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THE CONVERSION OF FERMENTATION PRODUCTS TO ELASTOMER INTERMEDIATES

by

John J. Kolfenbach

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Biophysical Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

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Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

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The author also takes pleasure in acknowledging the unselfish assistance of Mr. P. H. Figard, Mr. P. D. Raths, and Miss E. F. Tuller in conducting many catalytic experiments described herein.

INTRODUCTION

Undoubtedly one of the outstanding chemical developments of World War II has been the rise of the synthetic rubber industry in the United States from practically a "test tube" state in 1939 to an industry with the capacity to supply nearly 1,000,000 tons of vitally needed rubber each year. The growth of synthetic rubber has been accompanied, chronologically speaking, by important changes in two chemical industries, both of which supply raw materials for the production of synthetic rubber. The industries in question are the alcohol industry, which now supplies butadiene sufficient for 330,000 tons of synthetic rubber yearly, and the petroleum industry which is scheduled to produce butadiene sufficient for 600,000 tons of synthetic rubber yearly.

In the past few years, the alcohol industry has undergone an expansion from a yearly capacity of 100,000,000 gallons to a yearly capacity of 650,000,000 gallons, the increase being due only in part to the demands placed upon the industry for alcohol as a source of butadiene for rubber. During the same period, the petroleum resources of the country have been so seriously depleted by the increased demand for aviation gasoline and butadiene that today plans are being formulated for the production of gasoline from oil shale and from the hydrogenation of coal. The above facts indicate that alcohol will find relatively greater use in the field of synthetic rubber, as the nation's oil reserves sink lower and lower.

However, the true importance of the recent changes in the alcohol and petroleum industries is more fundamental than the previous paragraphs have indicated. The developments have served to demonstrate a trend away from petroleum and toward farm crops as a source of organic chemicals. As a means of conserving oil, an important raw material which is an irreplaceable natural resource, it is now very probable that farm products will be utilized more and more as raw materials wherever possible, thus vindicating the judgment of many chemists who have long advocated this very thing.

The diversity of organic chemicals derived from petroleum is astounding. There is little question that many, probably a majority, of the compounds now obtained from petroleum as a raw material will continue to be derived therefrom. However, there is every reason to believe that syntheses utilizing farm products as raw materials will receive favorable consideration now and in the future.

The purpose of the work upon which this thesis is based was to investigate the possibility of expanding the use of chemicals derived from agricultural crops in the field of synthetic elastomers. The study involved the production of monomers from chemicals obtained from farm crops through the intermediate step of fermentation. Attention was given not only to butadiene, but also to compounds needed for copolymers and to other compounds which could be utilized in the elastomer industry. The study was confined to fermentation products other than ethyl alcohol, the use of which has been so thoroughly studied and demonstrated in recent years. Attention was devoted principally to 2,3-butylene glycol, which has received less attention than ethyl alcohol, but which offers distinct promise, since it is a readily producible fermentation product.

HISTORICAL

Butadiene and Isomers

The field of synthetic elastomers is not a new field of study. Its sudden surge into prominence has suggested to many that only recently have the problems of synthetic elastomers been considered and solved. Actually, more than sixty years ago, a synthetic rubber had been prepared from a material other than natural rubber by Tilden (1882), and Fulmer (1943) pointed out in his survey of the literature on synthetic rubber that "practically all the basic information was known by 1913." A great deal of this basic information was gained by the utilization of fermentation products as starting materials for the production of monomers.

The earliest attempts at producing synthetic rubber involved the polymerization of isoprene, since it had been determined by Williams (1860) that isoprene was the "building block" of natural rubber. The production of isoprene was limited by the raw material, turpentine, which was not available in large quantity. Research was conducted in two directions; first to find new sources of isoprene and secondly to polymerize materials other than isoprene. Both lines of research were successful, but the second proved far more fruitful. It is worthy of mention, however, that one of the new sources of isoprene in those early days of experimentation was fusel oil, a product of fermentation; Perkin (1912).

The polymerization of homologs of isoprene proved to be of greatest industrial interest. Not only were the products superior to those produced from isoprene, but the raw materials for production of the monomers were more readily available.

The first synthetic rubber to be produced on a commercial scale was methyl rubber used by the Germans in World War I. Methyl rubber was a polymer of 2,3-dimethylbutadiene-1,3 and was prepared from acetone through pinacol by Couturier (1892). Since the acetone was a product of fermentation, one can safely state that the first commercial synthetic rubber employed a fermentation product as a starting material.

However, methyl rubber was not very satisfactory, and butadiene-1,3 came into prominence. Butadiene was first prepared by Caventou (1862) by passing amyl alcohol through red hot tubes and it was first polymerized to rubber by Lebedeff (1910). It was immediately recognized by Harries (1911) that butadiene rubber was superior to that prepared from isoprene, and the attention of most chemists interested in synthetic rubber was shifted to butadiene. Again fermentation products proved to be satisfactory starting materials.

Perkin (1912) described methods for preparing butadiene from either butyl alcohol or ethyl alcohol, both of which were produced by fermentation. The synthesis from ethyl alcohol involved the formation of acetaldehyde, condensation of the acetaldehyde to acetaldol, reduction of the acetaldol to 1,3-butylene glycol, and dehydration of the glycol to 1,3-butadiene. Equations indicating the steps involved follow:

$$2CH_3CH_2OH \xrightarrow{-H_2} 2CH_3CHO \longrightarrow CH_3CHOHCH_2CHO \xrightarrow{+H_2} CH_3CHOHCH_2CH_2OH \xrightarrow{-H_2O} CH_2{=}CH{-}CH{=}CH_2$$

This process is receiving considerable attention today, although the starting material is now acetylene rather than alcohol; Gamma and Inouye (1942 and 1943).

Ostromisslenski and Kelbasinski (1916) developed a method for preparing butadiene by passing a mixture of acetaldehyde and ethyl alcohol over catalysts, and Lebedeff (1928) developed the important process which bears his name, a process which consists of passing alcohol vapor over a mixed dehydration-dehydrogenation catalyst. The Lebedeff process made synthetic rubber feasible, and it was generally used throughout continental Europe. Aided by the experience gained from years of research in Russia, Poland, etc., this country today is using the Lebedeff process, or variations thereof, to produce about 330,000 tons of synthetic rubber yearly from ethyl alcohol, much of which is produced by fermentation.

Butadiene has also been prepared from 2,3-butylene glycol, a chemical produced in excellent yield by fermentation. Best results have been obtained by what might be termed an indirect dehydration of the glycol. This procedure involves esterification of the glycol with a carboxylic acid, usually acetic, and subsequent pyrolysis of the diester at a temperature of 550° C.; Hill and Isaacs (1938 and 1941) and Denivelle (1939). Investigators at the Northern Regional Research Laboratory at Peoria have conducted extensive research on the pyrolysis of the diacetate of 2,3-butylene glycol and have demonstrated on the pilot plant scale that high yields of butadiene can be attained by this process.

A number of other esters of 2,3-butylene glycol can be pyrolyzed to butadiene. Kosternaya (1938) prepared butadiene from the xanthate of 2,3-butylene glycol by heating the xanthate to 230°-240° C. The neutral sulfite of glycol also yields about 8-10 per cent butadiene at 575° C., according to Denivelle (1939). The similarity between the neutral sulfite and the inner carbonate suggests that the carbonate might also be pyrolyzed to butadiene. However, no record of the pyrolysis of the carbonate has been unearthed and no data on the compound itself were found. The classic paper of Ritchie (1935) dealing with the conversion of difficultly dehydrated alcohols to unsaturated hydrocarbon derivatives states that alkyl carbonates can be pyrolyzed to unsaturated hydrocarbons by heating to 500°- 600° C.

In addition to esters, ethers have been pyrolyzed to unsaturated hydrocarbons. Desaturation of methoxy compounds has received considerable attention and Norris, Verbanc, and Hennion (1938) have reported a series of unsaturated compounds produced by the desaturation of 1,3,3-trimethoxybutane at temperatures of 300°-320° C. 2,3-Butylene glycol lends itself readily to the formation of methoxy compounds according to Chappell (1935), but the preparation of butadiene from methoxy compounds has not been reported.

The direct dehydration of 2,3-butylene glycol to butadiene has offered considerable difficulty. Various investigators have reported that attempts to prepare butadiene from the glycol yield methyl ethyl ketone; Backer (1936), and Taira (1927), Akabori (1938), Denivelle (1939), Bouveault and Locquin (1906), and Tiffeneau, Levy and Weill (1931). Unpublished reports from the Northern Regional Research Laboratory and from a number of industrial concerns confirm the reported difficulty. Ipatieff

(1936) has stated that glycols upon dehydration yield carbonyl compounds rather than unsaturated hydrocarbons and attributed this effect to the formation of an epoxy compound, followed by isomerization to carbonyl compounds.

Small amounts of butadiene from direct dehydration of 2,3-butylene glycol have been reported in private communications from various industrial concerns and from the Northern Regional Research Laboratory. Chappell (1935) reported the production of butadiene from 2,3-butylene glycol by dropping the glycol into sulfuric acid-pumice mixtures at 175° C. In general, however, quantitative determinations of butadiene have never indicated that high yields of butadiene could be produced from 2,3-butylene glycol by direct dehydration.

Since the work reported in this thesis was confined to the utilization of fermentation products, no attempt will be made to review the large amount of literature reporting the production of butadiene from other raw materials, such as petroleum. An excellent survey of the methods of preparing butadiene has been made by Egloff and Hulla (1942), and the reader is referred to that article for complete lists and references to methods of preparation.

Methyl Vinyl Ketone

One of the great contributions to synthetic rubber has been the development of copolymerization. Copolymerization has made possible the production of synthetic rubbers with more desirable mechanical properties and has increased the versatility of synthetic rubbers. Mark (1942) attributed the differences between copolymers to changes in the intermolecular forces and incapability of the individual chains to fit into crystal lattices. Various substances used in forming copolymers affect the intermolecular forces to varying degrees and affect the ease with which the chains will fit together to form crystal-like lattices.

Substances which are used most extensively in producing copolymers are styrene and acrylonitrile. Styrene is the monomer used with butadiene to produce Buna S or GRS rubber, and acrylonitrile is used for the Buna N rubbers. Other copolymers have been investigated however, and copolymers of methyl vinyl ketone and butadiene show great promise. Rubber produced by the copolymerization of butadiene and methyl vinyl ketone has the highly desirable quality of excellent plasticity at extremes of high and low temperatures, in contrast to many synthetic rubbers and also to natural rubber, which have a tendency to become brittle at lower temperatures. The use of methyl vinyl ketone in copolymerization reactions with butadiene was first practiced by I. G. Farbenindustrie, A.-G. (1932), although Bayer, F. and Co. (1920) had first shown the autopolymerization of the ketone.

In recent years the references to methyl vinyl ketone in scientific literature have been very numerous. The vast majority of the literature on methyl vinyl ketone has been patent literature which describes uses, preparations, methods of polymerization, and stabilization of the compound. It has been found that the compound is valuable not only as a monomer for rubber copolymers, but also as a synthetic resin intermediate, yielding clear solids on autopolymerization. The synthetic resin produced finds utilization for coatings, heat hardened products, cements for glass and other articles, and glue in water soluble form. Methyl vinyl ketone may be condensed with formaldehyde to yield water soluble condensation products which are then converted to resins by addition of polycarboxylic acids or anhydrides, chlorides, esters, or amides.

One of the early syntheses of methyl vinyl ketone involved the condensation of acetone with formaldehyde, followed by dehydration of the condensation product.

$$CH_3COCH_3 + HCHO \longrightarrow CH_3COCH_2CH_2OH \xrightarrow{-H_2O} CH_3COCH{=}CH_2$$

Wohl and Prill (1924) give definite directions for the preparation of this compound and their method and variations thereof have been exhaustively investigated. Later workers employing variations of the reaction employed by Wohl and Prill are Drinberg and Bulygina (1940), Morgan and Holmes (1932), Germann (1936), and White and Haward (1943). Difficulty in controlling the mode of condensation of the formaldehyde with the acetone, as is evidenced by the isolation of such compounds as methylene butanolone by Gault and Germann (1933) limits the yields of methyl vinyl ketone possible from this reaction. Although the starting materials are readily available, the reaction has never been shown to be practicable on an industrial scale.

In recent years, a synthesis of methyl vinyl ketone from acetylene has come into prominence. The patent literature would indicate that most of the methyl vinyl ketone being prepared today is being made from acetylene. The first step in the synthesis is formation of vinyl-acetylene by use of the famed Nieuwland (1931) reaction.

$$1)\ 2CH{\equiv}CH \longrightarrow CH{\equiv}C{-}CH{=}CH_2$$

The vinylacetylene is then hydrolyzed to methyl vinyl ketone using mercury salts and sulfuric acid as catalysts.

$$2)\ CH{\equiv}C{-}CH{=}CH_2 + H_2O \xrightarrow[H_2SO_4]{HgSO_4} CH_3COCH{=}CH_2$$

Churbakov and Ryantsev (1940) claim 90 per cent yields on the hydrolysis step of the reaction and the feasibility of the first step has been convincingly demonstrated in the development of chloroprene which is based on the reaction (1) above. Continuous processes for the production of methyl vinyl ketone from acetylene have been devised, and there is every reason to believe that this compound will become one of the more common chemicals.

In addition to the above methods of synthesis, there are other methods available which have been exploited less extensively. The first of these is the oxidation of methylvinylcarbinol.

Groll (1935) patented methods for the production of unsaturated carbonyl compounds from unsaturated alcohols by catalytic dehydrogenation. He claimed 33 per cent yields on the catalytic dehydrogenation of methylvinylcarbinol to methyl vinyl ketone. Groll and deJong (1936) investigated the catalytic vapor phase oxidation of various unsaturated alcohols, and considerably higher yields of unsaturated carbonyl compounds were claimed. The essential difference in the two methods is the removal of hydrogen by combination with oxygen in the case of catalytic oxidation. It is necessary to remove the hydrogen by some method in order to prevent its reaction with the unsaturated methyl vinyl ketone to yield methyl ethyl ketone.. Oxygen from the air accomplishes this purpose very effectively, but also introduces the possibility of complete combustion of the molecule to carbon dioxide and water. The recent development of unsaturated alcohol production through high temperature chlorination of unsaturated hydrocarbons followed by hydrolysis, a process described by Groll and Hearne (1939) and by Williams and Associates (1940) probably will be a stimulus to research employing unsaturated alcohols as starting materials, and catalytic oxidation may well be one of the reactions which will be thoroughly investigated. There is also a possibility that fermentation products may be converted to unsaturated alcohols. Unpublished and unconfirmed reports indicate rather high yields of methylvinylcarbinol from 2,3-butylene glycol. These reports, if confirmed, will indicate that 2,3-butylene glycol may become a source of many unsaturated chemicals.

Another synthesis of methyl vinyl ketone utilizes acetylmethylcarbinol, a fermentation product, as a starting material. Direct dehydration of acetylmethylcarbinol would yield methyl vinyl ketone. However, the dehydration of an α-keto alcohol is very difficult, and the direct dehydration of acetylmethylcarbinol is reported in but a single patent issued to N. V. deBataafsche Petroleum Maatschappij (1939) in which it is stated that sodium bisulfate is the catalyst employed. Generally, however, indirect dehydration of acetylmethylcarbinol is employed. Allen and Haury (1941) and Long (1941) patented methods for the production of methyl vinyl ketone by pyrolysis of the acetate of acetylmethylcarbinol. The pyrolysis is effected at 500°-550° C. in the presence of an inert gas, such as nitrogen. It is of interest to note that the first synthesis of methyl vinyl ketone studied extensively was based on a fermentation product, acetone, as a starting material and that the latest synthesis of methyl vinyl ketone is based on yet another, less studied fermentation product, acetylmethylcarbinol.

Diacetyl

Diacetyl as the simplest of the "diketo" compounds is of interest in polymerization reactions. Until recently, the compound had not received a great deal of attention in the field of synthetic resins and rubber, but recent developments in the production of the compound suggest that it will become available in increasing quantities. With an increase in quantity will come an increase in research designed to find uses for the compound.

As a "diketo" compound, diacetyl has a number of α-hydrogen atoms which are available for condensation type reactions. For this particular type of reaction, it may be stated that diacetyl is polyfunctional in character. The advantages of the polyfunctional nature of diacetyl are enhanced by the fact that the molecule also has a system of conjugated linkages. The conjugated system is characteristic of all the common copolymers in synthetic rubber. However, it should be pointed out that at least one of the double bonds in common chemicals used in copolymers is a $C=C$ double bond, whereas both the double bonds involved in the diacetyl conjugated system are $C=O$ double bonds.

The polyfunctional nature of diacetyl has been utilized by I. G. Farbenindustrie, A.-G. (1937) which patented a method for the production of resins by condensing diacetyl with primary or secondary alkyl or aryl amines. The reaction product could be modified by treating with urea or phthalic anhydride. Ellis (1935) suggested possible uses of diacetyl in resins but there is no record of any experimental work which carried out his suggestions.

Diacetyl has been prepared to some extent by treating methyl ethyl ketone with a nitrite to form an oxime which is decomposed to diacetyl by nitric acid. However, later syntheses seem much more feasible. In particular, a method using vinylacetylene or methyl vinyl ketone as starting material is being thoroughly investigated. Carter (1939) patented methods for the production of diacetyl from methyl vinyl ketone, employing mercuric salts as oxidizing agents. Eberhardt and Stadler (1941) converted methyl vinyl ketone to diacetyl in good yield by heating the reaction product of hypochlorous acid and methyl vinyl ketone with a mineral acid. Eberhardt and Lieseberg (1938) converted vinylacetylene to diacetyl using mercuric salts as hydration catalysts and also as oxidizing agents.

A second method of synthesis utilizes fermentation products as raw materials. DeSimo and McAllister (1936) patented methods for the oxidation of acetylmethylcarbinol to diacetyl using cupric oxide and free oxygen. McAllister and deSimo (1936) claimed excellent yields for the conversion of 2,3-butylene glycol to diacetyl by vapor phase oxidation.

Diacetyl can also be made directly by fermentation. Kluyver and Scheffer (1933) were granted patents covering the production of both diacetyl and acetylmethylcarbinol by the fermentation of a variety of carbohydrate materials. The fermentation is very similar to the 2,3-butylene glycol fermentation, but a higher rate of aeration of the mash is employed. The increased aeration maintains the fermentation product in a higher oxidized form and prevents reduction of the product to

2,3-butylene glycol. There is a distinct possibility that diacetyl could be produced commercially by fermentation, either directly, or indirectly through catalytic oxidation of 2,3-butylene glycol.

Acrylates

Esters of acrylic acid have found extensive use in recent years as the monomers for production of synthetic resins. The industrial development has been due, in large part, to the researches of Dr. Otto Rohm. Commercial quantities first became available in 1931; Anon. (1942). The resins are used extensively as adhesives in which role their elasticity and extensibility offer distinct advantages.

The esters have been used to some extent in the field of synthetic rubber, although the nitrile has been used more extensively. I. G. Farbenindustrie, A.-G. (1931) patented a method for the production of rubber-like materials from the emulsion polymerization of acrylate esters. Ziegler (1938) has stated that acrylate esters may be used in forming copolymers with butadiene in the emulsion polymerization process, although mixtures of the pure chemicals alone yield Diels-Alder type reaction products.

The commercial production of acrylate esters today is based on ethylene as a starting material. The ethylene, which may be derived from ethyl alcohol or from petroleum, is converted to ethylene chlorohydrin, thence to the cyanohydrin by the reactions below.

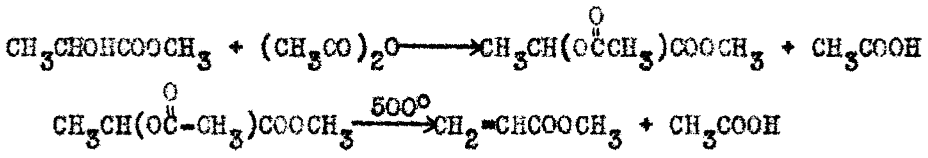
$$CH_2{=}CH_2 + HOCl \longrightarrow CH_2OH\text{-}CH_2Cl \xrightarrow{NaCN} CH_2OHCH_2CN$$

The cyanohydrin is converted to esters of acrylic acid by treating with an alcohol and sulfuric acid.

$$CH_2OHCH_2CN + ROH + H_2SO_4 \longrightarrow CH_2{=}CHCOOR + NH_4HSO_4$$

A new process which offers promise of attaining commercial importance is the conversion of esters of lactic acid to esters of acrylic acid. Lactic acid is a readily producible fermentation product and is derived from a variety of carbohydrates. Molasses, whey, and corn sugar have been used extensively in this country as raw materials. The acid in turn is converted readily to esters of lactic acid.

Burns, Jones, and Ritchie (1935) demonstrated the feasibility of converting lactates to acrylates by pyrolysis of acetate esters of lactic acid esters. Methyl lactate was converted to methyl α-acetoxy propionate in excellent yields, and the methyl α-acetoxy propionate was pyrolyzed to methyl acrylate in 90 per cent yields. The reactions are shown in the following equations.



$$CH_3CHOHCOOCH_3 + (CH_3CO)_2O \longrightarrow CH_3CH(O\overset{O}{\overset{\|}{C}}CH_3)COOCH_3 + CH_3COOH$$

$$CH_3CH(O\overset{O}{\overset{\|}{C}}{-}CH_3)COOCH_3 \xrightarrow{500^{\circ}} CH_2{=}CHCOOCH_3 + CH_3COOH$$

The authors state that esters other than the acetates can be pyrolyzed and mention the benzoates and carbonates specifically. This is another example of the indirect dehydration of difficultly dehydrated alcohols by pyrolysis of an ester.

Since the fundamental work of Burns, Jones, and Ritchie in 1935, a great deal of work has been done on the utilization of lactic acid, especially by the staff of the Eastern Regional Research Laboratory. Smith, Fisher, Ratchford, and Fein (1942) studied the effect of various contact materials, temperature, and contact time upon the production of acrylate esters and stated that a temperature of 500° C. with contact agents of quartz chip, strip aluminum, or iron would produce highest yields of methyl acrylate. Smith and Claborn (1939) stated that methyl acrylate could be produced as cheaply from fermentation lactic acid as from ethylene by the present commercial process.

Stearn, Makower, and Groggins (1940) stressed the possibilities of lactic acid in synthetic resins, not only from the viewpoint of acrylate raw material, but also in the formation of glyptal modified resins. They suggest that lactic acid be used to esterify the α-hydroxy groups of glycerol to yield an ester, glycerol dilactate. Glycerol dilactate is itself a compound having three alcoholic OH groups capable of reacting with dibasic acids to yield three dimensional polymers. Fisher, Rehberg, and Smith (1943) discussed the pyrolysis of esters of acetoxy propionic acid and demonstrated that esters higher than the methyl ester were not as satisfactory for pyrolytic reaction as the methyl esters. Fisher, Ratchford, and Smith (1944) discussed the effect of various contact materials on yields of methyl acrylate from methyl lactate and demonstrated that catalytic tubes constructed of stainless steel would be suitable. Fein and Fisher (1944) studied the acetylation of alkyl lactates and claim practically quantitative yields for the acetylation process. The commercial possibilities of the process are evidently great, and it now seems likely that lactic acid of fermentation may become an important factor in the future production of acrylate esters.

MATERIALS AND APPARATUS

Materials

1. The 2,3-butylene glycol used in this investigation was made by the fermentation of glucose by *Aerobacter aerogenes*. The fermentations were carried out by Mr. E. R. Kooi of these laboratories. In order to facilitate recovery of the glycol from the mashes, a counter-current liquid-liquid extractor was constructed, the details of which are described by Kolfenbach, Kooi, Fulmer, and Underkofler (1944). The glycol had the following physical constants: b.p. 178°-182° C. at 750 mm., $n^{20}_{D} = 1.438$, $d^{25}_{4} = 0.999$.

2. The acetylmethylcarbinol was prepared by the fermentation of 2,3-butylene glycol by *Acetobacter suboxydans*, as described by Fulmer, Underkofler, and Bantz (1943). The material was supplied by Mr. Bantz and had the following physical properties: b.p. 142°-144° C., $n^{15}_{D} = 1.4192$.

3. Methylvinylcarbinol was purchased from Shell Chemical Co. and possessed the following characteristics: b.p. 96°-97° C. at 745 mm., $n^{24}_{D} = 1.4130$, $d^{25}_{4} = 0.8357$.

4. Methyl lactate was purchased from Eastman Kodak Co., and after redistillation boiled at 141°-143° C., $n^{23}_{D} = 1.4118$.

5. Diacetyl was bought from Eastman Kodak Co. and from Forest Products Co. The material was redistilled, and the fraction boiling from 86° to 87.5° C. at 750 mm. was collected. This fraction had a density $^{25}_{4} = 0.980$ and $n^{26}_{D} = 1.3910$.

6. Alumina was bought from the Aluminum Ore Co., and was classified as Activated Alumina, Grade A, 8-14 mesh.

7. Silica gel was bought from the Davidson Co. One lot was in impalpable powder form, and the other was in granular form having a mesh size of 6-16.

8. Common chemicals used throughout this investigation were of C.P. grade.

Apparatus

Catalysis apparatus.

The apparatus used for the catalytic reactions is shown in Figure I. Standard taper joints were used for all connections from the vaporizer flask E to the ice bath J in order to eliminate sources of contamination of the catalyst.

A represents a compressed gas cylinder equipped with a pressure reducing valve. Various gases were used, including N_2, CO_2, H_2, and air.

B represents a wet test gas meter which was used to measure the volume of gas passing into the vaporizing flask E.

C represents gas wash bottles which were used to purify the gases being introduced into the vaporizer flask. The contents of the wash bottles varied with the different gases used. When nitrogen was used, as in the majority of the runs, the wash bottles were filled with alkaline pyrogallol to remove oxygen.

D represents a calcium chloride drying tower.

E represents a vaporizer flask. This flask was immersed in a bath

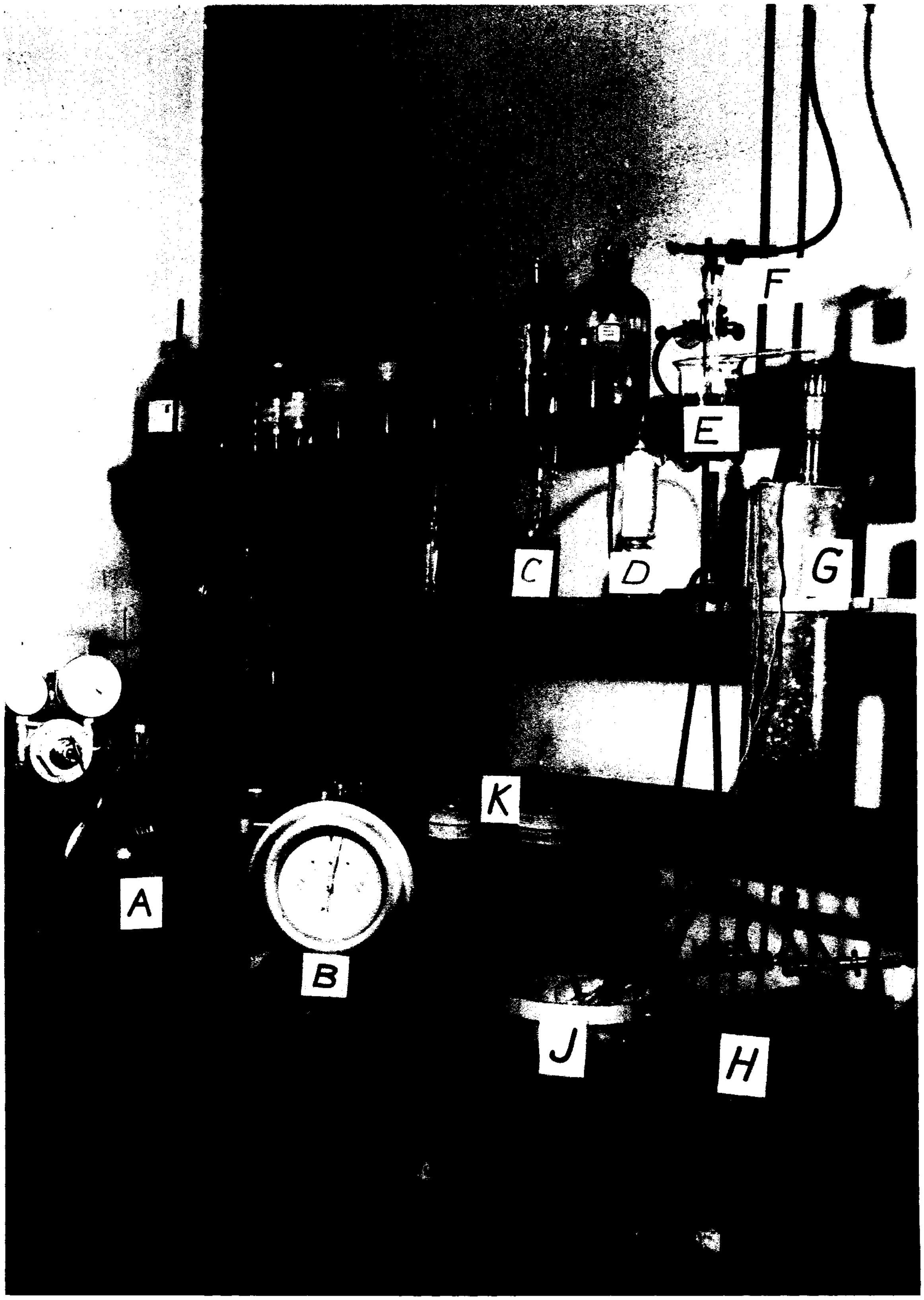


Figure I. Catalysis Apparatus

which could be heated to 225° C. The flask of 250 ml. volume was equipped with a gas inlet tube, which extended almost to the bottom of the flask, a side arm equipped with a 10/38 standard taper joint leading to the catalysis tube, and a slightly elongated neck leading to the drop rate regulator. In the vaporizer, the material was vaporized and mixed with gas which served to sweep the vaporized material into the catalysis chamber.

F, the drop rate regulator, consisted of a valve from a compressed gas tank. The regulator was attached by means of rubber tubing to a reservoir containing the material to be introduced into the catalyst chamber. With this method of introduction of material and by maintaining a head of approximately 45 cm. of liquid, excellent control of addition rate could be maintained.

G represents the furnace through which the glass catalysis tube passed. The furnace was electrically heated and was well insulated. The portion immediately surrounding the catalysis tube was constructed from a brass tube to which were sealed three thermocouples, one at each end and one in the middle. The furnace was 17-1/2 inches long, 6 inches in diameter, and the brass tube surrounding the catalysis tube was 35 mm. inside diameter.

The catalysis tube was constructed of pyrex glass and was equipped with standard taper joints at both top and bottom. The tube was 62 cm. long and 32 mm. in diameter.

The furnace was calibrated by relating the temperature of the bed of the catalyst, measured by a thermometer, to the millivolt reading of the thermocouples placed in the brass tube surrounding the catalysis tube. The relationship was derived under simulated reaction conditions--

with gas flowing but without introduction of reaction material. After calibration, thermocouple readings alone were used to measure the temperature of the catalysis tube.

H represents a transformer used to regulate the voltage applied to the furnace and thus to regulate the temperature of the furnace.

J represents an ice bath, and K represents dry ice baths used to insure more complete condensation of reaction products.

Pyrolysis apparatus.

The pyrolysis apparatus was similar to the catalysis apparatus, with the exception that no vaporizer flask was used. The material was dropped directly into the pyrolysis tube from the drop rate adjuster. The pyrolysis tube was constructed of Vycor tubing. The pyrolysis furnace was a Hoskins electric furnace, type FD 303. The furnace was calibrated in the same manner as the catalysis furnace.

Carbonate apparatus.

The carbonate of 2,3-butylene glycol was produced by a counter-current liquid vapor reaction. The apparatus employed is shown in Figure II.

A represents a cylinder of phosgene which was connected to a flowmeter B. The gaseous phosgene was led through the adapter D and passed up through the reaction tube, where it came into contact with liquid butylene glycol. The butylene glycol was added dropwise, the drop rate being controlled by the drop rate adjuster F, and fell into the reaction tube which was packed with glass beads. The temperature of the reaction tube was regulated by the transformer K. The high boiling reaction pro-

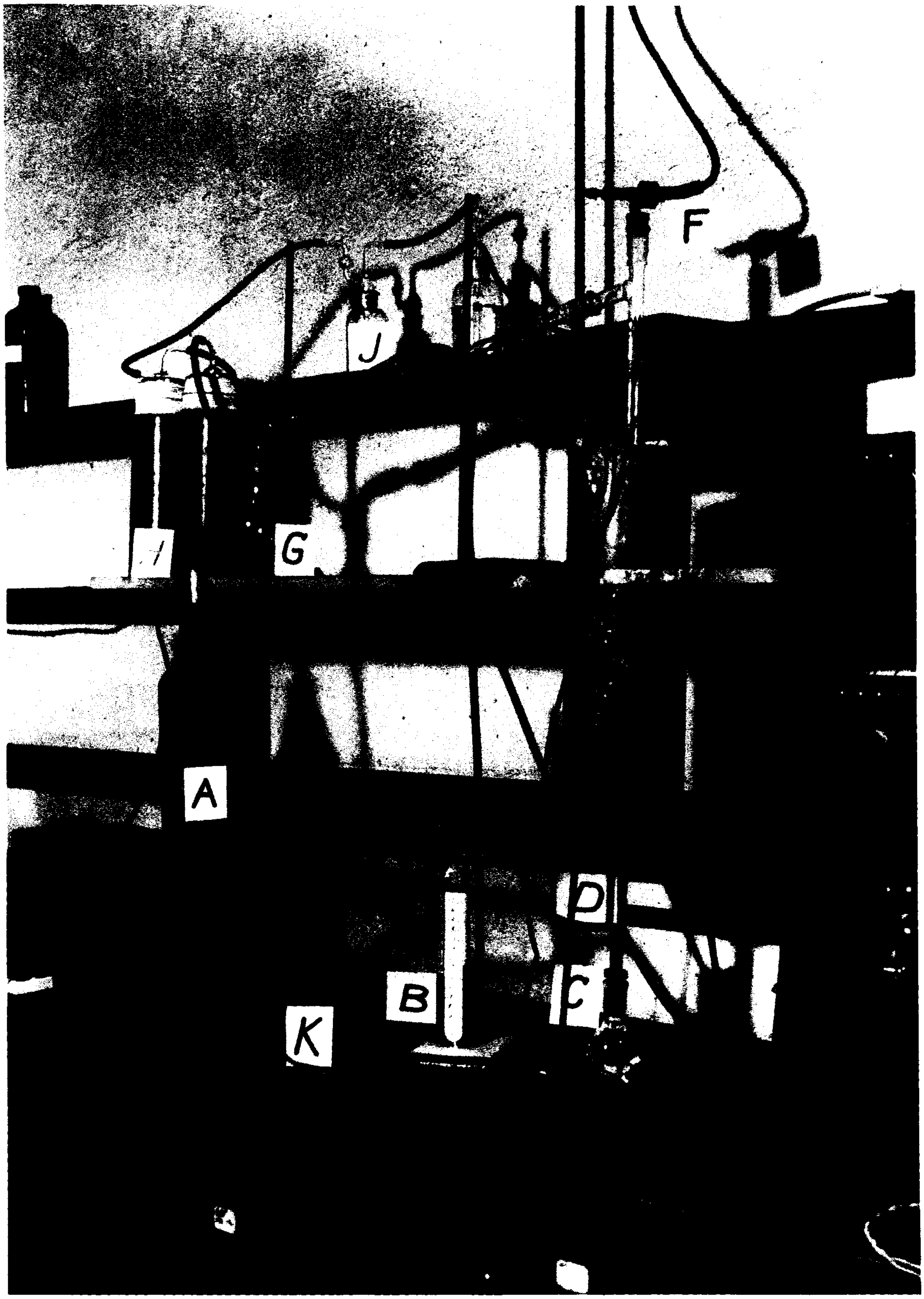


Figure II. Carbonate Production Apparatus duct was collected in flask C, while excess phosgene and low boiling products passed into the condensing system. The flask G was a receiver for materials boiling above room temperature. More volatile materials, including excess phosgene were led through dry ice traps to liquefy phosgene and thence through wash bottles containing sodium hydroxide solution. Any products not reacted nor condensed were led from the wash bottles into a hood and were removed from the laboratory.

Butadiene analysis apparatus.

Butadiene was analyzed by the maleic anhydride method. The apparatus employed was essentially the same as that described by Tropsch and Mattox (1934).

Polarograph apparatus.

The polarographic method was used for the quantitative analysis of methyl vinyl ketone and diacetyl. The instrument was manually manipulated and was similar to the instrument described by Lingane and Kolthoff (1939). A 7 cm. section of Heyrovsky tubing was used as the dropping electrode and this electrode was attached to a mercury reservoir by a section of pressure tubing. By raising or lowering the reservoir, the pressure on the dropping electrode could be varied. The voltage was measured against an external saturated calomel electrode, and the current was calculated from the IR drop across a resistance of 7000 ohms. Temperature was maintained at 25° C. by means of a thermostatically controlled heater fitted into a large de Khotinsky water bath. Nitrogen was used as the inert gas to flush all oxygen from the electrolysis vessel, and all analyses were made in an atmosphere of nitrogen.

METHODS

Catalyst Preparation

The preparation of catalysts for vapor phase work on a laboratory scale is complicated by the necessity of maintaining the catalyst in a form which will permit passage of the vapor. Obviously, a catalyst in powder form or a catalyst which will produce a fine powder on heating is not suitable for laboratory work, although the interesting fluid catalyst principle used in industry utilizes powders. The methods described were designed to produce a catalyst in a form through which gas could easily be passed.

"Paste" method with modifications.

The method used most generally in this investigation was a method termed the "paste" method. In this method, the materials to be incorporated into the catalyst were ball-milled to approximately 100 mesh. The components of the catalyst were then weighed out and placed in a small homogenizing apparatus. The homogenizing apparatus was merely a small ball mill, constructed from a wide mouth chemical reagent bottle of about 500 ml. capacity. The bottle was placed on a set of rubber stoppers which fitted on 2 glass rods, one of which was attached to a variable speed motor. The glass rods were supported from below by wood supports and were held in place by nails, but were free to revolve. The motor revolved the rod attached to it, and the revolution of the rod caused the bottle to revolve. Small stones in the bottle insured homogenization of the powders.

The stones were removed from the catalyst material and enough water was added to form a heavy paste which was of such consistency that it could be molded, but lost no water on molding. The amount of water to be added for a given weight of catalyst varied with the materials making up the catalyst. However, variation in the amount of water added to a given catalyst had little effect upon the activity of the catalyst.

The paste could be handled in several ways. Ordinarily the paste was spread on glass plates to a depth of about 3.5 mm. The catalyst was then divided into squares of about 6-7 mm., and was allowed to dry overnight at about 60° C. At times it was necessary to evaporate some of the water before cutting the catalyst into squares, a fact which became apparent immediately upon attempting to form the squares. The catalyst, however, should be cut before cracks appear on the surface.

The paste could also be handled by forcing it through a series of rather small holes of about 1 mm. diameter. This procedure produces a series of long strands which can be cut to desired lengths. In general, the method previously described was found more suitable from the viewpoint of stability as the second process has the serious disadvantage that the pressure required to force the paste through the holes may also force the water out of the paste.

Pill machines for handling catalyst pastes have been developed, but this laboratory was not equipped with one.

The "paste" method was adopted to insure a perfectly reproducible catalyst. However, not all materials can be handled in this fashion, and it is difficult to generalize as to the possibilities of using the "paste" method for different catalysts. Certain materials lend themselves readily to such use, and zinc oxide and calcium hydroxide are especially effective in producing sturdy catalysts in the "paste" method. Alumina and silica gel do not tend to form strong, stable catalysts from paste, but addition of salts, such as primary sodium phosphate to either alumina or silica, or mixtures of the two produces an exceedingly hardy catalyst.

Modifications of the paste method were used to some extent. In the first of the modifications, a salt which would decompose upon heating was incorporated into the paste. After the catalyst was dried, the salt was decomposed by raising the temperature. In this fashion, the catalyst of zinc oxide mixed with vanadium pentoxide was prepared, the decomposable salt in this case being ammonium metavanadate.

A second modification involved the incorporation of a reducible material, usually an oxide, into the paste. For example, pastes including zinc oxide and cupric oxide were prepared, and the cupric oxide was reduced to free copper by hydrogen at 350° C. Pastes incorporating tungstic oxide were also prepared, and the tungstic oxide was reduced to the blue oxide with hydrogen at 550° C.

Deposition method with modifications.

A second method of preparation of catalysts involved the deposition of an active component on a carrier which was in granular form. Carriers used most extensively in this work were silica gel, alumina, and asbestos.

In order to deposit the active ingredient several procedures were adopted. If soluble, the component was dissolved in water and the solution was poured on the carrier. The water was then evaporated from the mixture which was stirred continuously, and the active material was left on the surface of the carrier.

A second method of deposition was the addition of a carrier to a molten salt which was to act as the active ingredient. This method was used for the catalyst composed of zinc chloride on asbestos, and also for the catalyst composed of primary sodium phosphate on asbestos.

A third deposition method was the precipitation of an insoluble body from a solution in the presence of a carrier.

Modifications of the deposition method were also used. In the first modification, deposition was combined with decomposition. A material was deposited on the carrier and decomposed by heating. For example, the catalysts using alumina as a carrier on which primary sodium phosphate and copper formate were deposited, were subjected to a temperature of approximately 300° C. At that temperature the copper formate would be decomposed to copper or an oxide of copper.

In the second modification of the deposition procedure, a reducible material, usually an oxide, was deposited on the carrier. For example, copper hydroxide was deposited on asbestos, was dried, and then reduced to free copper by hydrogen at 350° C.

Reduction methods.

A third method involved the reduction of oxides in wire form. Specifically copper catalysts were made by reduction of copper oxide wire. Repeated oxidation and reduction may be used, and this procedure is reported to produce a more highly activated catalyst.

Single component catalysts.

Catalysts consisting of a single component were used for some experiments. In this classification, silica gel and alumina were used most extensively. The silica gel was prepared according to the directions of Patrick (1919). Alumina was prepared from aluminum nitrate by precipitating with ammonia. Thorough washing to remove ammonium salts, followed by drying at 60° C. overnight, and drying at 100° C. the following day, left a considerable portion of the material in granular form suitable for vapor phase catalysis.

Analytical Procedures

Butadiene analysis.

The yields of butadiene were determined by measuring the volume of gases which boiled between -78° C. and +5° C., and by determining the percentage of butadiene by volume. The volume of gases was measured by displacement of a saturated salt solution. The percentage of butadiene was determined by the method of Tropsch and Mattox (1934). Perfect gas laws were assumed, since no van der Waals' constants were known.

The theoretical volume of butadiene which could be produced from a given weight (g) of starting materials used in this investigation is given by the equation

$$V_t = g/M\frac{RT}{P}$$

where V_t = theoretical volume
M = molecular weight of starting material
R = gas constant
T = absolute temperature
P = pressure

The actual volume of butadiene is the product of total volume of gases multiplied by the fraction of butadiene in the gas.

The percentage yield is then

$$\frac{V_a}{V_t} \times 100, \text{ which is } \frac{V_a \times 100}{g/M \frac{RT}{P}}$$

Polarographic analysis.

Polarographic analysis was utilized for the quantitative determination of methyl vinyl ketone and diacetyl. This analysis was adopted for several reasons, the most important reasons being, (1) the difficulty of analysis of the mixtures encountered by any other means, and (2) the rapidity and accuracy of the polarographic method for the above-mentioned compounds. The difficulty of analysis by chemical means was due to the fact that other materials were present which distilled at temperatures in the same range as the material to be determined and also had functional groups similar to the groups present in the desired compound. For example, in the preparation of methyl vinyl ketone from methylvinylcarbinol, one would expect unchanged methylvinylcarbinol, methyl vinyl ketone, methyl ethyl ketone, and water. The boiling points are 97° C., 79° C., 80° C., and 100° C. respectively. The difficulty of separating the components of this mixture is readily apparent—especially the separation of the methyl vinyl ketone from methyl ethyl ketone. In addition each of the two functional groups of methyl vinyl ketone, namely the C=C and the C=O, is present in one or another of the molecules with which the methyl vinyl ketone is associated. The polarographic method was ideally suited for this determination, because methyl vinyl ketone is the only constituent of the mixture which is reducible at the dropping mercury electrode. The other materials neither reduce nor affect the reduction of the methyl vinyl ketone. In addition, a complete analysis can be made in 25 minutes.

Quantitative polarographic work is based on the variation of wave height of the reducible compound with concentration of the reducible compound. Quantitative polarography is similar in application to other comparator methods of analysis, for example, colorimetry. Unknown solutions are compared with standard solutions in order to determine concentrations in the unknowns. Impurities present in the unknown solution should be approximated in the standard solutions, or should be shown to have no effect upon the properties being compared. By reference to the standard solutions, the concentration in the unknown solution can be determined.

In this investigation, the total volume of organic material was measured, and one ml. of the organic layer diluted to proper volume was used for the polarographic determination of volume per cent of methyl vinyl ketone. A sample calculation for methyl vinyl ketone from methylvinylcarbinol follows and serves to demonstrate what data are necessary.

wt. of methylvinylcarbinol (M.V.C.) used = 36 g.
vol. of organic layer = 18 ml.
vol. % of methyl vinyl ketone (M.V.K.) = 70
density of methyl vinyl ketone = 0.86
mol. wt. of methyl vinyl ketone = 70
mol. wt. of methylvinylcarbinol = 72

$$\text{Actual yield} = \frac{(\text{total vol.})(\text{vol.\%M.V.K.})(\text{dens. M.V.K.})}{100}$$

$$\text{Theoretical yield} = \frac{\text{wt. M.V.C.}}{\text{mol. wt. M.V.C.}} \times \text{mol. wt. M.V.K.}$$

$$\%\ \text{yield} = \frac{(\text{total vol.})(\text{vol.\% M.V.K.})(\text{dens. M.V.K.})(\text{mol. wt. M.V.C.})}{(\text{wt. M.V.C.})(\text{mol. wt. M.V.K.})}$$

$$= \frac{(18)(70)(0.86)(72)}{(36)(70)} = 31\%$$

Direct analysis by distillation.

For the quantitative determination of other reaction products, direct weighing of distillation products was used. Per cent yields were calculated in the ordinary manner.

EXPERIMENTAL

Butadiene

Direct dehydration.

Since there were no quantitative data on the production of butadiene from 2,3-butylene glycol by direct dehydration, there was little precedent to follow in the choice of a catalyst. Single component catalysts were first investigated, although confidential reports had indicated that only small amounts of butadiene could be produced with such catalysts. Alumina and silica were chosen as catalysts for a series of runs. Mixed catalysts were next tested. The general procedures for all of these experiments are discussed in the following paragraphs.

Before making a run, the catalyst tube was filled with catalyst and was connected to the system. The temperature was then raised to approximately 300° C. and maintained at that temperature for several hours in order to activate the catalyst. In case the catalyst contained any oxidizable material, nitrogen was used to sweep out oxygen before heating, and the activation procedure was carried out in an atmosphere of nitrogen.

After activation of the catalyst, the temperature was adjusted to the desired level by means of the transformer. The 2,3-butylene glycol was weighed and placed in the reservoir above the drop rate adjuster. The temperature of the bath in which the vaporizer flask was immersed was increased to approximately 225° C. by means of a Bunsen burner. The rate of flow of inert gas was adjusted roughly, an interval timer was started, and the glycol was allowed to drip upon a pad of glass wool at the bottom of the vaporizer flask. The drop rate was carefully adjusted and finally the inert gas rate was adjusted to the exact value desired. The temperature, gas rate, and drop rate were checked from time to time during the run.

After all the glycol had been introduced, the time was recorded, and the inert gas was used to flush out the apparatus. Usually about 3 liters of gas were used for this purpose. At the close of the flushing out period, the dry ice flasks were detached from the system and were connected to a large bottle completely filled with saturated salt solution. The outlet tube from the large bottle was maintained at the level of the liquid inside the bottle. The flasks containing the butadiene were then placed in an ice bath at about 0° C., which vaporized products volatile at 0° C. into the large bottle and displaced salt solution from the bottle. The levels were carefully adjusted, after all the volatile material had distilled, and the volume of the displaced salt solution was recorded as were the temperature and pressure. The inlet tube to the large bottle was then connected to the butadiene analysis apparatus and a gas sample was withdrawn into the butadiene analysis apparatus in the customary manner. After determination of the percentage of butadiene in the gas sample, the percentage yield was determined by substitution into the equation on page 29.

The data for single component catalysts are collected in Table I. The catalysts were prepared as described in the section entitled "Methods."

Table I

Butadiene Yields from Alumina and Silica Gel Catalysts at Various Temperatures

Catalyst	Temp., ° C.	Glycol, grams	Time, min.	Rate of N_2 Flow ml. per min.	Butadiene %
Al_2O_3	250	53	60	150	0
Al_2O_3	275	50	42	150	0
Al_2O_3	300	41	58	150	trace
Al_2O_3	300	50	43	150	0
Al_2O_3	350	51	58	150	1
Al_2O_3	400	49	60	150	1.5
Al_2O_3	450	25	27	150	2.5
Al_2O_3	500	25	28	150	5
Silica gel	400	25	27	150	0
Silica gel	450	25	29	150	trace

The above data confirm the reported difficulty of dehydrating 2,3-butylene glycol, and also indicate that higher temperatures favor the formation of butadiene. However, the practical upper limit of temperature had already been reached at a temperature of 500° C., at which temperature the catalyst was thoroughly blackened from end to end of the tube by decomposition products. In the case of silica gel catalysts, this decomposition takes place at even lower temperatures.

The liquid condensate in all the runs contained a great deal of methyl ethyl ketone, and the major portion of the liquid boiled from 70° C. to 85° C. It was thought that the methyl ethyl ketone was produced not by isomerization of an epoxy compound, as Ipatieff suggests, but rather by a ketonization of an enol form of methyl ethyl ketone:

$$CH_3CHOHCHOHCH_3 \xrightarrow{-H_2O} CH_3CH{=}C(OH)CH_3 \longrightarrow CH_3CH_2COCH_3$$

All attempts at isolating the epoxy compound were unsuccessful.

The fact that butadiene is produced in excellent yields by the pyrolysis of glycol diacetate leads one to believe that the effect of the acetate radical is an orientation effect or a steric effect, which causes easier removal of the hydrogen atoms of the methyl group. Any hope of preparing butadiene directly from 2,3-butylene glycol probably lies in the production of a similar "orientation" effect, which would cause the molecule to dehydrate in such a manner that the hydrogen atom would come from a position on the end carbon rather than from a position on a carbon holding a hydroxyl group.

A series of runs totaling well over 100 was made in an attempt to find some material which would produce the desired effect. In all the runs particular attention was directed toward two compounds, butadiene and methylvinylcarbinol. The latter would be an expected intermediate in the formation of butadiene-1,3 from 2,3-butylene glycol. In no case was methylvinylcarbinol isolated, although private, unconfirmed reports indicate that methylvinylcarbinol has been produced from 2,3-butylene glycol in rather high yields.

The attempts at "orientation" effects were made in two directions. First, attempts were made to use a material having a somewhat basic effect to stabilize the enol form, and secondly, attempts were made to use a slightly dehydrogenating material to loosen the hydrogen atoms attached to the methyl groups. The incorporation of such materials into the catalysts was accomplished by the deposition and "paste" methods with modifications, as described above, under "Methods of Catalyst Preparation." Typical catalysts and results are listed in Table II.

Table II

Butadiene Yields Using Mixed Catalysts

22.5 grams butylene glycol used in each run

Catalyst	Method of Preparation	Temp. °C.	Time for Run, min.	Inert Gas	Rate Gas Flow, ml. per min.	Butadiene %
(A) Al_2O_3 as carrier						
$Ca_3(PO_4)_2$ on Al_2O_3 [a]	deposition	350	42	N_2	150	1.5
$Ca_3(PO_4)_2$ Fe_2O_3 (trace)[b] Al_2O_3	dep. & decomp.	300	40	N_2	150	0
$Hg_3(PO_4)_2$ Al_2O_3	deposition	350	44	N_2	100	0
$K_2CO_3(15)$ $Al_2O_3(100)$	deposition	400	37	N_2	150	0
Cu(trace) Al_2O_3	dep. & decomp.	340	40	N_2	165	0
Cu(20) $Al_2O_3(100)$	dep. & red.[c]	400	35	N_2	65	0
ZnO(20) $Al_2O_3(80)$	paste	400	40	CO_2	46	0
Cu(trace) $KH_2PO_4(1)$ $Al_2O_3(40)$	dep. & decomp.	350	40	CO_2	200	2
Cu(trace) $KH_2PO_4(1)$ $Al_2O_3(40)$	dep. & decomp.	400	55	CO_2	125	3.5
Cu(trace) $KH_2PO_4(1)$ $Al_2O_3(40)$	dep. & decomp.	400	30	CO_2	123	4
Cu(trace) $KH_2PO_4(1)$ $Al_2O_3(40)$	dep. & decomp.	400	70	CO_2	68	7.5
Cu(trace) $NaH_2PO_4(1)$ $Al_2O_3(40)$	dep. & decomp.	390	30	CO_2	105	1.5
$KH_2PO_4(1)$ $Al_2O_3(40)$	deposition	400	40	CO_2	30	4.5
$KH_2PO_4(1)$ $Al_2O_3(40)$	deposition	375	60	CO_2	20	1.5
$KH_2PO_4(1)$ $Al_2O_3(40)$	deposition	400	45	CO_2	70	2
$NaH_2PO_4(1)$ $Al_2O_3(40)$	deposition	400	47	CO_2	65	1
(B) Silica Gel as carrier						
$NaH_2PO_4(30)$ Silica(30)	deposition	400	50	CO_2	50	0
Cu(trace) $NaH_2PO_4(1)$ Silica(30)	dep. & decomp.	350	60	N_2	40	1

Table II (continued)

22.5 grams butylene glycol used in each run

Catalyst	Method of Preparation	Temp. °C.	Time for Run, min.	Inert Gas	Rate Gas Flow, ml. per min.	Butadiene %
Cu(trace) NaH_2PO_4(30) Silica (30)	dep. & decomp.	350	45	CO_2	90	3
Cu(trace) NaH_2PO_4(30) Silica (30)	dep. & decomp.	350	60	CO_2	50	1
Cu(trace) KH_2PO_4(30) Silica (30)	dep. & decomp.	360	50	CO_2	100	2
NaH_2PO_4(5) H_2WO_4(5) Silica (40)	deposition	400	45	CO_2	50	2.5
(C) Asbestos as carrier						
NaH_2PO_4(10) Asbestos (10)	deposition	400	40	CO_2	250	1.5
NaH_2PO_4(20) Asbestos (20)	deposition	400	40	CO_2	90	1.5
NaH_2PO_4(20) Asbestos (20)	deposition	450	40	CO_2	60	2

[a] Where specific quantities are not listed, the carrier was saturated with catalytic material.

[b] Trace amounts were added by addition of a formate solution to the catalyst, drying, and decomposing the formate at 300° C.

[c] Reduction of CuO.

The tabulated results indicate that high yields of butadiene from 2,3-butylene glycol by direct dehydration are difficult, if not impossible, to obtain. No definite trends could be noted with the exception that higher temperatures again favored butadiene formation, but also favored marked decomposition. The most favorable catalyst was the combination of KH_2PO_4 on Al_2O_3, modified by a trace of copper. Thorough investigation of this catalyst failed to increase yields to any appreciable extent, however. Attempts at finding basic materials to effect the desired change were abandoned early because of the fact that basic materials tended to inhibit all dehydrations, even dehydration to methyl ethyl ketone.

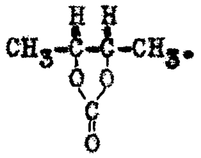
A variety of other catalysts was tried with equally unsatisfactory results. In particular, W_2O_5 catalysts, catalysts in which red phosphorus was mixed with NaH_2PO_4, and a variety of "paste" catalysts were investigated but failed to produce yields of more than 4-5 per cent butadiene. In every case, methyl ethyl ketone was the predominating reaction product, although traces of isobutyraldehyde, the cyclic acetal of methyl ethyl ketone and 2,3-butylene glycol, butadiene-1,2, and dimethyl acetylene were also found.

Indirect dehydration.

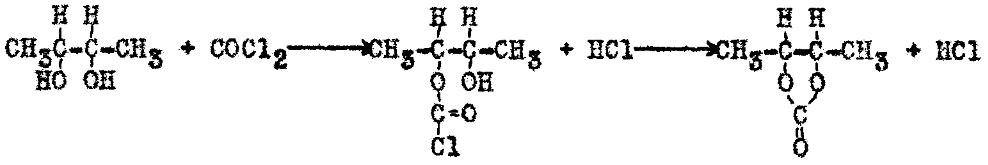
The possibility of converting the glycol to a carbonate was first investigated. Forty-five grams of 2,3-butylene glycol was placed in a 3-neck flask equipped with a stirrer, reflux condenser the outlet of which was connected to a dry ice trap, and a dropping funnel. To the dropping funnel was added 100 grams of liquid phosgene, maintained in the liquid state by addition of dry ice at intervals. The reflux condenser water was siphoned from a bath containing an ice-salt mixture at approximately -8° C. The phosgene was dropped into the liquid glycol, maintained at 50° C. The unreacted phosgene was condensed, either in the reflux condenser or in the dry ice trap, and was returned for further reaction. After all the phosgene had reacted, the mixture was heated for several hours, during which copious evolution of HCl was observed. The mixture was then subjected to atmospheric distillation and products boiling at temperatures up to 120° C. were removed. The remainder was then subjected to vacuum distillation and 37 g. of product boiling at 95° C. under 8 mm. pressure was collected. The product was water white and had the following physical properties:

$n_D^{26} = 1.4226$, $d_4^{26} = 1.129$, b.p. at 740 mm. = 240° C.
molecular weight = 116 in phenanthrene
molecular weight in bornyl bromide = 228, indicating association in that solvent

%C	Calculated:	51.7	Found:	51.5
%H	Calculated:	6.96	Found:	7.10

These data indicate that the compound is the inner carbonate of 2,3-butylene glycol, having the formula  $\begin{array}{c} CH_3-\overset{H}{\underset{O}{C}}-\overset{H}{\underset{O}{C}}-CH_3 \\ \diagdown\ \diagup \\ C \\ \| \\ O \end{array}$. A yield of 37 grams corresponds to 65 per cent of theoretical.

The possibility of preparing the carbonate by a continuous process was next investigated, and the apparatus employed is shown in Figure II, p. 22. Ninety grams of glycol was placed in the reservoir attached to the drop rate adjuster, F. The furnace was heated to 150° C., the phosgene gas flow was adjusted to 200 ml. per minute and the glycol was dropped into the reaction tube at the rate of 44 grams per hour. The reaction product dropped into the flask C and excess phosgene and low boiling by-product materials passed out the top of the furnace into the condensing system. After all the glycol had been introduced, about one liter of gaseous phosgene was passed through the system to insure complete reaction of the glycol. At the end of this period, the flask C was removed from the system and placed in a bath heated to 100° C. After heating for 2 hours, during which vile smelling gases, largely HCl and perhaps some phosgene, were driven off, the material was distilled under vacuum. The purpose of the heating was to complete the reaction, which evidently occurs in stages. The first stage is formation of the chlorocarbonate in which only one of the hydroxyl groups reacts. Extended heating causes the remaining hydroxyl group to react with the chlorocarbonate, splitting out HCl and forming the cyclic carbonate as shown in the following equations:



After HCl was no longer evolved, the reaction mixture was distilled under vacuum, and the product boiled very sharply at 95° C. under 8 mm. pressure; yields of 75 per cent of theory were realized.

The carbonate was pyrolyzed at various temperatures using either steel turnings or quartz chips as contact agent. The results are listed in Table III.

Table III

Butadiene Yields from Pyrolysis of Glycol Carbonate

Contact Agent	Temp. °C.	Wt. of Carbonate, grams	Time, min.	Inert Gas	Rate of Flow, ml. per min.	Butadiene %
Steel turnings	620	43	40	---	----	1
Steel turnings	550	28	30	N_2	200	trace
Steel turnings	475	26	30	N_2	200	trace
Quartz	460	24	35	N_2	150	0
Quartz	630	29	28	N_2	250	0
Quartz	670	35	30	N_2	250	trace

In all the runs much decomposition occurred. This was also true when using alumina or porous plate as contact agents. Even at the temperature of 670° C. a considerable portion of the carbonate was unchanged, when quartz was used as the contact agent. Iron evidently leads to decomposition at a lower temperature, as large amounts of carbon were deposited on the contact material at 620° C. The negligible yields of butadiene indicate that inner carbonates do not pyrolyze to unsaturated hydrocarbons, as do the ordinary carbonates, but rather decompose completely.

A second approach to the production of butadiene from 2,3-butylene glycol by indirect dehydration was made using the monomethyl ether of the glycol. It was thought that the methyl ether might be dehydrated to an unsaturated methoxy compound, which in turn could be desaturated to butadiene. The advantage in this procedure would arise from the fact that the methoxy group attached to a carbon involved in a double bond does not undergo rearrangement as does the hydroxyl group in a similar position. The removal of the one molecule of water from the starting material would produce not methyl ethyl ketone, but rather an unsaturated methoxy compound which has the possibility of conversion to butadiene.

The monomethyl derivative of glycol was prepared according to the directions of Chappell (1935), who prepared the monosodium derivative in excess glycol and then methylated with dimethyl sulfate. The methyl ether was then distilled from the reaction mixture under vacuum and was redistilled at atmospheric pressure. Excellent yields were realized, based on the sodium used, but great difficulty was encountered in attempting to distill the excess butylene glycol from the mixture. The sodium methyl sulfate, formed by the action of dimethyl sulfate on the sodium derivative of glycol, effectively prevented distillation of the glycol and acted as a dehydration catalyst. Even at reduced pressures, the glycol was partially dehydrated before it could be distilled. The cyclic acetal, formed from methyl ethyl ketone and glycol, could be isolated, along with large amounts of methyl ethyl ketone. The glycol could be extracted from the mixture by dissolving the mixture in water and using a continuous extractor employing ether as the immiscible solvent.

The monomethyl ether of glycol was passed over various catalysts at temperatures ranging from 265° C. to 375° C. The material was prevaporized, and nitrogen was used as the inert gas to sweep the vaporized material into the catalysis tube. All catalysts were prepared by the "paste" method. The results are listed in Table IV.

Table IV

Butadiene Yields from Simultaneous Dehydration-Desaturation of Mono Methyl Ether of 2,3-Butylene Glycol

25 grams methoxy compound in each run				
Catalyst	Temp., °C.	Time, min.	ml. N_2 Per Min.	Butadiene %
Al_2O_3(40) Silica(40) $AlPO_4$(20)	330	30	150	1
Pumice(100) P(5) Cu_2O(20)	265	40	250	0
Pumice(100) P(5) NaH_2PO_4(20)	335	40	125	0
Pumice(100) P(5) NaH_2PO_4(20)	325	35	125	0
Pumice(100) P(5) NaH_2PO_4(20)	375	38	125	0
Silica(26) Al_2O_3(26) W_2O_5(6.5) NaH_2PO_4(6.5)	325	38	125	1
Silica(26) Al_2O_3(26) W_2O_5(6.5) NaH_2PO_4(6.5)	375	50	150	11

In all the runs, the condensate in the ice bath was a complex mixture, most of which boiled from 75° C. to 85° C. It is suspected that a considerable fraction of this material was methyl ethyl ketone, which was produced by desaturation rather than by dehydration. Methyl alcohol was probably split out of the methoxy compound and left the enol form of methyl ethyl ketone. Unfortunately, the methoxy compound requires a higher temperature for dehydration than does the glycol, and at the temperature required for dehydration, desaturation also takes place.

Methyl Vinyl Ketone

The production of methyl vinyl ketone was investigated from three distinct angles, (1) the catalytic oxidation of methylvinylcarbinol, (2) the dehydration of acetylmethylcarbinol, and (3) the simultaneous dehydration-oxidation of 2,3-butylene glycol.

All the methods gave rise to certain by-products, which seriously complicated ordinary analytical procedures, and the possibility of using the polarographic method for the determination of methyl vinyl ketone in the mixtures was investigated.

Polarographic analysis.

Pure methyl vinyl ketone was prepared by the catalytic oxidation of methylvinylcarbinol as described later in this section. The material was dried with anhydrous sodium sulfate and was redistilled after addition of a few drops of butyric acid to prevent polymerization. The fraction boiling from 78° C. to 79° C. was collected. The refractive index at 20° C. was 1.4081, and the d^{25}_{4} was 0.862.

Immediately after distillation, one ml. of the pure methyl vinyl ketone was diluted to 100 ml. with 0.1 N potassium chloride solution. This solution of methyl vinyl ketone was termed the stock solution, and further dilutions were made from the stock solution.

A concentration series was run in order to determine the variation of wave height with concentration. The concentration series consisted of 3 solutions, each of which contained 1 ml. of the stock solution and each of which had been diluted to the proper volume with 0.1 N potassium chloride. The volumes for the three solutions were 250 ml., 100 ml., and 50 ml. respectively, and the concentrations in molarity were 0.494×10^{-3}, 1.23×10^{-3}, and 2.47×10^{-3} respectively. The solutions were placed in the electrolysis vessel, and nitrogen was bubbled through the solution for 15 minutes. During a determination, the nitrogen flow was continued, but the gas inlet tube was raised above the surface of the liquid, so that stirring effects would be avoided, but the nitrogen atmosphere would be maintained. The reservoir of mercury was raised and the increased pressure caused the mercury to drop from the tip of the electrode. The voltage was then gradually increased, and the current reading at each voltage level was determined by measuring the IR drop across a resistance of 7000 ohms.

The data for the three solutions comprising the concentration series follow in Table V.

Table V

Current-Voltage[a] Data for Methyl Vinyl Ketone Solutions

Molarity x 10^3					
0.494		1.23		2.47	
Volts	Current Micro-amps	Volts	Current Micro-amps	Volts	Current Micro-amps
1.245	0.56	1.250	0.53	1.080	0.57
1.338	0.57	1.330	0.71	1.215	0.57
1.412	1.31	1.400	1.71	1.290	0.90
1.478	2.21	1.454	3.43	1.407	4.93
1.545	2.46	1.515	4.71	1.462	7.74
1.615	2.46	1.581	5.20	1.527	9.07
1.680	2.36	1.650	4.96	1.577	9.50
1.745	2.36	1.718	4.99	1.640	9.57
1.820	2.36	1.800	4.99	1.720	9.57
Diffusion Current[b]	1.86		4.46		9.00

[a] Potential difference between dropping electrode and saturated calomel electrode

[b] Diffusion current = limiting current - residual current

These data demonstrate that the diffusion current is linearly proportional to the concentration, and hence perfectly suited to quantitative polarographic analysis. The relationship between the current and concentration can be expressed by the equation $dc = 3.65(M \times 10^3)$

where dc = current in microamps
M = molarity

The calculated values for the diffusion current using the above equation are compared with the experimental values in Table VI. Also included in Table VI are the half-wave potentials for the three solutions.

Table VI

Diffusion Current (dc) and Half-Wave Potentials ($E_{1/2}$) for Methyl Vinyl Ketone

$M \times 10^3$	dc exp.	dc calc.	$E_{1/2}$
0.494	1.80	1.79	1.43
1.234	4.43	4.50	1.42
2.468	9.00	9.01	1.41

These figures serve to demonstrate further the strict linearity between diffusion current and concentration. The half-wave potentials, the potentials at which half the reducible material in the mercury-solution interface is reduced, are practically constant. The slight decrease in $E_{1/2}$ with concentration is due to the slight IR drop within the solution itself.

While the above results demonstrate that pure methyl vinyl ketone in solution can be determined quantitatively by the polarographic method, it is necessary to demonstrate that the impurities likely to be present with the methyl vinyl ketone do not interfere with the polarographic analysis. In order to demonstrate this fact, methyl ethyl ketone and methylvinylcarbinol, the two compounds most likely to be present in a run, were added in varying ratios to the methyl vinyl ketone. The concentrations of the various constituents of the mixtures and the polarographic data for the mixtures are given in Table VII.

Table VII

Current-Voltage[a] Data for Mixtures of Methyl Vinyl Ketone (MVK), Methylvinylcarbinol (MVC), and Methyl Ethyl Ketone (MEK)

Molarity x 10^3					
MVK=0.494 MEK=0.448 MVC=0.469		MVK=1.23 MEK=1.12 MVC=1.17		MVK=1.87 MEK=0.224 MVC=0.234	
Volts	Current Micro-amps	Volts	Current Micro-amps	Volts	Current Micro-amps
1.265	0.50	1.200	0.40	1.220	0.53
1.314	0.53	1.283	0.46	1.270	0.57
1.422	1.57	1.352	0.89	1.346	1.06
1.506	2.33	1.433	2.79	1.418	2.86
1.580	2.33	1.490	4.36	1.470	5.14
1.653	2.33	1.557	5.04	1.530	6.71
1.714	2.33	1.621	4.93	1.594	7.07
		1.695	4.94	1.655	7.71
		1.760	4.93	1.725	7.43
				1.789	7.37
				1.850	7.37
Diffusion Current[b]	1.81		4.47		6.80

[a] Potential difference between dropping electrode and saturated calomel electrode.

[b] Diffusion current = limiting current - residual current

Table VII demonstrates that the values for the diffusion current of methyl vinyl ketone in mixtures with non-reducing impurities are the same as values for the pure compound alone.

The accuracy of the method can be illustrated by comparing the experimental values with the values calculated from equation (1) on page 45. The comparison is shown in Table VIII.

Table VIII

Diffusion Currents for Mixtures of Methyl Vinyl Ketone, Methylvinylcarbinol,[a] and Methyl Ethyl Ketone

$M^b \times 10^3$ exp.	dc calc.	dc exp.
0.494	1.80	1.81
1.23	4.49	4.47
1.87	6.83	6.80

[a] Concentration of methylvinylcarbinol and methyl ethyl ketone as in Table VII

[b] M = molarity of methyl vinyl ketone

These data indicate that methyl vinyl ketone in mixtures can be determined quantitatively within 2 per cent by the polarographic method.

In the production of methyl vinyl ketone from 2,3-butylene glycol by a simultaneous oxidation-dehydration procedure, there is a distinct possibility of producing diacetyl, along with methyl vinyl ketone. It was, therefore, of interest to investigate the possibility of utilizing the polarographic method for the quantitative determination of both diacetyl and methyl vinyl ketone from a single solution. It was known that diacetyl is reducible at the dropping mercury electrode, since Winkel and Proske (1936) reported its reduction potential.

The determination of the current-concentration relationship for diacetyl was carried out in the same manner as was used for methyl vinyl ketone. One ml. of pure diacetyl, the properties of which are described above in the section "Materials", was diluted to 100 ml. with 0.1 N potassium chloride to form the stock solution. Various concentrations were prepared from the stock solution and were analyzed polarographically. The data are presented in Table IX.

Table IX

Current-Voltage Data for Diacetyl

Molarity x 10^3									
1.136		0.909		0.568		0.454		0.379	
Volts[a]	Current Micro-amps	Volts[a]	Current Micro-amps	Volts[a]	Current Micro-amps	Volts[a]	Current Micro-amps	Volts[a]	Current Micro-amps
0.459	0.53	0.521	0.46	0.484	0.51	0.507	0.39	0.575	0.39
0.517	0.56	0.633	0.47	0.593	0.51	0.615	0.40	0.680	0.40
0.626	0.57	0.675	0.49	0.673	0.54	0.688	0.43	0.786	0.59
0.690	0.60	0.735	0.59	0.774	0.71	0.790	0.67	0.840	1.17
0.788	1.39	0.822	1.69	0.860	1.97	0.834	1.34	0.928	1.61
0.824	2.29	0.905	3.00	0.946	2.36	0.924	1.94	1.020	1.67
0.875	3.57	0.991	3.23	1.036	2.40	1.013	1.97	1.120	1.69
0.963	3.97	1.080	3.24	1.120	2.41				
1.053	3.97								
Diffusion Current[b]	3.37		2.76		1.86		1.52		1.28

---

[a] Volts represent the potential difference between the dropping electrode and saturated calomel electrode

[b] Diffusion current = limiting current - residual current

The data of Table IX indicate that the current is not linearly proportional to concentration. Rather the data follow the equation

$$\log dc = 0.877 \log (M \times 10^4) - 0.397$$

where dc = diffusion current in microamperes
M = molarity of diacetyl

The agreement between experimental values and calculated values is shown in Table X. Also included are the half-wave potentials for the various solutions.

Table X

Diffusion Currents and Half-Wave Potentials ($E_{1/2}$) for Diacetyl

$M \times 10^4$	dc exp.	dc calc.	$E_{1/2}$
11.36	3.37	3.38	0.82
9.09	2.76	2.78	0.83
5.68	1.81	1.84	0.82
4.54	1.51	1.51	0.83
3.79	1.29	1.29	0.83

Table X shows that pure diacetyl can be analyzed polarographically within 2 per cent. It was found more convenient to use the data of Tables IX and X in graphic form and to plot directly the "per cent" of diacetyl against diffusion current. In this particular case, the solution, 1.136 x 10^{-3} M, which contained one ml. of stock solution diluted to 100 ml. with 0.1 N potassium chloride was termed 100 per cent and the percentages of the other solutions were based upon the 1.136 x 10^{-3} M solution. For example, the solution, 0.454 x 10^{-3} M, which contained one ml. of stock solution diluted to 250 ml. was only 0.4 as concentrated as the 1.136 x 10^{-3} M solution and hence was termed 40 per cent. When unknown solutions were prepared, they were prepared exactly like the 1.136 x 10^{-3} M solution, with one ml. of unknown substituted for the one ml. of pure diacetyl. After determination of the wave height, the per cent diacetyl could be read directly from the graph. The graph of diffusion current against both molarity and per cent diacetyl is shown in Figure III.

The possible effects of the presence of the two reducible materials upon their individual reductions was next studied. Various dilutions of methyl vinyl ketone and diacetyl were prepared, and methyl ethyl ketone was also added. The current-voltage data for the various dilutions are presented in Table XI.

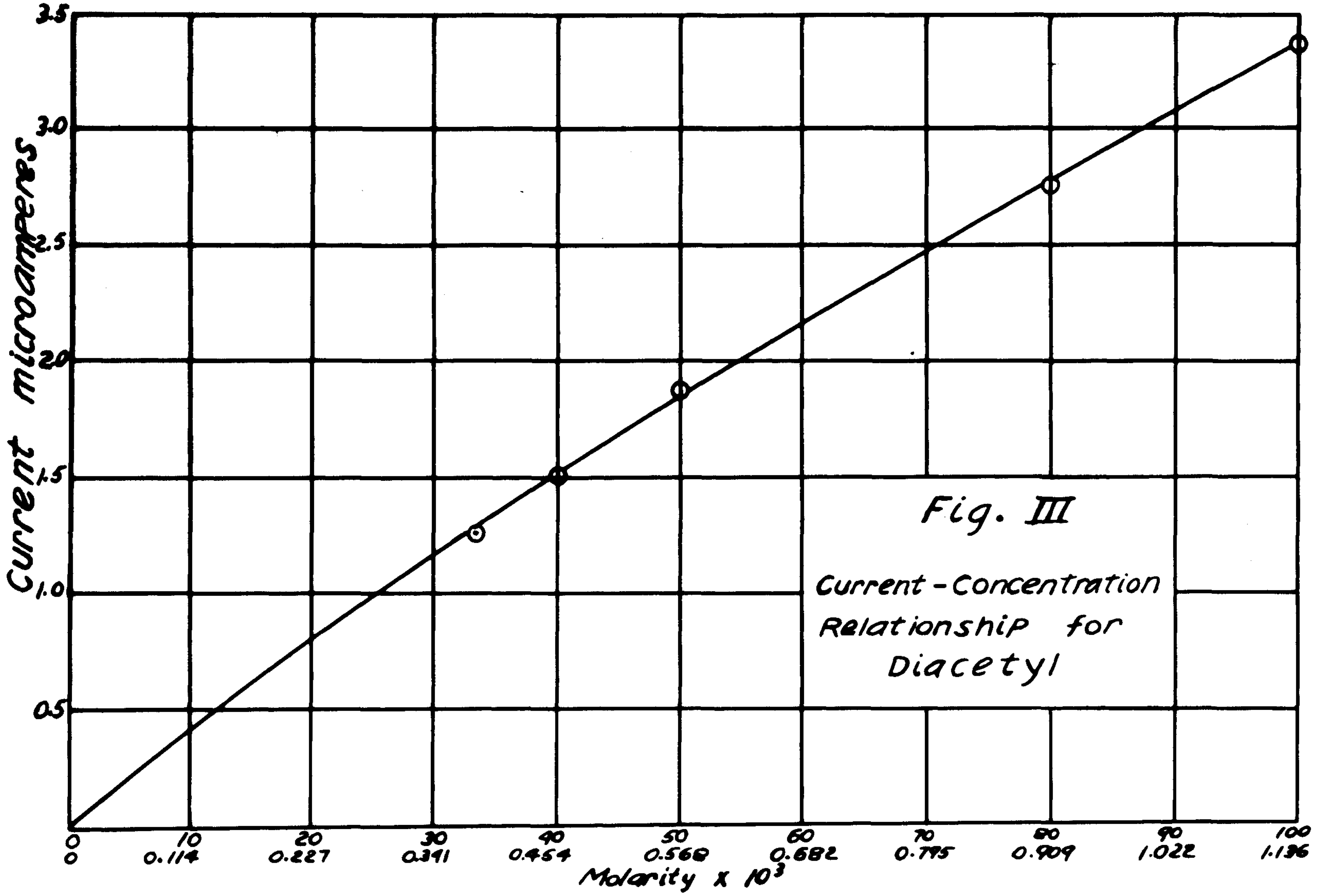


Fig. III

Current-Concentration Relationship for Diacetyl

Table XI

Current-Voltage[a] Data for Mixtures of Diacetyl (DA), Methyl Vinyl Ketone (MVK) and Methyl Ethyl Ketone (MEK)

Molarity x 10^3							
DA=0.385 MVK=0.834 MEK=0.834		DA=0.462 MVK=0.501 MEK=0.501		DA=0.462 MVK=0.750 MEK=0.750		DA=0.923 MVK=0.250 MEK=0.250	
Volts	Current Micro-amps	Volts	Current Micro-amps	Volts	Current Micro-amps	Volts	Current Micro-amps
0.480	0.37	0.526	0.31	0.459	0.47	0.475	0.39
0.590	0.39	0.633	0.36	0.576	0.53	0.580	0.41
0.695	0.41*	0.700	0.43*	0.680	0.60*	0.685	0.44*
0.791	0.67	0.807	1.36	0.792	0.89	0.733	0.50
0.843	1.21	0.873	1.93	0.885	1.93	0.772	0.64
0.931	1.71	0.965	2.00	0.975	2.10	0.845	2.37
1.023	1.79	1.060	1.96	1.067	2.14	0.936	3.07
1.110	1.77**	1.140	1.96**	1.152	2.14**	1.020	3.14**
1.200	1.77	1.225	1.94	1.240	2.14	1.108	3.14
1.281	1.77	1.290	2.00	1.322	2.16	1.193	3.13
1.335	1.77	1.369	2.71	1.400	2.43	1.277	3.13
1.411	2.36	1.439	3.57	1.466	3.61	1.355	3.13
1.470	3.83	1.506	3.77	1.528	4.60	1.433	3.31
1.533	4.56	1.577	3.77	1.600	4.81	1.500	3.86
1.590	4.73	1.649	3.77	1.705	4.81	1.573	3.97
1.668	4.74					1.642	3.97
1.735	4.74						

[a] Potential difference between dropping electrode and saturated calomel electrode

* Residual current

** Limiting current for diacetyl and residual current for methyl vinyl ketone

The results indicate the feasibility of applying the polarographic technique for the analysis of both diacetyl and methyl vinyl ketone. The diffusion currents for both diacetyl and methyl vinyl ketone are compared with calculated values in Table XII.

Table XII

Diffusion Currents for Diacetyl and Methyl Vinyl Ketone in the Presence of Methyl Ethyl Ketone[a]

Diacetyl			Methyl Vinyl Ketone		
M x 10^4	dc (exp.)	dc (calc.)	M x 10^4	dc (exp.)	dc (calc.)
3.85	1.36	1.31	0.834	2.97	3.04
4.62	1.53	1.53	0.501	1.83	1.83
4.62	1.54	1.53	0.750	2.67	2.74
9.23	2.70	2.81	0.250	0.84	0.91

[a] Methyl ethyl ketone concentrations as listed in Table XI

The agreement between calculated results and experimental results is entirely satisfactory for diacetyl, and the largest error is about 4 per cent. In the case of methyl vinyl ketone, the agreement between calculated and experimental values is very good with the exception of the most dilute solution. In this case, the previous reduction of diacetyl evidently depleted the hydrogen ions at the electrode too greatly for quantitative reduction of the methyl vinyl ketone. In actual determinations, however, the methyl vinyl ketone was usually present in higher concentration than the diacetyl, a fact which improved the accuracy of the determination. The analysis on actual determinations is reliable to within 3 per cent.

Methyl vinyl ketone from 2,3-butylene glycol.

The production of methyl vinyl ketone from 2,3-butylene glycol involves the removal of the elements of water and also a molecule of hydrogen. There are recorded instances of simultaneous dehydration and dehydrogenation of which the best known is the production of butadiene from ethyl alcohol. However, in the production of methyl vinyl ketone from glycol, it is necessary to remove the hydrogen by means of oxygen because of the ease of reduction of methyl vinyl ketone to methyl ethyl ketone. Thus, the process becomes a reaction involving catalytic dehydration combined with oxidation rather than dehydrogenation.

There is no well-known precedent for simultaneous catalytic dehydration-oxidation reactions and the type of catalyst to be used was not known. However, in a few attempts at preparing butadiene from butylene glycol, using primary sodium phosphate on asbestos as a catalyst, methyl vinyl ketone had been detected. In every case in which methyl vinyl ketone was produced, air had been introduced into the system. Because of this observation, phosphate catalysts were investigated to a relatively greater extent than others, and various catalysts employing combinations of dehydration and dehydrogenation materials were investigated.

The amount of methyl vinyl ketone produced was determined by the polarographic method, and all yields were based on the amount of glycol introduced into the vaporizer flask. The results are presented in Table XIII.

Table XIII

Methyl Vinyl Ketone from 2,3-Butylene Glycol

22.5 grams of glycol used in each run

Catalyst	Method of Preparation	Temp., °C.	Time, min.	Air flow, ml. per min.	M.V.K. %
NaH_2PO_4(30) Asbestos(30)	deposition	350	30	400	0
NaH_2PO_4(30) Asbestos(30)	deposition	400	30	400	trace
NaH_2PO_4(50) Asbestos(25)	deposition	325	30	250	0
NaH_2PO_4(50) Asbestos(25)	deposition	400	30	400	1.5
NaH_2PO_4(50) Asbestos(25)	deposition	450	30	400	6
NaH_2PO_4(54) Asbestos(18)	deposition	375	20	400	trace
NaH_2PO_4(54) Asbestos(18)	deposition	425	35	250	2
NaH_2PO_4(46) Asbestos(23) Cu(5)	dep. & red.[a]	325	45	200	0
NaH_2PO_4(46) Asbestos(23) Cu(5)	dep. & red.[a]	400	40	200	trace
NaH_2PO_4(100) Al_2O_3(100) CuO(20)	paste	390	30	0	1
NaH_2PO_4(50) Silica gel(25)	deposition	400	35	485	3.5
Al_2O_3(100) ZnO(50)	paste	400	30	0	0
Al_2O_3(100) ZnO(50)	paste	450	30	0	0
Al_2O_3(100) CuO(20)	deposition	350	30	100	0

[a] Reduction of cupric acetate at 300° C. with H_2.

The results of Table XIII indicate that the production of methyl vinyl ketone from 2,3-butylene glycol by catalytic dehydration combined with catalytic oxidation is very difficult. Again the chief obstacle is the inherent ease of formation of methyl ethyl ketone from the glycol. While methyl ethyl ketone itself produces a trace of methyl vinyl ketone in catalytic oxidation, most of the methyl vinyl ketone probably arises from methylvinylcarbinol.

Of the catalysts employed, primary sodium phosphate was the only material which showed any promise. However, the high temperature necessary for the sodium phosphate to become active militates against its use for the reason that considerable combustion occurs at the elevated temperatures. Attempts to find materials which would render the sodium phosphate active at lower temperatures were unsuccessful. Dehydrogenation materials were added but served to increase the yields of diacetyl rather than methyl vinyl ketone. However, the results do show that methyl vinyl ketone very definitely was formed directly from 2,3-butylene glycol by a process employing simultaneous catalytic dehydration and oxidation, even though the yields were poor.

Methyl vinyl ketone from methylvinylcarbinol.

Methyl vinyl ketone can be produced from methylvinylcarbinol by means of catalytic dehydrogenation, but the product is mixed with methyl ethyl ketone from which it is separated only with great difficulty. A much purer product can be made by means of catalytic oxidation.

The general topic of catalytic oxidation in the vapor phase has been discussed very thoroughly by Marek and Hahn (1932). Various catalysts are described and recommended by the above authors. Parks and Yula (1941) described the preparation of several catalysts for catalytic oxidations and generalized on the relative degree of oxidation ability of various oxide catalysts. In addition to knowledge of the general type of catalyst used, the patent of Groll and deJong (1936) makes claims for specific catalysts in the catalytic oxidation of various unsaturated alcohols.

Various catalysts, some of which had been described previously for catalytic oxidations, were investigated. The best catalysts found, however, had never been previously proposed for catalytic oxidation of unsaturated alcohols and were those composed of zinc oxide mixed with copper or oxides of copper. These catalysts were prepared by the paste method, were quite sturdy, and retained activity for a long period of time.

Table XIV lists the results using the catalysts composed of zinc oxide mixed with copper or the oxides of copper. In addition, the results using the individual components of the catalysts are listed at the end of the Table. All percentage yields are based on the amount of methylvinylcarbinol introduced into the vaporizer flask, and all yields were determined by the polarographic method. The temperatures listed in the Tables are temperatures of the catalyst bed before introduction of the reaction materials. Invariably, the temperature rose somewhat upon introduction of methylvinylcarbinol and air because of the highly exothermic nature of the reaction. No provision was made for removal of the heat of reaction in order to maintain a constant temperature.

Table XIV

Production of Methyl Vinyl Ketone (MVK) from Methylvinylcarbinol Using Zinc Oxide Mixed with Copper Oxide or Copper

36 grams of methylvinylcarbinol used in each run				
Catalyst	Temp., °C.	Air flow, ml. per min.	Time for Run, minutes	MVK %
CuO(22) ZnO(100)	390	650	60	46
CuO(22) ZnO(100)	300	620	60	59
CuO(30) ZnO(100)	300	500	60	63
CuO(30) ZnO(100)	250	600	60	trace
CuO(30) ZnO(100)*	300	600	60	61
CuO(30) ZnO(100)*	300	300	60	62
CuO(30) ZnO(100)*	300	0	60	23
CuO(40) ZnO(100)	325	500	80	49
CuO(40) ZnO(100)	300	600	60	60
CuO(40) ZnO(100)	250	600	60	6
CuO(40) ZnO(100)	300	500	80	58
Cu_2O(10) ZnO(100)	300	600	60	trace
Cu_2O(10) ZnO(100)	250	600	60	trace
Cu_2O(20) ZnO(100)	400	500	60	25
Cu_2O(20) ZnO(100)	380	650	60	46
Cu_2O(20) ZnO(100)	300	620	60	53
Cu_2O(20) ZnO(100)	250	600	60	61
Cu_2O(20) ZnO(100)	250	500	85	66
Cu_2O(20) ZnO(100)	250	500	85	61
Cu_2O(30) ZnO(100)	300	600	60	50
Cu_2O(30) ZnO(100)	250	600	60	51
Cu_2O(30) ZnO(100)	200	600	60	51
Cu_2O(40) ZnO(100)	250	600	60	46
Cu_2O(40) ZnO(100)	200	600	60	55
Cu[a](30) ZnO(100)	275	600	60	37
CuO (Wire)	300	500	80	0
CuO (Wire)	250	500	80	0
ZnO	300	500	80	0
ZnO	250	500	80	0

* Effect of varying quantity of air.

[a] Copper made previously by decomposing copper formate in the presence of potassium formate and formic acid.

The above results indicate that methyl vinyl ketone can be prepared in rather high yields from methylvinylcarbinol by catalytic oxidation. The product obtained was relatively pure, and after drying over anhydrous sodium sulfate, the reaction product boiled from approximately 77° C. to 82° C. and had a refractive index of about 1.407 at 23° C. The boiling point of pure methyl vinyl ketone is 80° C., and the refractive index at 20° C. is 1.4086. The refractive index value indicates that the product was not contaminated with methyl ethyl ketone to any great extent, since methyl ethyl ketone has a refractive index of 1.3807 at 16° C.

The results further indicate that there is little difference between cuprous oxide and cupric oxide for this reaction. The cuprous oxide is active at a slightly lower temperature, but produces yields approximately the same as the cupric oxide. Copper itself is not quite as active as the oxides of copper.

In general, with the various catalysts the yields increased as the temperature was reduced. Higher temperatures gave equally pure methyl vinyl ketone, but losses due to complete combustion to carbon dioxide and water were considerably greater. Almost all the carbinol which was not oxidized completely to carbon dioxide and water was oxidized to methyl vinyl ketone.

The ratio of cuprous or cupric oxide to zinc oxide is not critical. Varying the amounts of copper oxide between 20 and 40 grams per 100 grams of zinc oxide failed to affect the yields appreciably. However, when the amount of cuprous oxide was reduced to 10 grams per 100 grams of zinc oxide, the yields were reduced practically to zero. Increased amounts of either cuprous or cupric oxide rendered the catalyst active at lower temperatures, and the cuprous oxide was active at a slightly lower temperature than the cupric oxide.

The runs marked in the table by * demonstrate that air is necessary for this conversion. The run made with 600 ml. of air per minute--or slightly more than the theoretical quantity needed to effect the oxidation --produced a yield of 61 per cent. The next run, with 300 ml. of air per minute, produced a yield of 62 per cent. This yield was produced at the expense of the catalyst, however, and the cupric oxide was reduced to the cuprous state. The run made in the absence of air produced only 23 per cent methyl vinyl ketone, again at the expense of the catalyst. Moreover, the methyl vinyl ketone was contaminated with methyl ethyl ketone, the refractive index being in the neighborhood of 1.394.

The runs using zinc oxide and cupric oxide alone indicate that the individual components of the catalyst are not active. Only upon combining the zinc oxide and the copper oxide is catalytic activity shown.

Several runs were made using various catalysts, most of which were prepared by the paste method. Some were variations of the catalysts used in the previous runs and others were entirely different. The results follow in Table XV.

Table XV

Production of Methyl Vinyl Ketone from Methylvinylcarbinol Using Various Catalysts

36 grams of methylvinylcarbinol used in each run

Catalyst	Temp., °C.	Time, min.	Air flow, ml. per min.	MVK %
CuO(30) $Ca(OH)_2$(65)	300	75	600	28
CuO(22) C(0.75) ZnO(75)	300	65	600	57
CuO(22) C(0.75) ZnO(75)	300	65	600	58
CuO(30) MoO_3(5) ZnO(100)	300	60	600	trace
CuO(30) MoO_3(5) ZnO(100)	250	60	600	trace
MnO_2(25) ZnO(100)	300	60	600	trace
V_2O_5[a](14) ZnO(100)	300	65	600	trace
V_2O_5[b](14) ZnO(100)	300	65	600	trace
Brass	300	60	600	trace

[a] V_2O_5 made by decomposing ammonium metavanadate at 300° C. in the presence of air.

[b] Catalyst treated with Na_2CO_3 solution.

The catalysts composed of cupric oxide, zinc oxide and carbon acted very similarly to catalysts composed of zinc oxide and cupric oxide alone. It had been noticed that there was less smoke in the exit gasses--indicating less decomposition--toward the latter part of the run, when the cupric oxide-zinc oxide catalysts were used. It was thought that the carbon which deposited on the catalyst was causing the decrease in decomposition. Addition of carbon to the catalyst before a run had little effect on the yield, however.

The molybdic oxide was added in the hope that it would act as a promoter for the cupric oxide. Actually, it inhibited the action of the cupric oxide. Molybdic oxide is probably a poor choice of promoter for the reason that it has considerable tendency to dehydrate alcohols.

Brass has been used by other investigators for the catalytic oxidation of various alcohols and was investigated for that reason. It showed little catalytic activity in the temperature range at which the cupric oxide-zinc oxide catalysts performed most capably.

Vanadium pentoxide has been highly recommended as an oxidation catalyst. In the catalytic oxidation of methylvinylcarbinol, however, it was ineffective. Again, the tendency was toward dehydration rather than oxidation. In order to reduce the dehydration, the catalyst was treated with sodium carbonate solution, which is stated by Taylor (1926) to be a dehydration inhibitor. Yields were not improved by this treatment.

Manganese dioxide has activity for certain catalytic oxidations, but produced no more than trace amounts of methyl vinyl ketone from methylvinylcarbinol under the conditions at which the zinc oxide-copper oxide catalysts were decidedly active. The physical characteristics of the copper oxide-zinc oxide catalysts as well as their activity at low temperatures indicate that these catalysts should find increasing use for catalytic oxidations.

Methyl vinyl ketone from acetylmethylcarbinol.

A few runs were made in an attempt to dehydrate acetylmethylcarbinol to methyl vinyl ketone. Sodium bisulfate has been stated to effect this dehydration, but no other catalyst has been reported as effective.

Table XVI lists the runs for which quantitative data on the yields of methyl vinyl ketone were secured. In addition, several runs were made in which W_2O_5 was employed as catalyst. No quantitative data were secured, because the analytical procedure had not been developed as yet. In general, the runs made using W_2O_5 as catalyst produced materials which boiled in the range of 75° C. to 85° C. but did not possess the characteristic piquant odor of methyl vinyl ketone. It is now believed that the material was a mixture which included among its components methyl ethyl ketone and diacetyl. The diacetyl was produced by oxidation of the acetylmethylcarbinol at the expense of the W_2O_5 which was reduced to WO_2.

Table XVI

Methyl Vinyl Ketone from Acetylmethylcarbinol

29 grams of acetylmethylcarbinol used in each run				
Catalyst	Temp., °C.	Time, min.	mls. N_2 per min.	MVK %
$AlPO_4$(20) Silica(40) Al_2O_3(40)	350	45	0	0
H_2WO_4(30) NaH_2PO_4(30) Al_2O_3(60)	320	50	180	0
$NaHSO_4$(60) Al_2O_3(60) Silica(60)	315	50	160	0
NaH_2PO_4(20) P(5) Pumice(100)	375	46	150	13

The sodium phosphate-phosphorus-pumice catalyst was the only catalyst effective for the reaction. The sodium bisulfate showed no promise whatsoever. The bisulfate was reduced to hydrogen sulfide, which could be detected in the exit gases by means of lead acetate paper. Rather copious evolution of hydrogen sulfide was observed. The tungstic acid was also reduced, largely to the blue oxide of tungsten. Evidently acetylmethylcarbinol is so easily oxidizable at 300° C. and above that many of the common oxides used in catalysts are reduced in its presence. Phosphate catalysts are most suitable from this viewpoint, and in addition the catalyst gave an encouraging yield of methyl vinyl ketone.

Diacetyl

Production of diacetyl from 2,3-butylene glycol.

Dehydrogenation. Upon direct dehydrogenation, 2,3-butylene glycol would yield diacetyl. For some reason, glycols dehydrogenate with difficulty however, and poor yields of diketones are produced. Several runs were made in an attempt to produce diacetyl from 2,3-butylene glycol by dehydrogenation, but poor results were obtained. The catalysts investigated required high temperatures before they became active. Much decomposition of glycol resulted, and most of the starting material was lost. Table XVII lists the runs made with the object of direct dehydrogenation of 2,3-butylene glycol. All analyses of yields of diacetyl were made by the polarographic method.

Table XVII

Dehydrogenation of 2,3-Butylene Glycol

22.5 grams of 2,3-butylene glycol used in each run				
Catalyst	Method of Preparation	Temp., °C.	Time, min.	Diacetyl %
$Cu_2O(20)$ $ZnO(100)$	paste	325	35	5
$Cu_2O(20)$ $ZnO(100)$	paste	400	35	0
ZnO	paste	325	50	2
ZnO	paste	400	50	2
$Fe_2O_3(20)$ $ZnO(100)$	paste	325	65	0
$Fe_2O_3(20)$ $ZnO(100)$	paste	400	65	0
Cu	reduction[a]	325	40	0
Cu	reduction[a]	400	40	0
Ni on charcoal	deposition	250	30	0
Ni on charcoal	deposition	350	30	0
Ni on charcoal	deposition	450	30	0
Zn on charcoal	deposition	325	60	0
Zn on charcoal	deposition	400	50	0
CuO, CeO_2 on charcoal	deposition	300	60	0
CuO, CeO_2 on charcoal	deposition	375	60	0

[a] Reduction of CuO wire with H_2 at 350° C.

Direct dehydrogenation of 2,3-butylene glycol is not feasible on the basis of these results. In some cases methyl ethyl ketone was produced in high yields. This was especially true in the case of the metals deposited on charcoal. Copper on charcoal is reputedly a dehydration catalyst, and evidently other elements which usually act as dehydrogenation catalysts will act as dehydration catalysts when placed on a carbon carrier.

The metallic copper was without action at 325° C. and left considerable unchanged glycol at 400° C. The zinc oxide-cuprous oxide catalyst produced low boiling materials but only small amounts of diacetyl. Zinc oxide alone showed slight activity. The fundamental difficulties seemed to be dehydration of the glycol in the case of the paste catalysts, and decomposition and dehydration of the glycol in the case of the other catalysts.

Catalytic oxidation. Results of runs employing catalytic oxidation rather than dehydrogenation were considerably more encouraging. The catalysts which exhibited activity were active at considerably lower temperatures and produced higher yields in catalytic oxidation than in dehydrogenation reactions. There is a possibility that the equilibrium is very unfavorable to the formation of diacetyl in the case of catalytic dehydrogenation. The equilibrium would be more favorable in the case of catalytic oxidation because of the removal of hydrogen after its formation from the glycol.

Results of various runs employing zinc oxide with copper oxide as catalysts are listed in Table XVIII.

Table XVIII

Catalytic Oxidation of 2,3-Butylene Glycol to Diacetyl Using Zinc Oxide-Copper Oxide Catalysts

22.5 grams 2,3-butylene glycol used in each run

Catalyst	Method of Preparation	Temp., °C.	Time, min.	Air flow, ml. per min.	% Diacetyl
Cu_2O(15) ZnO(100)	paste	260	30	400	26
Cu_2O(15) ZnO(100)	paste	330	30	400	29
Cu_2O(20) ZnO(100)	paste	260	30	400	40
Cu_2O(20) ZnO(100)	paste	260	30	850	37
Cu_2O(20) ZnO(100)	paste	300	30	890	37
Cu_2O(20) ZnO(100)	paste	325	30	400	33
Cu_2O(20) ZnO(100)	paste	375	30	400	18
Cu_2O(30) ZnO(100)	paste	275	45	400	34
Cu_2O(30) ZnO(100)	paste	360	35	400	0
CuO(16) ZnO(100)	paste	275	30	430	33
CuO(34) ZnO(100)	paste	265	30	800	17
CuO(34) ZnO(100)	paste	325	30	800	11
CuO(40) ZnO(100)	paste	350	20	850	13

The data indicate again that catalysts composed of zinc oxide and oxides of copper have decided advantages for the catalytic oxidation of alcohols. The cuprous oxide was slightly more effective than the cupric oxide and was most effective at lower temperatures. The most favorable temperature was about 270° C. which is the temperature reported by McAllister and de Simo (1936) as being most favorable for the catalytic oxidation of 2,3-butylene glycol. The patent of McAllister and de Simo states that higher yields of diacetyl are produced when oxygen is added to the amount of not more than one mol per two carbinol groups. The data in Table XVIII indicate that oxygen to the extent of only one half mol per two carbinol groups is as effective as one mol of oxygen per two carbinol groups. Air flow of 400 ml. per minute corresponds to one half mol of oxygen per two carbinol groups when the time for a run is 30 minutes. The yields using 400 ml. of air per minute were as high as yields obtained when using 800 ml. of air per minute.

The patent of McAllister and de Simo claims that acetylmethylcarbinol is also formed in this reaction. Various attempts were made to isolate this compound but failed. It may be that the acetylmethylcarbinol formed constant boiling mixtures with other materials present. In any case, distillation failed to yield any material which might indicate appreciable yields of acetylmethylcarbinol.

Other catalysts were investigated for the purpose of attempting to duplicate results claimed in the patent of McAllister and de Simo and to find a more efficient catalyst. The results are listed in Table XIX.

Table XIX

Catalytic Oxidation of 2,3-Butylene Glycol to Diacetyl

22.5 grams of 2,3-butylene glycol used in each run

Catalyst	Method of Preparation	Temp., °C.	Time, min.	Air flow, ml. per min.	Diacetyl %
V_2O_5(14) ZnO(100)	paste & decomp.[a]	240	50	300	10
V_2O_5(14) ZnO(100)	paste & decomp.[a]	260	40	400	13
V_2O_5(14) ZnO(100)	paste & decomp.[a]	325	30	430	11
V_2O_5(14) ZnO(100)	paste & decomp.[a]	385	35	430	1
Cr_2O_3(30) ZnO(100)	paste	320	40	400	14
ZnO	paste	275	30	400	16
ZnO	paste	350	30	400	10
Cu on carbon	dep. & red.[b]	250	30	800	5
Cu on carbon	dep. & red.[b]	275	30	800	1
Cu on carbon	dep. & red.[b]	300	30	800	0
Cu on asbestos	dep. & red.[b]	325	30	400	1
Cu on asbestos	dep. & red.[b]	375	30	400	14
Cu on Zn	red.[c] & dep.	300	30	400	8.5
Cu on Al	dep. & red.[d]	300	30	400	5
Brass turnings		380	33	420	11
Cu	reduction[e]	300	30	800	14
Cu	reduction[e]	350	30	500	6.5
Cu	reduction[e]	400	30	800	trace
Cu	reduction[f]	300	30	400	15.5
Cu	reduction[f]	350	30	400	14

[a] Decomposition of ammonium metavanadate at 300° C. in presence of air.

[b] Deposition of cupric acetate by evaporation of a cupric acetate solution followed by reduction.

[c] Zinc pellets added to cupric acetate solution; zinc displaced copper from solution and the surface of the zinc was partially coated with copper.

[d] Aluminum pellets were ground with cupric acetate, which coated the pellets; the cupric acetate was then reduced with hydrogen at 300° C.

[e] Copper in wire form was coated with cupric acetate, which was subsequently reduced with hydrogen at 300° C.

[f] Copper turnings coated with $Cu(OH)_2$ which was subsequently reduced with hydrogen at 300° C.

Yields claimed by McAllister and de Simo (1936) were somewhat higher than realized in this investigation. For the copper catalyst which was made by the reduction of cupric oxide wire they claimed yields of about 45 per cent diacetyl and 38 per cent dimethyl ketol, or acetylmethylcarbinol. The copper catalysts used in this investigation produced yields no higher than 16 per cent, and no acetylmethylcarbinol was detected. The zinc oxide-cuprous oxide catalyst approached the copper catalyst used by McAllister and de Simo as regards yields of diacetyl, but yields of acetylmethylcarbinol were not appreciable.

The various copper catalysts were prepared in order to attempt to find a catalyst as active as McAllister and de Simo's material. In spite of the many different methods of preparation and in spite of the use of different carriers, the copper catalysts used in this investigation were not especially active. Furthermore, the patent claims that brass turnings are effective for the catalytic oxidation of polyhydric alcohols, but the brass turnings used in this investigation produced yields of only 11 per cent of theory. On the basis of data included in Tables XVIII and XIX, the zinc oxide-copper oxide catalysts are the most effective for the catalytic oxidation of 2,3-butylene glycol to diacetyl.

Diacetyl in resins.

The possibility of utilizing diacetyl in synthetic resins was investigated in a few exploratory experiments. Diacetyl was mixed with glyoxal (40 per cent solution) in equimolar quantities, and the pH was adjusted to 8.0 by means of sodium carbonate. The mixture was stirred vigorously and the temperature rose spontaneously to 35° C. After a time the mixture became homogeneous and was set aside for 24 hours. The condensation product was extracted from water by means of ether, which was subsequently removed by distillation. The residue in the distillation flask was very viscous. It was placed in an oven at 100° C. for 40 hours after which it had become solid and somewhat dark colored, although it had not carbonized. The solid was soluble in alcohol, producing a solution which was somewhat like varnish. Upon spreading the solution over a surface and allowing to dry, a glossy coating was produced. The material was somewhat soluble in water, however, and as such would not be suitable for varnish. However, esterification of the alcohol groups, present after condensation of the dialdehyde with the diketone, by such agents as phthalic anhydride would reduce the solubility and might yield a substance more suitable as a varnish. The material without modification was quite stable to heating and maintained a hard coating on metal heated to a temperature of 110° C.

The possibility of condensing formaldehyde with diacetyl was also investigated. Two hundred twenty five ml. of 40 per cent formaldehyde (3 mols) was mixed with 86 grams (1 mol) of diacetyl, and the pH was adjusted to 8.0 by means of sodium carbonate. The condensation was so rapid that the temperature rose to approximately 75° C. in spite of cooling the reaction flask with water, and a small amount of acid was added to decrease the rate of condensation. The mixture was allowed to stand overnight, and on the following day was extracted with ether. Removal of the ether left a viscous liquid. The liquid decomposed on maintaining at a temperature of 100° C. However, esterification of the alcoholic hydroxyl groups with phthalic anhydride produced a semi-solid product.

Methyl Acrylate

Methyl lactate to methyl acrylate polymer.

An attempt was made to prepare methyl acrylate from methyl lactate using a variation of the method which involves pyrolysis of the acetate of methyl lactate. In this work, the possibility of utilizing phosgene rather than acetic acid as the esterifying agent was investigated. While the results involving pyrolysis of the carbonate of 2,3-butylene glycol had not offered any encouragement it was considered that the difficulty in that particular pyrolysis was due to the fact that the glycol had formed a cyclic carbonate which was very stable to heating. Methyl lactate, on the other hand, could form no such cyclic carbonate and the carbonate of methyl lactate would probably be less stable to heat.

Twenty five grams of methyl lactate was mixed with an equal weight of phosgene and was placed in a dry ice bath overnight. No reaction occurred. The flask was attached to a reflux condenser maintained at -8° C. and the contents were heated to about 30° C. Phosgene not condensed in the reflux condenser was caught in a dry ice trap and returned to the reaction flask through a dropping funnel. Reaction took place at 30° C. and hydrogen chloride was evolved. The reaction mixture was maintained at 30° C. for several hours and was then heated to 100° C. for one hour. Very copious evolution of hydrogen chloride was observed during the latter period. Distillation yielded products boiling from 70° C. to 215° C. without any constant boiling point but with very definite assurance that reaction had taken place. A small residue which failed to distill turned solid upon cooling to room temperature.

A counter-current, phosgene-methyl lactate run was made to determine if the monomeric methyl acrylate could be isolated. The apparatus which had been used for the production of butylene glycol carbonate was also used for this run. The temperature was maintained at 70° C., the gaseous phosgene flow was maintained at 200 ml. per hour and the methyl lactate flow was maintained at 47.5 ml. per hour.

The product at the bottom of the furnace was colored a slightly brownish yellow. The product was refluxed for eight hours at 100° C. The gases evolved were bubbled through sodium hydroxide solution from which carbonates had been removed by addition of barium hydroxide. Gas was evolved at 100° C. continuously, and a precipitate formed in the sodium hydroxide solution. The precipitate was barium carbonate and upon treating the precipitate with acid, carbon dioxide was evolved.

The product was then heated to 150° C. under total reflux for 20 hours. At the end of this time, the mixture was subjected to distillation, and again the material distilled over a wide range. The residue was very viscous, somewhat darkened, and could not be distilled. It is thought that this material was a methyl acrylate polymer. The yield of this material was 40 per cent of theoretical.

Attempts to prepare monomeric methyl acrylate were unsuccessful. During the long heating periods, the monomer evidently polymerized. The extremely noxious vapors arising during the heating period made direct distillation without previous heating somewhat difficult. However, a distillation made immediately after the counter-current reaction failed to yield methyl acrylate, and the material boiled continuously through a range of almost 150° C. Redistillation of this material left a residue which could not be distilled. Very probably this residue again was methyl acrylate polymer, which had previously distilled as monomeric methyl acrylate at a temperature above that at which it normally distills because it had been formed from the chlorocarbonate at a temperature higher than its normal boiling point.

The polymer had some rather interesting properties. Preliminary tests indicated that it could be used as a baked enamel type resin. It was very adhesive and joined paper to paper very strongly and also acted as a binding agent for glass to glass. It had the disadvantage of becoming quite fluid at relatively low temperatures. However, hardness could be improved by addition of a small percentage of allyl acrylate, a procedure which is fairly common practice. The resin was impervious to water but was soluble in alcohol.

DISCUSSION

Butadiene

The possibility of direct dehydration of 2,3-butylene glycol to butadiene is seriously questioned on the basis of the experiments made during this investigation. The first obstacle is the ready formation of methyl ethyl ketone, probably by ketonization of an enol form. Once methyl ethyl ketone has been formed, there is little possibility of directly producing butadiene from that particular molecule. While methyl ethyl ketone has been used as a source of butadiene, the reactions involved are so numerous that the process loses practicability.

The second obstacle is suggested by the reported difficulty of dehydrating unsaturated alcohols, such as methylvinylcarbinol. This compound is very probably an intermediate in the formation of butadiene-1,3 from 2,3-butylene glycol, and Dumoulin (1926) stated that butadiene yields of only 35 per cent were produced by direct dehydration of methylvinylcarbinol, and the reaction was further complicated by rearrangement of the molecule. A few runs were made in order to check this statement and butadiene yields of about 50 per cent were realized. So it seems that a combination of circumstances renders the direct dehydration of 2,3-butylene glycol to butadiene-1,3 very difficult.

The indirect dehydration of 2,3-butylene glycol using the carbonate or the monomethyl derivative of the glycol was not encouraging. However, the production of the carbonate by the counter-current method may have considerable interest. The carbonate, which could be made quite cheaply, might find considerable application as a plasticizer for various resins, including nitrocellulose and cellulose acetate. The compound is high boiling, insoluble in water, very stable to light and heat, very faint in odor, colorless, and a good solvent for nitrocellulose and cellulose acetate, characteristics which are ideal for plasticizers. In addition, carbonates in general are less readily hydrolyzed than the ordinary type of ester, such as phthalate and acetate esters, both of which are used extensively as plasticizers. In this connection, the reaction product of glycerol and phosgene might be even more favorable, since it would probably be higher boiling than the glycol carbonate.

Methyl Vinyl Ketone

The polarographic method of analysis described in this investigation would be applicable in the analysis of many complex mixtures met in catalytic oxidation reactions. In particular, unsaturated aldehydes and ketones could be readily determined in the presence of the corresponding saturated compounds. Very possibly such mixtures might be analyzed also by spectrophotometric methods, but it is doubtful if the accuracy and ease of such a method would be comparable to the polarographic method.

The production of methyl vinyl ketone was very encouraging when using methylvinylcarbinol as a starting material. The fact that yields of 60 per cent and above were realized in spite of inability to remove the heat of reaction suggests that the yields might be excellent when industrial catalytic vapor phase oxidation apparatus, which is constructed so that a given temperature can be maintained, is used. The cupric oxide-zinc oxide catalyst is evidently an excellent one for this reaction. It was effective at a temperature of only 250° C. which is considerably lower than the temperature suggested by Groll and deJong (1936) for their copper catalyst. It is considered that catalysts which are effective at lower temperatures would give rise to less combustion to carbon dioxide and water and hence would produce higher yields of methyl vinyl ketone. Moreover, the zinc oxide-cupric oxide catalyst is very easily prepared and could be regenerated easily by merely powdering the catalyst, igniting to remove carbon, and reforming into proper shape by the "paste" method. However, it does have the disadvantage that the oxides are not good conductors of heat, and the problem of maintaining a given temperature in an industrial process would be more difficult than is the case with metallic catalysts, such as copper or silver.

The experiments on the production of methyl vinyl ketone from acetylmethylcarbinol and from 2,3-butylene glycol were not too successful. However, in the case of acetylmethylcarbinol, it is of interest to note the extreme ease of oxidation of the compound at high temperatures. This observation should merit the attention of future workers who may attempt the dehydration. Many catalysts commonly used in dehydrations are reduced by acetylmethylcarbinol at high temperature, and the choice of catalysts will be limited because of this fact. It is felt that the phosphate catalysts deserve more attention, should acetylmethylcarbinol become available in larger quantity.

Diacetyl

The production of diacetyl by catalytic oxidation of 2,3-butylene glycol may be of interest should diacetyl find more extensive use. The yields produced in this investigation were only 40 per cent of theoretical on a single pass. The patent claims of McAllister and de Simo (1936) are approximately the same, but the patent in addition claims that acetylmethylcarbinol is produced along with the diacetyl and in approximately equal amounts. This claim, if confirmed, would indicate a cheap source of diacetyl, since acetylmethylcarbinol can be converted to diacetyl quite readily. One might have difficulty in purifying the product, since diacetyl forms constant boiling mixtures with most of the common organic solvents, but the actual production could probably be improved, until excellent yields were obtained.

The resins produced using condensation products of diacetyl and aldehydes would be very interesting from a chemical viewpoint, although commercially they might not be feasible at this time. The resins of dialdehydes and diacetyl would contain two hydroxy groups and two keto groups for each molecule of diacetyl and dialdehyde condensed. The possibilities of modification of this resin would be tremendous. Either by esterification of the hydroxyl groups or by conversion of the keto groups, one might produce many interesting and useful resins.

Acrylates

The conversion of methyl lactate to a polymer of methyl acrylate by use of phosgene deserves further investigation. The use of phosgene for any chemical reaction has some very obvious disadvantages, first, the toxic nature of phosgene, and secondly, the loss of phosgene as reaction products. Another disadvantage is the inability to obtain the monomer so that the control of polymerization is not as complete as desirable. However, this disadvantage might be overcome. On the other hand, the use of phosgene has certain advantages over the method employing methyl-α-acetoxypropionate. The pyrolysis products, when phosgene is used, are hydrogen chloride and carbon dioxide, neither of which is corrosive at high temperature, if dry. This is in contrast to the pyrolysis of acetoxypropionate which gives rise to acetic acid, which is highly corrosive at high temperatures. Moreover, the temperature of pyrolysis is evidently much lower when phosgene is used.

Another possible synthesis of acrylic acid and its derivatives is suggested by the success encountered in the catalytic oxidation of methylvinylcarbinol. By catalytic oxidation of allyl alcohol, a chemical which probably will be relatively inexpensive, acrolein and/or acrylic acid should be produced. Very possibly acrylic acid might be prepared cheaply enough by this process to compete with acrylic acid made by customary methods.

Future Utilization of Fermentation Products in Elastomers and Plastics

It is difficult to predict the future of fermentation products in the elastomer industry. The uncertainty regarding the position of the elastomer industry itself after the war renders the position of the sources of raw materials for that industry uncertain. However, there is every reason to feel that the alcohol industry will supply a generous portion of the raw material for butadiene at the close of the war. The ability of the butylene glycol diacetate process for preparing butadiene to compete with the alcohol process is questionable.

Lactic acid will very probably enter into the elastomer and resins field more extensively. Its conversion to acrylates has been thoroughly investigated, and it has been used to modify glyptal type resins, in which case it esterifies the polyhydric alcohol without changing the number of hydroxyl groups present.

Butyric acid has been used extensively in cellulose acetate butyrate plastics, which are displacing cellulose acetate plastics in many instances. Undoubtedly with increased demands, the fermentation industry will exploit the butyric acid fermentation.

The polyvinyl butyrals, used in safety glass and as a bonding resin, may utilize another fermentation product, butyl alcohol. The butyl alcohol from the butyl-acetonic fermentation could be converted to butyraldehyde quite readily, and subsequent reaction with polyvinyl alcohol would yield the valuable polyvinyl butyral. In addition butyl alcohol is used extensively in the production of various butyl esters, including the phthalate and citrate esters, which are among the leading plasticizers.

In the alkyd type resins, fermentation products should find a considerable outlet. Polyhydric alcohols are not produced by fermentations to any great extent, although the glycerol fermentation has been studied extensively. On the other hand, citric acid with three carboxylic groups is an important fermentation product. This acid should be capable of forming three dimensional polymers with glycols, such as 2,3-butylene glycol. C. Pfizer and Company now sells fumaric acid within the price range necessary for a raw material for synthetic resins, and this unsaturated acid would produce three dimensional polymers with polyfunctional alcohols.

Plasticizers for synthetic rubber and resins may also prove to be an outlet for fermentation products. C. Pfizer and Company already advertises various citrates for use as plasticizers. It is felt that the carbonate of 2,3-butylene glycol might find application as a new plasticizer, perhaps for use with Buna N rubber which employs considerable quantities of plasticizers of the ester type.

With the great demand for the many and varied types of compounds used in elastomers and resins, the fermentation industry will undoubtedly continue to contribute chemicals needed in that field. More extensive research leading to the production of chemicals useful in the elastomer and resins field is necessary, if the use of fermentation products in this rapidly growing industry is to be expanded.

SUMMARY AND CONCLUSION

1. The direct dehydration of 2,3-butylene glycol to butadiene has been found to be very difficult, and yields of only 10 per cent or lower have been obtained.

2. The indirect dehydration of 2,3-butylene glycol involving the pyrolysis of the monomethyl derivative and the inner carbonate of 2,3-butylene glycol has proven unsuccessful. The production of the carbonate using the counter-current principle with phosgene has been shown to be entirely practical, and utilization of the carbonate as a new plasticizer has been suggested.

3. The polarographic method of analysis of methyl vinyl ketone and diacetyl in mixtures has been developed and shown to be a very quick, accurate method of analysis.

4. Methyl vinyl ketone has been produced in yields of 65 per cent of theoretical by catalytic oxidation of methylvinylcarbinol, and a new catalyst for catalytic oxidations, cupric oxide on zinc oxide, has been developed. 2,3-Butylene glycol has been converted to methyl vinyl ketone, but poor yields were realized. Acetylmethylcarbinol has also been converted to methyl vinyl ketone in rather poor yield. Attention has been called to the marked reducing ability of acetylmethylcarbinol at high temperature, and its consequent action on many of the usual dehydration catalysts including WO_3, W_2O_5, and $NaHSO_4$.

5. Diacetyl has been prepared by the catalytic oxidation of 2,3-butylene glycol in yields of 40 per cent. Diacetyl was used along with

glyoxal in the formation of a condensation type polymer containing hydroxyl groups and carbonyl groups. Various ways in which this polymer could be modified have been suggested.

6. Methyl lactate has been converted to a polymer of methyl acrylate by the action of phosgene and heat. The mechanism of this reaction has been discussed.

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