THE VAPOUR-PHASE DEHYDRATION
OF
BUTANEDIOLS

A Thesis

by

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Ph.D. Chemistry

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THE VAPOUR-PHASE DEHYDRATION OF BUTANEDIOLS

Activated Morden Bentonite has been investigated as a vapour-phase catalyst for the decomposition of three butanediols and butanediol-2,3 diacetate.

Butanediol-2,3 at low temperatures gave 85 per cent yields of butanone-2, with isobutyraldehyde and the isobutyral of butanediol-2,3 as by-products. At high temperatures, gaseous decomposition occurred producing small yields of butadiene increasing to 14.9 per cent in the presence of water vapour.

Butanediol-2,3 diacetate gave chiefly acetic acid, butanone-2, and butadiene. Highest yields (57.5 per cent) of the diene were obtained at low temperatures and at fast feed-rates.

Butanediol-1,4 at low temperatures gave practically theoretical yields of tetrahydrofuran. At high temperatures, propene, butene and formaldehyde were formed with a small amount of n-butyraldehyde and condensation products.

Butanediol-1,3 gave butadiene (maximum yield 28.8 per cent), propene and butene. Increase in temperature and dilution with water increased gaseous decomposition but decreased the butadiene content of the gas. n-Butyraldehyde, 1-butenol-4, n-butyral of butanediol-1,3 and formaldehyde were also formed.

GENERAL INTRODUCTION

High-temperature, vapour-phase catalysis is a new field in organic chemistry. Pyrogenic reactions had received considerable attention before it was realized that factors other than temperature must be considered. It was not until 1900 that Ipatieff was definitely able to show that, at high temperatures, a catalyst could influence the course of a decomposition and force the reaction to go in one direction. It soon became evident that catalysis could be used for the industrial synthesis of numerous organic materials and rapid advances were made. Today, many chemical processes and industries are based on the use of catalysts under conditions of high temperature. The cracking of high boiling petroleum components has been developed into an exact science. Polymerization and isomerization of hydrocarbons are important industrial processes. The production of olefins, alcohols, ketones, aldehydes, esters and a variety of other types of organic compounds are produced by vapour-phase catalytic reactions.

The dehydration of alcohols to olefins received early investigation. Catalysts such as activated alumina, clay-like substances, phosphoric acid, phosphoric anhydride, and the metal phosphates proved to be particularly efficient.

It soon became evident that dihydric alcohols (glycols) could also be used as a fruitful source for the production of organic materials. In the case of these compounds, it was found that the removal of one molecule of water resulted in the formation of cyclic oxides, aldehydes, ketones or mixtures of the same. Moreover, the removal of two molecules of water resulted in the formation of diene hydrocarbons. The nature of the products obtained was dependent not only upon temperature but also upon the catalyst used.

The isomeric butanediols (butylene glycols) proved to be of particular interest. Since these compounds contain four carbon atoms, the mono-dehydration products include the ketone, butanone-2 (methyl ethyl ketone), and the aldehydes n- and iso- butyraldehyde. The cyclic oxide, obtained only in the case of butanediol-1,4 (1,4-butylene glycol), is tetrahydrofuran. Butanone-2 and tetrahydrofuran are of great practical importance because of their excellent solvent properties. Butanone-2 is used in place of acetone where a less volatile solvent is required. Tetrahydrofuran is useful in the refining of hydrocarbon oils and also as a solvent for lacquers and varnishes. The removal of two molecules of water from the straight-chained butanediols results in the formation of the diolefin, butadiene. The importance of the latter product requires little comment.

The fall of the Malay Peninsula, resulting in the loss of almost our entire source of natural rubber, initiated the present synthetic rubber program. It was decided, at an early stage, to concentrate on the production of GR-S (Buna S), a copolymer of butadiene and styrene. This initiated, in its turn, an exhaustive investigation of all possible methods, both new and old, for the production of butadiene (1). One of the first methods considered was the direct dehydration of butanediol-2,3 (2,3-butylene glycol). This compound can be obtained in good yields from grain by a special fermentation process.

The investigation, described in this thesis, began with a study of the dehydration of this glycol to butadiene by a high-temperature catalytic method. It soon became evident, however, that the direct dehydration of butanediol-2,3 (2,3-butylene glycol) would not give practical yields of the diolefin. The work was then extended to a study of the decomposition of the corresponding diacetate and further to the dehydration of butanediol-1,3 (1,3-butylene glycol) and of butanediol-1,4 (1,4-butylene glycol). The investigation was begun at the instigation of the National Research Council of Canada and carried on in close cooperation with the Division of Applied Biology.

Investigation was not restricted, however, to the production of butadiene from these compounds. The mono-dehydration of the glycols, in particular the dehydration of butanediol-2,3 to butanone-2, and of butanediol-1,4 to tetrahydrofuran, was also studied. The theoretical implications involved in the decomposition of these compounds proved to be of considerable interest. Consequently, the work was extended so as to include a study of the actual mechanisms involved in the dehydration of the three glycols and the decomposition of the 2,3-butylene glycol diacetate.

The catalyst used throughout this investigation was activated Morden bentonite. This material is a Canadian clay mined at Morden, Manitoba, and can be obtained in considerable quantities at a relatively low cost. Morden bentonite as a vapour-phase catalyst has been investigated in this University by several workers (2,3,4). Wasson's work (3) on the dehydration of alcohols and ketones has shown this clay to be a particularly efficient dehydration catalyst, more efficient even than activated alumina. This fact, combined with the availability of the material, contributed to the choice of Morden bentonite as the catalyst in the present investigation.

HISTORICAL INTRODUCTION

Dehydration of Butanediols

The discovery in the last century that isoprene, on standing or under the influence of certain reagents, polymerizes into an artificial rubber (5) marked the beginning of synthetic rubber chemistry. It was soon found that other diolefinic hydrocarbons could be made to polymerize into rubber-like masses, and numerous synthetic methods for these compounds were investigated. One of the earliest processes was developed by Matthews, Strange and Bliss in 1912 (6), and consisted of the dehydration of primary, secondary or primary-secondary glycols to butadiene and its homologues. This was followed by extensive research on the conversion of glycols to diolefinic hydrocarbons.

Although the dehydration of α-glycols to aldehydes and ketones has been subject to much theoretical investigation, it has only been in recent years that glycols in general have been considered as a practical source for carbonyl compounds. Comparatively little investigation has been carried out on this process, however, and the method has not been able to compete with other processes for the synthesis of these materials. The formation of cyclic oxides, which occurs in the dehydration of glycols, in which the hydroxyl groups are separated by four or more carbon atoms, has also only recently received consideration.

In the following pages, a comprehensive survey will be given of the previous work on the dehydration and decomposition of butanediol-2,3 and its diacetate, butanediol-1,4 and butanediol-1,3. In general, only the high-temperature catalytic studies will be reviewed. However, when of particular interest, certain liquid-phase dehydrations will also be mentioned.

Butanediol-2,3 and its Diacetate

Of the three butanediols (butylene glycols), butanediol-2,3 has received the least attention. Previous to the present synthetic rubber program, studies on butanediol-2,3, for the most part, had been restricted to mono-dehydration. Several attempts to produce butadiene from this compound have been reported, but in all cases, only mono-dehydration products were obtained.

The dehydration of the 2,3-glycol to methyl ethyl ketone was first reported by Krassoutsky (7) in 1903 during an investigation of the dehydration of α-glycols and the isomerization of substituted ethylene oxides to aldehydes and ketones.

Gutner and Tischtschenko (8), in an attempt to determine the mechanism of the conversion of 2,3-dichlorobutane to butadiene over various catalysts in the presence of steam, studied the behaviour of 2,3-butylene glycol under the same conditions. They obtained mainly methyl ethyl ketone as well as a little butadiene.

Langedijk (9), in a review article on methyl ethyl ketone published in 1938, listed the dehydration of butanediol-2,3 as one of the methods for the production of this ketone. Details of the process, or literature references, were not given, however. Recently a process has been patented (10) describing the liquid-phase dehydration of glycols to aldehydes and ketones. The conversion of butanediol-2,3 to methyl ethyl ketone is given as an example.

Recently, Akabori (11) has investigated the mono-dehydration of the 2,3-glycol in the presence of twenty-five per cent sulphuric acid and obtained an aldehyde, isobutyraldehye, in addition to the expected product, methyl ethyl ketone. The mechanism of these changes will be discussed later.

Denivelle (12) carried out the dehydration of butanediol-2,3 with a variety of catalysts, including sulphuric acid, phosphoric acid, phosphoric anhydride, basic oxides, and zinc chloride, in an attempt to produce butadiene. In all cases methyl ethyl ketone only was obtained.

At the onset of the present synthetic rubber program, efforts to obtain butadiene directly from the butanediol-2,3 were renewed. The glycol could now be obtained very cheaply from grain (13) and consequently was a most desirable starting material. This investigation was conducted in the United States by the Northern Regional Research Laboratories at Peoria, Ill., and by Joseph E. Seagram & Sons Inc., Louisville, Ky. The work in this University was carried on concurrently. A report from the Northern Regional Laboratories (14) disclosed that seventy catalysts in all had been studied in the course of their research on the direct dehydration of the glycol. One-pass yields of butadiene seldom reached more than twenty per cent, the main product being methyl ethyl ketone, with methyl vinyl carbinol and butylene oxide as possible by-products. These laboratories then turned their attention to the decomposition of butanediol-2,3 diacetate to butadiene.

The conversion of the diacetate of the glycol to butadiene was first reported in a British patent granted in 1938 (15). The process consisted of the passage of the diacetate of butanediol-2,3 over quartz chips or unglazed earthenware rings, contained in a quartz tube, at a temperature of 500-550°C. A 90 per cent yield of butadiene was claimed using a recirculating process.

Denivelle (12) studied the decomposition of the diacetate over kaolin at temperatures ranging from 350-575°C. Good yields of butadiene were obtained at the higher temperatures. (Actual percentages were not given). Over quick lime, however, he found that the diacetate decomposed to methyl ethyl ketone and 2,3-butylene oxide.

The Northern Regional Laboratories (14) investigated the straight pyrolysis of the diacetate of butanediol-2,3 quite thoroughly. They determined the optimum conditions of the decomposition and were able to obtain 80 per cent conversions to butadiene at 550°C. and at feed rates of 15 gramsper minute. Liquid products consisted of acetic acid and unsaturated esters, including the acetate of methyl vinyl carbinol and the enol acetate of methyl ethyl ketone. A repass of the liquid products increased the yield to 83 per cent, while a repass of the isolated esters gave a total yield of 88 per cent.

The research of the Joseph E. Seagram Laboratories confirmed these results (16). They reported a 55-65 per cent yield of butadiene, increased to 75 per cent on recycling, using a one and one-half inch unpacked stainless steel pipe, at a temperature of 600°C., and feed rates of one-half pound per hour per foot. Using an all glass apparatus, 75 per cent yields were obtained, increased to 80 per cent on recycling.

Butanediol-1,4

The butanediol-1,4 was the last of the three butylene glycols to receive consideration as a practical source for the production of organic materials. This was primarily due to the fact that, up until recent years, this compound could not be obtained readily enough to justify its use as an intermediate in organic synthesis. Two methods of preparation, recently patented, have brought the glycol into the class of available materials. The first (17) consists of the high-pressure catalytic hydrogenation of the esters of succinic acid, as for example, butyl succinate. The second process (18), of even greater importance, involves the hydrogenation of 1,4-dihydroxybutyne-2 under conditions of high pressure over a variety of catalysts. The latter compound can be obtained easily by causing acetylene and formaldehyde to react in the liquid phase, under a pressure of twenty-five atmospheres, and in the presence of acetylenic compounds of the heavy metals in Groups I and II of the Periodic System.

This glycol has been studied in respect to both its mono-dehydration and di-dehydration products. With 1,4-glycols, however, it has been found that the mono-dehydration products are not carbonyl compounds but cyclic oxides; the butanediol-1,4 thus yielding tetrahydrofuran. The di-dehydration product is, as expected, butadiene.

Considerable work has been done on the liquid-phase dehydration of butanediol-1,4 to tetrahydrofuran. One method involves the heating of a mixture of the glycol and catalyst to such a temperature that a mixture of tetrahydrofuran and water distills off. By refluxing the glycol with thirty-two per cent sulphuric acid for two hours and distilling, Hurd (19) obtained a seventy-six per cent yield of tetrahydrofuran. Other liquid catalysts, which have been investigated, are thionyl chloride (20), and oxygenated acids of phosphorus, such as otho-, meta-, and pyro-phosphoric acid (21). Numerous solid catalysts have also been used. Patents (22,23) have been granted for such solid catalysts as oxides of silicon (silica gel), aluminium, zinc and thorium; sulfates of aluminium and copper; neutral phosphates of aluminium, iron, cerium and silver; chlorides of aluminium, magnesium, calcium and zinc; silicates of aluminium (bleaching earths), as well as solid organic acids.

The vapour-phase dehydration of butylene glycol is an excellent example of the influence of temperature and catalyst on the course of a reaction. Two very similar patents (24), describing the vapour-phase dehydration of the glycol to both tetrahydrofuran and butadiene, have been granted. For the sake of convenience, these will be considered together.

Tetrahydrofuran was obtained in almost theoretical yields at temperatures ranging from 200-350°C. with such catalysts as cuprous oxide, aluminium oxide and chromium oxide. At higher temperatures the formation of propylene and formaldehyde was favoured. Temperatures as high as 450°C. were used in the case of alkali and alkali earth metal salts, such as, calcium chloride, calcium carbonate, and aluminium phosphate, the most favourable temperature for tetrahydrofuran formation being from 400-450°C.

Acidic catalysts or catalysts which react acid under the conditions of the reaction, as for example, primary sodium pyrophosphate, calcium phosphate, and acidic oxides of tungsten and molybdenum, were also used for the production of tetrahydrofuran at temperatures below 350° C. At higher temperatures, however, the formation of butadiene was favoured, the optimum conditions for this product ranging from 300-400° C. and yields of 25-60 per cent were obtained. A later patent (25) describes a process whereby a 95 per cent yield of butadiene was obtained by passing 1,4-butylene glycol, together with steam, over calcium phosphate at 280° C., followed by recycling the tetrahydrofuran formed in the first pass.

It may be mentioned that tetrahydrofuran has also been dehydrated to butadiene (26). The catalysts employed were, in general, those which yield butadiene in the dehydration of butanediol-1,4. Yields ranging from 65-70 per cent were obtained.

Butanediol-1,3

Of the three butanediols, the 1,3-isomer has received the greatest amount of study. The glycol is readily obtained by the hydrogenation of acetaldol (27) which is prepared by a process involving either ethyl alcohol or acetylene as the starting material. Recently, the corresponding diacetate of this glycol has been obtained as a by-product in the production of ethyl acetate by the Tishchenko reaction (28). This may possibly be applied to the industrial production of 1,3-butanediol itself.

Patents (29) have been granted on the mono-dehydration of the 1,3-glycol to methyl ethyl ketone over catalysts comprising one or more of the heavy metals in Groups I and VIII of the Periodic System, with or without activating agents, and supported on carrier substances. However, it is by the di-dehydration to butadiene that butanediol-1,3 has attained its importance.

It is beyond the scope of this thesis to present a complete review of the literature on the production of butadiene from this glycol. Innumerable patents have been granted on this process, using a wide variety of catalysts under varying conditions. The following table adapted from a review article by Gamna and Inouye (30), with several additions, permits an adequate survey of this work.

TABLE I

Catalyst	Temp. °C.	% Yield	Reference
Aluminium oxide	300	19.4	31
Ferric oxide on kaolin in KOH	300	40.1	31
Sulphuric acid 1%	140-200	80	32
Calcium sulphate	350	24	31
Anhydrous iron sulphate	300-400	60	33
Sulphonic acids of aromatic hydrocarbons	180-240	78	34
Primary sodium phosphate	270	85-90	35
Sodium phosphate impreg. with 2% H_3PO_4 plus water vapour	270	85-90	36
Primary sodium phosphate with graphite	250	90	35
Anhydrous primary sodium phosphate, primary n-butylamine phosphate, and graphite	260	90	35,37
Sec-calcium phosphate, sec-ammonium phosphate, and graphite	320-330	90	35
Sec-calcium phosphate, ammonium oxalate, and primary ammonium phosphate	260	90	37
Acid phosphates such as KH_2PO_4, $Na_2H_2P_2O_7$, $Ca(H_2PO_4)_2$ with potassium or ammonium alum	200-300	80	38
Neutral pyro- and ortho-phosphates of magnesium and alkaline earth metals	400	90	35

TABLE I (cont'd)

Catalyst	Temp.° C.	% Yield	Reference
Acid bismuth ortho-phosphate with graphite	320-330	90	35
Acid cerium phosphate on pumice	320-330	90	35
Cerium phosphate and water vapour		90	39
Red phosphorus, 1.0% on pumice	300	99	40
Red phosphorus plus mono-sodium phosphate	250-300	98-99	40
Red phosphorus and potassium alum	270	98	40
Phosphorus pentoxide on kaolin	500	37	31
Phosphorus oxychloride 0.2%	300-350	85	41
Volatile derivatives of phosphorus as $POCl_3$, PCl_3, and tri-ethyl phosphate	300-350	90	42

The yields of butadiene may be increased considerably by recirculating the liquid products. Wellman (43) has patented a process whereby the liquid products are fractionated to yield a constant boiling mixture of 1-butenol-4 and water. Catalytic dehydration of this mixture increases the conversion to butadiene from 70 or 80 per cent to 90 or 95 per cent.

It is interesting to note the effect of water as a diluent in the dehydration of 1,3-butylene glycol. Several patents (44,45) have been taken out on this process. The results are summarized in the following table.

TABLE II

Catalyst	Temp.°C.	Parts of Butadiene per 100 parts of glycol		
		100% glycol	80% glycol	30% glycol
Activated alumina	300	27	33	65
Aluminium silicate	270-280	The yield is increased 30-35 per cent by addition of water.		
Red phosphorus on pumice	270-280	49	63	72.5
Phosphoric acid on pumice	290	55.3	60	65
Thorium nitrate	300	The yield is increased 30-35 per cent by addition of water.		

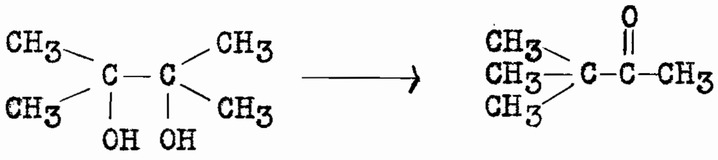
Theoretical Considerations on the Dehydration of Glycols

Dehydration of α-Glycols

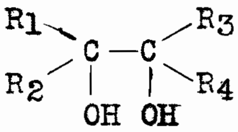
General Considerations

The dehydration of α-glycols to aldehydes and ketones is a classical example of molecular rearrangement in organic chemistry. Extensive studies have been made of the mechanism of the dehydration process itself, and also of the factors which influence the resulting rearrangement, in an effort to predict the nature of the carbonyl compounds obtained. It is beyond the scope of this thesis to attempt a complete survey of these investigations. An outline of the various theories that have been enunciated will be given, including the pertinent evidence that has been accumulated either in their favour or disfavour. It must be borne in mind, however, that almost all theoretical studies on α-glycols have been carried out in the liquid phase. Consequently, mechanisms which serve to explain these dehydrations do not necessarily hold for the same reactions carried out in the vapour state. Nevertheless, conclusions drawn concerning the mechanism of liquid-phase dehydrations may be of great value in a consideration of the vapour-phase reactions, which are the subject of this thesis.

In 1860, Fittig (46) observed that the glycol, pinacol, when heated with sulphuric acid, will undergo a rearrangement to form a ketone, pinacolone.

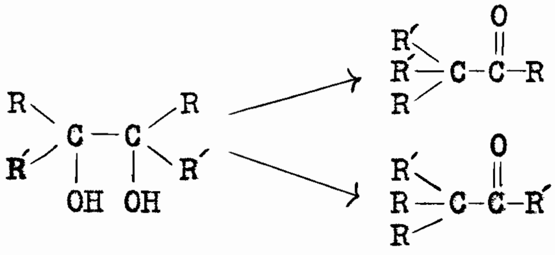


Since this discovery, numerous examples of the so-called pinacol-pinacolone rearrangement have been studied. Glycols of the general formula



in which R_1, R_2, R_3, and R_4 are hydrogen atoms, aliphatic or aromatic groups, have been prepared and made to undergo a dehydration reaction.

It can readily be seen, that in the case of symmetrical glycols of the type RR′(COH).(COH)RR′, two ketones may be obtained depending, apparently, upon what Tiffeneau (47) calls the relative "migration aptitude" of the groups R and R′, thus:



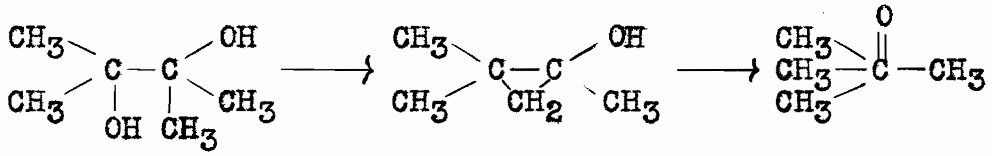
In the case of unsymmetrical glycols of the type RR(COH).C(OH)R′R′, the product on dehydration will depend upon which hydroxyl group is eliminated in the dehydration process. This in turn, will depend, apparently, upon what Meerwein (47,48) calls the relative "capacity affinity" of the radicles R and R'. The greater the "capacity affinity" of the radicles for the carbon atom to which they are bound, the smaller will be the affinity between that carbon atom and its attached hydroxyl group. Consequently, in the dehydration process, this hydroxyl radicle will be eliminated. For glycols of the type $R_1R_2C(OH).C(OH)R_3R_4$, the resulting products will depend on both the "affinity capacity" and the "migration aptitude" of the groups concerned.

Tiffeneau (49), McKenzie (50), Bachmann (51) and others have carried out extensive work on the relative "affinity capacity and "migration aptitude" of various radicles. An understanding of the dehydration process itself, however, is necessary in order to suggest a theoretical basis for the results of these investigations.

Mechanism of the Dehydration Process

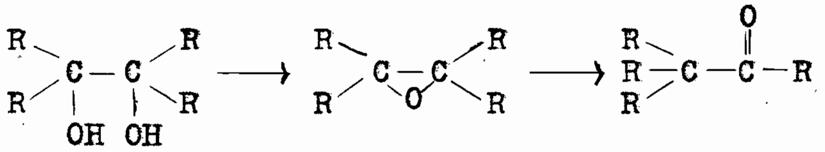
A careful examination of the many theories which have been proposed to explain the dehydration of α-glycols shows that they may be divided into two groups. The first type of theory assumes that some form of intermediate is involved in the reaction. This intermediate may be of such a type that, if the proper conditions could be realized, actual isolation would be possible. Postulated intermediates have been cyclopropane rings, cyclic ethers and olefinic compounds. On the other hand, the intermediate may take the form of a non-isolable free radicle, carbanion, or carbonium ion. The theories of the second type are based on an electronic mechanism which does not involve the formation of intermediates during the course of the reaction.

Intermediate compounds:- One of the earliest mechanisms was proposed by Erlenmeyer (52) in 1881. He assumed an intermediate cyclopropane ring to be formed in the first step of the reaction, followed by a rupture of the ring in a different position from which it was formed. For pinacol this may be expressed thus:



It was first shown by Montagne (53) and later by Acree (54), that such a mechanism was not in agreement with the results observed during the dehydration of aromatic glycols. Montagne studied the rearrangement of p, p′, p″, p‴-tetrachlorobenzpinacol into the corresponding ketone. The product contained only para chlorine while, according to the Erlenmeyer mechanism, the meta chlorine isomer should have been formed.

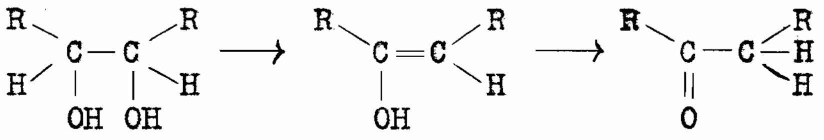
Breuer and Zincke (55) postulated in 1879 that an intermediate cyclic ether (oxide) is formed during the dehydration process. According to these workers, the reaction can be expressed as follows:



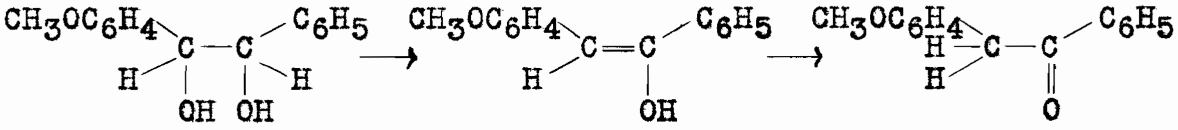
A considerable amount of evidence has been accumulated against this theory, however, and it has been generally discarded.

Eltekow (56) has shown that certain cyclic ethers are converted into glycols under conditions customary for pinacol rearrangement. Furthermore, Meerwein (57) has pointed out that very often oxides will not always lead to the same ketonic product as does the corresponding glycol. Meerburg (58) has concluded that ethylene oxides are not formed as intermediates by comparing the rates of rearrangement of certain glycols and their corresponding oxides. A comparison of the results, in the case of tetrachlorobenzpinacol and its oxide, show that for both compounds the reaction is of first order, and the rate of reaction is slower for the oxide.

An intermediate olefinic compound has been postulated by several workers in the case of primary-secondary, bi-secondary, and secondary-tertiary glycols. This mechanism, named by Tiffeneau (59) "vinyl dehydration", can be expressed as follows:



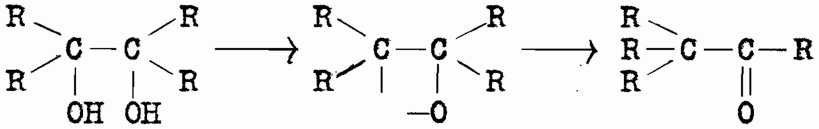
Tiffeneau (60) has presented very strong evidence for this intermediate based on the fact that the dehydration product from sym-anisylphenyl glycol is ketonic. Since the "migration aptitude" of aromatic groups has been shown to be greater than that of hydrogen (61), an aldehyde is the expected product. This discrepancy, he explains on the basis of vinyl dehydration in which the hydrogen of the hydroxyl group undergoes migration thus:



Although it has been shown that an olefinic mechanism does not hold for certain molecular rearrangements, direct evidence against this theory in the case of the dehydration of α-glycols is lacking. Apparently Wallis (62) assumes that the rearrangement of phenolic ethers to alkyl phenols and the rearrangement of N-alkylated anilines to alkyl anilines is comparable to the rearrangement of α-glycols, and uses evidence which is unfavourable to the olefinic mechanism in the former rearrangements (63,64) as evidence against a similiar mechanism in the latter rearrangement. We take exception to this view, however, and hold with Ingold (65) that an olefinic mechanism remains a possibility.

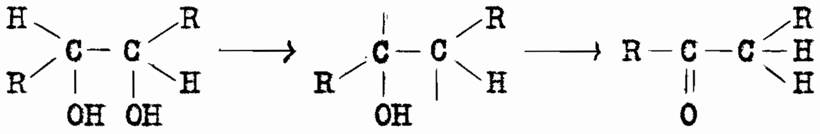
From this discussion, it would appear that little dependence can be placed on the hypothesis of intermediate compounds such as cyclopropane and ethylene oxide rings in the dehydration of glycols. It is possible that intermediate olefinic compounds (vinyl dehydration) may occur in the case of glycols containing at least one hydrogen atom attached to an hydroxyl-bearing carbon atom. This theory, however, can not be applied in the case of bi-tertiary glycols, and it would appear that one must search further in order to find an adequate explanation for these reactions.

Free radicles and ions as intermediates:- Tiffeneau (66) was the first to apply the concept of free valences to the pinacol rearrangement. He formulated the mechanism of dehydration in the following manner:



Meerwein (67) adopted the Tiffeneau concept of free valences and was able to show definitely that the elimination of water was the first step, followed by the migration of an R group. He postulated the same form of intermediate as Tiffeneau, and assumed that the rearrangement of this intermediate to product occurs at such a speed that the ethylene oxide has no chance to form. Both workers considered this rearrangement to be intramolecular, in contrast to an intermolecular rearrangement involving intermediate compounds.

In the Tiffeneau mechanism, the hydrogen atom, which unites with the eliminated hydroxyl group to form water, comes from the adjacent hydroxyl group. It is possible, however, for glycols in which one or more of the R radicles is hydrogen, that the elimination may occur between an hydroxyl group and a hydrogen attached to the adjacent carbon atom. For example:

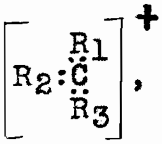
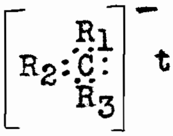


This is essentially a vinyl dehydration without the actual formation of an olefinic double bond.

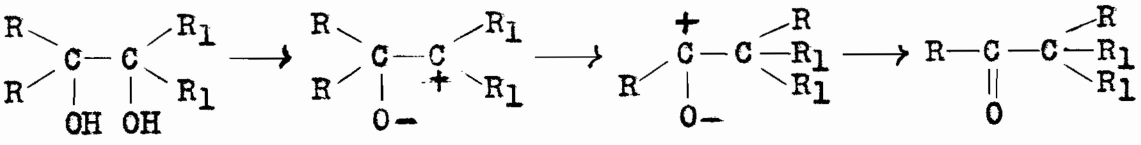
Molecules having free valences may be considered as either free radicles or ions. Very striking evidence against the intermediate formation of free radicles is found in the investigations of Wallis (68), who studied the rearrangement of a number of compounds in the presence of triphenylmethyl. This compound is known to unite with other free radicles to form addition products. Since in all cases the normal product was obtained, Wallis concluded that the rearrangement does not involve free radicles or that, if present, these radicles are never entirely free from the molecule.

The studies of McKenzie and others (69) on certain optically-active pinacols and amino glycols supply additional evidence against the formation of free radicles. These workers found that in many cases the optical activity was maintained during the dehydration process. If the asymmetric carbon atom were to exist at any time in the form of a free radicle, this would not be possible, since it has definitely been shown (70) that free radicles can not maintain an asymmetric configuration.

Caution must be exercised, however, in applying this evidence against free-radicle formation to the case of vapour-phase dehydrations. Although the conditions used in the present investigation for the dehydration of butanediol-2,3 to butanone-2 were extremely mild, free radicle intermediates might readily be involved.

The possibility of the migrating radicle assuming the form of a carbonium ion is also excluded by the previously mentioned studies on optically active glycols. An investigation by Wallis and Adams (70) has shown that carbonium ions  $\left[R_2:\overset{R_1}{\underset{R_3}{\overset{\cdot}{\underset{\cdot\cdot}{C}}}}\right]^{+}$, in the absence of a special mechanism leading to Walden inversion, are optically unstable. It is only when the radicle assumes the form of a carbanion  $\left[R_2:\overset{R_1}{\underset{R_3}{\overset{\cdot}{\underset{\cdot\cdot}{C}}}}:\right]^{-}$ that the spatial arrangement is stable enough to maintain its asymmetric configuration.

Haworth (71) has postulated the migration of such a carbanion in the pinacol rearrangement. He represents the course of the reaction as follows:



It is seen that the first step is the elimination of water leaving an open sextet on the carbon atom from which the hydroxyl group was removed. This is followed by the migration of an R ion with its electron pair.

Serious objection to this mechanism is found in the results of McKenzie, Roger and Wills (50). They found that certain optically-active glycols, in which the eliminated hydroxyl group is attached to the asymmetric carbon atom, retain their activity during the dehydration process. This would not be possible if this carbon atom were to exist at any time as an open sextet.

From the preceding discussion, it would seem that the hypothesis of an intermediate, either of a compound, free radicle, or ion, is inadequate in explaining the mechanism of the dehydration of α-glycols. Wallis (72) makes the following comment concerning this problem:

> "The failure of these interpretations as explanations of the mechanism of molecular rearrangement is due to the fact that the investigators who proposed them did not realize that such reactions are often dependent on the properties inherent in the molecules themselves, and for that reason can not take place in a step-by-step fashion, but must be continuous processes which involve simple displacements or transfer of electrons from one atom to another within the molecule."

<u>The electronic mechanism</u>:- The application of the electronic concept of valence to intramolecular rearrangement is due to Whitmore (73). According to him, the structure of organic molecules which undergo intramolecular rearrangement can be represented by the following formula:

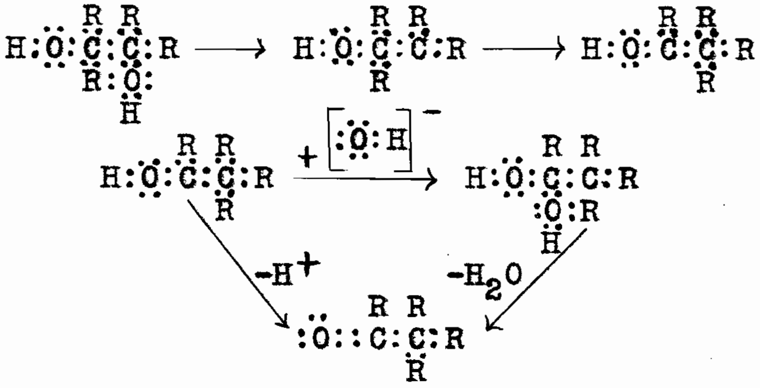
$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{A}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{B}}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:$$

in which X is a strongly electronegative atom, and A and B are neither electronegative or electropositive. In chemical reaction, X is eliminated together with its shared pair of electrons leaving the fragment $:\ddot{\underset{..}{A}}:\ddot{\underset{..}{B}}$. This fragment may stabilize itself by adding another negative ion Y to form the compound $:\ddot{\underset{..}{A}}:\ddot{\underset{..}{B}}:\ddot{\underset{..}{Y}}:$. On the other hand, if one of the groups attached to either A or B is hydrogen, the fragment may lose a proton to form an olefin. A third possibility must also be considered. If the fragment $:\ddot{\underset{..}{A}}:\ddot{\underset{..}{B}}$ is of such a nature that B has a greater affinity for electrons than A, an electron pair, together with its accompanying atom or group, may shift so as to leave A with an open sextet.

$$:\ddot{\underset{..}{A}}:\ddot{\underset{..}{B}} \longrightarrow \ddot{\underset{..}{A}}:\ddot{\underset{..}{B}}:$$

This will then be followed by the addition of the negative ion Y to form the rearrangement product YAB.

Applying this concept to the dehydration of α-glycols, Whitmore (73) explains the reaction in the following manner. The more reactive hydroxyl group is eliminated accompanied by its shared electrons, leaving an open sextet which is completed by the rearrangement of an R radicle. The rearranged fragment can then re-add the hydroxyl ion followed by the elimination of water, or it may stabilize itself by the loss of a proton, both processes leading to the final product. This mechanism may be expressed as follows:



It should be noted that this is not an ionic mechanism, in which the group R migrates as a carbanion. Whitmore (74) suggested that the half-life of the postulated fragment is in the vicinity of 10^{-7}sec., while the half-life of an ordinary ion is 10^{-4}sec. In fact, one can assume that the open sextet never does exist as such, but that the removal of the hydroxyl group with its electron pair and the rearrangement of the R radicle can occur simultaneously. This would explain why certain optically active glycols on rearrangement retain their activity.

This theory also forms a theoretical basis for the relative "affinity capacities" and "migration aptitudes" of various groups (75). In the case of unsymmetrical glycols of the type RRC(OH).C(OH)R'R', the hydroxyl group eliminated will be that to which is attached the more electronegative groups, since this hydroxyl will have negative polarity. Furthermore, in the case of symmetrical glycols of the type RR'C(OH).C(OH)RR', the more electronegative group will undergo migration, since the carbon atom to which it migrates tends to exist as an open sextet on elimination of an hydroxyl ion.

Again, it must be emphazied that these conclusions are based on liquid-phase reactions and can not with certainty be applied to those carried out in the vapour phase. However, Egloff, Hulla and Komarewsky (76), in a consideration of the mechanism involved in the vapour-phase isomerization of alkanes, make the following interesting suggestion:

> "The observed formation of over 50 per cent of isomers in several catalytic isomerizations of alkanes can not be overlooked, since such yields appear high for a statistical redistribution of fragments, including free radicles.
>
> Much more reasonable than this theory appears to be the one which postulates that under the influence of a powerful catalyst the interatomic bonds of the alkane are loosened sufficiently to allow a rearrangement of the molecule as a whole to a thermodynamically more stable form by the slippage of atoms or groups without their ever completely leaving the sphere of influence of the molecule as a whole."

This statement is essentially an extension of the Whitmore hypothesis to high-temperature catalytic reactions. The concept of the slippage of atoms or groups is extremely fruitful in consideration of rearrangement reactions carried out in the vapour phase.

Dehydration of β-Glycols

As far as the writer is aware, no theoretical studies have been made on the catalytic dehydration of β-glycols. Investigation for the most part has been restricted to the practical production of diolefins from butanediol-1,3 and its homologues. This reaction, it would appear, merely involves the elimination of two water molecules resulting in the formation of two double bonds. In the dehydration of butanediol-1,3 itself, the organic liquid products contain, for the most part, 1-butenol-4 (43). It can be assumed then, that the first step in the dehydration process is the elimination of the secondary hydroxyl group along with a hydrogen from the terminal carbon atom, followed by a further dehydration of the resulting unsaturated alcohol to form butadiene.

$$CH_3CHOHCH_2CH_2OH \longrightarrow CH_2{=}CHCH_2CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2$$

This is further substantiated by the fact that 1-butenol-4 will yield butadiene when passed over catalysts which dehydrate the glycol to the diene.

Nagai (31) has found that when butanediol-1,3 is passed over such catalysts as alumina, silica gel, or aluminium silicates, the gas evolved contains considerable quantities of unsaturated hydrocarbons other than butadiene. These unsaturates, he concludes, are a mixture of propene and butenes since they are absorbed by 87 per cent sulphuric acid. No attempt, however, was made to determine the exact quantities of each olefin, nor was a mechanism postulated to account for their formation.

From Table I of the preceding section on the dehydration of butanediol-1,3 to butadiene, it was seen that the most efficient catalysts for diolefin formation were phosphorus, metal phosphates, and volatile derivatives of phosphorus.

Catalysts such as alumina and iron oxide, on the other hand, gave appreciably lower yields of butadiene. It would appear that these latter substances favour a reaction producing mono-olefins.

Reference has also previously been made to the mono-dehydration of butanediol-1,3 to methyl ethyl ketone. This reaction was carried out in the vapour phase at reduced pressure and n-butyraldehyde was formed as a by-product.

Further investigation on the mono-dehydration of 1,3-glycols was carried out by Beati and Mattei (77). These workers studied the dehydration of pentanediol-1,3 over kaolin, alumina, and phosphorus. Over kaolin and alumina an aldehyde-ketone mixture was obtained, while over phosphorus the dehydration product was pentadiene. They concluded that the formation of the carbonyl compounds arises through an intermediate cyclic ether which, being unstable, rearranges to the final product. This reference is available only in the abstract and further details are lacking.

The problem of the mechanism of both the mono- and di-dehydration of butanediol-1,3 will be further discussed in a later section of this thesis.

Dehydration of γ-Glycols

The dehydration of γ-glycols also has been studied only in respect to its application in the practical production of other organic compounds. However, from the results given in several patents (24) covering the conversion of butanediol-1,4 and its homologues to tetrahydrofurans and diolefins, several conclusions may be made.

Basic oxides, neutral salts, and acidic catalysts at the lower temperatures favour the elimination of a water molecule between the two hydroxyl groups, resulting in the ring closure and the formation of a five-membered heterocyclic ring. The stability of five-membered rings in contrast to the relative instability of three- and four-membered rings (78) accounts for ring formation in the case of the γ-glycols. At higher temperatures, it would appear that basic and acidic catalysts behave differently. The former favour carbon-carbon fission resulting in the formation of propylene and formaldehyde. The acidic catalysts, on the other hand, produce butadiene. Whether these gaseous products arise directly from the glycol or through the intermediate formation of tetrahydrofuran is open to question. The mechanism of these reactions will be discussed more fully in a later section of this thesis.

Bentonites

The catalyst used throughout this present investigation was Morden bentonite. A brief description of bentonites in general followed by an outline of work previously carried out in this University on Morden bentonite as a vapour-phase catalyst will now be given.

Bentonite was first described by Knight in 1898. It is a colloidal clay, whose particle size lies between 10-200mu. (79). This clay, which has been derived from the alteration of volcanic ash or turf, is usually largely composed of montmorillonite. Montmorillonite, an hydrous aluminium silicate of the general formula $(Mg,Ca)O.Al_2O_3.5SiO_2.nH_2O$ where $n = 5-7$, is a massive clay-like substance showing an X-ray pattern of kaolinite and may be composed of that mineral enclosing colloidal particles within the structure (80).

Bentonites are deposited widely in the United States, Western Canada, Italy, Japan, Germany, Russia and Poland. Many of the deposits are too thin to be worked economically, but Morden bentonite occurs in a large bed in Manitoba with a total thickness of eight feet. A yield of 6000 tons may be recovered from one acre (81).

Bentonites consist chiefly of hydrous aluminium silicate and they usually contain small amounts of oxides of alkalis and alkaline earths. They have no narrow chemical composition and their physical properties are not constant. Morden bentonite analyzes for approximately twenty per cent alumina, forty-five per cent silica, and for traces of ferric oxide, magnesium oxides, and calcium oxide. About twenty-five per cent is lost on ignition representing adsorbed water and water of crystallization (82).

Bentonites are seldom used as catalysts in the raw state but are usually activated by boiling the clay with dilute sulphuric acid for several hours, followed by filtering, washing, drying, and screening to the desired mesh (83).

Bentonites have found important industrial uses in recent years. Gallay (81) used bentonites to refine and bleach petroleum and fatty oils and found Morden bentonite to be superior to many earths being imported into this country. Bentonites have been used as catalyst carriers in a few organic vapour-phase reactions, as for example, the cyclization of aliphatic compounds in the presence of bentonite and oxides of vanadium, neodymium, or tantalum (84). They have also been used as catalysts themselves in the desulphurization of petroleum oils (85).

In recent years, clays in general have found increasing use in a great variety of high-temperature catalytic reactions. An investigation was begun in this University to determine the catalytic activity of Morden bentonite in several types of organic reactions (2,3,4).

A summary of the types of compounds studied and the main reactions observed is as follows:

Compound	Type of Reaction
Aliphatic alcohols	Dehydration
Aliphatic and cyclic ketones	Dehydration and fission to carbon monoxide and olefinic hydrocarbons.
Aliphatic acids	Fission to saturated hydrocarbons and carbon dioxide.
Aromatic hydrocarbons	Dealkylation

Wasson (3) in particular studied the dehydration of primary, secondary, and tertiary alcohols over Morden bentonite. Pentanol-1 was dehydrated almost completely to isomeric pentenes. At temperatures ranging from 300-400°C. and at feed rates of one to two cubic centimetres per minute, the pentenes were obtained in 85-93 per cent yield. This yield was slightly higher than that obtained by other workers using activated alumina (86,87). Pentanol-3 was dehydrated to form olefinic hydrocarbons under somewhat milder conditions than the primary isomer. Pentene-2 (cis and trans) was obtained in yields ranging from 93-95 per cent at temperatures of 275-350°C. and feed rates of one to two cubic centimetres per minute. The dehydration was quite complete with only small amounts of the alcohol remaining unchanged. Pentanol-3 has been dehydrated over alumina by Leenderste, Tulleners and Waterman (88) at 380-400°C. A yield of 81 per cent of pentene-2 was obtained. This would indicate that bentonite is superior to alumina in the dehydration of secondary alcohols.

The tertiary-isomer, 2-methylbutanol-2 (dimethyl ethyl carbinol) was also studied. It was found to produce two olefins, 2-methylbutene-2 and 2-methylbutene-1, in yields of 92-94 per cent at temperatures of 300-400°C. and feed rates of one to two cubic centimetres per minute. This again indicates the efficient dehydration action of Morden bentonite.

Wasson has also studied the action of Morden bentonite on the aliphatic ketones, acetone and methyl isobutyl ketone, as well as the cyclic ketone, cyclohexanone. Two reactions were observed in the case of acetone. The first involved the elimination of a molecule of water to form allene.

$$CH_3COCH_3 \longrightarrow CH_2{=}C{=}CH_2 + H_2O$$

This reaction was predominate at the lower temperatures, particularly at 350°C. At higher temperatures, large quantities of methane, ethylene and carbon monoxide were formed. These gases were assumed to arise through the formation of ketene and methane followed by decomposition of the ketene to carbon monoxide and ethylene.

$$CH_3COCH_3 \longrightarrow CH_2{=}C{=}O + CH_4$$

$$2CH_2{=}C{=}O \longrightarrow 2CO + CH_2{=}CH_2$$

In the case of methyl isobutyl ketone the same two types of reaction were observed. At the lower temperatures part of the ketone was dehydrated to form the diene, 4-methylpentadiene-1,3.

$$CH_3COCH_2CH(CH_3)_2 \longrightarrow CH_2{=}C{=}CHCH(CH_3)_2 + H_2O$$
$$CH_2{=}C{=}CHCH(CH_3)_2 \longrightarrow CH_2{=}CH{-}CH{=}C(CH_3)_2$$

As the temperature was progressively increased, however, quantities of isobutylene, methane and carbon monoxide were formed. This reaction was thought to involve the intermediate formation of a ketene derivative and methane followed by decomposition of this ketene to carbon monoxide and isobutylene.

$$CH_3COCH_2CH(CH_3)_2 \longrightarrow CH_4 + (CH_3)_2CHCH{=}C{=}O$$
$$(CH_3)_2CHCH{=}C{=}O \longrightarrow (CH_3)_2C{=}CH_2 + CO$$

Cyclohexanone was also dehydrated by passage over Morden bentonite, the main product at temperatures up to 500°C. being the diolefin, cyclohexadiene-1,3. Yields were small, however, with the greater part of the ketone passing through unchanged. At higher temperatures, cracking to gaseous products was found to occur.

It is to be noted that the dehydration of ketones to diolefins has rarely been observed. The results of Wasson's investigation on these three ketones indicate that Morden bentonite is exceptional in its dehydration activity.

The decomposition of acetic acid over this bentonite has also been studied. In the case of this compound, the main reaction is fission to carbon dioxide and methane, with dehydration to acetic anhydride and formation of acetone occurring only to a slight extent.

Several workers in this department have found Morden bentonite to be efficient as a dealkylation catalyst for substituted aromatic hydrocarbons. Deans (2) obtained excellent yields of toluene by passing p-cymene over this catalyst at a temperature of 500°C. Morton (4) has found that 1,1-diphenylethane can be converted to styrene and benzene in good yields by passing the compound together with water vapour over Morden bentonite at 550°C. and at rates of one to three cubic centimetres per minute.

From this survey, it would appear that Morden bentonite is highly active for both dehydration reactions, and reactions involving carbon-to-carbon fission. It was because of its high dehydration activity that Morden bentonite was chosen as a catalyst in the present investigation.

EXPERIMENTAL PROCEDURES AND DISCUSSION OF RESULTS

Apparatus

Catalysis Apparatus

Two types of catalysis apparatus were employed in the present investigation. The first was an all-glass apparatus consisting of a separate preheater and a horizontal furnace. The second apparatus had the preheater incorporated into the furnace itself, which was of the vertical type with an iron catalyst tube. A description of each type together with the advantages and disadvantages of each will follow.

The all-glass apparatus is shown in Figure I. A is a constant-level mercury reservoir from which mercury is fed into a graduated chamber, B, containing the liquid under investigation. The connecting tubing is capillary and the rate of flow is regulated by means of a stop-cock. The mercury, by displacement, forces the liquid into the preheater, C. The preheater consists of a 250 m.l. flask immersed in an electrically-heated oil-bath which is maintained at a temperature sufficient to vaporize the liquid as it passes from the graduated chamber. The preheater is connected to the catalyst tube, D, by a tube wound with Nichrome ribbon and maintained at a temperature 30-40°C. above the boiling point

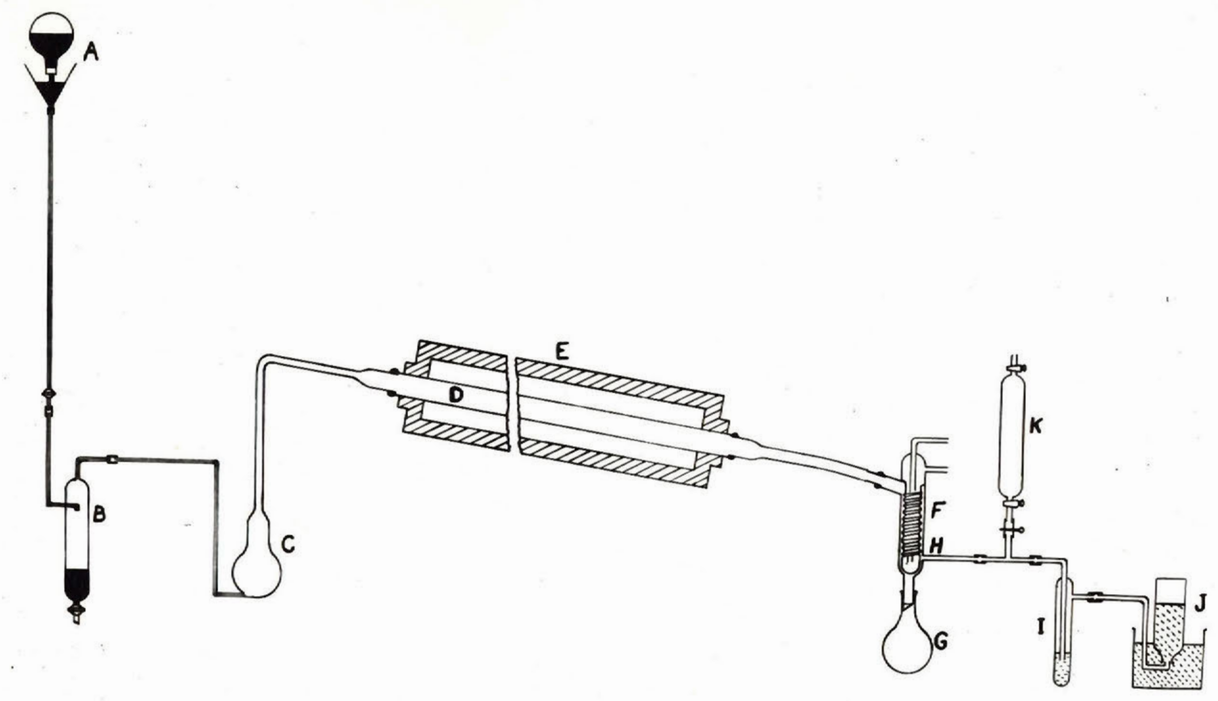


FIGURE I

HORIZONTAL-TYPE CATALYSIS APPARATUS

of the liquid. The catalyst tube is made of No.172 Pyrex resistant glass. It is 100 c.m. in length by 1.5 c.m. inside diameter and is contained in a slightly inclined electrical furnace, E. This furnace consists of two oversize Hoskins F.D.303 heating elements arranged so as to permit operation in series or in parallel. The heating elements are surrounded by a 36 inch section of asbestos pipe-covering, two and one-half inches in thickness, for insulation purposes. A chromel-alumel thermocouple is placed in the furnace and immediately outside the catalyst tube. The catalyst tube is connected by means of a short adapter to a Frederich condenser, F, which is fitted with a receiver, G, for liquid products and has an outlet, H, for gaseous products. The gaseous products pass through a small bubbler trap, I, into the gasometer, J. A gas sample for analysis is taken during the course of a run into an evacuated gas sampling tube, K, at such a rate that a small portion of the gas still passes through trap I, thus maintaining atmospheric pressure in the apparatus.

This type of apparatus is suitable only in the case of low-boiling liquids and at the lower feed-rates. Liquids boiling higher than 180°C. cannot be vaporized conveniently by means of an oil bath and, in general, for all liquids feed-rates of over four cubic centimetres per minute cause a liquid build-up in the preheater vessel. This type of catalyst tube, however, has the advantage of low holdup, non-interference in the catalysis reaction, and convenience in the recharging and reactivation of the catalyst.

For the higher boiling compounds studied in this investigation, and at the faster feed-rates, the vertical-type furnace was employed.* This apparatus is shown in Figure II. A is, as previously described, a constant-level mercury reservoir from which mercury can be fed into the 200 c.c. graduated vessels, B and C, which contain the liquid to be studied and water, respectively. (The vessel C only was used in the case of water-vapour runs involving a liquid with which water is immiscible). These feeders are connected by capillary tubing to the catalyst tube, D, which consists of a one-inch iron pipe, forty-two inches in length, and suspended vertically. A T-coupling is attached to the upper end and is fitted with one-inch nipples to accomodate the feeder capillaries and the thermocouple, L, which is inserted inside the tube. The lower end of the tube is connected by means of a union to a one-quarter inch iron tube of which a four-inch length is water-jacketed. The remaining length is curved to make contact with a Frederich condenser which is connected to receivers for gas and liquid products as described in the all-glass apparatus.

The lower portion of the catalyst tube is packed with the catalyst, immediately above which is placed the metal junction of the thermocouple L. This thermocouple is

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*This furnace was designed and constructed by Morton and Nicholls (4).

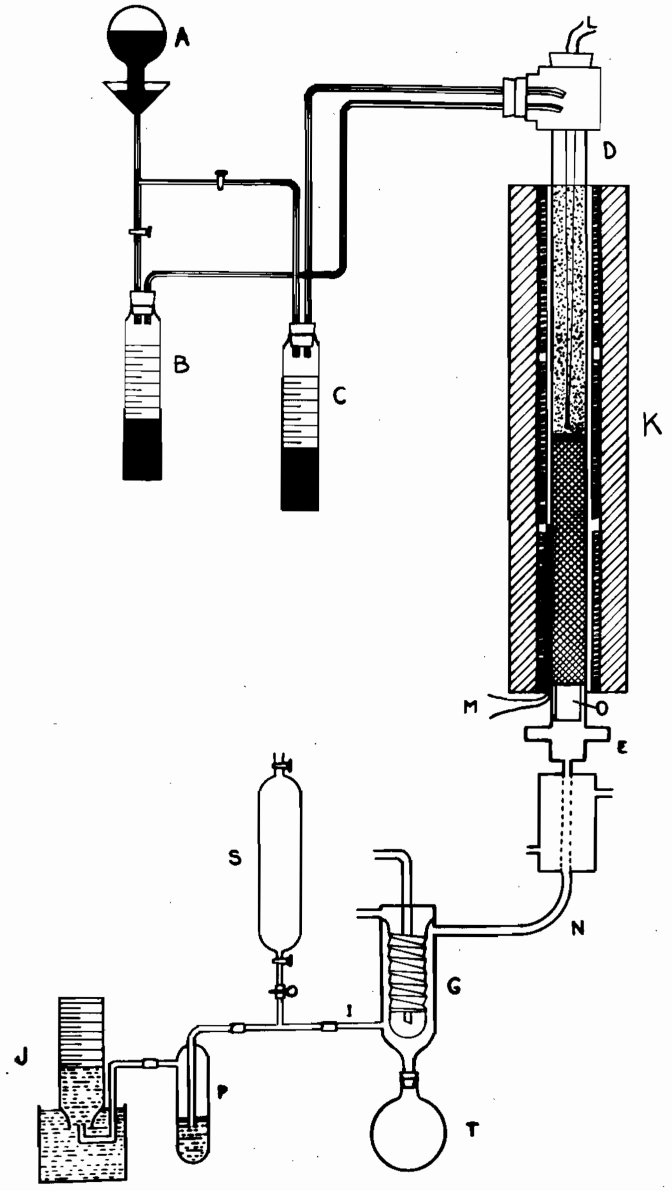

FIGURE II

VERTICAL-TYPE CATALYSIS APPARATUS

suitably insulated and surrounded by pumice or steel-wool which serves as a heat-transfer medium for the vaporization and preheating of the material before its entry into the catalyst. Another thermocouple, M, is placed outside the catalyst tube with the metal junction lying about two-thirds up the column of catalyst. With this arrangement, it is possible to measure the temperature of the vapours entering the catalyst, and also that of the main body of the catalyst itself. The furnace, K, consists of three Hoskins heating elements surrounded by asbestos pipe-insulation. The top heater is separately controlled to maintain any desired heat input for vaporization and preheating of the vapours. The two lower heaters are wired in series and in parallel, and are maintained at any desired temperature for the catalytic reaction.

Gas Analysis Apparatus

Since a study of gaseous products played an important part in this investigation, it was found desirable to construct more accurate Gas Analysis Apparatus than had been used in previous catalytic studies in this University. A Bone and Wheeler apparatus was constructed for the general gas analysis, while a special apparatus was constructed for butadiene analysis.

Bone and Wheeler Apparatus:- This apparatus, shown in Figure III, is a modification of the standard type of Bone

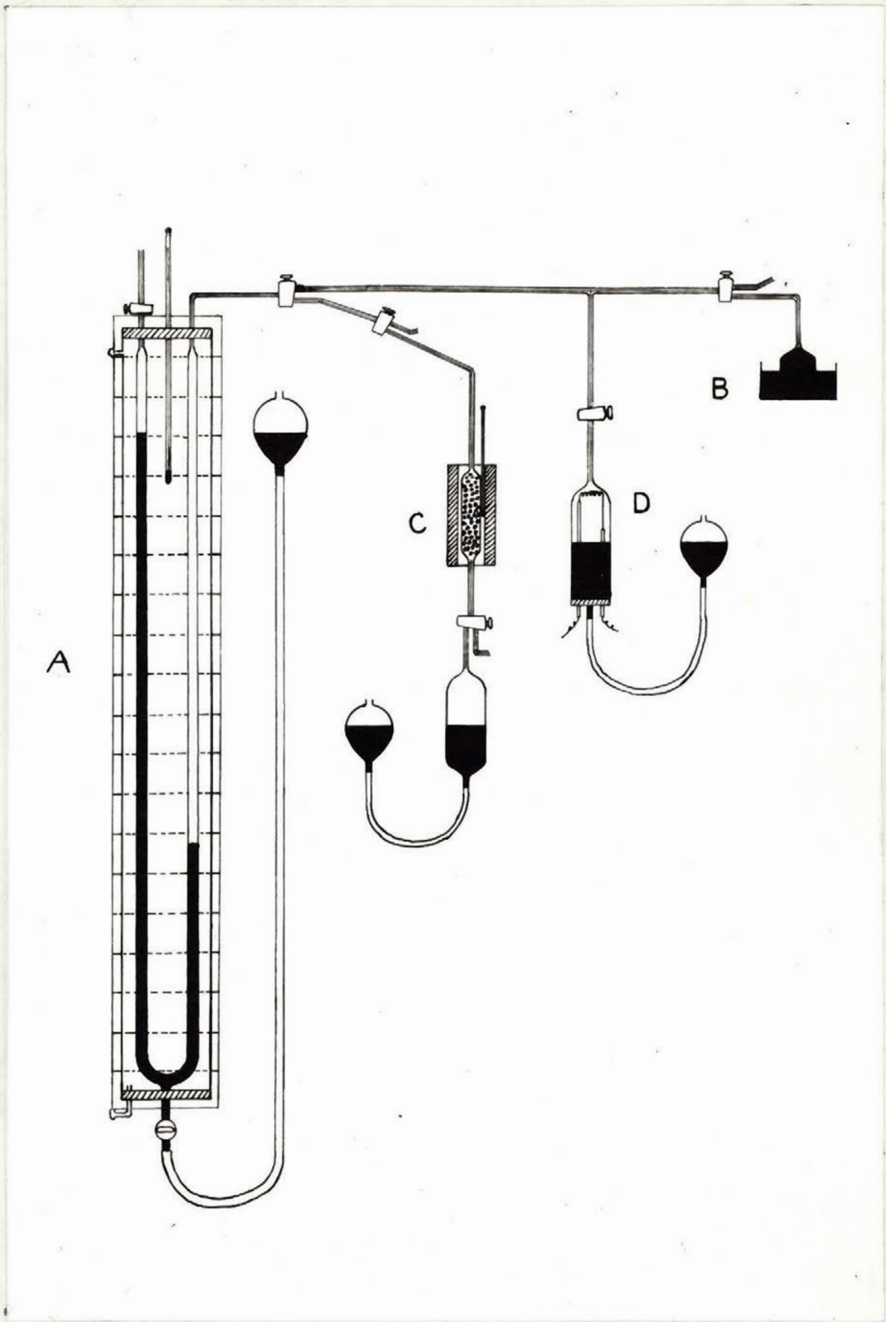

FIGURE III

BONE AND WHEELER GAS ANALYSIS APPARATUS

and Wheeler Apparatus described by Grice and Payman (89). It consists essentially of four main parts, namely, a U-tube, A, which is water jacketed and backed by a mirror scale for measurement of the gas, an absorption dome, B, connected to the U-tube by capillary tubing and inverted over a mercury trough, a copper-oxide slow-combustion furnace, C, and a platinum-coil slow-combustion pipette, D. The copper-oxide furnace is an addition to the standard apparatus, while the platinum-coil pipette is substituted for an explosion pipette.

The gas is measured at constant volume and passed into the absorption dome, where it is treated with various reagents. The reagents for the various gases are listed below in the order in which they are used.

TABLE III

Reagent	Gas Absorbed
Concentrated KOH solution	Carbon dioxide
Sulphuric acid 67% [a]	Isobutylene
Sulphuric acid 90% [b]	All other unsaturates excluding ethylene
Bromine water	Ethylene
Alkaline pyrogallol solution	Oxygen
Ammoniacal cuprous chloride solution	Carbon monoxide

a. This concentration of sulphuric acid was used by Dobrjanski (90) for separating isobutylene from other olefins. Davis and Schuler (91) have shown that isobutylene is absorbed eighty times faster than butene-2 with 70% sulphuric acid which, in turn, is absorbed faster than propene or butene-2. In our experience, 67% sulphuric acid absorbs some butadiene as well as isobutylene, but gives an analysis within one to two per cent of the actual value.

b. Davis and Schuler (91) have shown that ethylene is only very slowly absorbed by 90% sulphuric acid.

For hydrogen determination, the copper-oxide tube is evacuated by Toepler pump action and the gas passed over the oxide at 250-270°C., followed by re-evacuation and measurement of the residual gas. This is repeated until no further contraction occurs. Saturated hydrocarbons are determined in the usual manner by combustion over a glowing platinum coil.

Butadiene Apparatus:- A prolonged study of Universal Oil Products Apparatus for butadiene analysis failed to give satisfactory results. A modification of an apparatus designed by Cambron at the National Research Council, Ottawa, (93) was then constructed. It is based on the Diels-Alder reaction between butadiene and maleic anhydride. The apparatus is shown in Figure IV. It consists of four main parts, namely, a gas sampling tube, A, provided with a mercury levelling-bulb, a drying tube, B, a water-jacketed gas measuring-burette, C, with a mercury levelling-bulb, and and Orsat gas absorption pipette, D, surrounded by an electrically-heated water-jacket and provided with a levelling bulb.

In operation, the first step involves the charging of the Orsat pipette with maleic anhydride. The water

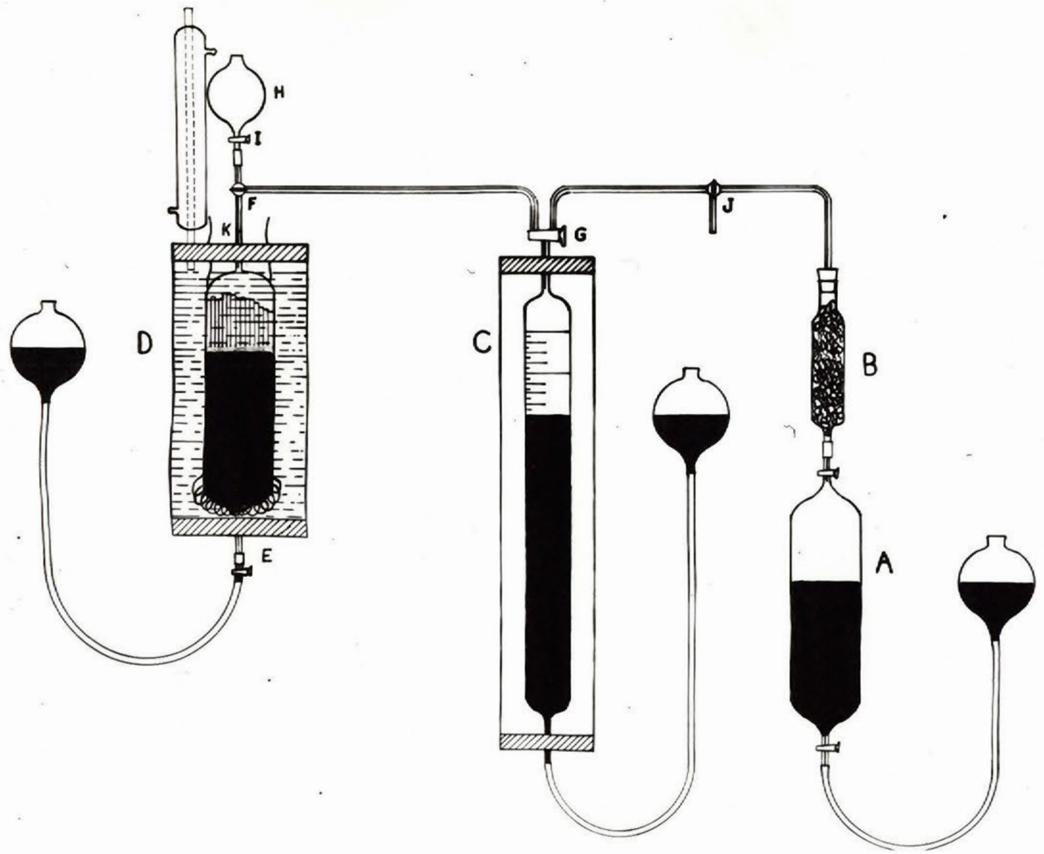

FIGURE IV

BUTADIENE GAS ANALYSIS APPARATUS

surrounding the pipette is heated to boiling, and the mercury levelling-bulb is detached above the stop-cock E. Stop-cocks F and G are turned so as to connect the pipette with the measuring burette, and two to three grams of molten anhydride are drawn into the pipette by slowly lowering the burette levelling-bulb. The pipette levelling-bulb is again connected to the pipette. The anhydride is then raised to the mark K and the stop-cock F turned so as to connect the bulb H with the burette.

The drying tube and capillary tubing to stop-cock G are evacuated by Toepler pump action, and G is turned to connect the burette with the bulb H. The burette levelling-bulb is raised until a little mercury flows beyond the stop-cock I, which is then closed. A gas sample is now passed slowly from the sampling tube A into the burette and measured at atmospheric pressure. (For samples containing over 90 per cent butadiene the gas is diluted with approximately an equal volume of air taken in at J). The gas is then passed into the absorption pipette. After ten to fifteen minutes, the gas is returned to the measuring burette, the maleic anhydride being raised to the level K as before. This process is repeated until no further absorption of gas occurs. After the final pass, the gas in the connecting capillary is displaced by allowing the mercury from H to flow down to the stop-cock G. The final gas volume is then measured.

The first gas sample serves only to saturate the maleic anhydride with soluble hydrocarbons other than butadiene. This is followed by analysis of another sample from A, the contraction in volume this time being due to the removal of butadiene alone. Two successive samples following the "saturation sample" were found to check within one per cent.

A single maleic anhydride charge may be used for several different butadiene determinations. However, before each new analysis, a preliminary saturation must be made. After discarding the maleic anhydride, the pipette is washed with acetone and dried. After two charges of anhydride, the apparatus becomes quite dirty and both the pipette and measuring burette are cleaned by filling with cleaning solution.

Fractionation Columns

In previous work carried out at this University, the liquid products were separated into main fractions by distillation in a modified Claisen flask, followed by a fractionation of combined similiar fractions from successive runs for identification purposes. For this investigation, a more accurate method of analysis was required. It was decided to attempt to construct a fractionation column which had the following characteristics:

1. A reasonably small hold-up, not greater than ten per cent of the liquid being fractionated which usually amounted to 50-70 c.c.
2. An efficiency which would enable adequate separation and identification of the various components in one fractionation.

3. A high rate of through-put, so as to permit the fractionation of a 50 c.c. sample in ten to twelve hours.

Two fractionation columns were constructed. The first column was 10 m.m. internal diameter and had a packed section 38 c.m. in length. It was packed with single turn wire helices, 3/64 inch in diameter, made from B.&S.No.40 Nirosta Stainless Steel Wire, manufactured by Driver-Harris Company, Harrison, N. J.* This wire was wound into spirals on a steel shaft, 3/64 inch in diameter, and the spirals were cut lengthwise by a fine pair of scissors into single turn helices. In packing the column, care was taken that all helices were separated from one another and passed into the column approximately one at a time. The column head was of the total condensate, partial take-off variety. In order to attain maximum efficiency, care must be taken to insure complete wetting of the packing throughout the distillation. This was accomplished by a preliminary flooding.

The efficiency of this column was determined using a test mixture of n-heptane and methylcyclohexane (94). The holdup was determined by a method described by Tongberg, Quiggle and Fenske (95). The efficiency and holdup values at various through-put rates under total reflux are listed below:

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*This type of packing was the suggestion of Dr. R.W. Schiessler of Pennsylvania State College

TABLE IV

Reflux Rate c.c./hr.	Liquid Holdup c.c.	No. of Theoretical Plates	H.E.T.P. in c.m.
30	---	45.7	.83
60	5.1	46.2	.82
90	6.7	43.2	.88

From this data, it is seen that the column fulfils the requirements of efficiency and holdup. In fact, this H.E.T.P. value is one of the lowest reported in the literature. However, the rate of through-put was extremely low. It was found very difficult to operate the column at reflux rates faster than 60 c.c. per hour and even at this rate flooding occurred with certain liquids. Operating at a suitable reflux ratio, little more than 2 c.c. per hour could be taken off. Because of this fact, the column was not considered suitable for the analysis of the liquid products from individual runs. It was used, however, to great advantage in the separation and identification of very small and closely boiling components.

A small glass helices column was then constructed for the analysis of products from individual runs. This column was 45 c.m. in length by 10 c.m. internal diameter and was packed with single-turn glass helices 3/32 inch in diameter. The column head was of the total condensate, partial take-off type. Preliminary flooding was made to insure complete wetting of the packing during a distillation. Data on the efficiency and holdup of this column are listed below.

TABLE V

Reflux Rate c.c. per hr.	Reflux Ratio	Liquid Holdup c.c.	No. of Theoretical Plates	H.E.T.P. in c.m.
96	Total	5.0	30	1.5
240	Total	---	23	2.0
360	Total	6.5	22	2.0
240	20:1	---	14	3.2

From this data it was seen that the glass helices column fulfils the requirements of through-put and holdup. Efficiency has been sacrificed, but was found adequate for most separations required in this investigation.

Preparation of the Catalyst

A sample of Morden bentonite was obtained from the Pembina Mountain Clays Company of Winnipeg.* It was light brown in color and very finely powdered. It readily passed through a 200-mesh screen.

The bentonite was activated according to a method outlined by Gallay (81). The material was treated with a twenty-percent aqueous solution of sulphuric acid of such a volume that the weight of concentrated acid was fifty per cent of the weight of the clay being reactivated. This mixture was boiled gently for three hours with frequent stirring insuring an even dispersion throughout. After cooling, the slurry was diluted to three times its volume, filtered, and

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*This sample was the gift of the Pembina Mountain Clays Company, which we hereby acknowledge with thanks.

the clay washed thoroughly. In order to insure a catalyst of uniform activity from successive activations, the washing was continued until the acidity of the wash-water was approximately one-fiftieth normal. The moist cake was dried at 110°C. for twelve hours, broken up, and screened to a material ranging from 4 to 8 mesh. The catalyst was then ready for use.

After a catalysis run, the catalyst usually carried some deposited carbon which impaired its activity. This carbon was removed and the activity restored by passing air slowly over the catalyst at a temperature of 550-600°C. for five to eight hours. A small decrease in activity compared to fresh catalyst was found after the first reactivation. Subsequent reactivations caused no change. On the other hand, if the reactivation process is carried out too rapidly causing high local heating as the carbon is oxidized, or if the temperature of the furnace is allowed to rise above 700°C., sintering of the catalyst results and its activity is greatly impaired. In order to obtain comparable results, a reactivated catalyst was used for each run of this investigation. A single charge of catalyst was reactivated six to eight times before recharging.

Through the courtesy of the Department of Mines and Resources an analysis of the unactivated, activated and reactivated Morden bentonite was obtained. The results of this analysis are as follows:

TABLE VI

ANALYSIS OF MORDEN BENTONITE AFTER IGNITION [a].

	Unactivated	Activated	Reactivated
SiO_2	61.67	71.73	72.93
Al_2O_3	22.86	19.68	19.84
Fe_2O_3	4.89	0.87	0.28
CaO	2.18	0.51	0.53
MgO	4.77	4.08	3.68
Other Bodies (by difference)	3.64	3.15	2.73

a. The ignition was carried out at 1700°C. for two hours. Loss included uncombined moisture and water of hydration. The loss on ignition for the unactivated sample was 24.94%, for the activated 22.28%, and for the reactivated 2.77%.

It would appear that the activation process removes the greater portion of the iron and calcium content of the clay as well as a small portion of the aluminium content thus increasing the catalytic surface. The drop in activity in the reactivated catalyst is probably due to sintering during heat treatment.

The Dehydration of Butanediol-2,3 over Activated Morden Bentonite

Source and Purification of Butanediol-2,3

The laevo form of butanediol-2,3 was chosen for this investigation. This was due to the fact that the Division of Applied Biology of the National Research Council, Ottawa, has developed a method for the production of this glycol from wheat starch. This method involves cooking the wheat and fermenting it by a soil organism known as aerobacillus, which acts directly on the starch to produce laevo-butanediol. The glycol was obtained from two sources, the Northern Regional Research Laboratory, Peoria, Ill. and the National Research Council, Ottawa.*

The material used in the catalysis investigation was purified in the following manner. The glycol was diluted with an equal volume of water and 200 grams of calcium oxide per litre of solution added. This mixture was heated on a steam bath for several hours with occasional shaking. The hydrated oxide was removed by filtration, and the greater portion of the water removed by simple distillation. The material was finally fractionated and the fraction having the constants b.p. 177°C., d_4^{20} 0.992, n_D^{20} 1.4312 was used for the catalysis investigation. Wilson and Lucas (96) have

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*We hereby acknowledge with thanks the generous gift of samples of laevo-butanediol-2,3 from the Northern Regional Research Laboratory of the U.S. Bureau of Agricultural Chemistry and Engineering and the Division of Applied Biology of the National Research Council.

reported a boiling point of 176.7°C. for the laevo glycol. Density and refractive index contents were not given, however.

Procedure

In the investigation with butanediol-2,3 the horizontal-type of catalysis apparatus was employed. Forty grams (approximate volume 105 c.c.) of activated Morden bentonite was used in each catalyst run. The catalyst was placed in the catalyst tube and held in place by two small plugs of glass wool. The temperature of the furnace was raised to 500°C. and held there for one hour, whereby the greater portion of the water contained in the catalyst was removed.

The furnace was then quickly adjusted to the desired temperature and maintained throughout the course of the run. The glycol in the graduated chamber B was displaced by mercury from the reservoir A and regulated to the desired rate. The liquid flowed into the preheater which was maintained at 220°C. The vaporized material then passed into the catalysis tube and over the activated bentonite. The liquid products were condensed in the Frederich condenser while the gaseous products passed through the outlet H. A fore-run of 15-20 c.c. was made, during which time the temperatures and rate were given final adjustment. The liquid receiver was then changed and the run carried out under carefully regulated conditions. The rate of gas evolution was measured in a 2-litre calibrated vessel by displacement of water previously saturated with carbon dioxide. The rate was determined several times during the course of a run by measuring the volume of gas evolved during the passage of a given amount of liquid glycol measured in B. The amount usually varied from 10-15 c.c. depending upon the rate of gas evolution. A gas sample for analysis was collected in the sampling tube K at about the middle of the run.

The liquid products consisted of two layers, an upper organic layer and a lower aqueous layer. The organic layer was salted out, separated, and dried by the addition of a little sodium sulphate. Because of the considerable mutual solubility of butanone-2 and water, a large quantity of the drying agent was required to accomplish complete drying of the organic layer. Complete drying was not attempted, however, as it would involve excessive losses. The drying agent was removed by filtration, and the organic liquid given a preliminary distillation through an ordinary Claisen flask. The product was separated into three fractions, the major fraction distilling below 150°C., a small fraction between 150-200°C., and some tarry residue. The lower boiling fraction was then carefully fractionated in the small glass helices column. An inert booster, p-cymene (b.p.177°C.), was added to keep distillation losses at a minimum. In the case of small and closely boiling components further fractionation was accomplished using the wire helices column. The boiling point, refractive index, and density were taken of the purified products. In all cases, where the physical constants were not in close agreement with literature values, due to difficulties in purification, derivatives were prepared for further identification.

The gaseous products were analyzed in the Bone and Wheeler Apparatus. A separate analysis was made for butadiene content. For the determination of individual olefins, a typical run was made in which the gaseous products were passed into liquid bromine. The resulting dibromides were washed, dried, and given a preliminary vacuum distillation. The material boiling below 85°C. at 50 mm. was carefully fractionated under reduced pressure using p-bromotoluene (b.p. 90°C. at 50 mm.) as an inert booster. The identity of the saturated hydrocarbons was determined by passing the gas, from which carbon dioxide and unsaturated hydrocarbons had previously been removed, through a series of cold traps. The first trap was maintained at -80°C. for the condensation of butane and propane, the second was maintained at -110°C. for ethane, and the third trap was immersed in liquid air for the condensation of methane.

Results and Discussion

The various temperatures and feed -rates at which the dehydration of butanediol-2,3 was investigated, together with the amounts of liquid and gaseous products obtained, are given in Table VII. In this Table, the runs are divided into two groups, low-temperature non-gaseous and high-temperature

TABLE VII

DEHYDRATION OF BUTANEDIOL-2,3 OVER ACTIVATED MORDEN BENTONITE

Low-temperature Non-gaseous Runs

Run No.	Furnace °C.	Rate c.c./min.	Glycol g.	Total Liquid Products-g.	Organic Layer-g.	Aqueous Layer-g.	Vapour Products and loss-g.	Total Gas-l.
15	225	1	100	99.5	79.3	20.2	0.5	---
11	275	1	100	100.0	79.0	21.0	0.0	---
16	225	3	100	99.5	80.5	19.3	0.5	---
12	275	3	100	99.2	79.2	20.0	0.8	---
13	350	3	100	94.7	74.3	20.4	5.3	small

High-temperature Gaseous Runs

Run No.	Furnace °C.	Rate c.c./min.	Glycol g.	Total Liquid Products-g.	Organic Layer-g.	Aqueous Layer-g.	Vapour Products and loss-g.	Total Gas-l.
3	450	1	100	88.3	62.1	26.2	11.7	2.88
4	550	1	100	76.7	46.5	30.2	23.3	11.20
6	650	1	100	58.0	29.3	27.7	42.0	24.00
7	700	1	100	39.5	12.3	27.2	60.5	38.00
5	550	3	100	82.1	55.8	26.3	17.9	5.30
8	650	3	100	71.6	45.4	26.2	28.4	12.00
9	700	3	100	64.3	37.0	27.3	35.7	20.00

gaseous runs. One rate is considered at a time in order to show more clearly the effect of temperature upon the reaction.

The analysis of the organic liquid products, expressed in per cent composition, is shown in Table VIII. Five fractions were obtained in addition to a thick tarry residue remaining after the preliminary distillation. (A small residue, formed by polymerization during the fractionation, was found to remain with the booster. This was included in the residue percentage). Fraction I, distilling below 60°C., was present only in traces and was not identified. Fraction 2, boiling between 60-70°C. (mainly at 64-66°C.) consisted of isobutyraldehyde, identified by its physical constants and by the preparation of a derivative. Fraction 3, collected between 77-82°C., the majority of which distilled at 79-80°C., was practically pure butanone-2. Fraction 4, distilling between 125-145°C. with a flat in the distillation curve at 137-138°C. in the case of the lower temperature runs, was found to consist mainly of the cyclic acetal formed by the condensation of the glycol with isobutyraldehyde. This compound was identified by synthesis and by hydrolysis to the glycol and isobutyraldehyde. Fraction 5, distilling over a continuous range of 100 Centigrade degrees, could not be separated into any single component. It was believed to be a complex mixture of high boiling condensation products from butanone-2 similiar to that found by Mitchell and Reid

TABLE VIII

ANALYSIS OF ORGANIC LIQUID PRODUCTS FROM BUTANEDIOL-2,3 EXPRESSED AS PER CENT COMPOSITION

Low-temperature Non-gaseous Runs

Run No.	Total Organic Layer Analyzed-g.	1. -60°C. in %	2. 60-70°C. in %	3. 77-82°C. in %	4. 125-145°C. in %	5. 150-250°C. in %	6. Residue in %
15	79.3	1.8	3.0	85.7	4.7	2.0	2.8
11	79.0	3.4	5.7	83.9	2.1	3.2	1.7
16	80.5	1.7	2.6	85.5	6.2	1.4	2.6
12	79.2	2.0	6.5	84.5	2.8	2.0	2.2
13	74.3	4.9	13.0	75.5	1.8	1.4	3.4
High-temperature Gaseous Runs							
3	62.1	3.8	7.3	73.8	2.9	5.1	8.0
4	46.5	6.7	6.1	68.6	3.8	7.5	7.3
6	29.3	3.3	3.7	73.5	2.2	8.9	8.4
7	12.3	2.0	3.0	69.0	3.0	8.0	15.0
5	55.8	3.7	8.3	74.9	1.4	5.0	6.7
8	45.4	5.0	5.7	79.3	1.4	3.6	5.0
9	37.0	3.3	4.9	80.0	1.6	3.7	6.4

(97) when butanone-2 is passed over silica gel.

In order to show more clearly the effect of variation in temperature and feed-rates, the three main organic liquid fractions; Fraction 2, isobutyraldehyde; Fraction 3, butanone-2; and Fraction 4, the cyclic acetal; are expressed in per cent of the theoretical yield in Table IX. The number of moles of water eliminated per mole of the glycol is also given. The yields were calculated with the assumption that the dried material can be considered as an aliquot sample of the original organic layer. This appears justifiable for two reasons. In the low-temperature runs, no trace of unchanged glycol was detected, and the weight of the aqueous layer was exactly one mole per mole of glycol dehydrated. Furthermore, on mixing pure butanone-2 and water in molar proportions, it was found that the weight of the undried upper layer was approximately the weight of butanone-2 in the mixture. Consequently, it would appear that the weight of undried organic layer from the glycol runs closely approximates the true weight of organic products.

The analysis of the gaseous products expressed in volume per cent and the per cent yield of butadiene are given in Table X. The saturated hydrocarbons were found to consist of methane and ethane only by the cold trap condensation method. They were determined quantitatively by combustion analysis.

The results of the fractionation of the olefin

TABLE IX

YIELDS OF LIQUID PRODUCTS FROM BUTANEDIOL-2,3 RUNS

Low-temperature Non-gaseous Runs

Run No.	Furnace °C.	Rate c.c. /min.	60-70°C.Fract. % Yield as Isobutyraldehyde	77-82°C.Fract. % Yield as Butanone-2	125-145°C.Fract. % Yield as Cyclic Acetal	Moles of water Removed
15	225	1	3.0	85.0	4.7	1.00
11	275	1	5.6	82.9	3.2	1.05
16	225	3	2.6	86.0	6.2	0.97
12	275	3	6.5	83.7	2.8	1.00
13	350	3	12.1	70.1	1.7	1.02

High-temperature Gaseous Runs

Run No.	Furnace °C.	Rate c.c. /min.	60-70°C.Fract. % Yield as Isobutyraldehyde	77-82°C.Fract. % Yield as Butanone-2	125-145°C.Fract. % Yield as Cyclic Acetal	Moles of water Removed
3	450	1	5.7	57.3	2.2	1.31
4	550	1	3.6	39.9	2.2	1.51
6	650	1	1.4	26.9	0.8	1.39
7	700	1	0.45	10.3	0.45	1.36
5	550	3	5.8	52.2	1.0	1.31
8	650	3	3.2	45.0	0.8	1.31
9	700	3	2.3	36.9	0.7	1.36

TABLE X

ANALYSIS OF GASEOUS PRODUCTS FROM BUTANEDIOL-2,3 RUNS

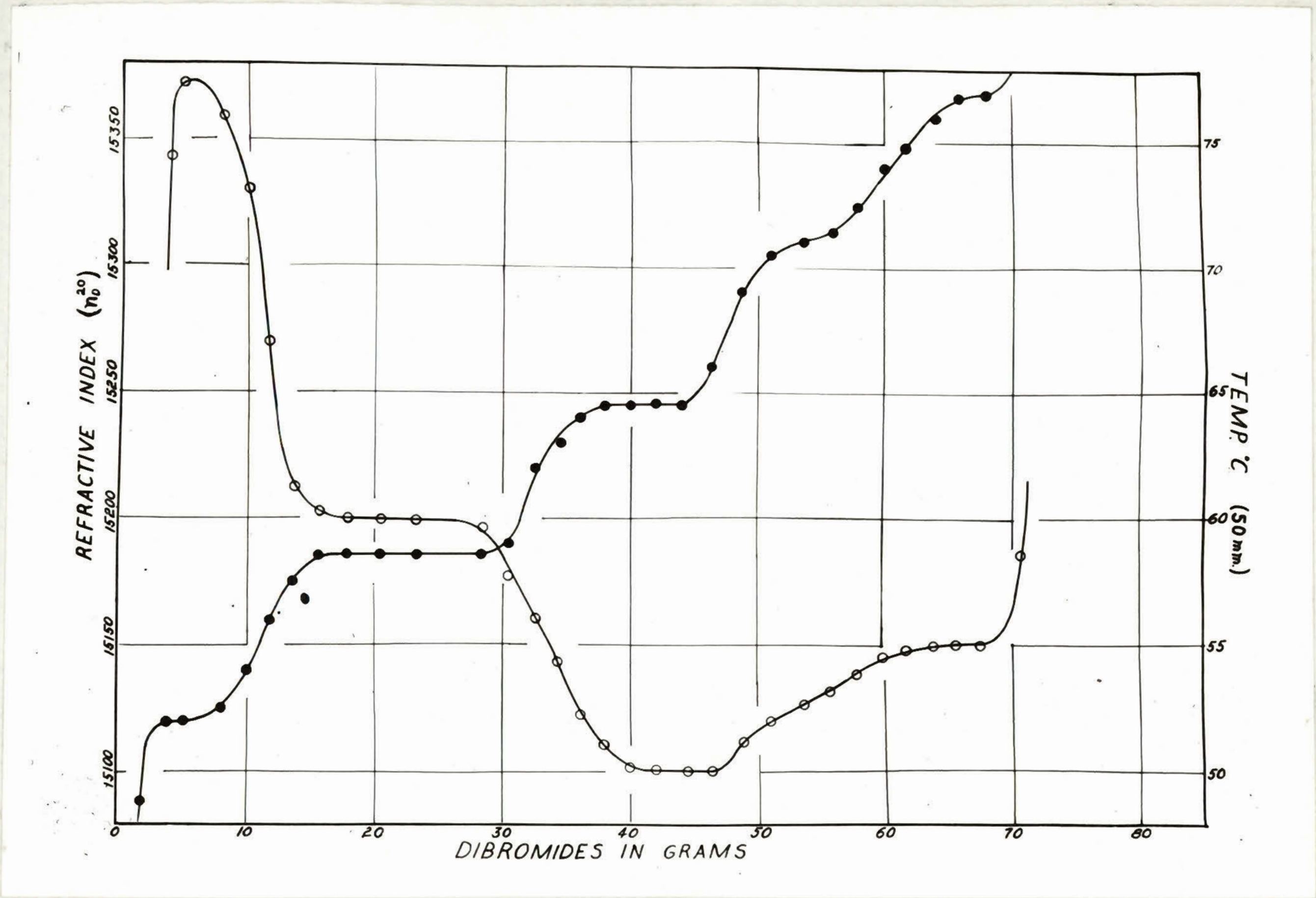
General Gas Analysis in Volume Per cent									Butadiene Analysis	
						Saturates				
Run No.	CO_2	CO	H_2	$CH_2{=}CH_2$	Other Unsats. including Butadiene	Total	CH_4	C_2H_6	Volume %	Yield %
3	17.4	14.7	0.0	2.2	43.3	19.2	3.5	15.8	5.3	0.8
4	7.3	16.7	4.1	3.0	39.1	28.3	10.4	17.9	4.2	2.0
6	1.7	27.2	11.6	5.0	27.8	25.1	12.5	12.5	4.2	4.1
7	1.9	27.2	14.1	8.2	20.6	26.4	17.0	9.3	4.4	6.7
5	6.7	19.2	2.5	2.7	43.3	24.1	9.0	15.1	8.5	2.2
8	2.7	20.1	6.6	4.6	39.7	24.9	14.5	10.4	8.4	4.3
9	2.1	24.6	11.5	6.5	31.5	23.8	14.9	8.6	7.6	6.1

dibromides formed from a run carried out at 650°C. and at a feed-rate of one cubic centimetre per minute, are shown in Graph I. Examining this graph, it is seen that the first flat in the temperature and refractive index curves appears at 52°C. and n_D^{20}1.537, respectively. This corresponds to 1,2-dibromoethane. The second flat, occurring at 58.5°C. and n_D^{20}1.5200 is 1,2-dibromopropane. A third flat is found at 64.5°C. and n_D^{20}1.5101 and corresponds to 1,2-dibromo-2-methyl-propane (the dibromide of isobutylene). Both the temperature and refractive index curves rise with gentle slopes between 72-77°C. and n_D^{20}1.5110-1.5150. This corresponds to a mixture of racemic and meso 2,3-dibromobutane. The literature reports the meso form boiling at 73°C. at 50 mm. and n_D^{20}1.5116. The racemic form has a boiling point of 75.6-75.8°C. at 50 mm. and n_D^{20}1.5147. Beyond this fraction, both temperature and refractive index rise rapidly to that of the booster. By careful analysis of the two curves, a close approximation of the relative amounts of the individual dibromides can be made.

1,2-dibromoethane	10.4
1,2-dibromopropane	34.4
1,2-dibromo-2-methyl-propane	22.4
2,3-dibromobutane	32.8

As far as the writer is aware this method has not previously been used as such for the quantitative estimation of olefinic hydrocarbons. Hurd (98) analyzed an ethylene,

GRAPH I



FRACTIONATION OF THE OLEFIN DIBROMIDES FROM BUTANEDIOL-2,3

○ Refractive Index Curve

● Boiling Point Curve

propylene, and isobutylene mixture by converting the olefins into dibromides and fractionating them into two component mixtures. Each mixture was analyzed by the index of refraction method, using synthetic two component mixtures for reference.

Three runs were carried out in the presence of water vapour. These were investigated in respect to gaseous products only, since the solubility of the organic liquid products in the large volume of water present made a quantitative liquid analysis impossible. The conditions of the reaction and the analysis of gaseous products are shown in Table XI.

The physical constants found for the products obtained in the dehydration of the glycol together with the literature values are shown in Table XII. In certain cases, derivatives were formed for further identification.

Considering the low-temperature non-gaseous runs, it is seen from Table VII that the glycol is completely converted to mono-dehydration products and one mole of water is eliminated per mole of glycol. Gaseous products do not form until a temperature of 450°C. is reached and considerable quantities not until 550°C. From Table IX, it is seen that yields of 84-86 per cent butanone-2 are obtained at temperatures of 225°C. and 275°C. and at feed-rates of 1 and 3 c.c. per minute. At 350°C., however, the yield of this ketone is reduced to 70.1 per cent. At 225°C., the main by-product is the cyclic

TABLE XI

DEHYDRATION OF BUTANEDIOL-2,3 OVER ACTIVATED MORDEN BENTONITE IN THE PRESENCE OF WATER VAPOUR

Run No.	Furnace °C.	Rate[a] c.c./min.	Glycol g.	Water g.	Total gas-l.
14	650	2	100	100	11.20
17	700	2	100	100	27.20
18	700	3	100	200	15.40

	General Gas Analysis in Volume Per cent								Butadiene Analysis	
						Saturates				
Run No.	CO_2	CO	H_2	$CH_2=CH_2$	Other Unsats. including Butadiene	Total	CH_4	C_2H_6	Volume %	Yield %
14	2.5	17.4	7.7	5.6	43.4	21.5	14.9	6.6	13.6	5.8
17	1.9	17.9	13.8	6.5	34.1	23.5	16.0	7.5	7.7	8.4
18	1.8	15.4	15.0	6.7	45.0	13.9	8.5	5.4	24.0	14.9

a. This is the total rate including glycol and water.

TABLE XII

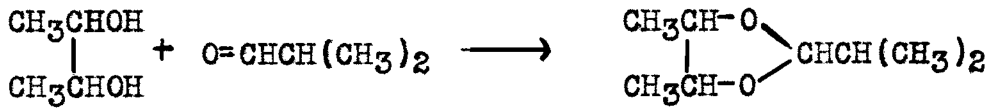
IDENTIFICATION OF PRODUCTS FROM THE DEHYDRATION OF BUTANEDIOL-2,3

Compound		Boiling Point °C.	Density d_4^{20}	Ref. Index n_D^{20}	Deriv. Melt. Point °C.
Isobutyraldehyde	Given	65	0.794	1.3730	
	Found	64-65	0.798	1.3747	
2,4-dinitrophenylhydrazone	Given				183
	Found				183-183.5
Butanone-2	Given	79.6	0.805	$1.3708^{(15.9)}$	
	Found	79.6	0.804	$1.3707^{(15.9)}$	
Water	Given	100	0.998	1.3333	
	Found	100	0.998	1.3337	
Isobutyral of butanediol-2,3	Given[a]	139	0.890	1.4095	
	Found	136-139	0.893	1.4078	
1,2-Dibromoethane	Given	52/50 mm.		1.5379	
	Found	52-53/50 mm.		1.5373	
1,2-Dibromopropane	Given	141.6	$1.925^{(25)}$	1.5203	
	Found	141.8	$1.916^{(25)}$	1.5199	
Isobutylene dibromide	Given[b]	65/50 mm.	1.790	1.5102	
	Found	64.5/50 mm.	$1.761^{(25)}$	1.5101	
2,3-Dibromobutanes meso	Given	73/50 mm.	$1.775^{(25)}$	1.5116	
rac.	Given	76/50 mm.	$1.784^{(25)}$	1.5147	
	Found	72-77/50 mm.	$1.777\text{-}1.782^{(25)}$	1.5110-1.5147	
Tetrabromobutane	Given				118-119
	Found				117-118

a. These values are for the product synthesized in the liquid phase.

b. These values are for a synthesized product, literature values being in disagreement with themselves.

acetal formed by the elimination of water between isobutraldehyde and the glycol.

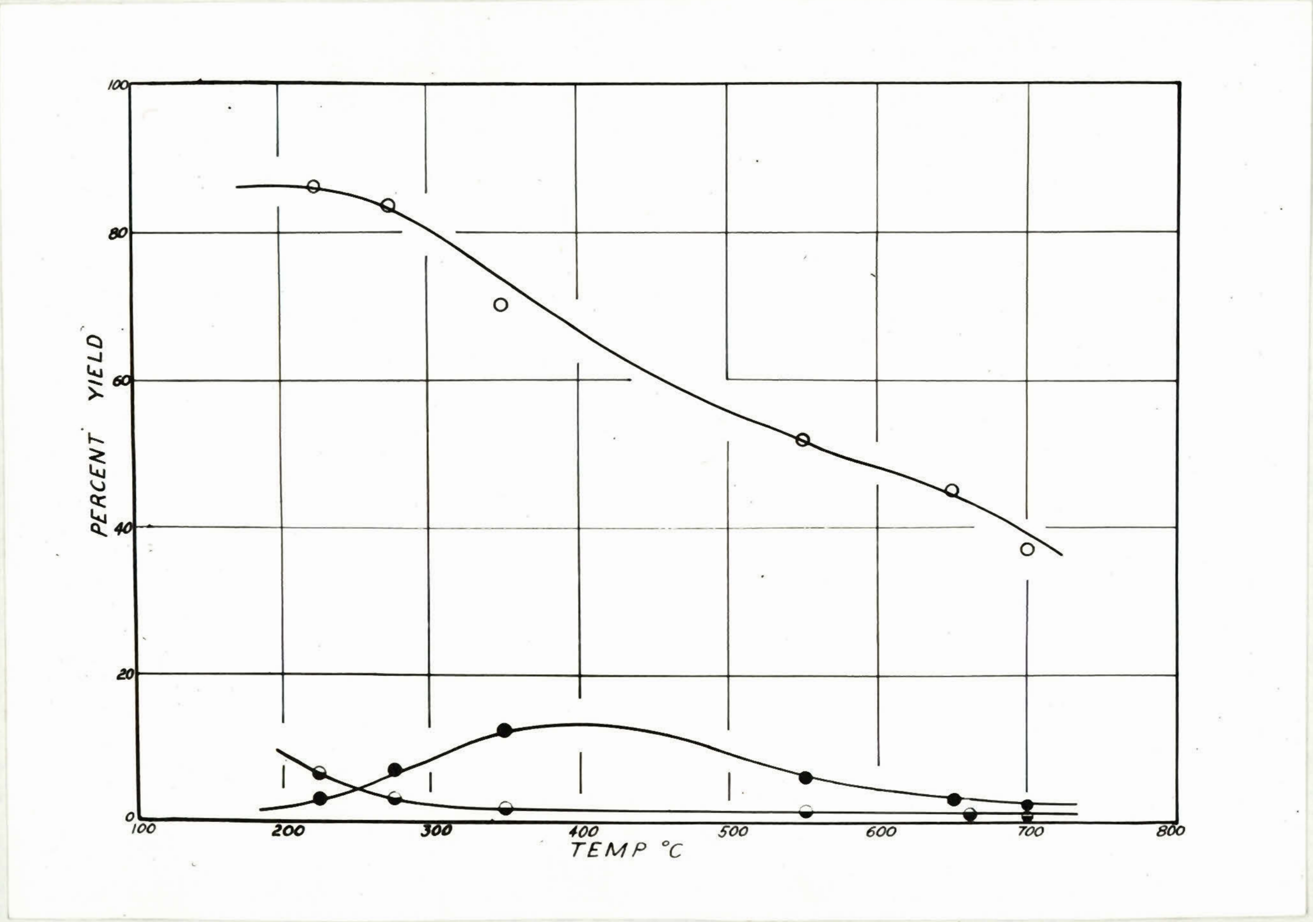


As the reaction temperature is increased, less of the cyclic acetal is formed since the glycol is converted completely to carbonyl compounds before acetal formation can occur. As far as the writer is aware, this acetal has not been prepared before. It is interesting to note, however, that Backer (99) obtained the acetal of butanediol-2,3 and butanone-2 by passing the glycol over alumina, in an attempt to produce butadiene.

At higher temperatures, increasing amounts of isobutyraldehyde are formed, amounting to as much as 12 per cent at 350°C. Above this temperature, the yields of both the ketone and aldehyde are reduced due to decomposition into gaseous products. Graph II shows the effect of temperature on the yields of these products.

Turning to a consideration of the high-temperature decomposition, it is seen that increasing quantities of water are eliminated and gaseous products are formed. Table X shows that at the lower temperatures over forty per cent of the gaseous products are unsaturated hydrocarbons other than ethylene, the remainder consisting mainly of carbon monoxide, carbon dioxide, and saturated hydrocarbons. As the temperature is increased, the percentage of unsaturates

GRAPH II



EFFECT OF TEMPERATURE ON THE YIELDS OF LIQUID PRODUCTS FROM BUTANEDIOL-2,3

Rate: 3 c.c./min.

○	Butanone-2
●	Isobutyraldehyde
◒	Cyclic Acetal

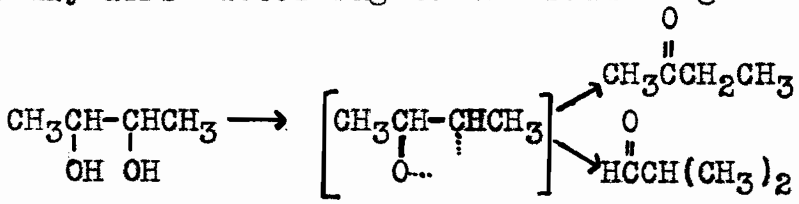
decreases, while increasing amounts of hydrogen, carbon monoxide, and ethylene are formed. Less carbon dioxide, however, is formed at the higher temperatures. The volume of the saturated hydrocarbons remains about the same above 550°C., while the ratio of methane to ethane increases greatly with increasing temperature. An increase in the feed-rate from 1 c.c. to 3 c.c. per minute is approximately the same as a decrease in temperature of 100 Centigrade degrees.

Butadiene yields are small. A slightly lower percentage in the gas evolved is found at the higher temperatures, but an increased decomposition causes the butadiene yield to rise with temperature. An increase in feed-rate increases the per cent composition of butadiene in the gas, but owing to a smaller evolution of this gas, the over-all yield remains approximately the same.

From Table XI, it is seen that the addition of water vapour greatly affects the course of the high-temperature decomposition. As expected, the volume of gaseous products is decreased in the water-vapour runs, owing to a decrease in catalyst contact time. On the other hand, the percentage of unsaturated hydrocarbons (other than ethylene) is greatly increased. At 700°C. and at a rate of 1 c.c. per minute, the gas evolved from a dry run analyzes for 20.6 per cent unsaturates, the addition of one volume of water increases this to 34.1 per cent, while the addition of two volumes gives 45 per cent. The butadiene content of the gas increases accordingly. The gas from the 700°C. dry run contains 4.4 per cent butadiene. When one volume of water is used, this increases to 7.7 per cent, and for two volumes to 24.0 per cent. The over-all butadiene yield is 6.7 per cent, 8.4 per cent and 14.9 per cent respectively. The highest yield obtained by the Northern Regional Research Laboratories with any catalyst was about 20 per cent. (14)

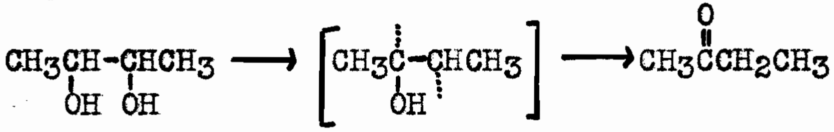
The mechanism of the dehydration process will now be considered. In the dehydration of butanediol-2,3, water may be eliminated in two ways. A molecule of water may be formed by the removal of a hydroxyl group and either a hydrogen atom from the second hydroxyl group or a hydrogen atom attached to the carbon atom containing the second hydroxyl group. In either case, a carbonyl type of compound will result. On the other hand, water may be eliminated between a hydroxyl group and a hydrogen from the terminal methyl group, resulting in the unsaturated alcohol, methyl vinyl carbinol. The removal of a second molecule of water in the same manner will produce butadiene.

In the low-temperature, non-gaseous runs, carbonyl compounds only are obtained, the main product being butanone-2 with small quantities of isobutyraldehyde. Both of these products may arise according to the following reaction.



$$CH_3\underset{OH}{\underset{|}{C}}H-\underset{OH}{\underset{|}{C}}HCH_3 \longrightarrow \left[CH_3\underset{O\cdots}{\underset{|}{C}}H-\underset{\vdots}{C}HCH_3\right] \begin{cases} \nearrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3 \\ \searrow H\overset{O}{\overset{\|}{C}}CH(CH_3)_2 \end{cases}$$

A water molecule is eliminated between one hydroxyl group and the hydrogen atom of the second hydroxyl group, this being followed by the migration of a hydrogen atom to form butanone-2, or by the migration of a methyl group to form isobutyraldehyde. The "migration aptitude" of hydrogen is known to be greater than that of a methyl radicle (100), which will explain the large proportion of ketone in the reaction product. On the other hand, butanone-2 may arise from a different mechanism.



$$CH_3\underset{OH}{CH}-\underset{OH}{CH}CH_3 \longrightarrow \left[CH_3\underset{OH}{C}-CHCH_3\right] \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$$

This is essentially a "vinyl dehydration". It is to be noted that butanone-2 only can be formed by this reaction.

Since considerable quantities of isobutyraldehyde are formed in the dehydration process, it would appear that the first mechanism is the correct one. The possibility must be recognized, however, that the two types of reaction may be going on simultaneously, the first producing both ketone and aldehyde, the second ketone alone. Nevertheless, if the "vinyl dehydration" reaction were to take place to any great extent, then the ratio of isobutyraldehyde to butanone-2 formed by the first reaction is greater than would be expected from the relative "migration aptitudes" of the hydrogen atom and the methyl radicle as observed in the rearrangement of other glycols. This is particularly evident at 350° C. where a 12.1 per cent yield of the aldehyde was obtained.

Further evidence against the "vinyl dehydration" mechanism is found by analogy with the decomposition of the corresponding diacetate over Morden bentonite. In addition to butadiene, butanone-2 and isobutyraldehyde were obtained in considerable quantities while unsaturated esters were present only in traces. These carbonyl compounds can only be formed by the elimination of acetic anhydride between the two acetate groups. In the absence of water causing hydrolysis, this anhydride was isolated. While this analogy to the dehydration of butanediol-2,3 may be open to criticism, in the writer's opinion, it is a more direct argument against vinyl dehydration than that furnished by Wallis (62) in a consideration of the rearrangement of phenolic ethers and alkylated anilines.

Whether the dehydration reaction involves the formation of free radicles or occurs through an electronic mechanism, as postulated by Whitmore for the liquid-phase reaction, is open to question. It might be added, however, that the concept of a slippage of atoms or groups without the existence at any time of an intermediate independent radicle may well apply to the rearrangement of butanediol-2,3 in the vapour phase over bentonite.

Turning now to a consideration of the high-temperature gaseous runs, the following question arises. Are the high-temperature decomposition products formed directly from the glycol, or are they formed through the intermediate formation of mono-dehydration products? In view of Wasson's results on the dehydration of ketones, it is possible that the small amount of butadiene in the gaseous products does not arise directly from the glycol, but from a dehydration of butanone-2 to methyl allene, followed by isomerization to butadiene.

$$CH_3CH_2COCH_3 \longrightarrow CH_3CH{=}C{=}CH_2$$
$$CH_3CH{=}C{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2$$

Consequently, the investigation was extended to a short study of the decomposition of butanone-2 over activated Morden bentonite. It was hoped that this work might assist in establishing the most favorable conditions for the dehydration of the glycol to butadiene, and also might assist in establishing the mechanism of the high-temperature decomposition.

The various conditions used in the butanone-2 decomposition and the analysis of the gaseous products are given in Table XIII. Liquid products were also analyzed and found to contain, besides unchanged butanone-2, considerable amounts of isomeric pentenes and hexenes. From these results, it is seen that bentonite does remove water from the ketone molecule. At 550°C. and at a feed-rate of 1 c.c. per min. as much as 0.5 mole of water was obtained per mole of butanone-2. Methyl allene could not be isolated, however, and butadiene is present only in very small amounts. The gaseous products contain a smaller percentage of unsaturated hydrocarbons than the gas evolved under similiar conditions in the case of the glycol, while larger quantities of carbon monoxide and saturated hydrocarbons are formed. Isobutylene is one of the major

TABLE XIII

DECOMPOSITION OF BUTANONE-2 OVER ACTIVATED MORDEN BENTONITE

Run No.	Furnace °C.	Rate c.c./min.	Ketone g.	Total Liquid Products g.	Organic Layer g.	Aqueous Layer g.	Vapour Products and loss g.	Total Gas l.
21	450	1	80.4	72.0	68.0	4.0	8.4	3.16
19	550	1	80.4	52.1	42.2	9.9	28.3	15.00
20	650	1	80.4	40.7	31.7	9.0	39.7	30.00
22	550	2.5	80.4	70.0	63.9	6.1	10.4	5.75
23	650	3	80.4	54.5	49.7	4.8	25.9	12.80
70	650	0.8plus 1.2H_2O	80.4 plus 122.0 H_2O	--	--	--	--	14.83

	General Gas Analysis in Volume Per cent									Butadiene Analysis	
Run No.	CO_2	CO	H_2	$CH_2=CH_2$	Iso-butene	Other Unsats. including Butadiene	Saturates Total	CH_4	C_2H_6	Volume %	Yield %
21	43.4	12.4	0.0	1.5	14.8	10.6	15.9	3.4	12.5	4.3	0.5
19	18.2	15.3	4.8	2.7	14.4	14.2	30.1	14.1	16.0	1.7	1.0
20	5.3	15.8	13.1	5.7	12.0	9.5	37.0	25.5	11.7	3.7	4.4
22	23.1	17.8	1.9	2.3	15.2	12.5	26.1	11.9	14.2	3.1	0.7
23	8.0	17.8	5.9	5.9	11.1	10.8	35.5	25.1	10.4	3.6	1.8
70	1.7	12.4	10.2	4.9	4.0	37.3	29.4	--	--	11.2	7.4

components of the unsaturated hydrocarbons.

Very little work has been done on the vapour-phase decomposition of butanone-2. Hurd (101) found that, under the influence of heat alone, the ketone forms small quantities of ketene and methyl ketene. Mitchell and Reid (97) studied the decomposition of butanone-2 over silica gel. They obtained high-boiling condensation products accompanied by considerable gas formation. This gas gave an analysis closely approximating that found by passing the ketone over bentonite in the present investigation.

Based on an analogy with Wasson's results with other ketones, and supported by the fact that a considerable amount of water was obtained in the liquid products, one may assume that one reaction involved in the decomposition of butanone-2 over bentonite is a dehydration to methyl allene (butadiene-1,2). That this does not isomerize to butadiene-1,3 is not surprising. Slobodin (102) has found that methyl allene, when passed over floridin at 245-330°C., yields a small amount of ethyl acetylene and only traces of butadiene. Furthermore, Hurd and Meinert (103) have found from a non-catalytic treatment of methyl allene at 500-550°C., that a complete decomposition is effected in 36 seconds, the decomposition products consisting of carbon, hydrogen, methane, ethane, propene, allenes, acetylenes, and liquids of a polymeric nature. This would account for the fact that methyl allene could not be isolated and only traces of butadiene were formed.

Other reactions appear to occur simultaneously with the dehydration reaction. These involve the formation of carbon monoxide, carbon dioxide, olefins including isobutylene, and large quantities of saturated hydrocarbons. Wasson's hypothesis, involving the intermediate formation of a ketene derivative followed by its decomposition to carbon monoxide and an olefin, does not provide an adequate explanation for the formation of these products, particularly for the large quantity of carbon dioxide, and the branched-chain olefin, isobutylene. A more complete investigation of the decomposition of butanone-2 is necessary before offering a mechanism for these changes.

Although the analysis of the gaseous products obtained from butanone-2 differs considerably from the analysis of the glycol gaseous products, it must be remembered that in the case of the glycol the decomposition occurs in the presence of one mole of water. That water can greatly increase the unsaturated hydrocarbon content of the gas at the expense of other components was shown clearly in the results obtained in the glycol water-vapour runs. Accordingly, a butanone-2 run (Run 70, Table XIII) was carried out in the presence of such a volume of water that the same dilution was realized as in the case of a glycol run carried out in the presence of one volume of water. It was found that both the total unsaturated content of the gas and the butadiene content compared favorably with that found in the case of this glycol water-vapour run. This would strongly indicate that at high temperatures the gaseous decomposition takes place through the intermediate mono-dehydration products.

It must be remembered that superimposed upon the decomposition of the intermediate butanone-2 in the glycol runs, a small amount of isobutyraldehyde is also undergoing decomposition. Nef (104) has shown that isobutyraldehyde at high temperatures decomposes to carbon dioxide, hydrogen, methane, ethane, ethylene, and propylene.

On the basis of these results, it would appear that the butadiene was formed through the intermediate ketone in both the dry-glycol and the water-glycol runs. The effect of water vapour in increasing the butadiene content of the gas is difficult to explain. Patents (105) have been taken out for the use of water vapour in reducing char formation on vapour-phase catalysts, thus maintaining their activity. Furthermore, it may be pointed out that because of its low molecular weight, a small weight of water greatly increases the volume of vapour passing over the catalyst, consequently decreasing catalyst contact time. It is probably by this latter effect that water increases the butadiene yield. The methyl allene formed from the intermediate ketone in the case of a dry glycol run decomposes almost entirely to other products. However, in the presence of water vapour, it is possible that the contact time is so decreased that part of the allene is not decomposed but rearranges to butadiene. Although it is known that at 300°C. over floridin this rearrangement occurs only to a slight extent, the course of the reaction may be entirely different at 650-700°C. over bentonite and in the presence of water vapour.

The results of this investigation on the direct dehydration of butanediol-2,3 over activated Morden bentonite confirm the work of the Northern Regional Laboratories and others in showing that this method cannot be used for the practical production of butadiene. On the other hand, it has been shown that excellent yields of butanone-2 may be obtained by a low-temperature dehydration of the glycol over bentonite. A yield of 85 per cent has been obtained and it is possible that this might be increased to as high as 90 per cent by working on a larger scale. A definite limitation in the yield is seen, however, in the formation of small quantities of isobutyraldehyde and the cyclic acetal.

This method for the conversion of butanediol-2,3 to butanone-2 has the advantage of an extremely cheap catalyst, low temperatures, and fast rates of through-put. Whether this method can be used for the industrial production of butanone-2 depends, in the writer's opinion, entirely upon the availability of the butanediol-2,3. Recent reports from the National Research Council indicate that this glycol can be produced cheaply and in large quantities by making use of our large wheat supplies. It is conceivable that by this method, Canada can manufacture large quantities of this very useful and, at present, relatively scarce material.

The Decomposition of Butanediol-2,3 Diacetate over Activated Morden Bentonite

Preparation of the Diacetate

At this stage of the investigation, an adequate supply of laevo butanediol-2,3 could not be obtained for the preparation of the laevo diacetate. Material was obtained, however, from the Heyden Chemical Corporation, New York, consisting of a mixture of the meso and dextro forms, the major portion being meso. Two methods were examined for the preparation of the diacetate. The first was a method reported by the Northern Regional Research Laboratories (14, 106) and consisted of the reaction of acetic acid and the glycol in the presence of a small amount of concentrated sulphuric acid. Isopropyl acetate was used as an entrainer liquid, and the water formed in the esterification process was removed continuously by azeotropic distillation. Upon fractionation, a constant boiling material was obtained with a high and varying refractive index. A saponification equivalent was determined according to the method of Redemann and Lucus (107) and found to be 97.1, while the theroetical value for the diacetate is 87.0. This, together with the high refractive index, indicated the presence of a considerable quantity of mono-acetate.

The second method, employing acetic anhydride, was essentially that described by Wilson and Lucas (96).

Forty-five grams of butanediol-2,3 was mixed with 117 grams of acetic anhydride and one to two drops of sulphuric acid was added. The temperature of the mixture rose very slowly over the course of five to ten minutes to 40-50°C. At this point, a violent reaction was found to occur, the temperature rising almost instantaneously to the boiling point of the anhydride, necessitating external cooling in an ice bath. This reaction subsided in a few minutes and the mixture was allowed to stand without further cooling. In some instances an initial heating to 40°C. was necessary in order to start the reaction. Several lots were treated in the above manner, combined, and allowed to stand for twenty-four hours. The material was then fractionated through a three-foot Whitmore-Fenske column, packed with 3/32 inch glass helices, under reduced pressure and a product boiling at 76°C. at 50 mm. was obtained in a yield of 88 per cent. This material had the following constants: b.p.$_{760}$ 192°C., d_4^{25}1.021, n_D^{25}1.4121 and a saponification equivalent of 87.1. Winstein and Wood (108) report the following physical constants for the pure meso isomer of butanediol-2,3 diacetate: d_4^{25}1.021, n_D^{25}1.4122. The theoretical saponification equivalent is 87.0.

Procedure

The horizontal-type catalysis furnace was used for the work on this compound carried out at the slow feed-rates, while for the faster feed-rates, the vertical-type furnace was employed. Pumice was first used as a heat-transfer medium in the preheater of the vertical furnace, having been found satisfactory for hydrocarbon studies in this University. In the case of the diacetate, however, it was found to be entirely unsatisfactory, causing extensive carbonization and the evolution of large volumes of hydrogen. Steel wool was then employed and gave satisfactory results.

Varying amounts of the catalyst were employed in the investigation of the diacetate. Before use, water was removed from the catalyst by a preliminary heating to 500°C. The procedure followed in the case of the diacetate runs carried out in the horizontal-type furnace was essentially that previously described for butanediol-2,3. For the work involving the vertical-type furnace, the following procedure was employed. The furnace temperature was first adjusted so that both thermocouples registered the desired temperature for the run. The diacetate was then passed into the catalyst tube from the graduated vessel B and, in the case of the water -vapour runs, water was passed into the tube from the vessel C. Shortly after the entry of the liquids into the catalyst tube, a drop in temperature was registered in the top thermocouple L. Additional heat was then supplied to the preheater element. This was so adjusted that the vapours entering the catalyst were at a temperature no lower than 30°C. below the desired run temperature. Care was taken, however, to prevent over-heating in the preheater zone of the furnace causing pre-cracking of the material before its entry into the catalyst. In the case of the very fast feed-rates, additional heat was also supplied to the lower heating elements in order to maintain the catalyst at the desired temperature. A fore-run of 25-35 c.c. was required in order to establish equilibrium conditions. Gas and liquid products were collected and measured as described in the investigation of butanediol-2,3.

The liquid products contained a large quantity of dissolved gas of high butadiene content. This was removed by heating the liquid to boiling under a reflux condenser connected to an aspirator bottle inverted over a water trough. The liquid was refluxed until gas was no longer evolved. This gas was measured and analyzed for butadiene content only. The liquid products were given a preliminary distillation and separated into a fraction distilling below 200°C. and a tarry residue. The distillate was then carefully fractionated in the small glass-helices column using the diacetate itself as an inert booster. When unchanged diacetate was present in the liquid products, it was determined by collecting fractions up to the boiling point of the ester and measuring the volume of residue remaining in the pot. The wire-helices column was used for the separation and identification of small and closely boiling components. The boiling point, density, and refractive index were determined for each component. When these constants did not check closely with the literature values, derivatives were formed for further identification. The gaseous products evolved in the catalysis runs were analyzed in the Bone and Wheeler apparatus. A separate analysis was made for butadiene content.

Results and Discussion

The conditions of each run and the amount of liquid and gaseous products obtained are given in Table XIV. This tabulation includes the dry runs using both the horizontal and vertical-type furnace, as well as certain runs carried out in the presence of water vapour. Liquid products are expressed as the net weight after the removal of the dissolved gases. This gas volume is added to the volume of gas evolved to give the total gas produced in each run.

The analysis of liquid products expressed in per cent composition is given in Table XV. Eight fractions were obtained in addition to a small amount of tarry residue remaining after the preliminary distillation. Fraction 1, boiling at 54-58°C., consisted mainly of acetone which was identified by its physical constants and by the preparation of a derivative, dibenzylidene acetone. Fraction 2, distilling between 62-68°C. and present only in traces, was identified as isobutyraldehyde by the formation of a 2,4-dinitrophenylhydrazone. Fraction 3, distilling at 71-74°C., was an azeotropic mixture of butanone-2 and water. This azeotrope contains 33 mole per cent (10 per cent by weight) of water and has a boiling point of 73.5°C. (109).

TABLE XIV

DECOMPOSITION OF BUTANEDIOL-2,3 DIACETATE OVER ACTIVATED MORDEN BENTONITE

Run No.	Catalyst g.	Furnace °C.	Rate c.c. /min.	Diacetate g.	Net Liquid Products g.	Vapour Products and loss g.	Gas Evolved l.	Gas in liq. Products l.	Total Gas l.
Horizontal Glass Furnace									
26	50	400	3.6	100	81.5	18.5	5.03	3.0	8.03
25	50	450	3.6	100	69.3	30.7	12.65	1.5	14.15
24	50	450	1.0	100	56.3	43.7	23.00	0.5	23.50
Vertical Iron Furnace									
39	50	450	6.0	100	84.1	15.9	5.83	4.10	9.93
38	50	500	10.0	100	73.9	26.1	8.00	3.55	11.55
35	90	450	6.0	100	73.5	26.5	11.25	2.75	14.00
34	90	490	10.0	100	70.9	29.1	13.75	1.6	15.35
33	90	500	6.0	100	46.1	23.9	29.58	0.45	30.03
Water Vapour Runs using Iron Furnace									
36	90	500	6.0[a]	100 plus 92 H_2O	172.4	19.6	11.00		11.00
37	90	500	2.0[a]	100 plus 102 H_2O	165.2	36.8	18.00		18.00

a. This is total rate including diacetate and water.

TABLE XV

ANALYSIS OF LIQUID PRODUCTS FROM BUTANEDIOL-2, 3 DIACETATE EXPRESSED AS PER CENT COMPOSITION

RUN No.	TOTAL LIQUID g.	1 54-58°C. Acetone %	2 62-68°C. Isobutyraldehyde %	3 72-75°C. Butanone Azeotrope %	4 77-81°C. Butanone %	5 90-110°C. Water %	Organic Layer %	6 116-120°C. Acetic Acid %	7 137-140°C. Acetic Anhydride %	8 187-192°C. Unchanged Diacetate %	9 Residue %
Horizontal Glass Furnace											
26	81.5	4.0	0.9	1.3	12.8	-	1.9	56.0	1.9	17.4	3.8
25	69.3	5.8	1.2	17.0	1.6	-	2.2	60.0	-	9.4	2.8
24	56.5	7.1	1.2	22.4	-	7.5	3.0	54.3	-	-	4.4
Vertical Iron Furnace											
39	84.1	2.4	0.8	-	11.2	-	1.8	63.8	4.6	13.0	2.4
38	73.9	3.0	1.3	5.0	4.6	-	2.1	77.1	-	4.2	2.7
35	73.5	5.9	1.4	4.7	11.0	-	2.5	67.9	-	3.8	2.8
34	70.9	6.2	1.2	20.0	-	-	2.2	66.7	-	-	3.7
33	46.1	11.2	1.8	16.6	-	20.2	5.1	39.8	-	-	5.4
Water Vapour Runs Using Iron Furnace											
36	172.4	1.2	0.9	10.7	-	50.3	0.3	34.5	-	-	2.1
37	165.2	1.9	0.6	9.2	-	59.2	-	28.1	-	-	0.9

Fraction 4, obtained only in the cases in which all the water in the liquid products was removed in Fraction 3, distilled at 77-81°C. and consisted of butanone-2. This ketone, from both Fractions 3 and 4, was identified by its physical constants. Fraction 5, boiling over a continuous range from 90-110°C., consisted of two layers in the case of runs in which the formation of water was large. For those runs in which all the water was removed in the azeotropic mixture, this fraction consisted of one phase only. Repeated fractionation failed to isolate any single component, but the boiling point range and the odor of the material indicated that it consisted of a mixture of unsaturated esters. Fraction 6, the main fraction of the liquid products, distilled at 116-120°C. and was identified by its physical constants as acetic acid. Fraction 7, obtained only in the two runs in which no water was formed in the reaction, distilled at 137-139°C. and was acetic anhydride. This compound was identified by its physical constants and by the formation of a derivative, acetanilide. Fraction 8, distilling at 187-192°C., was unchanged butanediol-2,3 diacetate.

In Table XVI, the major liquid components are expressed as per cent of the theoretical yield in order to show more clearly the effect of temperature, feed-rates, and the amount of catalyst. The ratio of the yields of butadiene to butanone-2 are also given. This ratio will receive further consideration later.

TABLE XVI

YIELD OF PRODUCTS FROM BUTANEDIOL-2,3 DIACETATE RUNS

Run No.	Catalyst g.	Furnace °C.	Rate c.c./min.	Acetone as % Yield	Acetic Acid as % Yield	Butanone-2 as % Yield	Butadiene as % Yield	Ratio of Butadiene to Butanone-2
Horizontal Glass Furnace								
26	50	400	3.6	9.6	65.0	27.0	35.6	1.32
25	50	450	3.6	11.8	59.1	27.4	34.3	1.25
24	50	450	1.0	11.8	43.6	26.6	25.7	0.96
Vertical Iron Furnace								
39	50	450	6.0	5.9	76.2	22.3	47.3	2.12
38	50	500	10.0	6.5	81.0	15.8	57.5	3.64
35	90	450	6.0	12.8	70.8	24.8	49.9	2.01
34	90	490	10.0	13.0	67.2	29.9	47.1	1.57
33	90	500	6.0	15.2	30.0	16.2	35.3	2.18
Water Vapour Runs using Iron Furnace								
36	90	500	6.0	6.1	84.5	38.8	30.4	0.78
37	90	500	2.0	9.2	66.0	32.1	24.7	0.77

The analysis of the gaseous products in volume per cent is given in Table XVII. From the absorption analysis, it is seen that the unsaturated hydrocarbons consist mainly of butadiene and isobutylene. A preparation and fractionation of the olefin dibromides was not attempted. It must be pointed out that while a general gas analysis was determined for the gas evolved only, the volume per cent of butadiene expressed in Table XVII includes the butadiene content of both the gas evolved and the gas dissolved in the liquid products. The dissolved gas has a very high butadiene content. Consequently, in runs in which the amount of dissolved gas was large, the percentage of butadiene expressed in this table is larger than the value given for the total olefin content of the gas.

The physical constants of the products obtained and the derivatives formed in this investigation, together with the literature values, are found in Table XVIII.

From these results, it is seen that variations in temperature, feed-rates, and the amount of catalyst greatly affected the course of the reaction. Under the more drastic conditions of higher temperatures, lower feed-rates, and with larger amounts of catalyst, the percentage of butanone-2 in the liquid products was increased, as shown in Table XV. This percentage is calculated from the azeotropic fraction and the pure butanone-2 fraction. The effect of temperature is seen by comparing Runs 26 and 25. Both runs were carried

TABLE XVII

ANALYSIS OF GASEOUS PRODUCTS FROM BUTANEDIOL-2,3 DIACETATE RUNS

	General Gas Analysis in Volume Per cent							Butadiene Analysis	
Run No.	CO_2	CO	H_2	$CH_2=CH_2$	Iso-Butene	Other Unsats.Incl. Butadiene	Saturated Hydro-carbons	Volume %	Yield %
Horizontal Glass Furnace									
26	32.2	7.0	0.0	0.0	3.0	51.1	6.3	58.1	35.6
25	23.8	21.4	0.0	0.0	10.3	30.7	13.5	31.7	34.3
24	28.6	22.9	0.2	0.8	12.3	19.2	14.9	14.3	25.7
Vertical Iron Furnace									
39	21.6	11.7	0.0	0.4	1.2	53.2	11.9	62.4	47.3
38	20.0	8.2	0.0	0.2	1.2	60.4	10.0	65.2	57.5
35	22.9	14.1	0.0	0.6	0.9	50.8	9.5	46.7	49.9
34	22.5	18.0	0.0	0.4	4.0	43.2	9.8	40.2	47.1
33	21.6	28.6	0.4	0.8	4.5	24.9	19.5	15.4	35.3
Water Vapour Runs using Iron Furnace									
36	13.7	20.0	5.2	0.9		47.2	11.9	36.2	30.4
37	16.9	23.2	13.7	1.0		29.7	14.3	18.1	24.7

TABLE XVIII

IDENTIFICATION OF PRODUCTS FROM THE DECOMPOSITION OF BUTANEDIOL-2,3 DIACETATE

Compound		Boiling Point °C.	Density d_4^{20}	Ref. Index n_D^{20}	Deriv. Melt. Point °C.
Acetone	Given	56.5	0.792	1.3592	
	Found	56-57	0.794	1.3602	
Dibenzylidene acetone	Given				111-112
	Found				111-112
Butanone-2	Given	79.6	0.804	1.3804$^{(15.9)}$	
	Found	79.6	0.804	1.3807$^{(15.9)}$	
Isobutyraldehyde 2,4-dinitrophenylhydrazone	Given				183
	Found				182-183
Water	Given	100	0.998	1.3333	
	Found	100	0.998	1.3343	
Acetic acid	Given	118.1	1.049	1.3718	
	Found	117-118	1.046	1.3719	
Acetic anhydride	Given	140		1.3904	
	Found	137-139		1.3907	
Acetanilide	Given				114
	Found				114-115
Butanediol diacetate	Given	---	1.021$^{(25)}$	1.4122$^{(25)}$	
	Found	191.5	1.021$^{(25)}$	1.4121$^{(25)}$	
Tetrabromobutane	Given				118-119
	Found				117-118

out using 50 grams of catalyst and at a feed-rate of 3.6 c.c. per min. Run 26, at a temperature of 400°C., yielded a liquid product containing 14 per cent butanone-2; while Run 25, at a temperature of 450°C., gave a product containing 16.9 per cent butanone-2. The effect of decreasing feed-rates is seen by a comparison of Runs 39, 25 and 24, which were all carried out using 50 grams of catalyst and at a temperature of 450°C. Run 39, at a feed-rate of 6 c.c. per min., gave 11.2 per cent butanone-2; Run 25, at 3.6 c.c. per min., gave 16.9 per cent; while Run 24, at 1 c.c. per min., yielded 20.4 per cent butanone-2 in the liquid products.

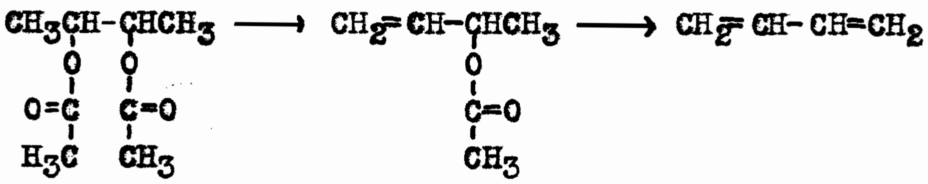
The effect of increasing the amount of catalyst is seen from Runs 39 and 35. Each run was carried out at 450°C. and at a feed-rate of 6 c.c. per minute. Run 39, using 50 grams of catalyst, gave 11.2 per cent butanone-2, while Run 35, using 90 grams of catalyst, gave 15.3 per cent ketone. The same effect is seen by comparing Runs 38 and 34 which were carried out at 500°C. and at 10 c.c. per minute. The former, using 50 grams of catalyst, gave 9.1 per cent butanone-2 in the liquid products; the latter, using 90 grams of catalyst, gave 18.0 per cent. The same trends are seen from Table XVI in which butanone-2 is expressed as percentage yield. Some discrepancy is seen in the case of the 500°C. runs due to extensive decomposition of the ketone into gaseous products.

A further examination of these runs at various conditions of temperature, feed-rates and catalyst shows that under the more drastic conditions increasing amounts of acetone and water were also formed. On the other hand, under milder conditions, a larger per cent (both per cent composition and per cent yield) of acetic acid was obtained. This was to be expected since, under the more drastic conditions, a greater decomposition of the acid into acetone and gaseous products occurred. It was only under extremely mild conditions that acetic anhydride and unchanged diacetate were obtained. The addition of water vapour, on the other hand, increased the yield of butanone-2, while acetic acid was also increased at the expense of the acetone yield.

Turning now to a consideration of the gaseous products as shown in Table XVII, it is seen that the effect of varying conditions was as pronounced as in the case of the liquid products. The unsaturated hydrocarbon content of the gaseous products was greatest under the milder conditions, namely, the lower temperatures, faster feed-rates, and smaller amounts of catalyst. Furthermore, under these conditions, the unsaturates contained the smallest percentage of isobutylene and the largest percentage of butadiene. The amounts of carbon monoxide and saturated hydrocarbons, on the other hand, were greatest under the more drastic conditions.

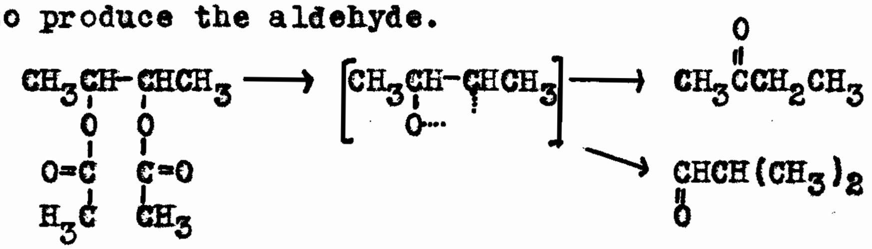
A very significant point is demonstrated by the ratio of the percentage yield of butadiene to that of butanone-2 under varying conditions as shown in Table XVI. It has been shown above that under the milder conditions of temperature, rate and catalyst, the highest yields of butadiene and the lowest yields of butanone-2 were obtained. Consequently the ratio of butadiene to butanone-2 was greatest under these conditions. Expressed differently, as the severity of the reaction conditions was increased butanone-2 was formed at the expense of butadiene. One exception to this is found in the case of Run 33. In this run, the conditions were so severe that a large portion of the ketone was decomposed to gaseous products, thus increasing the ratio even though the yield of butadiene was extremely small. From these results, it would appear that the decomposition of butanediol-2,3 diacetate over Morden bentonite involves two competing reactions, the first producing butadiene and the second producing the carbonyl compounds, butanone-2 and isobutyraldehyde.

The effect of Morden bentonite on the decomposition of the diacetate is very surprising. The results of the investigation of the Northern Regional Research Laboratories (14) and the Research Laboratories of Joseph E. Seagram (16) have shown that the non-catalytic pyrolysis of the diacetate produces butadiene in yields of 80-90 per cent at temperatures above 500°C. Below this temperature, considerable quantities of unsaturated esters, in particular the acetate of methyl vinyl carbinol, are formed. Carbonyl compounds, on the other hand, are not obtained. The course of the pyrogenic reaction can be expressed as follows:



$$\underset{\underset{\underset{H_3C}{|}}{O=\overset{|}{C}}}{\overset{|}{O}}\!\!\!\!\!\!\!\!CH_3CH-\underset{\underset{\underset{CH_3}{|}}{\overset{|}{C}=O}}{\overset{|}{O}}\!\!\!\!CHCH_3 \longrightarrow CH_2{=}CH-\underset{\underset{\underset{CH_3}{|}}{\overset{|}{C}=O}}{\overset{|}{O}}\!\!\!\!CHCH_3 \longrightarrow CH_2{=}CH-CH{=}CH_2$$

Under the influence of Morden bentonite, another reaction occurs involving the formation of butanone-2 and isobutyraldehyde. This reaction can only take place by the elimination of acetic anhydride, followed by the migration of a hydrogen atom to produce the ketone, or of a methyl group to produce the aldehyde.



$$CH_3CH(OCOCH_3)-CH(OCOCH_3)CH_3 \longrightarrow \left[CH_3\underset{O\cdots}{CH}-\dot{C}HCH_3\right] \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3$$
$$\searrow \underset{\underset{O}{\|}}{C}HCH(CH_3)_2$$

In the absence of water causing hydrolysis acetic anhydride was isolated. It is interesting to note that Denivelle (12) obtained 2,3-butylene oxide and butanone-2 by a decomposition of the diacetate over calcium oxide.

In the case of the non-catalytic decomposition, considerable quantities of the unsaturated esters were obtained even at temperatures as high as 500°C. The Northern Regional Research Laboratories obtained an 80 per cent yield of unsaturated esters at 450°C., and even at 500°C. as much as 20 per cent of these esters remained unconverted to butadiene. From the results of the present investigation it would appear that bentonite is a catalyst for the removal of acetate groups, since it was only at 400°C. and at the faster feed-rates at 450°C. that unchanged diacetate was obtained. Under all conditions only traces of the unsaturated esters could be isolated. Since it was found that a higher yield of butadiene relative to butanone-2 could be obtained at the lower temperatures, it was hoped that this catalyst would yield butadiene with good conversion at temperatures much lower than the pyrogenic reaction. However, before the over-all butadiene yield reached 60 per cent, considerable quantities of unchanged diacetate were recovered, and the effect of an increase in the ratio of the diolefin to carbonyl compounds was counteracted by the effect of decreasing conversions. Thus in Run 39, carried out at 450°C. at a feed-rate of 6 c.c. per minute and 50 grams of catalyst, the butadiene content in the gas was 62.4 per cent, while the over-all yield of the diolefin was reduced to 47.3 per cent because of incomplete conversion of the diacetate. A reduction in feed-rates at these lower temperatures increased the yield of butanone-2.

The products other than butadiene, butanone-2 and isobutyraldehyde can easily be explained. Acetic acid results from the reaction producing butadiene and also by the hydrolysis of the acetic anhydride formed in the ketone-aldehyde producing reaction. The acetic acid then undergoes two reactions. The major reaction involves a cracking to methane and carbon dioxide.

$$CH_3CO_2H \longrightarrow CH_4 + CO_2$$

This is confirmed by the large amount of carbon dioxide and saturated hydrocarbons present in the gaseous products. A minor reaction involves the formation of acetone from two molecules of the acid.

$$2CH_3CO_2H \longrightarrow CH_3COCH_3 + CO_2 + H_2O$$

The formation of carbon monoxide and isobutylene results, apparently, through the same reaction which accounts for their formation in the high temperature decomposition of butanediol-2,3. That is, they arise from the decomposition of intermediate carbonyl compounds, or from the decomposition of some unstable fragment intermediate in the formation of these carbonyl compounds.

Since the effect of increased feed-rates (decreased catalyst contact time) was to increase the yield of butadiene relative to butanone-2, one would expect that the added water in the water-vapour runs would greatly increase this ratio. Actually the butanone-2 yield was increased at the expense of butadiene. This indicates that the diacetate upon entering the furnace in the presence of water vapour underwent a partial hydrolysis to butanediol-2,3 before undergoing further decomposition.

The Dehydration of Butanediol-1,4 over Activated Morden Bentonite

Preparation of Butanediol-1,4

Butanediol-1,4 was not available commercially and had to be synthesized for the present catalysis study. It was prepared by the high-pressure hydrogenation of diethyl succinate. This ester was prepared by a method similiar to that described in the literature for the preparation of diethyl oxalate (110). It involved the prolonged heating of a mixture of succinic acid and ethyl alcohol. The water formed in the esterification reaction was removed continuously using carbon tetrachloride as an entrainer liquid. The ester was carefully fractionated before being used in the hydrogenation reaction, and the pure material gave the following physical constants: b.p. 108°C. at 13 mm., and n_D^{20} 1.4199.

Diethyl succinate was hydrogenated over copper-chromium oxide according to a method described by Adkins (111).* Three moles (523 g.) of pure ester and hydrogen were allowed to react under a pressure of approximately 300 atm. at 250°C. for one-half hour over 30 g. of copper-chromium oxide. The reaction mixture was then allowed to cool under the pressure of hydrogen. The catalyst was removed by filtration and the

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* Grateful acknowledgement is hereby made to Dr. J. M. Pepper of this University who carried out the hydrogenation reaction.

ethyl alcohol formed in the reaction removed by a rapid fractionation. Very careful fractionation of the high boiling material through a three-foot Stedman column gave 7.5 g. of butyl alcohol, 14 g. of butyralactone, 5 g. of unchanged diethyl succinate, and 200 g. (80% yield) of butanediol-1,4. It was found the higher the pressure of hydrogen used and the shorter the reaction time, the smaller were the quantities of by-products formed. The physical constants of the purified material were: b.p.$_{760}$ 230°C., d_4^{20}1.016 and n_D^{20}1.4459. The following constants have been reported in the literature: b.p.$_{760}$ 230°C., d_4^{20}1.016, n_D^{20}1.4467 (112).

Procedure

The vertical-type catalysis furnace was used in the investigation of the dehydration of butanediol-1,4. One hundred grams of activated Morden bentonite was used for each run. The procedure employed was essentially the same as that used for the vertical-furnace runs in the study of butanediol-2,3 diacetate. In the case of the low-temperature runs with butanediol-1,4, particularly those carried out in the proximity of the boiling point, the temperature of the preheater had to be carefully adjusted so that the vapours entering the catalysts were at a temperature no higher than the desired run temperature. Furthermore, the preheater temperature had to be held constant throughout the course of a run in order to maintain a constant hold-up of liquid glycol in the preheater. In the case of the water-vapour runs, the glycol and water, being miscible, were passed into the catalysis tube together from vessel B. The gas evolved at the higher temperatures was passed through a water trap for the absorption of gaseous formaldehyde escaping entrainment in the liquid products.

The liquid products obtained from the low-temperature runs consisted of one phase only and mainly of a mixture of tetrahydrofuran and water. By salting-out with sodium chloride, the liquid products were separated into two layers. The mixture was cooled to -40°C. whereby the salt solution froze to a solid mass and the organic layer was then decanted. This served to minimize the mutual solubility of the two layers. On melting, the salt solution was extracted with small portions of diethyl ether in order to remove the remaining organic material. The ether extracts were combined with the organic layer and dried over sodium sulphate. The drying agent was removed by filtration and washed with a little anhydrous ether. These washings were combined with the filtrate. The ether solution of the organic products was given preliminary distillation and separated into a fraction distilling below 130°C. and a small amount of high boiling residue. The distillate was then carefully fractionated in the small glass helices column using isoamyl acetate, b.p. 142.5°C., as an inert booster. Employing this technique, it was found that the total losses involved in all operations did not exceed one to two grams of the organic liquid products.

In the case of the high-temperature runs, 400°C. and higher, the liquid products consisted of two layers. A weighed sample was taken from each layer for formaldehyde determination. The aqueous layer was salted out and extracted with ether, while the ethereal solution of the organic layer was dried followed by a preliminary distillation. In this distillation, the product was separated into three fractions, the major fraction distilling below 120°C., a fraction between 120-200°C., and some tarry residue. The first fraction was fractionated in the glass-helices column. Identification of liquid products was made by physical constants and by the formation of derivatives.

The gaseous products were analyzed in the Bone and Wheeler Apparatus. A separate analysis was made for butadiene content. For the determination of individual olefins, a typical run was made in which the gaseous products were passed into liquid bromine. The resulting dibromides were fractionated under reduced pressure as previously described.

The formaldehyde present in the liquid products from the high-temperature runs was detected by the resorcinol test. Further identification was made by the preparation of a derivative, methylene-di-β-naphthol. A quantitative determination of formaldehyde was made of/the organic layer, the aqueous layer and of the water in the absorption trap. The method employed was the hydrogen peroxide method described by Haywood and Smith (113).

Results and Discussion

The various temperatures and feed-rates at which the dehydration of butanediol-1,4 was investigated, together with the amounts of liquid and gaseous products obtained are given in Table XIX. In this table, the runs are divided into low-temperature non-gaseous, high-temperature gaseous and high-temperature water-vapour runs.

The analysis of the organic liquid products expressed in per cent composition is given in Table XX. In the low-temperature runs, following the removal of diethyl ether, three fractions were obtained. Fraction 2, the major fraction and boiling at 64-66°C., was practically pure tetrahydrofuran identified by its physical constants. Fraction 1, boiling below 64°C., and Fraction 3, boiling between 67-130°C., were present only to the extent of two to three per cent. The lower boiling fraction was undoubtedly a mixture of diethyl ether and tetrahydrofuran. The higher boiling fraction was not identified.

Four fractions, in addition to a considerable amount of residue, were obtained from the liquid products of the high-temperature runs. Fraction 1, boiling below 64°C. was present to an appreciable extent only in the case of the 500°C. dry run. Even in this run only one gram was obtained which was not identified. Fraction 2, distilling between 64-66°C.,was tetrahydrofuran. Fraction 3, distilling between 74-76°C., was n-butyraldehyde, identified by its boiling point and by

TABLE XIX

DEHYDRATION OF BUTANEDIOL-1,4 OVER ACTIVATED MORDEN BENTONITE

Run No.	Furnace °C.	Rate c.c./min.	Glycol g.	Total Liquid Products-g.	Organic[b] Layer-g.	Aqueous[b] Layer-g.	Vapour Products and loss-g.	Total Gas-l.
Low-temperature Non-gaseous Runs								
42	250	1	60	59.6	47.8	11.8	0.4	---
43	250	3	60	60.0	48.3	11.7	0.0	---
46	300	1	60	59.7	48.3	11.4	0.3	---
41	300	3	60	59.7	48.5	11.2	0.3	---
High-temperature Gaseous Runs								
45	400	1	60	56.2	42.8	13.4	3.8	.73
47	450	1	60	50.4	34.9	15.5	9.6	5.50
44	500	1	60	30.7	9.3	20.6	29.3	12.29

Water Vapour Runs

Run No.	Furnace °C.	Rate[a] c.c./min.	Glycol g.	Water g.	Total Gas-l.
48	500	2	60	60	8.75
49	500	3	60	120	13.50

[a] This is the total rate including glycol and water.

[b] The amount of aqueous layer was obtained by weighing this layer after extraction and substracting the weight of salt added during the salting-out process. The amount of organic layer was the difference between the amount of aqueous layer and the total liquid products.

TABLE XX

ANALYSIS OF ORGANIC LIQUID PRODUCTS FROM BUTANEDIOL-1,4 DRY RUNS

Low-temperature Non-gaseous Runs

		Per cent Composition				Per cent Yield
Run No.	Org.Prod.[a] in g.	1. -64°C. in %	2. 64-66°C. in %	3. 67-130°C. in %	4. Residue in %	Apparent Yield of Tetrahydrofuran[b]
42	46.7	0.6	96.7	1.8	0.9	92.8
43	46.6	0.6	96.5	1.9	1.0	92.1
46	46.7	0.7	96.9	1.4	1.0	92.7
41	46.2	0.7	96.3	1.8	1.2	91.4

High-temperature Gaseous Runs

Run No.	Org.Prod. in g.	1. -64°C. in %	2. 64-66°C. in %	3. 74-76°C. in %	4. 76-200°C. in %	5. Residue in %	Apparent Yield of Tetrahydrofuran
45	40.5	0.9	88.5	3.0	4.6	3.0	73.4
47	32.7	---	80.8	2.3	12.7	4.3	54.1
44	8.8	12.5	16.6	7.8	38.6	24.5	3.1

a. This column gives the total weight of the organic fractions obtained after fractionation.

b. This yield is calculated from the actual weight of the tetrahydrofuran obtained after fractionation without any allowance for losses in drying and distillation.

the preparation of the 2,4-dinitrophenylhydrazone. Fraction 4, distilling over a continuous range from 76-200 C., could not be separated into any single component even by the most careful fractionation in the wire-helices column. It was thought to consist of a complex mixture of condensation products of formaldehyde and tetrahydrofuran.

Table XX also gives the apparent yield of tetrahydrofuran. This yield is calculated from the actual weight of tetrahydrofuran obtained after fractionation and does not take into account any losses which occur during the working up of the liquid products. Since in the low-temperature runs, no gas was formed and no unchanged glycol could be detected, it would appear that for these runs the value expressing the per cent tetrahydrofuran in the organic liquid products is a closer approximation to the true yield than is the "apparent yield".

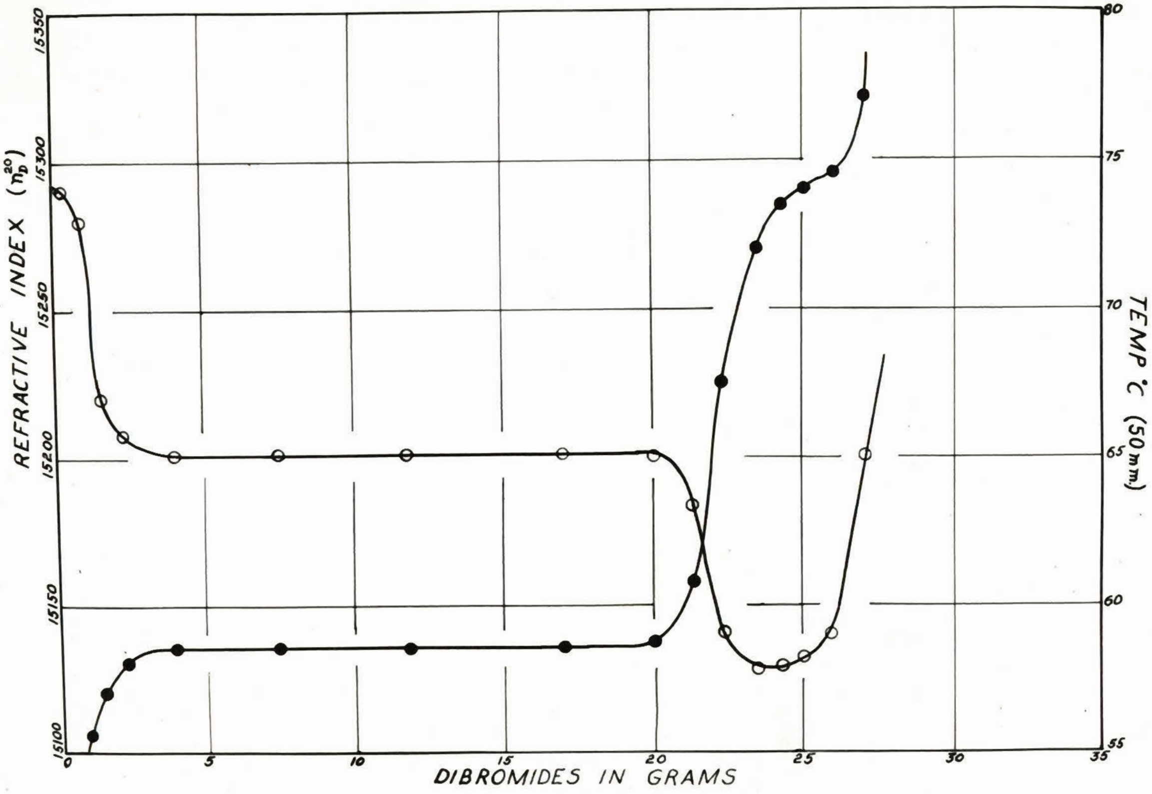
The analysis of the gaseous products expressed in volume per cent and the per cent yield of butadiene are given in Table XXI. The results of the fractionation of the olefin dibromides, formed from the gaseous products evolved in Run 44, are given in Graph III. The major fraction, distilling at 58.5° C. at 50 mm. and with a refractive index of n_D^{20}1.5200, was 1,2-dibromopropane. A small amount of meso and racemic 2,3-dibromobutanes was also found, indicated by a rise in the temperature curve to 73° C. and a drop in the refractive index curve to n_D^{20}1.5125 where small flats were obtained. From this graph, it can be estimated that the olefins contained

TABLE XXI

ANALYSIS OF GASEOUS PRODUCTS FROM BUTANEDIOL-1,4 RUNS

General Gas Analysis in Volume Per cent								Butadiene Analysis	
Run No.	CO_2	CO	H_2	$CH_2{:}CH_2$	Iso-Butene	Other Unsats. incl. Butadiene	Saturated Hydro-Carbons	% in Gas	% Yield
Dry Runs									
45	2.9	6.2	5.7	2.3	0.0	71.0	11.9	7.3	0.2
47	8.1	7.1	12.0	1.6	0.0	62.8	8.0	8.9	1.9
44	3.6	13.6	6.5	2.7	0.0	60.7	11.0	2.0	1.0
Water Vapour Runs									
48	4.1	5.1	6.8	1.0	0.0	77.7	3.9	13.0	4.5
49	5.2	4.8	9.3	1.0	0.0	75.9	2.8	15.1	8.0

GRAPH III



FRACTIONATION OF THE OLEFIN DIBROMIDES FROM BUTANEDIOL-1,4

○ Refractive Index Curve

● Boiling Point Curve

75-80 per cent propene, the remainder consisting mainly of butenes.

The physical constants of the products obtained and the derivatives formed in this investigation, together with the literature values are found in Table XXII.

Table XXIII gives the results of the formaldehyde determinations for the high-temperature runs. The theroetical amount of formaldehyde based on the amount of propene formed is also given.

TABLE XXIII

FORMALDEHYDE ANALYSIS

Dry Runs

Run No.	Amount of CH_2O found g.	Theoretical Amount of CH_2O g.[a]
45	1.3	0.6
47	2.9	3.7
44	2.3	8.0
Water Runs		
48	6.4	7.3
49	6.5	11.0

a. This was calculated assuming that the olefins contain 80 per cent propene.

A small amount of n-butyraldehyde in the organic layer was found to give high results for the formaldehyde analysis of the dry runs. In the case of the water runs, however, the error due to n-butyraldehyde was small since almost all the formaldehyde was in the aqueous layer. The significance of

TABLE XXII

IDENTIFICATION OF PRODUCTS FROM THE DEHYDRATION OF BUTANEDIOL-1,4

Compound		Boiling Point °C.	Density d_4^{20}	Ref. Index n_D^{20}	Deriv. Melt. Point °C.
Tetrahydrofuran	Given	65.6-65.8	0.888	1.4073	
	Found	65.7	0.887	1.4073	
n-Butyraldehyde	Given	75			
	Found	74-76			
2,3-Dinitrophenyl-hydrazone	Given				122
	Found				122.5-123.5[a].
Water	Given	100	0.998	1.3333	
	Found	100	0.998	1.3340	
1,2-Dibromopropane	Given	141.6	1.933	1.5203	
	Found	141-142	1.929	1.5201	
2,3-Dibromobutane rac.	Given	73/50 mm.		1.5116	
meso	Given	77/50 mm.		1.5147	
	Found	73-75/50 mm.		1.5125-1.5150	
Tetrabromobutane	Given				118-119
	Found				117-118
Formaldehyde methylene-di-β-naphthol	Given				189-192
	Found				190-192.5

a. Mixed melting point was made.

of these results will be discussed later.

From a consideration of the results obtained in the low-temperature runs, it is seen that one mole of water was removed per mole of glycol and practically theoretical yields of the mono-dehydration product, tetrahydrofuran, were obtained. Even at a temperature of 250°C. (only 20°C. above the boiling point of the glycol) no unchanged butanediol-1,4 was recovered and tetrahydrofuran was obtained in a 93 per cent yield.

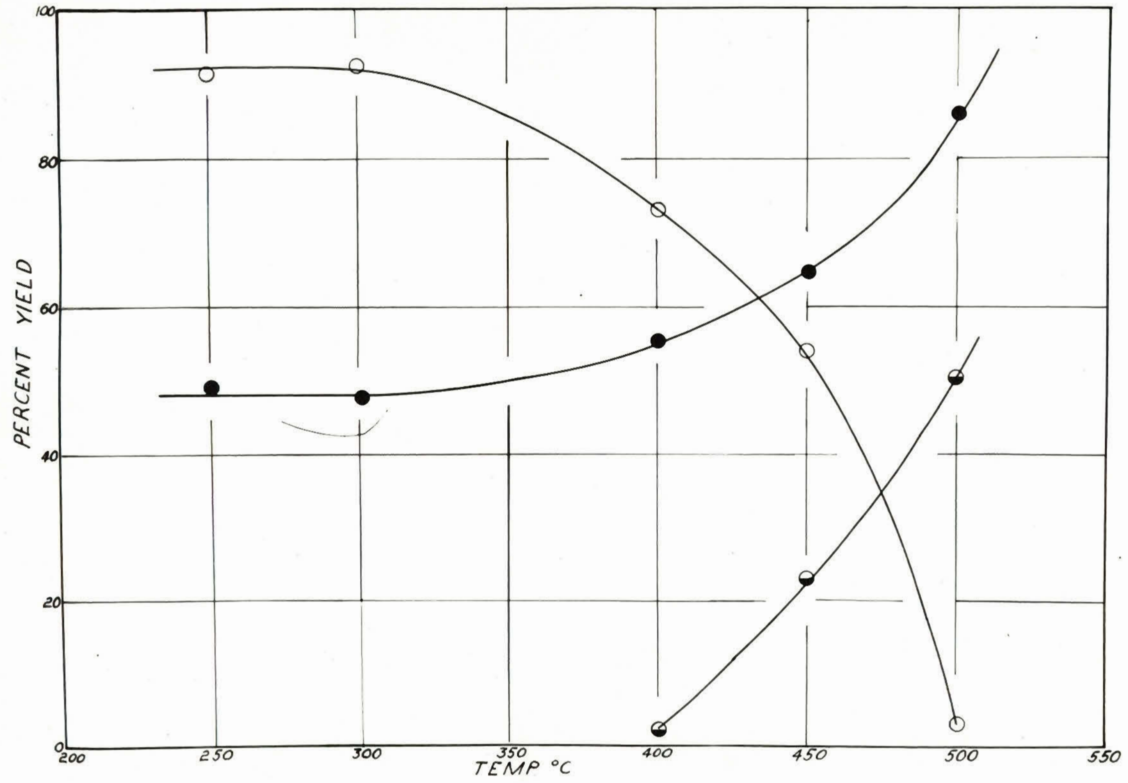
These results compare favorably with those obtained by other workers (24) for the dehydration of butanediol-1,4 to tetrahydrofuran in the presence of various catalysts. It would appear that the dehydration over Morden bentonite is as efficient and takes place at as low an operating temperature as for any catalyst previously investigated. Activated alumina is as efficient as bentonite at the low-temperatures but is more expensive. Catalysts such as calcium chloride and primary calcium phosphate require much higher temperatures. Morden bentonite, on the other hand, combines the features of a very cheap and readily available catalyst and a low temperature of dehydration.

The results of the higher temperature work show definitely that Morden bentonite cannot be used as a catalyst for the production of butadiene from butanediol-1,4. This was not unexpected since basic catalysts have previously been shown to be unsatisfactory for this reaction (24). From Table XIX it is seen that little decomposition into gaseous products occurred until a temperature of 450°C. was reached, while considerable quantities of gas were obtained only in the case of Run 44 carried out at 500°C. The amount of water removed in the reaction increased with temperature, however, while the yield of organic liquid products was considerably decreased. From the results obtained in the water-vapour runs, it is seen that one volume of water decreased the amount of gaseous decomposition, possibly through a decrease in catalyst contact time. On the other hand, it is seen that two volumes of water increased the amounts of gaseous decomposition, possibly through an increase in catalyst activity.

The liquid analysis of the high-temperature runs differed considerably from that found in the low-temperature work. A small amount of n-butyraldehyde was isolated, while a considerable quantity of high-boiling material was obtained. At 500°C., this latter material comprised the greater portion of the liquid products. The yield of tetrahydrofuran decreased with increasing temperature. The effect of temperature upon the per cent yield of tetrahydrofuran, the per cent of water eliminated (two moles being theoretical), and the per cent of gaseous decomposition is shown in Graph IV. The percentage decomposition was calculated assuming that one mole of olefinic hydrocarbons is equivalent to the decomposition of one mole of the glycol.

The liquid products from the water-vapour runs were not analyzed quantitatively because of the large volume of water present. It was found, nevertheless, that considerably more

GRAPH IV



EFFECT OF TEMPERATURE ON THE DEHYDRATION OF BUTANEDIOL-1,4

Rate: 1 c.c./min.

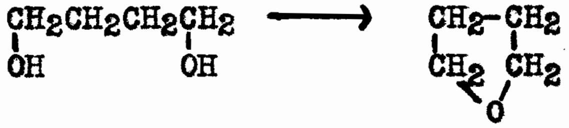
○ Tetrahydrofuran
● Water
◒ Gaseous Decomposition

tetrahydrofuran and less high-boiling material were obtained in the presence of water vapour at 500°C. than in the case of the dry glycol runs at the same temperature.

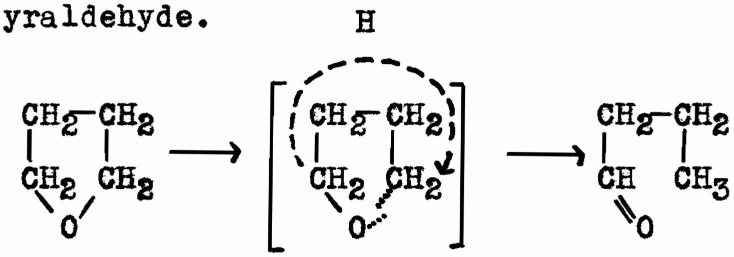
The gas evolved in the high-temperature runs consisted chiefly of unsaturated hydrocarbons which were found to contain over 75 per cent propene, the remainder being mainly butene-2. Saturated hydrocarbons were present to the extent of 8-11 per cent in the dry runs, while varying quantities of carbon dioxide, carbon monoxide and hydrogen were also formed. At the higher temperatures, the unsaturated hydrocarbon content of the gas decreased. The presence of water vapour, on the other hand, increased the volume of unsaturated hydrocarbons considerably. Butadiene was present to a very small extent in the dry runs increasing to 15 per cent when two volumes of water was used at 500°C. The maximum overall yield of butadiene obtained was 8.0 per cent.

Formaldehyde was present in very small amounts in the case of the dry glycol runs. When water vapour was used, however, the amount of formaldehyde approached the theoretical amount calculated on the assumption that one mole of formaldehyde is formed for every mole of propene produced.

From these results, it is evident that at low temperatures one molecule of water is eliminated to form a cyclic ether, tetrahydrofuran.

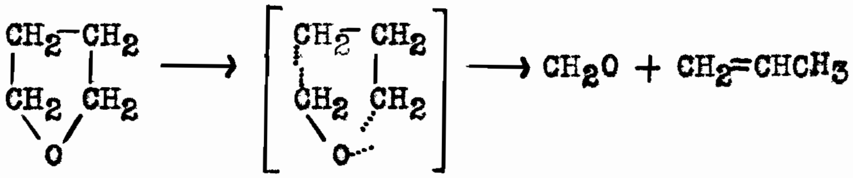


As the temperature is increased, it would appear that this ring undergoes fission. If this fission occurs at a carbon to oxygen linkage, then a fragment is formed which may stabilize itself by the migration of a hydrogen atom to form n-butyraldehyde.



Since n-butyraldehyde was isolated, it is apparent that this reaction actually does occur to some extent.

If, on the other hand, a carbon-to-carbon bond is also broken, either simultaneously with or following the carbon to oxygen bond fission, the molecule will separate into two fragments. This would result in the formation of propene and formaldehyde.



That this actually occurs is shown by the formation of a large quantity of propylene in the gaseous products.

Formaldehyde, however, was not present in appreciable quantities in the case of the dry runs. This can be explained by the removal of formaldehyde by two reactions. The first reaction involves a decomposition of the aldehyde to carbon monoxide, hydrogen, carbon dioxide, and methane. By non-catalytic pyrolysis, Bone and Smith (114) have shown that the main decomposition products of formaldehyde are carbon monoxide and hydrogen, while under certain conditions considerable quantities of carbon dioxide and methane are also formed. The mode of the decomposition of this aldehyde, or of the -CH_2O- fragment which is intermediate in the formation of the aldehyde, may be entirely different.

The second reaction which may contribute to the removal of formaldehyde is a condensation reaction between formaldehyde and tetrahydrofuran involving the elimination of water. This is supported by the fact that at higher temperatures considerable quantities of high-boiling products were obtained. Furthermore, the large amount of aqueous layer obtained at these temperatures would indicate a dehydration reaction not explained by the above decomposition to gaseous products. This is further supported by the fact that, in the case of the water-vapour runs, much larger amounts of formaldehyde and tetrahydrofuran and smaller amounts of the high-boiling material were obtained than in the case of the dry runs carried out under the same temperature conditions. The formation of propylene and formaldehyde from butanediol-1,4 over basic catalysts has previously been observed (24). The results also are consistent with the high -temperature decomposition of open-chain ethers which produce an aldehyde and a paraffin (115,116).

The butadiene formed in the reaction may arise directly from the glycol or from tetrahydrofuran since both compounds have previously been shown to give high yields of butadiene over acid catalysts. The effect of water in increasing the butadiene yield may be due to a reduction of contact time. Since it is difficult to explain the presence of butenes in the dry runs excepting by a hydrogenation of butadiene, it is possible that water, by reducing the catalyst contact time, reduces the extent of this reaction.

The Dehydration of Butanediol-1,3 over Activated Morden Bentonite

Source and Purification of Butanediol-1,3

Great difficulty was encountered in obtaining commercially adequate supplies of this glycol. Although Germany is reported to manufacture large quantities of this compound for the production of butadiene, butanediol-1,3 is not used in any industrial process on this continent. The glycol finally was obtained in limited quantities from Shawinigan Chemicals Limited,* where it is produced as a by-product in the manufacture of ethyl acetate from acetaldehyde (28). This material was received in a fairly pure form, having been fractionated through a Stedman column in the Research Laboratories of Shawinigan Chemicals Limited, and was used in this investigation without further purification. The physical constants of this product were: b.p.$_{760}$ 207.5-208° C., d_4^{20}1.002 and n_4^{20}1.4404. The following values have been reported in the literature: b.p.$_{760}$ 205-208° C., d_4^{20}1.026 and $n_D^{19.5}$1.4418 (117).

Procedure

The vertical-type catalysis apparatus was used for the investigation of butanediol-1,3. Each run was carried out using one hundred grams of catalyst. The procedure employed

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* Grateful acknowledgment is made to Shawinigan Chemicals Limited for a sample of purified butanediol-1,3.

was essentially the same as that used in the study of butanediol-1,4. It was found that the greatest care must be taken to prevent overheating in the preheater zone of the catalysis tube. In a normal run, in which the glycol vapours entered the catalyst slightly below the desired run temperature, the evolved gases contained 94-98 per cent unsaturated hydrocarbons. A slight overheating in the preheater, however, reduced the unsaturated content to below 90 per cent, while considerable quantities of hydrogen were formed. In the case of the water-vapour runs, the glycol and water, being miscible, were passed into the catalyst tube together from vessel B. The amount of carbon deposited on the catalyst at the end of a dry butanediol run was found to be much greater than for any compound previously studied under the same temperature conditions. This necessitated a long and careful reactivation.

The liquid products obtained from the dry glycol runs consisted of two layers. The organic layer was separated by the salting-out and extraction technique as previously described for butanediol-1,4. The material was then dried using a small quantity of anhydrous sodium sulphate. Because of the considerable mutual solubility of water and the principle organic liquid product, 1-butenol-4 (allyl carbinol),a large quantity of the drying agent was required to accomplish complete drying of the organic layer. Complete drying was not attempted, however, since it would involve excessive losses. Following the drying process, the organic liquid product was treated as in the butanediol-2,3 diacetate runs for the removal of dissolved gas. This gas was measured and analyzed for butadiene content only.

A preliminary distillation was made in which the organic liquid products were separated into three fractions, the major fraction distilling below 170°C., a fraction distilling between 170-220°C., and a small amount of tarry residue. The lower boiling fraction was then carefully fractionated in the glass-helices column using the 1,3-glycol itself as the inert booster. In the case of one run carried out at 275°C., a considerable fraction distilling at 200-210°C. was obtained in the preliminary distillation. This was identified as unchanged butanediol-1,3. The liquid products obtained from the glycol water-vapour runs were not analyzed since the solubility of the organic layer in the large volume of water present made a quantitative analysis impossible.

Formaldehyde was detected in the liquid products by the resorcinol test and a derivative, methylene-di-β-naphthol, was prepared for further identification. Three methods, the iodometric, the hydrogen peroxide, and the sodium cyanide method were tried for the quantitative determination of formaldehyde. High results were obtained in each case since it was found that the considerable amount of n-butyraldehyde present interferred in the analysis. The results obtained, however, indicated that the amount of formaldehyde produced was greatest in the case of the water-vapour runs.

The gaseous products were analyzed in the Bone and

Wheeler Apparatus while a separate analysis was made for butadiene content. The gas evolved from a number of runs was passed into a carbon tetrachloride-bromine solution. The tetrabromobutane separating out was filtered off, followed by the removal of the carbon tetrachloride. The product was given a preliminary distillation and the fraction distilling below 85° C. at 50 mm. was fractionally distilled.

Results and Discussion

The various feed-rates and temperatures at which dry butanediol-1,3 was investigated together with the amounts of liquid and gaseous products obtained are given in Table XXIV. The conditions of the water-vapour runs are given in Table XXV. These were carried out at various feed-rates, temperatures and water dilutions. With the exception of Run 67, the feed-rates were such that the amount of glycol passing into the catalyst tube was one cubic centimetre per minute at all dilutions.

Table XXVI gives the analysis of the liquid products obtained from the dry glycol runs expressed in per cent composition. Eight fractions were obtained in addition to a small amount of tarry residue. Fraction 1, distilling below 60° C. and present in extremely small amounts, gave a positive test with Tollen's reagent but was not further identified. Fraction 2, distilling between 60-70° C. consisted mainly of n-butyraldehyde identified by the formation of the 2,4-dinitrophenylhydrazone. It also contained a considerable

TABLE XXIV

DEHYDRATION OF BUTANEDIOL-1,3 OVER ACTIVATED MORDEN BENTONITE
DRY RUNS

Run No.	Furnace °C.	Rate c.c./min.	Glycol g.	Total Liquid Products g.	Organic Layer g.	Aqueous Layer g.	Vapour Products and loss g.	Total Gas l.
53	250	1	80	62.6	46.5	16.1	37.4	5.57
54	300	0.4	80	49.7	24.1	25.6	50.3	11.32
57	300	1	80	54.4	29.5	24.9	45.6	9.80
69	325	0.6	80	52.3	24.5	27.8	47.7	11.70
56	325	1	80	51.7	24.9	26.8	48.3	11.15
58	325	2	80	54.1	29.7	24.4	45.9	9.70
59	325	3	80	61.6	40.9	20.7	38.4	6.96
55	350	1	80	49.9	21.8	28.1	50.1	12.75

TABLE XXV

DEHYDRATION OF BUTANEDIOL-1,3 OVER ACTIVATED MORDEN BENTONITE IN THE PRESENCE OF WATER VAPOUR

Run No.	Furnace °C.	Total Rate[a.] c.c./min.	Glycol g.	Water g.	Total Liquid Products g.	Vapour Products and loss g.	Total Gas l.
67	275	2	80	240	299.2	20.8	10.00
62	300	2	80	80	136.6	23.4	9.33
64	300	3	80	160	218.9	21.1	11.47
66	300	4	80	240	289.6	30.4	12.60
61	325	2	80	80	133.9	26.1	13.33
65	325	3	80	160	214.9	25.1	13.53

a. This rate includes the total rate for both the glycol and water.

TABLE XXVI

ANALYSIS OF ORGANIC LIQUID PRODUCTS FROM THE BUTANEDIOL-1,3 DRY RUNS EXPRESSED AS PER CENT COMPOSITION

Run No.	Total Liq. Analyzed g.	1. -60°C in %	2. 60-70°C in %	3. 70-75°C in %	4. 80-100°C in %	5. 112-116°C in %	6. 157-164°C in %	7. 164-200°C in %	8. 200-210°C in %	Residue in %
53	46.5	---	1.1	2.0	3.5	33.0	14.1	2.0	39.8	4.4
54	24.1	---	11.8	10.5	8.4	27.8	29.4	4.2	----	7.8
57	29.5	3.1	18.1	9.6	4.2	42.6	11.5	8.1	----	2.3
69	24.5	---	21.5	15.1	8.4	35.2	5.6	8.4	----	5.6
56	24.9	---	13.0	9.8	6.5	30.4	17.4	17.5	----	5.3
58	29.7	1.8	20.2	16.7	7.0	31.0	7.3	9.4	----	6.7
59	40.9	1.4	20.2	22.9	9.4	29.8	7.7	5.6	----	2.8
55	21.8	4.9	23.2	9.9	8.4	23.2	18.7	4.4	----	7.4

quantity of water and would appear to be an azeotropic mixture of water and the aldehyde. Fraction 3, distilling between 70-75°C., consisted chiefly of n-butyraldehyde contaminated with other unidentifiable products. Butanone-2 was expected in this fraction but careful refractionation in the wire-helices column failed to isolate any of this ketone. Fraction 4, boiling between 80-100°C., consisted mainly of the water remaining in the organic products after the drying treatment. Fraction 5, distilling at 112-116°C. with the major portion at 113.5°C., was 1-butenol-4, identified by its physical constants. Fraction 6, distilling between 157-164°C. with a flat at 161.3-161.5°C., was the cyclic acetal formed by the condensation of one mole of n-butyraldehyde with one mole of the glycol. This was identified by a comparison of its physical constants with those of the acetal synthesized in the liquid phase. This acetal was prepared by refluxing one mole of the glycol and one mole of n-butyraldehyde in the presence of a small amount of 40 per cent sulphuric acid for fifteen hours, followed by neutralization and fractionation. Fraction 7, distilling between 164-200°C., could not be separated into any single component. Fraction 8, consisting of unchanged butanediol-1,3, was obtained only in the case of Run 53. It was noted that during fractionation a considerable amount of a white amorphous solid collected on the cold finger of the fractionation column head. This was identified as paraformaldehyde.

In order to show more clearly the effect of varying conditions on the yields of the liquid products, Fractions 2 and 3 considered as n-butyraldehyde and Fraction 5 as 1-butenol -4 are expressed as per cent of the theoretical yield in Table XXVII. This table also gives the number of moles of water per mole of glycol eliminated in the dehydration reaction.

The analysis of the gaseous products expressed in volume per cent and the per cent yield of butadiene are given in Table XXVIII for the dry glycol runs and in Table XXIX for the runs carried out in the presence of water vapour. It is seen that the gaseous products contain from 94-100 per cent unsaturated hydrocarbons with only traces of other gaseous products being present. One exception to this is found in Run 66 of the water-vapour runs where an overheated preheater caused the evolution of a considerable quantity of hydrogen.

The results of the fractionation of the dibromides are shown in Graph V. The major fraction, distilling at 59.5° C. at 50 mm. and n_D^{20} 1.5202, was 1,2-dibromopropane. A small amount of meso and racemic 2,3-dibromobutanes was also obtained, indicated by a gentle slope in the temperature curve between 72-73° C. at 50 mm. and in the refractive index curve at n_D^{20} 1.5120-1.5140. From this graph it can be estimated that the mono-olefins in the evolved gas consist of 85-90 per cent propene and 10-15 per cent butene.

The identification of products, both liquid and gaseous, is shown in Table XXX.

It is seen from Table XXIV that, in the case of the dry glycol runs, the extent of gaseous decomposition was greatest

TABLE XXVII

YIELDS OF LIQUID PRODUCTS FROM BUTANEDIOL-1,3 DRY RUNS

Run No.	Furnace °C.	Rate c.c./min.	60-75°C. Fracts. % Yield as n-Butyraldehyde	112-116°C. Fract. % Yield as 1-Butenol-4	Moles of Water Removed
53	250	1	2.2	23.7	1.01
54	300	0.4	8.3	10.3	1.60
57	300	1	12.8	19.6	1.56
69	325	0.6	14.0	13.5	1.74
56	325	1	8.9	11.8	1.67
58	325	2	17.1	14.4	1.53
59	325	3	27.5	19.0	1.30
55	350	1	11.3	7.9	1.76

TABLE XXVIII

ANALYSIS OF GASEOUS PRODUCTS FROM BUTANEDIOL-1,3 DRY RUNS

			General Gas Analysis in Volume Per cent					Butadiene Analysis	
Run No.	Furnace ° C.	Rate c.c. /min.	CO_2	CO	$CH_2=CH_2$	Other Unsats. including Butadiene	Hydrogen and Sat. Hydrocarbons	Volume %	Yield %
53	250	1	0.0	0.0	0.4	99.6	0.0	65.9	18.4
54	300	0.4	1.3	0.5	0.4	95.9	1.9	49.8	28.3
57	300	1	0.9	0.7	9.2	97.2	1.0	54.3	26.7
69	325	0.6	2.0	0.3	0.9	94.1	2.7	42.2	24.8
56	325	1	1.6	1.0	0.2	95.7	1.5	46.6	26.1
58	325	2	2.0	0.7	0.5	94.8	2.0	47.1	23.0
59	325	3	1.6	0.5	1.0	94.6	2.1	46.3	16.2
55	350	1	2.8	1.2	0.8	91.8	3.4	37.0	23.7

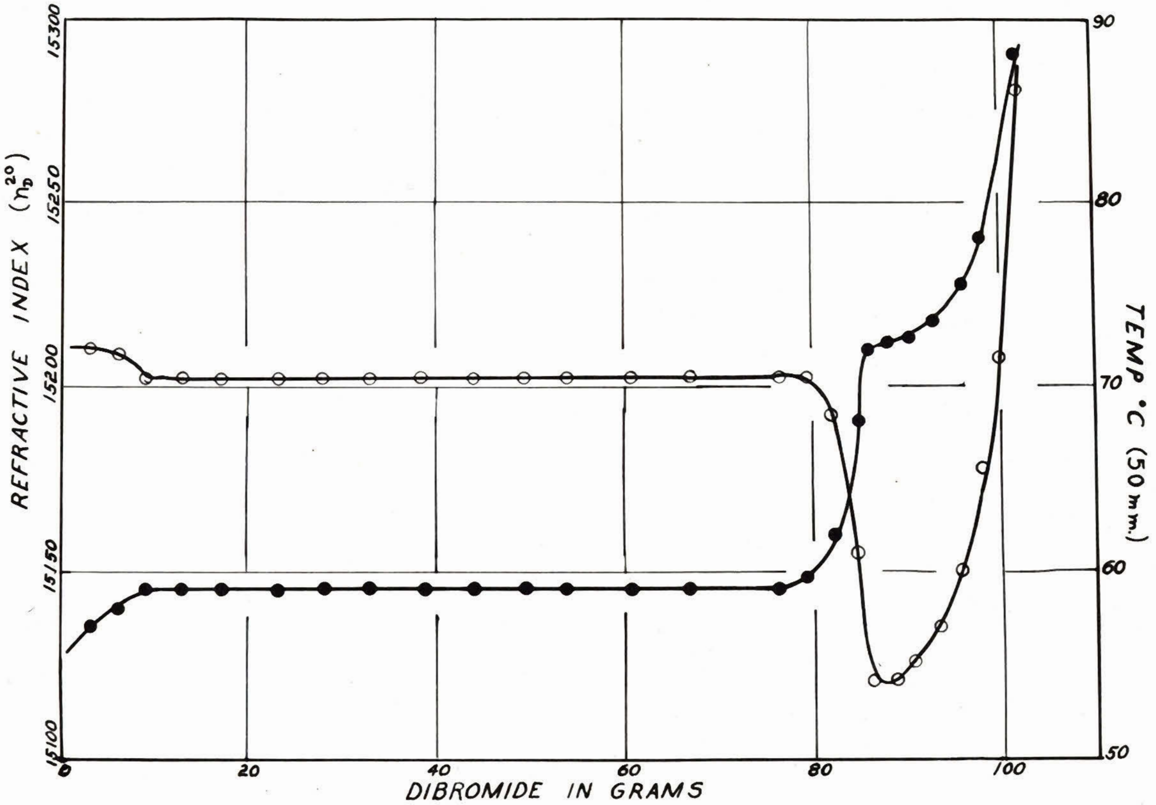
TABLE XXIX

ANALYSIS OF GASEOUS PRODUCTS FROM BUTANEDIOL-1,3
WATER VAPOUR RUNS

General Gas Analysis in Volume Per cent									Butadiene Analysis	
Run No.	Furnace °C.	Rate c.c./min. Glycol	H_2O	CO_2	CO	$CH_2=CH_2$	Other Unsats. including Butadiene	Hydrogen and Sat. Hydrocarbons	Volume %	Yield %
67	275	0.5	1.5	0.5	0.2	0.2	97.9	1.2	57.7	29.0
62	300	1	1	0.6	0.2	0.3	98.0	1.0	53.6	25.1
64	300	1	2	1.3	0.2	0.4	96.7	1.3	50.0	28.8
66	300	1	3	1.4	0.4	0.4	88.1[a.]	9.7	41.5	26.3
61	325	1	1	1.9	0.4	0.4	95.4	1.9	40.3	27.0
65	325	1	2	1.5	0.2	0.5	95.3	2.5	40.8	27.7

a. The lowering in unsaturated hydrocarbon content was due to overheating in the preheater.

GRAPH V



FRACTIONATION OF THE OLEFIN DIBROMIDES FROM BUTANEDIOL-1,3

○ Refractive Index Curve

● Boiling Point Curve

TABLE XXX

IDENTIFICATION OF PRODUCTS FROM BUTANEDIOL-1,3

Compound		Boiling Point °C.	Density d_4^{20}	Refr.Index n_D^{20}	Deriv.Melt. Point °C.
n-Butyraldehyde	Given	75		1.3843	
	Found	72-78		1.3894	
2,4-Dinitrophenylhydrazone	Given				122
	Found				122.5-123.5
Water	Given	100	0.998	1.3333	
	Found	100	0.998	1.3337	
1-Butenol-4	Given	114	0.853	1.4209	
	Found	113.5	0.850	1.4210	
n-Butyral of butanediol-1,3	Given[a]	161.5	0.913	1.4235	
	Found	161.3-161.5	0.915	1.4254	
1,2-Dibromopropane	Given	141.6	1.933	1.5203	
	Found	141	1.929	1.5202	
2,3-Dibromobutane rac.	Given	73/50 mm.		1.5116	
meso	Given	77/50 mm.		1.5147	
	Found	72-76/50 mm.		1.5120-1.5140	
Tetrabromobutane	Given				118-119
	Found				117-118
Formaldehyde Methylene-di- - naphthol	Given				189-192
	Found				191-193

[a] These values are for the product synthesized in the liquid phase.

at the higher temperatures and at the slower feed-rates. The same effect of increased temperatures is also shown in Table XXV which gives the extent of gaseous decomposition of the glycol in the presence of water vapour. Furthermore, in the case of the water-vapour runs, the gaseous decomposition was greatest at the higher dilutions. This would indicate that the effect of water in maintaining the activity of the catalyst by preventing carbonization was greater than the effect of a decreased catalyst contact time. It was noted that, in the case of the dry butanediol-1,3 runs, the amount of carbon deposited on the catalyst was abnormally large. In fact, with the other compounds studied, the carbonization at temperatures below 350° C. was almost negligible, while in the case of the 1,3-glycol, carbon was deposited in considerable quantities. It has generally been considered that water acts by means of the water-gas reaction in removing carbon from the catalyst. It would appear, however, that in the case of butanediol-1,3, water vapour prevents a decomposition of formaldehyde to carbon and water. This is supported by the fact that, in the water vapour runs, much less carbon and much larger quantities of formaldehyde were formed. This will receive further discussion later.

The effect of temperature and feed-rates upon the composition and yields of the liquid products is shown in Tables XXVI and XXVII. It is seen that, in general, the percentage of n-butyraldehyde (Fractions 2 and 3) in the liquid products increased with temperature, while the over-all yield of this compound increased accordingly. The percentage of 1-butenol-4 in the liquid products decreased only slightly with increasing temperatures. The over-all yield of this unsaturated alcohol, on the other hand, was decreased considerably at the higher temperatures. The amount of water eliminated from the glycol also increased with temperature. The effect of an increased feed-rate, on the other hand, was to increase the yield of both n-butyraldehyde and 1-butenol-4. The amount of water eliminated, as expected, decreased with increasing feed-rates. Great difficulty was found in obtaining an accurate analysis of the liquid products due to inadequate drying. Consequently, deviations in these trends were frequently encountered.

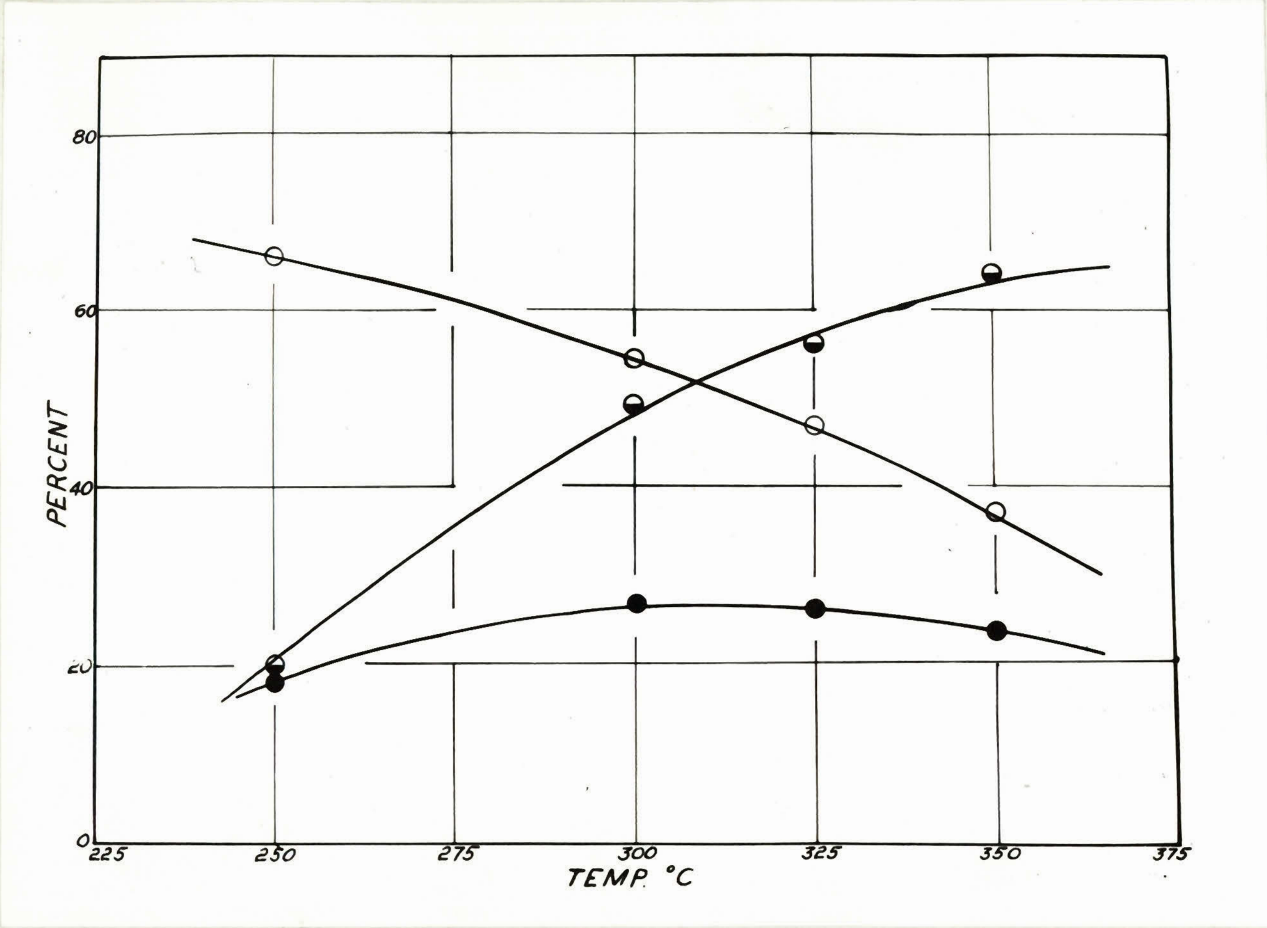
Turning now to a consideration of the results of the analysis of gaseous products as given in Tables XXVIII and XXIX, it is seen that, in the case of both the dry and water-vapour runs, the gases consisted almost entirely of unsaturated hydrocarbons. Only traces of other components were present. Considering first the analysis of the gas evolved in the dry glycol runs, it is seen that the unsaturated hydrocarbon content decreased slightly with increasing temperature. Thus, at 250° C. and 1 c.c. per minute, 99.6 per cent unsaturates were obtained decreasing to 91.8 per cent at 350°C. and at the same feed-rate. The percentage butadiene in the gas, on the other hand, was greatly effected by increasing temperatures. This is seen by a comparison of Runs 53, 57, 56 and 55 which were each carried out at a feed-rate of 1 c.c. per min. Run 53, at 250°C., gave 65.9 per cent butadiene in the gaseous products; Run 57, at 300°C., gave 54.3 per cent; Run 56, at 325°C., gave 46.6 per cent; while Run 55, carried out at 350°C., furnished only 37.0 per cent butadiene in the gaseous products.

The over-all yield of butadiene, in the case of these runs, increased with temperature to a maximum of 26.7 per cent at 300°C., decreasing to 26.1 per cent at 325°C., and to 23.7 per cent at 350°C. This would indicate that at first the effect of an increased gaseous decomposition at the higher temperatures was greater than the effect of a reduction in the butadiene content of the gas. Above 300°C., however, the latter effect became predominate. This is shown more clearly in Graph VI in which temperature is plotted against per cent gaseous decomposition, per cent butadiene content in the gas, and the over-all butadiene percentage yield.

The effect of feed-rate upon the butadiene content of the gaseous products was not nearly as pronounced as the temperature effect. A slight increase in butadiene content was obtained at the higher feed-rates, while the over-all butadiene yield was reduced considerably due to a reduction in the extent of gaseous-product formation.

Turning now to a consideration of the analysis of the gaseous products from the water-vapour runs, it is seen that an increase in the ratio of water to glycol decreased the butadiene content of the gas. This is shown by a comparison of Runs 57, 62, 64 and 66 which were carried out at 300°C.

GRAPH VI



EFFECT OF TEMPERATURE ON THE YIELD OF BUTADIENE FROM BUTANEDIOL-1,3

Rate: 1 c.c./min.

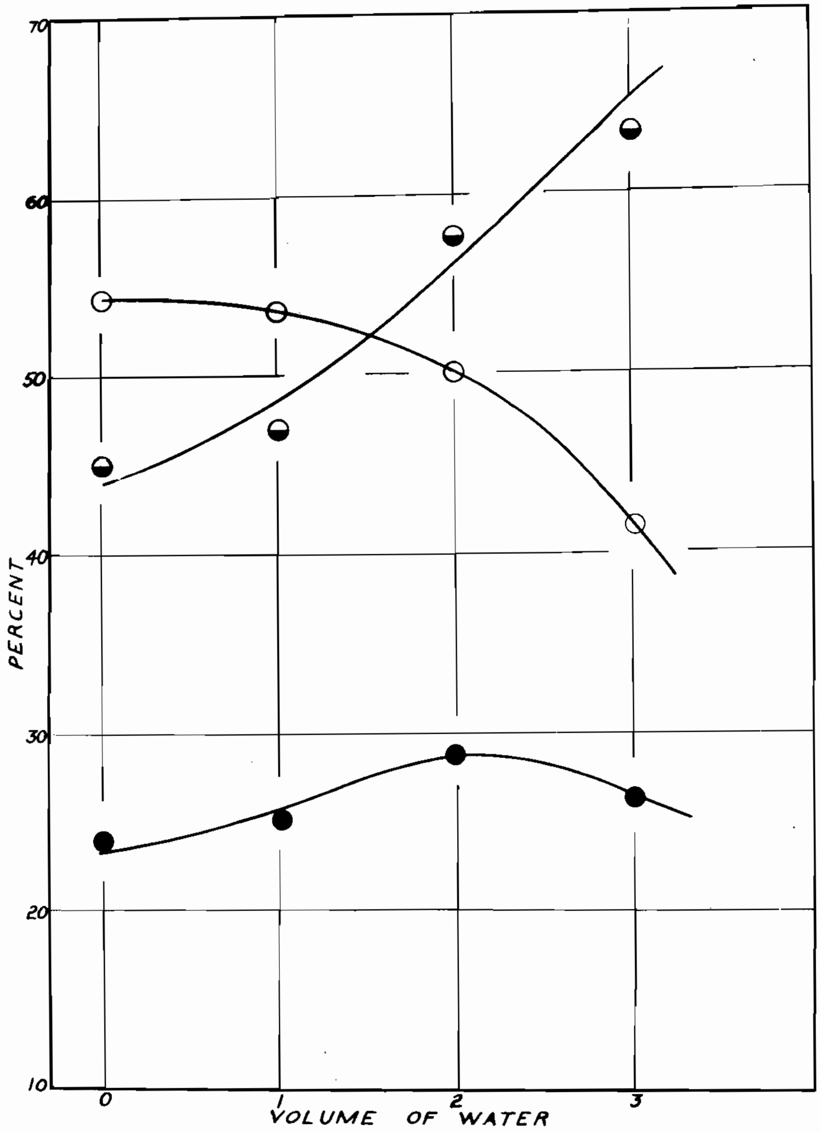
○ Per cent Butadiene in Gaseous Products
◒ Per cent Gaseous Decomposition
● Per cent Yield of Butadiene

and at a feed-rate of 1 c.c. of glycol per minute. Run 57, without added water vapour, gave a gaseous product containing 54.3 per cent butadiene; Run 62, using one volume of water per volume of glycol, gave 53.6 per cent; Run 64, using two volumes of water, gave 50.0 per cent; while Run 66, with three volumes of water, gave41.5 per cent butadiene in the gaseous products. The over-all yield of butadiene, on the other hand, increased to a maximum of 28.8 per cent using two volumes of water, decreasing again to 26.3 per cent with three volumes. The effect of increased dilution on the extent of gaseous decomposition, the butadiene content of the gas, and the over-all butadiene yield is shown in Graph VII. It is to be noted that the points on this graph are plotted from values obtained from the gas evolved only and do not include dissolved gases which were not analyzed in the case of the water-vapour runs.

As far as the writer is aware, the decomposition of butanediol-1,3 at high temperatures over dehydration catalysts has not been studied with respect to the mechanism of the decomposition reactions. Numerous patents have been taken out covering the production of butadiene from this glycol. However, no mention was made concerning the nature of the by-products formed in this reaction.

Recently Nagai (31) investigated the dehydration of butanediol-1,3 over aluminium oxide and various clay catalysts. It was found that, for the most part, less than fifty per cent of the gaseous products consisted of butadiene, the remainder

GRAPH VII



EFFECT OF WATER DILUTION ON THE YIELD OF BUTADIENE FROM BUTANEDIOL-1,3

Rate: 1 c.c./min.

○ Per cent Butadiene in Gaseous Products
◒ Per cent Gaseous Decomposition
● Per cent Yield of Butadiene

being mono-olefins which were considered to be a mixture of propene and butene. The results of the present investigation compare with the results of this worker both with respect to the extent of the gaseous decomposition and the butadiene content of the gas. It has been shown, moreover, that the mono-olefins consist mainly of propene with only very small amounts of butenes being present. Furthermore, formaldehyde is also formed in the reaction while a considerable amount of carbon is deposited on the catalyst at the expense of the formaldehyde yield.

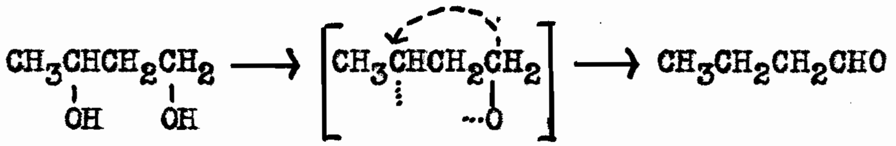
From a consideration of the mechanism of the decomposition of butanediol-1,3 over activated Morden bentonite, several conclusions may be made. It would appear that the butadiene formed in the reaction results from the elimination of one molecule of water from the secondary-hydroxyl group and a hydrogen from the terminal methyl group to form the unsaturated alcohol, 1-butenol-4, this being followed by further dehydration to butadiene.

$$CH_3CHOHCH_2CH_2OH \longrightarrow CH_2{=}CHCH_2CH_2OH \longrightarrow CH_2{=}CHCH{=}CH_2$$

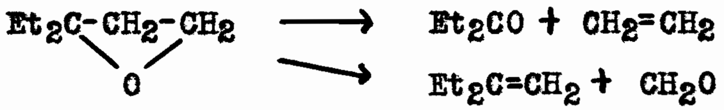
This is supported by the fact that considerable quantities of the unsaturated alcohol were isolated. Furthermore, it has previously been shown that 1-butenol-4, in the presence of dehydration catalysts, produces butadiene (43).

A second reaction which occurs in the decomposition of this glycol over bentonite involves the formation of n-butyraldehyde. By an analogy with the dehydration of the 2,3- and the 1,4-glycol, it would appear that this aldehyde results from the elimination of one water molecule between the two hydroxyl groups. This mode of dehydration may first result in the formation of a four-membered oxide ring, followed by a carbon to oxygen fission and the rearrangement of a hydrogen atom to form the aldehyde.

On the other hand, the rearrangement may occur without an actual ring closure as in the case of the mono-dehydration of butanediol-2,3.



In either case, by this mode of dehydration, it is also possible to explain the formation of propylene and formaldehyde. This would involve carbon-to-carbon fission similiar to that occurring in the decomposition of tetrahydrofuran to the olefin and aldehyde. This mechanism for the formation of these compounds is further supported by the work of Barbot (118). This worker has shown that the diethyl substituted four-membered cyclic ether decomposes under the influence of heat as follows:



On the other hand, a serious argument against this mechanism for the formation of propylene and formaldehyde is seen from the results of Dojarenko (119) and Prévost (120).

Dojarenko studied the decomposition of the unsaturated alcohol, 1-butenol-4, over aluminium oxide and obtained only traces of butadiene, the main products being propylene, carbon and water. Formaldehyde was not identified and the investigator discarded the idea that formaldehyde might be intermediate in the formation of carbon and water on the basis that this aldehyde, at high temperatures, is known to decompose to carbon monoxide and hydrogen. A fallacy in this argument can be pointed out, however. The mode of the decomposition of the $-CH_2-O-$ fragment as it is first formed in the reaction (nascent formaldehyde) may be entirely different from the decomposition of a stabilized formaldehyde molecule.

This assumption, that formaldehyde is an intermediate in the formation of carbon and water produced by the decomposition of butenol-4, is supported by the results of Prévost with this unsaturated alcohol. This worker studied the decomposition over aluminium oxide of the unsaturated alcohols of the type $RCHOH\overset{CH_2}{C}H=CH_2$, in which R is a hydrogen atom, or a methyl, ethyl or vinyl group. It was found that, in all cases, only traces of diolefins and water were formed, the main products being an aldehyde and propylene.

$$RCHOHCH_2CH=CH_2 \longrightarrow RCHO + CH_3CH=CH$$

The mechanism of this reaction could not be explained, however.

From these results on the decomposition of 1-butenol-4, it is seen that one can equally as well explain the formation of formaldehyde and propylene in the decomposition of butanediol-1,3 through the intermediate formation of the unsaturated alcohol. How this intermediate alcohol decomposes to the final products, however, is difficult to explain.

It would appear, then, that there are two possible mechanisms for the decomposition of butanediol-1,3 to propylene and formaldehyde. The first involves the elimination of water between the two hydroxyl groups, with or without ring closure, followed by carbon-to-carbon fission to propylene and formaldehyde. Each of these steps is explicable by analogy with the decomposition of the 1,4-glycol to the same products. Furthermore, it is difficult to explain the formation of n-butyraldehyde excepting through this mode of dehydration. The second mechanism involves the elimination of the first molecule of water between the secondary hydroxyl and a hydrogen from the terminal methyl group to give 1-butenol-4, which then decomposes to the aldehyde and mono-olefin. This mechanism has the advantage in that it involves an isolable intermediate.

It is difficult to postulate a mechanism for this decomposition of 1-butenol-4 to formaldehyde and propylene. It is possible that the unsaturated linkage by an inductive effect sufficiently weakens the bond between the hydroxyl-bearing carbon atom and its adjacent carbon to cause a carbon-to-carbon fission. The resulting $-CH_2OH$ radicle could then lose hydrogen to form formaldehyde followed by an addition of this hydrogen to the $CH_2=CHCH_2-$ radicle to form propylene. Another possibility is that the decomposition occurs through the same intermediate as postulated in the first mechanism for the glycol decomposition. This would involve the addition of the hydrogen of the hydroxyl group across the double bond to form the fragment  $\mathrm{CH_3\underset{\vdots}{C}HCH_2\underset{\underset{\cdots O}{|}}{C}H_2}$ which then decomposes by carbon-to-carbon fission to formaldehyde and propylene.

The effect of water in increasing the gaseous decomposition of the glycol can be explained on the basis that water prevents carbonization on the catalyst. This is supported by the experimental fact that in the case of water-vapour runs a smaller amount of carbon and a larger amount of formaldehyde was obtained. On the other hand, increased dilution was found to decrease the butadiene content of the gas. Furthermore, the relation between butadiene content and the extent of gaseous decomposition at various dilutions compared closely with the same relation found at various temperatures. This is shown clearly by a comparison of Graphs VI and VII. It is to be noted that this effect of water vapour in decreasing the butadiene content of the gaseous products is in direct contradiction to the claims of various patents on the use of water in the production of butadiene (44,45).

SUMMARY

1. Activated Morden Bentonite was investigated as a catalyst for the vapour-phase dehydration of three butanediols namely, butanediol-2,3, butanediol-1,4, and butanediol-1,3, and as a catalyst for the decomposition of butanediol-2,3 diacetate.

2. The dehydration of butanediol-2,3 was studied at temperatures of 225-700°C. and at various feed-rates, with and without the addition of water vapour. At low temperatures, 225-350°C., high yields (a maximum of 85 per cent) of butanone-2 as well as small amounts of isobutyraldehyde and the cyclic acetal, the isobutyral of butanediol-2,3, were obtained from the dry glycol. At 225°C., the cyclic acetal was the main by-product, while at 350°C., isobutyraldehyde was formed to the extent of 12.1 per cent. The effect of increased feed-rates was slight. At high temperatures, 450-700°C., decomposition to gaseous products was found to occur. Only small yields of butadiene (2-7 per cent) were obtained from the dry glycol while this yield was increased to 14.9 per cent in the presence of two volumes of water at 700°C. The extent of the gaseous decomposition was greatest at the higher temperatures and the slower

feed-rates. The mechanism of the low and high temperatures has been discussed.

3. The decomposition of butanediol-2,3 diacetate was investigated at temperatures of 400-500° C. and at various feed-rates in the dry state and in the presence of water vapour. Various quantities of catalyst were used. The main products were acetic acid, butanone-2, isobutyraldehyde and butadiene. Secondary products, both liquid and gaseous, were formed by further decomposition of acetic acid and the carbonyl compounds. Under the more drastic conditions of high temperatures, slow feed-rates and with increasing amounts of catalyst, butanone-2 was formed at the expense of the butadiene yield. A mechanism was suggested for the formation of these products.

4. Butanediol-1,4 was studied at temperatures of 250-500° C. and at various feed-rates, with and without the addition of water vapour. At the lower temperatures, 250-300° C., practically theoretical yields of tetrahydrofuran were obtained at all feed-rates. At higher temperatures, 400-500°C., decomposition to gaseous products was found to occur, the main products being propylene and formaldehyde. The liquid products, in addition to water and tetrahydrofuran, contained a small amount of n-butyraldehyde and high-boiling condensation products. An increase in temperature greatly increased the extent of gaseous decomposition. Butadiene was obtained in an 8.0 per cent yield in the presence of water vapour. A mechanism for these reactions has been considered.

4. Butanediol-1,3 was investigated at temperatures of 250-350° C. and at different feed-rates both in the dry state and in the presence of various amounts of water. The liquid products consisted of water, n-butyraldehyde, 1-butenol-4, and the n-butyral of butanediol-1,3. The gaseous products consisted mainly of propylene and butadiene. Formaldehyde was dissolved in the liquid products and carbon was deposited in considerable quantities on the catalyst. The extent of gaseous decomposition increased with temperature and with water dilution while the butadiene content of the gas decreased. A maximum yield of 28.8 per cent was obtained at 300° C. using two volumes of water. Increased feed-rates increased the butadiene content of the gas but greatly decreased decomposition to gaseous products. A mechanism for these reactions has been postulated.

CLAIMS TO ORIGINAL RESEARCH AND CONTRIBUTIONS TO KNOWLEDGE

It is claimed that the work reported in this thesis constitutes:

1. The first reported study of the vapour-phase dehydration of butanediol-2,3 over an aluminium silicate catalyst.

2. The first reported study of the dehydration of butanediol-2,3 over any catalyst in which the by-products have been thoroughly investigated.

3. An original contribution to the study of the mechanism of the rearrangement of α-glycols.

4. An original contribution to the knowledge of the catalytic activity of aluminium silicates acquired by a study of the decomposition of butanediol-2,3 diacetate.

5. The first reported vapour-phase study of the dehydration of butanediol-1,4 over an aluminium silicate catalyst.

6. The first reported study of the catalytic pyrolysis of butanediol-1,3 in which all products have been thoroughly investigated.

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