide. In the presence of alcohol or cellosolve, the peroxide $E_{\frac{1}{2}}$ is shifted to more negative values and there are two reduction waves instead of one.

3. A reaction cell has been designed and built to measure the oxygen uptake of α- and β-angelicalactone in correlation with the diffusion current of the peroxide. The main feature of this new cell is a dropping mercury electrode which is introduced into the reaction cell by means of a ground glass joint on the end of the capillary.

4. The oxygen uptake of α- and β-angelicalactone has been studied in conjunction with the diffusion currents of the peroxide. The polarograph cannot be used for analysis of the peroxide content with an accuracy greater than 10% because no calibration curve can be made with an accuracy greater than 10%. This is because the true concentration of peroxide cannot be ascertained from the oxygen uptake due to a secondary reaction of the peroxide. It is postulated that this secondary reaction is polymerization. The maximum conversion of lactone to peroxide is

probably no more than 10-12%.

5. A logical ionic mechanism for the formation of the peroxide by a first order reaction has been formulated. This proposed mechanism results in the formation of a hydroperoxide group at the γ-carbon atom and a double bond between the α and β carbon atoms. The hydroperoxide has the same structure when formed from either α- or β-angelicalactone. The structure of this peroxide agrees with the structures postulated by Farmer (cf. History) of olefinic peroxides with a hydroperoxide group alpha to the double bond.

6. The values of n_D^{25} are reported. This physical constant has not perviously been reported in reference to the D line of sodium.

BIBLIOGRAOHY

1. Wolff, Ann, 229, 251 (1885).
2. Thorne, Ber. 18, 2263 (1885).
3. Thiele, Tischbein and Lossow, Ann. 319, 180 (1901).
4. Jacobs and Scott, J. Biol. Chem. 87, 601 (1930).
5. Jacobs and Scott, ibid. 93, 139 (1931).
6. Mannich and Butz, Ber. 62, 461 (1929).
7. LaForge and Smith, J. Am. Chem. Soc. 51, 2574 (1929).
   ibid. 52, 1088 (1930).
8. Borsche and Peitzsch, Ber. 62, 360 (1929).
9. Jacobs and Gustus, J. Biol. Chem. 86, 203 (1930).
10. Packendorff, Ber. 67, 905 (1934).
11. Michael and Weiner, J. Org. Chem. 4, 531 (1939).
12. Kharasch, Rossin and Fields, J. Am. Chem. Soc. 63, 2558 (1941).
13. Kharasch and Hannum, ibid. 56, 712 (1934).
14. Kharasch, Kritchevsky and Mayo, J. Org. Chem. 2, 489(1939).
15. Kharasch, Engelman and Mayo, ibid. 2, 288 (1938).
16. Kharasch, Norton and May, ibid. 3, 48 (1938).
17. Kharasch and Hannum, J. Am. Chem. Soc. 56, 1782 (1934).
18. Kharasch, Norton and Mayo, ibid. 62, 81 (1940).
19. Grosse and Linn, J. Org. Chem. 3, 26 (1938).
20. Walling, Kharasch and Mayo, J. Am. Chem. Soc. 61, 1711 (1939).
21. Kharasch and Potts, J. Org. Chem. 2, 195 (1938).
22. Kharasch and Mayo, J. Am. Chem. Soc. 55, 2468 (1933).
23. Kharasch, Hannum and Gladstone, ibid. 56, 244 (1934).

24. Ashton and Smith, J. Chem. Soc. , 439, 1934.
25. Whitmore and Hameyer, J. Am. Chem. Soc. 55, 4555 (1933).
26. Kharasch and Hinckley, ibid. 56, 1212 (1934).
27. Scott, News Ed. (Am. Chem. Soc.), 18, 404 (1940).
28. Young, Vogt and Nieuwland, J. Am. Chem Soc. 58, 55, 1806 (1936).
29. Kharasch and Hinckley, ibid. 56, 1243 (1934).
30. Kharasch, Hinckley and Gladstone, ibid. 56, 1642 (1934).
31. Kharasch, Margolis and Mayo, J. Org. Chem. 1, 393 (1937).
32. Kharasch and Potts, J. Am. Chem. Soc. 58, 57 (1936).
33. Kharasch, McNab and McNab, ibid. 57, 2463 (1935).
34. Kharasch, McNab and Mayo, ibid. 55, 2531 (1933).
35. Walling, Kharasch and Mayo, ibid. 61, 2693 (1939).
36. Kharasch, Kleiger and Mayo, J. Org. Chem. 4, 428 (1939).
37. Kharasch, McNab and Mayo, J. Am. Chem. Soc. 55, 2521 (1933).
38. Walker and Lumsden, J. Chem. Soc. 29, 1191 (1901).
39. Kharasch, Margolis and Mayo, Chem. and Ind. 53, 663 (1936).
40. Young, Vogt and Nieuwland, J. Am. Chem. Soc. 56, 1822 (1934).
41. Kharasch and McNab, Chem. and Ind. 54, 989 (1935).
42. Sherrill, Mayer and Walter, J. Am. Chem. Soc. 56, 926(1934).
43. Ingold and Smith, J. Chem. Soc. 2746, 1931.
44. Linstead and Rydon, Nature, 132, 643 (1933).
45. Lucas, Dillon and Young, J. Am. Chem. Soc. 52, 1949 (1930).
46. O'Conner, Baldinger, Vogt and Hennion, ibid. 61, 1454 (1939).
47. Kharasch, Haeffle and Mayo, ibid. 62, 2047 (1940).
48. Mayo and Gregg, ibid. 70, 1284 (1948).

49. Price, Kell and Krebs, ibid. 64, 1103 (1942).
50. Kolthoff and Dale, ibid. 69, 441 (1947).
51. Kolthoff and Dale, ibid. 67, 1672 (1945).
52. Bovey and Kolthoff, ibid. 69, 2143 (1947).
53. Snow and Frew, Ind, Eng. Chem. 30, 176 (1938).
54. Marvel, Davis and Glavis, J. Am . Chem. Soc. 60, 1450 (1938).
55. Meunier and Vaissiere, Compt. rend, 206, 677 (1938).
56. Kharasch, May and Mayo, J. Org. Chem. 3, 175 (1938).
57. Kharasch, Read and Mayo, Chem. and Ind., 752, 1938.
58. Kharasch and Brown, J. Am. Chem. Soc. 61, 3432 (1939).
59. Kharasch, Skell and Fisher, ibid. 70, 1055 (1948).
60. Kharasch, Jensen and Urry, ibid. 69, 1100 (1947).
61. Weizmann, Israelaslivili, Halevy and Bergman, Ibid. 69, 2569 (1947).
62. Jones and Reid, ibid. 60, 2452 (1938).
63. Rust, Senbold and Vaughan, ibid. 70, 95 (1948).
64. George and Walsh, Trans. Faraday Soc. 42, 94 (1946).
65. Thomson, J. Am. Chem. Soc. 56, 2744 (1934).
66. Albers and Schmidt, J. prakt. Chem. 162, 91 (1943).
67. Engler, Ber. 33, 1094 (1900).
68. Engler and Frankenstein, ibid.34, 2933 (1901).
69. Staudinger, ibid. 58, 1075 (1925).
70. Jacquemain, Compt. rend. 215, 200 (1942).
71. Zelinskij and Borissow, Beer. 63, 2362 (1930).
72. Hock, Oel, Kohl, Erdoel, Teer, 13, 697 (1937). C. A. 31, 8875 (1937).
73. Creigee, Pilz and Flygare, Ber.72, 1799 (1939).
74. Hock and Neuwirth, ibid. 72, 1562 (1939).

75. Farmer, Bloomfield, Sundralingam and Sutton,
Trans. Faraday Soc. 38, 348 (1942).
76. Water, J. Chem. Soc. 153, (1942).
77. Staudinger, Ber. 58, 1075 (1925).
78. Farmer, Trans. Faraday Soc. 38, 340 (1942).
79. Stephens, J. Am. Chem. Soc. 50, 568 (1928).
80. Farmer and Sundralingam, J. Chem. Soc. 121, 1942.
81. Farmer and Narracott, ibid. 185, 1942.
82. Heilberger, Rebay and Fettback, Ber. 72, 1643 (1939).
83. Milas and Harris, J. Am. Chem. Soc. 60, 2434 (1938).
84. Hock and Lang, Ber. 77, 257 (1944).
85. Hock and Lang, ibid. 76, 169 (1943).
86. Farmer and Sutton, J. Chem. Soc. 139, 1942.
87. Farmer and Narracott, ibid. 185, 1942.
88. Farmer and Sutton, ibid. 119, 1943.
89. Bergman and McLean, Chem. Rev. 28, 367 (1941).
90. Groll and Hearne, Ind. Eng. Chem. 31, 1530 (1939).
91. Stewart, Dod and Stenmark, J. Am. Chem. Soc. 59, 1765(1937).
92. Deanesly, ibid. 56, 250 (1934).
93. Morrell, Trans Faraday Soc. 262, 1942.
J. Oil Col, Chem. Assoc, 12, 183 (1939).
ibid. 10, 264 (1936).
94. Atherton and Hilditch, J. Chem. Soc. 105, 1944.
95. Armstrong and Hilditch, J. Soc. Chem. Ind. 44, 43T (1925).
96. Breitenbach and Bremer, Ber. 76, 1124 (1943).
97. Bartlett and Altschul, J. Am. Chem. Soc. 67, 812 (1945).
98. Mednedev and Alekeeva, Ber. 65, 133 (1932).

C. A. 26, 2412 (1932).

99. Hock and Lang, ibid. 76, 1130 (1943).

100. Windaus, Z. physiol. Chem. 276, 280 (1942).

101. Fieser, "Chemistry of Natural Products Related to Phenanthrene", page 174.

102. Treibs, Ber. 76, 670 (1943).

103. Franke and Jerchel, Ann. 533, 46 (1937).
C. A. 32, 3333 (1938).

104. Jacobs and Gustus, J. Biol. Chem. 86, 199 (1930).

105. Cavallito and Haskell, J. Am. Chem. Soc. 67, 1991 (1945).

106. Mendez, J. Pharmocology, 81, 151 (1944).
C. A. 38, 4684.

107. Krayer, Mendez, deEspenes and Linstead, ibid. 74, 372 (1942).

108. Precaul, Rev, combustibles liquids, 16, No. 155, 167 (1938).
C.A. 32, 6848 (1938).

109. Donnefelser, Oel und Kohle, 39, 903 (1943).
C.A. 38, 6066 (1944).

110. Denison, Ind, Eng. Chem. 36, 477 (1944).
C. A. 38, 3461 (1944).

111. Poist, Blout, Uhle and Elderfield, J. Org. Chem. 6, 260 (1941).

112. Hock and Schrader, Brennstoff Chem. 18, 6 (1937).
C. A. 31, 4619 (1937).

113. Liefhofsky and Sharkey, J. Am. Chem. Soc. 62, 190 (1940).

114. Marks and Morrell, Analyst 54, 503 (1929).
C. A. 23, 5439 (1929).

115. Paschke and Wheeler, Oil and Soap, 21, 52 (1944).
C. A. 38, 2228 (1944).

116. Nokumura, J. Soc. Chem.Ind., Japan. 40, Suppl. Binding, 206 (1937).
C. A. 31, 6910 (1937).
117. Yamada, ibid. 39, Suppl. Binding, 189 (1936).
C. A. 30, 6219 (1936).
118. Panyutin and Gindin, Bull. acad. sci., U.R.S.S., classe sci. math. nat., Ser. Chim. 841, 1938.
C. A. 33, 4161 (1939).
119. Kempf, Z. anal. chem. 89, 88 (1932).
120. Pratesi and Celeghini, C. A. 31, 2543 (1937).
121. Arakawa, J. Exptl. Med. 16, 252 (1930).
C. A. 25, 1854 (1931).
122. Poggi, Ann. Chim. applicata. 22, 493 (1932).
C. A. 26, 5868 (1932).
123. Gutmann, Z. anal. Chem. 66, 224 (1925).
124. Rupp and Stöbler, Pharm. zentralhalle, 66, 193 (1925).
C. A. 19, 1754 (1925).
125. Kiemstedt, Brennstoff Chem. 17, 83 (1936).
C. A. 30, 8204 (1936).
126. Calo and Muntoni, Ann. chim. applicata. 28, 59 (1938).
C. A. 32, 7583 (1938).
127. D'Este, Ball. chim. farm. 71, 437 (1932).
C. A. 27, 476.
128. Young, Vogt and Nieuwland, Anal. Ed., Ind. Eng. Chem, 8, 198 (1936).
129. Rostovtseva, Org. chem. Ind. (U.S.S.R.) 2, 166 (1936).
C. A. 31, 628 (1937).

130. Muller and Brenneis, Berg. huttenman Jahrb. montan. Hochschule Leoben 80, 101 (1932).

131. C. A. 27, 3896 (1933).

131. Heyrovsky and Shikato, Rec. trav. chim. 44, 496 (1925).

132. Kolthoff and Lingane, "Polarography", Interscience Publ.

133. Shtern and Pollyak, Acta Physicochim., U.R.S.S. 11, 797 (1939).

C. A. 34, 4698 (1940).

134. Dobrinskaya and Neiman, ibid. 10, 297 (1939).

C. A. 33, 6198 (1939).

135. Dobrinskaya and Neiman, Zavodskaya Lab. 8, 280 (1939).

C. A. 34, 55 (1940).

136. Vitek, Chimie et industrie, Special No., 215 (June, 1933).

C. A. 27, 5274 (1933).

137. Petering and Daniels, J. Am. Chem. Soc. 60, 2796 (1938).

138. Ingols, Ind. Eng. Chem., Anal. Ed., 14, 256 (1942).

139. Beecher, Followsbee, Murphy and Craig, J. Biol. Chem. 146, 197 (1942).

140. Kolthoff and Miller, J. Am. Chem. Soc. 63, 1013 (1941).

141. Zambotti, Arch, sci. biol. (Italy) 26, 80 (1940).

C. A. 34, 6864.

142. Whitnack, Anal. Chem. 20, 658 (1948).

143. Anwers, Ber. 56, 1672 (1923).

144. Kolthoff and Laitinen, "pH and Electro Titrations."

145. Schwaer, Collection Czechoslov. Chem. Commun. 7, 326 (1935).