THE VAPOR PHASE DEHYDRATION
OF
KETONES AND GLYCOLS

A Thesis

by

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M.Sc. Chemistry

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THE VAPOR PHASE DEHYDRATION OF KETONES AND GLYCOLS

A study was made of Canadian bentonites as vapor phase catalysts for the dehydration of butanone, butanediol-2,3 and butanediol-1,3. Optimum conditions of temperature and contact time were established for the production of butadiene from these compounds.

Samples of clays from the four Western Provinces were compared as to their activity as dehydration catalysts. The Manitoba bentonite was found to be the most efficient, followed by the Saskatchewan, Alberta, and British Columbia clays.

In an effort to determine the mechanism of the dehydration reactions, nitric oxide and methyl iodide were added to the butanone. The decrease in gaseous decomposition in the presence of nitric oxide is evidence for a free radical mechanism, the nitric oxide serving to terminate the chains perpetuated by other free radicals. An increase in the gaseous decomposition in the presence of methyl iodide further indicates a free radical mechanism, the methyl radicals from the pyrolysis of methyl iodide serving to initiate the chain reactions.

A mechanism for the dehydration of the glycols studied is also postulated.

INTRODUCTION

The launching of a vast synthetic rubber program following the loss early in the Pacific war of the United Nations' source of natural rubber, led to an exhaustive investigation of all possible methods for the production of butadiene (1). One of the avenues of approach was that of high temperature, vapor-phase catalysis. By this means, the production of olefins, alcohols, ketones, aldehydes, esters, and the carrying out of a variety of other types of organic reactions has been accomplished. It was believed that this type of reaction might be a fruitful source of both butadiene and styrene, the chief components of the particular synthetic rubber favored by the Government in its program. The field of high temperature catalysis, though relatively new in Organic Chemistry, has now been well explored with many types of compounds and catalysts under a wide variety of conditions.

Activated Morden bentonite, a clay mined at Morden, Manitoba, has been used successfully in this Department to carry out a number of reactions, notably dealkylation of straight and branched chain aromatics; dehydrogenation, polymerization and isomerization of aliphatic alcohols; dehydration of ketones (2) and dihydric alcohols (3). It was found that the removal of one molecule of water from dihydric alcohols (glycols) resulted in the formation of cyclic oxides, aldehydes, ketones, or mixtures of the same. The removal of two molecules of water resulted in the formation of diene hydrocarbons. Thus at low temperatures, the dehydration of butanediol-2,3 yielded a miximum of 85 per cent of butanone-2, as well as isobutyraldehyde and the cyclic acetal of the glycol and isobutyraldehyde. At high temperatures, a maximum of 15 per cent of butadiene was obtained in the presence of two volumes of water. The diacetate of butanediol-2,3 yielded acetic acid, butanone-2, isobutyraldehyde, and butadiene (57.5 per cent maximum). Butanediol-1,3 and butanediol-1,4 were also studied, and butadiene prepared from both.

An important discovery was the fact that the presence of water vapor markedly increased the percentage of unsaturated hydrocarbons, though the total volume of gaseous products is decreased. In an attempt to explain the mechanism of the dehydration of butanediol-2,3 by determining the products of pyrolysis of butanone-2, a product of the glycol decomposition, it was noted that large amounts of butadiene could be prepared. Thus it has been considered advisable to extend the work on the pyrolysis of butanone-2, using conditions not previously employed, in order to obtain the optimum conditions for the maximum production of butadiene. These conditions having been determined, they were extended to butanediol-2,3 and butanediol-1,3.

An attempt has been made to prove the free radical theory for the mechanism of the dehydration of butanone-2, by the use of nitric oxide as an inhibitor, and methyl free radicals as promoters of the reaction. The decomposition of octanone-2 has also been studied, resulting in the formation of hexenes, octadienes, and polymers of olefins.

It was considered possible that different clays might alter the course of the pyrolysis reactions. Bentonites mined in Saskatchewan, Alberta and British Columbia have been compared in their activity with the Manitoba Bentonite used in the remainder of the investigation. It was hoped that the results of this research might lead to a commercial development of Canadian bentonites, large quantities of which are readily accessible in Western Canada.

HISTORICAL

Pyrolysis of Ketones

Ketones early occupied the attention of investigators working in the field of thermal decomposition. During the last century, Barbier and Roulx (4) passed acetone through a copper tube and reported an almost quantitative yield at 1000° in accordance with the equation:

$$2CH_3COCH_3 \longrightarrow 2CH_4 + 2CO + C_2H_4.$$

Some of the ethylene decomposed to acetylene and hydrogen.

In 1901, Nef (5) passed acetone over pumice at 530°-580° during eighty minutes, and obtained a liquid which he thought to be a mixture of crotonaldehyde and acetaldehyde, but which was probably ketene, at that time still undiscovered.

Schmidlin and Bergman (6) passed acetone through a tube over clay heated to 500°-600° and were the first investigators to list ketene as a pyrogenic product. Peytral (7) concluded that the primary reaction when acetone is decomposed is the formation of ketene and methane. Ketene may then be broken into ethylene and carbon monoxide. Later, Hurd and co-workers (8) determined the optimum conditions for the production of ketene, now valuable as an acetylating reagent. They worked at a temperature of 700° and a flow of acetone of 5 cc. per minute, and obtained 35-45% of ketene.

By passing acetone vapor over heated thoria and alumina, mesityl oxide and phorone have been obtained (9). At high temperatures and pressures, Ipatieff and Petrov (10) report that mesitylene is the chief product formed in heating acetone with dehydrating catalysts. Greene (11) produced hexamethyl benzene by heating acetone with zinc chloride. Reckleben and Sheiber (12) prepared hexamethyl benzene by leading a mixture of acetone and methyl alcohol over alumina at 400°.

Considerable attention has been given to the products of the gaseous decomposition of acetone. Senderens (13) reports an equal mixture of carbon monoxide, carbon dioxide and ethylene at 400° over alumina.

Petrov (14) has shown that under conditions of high temperature and pressure, homologs of mesityl oxide and isophorone, with a trace of trimethyl benzene are formed from methyl ethyl ketone.

In presence of silica gel, Mitchell and Reid (15) obtained at 500° a 17% yield of 1,3,5-trimethyl benzene from acetone, the homogeneous decomposition into ketene and methane taking place only to a minor extent. The mechanism would seem to be dehydration to methyl acetylene, followed by polymerization of this compound. Mesityl oxide, phorone, isophorone, xylitone and other condensation products were isolated. From butanone, only ketonic condensation products appear, such as homomesityl oxide, homophorone, and homoisophorone.

Working on butanone-2, Hurd (16) found both ketene and methyl ketene as pyrogenic products, Thus

$$CH_3\text{-}CO\text{-}CH_2\text{-}CH_3 \begin{array}{l} \nearrow \; CH_2{=}C{=}O \; + \; C_2H_6 \\ \searrow \; CH_3\text{-}CH{=}C{=}O \; + \; CH_4 \end{array}$$

The combined yield of the ketenes is about 5 per cent.

Pinacolone $(CH_3)_3C\text{-}CO\ CH_3$ undergoes pyrolysis into gaseous products at 705° and a rate of 1cc. per minute (17). Only 2 per cent of ketene is produced, in spite of the presence of the acetyl group as in acetone. However, the tertiary carbon atom makes it impossible for methane to be a primary decomposition product.

Acetophenone at high temperatures decomposes into a variety of products, including benzene, diphenyl, 1,4-diphenylbenzene and toluene, of which benzene is undoubtedly the primary product (18). At lower temperatures, and over long periods of time, acetophenone forms 20% dypnone, 45% 1,3,5-triphenylbenzene and a little α,β'-diphenyl furan, the major reaction being the loss of three molecules of water from three of ketone (19). In a sealed tube for ten hours, as well as the above products, carbon monoxide, carbon dioxide, methane, and hydrogen were formed. If p-methoxy acetophenone is heated in a sealed tube for twenty hours at 360°-380°, water, a little oil, and a carbonized mass are the result. p-Methoxypropiophenone and p-methoxybutyrophenone are completely carbonized in 100 hours at the same temperature. These ketones are considerably more stable than the corresponding hydrocarbons. No simple products could be detected from the condensation products, due to rapid resinification and carbonization.

Acetophenone at 270°- 300° gives 35% of a mixture of symtriphenyl benzene and 3,4-diphenyl furan. At 380°-420°, a mixture of benzene, toluene, ethyl benzene and o-xylene is obtained (20). The ethyl benzene arises from hydrogenation of acetophenone, the hydrogen being due to the presence of iron in the tube. In a high pressure apparatus, in presence of ferric oxide, homoisophorone and pulegone give phenols, while 1-methyl-2-cyclohexanone liberates carbon monoxide and a mixture of hydrocarbons (21).

Dibenzyl ketone, if heated for 14 hours at 200°-360° gives rise to carbon monoxide, toluene, water and carbonaceous matter (22). The gas is over 75 per cent carbon monoxide. The yield of toluene is about 50 per cent. Engler assumed that hydrogen was liberated in the pyrolysis, and is the active agent in the formation of toluene and carbon monoxide.

$$(C_6H_5CH_2)_2CO + H \longrightarrow CO + 2C_6H_5CH_3$$

Another possible breakdown is a ketenic decomposition:

$$C_6H_5CH_2COCH_2C_6H_5 \longrightarrow C_6H_5\text{-}CH{=}C{=}O + C_6H_5CH_3$$

The phenyl ketene would probably decompose into carbon monoxide and polymerized phenyl methylene. Other workers (23) were unable to detect polymerized products as such.

Benzophenone breaks down completely at 500°-550° largely into carbon and gases, with about 12% of a liquid containing benzene and diphenyl methane (24). If refluxed for several days, 2,4- or 2,5-dimethyl benzophenone gives 2-methyl anthracene (25).

Cyclohexanone if refluxed for 115 hours at 153°-156° is one-sixth converted into cyclohexylidene cyclohexanone. At 700° it decomposes in a furnace into carbon monoxide, olefins, hydrogen and saturated hydrocarbons. A small quantity of liquid that was condensed after leaving the furnace proved to be a mixture of unchanged cyclohexanone, and cyclohexadiene-1,3. (26).

In a reaction now well known as the Elbs Reaction, Elbs and co-workers (27-33) studied the pyrolysis of various polyalkyl benzophenones, producing 20-25 per cent yields of anthracene homologs. This reaction has found significant use in the preparation of hydrocarbons not available by other known methods. Morgan and Coulson (34) obtained 2,6-dimethyl and 2,7-dimethyl anthracene in good yield from the pyrolysis of 2,5,4'-trimethyl and 2,4,4'-trimethyl benzophenone. A large number of 1,2,5,6-dibenzanthracene derivatives have been prepared from derivatives of 2,1'-dinaphthyl ketone; 1,2-benzanthracene derivatives from 1'-benzoylnaphthalene derivatives. Herschberg (35) observed that o-tolyl α -naphthyl ketone can be pyrolysed at 400°-410° in presence of zinc dust to give 1,2-benzanthracene in 61% yield.

Cyclic hydrocarbons have been obtained by passing the vapors of diaryl ketones or aryl alkyl ketones over silica gel and alumina (36).

Using a catalyst composed of alumina and copper at 600°-650°, Mailhe (37) studied the decomposition of aliphatic ketones. The products were almost entirely gaseous: carbon monoxide 18.9-30.9%, C_nH_{2n} 17.2-43.1%; C_nH_{2n+2} 12.5-35.3%; methane 7.5-23.5%; hydrogen 3.7-28.5%. He studied methyl isopropyl ketone, methyl isobutyl ketone, methyl butyl ketone, methyl isoamyl ketone, di-isobutyl ketone, isopropyl isobutyl ketone and dihexyl ketone. The radicals combined with the carbonyl group split off and break donw to give saturated and unsaturated hydrocarbons (38).

With aromatic ketones, Mailhe (39) found that the decomposition over copper turnings is analogous to that for aliphatic ketones. The decomposition is more difficult if the carbonyl group is attached directly to the ring. The chain is broken on each side of the carbonyl group, giving carbon dioxide, an aromatic residue which hydrogenates to an aromatic hydrocarbon, and an aliphatic hydrocarbon, which may further decompose.

From the foregoing survey, it is evident that a wide variety of compounds may be prepared from the pyrolysis of ketones, factors such as pressure, temperature, and catalyst having a profound effect on the nature of the products. At high temperatures, all ketones yield gaseous products, in which carbon monoxide and olefinic hydrocarbons predominate. At lower temperatures, simple straight chain ketones undergo a ketenic type of decomposition, producing ketene, substituted ketenes, and gaseous products. Alkyl aryl ketones form a wide variety of cyclic and substituted aromatic compounds. Diaryl ketones also yield cyclic hydrocarbons. Polyalkyl benzophenones yield many anthracene derivatives. In many cases, hydrogen liberated in the pyrolysis serves to hydrogenate primary decomposition products, and the original ketone, forming, as an example, ethyl benzene from acetophenone.

Free Radicals

The discovery of the free triphenylmethyl radical by Gomberg (40) in 1900 was a discovery of far-reaching effects, signalizing the birth of a new area of investigation affecting all fields of Chemistry. In attempting to prepare hexaphenyl ethane from triphenylchloromethane and a metal, he isolated a compound of which he reported: "The compound is extremely unsaturated. It absorbs chlorine, bromine and iodine .... The experimental evidence forces me to the conclusion that we have to deal here with a free radical, triphenylmethyl $(C_6H_5)_3C-$. On this assumption alone do the results become intelligible and receive an adequate explanation." Subsequent experiments on the molecular weight of the triphenyl methyl and radicals obtained by replacement of the phenyl groups by naphthyl, biphenyl, methoxyphenyl groups, etc., established beyond all doubt the existence of free triarylmethyls containing trivalent carbon. Later, radicals containing bivalent and quadrivalent nitrogen, univalent oxygen and univalent sulfur, were discovered.

In 1929, the work of Paneth and his co-workers (41) proved the existence of free alkyl radicals. Their apparatus consisted of a tube which was heated strongly at one point. Working at very low pressures, they passed a stream of hydrogen and the vapor of tetramethyl lead through the tube, and noticed the deposition of a lead mirror at the point of heating due to the reaction

$$(CH_3)_4Pb \longrightarrow 4CH_3\cdot + Pb \quad .$$

To detect the presence of the free radical, a lead mirror was deposited farther along the tube, and when decomposition of tetramethyl lead occurs, this lead mirror disappears by chemical combination with the methyl radicals and reforms tetramethyl lead. Iodine may also be used, with the formation of methyl iodide. The free ethyl radical was prepared in a similar manner, and undergoes the same reactions. If the lead mirror is too far from the source of the free radicals, it is not removed. This at once suggested that the free radicals have only a very brief existence as such. The half-life of the methyl radicals was calculated to be of the order of 0.006 seconds at a pressure of 2 mm.

The concept of free radicals was early applied to the mechanism of organic reactions. There is abundant evidence that many reactions proceed through the intermediate formation of the fragments, ions or neutral radicals. The ionic mechanism is successful in interpreting reactions which proceed in an ionizing solvent or in aqueous solution, and reactions such as hydrolysis, which are promoted in a polar environment and are catalysed by ions. On the other hand, many photochemical and thermal decompositions which occur in liquids of low dielectric constant and in gases, appear to depend on the formation and interaction of neutral radicals. To be successful, the statement of a free radical mechanism must satisfy the conditions of (1) accounting satisfactorily for the products, (2) predicting the correct order of reaction, (3) accounting for the measured activation energy.

Rice (42) assumes that when an organic compound decomposes at high temperature it is broken up into two or more radicals, depending on the number of bonds in the molecule. The radical may do one of three things: first, it may react with one of the surrounding molecules; second, it may decompose into a compound and a smaller radical; or, third, it may diffuse to the wall and be absorbed there. If only a 5 to 10 per cent decomposition of the organic compound is considered, the radicals can react only with the original substance, and the problem is less complicated. Noting that propane decomposes into propylene and hydrogen, and also into methane and ethylene, Rice considers that the use of free radicals is necessary to explain the mechanism of such decompositions.

In order to determine the nature of the different fragments produced when a paraffin hydrocarbon breaks, it is necessary to know the strength of the bonds involved. The strength of the C-H bond in methane, from thermochemical measurements is 93.3 kg. cal. The heat of formation of ethane from gaseous carbon and gaseous hydrogen is 630.8 kg. cal. Taking the strength of the C-H bonds in methane and ethane to be the same, the strength of the C-C bond in ethane is found to be $630.8 - (6 \times 93.3) = 71.0$ kg. cal. Therefore the breaking of a C-H bond is negligible compared with that of a C-C bond. Thus the decomposition of a paraffin hydrocarbon consists in the rupture of a C-C bond, producing two free radicals which fly apart.

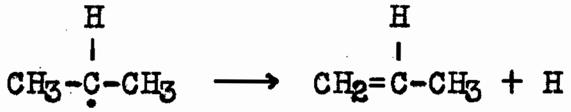
Only one reaction is probable for a methyl group formed in this way. It takes a hydrogen atom from a molecule of the hydrocarbon to form methane and another free radical. The energy of activation for this reaction is considerably lower than the minimum activation energy for the original hydrocarbon. It is to be noted that the methyl radical has a high chance of colliding with a hydrocarbon molecule under conditions of small decomposition, whereas the hydrocarbon radical produced has only a small chance of colliding with a methane molecule. Thus the probability that a methane molecule will lose a hydrogen atom to bring about the reverse reaction is very small.

Radicals higher than methyl free radicals can react in two different ways. First, they may take a hydrogen atom from the surrounding hydrocarbon molecules to form a saturated hydrocarbon. Second, they may decompose by giving off a hydrogen atom and forming an olefin, or they may break into a compound and a smaller free radical. Thus propane can decompose into a free methyl and a free ethyl group. The methyl group can form only methane, but the ethyl radical can either lose a hydrogen atom and form ethylene or take up a hydrogen atom and form ethane. From heats of reaction data, it may be shown that due to a process of internal compensation, it is possible for a free radical to form an olefin and hydrogen. It is much less probable that an ethyl radical would decompose into a methyl and methylene radical.

The n-propyl radical formed when a methyl or an ethyl group takes a hydrogen atom from propane can decompose in many ways. Of these the reaction

$$CH_3\text{-}CH_2\text{-}CH_2\cdot \longrightarrow CH_2{=}CH_2 + CH_3\cdot$$

is most probable, as it requires a minimum energy of activation. The isopropyl radical most probably follows the reaction



$$CH_3-\underset{\bullet}{\overset{\overset{H}{|}}{C}}-CH_3 \longrightarrow CH_2=\overset{\overset{H}{|}}{C}-CH_3 + H$$

Similarly, radicals higher than propyl can decompose in an even greater variety of ways, but without exception, one decomposition is much more probable than any other.

Rice pointed out that organic decompositions are chain reactions in which certain atoms or radicals start a cycle of reactions, and are themselves regenerated to start a new cycle. Thus if a hydrogen atom is produced in the decomposition of a free radical R, it will combine with a hydrogen atom of the surrounding hydrocarbon to form a hydrogen molecule and a free radical R'. The same radical is formed if the original radical R combines with a hydrogen atom of the hydrocarbon. Then R' decomposes into an olefin and either a smaller free radical or a hydrogen atom. These products then start a new cycle, and the process can presumably go on a great number of times. Thus the overall products of the decomposition are practically independent of the primary decomposition, provided the chains are fairly long. The radicals which perpetuate the chain are called carriers, and it is they which determine the saturated part of the products, as they are converted into paraffins in the succeeding cycle. The carriers are destroyed largely through collision, and to some extent through recombination on the walls of the vessel. Recognizing that the strengths of all C-H bonds in all hydrocarbons and radicals are not the same, Rice fixed an arbitrary value of 1200 calories as the difference in strength between a primary and secondary C-H bond, and 4000 calories as the difference between a tertiary and primary C-H bond. Using these values, the calculated and experimentally determined products agree.

Based on the preceding discussion, the decomposition of propane is represented as

$$CH_3\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH_2\cdot + CH_3\cdot$$

$$CH_2\text{-}CH_2\cdot \longrightarrow CH_2{=}CH_2 + H$$

$$CH_3\text{-}CH_2\cdot + CH_3\text{-}CH_2\text{-}CH_3 \longrightarrow C_2H_6 + CH_3\text{-}CH_2\text{-}CH_2\text{-} \longrightarrow$$

$$C_2H_6 + CH_2{=}CH_2 + CH_3\cdot$$

$$CH_3\text{-}CH_2\cdot + CH_3CH_2CH_3 \longrightarrow C_2H_6 + CH_3CH(CH_3)\cdot \longrightarrow$$

$$C_2H_6 + CH_3CH\ CH_2 + H$$

$$CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH_2CH_2\cdot \longrightarrow RH + CH_2{=}CH_2 + CH_3\cdot$$

$$CH_3CH_2CH_3 + R \longrightarrow RH + CH_3CH(CH_3)\cdot \longrightarrow RH + CH_3CH{=}CH_2 + H$$

$$R{=}CH_3\cdot,\ H$$

The last two reactions, which are alternative chain mechanisms depending on whether primary or secondary hydrogen reacts with the carrier complicate the decomposition. The composition of the products varies with the temperature and the relative probabilities of the last two reactions. It is possible to predict with fair accuracy both the nature and composition of the products at different temperatures.

Subsequently, Rice and co-workers (43) state that the scheme is highly satisfactory as a means of representing the thermal decomposition of a wide variety of compounds, including unsaturated hydrocarbons, ketones, aldehydes, acids and ethers. The outstanding difficulty in connection with the proposed mechanisms lies in the relative strengths of the C-H and C-C bonds, as the values determined by Mecke (44) were considerably above the maximum value for a primary rupture of a C-C bond to occur. However, at a temperature of 800 to 1000°, and a pressure of a few millimetres, it was found that hydrocarbon vapors remove mirrors of many metals even at considerable distances from the furnace.

The question remained as to whether the ordinary decomposition in the range 550°-650° is of the same nature as the higher temperature decomposition. Also, it was necessary to consider whether the removal of the mirrors was due to activated molecules as suggested by Burk (45), or by an alkylidene radical formed by the splitting off of two hydrogen atoms from the same carbon atom as suggested by Kassel (46). By carrying out the pyrolysis of acetone, propane and butane, and analysing the mercury dialkyls obtained in a reaction with metallic mercury, Rice concluded that the agent that removes the mirror is really free alkyl radicals. He did not determine whether the radicals are produced by a rupture of a C-C bond in the homogeneous gas phase, or by the rupture of a C-H bond at a hot silica surface. Working at a pressure of 70 mm. and 550°-650°, no removal of metallic mirrors occurred. Likewise, no removal occurred at 550°-650° at 1-2 mm. It was therefore concluded that free radicals must have been produced, but that they had all recombined before the mirror was reached.

Noting that in all attempts to prepare higher alkyl radicals by the Paneth method, only methyl and ethyl radicals could be detected, Rice (47) assumes that in ordinary pyrogenic decomposition of organic compounds, methyl and ethyl groups are the only stable radicals formed. Larger radicals decompose into olefins and either methyl groups, ethyl groups, or atomic hydrogen. These react with surrounding molecules to give methane, ethane, and molecular hydrogen. By taking the relative chances of reactions of primary, secondary and tertiary hydrogens as 1:2:10, the decomposition products of all paraffin hydrocarbons can be calculated quantitatively, assuming that they decompose according to the chain mechanism.

In a study of the decomposition of ethane, Frey and Smith (48) found a homogeneous, unimolecular reaction which they represent as the separation of a molecule of hydrogen from the ethane molecule to form ethylene. Pease (49) supported this mechanism as a result of studies on the formation of ethane from ethylene and hydrogen. Rice and Dooley (50) suggested that if the reaction can best be represented as the splitting off of molecular hydrogen, there should be a relation between the structure of a hydrocarbon and the extent of dehydrogenation. From a study of four hydrocarbons, they were unable to determine any such relation. However, if the decomposition is considered from the standpoint of free radicals, the agreement is much better. Furthermore, as neither ethylene or hydrogen have any effect on metallic mirrors, and as the pyrolysis of ethane causes the rapid removal of these mirrors, the reaction

$$C_2H_6 \longrightarrow 2CH_3.$$

must take place to some extent at least. The authors concede that a simple separation of hydrogen may occur simultaneously.

As it is necessary to know the activation energies of the various processes occurring during the different stages of the decomposition of an organic molecule in order to apply the free radical mechanism, Rice and Johnston (51) determined the strength of various bonds. Using the Paneth method of producing free radicals, the time of removal of a metallic mirror at different temperatures was noted. Assuming that the concentration of radicals at the end of the furnace is proportional to the rate of dissociation, the activation energy of the primary dissociation into free radicals, and thus the strength of the bond, may be determined. It was observed that the ethereal C-O bond is stronger than the C-H bond, which in turn is stronger than the C-N bond. There seems to be a definite diminution in stability as one passes from the lower to the higher members of a homologous series.

Staveley (52) states that the activation energy for the chain free decomposition of ethane is 74,500 cal. Although the C-C bond energy may be only 10,000-20,000 cal. greater than this, the author states that it does not follow that a relatively large fraction of activated ethane molecules decompose into radicals, since the activation energy is distributed in about fourteen square terms, and the chance that it allmigrates into the C-C link before the molecule is deactivated may be very small indeed. No quantitative calculations of the fraction of activated molecules which yield radicals can be made until more is known about the distribution of energy in molecules and of the exact values of bond strengths. There is one significant difference between ethane and dimethyl and diethyl ethers. With ethane there is a pronounced decrease in the mean chain length with increasing pressure. Hydrogen atoms seem to be the most likely chain carriers. With the ethers the mean chain length is independent of pressure, and probably methyl or ethyl radicals propagate the chains. Again it seems probable that only a small proportion of activated ethane molecules yield radicals, the great majority undergoing direct rearrangement to give ethylene and hydrogen. The absolute chain length must therefore be high. It was pointed out by Kassel (53) that the decomposition of ethane, acetone, and dimethyl ether follows the equation of a unimolecular reaction, whereas the decomposition of acetaldehyde follows an equation of an order between one and two. In order to substantiate the free radical theory, it is necessary to account for these facts. By measuring the reaction rates and energies of activation involved in these decompositions, Rice and Herzfeld (54) showed that these values fit the observed orders of reaction. Though there is no direct experimental demonstration of the presence of free radicals below 700°, the only way to avoid chain reactions as the explanation of the measured ratio would be to increase the heats activation to quite improbable values.

In a study of the reaction products resulting when the fragments formed during the thermal decomposition of propane and butane are brought into contact with metallic mercury, Rice and Evering (55) found more than 95% of dimethyl mercury. Thus the methyl groups are the only alkyl radicals formed to any extent. Ethyl and higher radicals were shown to be absent. This was confirmed by the use of metallic tellurium,--94% of dimethyl ditelluride being formed from the products of decomposition of butane, acetone and diethyl ether (56). The same workers were later able to prove the existence of free methylene radicals by working with diazomethane at temperatures under 500° (57). Kassel (58) and Belchetz (59) stated that free methylene radicals occurred in the decomposition of methane. By using metallic tellurium, Rice and Dooley (60) could detect no products of the combination of tellurium and methylene radicals, and concluded as a result that methane dissociates only into methyl groups and hydrogen.

Interesting information in the study of free radical mechanisms was obtained by the addition of nitric oxide to thermal decomposition reactions. Rice and Rodowskas (61) represent the overall decomposition of ethyl nitrite at higher pressures as

$$CH_3CH_2ONO \longrightarrow NO + 1/2\ CH_3CH_2OH + 1/2CH_3CHO \quad \ldots\ldots (1)$$

and at lower pressures as

$$CH_3CH_2ONO \longrightarrow NO + 1/2HCHO + 1/2CH_4 + 1/2CH_3CHO \quad \ldots\ldots (2)$$

Steacie and Shaw (62) have also concluded that equation (1) represents the overall reaction. The primary decomposition is

$$CH_3CH_2ONO \longrightarrow NO + CH_3{\cdot}CH_2O{\cdot}$$

Even if a free radical were introduced, it would immediately be removed and replaced by molecules according to the equations

$$R + CH_3CH_2ONO \longrightarrow RH + CH_3CH(ONO){\cdot}$$

$$CH_3CH(ONO){\cdot} \longrightarrow CH_3CHO + NO$$

Thus the ethyl nitrite itself is a chain terminator, and the reaction cannot be expected to occur through a chain mechanism. It was found that when ethyl nitrite was decomposed at 425°, no effect was observed on metallic mirrors. However if carbon dioxide was used as a diluent, mirrors were removed with great readiness as low as 400°. This indicated that methyl groups were produced from the $CH_3CH_2O{\cdot}$ radical formed in the primary decomposition, but unless a diluent was added, these methyl radicals were removed before they reached the metallic mirror. The authors therefore suggested that the introduction of a small quantity of ethyl nitrite into an organic substance decomposing according to a chain mechanism should inhibit the reaction by shortening the chains. Preliminary work on butane showed the rate of decomposition to be unaffected, but this was to be expected, because the life of an ethyl nitrite molecule is exceedingly short in the temperature range in which butane decomposes at a measurable rate.

The effect of nitric oxide on thermal decompositions was studied by Hinshelwood and Staveley (63). They state that in the course of a systematic study of the catalytic influence of nitric oxide on various organic decomposition reactions, small amounts of this gas, of the order of 0.1 - 1.0 mm., could reduce the rate of reaction to a well-defined limit, smaller than the original by a factor of up to two or three times. The effect is as though quite short reaction chains were broken by the nitric oxide. Direct experiment showed that the inhibition is not connected with a surface reaction. In connection with the free radical theory, it may be observed that in the electronic structure, nitric oxide is itself virtually a free radical. Travers and Seddon (64), though wishing to avoid the use of the term free radical, were forced by their experiments on the decomposition of acetaldehyde to the conclusion that the changes involve the formation of a short-lived intermediate. Investigating the thermal decomposition of dimethyl ether, Gay and Travers (65) discovered that small quantities of nitric oxide reduced the rate of reaction to a small fraction of the rate observed in the pure gas. As the concentration of nitric oxide is increased, the rate of reaction increases rapidly. The authors explain the observations on the basis of an oxidation reaction.

A later statement of Staveley and Hinshelwood (66) on the decomposition of diethyl ether shows that at 500°-600° the addition of considerable amounts of nitric oxide has a pronounced catalytic effect. However small amounts retard the reaction in a marked way. As there had been no previous evidence of a chain mechanism in the ether decomposition, a detailed investigation was undertaken. The authors state that the only possible causes of inhibition in a homogeneous reaction seem to be (a) the removal of adventitious catalyst by the inhibitor, (b) the specific deactivation of activated molecules, (c) the breaking of chains by the inhibitor. It is unlikely that (a) is a satisfactory explanation. With regard to (b), certain thermodynamic difficulties are encountered. We are therefore left to conclude that the reaction must involve at least short chains. The investigation was extended to numerous other ethers (67), and it was discovered that the rate of decomposition was reduced by nitric oxide in the case of methyl ethyl ether, ethyl propyl ether, dipropyl ether, and di-isopropyl ether. In all cases, a well-defined limiting rate is reached with one or two mm. of nitric oxide. Assuming that nitric oxide breaks chains, and that this limit represents the rate of the primary decomposition, the mean chain length falls steadily from about 17 for dimethyl ether at 540° to 1.4 for di-isopropyl ether. It is stated that most of the activated molecules decompose by internal re-arrangement, that is, by a chain of unit length, while a quite small proportion split into radicals which give rise to a few long chains. With dimethyl ether, nitric oxide is quite rapidly removed from the system. With the other ethers this effect is very much smaller. With increasing temperature the mean chain length for all the ethers decreases somewhat, necessitating the determination of new values for the activation energy on the fully inhibited reactions. The new values bear a more natural relation to the structure of the molecule than did the older ones. The activation energy of the chain free reaction is in all cases considerably less than the energy required to break the C-C or C-O bond.

Turning to aldehydes, Staveley and Hinshelwood (68) found that acetaldehyde is complete exempt from inhibition by nitric oxide, whereas propaldehyde shows marked inhibition. The absence of inhibition therefore shows a non-chain mechanism for the decomposition of acetaldehyde. Rice and Herzfeld (54) had suggested a chain mechanism, a concept supported by the work of Sickman and Allen (69), who found that the decomposition of acetaldehyde can be accelerated by the addition of azomethane and assumed that methyl radicals from the azomethane react with aldehyde molecules.

In explanation of their results, Staveley and Hinshelwood refer to a conclusion reached by Hinshelwood, Fletcher, Verhoek and Winkler (70) that in thermal decompositions there are several varieties of activated molecules, differing in the location of the energy and having different decomposition probabilities. The different types of activated acetaldehyde molecules react as though the aldehydes hydrogen migrates to the alkyl carbon atom, to form carbon monoxide and methane. Some of the propaldehyde molecules also behave in this way, but others undergo an alternative decomposition, yielding methane, ethylene, and hydrogen. It would seem that the activation energy is located in the C-H bonds of the alkyl group. In the case of acetaldehyde, the energy can migrate to permit the rupture of the molecule into methane and carbon monoxide, but then the activation energy is distributed in the ethyl group in propaldehyde, production of a free radical becomes more likely. Thus some propaldehyde molecules dissociate as

$$CH_3 \cdot CH_2 \cdot CHO \longrightarrow CH_3 \cdot + \cdot CH_2CHO$$

the methyl radicals then bringing about further decomposition. The authors conclude that only those molecules in which the activation energy is large and located in the region of the molecule most remote from the aldehyde group dissociate into radicals and so initiate chains or cause catalytic decomposition.

In the course of investigations on the inhibition of organic decompositions, Rice and Polly (71) noted that alkyl nitrites and propylene, as well as nitric oxide have an inhibitory effect. The action of alkyl nitrites is due to a dual effect, the molecules themselves inhibiting by taking up a free radical, as well as the nitric oxide liberated in the breakdown of the alkyl nitrite. Propylene removes some of the chain radicals R to give RH and the allyl radical, which combines with itself to form diallyl rather than continuing the chain.

Regarding the fate of the nitric oxide in decomposition reactions, Taylor and Bender (72) note that cyanides, ammonia, nitrogen, formamide and formaldoxime have been detected in the products of the reaction.

It has been reported by Frey (73), Leermakers (74) and others that thermal decompositions involving chain mechanisms are accelerated by the addition of free radicals. Frey added dialkyl mercury compounds to butane and obtained decomposition at a lower activation energy.

Bentonites

In industry there is a continual search for more efficient and more economical catalysts for high temperature, vapor phase reactions. Catalysts which induce specific reactions are especially needed, and among these, clays and clay-like substances have already been used successfully as catalysts for dehydration, polymerization, isomerization, condensation and dehydrogenation. Clays such as kaolin, kieselguhr and Japanese acid earth are widely used. Until the present, these have been imported into Canada. It would therefore be of advantage to develop our own clays to replace the imported ones.

In Western Canada there are deposits of clays which should be suitable for industrial development. In British Columbia, near Princeton, there is a seam fifteen feet thick, about a mile long, within a few feet of the railroad (75). In Alberta there are large deposits near Drumheller and in the Red Deer River Valley (76). In Saskatchewan there are several widely scattered deposits (77). The colors vary from white, grey, yellow to green and brown. They differ greatly in physical condition and texture. When damp, many are waxy or greasy, some are hard and flint-like. Canadian bentonites, unlike many others, show little expansion when wetted with water. In Manitoba, at Morden, there is a deposit in alternate yellow and black layers which has been commercially developed, the yellow only being used.

Bentonite is commonly composed of the mineral montmorillonite, having the following composition:

$$(Mg,Ca)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$$

where n is 4 approximately, and in certain cases, the Al_2O_3 is replaced by Fe_2O_3. It is generally conceded that bentonite is an alteration product of glassy volcanic ash following its deposition in water, the base materials of the original ash being removed by leaching or solution, leaving the colloidal silica and alumina behind as bentonite.

Perhaps the earliest use of bentonite was as a "soap clay" by early settlers, and for plastering and white washing purposes about their homes. There was little real development of bentonite on this continent until about 1920, when a marked expansion took place. At the present time, this little known mineral plays an important part in certain lines of industrial activities. Among the largest users may be cited the mineral-oil refiners (78) and producers of vegetable oils. It is also used for the sweetening (desulfurizing) of petroleum oils (79), as a drilling mud for oil wells, as a catalyst carrier, and for a host of other purposes such as a filler, a binder and surface coating for paper, in oil cloth, rubber, ceramics, etc.

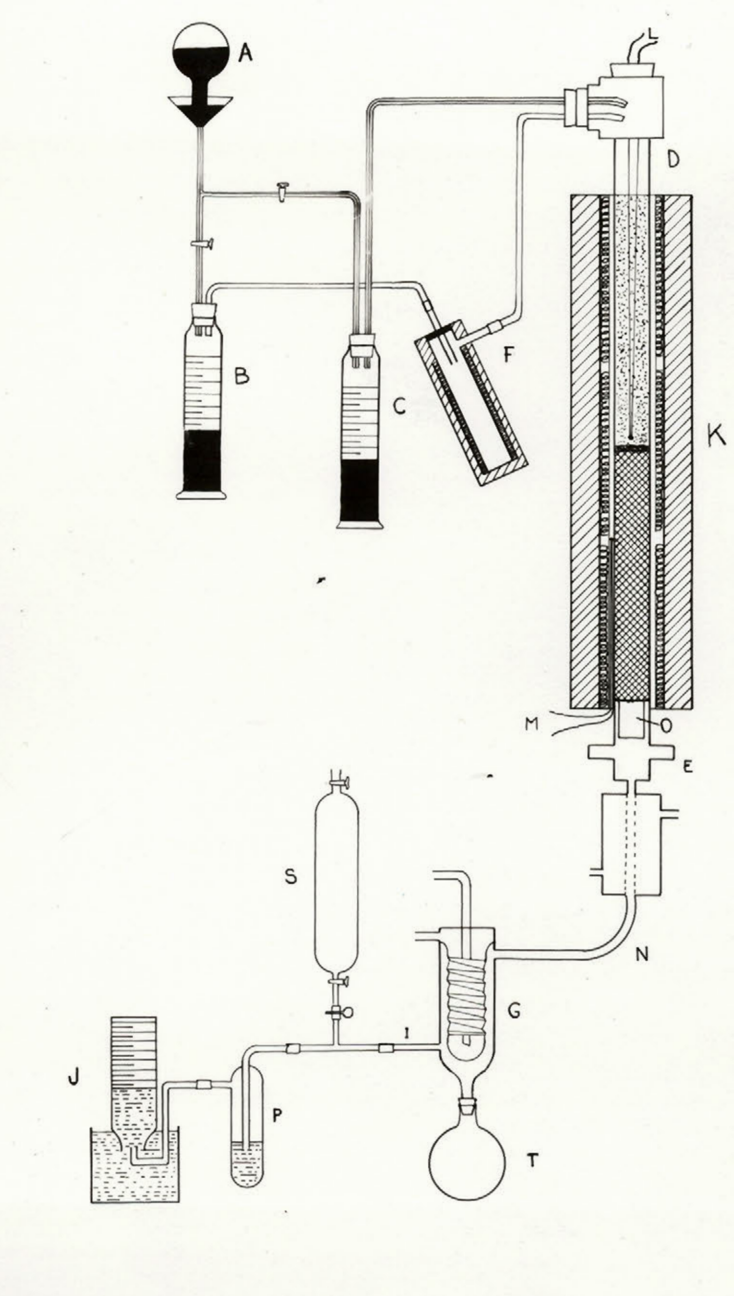
EXPERIMENTAL PROCEDURES AND DISCUSSION OF RESULTS

Apparatus

I. Catalysis Apparatus

In order to permit the use of high-boiling liquids and fast feed rates, the vertical type of pyrolysis furnace designed in this Department by Morton (80) was used in this investigation, modified by the addition of a vaporizer for the water used as a diluent in the pyrolysis reactions.

A is a constant level mercury reservoir from which mercury is fed through stopcocks into the 250-cc. graduated vessels B and C, which contain the liquid to be studied and water, respectively. B is connected directly by means of capillary tubing to the preheater section of the furnace D. C is connected to the water vaporizer F. This consists of one-inch iron pipe, 10 inches in length, wound with fifteen feet of B. & S. #22 Nichrome wire, which is sufficient to vaporize completely all the water employed. One end of the pipe is closed, the water entering through a nipple at the other end, and the steam leaving by way of the side arm, which is connected by asbestos-wrapped glass tubing to the preheater section of the furnace. The preheater is 15 inches long, made of one-inch iron pipe packed with steel wool to serve as a heat transfer medium. A T-coupling is connected to the top, through one arm of which the starting materials pass. A chrome-alumel thermocouple is inserted through the other arm,



Vertical Type Catalysis Apparatus

FIGURE 1

and extends to the end of the pre-heating section. By this means, the temperature of the vapors as they reach the catalyst may be determined. Connections between the glass tubing, the graduated cylinders, and the pyrolysis tube are made with neoprene stoppers. The catalyst section is thirty inches long, packed in most cases with 80 g. of activated bentonite of 4 to 8 mesh, supported by a wad of steel wool. The two sections of the furnace are joined by a metal union. The heat was obtained by three 550-watt cylindrical heaters, wound on 12-inch alundum cores (Hoskins FD-303 oversize) and placed end to end. The two bottom elements were wired in both series and parallel, and, controlled through rheostats to yield any desired temperature. The pre-heater section and the water vaporizer were both controlled by separate rheostats. A thermocouple (M) was inserted through the bottom of the furnace extending approximately half way up the catalyst section between the iron pipe and the heating elements. The whole furnace was surrounded by asbestos high temperature pipe covering, 2 inches in thickness for insulation purposes.

The bottom end of the furnace tube is connected by means of a union (E) to a length of 1/4-inch pipe (N) surrounded by a metal jacket through which water flowed, to act as a condenser. The lower end of this is curved to fit into a Frederick condenser (G) by means of a neoprene stopper to insure complete condensation of the liquid products of the pyrolysis. The side arm of the condenser (I) permits the passage of gaseous products through a bubbler (P) and thence into a Fisher Precision Wet Test gas meter, or a measuring vessel (J) as used in early runs. In this way the total volume of gas produced in the pyrolysis could be readily measured. A gas sample for analysis is taken during the course of a run into an evacuated gas sampling tube (S), care being taken to make sure that atmospheric pressure is maintained in the furnace, by maintaining a stream of bubbles through the bubbler. Liquid products were collected in the flask (T).

II. Gas Analysis Apparatus

A major feature of this investigation was the analysis of gaseous products. Use was made of a modified Bone and Wheeler apparatus previously constructed in this Department. It consists of 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. This differs from the usual apparatus by the addition of the copper-oxide furnace, and the substitution of a platinum-coil pipette for an explosion pipette.

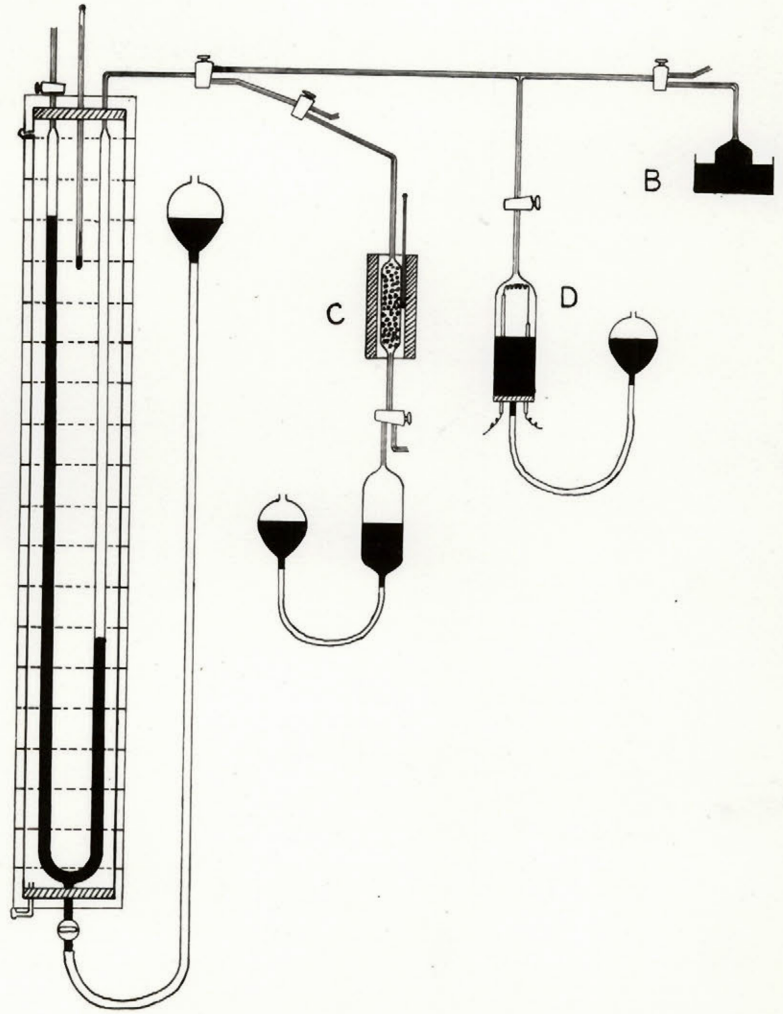
The gas is measured at constant volume and passed into the absorption dome, where it is treated with various reagents, listed in the order in which they are used:

TABLE I

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

Dobrjanski (81) used 67 per cent sulfuric acid to separate isobutylene from other olefins.

For hydrogen determination, the copper-oxide furnace is evacuated by means of Toepler pump action and the gas passed over the oxide at 260°-280°C., followed by re-evacuation and measurement of the residual gas. This is repeated until no further contraction occurs. Saturated hydrocarbons are burned in oxygen over the glowing platinum coil, and determined by measuring the contraction in volume, and volume of carbon dioxide produced.



Bone and Wheeler Apparatus

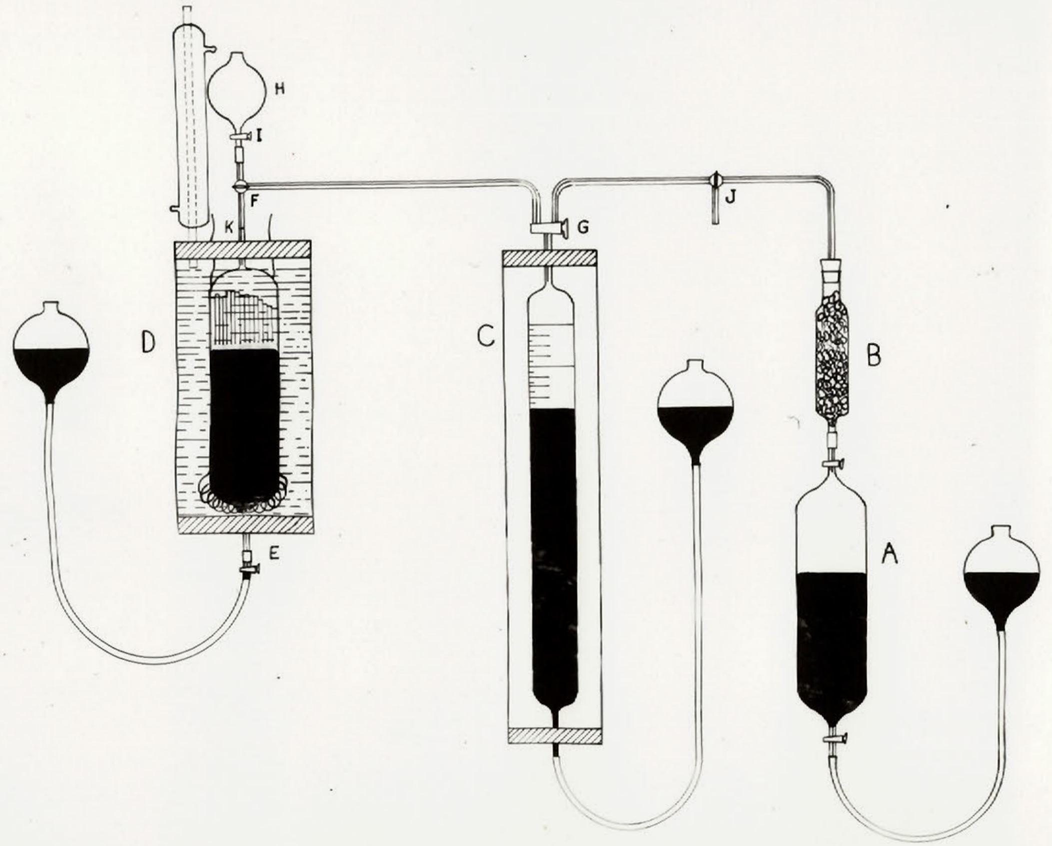
FIGURE 2.

III. Butadiene Apparatus

An apparatus for the analysis of butadiene as devised by Cambron based on the Diels-Alder reaction between butadiene and maleic anhydride had also been constructed in this Department. It is shown in Figure III. It consists of 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 the Orsat gas absorption pipette, D, surrounded by an electrically heated water jacket and provided with a levelling bulb. The Orsat pipette is charged with 3-4 grams of molten maleic anhydride, which is kept liquified by the surrounding hot water. The drying tube and capillary tubing to stopcock 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 stopcock I, which is then closed. A gas sample is passed into the burette and measured at atmospheric pressure. It is then passed into the absorption pipette, and left until no further absorption occurs. This serves to saturate the maleic anhydride with soluble hydrocarbons other than butadiene. Then a second sample is taken from A, the contraction in this case being due to butadiene alone. A single charge of maleic anhydride serves for several different butadiene determinations.

IV. Fractionation Columns

Two previously constructed fractionation columns were used in the purification of starting materials, and analysis of the



Butadiene Gas Analysis Apparatus

FIGURE 3.

liquid products in the case of the octanone-2 runs.

The first of these was a Stedman column, of the laboratory type, 90 cm. long by 1.5 cm. internal diameter, with an efficiency rated at 50 theoretical plates. This was used for the purification of starting materials, being suitable for distillation in vacuo. The second was a small colum packed with 3/16 inch glass helices, 45 cm. long with an internal diameter of 10 mm. Its efficiency was rated at 14 theoretical plates. The column head on both columns was of the total condensate, partial take-off type.

Preparation of the Catalyst

All of the clays used in this investigation were activated according to a method outlined by Gallay (78). The material was boiled gently for three hours with a twenty per cent aqueous solution of sulfuric acid. The volume of concentrated acid used was one-half the weight of the clay being activated. After cooling, the slurry was diluted to about three times its volume, filtered and washed on a vacuum filter, and dried at 110° for 12 hours. The cakes of clay were then broken up and screened into pellets of from 4 to 8 mesh.

After a pyrolysis run, the catalyst became coated with a deposit of carbon, which markedly decreased its activity. It was therefore necessary to remove this deposit after each run. This was accomplished by heating the catalyst to 550°-600° and drawing air through it for about 6 hours. After this reactivation process, the catalytic properties were slightly different from those of a fresh sample. Consequently reactivated catalyst was used for each run of this investigation in order to obtain comparable results. Each charge of catalyst could be used eight to ten times before renewing, provided the temperature during reactivation did not exceed 700°, as at this temperature, sintering occurs and catalytic activity is practically lost.

Through the courtesy of the Department of Mines and Resources, an analysis of the unactivated, activated and reactivated bentonites was obtained. The results are as follows, based on water-free bentonite:

TABLE II

Analysis of Morden Bentonite

	Unactivated	Activated	Reactivated
SiO_2	61.70	71.73	72.95
Al_2O_3	22.88	19.66	19.84
Fe_2O_3	4.89	0.87	0.28
CaO	2.13	0.59	0.53
MgO	4.78	4.08	3.68
Other Bodies (by difference)	3.63	3.07	2.72
	100.00	100.00	100.00
Loss on Ignition (a)	24.94	22.28	2.77

(a) In each case, the ignition was carried out at 1700° for 2 hours. The loss includes uncombined moisture and water of hydration.

TABLE III

Analysis of Saskatchewan Bentonite

	Unactivated	Activated	Reactivated
SiO_2	66.23	81.96	82.45
Al_2O_3	20.89	13.36	11.68
Fe_2O_3	4.28	1.75	1.79
CaO	1.65	Trace	Trace
MgO	5.43	1.42	1.64
Other bodies (by difference)	1.52	1.51	2.44
	100.00	100.00	100.00
Loss on Ignition (a)	15.69	9.32	3.47

(a) In each case, the ignition was carried out at 1700° for 2 hours. The loss includes uncombined moisture and water of hydration.

TABLE IV

Analysis of Alberta Bentonite

	Unactivated	Activated	Reactivated
SiO_2	72.48	80.85	81.04
Al_2O_3	16.45	13.99	14.04
Fe_2O_3	3.36	2.17	2.08
CaO	2.08	0.62	0.53
MgO	1.84	1.26	1.26
Other bodies (by difference)	3.79	1.11	1.05
	100.00	100.00	100.00
Loss on Ignition (a)	8.75	6.85	1.38

(a) In each case, the ignition was carried out at 1700° for 2 hours. The loss includes uncombined moisture and water of hydration.

TABLE V

Analysis of British Columbia Bentonite

	Unactivated	Activated	Reactivated
SiO_2	74.29	78.87	79.62
Al_2O_3	16.45	15.09	14.07
Fe_2O_3	3.71	3.22	3.21
CaO	1.82	Trace	0.22
MgO	1.72	1.32	1.33
Other bodies (by difference)	2.11	1.50	1.55
	100.00	100.00	100.00
Loss on Ignition (a)	8.75	6.15	1.23

(a) In each case, the ignition was carried out at 1700° for 2 hours. The loss includes uncombined moisture and water of hydration.

The Manitoba bentonite was mined at Morden, Manitoba, by the Pembina Mountain Clays Company of Winnipeg. The Saskatchewan bentonite was mined at Rockglen, Sask., Sample #3731. The Alberta bentonite was a composite of samples mined by Mr. Gordon L. Kidd, Mining Engineer, Drumheller, Alberta. The British Columbia bentonite was mined at Princeton, B.C. by the Princeton Properties, Ltd. (a)

It thus appears that the acid treatment removes the greater part of the iron and calcium content of the clays, and some of the aluminum. The percentage compositions of the four samples are seen to be remarkably similar. The difference in catalytic activity can therefore be attributed only to differences in particle size and surface area.

X-ray diffraction and spectroscopic studies were made on the clay samples (b) and electronmicrographs were also obtained (c). The results of the X-ray diffraction studies and the

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(a) We wish to express our thanks for the generous gifts of bentonites to the Pembina Mountain Clays Company, Winnipeg; Professor W.G. Worcester of the University of Saskatchewan, Saskatoon; Mr. Gordon L. Kidd, Drumheller, Alberta and Mr. Edward R. Hughes, Inspector of Mines, Princeton, B.C.

(b) For these studies we are indebted to the Research and Development Department of Canadian Industries Limited.

(c) We wish to express our thanks to the Department of Physics, University of Toronto, for the electronmicrographs.

conclusions drawn from them, with the spectrographic analyses appear in Appendix I. No conclusions relating to the efficiency of the clays as catalysts could be drawn from the electron-micrographs.

The Pyrolysis of Butanone over Activated Morden Bentonite

Butanone has been known for a long time as a by-product in the manufacture of acetone in the charcoal industry (82). It is an important component of the so-called acetone oil (last runnings from acetone distillation). In addition to this method of production, some new processes have been technically developed which give butanone as the main product and enable a high standard of purity to be guaranteed. These include a fermentation process and the use of the C_4 fraction from cracked gases in the petroleum industry (83). It is used as a dewaxing agent for lubricating oils, as a component of lacquer solvents and thinners (84) and as a solvent for cellulose acetate.

The butanone used in this investigation was purified by distillation in the Stedman Column. The fraction having the constants b.p. 79.5°, n_D^{20} 1.3795, d_d^{20} 0.805 was used in the pyrolysis reactions.

Procedure

The desired weight of catalyst, in most cases 80 g. of bentonite when newly activated, was placed in the catalyst section of the furnace, and the furnace and preheater raised to the desired temperature. Care was taken to prevent overheating of the preheater, as overheating in this region caused premature cracking with a large evolution of hydrogen. In most cases, the preheater temperature was maintained 50° below the furnace temperature.

The water and ketone were displaced from their containers by mercury at the desired rate. Except for very rapid rates, the rate could be easily and conveniently controlled by counting the drops of mercury. The water was vaporized in the vaporizer and the ketone in the preheater. The vapors then passed over the activated bentonite. Liquid products were condensed in the two condensers, while the gaseous products passed on and were measured in the gas meter. The rate of evolution of gas varied somewhat as the run progressed, the gas sample being taken at about the middle of the run.

Due to the large volumes of water used, and the mutual solubility of the liquid organic products and the water, no attempt was made to analyse the liquid products. The gaseous products were analysed in the Bone and Wheeler Apparatus, and a separate analysis made for the butadiene content.

Results and Discussion

The various temperatures and feed rates at which the pyrolysis of butanone was investigated are shown in Table VI.

From an examination of the analysis of the gaseous products it will be noted that an increase in temperature causes a marked increase in the volume of gas produced. The ketone proved to be extremely sensitive to small differences in temperature. However, as the temperature is increased, the percentage of unsaturated hydrocarbons other than ethylene drops quite rapidly, while an increase occurs in the percentage of ethylene, hydrogen,

TABLE VI

Dehydration of Butanone over Activated Modern Bentonite

80g. Bentonite

Run No.	Furnace ^{o}C.	Rate cc./min.		Ketone g.	Water g.	Total Gas l.
		Ketone	Water			
14	550	1	8	72.0	720.0	6.3
23	600	1	8	72.0	720.0	18.3
15	600	2	8	72.0	360.0	20.7
24	650	1	8	72.0	720.0	19.1
16	650	2	8	72.0	360.0	29.2
17	650	3	8	72.0	240.0	23.5
25	700	1	8	72.0	720.0	26.1
18	700	4	12	72.0	270.0	30.0
26	750	1	8	72.0	720.0	39.1
27	750	1	12	72.0	1080.0	32.6

40g. Bentonite

22	700	1	4	72.0	360.0	29.2
21	700	1	8	72.0	720.0	19.6

TABLE VII

Analysis of Gaseous Products from Butanone Runs

General Gas Analysis in Volume Per Cent								Butadiene Analysis	
Run No.	CO_2	Iso-butylene	C_2H_4	Other Unsats. Incl. Butadiene	CO	H_2	Saturates	Volume %	Yield %
14	6.4	6.2	8.3	18.9	5.3	39.2	14.0	12.3	3.7
23	13.1	5.4	5.0	34.7	7.5	14.0	17.8	24.5	20.0
15	11.2	8.0	7.2	34.5	8.5	10.0	18.0	24.5	22.6
24	11.3	4.9	4.2	41.3	9.3	18.2	9.7	35.5	30.3
16	8.4	4.0	12.6	28.0	14.7	14.8	16.5	19.0	24.5
17	8.3	6.0	11.8	27.4	15.0	10.2	19.1	18.1	18.7
25	7.5	3.0	8.1	36.3	11.2	20.0	10.9	31.3	36.6
18	7.0	5.1	17.8	21.3	18.7	9.3	19.5	10.2	13.6
26	4.5	3.5	11.8	26.1	11.0	29.8	11.1	22.0	38.4
27	6.4	4.0	9.0	28.1	10.2	27.1	13.5	22.5	32.7
22	9.0	4.0	10.1	29.8	10.4	19.6	15.5	21.3	32.2
21	7.3	4.3	9.5	28.6	13.5	20.9	15.1	23.6	20.6

and carbon monoxide. An increase in the percentage of carbon monoxide is accompanied by a decrease in the percentage of carbon dioxide. The effect of adding larger volumes of water is to decrease the total volume of gas, at the same time increasing the percentage of unsaturated components. The butadiene content of the gas increases accordingly. Thus the highest percentage yield of butadiene should occur at a high temperature to insure a high degree of cracking of the molecules, and when the volume of water added is large enough to produce a high percentage of unsaturates. This was found to be the case, a maximum of 38.4 per cent of butadiene being formed at a temperature of 750°C. and a rate of 8 volumes of water to one of ketone. From a study of the effect of both water and nitrogen as a diluent in pyrolytic reactions, Morton (80) concluded that the water serves two functions. Firstly, it removes carbon from the catalyst, with the formation of carbon dioxide, carbon monoxide and hydrogen. The result of this is to maintain a cleaner catalytic surface, hence to increase the extent of cracking. Secondly, the water greatly decreases the length of contact time, thus tending to minimize secondary reactions. It is possible that the water also exerts a directive influence on the course of the reaction, which is thought to be the result of two competing reactions. The use of large volumes of water is thus a factor of prime importance in securing the yield of butadiene obtained in these experiments.

It was considered possible that a smaller quantity of catalyst would be an aid in preventing severe cracking of the ketone molecules, with an increase in the butadiene production. Runs were therefore carried out with half the weight of catalyst. The results were disappointing. Not only was the butadiene content lower, but the volume of gas produced was greatly reduced. This resulted in a large decrease in yield per cent of butadiene. It would seem that with less catalyst, there is more simple thermal decomposition instead of selective dehydration to form butadiene. An increase occurs in the percentage of hydrogen, ethylene, carbon monoxide and saturated hydrocarbons with a smaller volume of catalyst, with a drop in the percentage of unsaturates other than ethylene from 36.3 per cent to 28.6 per cent at 700°. This effect is further noted in runs reported later in this thesis where no clay catalyst was used.

It must be pointed out that in all cases there was an inevitable reaction between the water vapor and the steel wool used as a heat transfer medium in the preheater with the evolution of hydrogen. No packing which was more inert than steel wool was available. Pumice was used in several early runs, but was found to have a marked effect on the decomposition of the ketone. The hydrogen reported in the gas analyses is therefore a composite of hydrogen produced from the water vapor and steel wool and hydrogen from the breakdown of the ketone molecules.

The Effect of Other Canadian Bentonites on the Pyrolysis of Butanone

In order to compare the catalytic activity of samples of bentonite mined in British Columbia, Alberta and Saskatchewan with that of the Manitoba bentonite heretofore used in this Department, butanone vapors were dehydrated over these clays. These samples were finely ground and activated with acid in precisely the same way as the Manitoba samples, and received identical treatment throughout. For purposes of comparison, the three conditions which produced the highest yields of butadiene with the Manitoba clay were used. In all cases, eighty grams of the activated clay were employed. The temperature conditions, rates of through-put used, and total gas produced are reported in Table VIII. The general gas analysis and separate butadiene analysis are shown in Table IX. To discover what the effect of having no catalyst in the furnace would be, the furnace tube was packed with steel wool and a similar series of runs carried out. These runs are also recorded in Tables VIII and IX. In the runs carried out at 750°, the preheater was kept at 650° to prevent excessive cracking in the preheater.

Discussion of Results

It is evident from the percentage yield of butadiene, that none of the clays from the three western provinces compare as dehydration catalysts with the Manitoba bentonite. The British

TABLE VIII

Dehydration of Butanone over Activated Canadian Bentonites

80 g. Bentonite

Run No.	Catalyst	Furnace °C.	Rate cc/min.		Ketone g.	Water g.	Total Gas l.
			Ketone	Water			
28	British Columbia	650	1	8	72.0	720.0	13.4
29	British Columbia	700	1	8	72.0	720.0	25.6
30	British Columbia	750	1	12	72.0	1080.0	42.3
31	Alberta	650	1	8	72.0	720.0	11.2
32	Alberta	700	1	8	72.0	720.0	23.8
33	Alberta	750	1	12	72.0	1080.0	43.2
34	Saskatchewan	650	1	8	72.0	720.0	15.2
35	Saskatchewan	700	1	8	72.0	720.0	25.3
36	Saskatchewan	750	1	12	72.0	1080.0	38.2
24	Manitoba	650	1	8	72.0	720.0	19.1
25	Manitoba	700	1	8	72.0	720.0	26.1
27	Manitoba	700	1	12	72.0	1080.0	32.6
37	None	650	1	8	72.0	720.0	5.7
38	None	700	1	8	72.0	720.0	9.8
39	None	750	1	12	72.0	1080.0	31.5

TABLE IX

Analysis of Gaseous Products from Butanone Runs

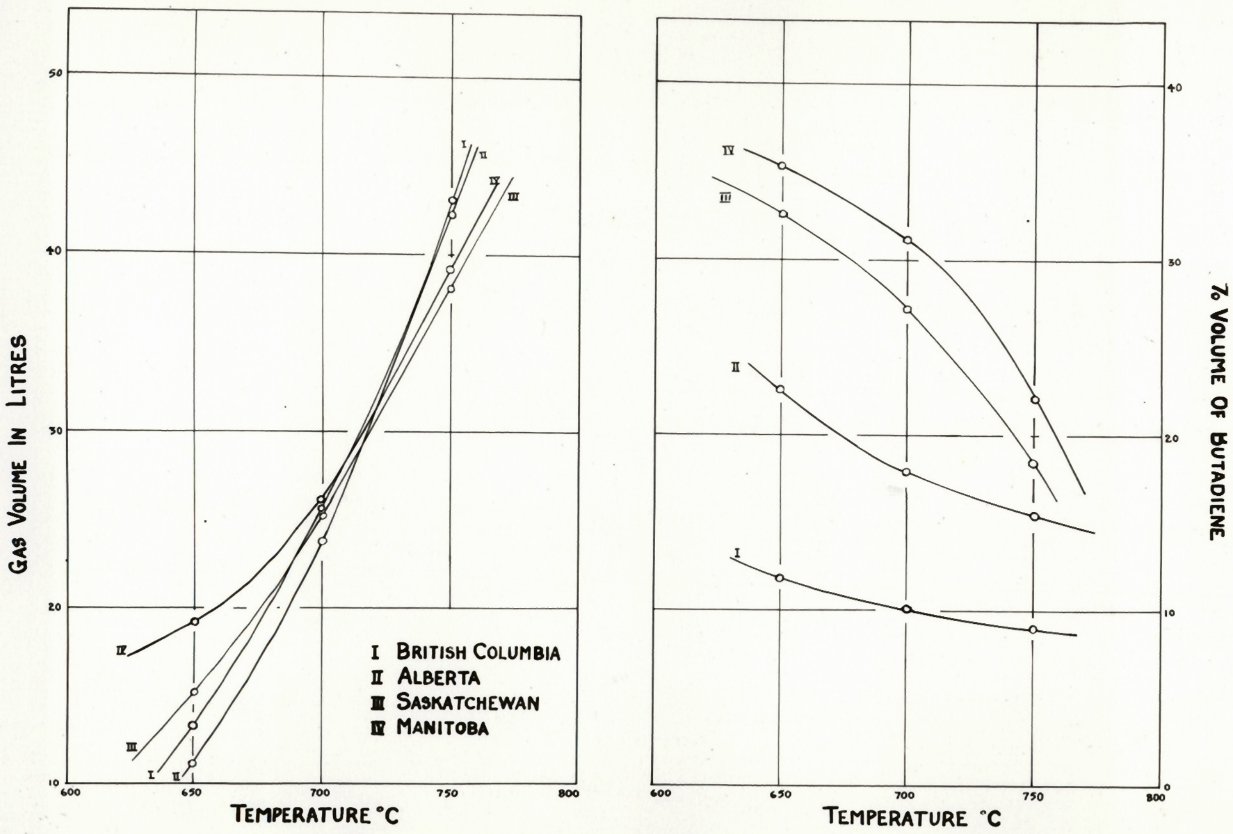
General Gas Analysis in Volume Per Cent									Butadiene Analysis	
Run No.	Catalyst	CO_2	Iso-butylene	C_2H_4	Other Un-Saturates Including Butadiene	CO	H_2	Saturates	% Volume	% Yield
28	British Columbia	6.2	2.8	3.2	16.5	3.6	53.3	12.0	12.0	7.2
29	British Columbia	5.0	2.5	9.2	15.7	7.4	43.0	15.6	10.1	11.5
30	British Columbia	6.4	2.1	13.1	14.6	10.6	35.0	16.7	9.2	17.0
31	Alberta	8.8	3.1	5.6	26.9	6.7	28.2	18.2	22.7	11.3
32	Alberta	6.4	2.3	10.6	24.2	12.9	28.5	14.2	18.0	19.1
33	Alberta	6.0	2.3	13.7	19.5	16.4	23.3	16.5	15.7	30.0
34	Saskatchewan	11.6	4.7	5.2	36.7	8.0	24.5	9.0	32.6	21.7
35	Saskatchewan	10.4	4.5	5.9	32.8	8.5	26.0	11.4	27.3	30.9
36	Saskatchewan	12.0	2.4	7.1	23.1	11.1	30.7	12.0	18.5	31.5
24	Manitoba	11.3	4.9	4.2	41.3	9.3	18.2	9.7	35.5	30.3
25	Manitoba	7.5	3.0	8.1	36.3	11.2	20.0	10.9	31.3	36.6
27	Manitoba	6.4	4.0	99.0	28.1	10.2	27.1	13.5	22.5	32.7
37	None	13.5	0.0	3.8	1.6	6.0	64.6	8.4	0.0	0.0
38	None	10.8	0.0	13.4	1.7	13.0	48.1	12.5	0.0	0.0
39	None	8.9	0.0	15.5	1.8	17.0	39.1	16.9	0.0	0.0

Columbia bentonite especially gave very low yields of butadiene, a maximum of 17.0 per cent being produced at 750° with a rate of 1 cc. of ketone and 12 cc. of water per minute. This does not compare with the 32.6 per cent yield of butadiene obtained from the Manitoba clay under the same conditions. Nearly half of the gas produced was hydrogen, and the percentage of saturates was also higher than in the Manitoba bentonite runs.

The Alberta bentonite gave better results than the Manitoba bentonite, a maximum of 30.0 per cent of butadiene being formed at 750°. While this value closely approximates the yield from the Manitoba bentonite, the volume per cent is considerably less, the increased volume of gas produced over the Alberta clay accounting for the higher yield per cent.

The Saskatchewan bentonite more closely approximates the Morden bentonite than either of the other two clays. The volume of gas produced is lower at the low temperatures and higher at the high temperatures than the corresponding runs over Manitoba bentonite. The per cent volume of butadiene is lower, and the per cent yield also correspondingly lower. For purposes of comparison, the results obtained are plotted in Graphs I to IV.

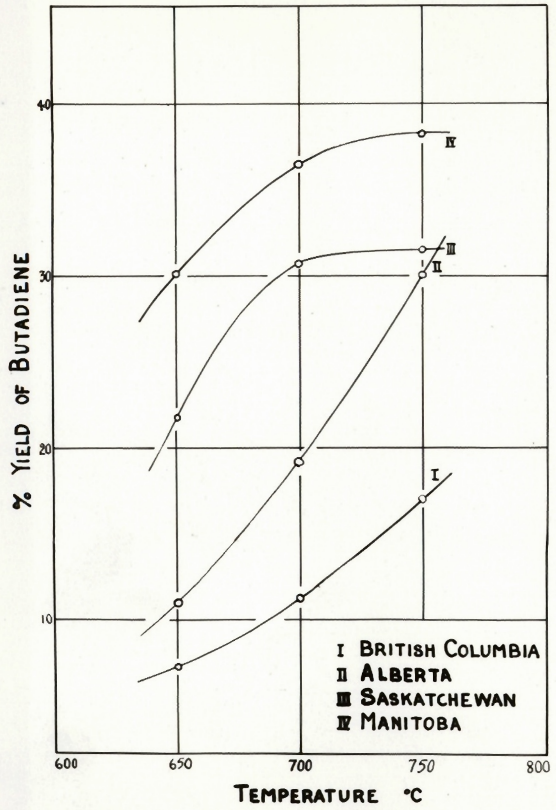
It is difficult to explain on the basis of work done to date the difference in activity of these clays as dehydration catalysts. It would seem that straight thermal decomposition predominates over the dehydration reaction with the poor quality clays. As the temperature is increased, the volume of gas, which is largely hydrogen, increases much more rapidly than



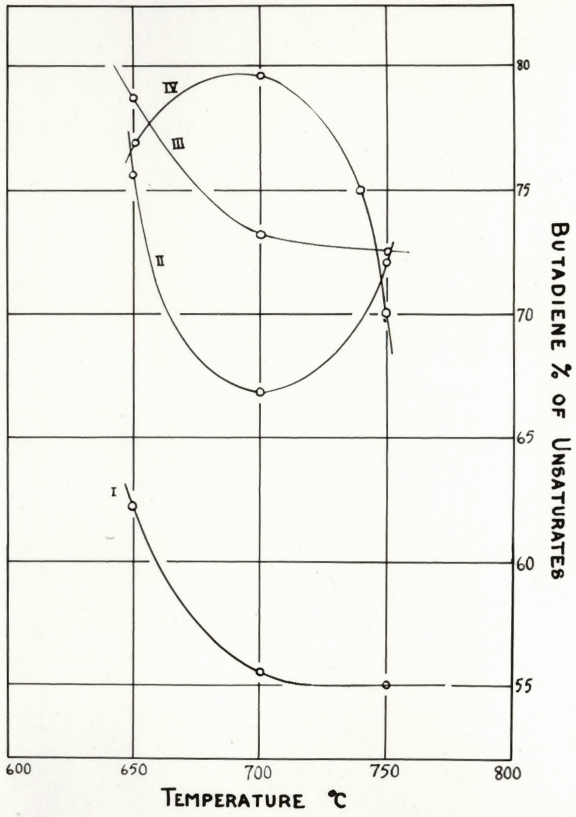
Graph I

Graph II

Pyrolysis of Butanone over Canadian Bentonites



Graph III



Graph IV

Pyrolysis of Butanone over Canadian Bentonites in the case of the Manitoba clay, where considerably more dehydration takes place. This effect is very noticeable in the runs done with no catalyst in the furnace. In these, the volume of gas jumps from 5.7 litres at 650° to 31.5 litres at 750°, hydrogen, saturated gases and ethylene being the main constituents. Large quantities of carbon were found deposited in the furnace.

From the electromicrographs, no significant differences in crystal size or shape could be noted to account for the difference in activity of the four clays. It might be suggested that all clays do not respond in the same way to the particular process of activation employed. Different activation procedures may possibly be found to increase the activity of the clays found to be relatively inert in this investigation.

Effect of Nitric Oxide on Decomposition of Butanone

In order to secure evidence as to the presence or absence of free radicals in the thermal decomposition of butanone, several runs were carried out in the presence of nitric oxide. The nitric oxide was conveniently introduced into the system by the addition of iso-amyl nitrite to the ketone. The two liquids are mutually soluble, and at the temperature at which the runs were carried out, the iso-amyl nitrite is split into nitric oxide, which may be regarded as a free radical, and the free radical $(CH_3)_2CHCH_2CH_2O$. Thus

$$(CH_3)_2CHCH_2CH_2ONO \longrightarrow (CH_3)_2CHCH_2CH_2O\cdot + NO \quad .$$

The procedure employed was otherwise the same as in previous runs, great care being taken to maintain the temperature accurately at the desired point, in order that the volumes of the gases produced may be compared. The rate of flow of ketone and water was also rigidly controlled. In this way the extent of decomposition, and the effect of increasing amounts of nitric oxide on the extent of decomposition may be noted. The calculated amount of iso-amyl nitrite was added which, assuming complete decomposition, would yield the indicated per cent by weight of nitric oxide of the butanone. At the temperature at which the runs were carried out, it was considered very improbable that any of the iso-amyl nitrite escaped decomposition. The conditions employed in these runs are reported in Table X and the general gas analysis and separate butadiene analysis in Table XI.

TABLE X

Decomposition of Butanone in the Presence of Nitric Oxide

Run No.	Nitric Oxide % By weight	Furnace °C.	Rate cc./min.		Ketone g.	Water g.	Total Gas l.
			Ketone	Water			
47	0.00	700	1	8	72.0	720.0	20.6
52	0.25	700	1	8	72.0	720.0	15.5
48	0.50	700	1	8	72.0	720.0	14.4
49	1.00	700	1	8	72.0	720.0	12.6
50	2.50	700	1	8	72.0	720.0	13.5
51	5.00	700	1	8	72.0	720.0	17.1

TABLE XI

Analysis of Gaseous Products

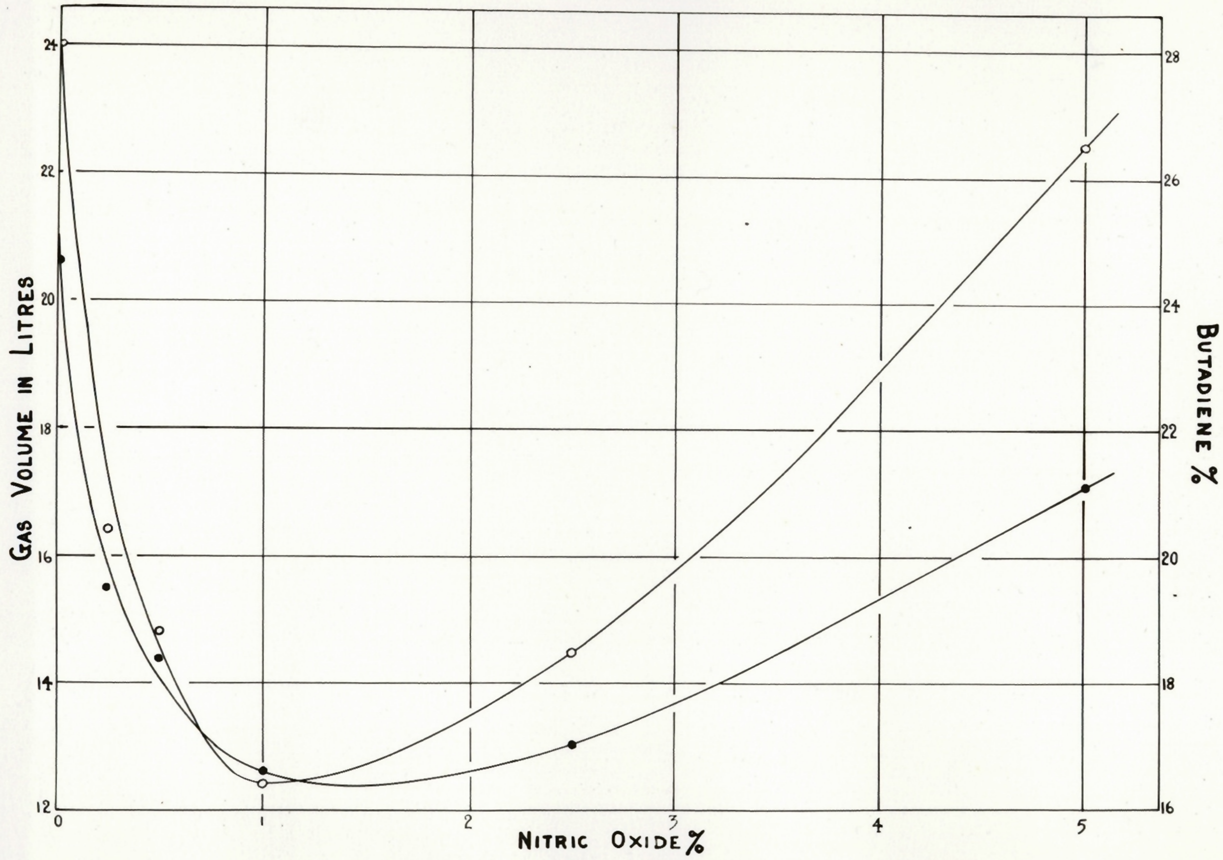
General Gas Analysis in Volume Per Cent								Butadiene Analysis	
Run No.	CO_2	Iso-butylene	C_2H_4	Other Un-Saturates Including Butadiene	CO	H_2	Saturates	% Volume	% Yield
47	6.0	2.4	8.7	36.2	14.1	18.7	12.2	30.5	28.0
52	6.3	3.2	8.0	37.1	12.3	17.5	13.7	29.6	20.4
48	6.8	3.8	8.3	39.8	11.9	16.3	12.3	29.3	18.8
49	6.2	4.3	7.2	34.9	12.2	20.5	12.7	29.2	16.4
50	6.4	4.6	7.9	36.1	12.7	17.6	12.4	30.7	18.5
51	6.8	5.8	8.1	39.0	13.7	13.0	11.7	34.8	26.5

In Graph V the per cent of nitric oxide is plotted against the total gas volume and the butadiene per cent.

Discussion of Results

It will be noted that on the addition of small amounts of nitric oxide there is a marked decrease in the gaseous decomposition. As the amount of nitric oxide is increased, the effect is lost, and the volume of gas increases again. The percentage composition of the gas, including the butadiene content, remains approximately the same in all the runs, the volume of gas and consequently the per cent yield of butadiene only being affected. This is precisely the effect reported by other workers with nitric oxide in the historical section of this thesis. These results are therefore considered to provide evidence for the presence of free radicals in the pyrolysis reaction.

Several objections and dissimilarities to previous work may at once be pointed out, notably that these reactions are carried out in a heterogeneous system, whereas previous work was done homogeneously. An unequivocal statement as to the presence of free radicals is therefore to be avoided, but in conjunction with the runs carried out in the presence of methyl iodide, an indication as to the most probable mechanism for the decomposition has been obtained. This will be further considered when the mechanism of the reaction is discussed.



Graph V

Effect of Nitric Oxide on Pyrolysis of Butanone

Gas Volume Curve ●   ○ Butadiene Curve

Effect of Methyl Iodide on the Decomposition of Butanone

In a further attempt to gain evidence for the free radical theory in the pyrolysis of butanone, several runs were carried out in the presence of methyl iodide. As in the case of the nitric oxide runs, the methyl iodide was dissolved in the butanone in the desired percentage by weight. The same procedure as previously used in the decomposition reactions, with the usual precautions as to temperature and rates was again employed. Eighty grams of activated Morden bentonite was used in the furnace for Runs No. 53-57. For Run No. 58 the furnace tube was packed with steel wool as a heat transfer medium to determine the difference in the products when no catalyst was present. The same conditions of temperature and rate were used as before, as reported in Table XII. The gas analyses are reported in Table XIII. In Graph VI the per cent of methyl iodide is plotted against the total gas in litres and the unsaturates in per cent.

Discussion of Results

The results from the methyl iodide runs are not very conclusive. In the first place, two different effects are possible. From energy of activation studies, Ogg (85) states that alkyl iodides may break down as

$$CH_3I \longrightarrow CH_3\cdot + I$$

Thus besides free methyl radicals, atomic iodine is also present in the reaction. Several workers have reported that iodine has a catalytic effect in the decomposition of organic compounds. Gantz and Walters (86) report that in the decomposition of acetone

TABLE XII

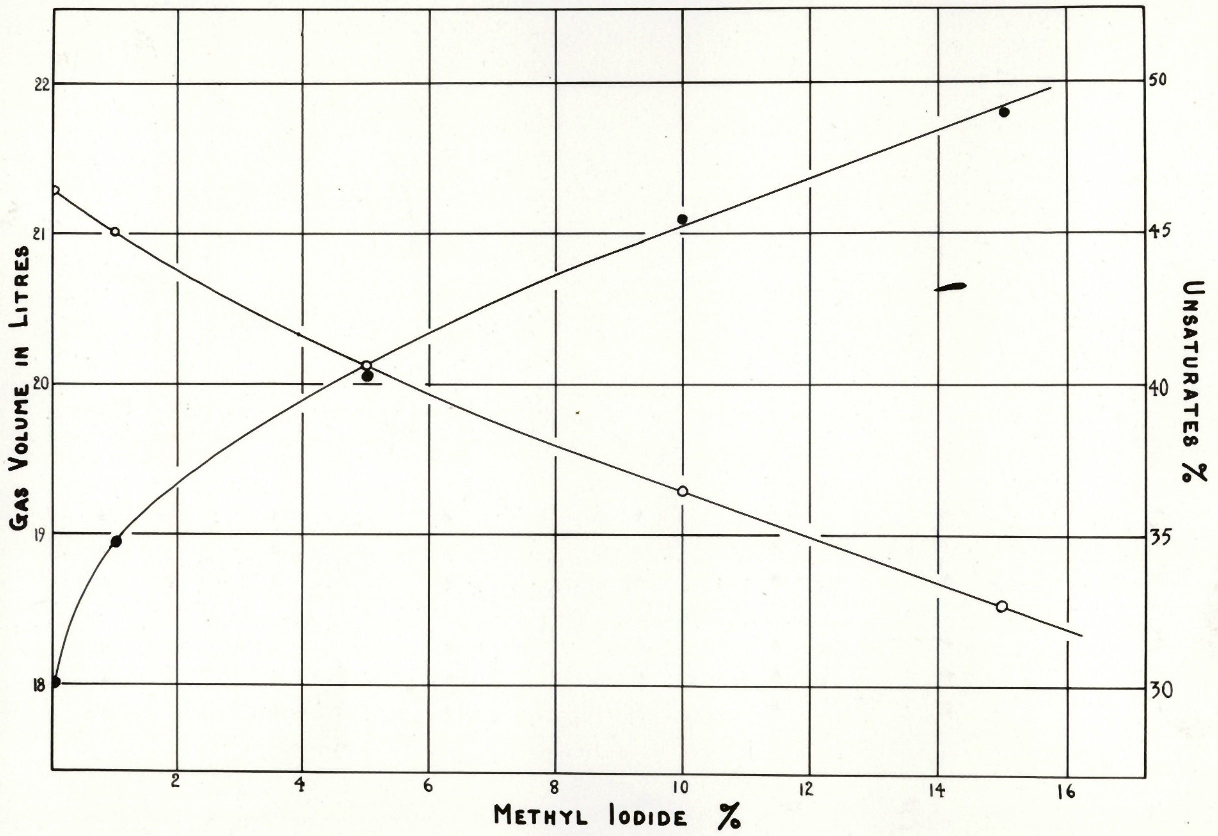
Decomposition of Butanone in the Presence of Methyl Iodide

Run No.	Methyl Iodide % By Weight	Furnace °C.	Rate cc./gm.		Ketone g.	Water g.	Total Gas l.
			Ketone	Water			
53	0.0	700	1	8	72.0	720.0	18.0
57	1.0	700	1	8	72.0	720.0	18.9
55	5.0	700	1	8	72.0	720.0	20.7
54	10.0	700	1	8	72.0	720.0	21.1
56	15.0	700	1	8	72.0	720.0	21.9
58	15.0	700	1	8	72.0	720.0	10.8

TABLE XIII

Analysis of Gaseous Products

General Gas Analysis in Volume Per Cent								Butadiene Analysis	
Run No.	CO_2	Iso-butylene	C_2H_4	Other Un-Saturates Including Butadiene	CO	H_2	Saturates	% Volume	% Yield
53	6.3	3.0	8.2	43.6	14.0	13.1	11.2	34.0	27.3
57	6.6	2.8	8.1	42.2	14.1	12.6	12.4	33.7	28.4
55	6.9	4.6	6.9	36.0	13.5	14.2	17.4	30.2	27.9
54	6.4	2.8	7.0	32.7	12.9	14.6	23.5	22.0	20.7
56	8.7	2.7	6.2	30.3	15.2	11.4	24.6	21.3	20.0
58	10.5	2.8	8.4	2.8	13.2	21.0	39.7	0.0	0.0



Graph VI

Effect of Methyl Iodide on Pyrolysis of Butanone

Gas Volume Curve ●   ○ Butadiene Curve

catalysed by iodine, the percentage of unsaturated gases is lower, and of saturated gases higher than in the case of the decomposition of pure acetone. Rice and Weiler (87) observed that the decomposition of acetone containing methyl iodide is appreciably faster than the rate for pure acetone. The decomposition of butanone is not catalysed by iodine to so great an extent as is acetone. The effect observed on the addition of methyl iodide is therefore a combination of the effect of free methyl radicals, and iodine atoms.

The results obtained are in agreement with those reported by other workers. It will be noticed that there is an increase in the decomposition, as evidenced by greater gas formation as the amount of methyl iodide is increased. It must be borne in mind that the methyl radicals formed in the breakdown of methyl iodide will recombine to form ethane. This alone will make for an increase in the gas volume. However, there is not a linear increase in gas formation, the curve tending to flatten off when large amounts of methyl iodide are used. Thus the iodine and possibly also the methyl radicals are catalysing the decomposition of the butanone. In accord with other workers, the percentage of unsaturated gases was found to drop from 54.8 per cent with no methyl iodide to 39.2 per cent with 15 per cent of methyl iodide. The saturated gases increase from 11.2 per cent to 39.7 per cent. The production of ethane from the methyl iodide must be taken into account in the latter figure. These results will be further considered when an attempt is made to explain the mechanism of the reaction.

Mechanism of the Reaction

From the results obtained in this investigation, it appears that the decomposition of butanone involves at least two competing reactions. The first of these is a dehydration to methyl allene, and subsequent rearrangement to butadiene, and the second a molecular fission reaction involving free radicals in a chain mechanism resulting in a mixture of products. Hurd (88) produced small quantities of ketene and methyl ketene from butanone by heat treatment alone. Mitchell and Reid (15) obtained high boiling condensation products and gas whose analysis closely resembles that obtained in the present investigation, from the decomposition of butanone in the presence of silica gel. Based on an analogy with the suggestion of Wasson (2) and Bourns (3), it appears that bentonite dehydrates butanone to methyl allene (butadiene-1,2) which isomerizes to butadiene-1,3. Thus

$$CH_3CH_2COCH_3 \longrightarrow H_2O + CH_3\text{-}CH\text{=}C\text{=}CH_2$$

$$CH_3CH\text{=}C\text{=}CH_2 \longrightarrow CH_2\text{=}CH\text{-}CH\text{=}CH_2$$

Slobodin (89) produced only traces of butadiene by passing methyl allene over floridin at 245-330°. This is explained by the work of Hurd and Meinert (90), who found that methyl allene completely decomposes in 36 seconds at 500-550°C. into carbon, hydrogen, methane, ethane, propene, allenes, acetylenes, and liquids of a polymeric nature. The fact that butadiene was produced in this investigation suggests that the rapid rate of throughput prevents the breakdown of methyl allene into fragmentary products, but permits its isomerization into butadiene-1,3. Thus it might be expected that the more rapid the rate of throughput, provided the molecules reach a temperature sufficiently high to bring about the dehydration, the higher would be the yield of butadiene. This is in accord with experimental results, practically no butadiene being produced in dry runs, up to nearly 40 per cent yield when 8 volumes of water are used to decrease the time of contact.

Simultaneously with the dehydration reaction, other reactions are occurring resulting in the formation of carbon monoxide, carbon dioxide, olefins, saturated hydrocarbons, hydrogen, and carbon. It is believed that these involve a chain mechanism with free radicals as intermediates. The decomposition of butanone is complicated by the three different kinds of C-H bonds. The chain mechanism may be represented as follows (91):

1. $CH_3COCH_2CH_3 + R\cdot \longrightarrow RH + CH_3COCH_2CH_2\cdot \longrightarrow$
   $RH + CH_2{=}CH_2 + CO + CH_3\cdot$
2. $CH_3COCH_2CH_3 + R\cdot \longrightarrow RH + \cdot CH_2COCH_2CH_3 \longrightarrow$
   $RH + CH_2{=}C{=}O + CH_3CH_2\cdot$
3. $CH_3COCH_2CH_3 + R\cdot \longrightarrow RH + CH_3CO\dot{C}HCH_3 \longrightarrow$
   $RH + CH_3CH{=}CO + CH_3\cdot$

R represents a radical formed in the primary decomposition. The products are therefore ethylene, methane, ketene, ethane, methyl ketene and carbon monoxide. It is believed that at the temperatures employed, ketene and methyl ketene undergo further decomposition, as they have not been detected in the reaction products.

The fact that the decomposition of butanone is retarded to quite a marked extent by the addition of nitric oxide, is further evidence for the existence of the free radical chain mechanism. It is known that nitric oxide functions as a chain terminator, thus removing the free radicals which are responsible for the progressive decomposition.

It must be noted that there is no significant change in the volume per cent of butadiene, although the yield per cent drops due to a decrease in the total volume of gas produced. Thus it might be postulated that the dehydration reaction itself occurs through intermediate free radicals. Were this not the case, it would be expected that the addition of nitric oxide would not interfere with the dehydration reaction, and hence would increase the volume of butadiene relative to the other gases. This, however, is not the case.

Likewise, the addition of methyl free radicals affords further evidence for the free radical mechanism. The methyl radicals from the decomposition of methyl iodide act as chain initiators, helping to start all three of the above reactions. Thus the increase in the extent of gaseous decomposition is explained. It is to be noted that the volume per cent of butadiene decreases in the case of the methyl iodide runs. This may be due to the presence of the methyl radicals favoring the free radical decomposition of butanone over the straight dehydration reaction. However, as already noted, the methyl radicals result in the formation of ethane, which decreases the volume per cent of butadiene, and iodine alone has a catalytic effect on the thermal decomposition of ketones.

Further work, possibly with metal-alkyl compounds, will be necessary before the reaction mechanism can be definitely stated. At present the evidence indicates that the decomposition of butanone involves two competing reactions: firstly, a fission of the molecule involving methyl free radicals and hydrogen atoms in a chain mechanism leading to a variety of products and secondly, a dehydration reaction producing methyl allene which re-arranges to butadiene. This reaction also may proceed by a free radical mechanism.

The Dehydration of 1-Butanediol-2,3 over Activated Morden Bentonite

As noted earlier in this thesis, work was carried out in this Department by Bourns (3) on the pyrolysis of butanediol-2,3. For this work, a horizontal type of catalysis apparatus was employed, and only three runs were carried out in the presence of water vapor. He reported that at low temperatures the glycol is completely converted to mono-dehydration products and one mole of water is eliminated per mole of glycol. Large yields of butanone are obtained at temperatures of 225°-275°, and it was thought that butadiene was formed only after the preliminary formation of butanone. In the dry runs, the percentage yield of butadiene was small, but increased considerably on the addition of water vapor. The furnace then in use did not permit the use of large volumes of water. It was thought advisable therefore to extend the investigation of butanediol-2,3 under conditions of rapid throughput with high dilution by water vapor, and high temperature.

Source and Purification of Butanediol-2,3.

The glycol was obtained from the Division of Applied Biology of the National Research Council, Ottawa, and is produced from wheat starch. The wheat is cooked and fermented by a soil organism known as aerobacillus, the laevo form of the glycol being the one produced.

The material as received corresponded to 99.7 per cent of the glycol in water, with a titratable acidity based on acetic acid of 0.77 per cent. It was purified by shaking 500-cc. portions with 200 cc. of 5 per cent sodium carbonate solution. A simple distillation was then carried out to remove most of the water. The glycol was then fractionally distilled in a Whitmore column. The fraction having the constants b.p. 176.7°, d_4^{20} 0.992, n_D^{20} 1.4314 was used for the catalysis investigation.

Procedure

The procedure employed was similar to that used in the pyrolysis of butanone. The rate of input of water and glycol, and the temperature were carefully controlled. Again due to the large volume of water employed, no attempt was made to identify the liquid products, some of which are soluble in water. The gaseous products were measured in the wet test gas meter, and analysed in the Bone and Wheeler apparatus, with a separate analysis for butadiene content. The conditions employed are reported in Table XVI and the gas analyses in Table XVII.

TABLE XVI

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

80.0 g. Bentonite

Run No.	Furnace °C.	Rate cc./min.		Glycol g.	Water g.	Total Gas l.
		Glycol	Water			
43	500	1	4	90.0	360.0	18.9
40	600	1	8	90.0	720.0	25.2
41	625	1	8	90.0	720.0	30.6
42	650	1	8	90.0	720.0	47.6
44	650	1	12	90.0	1080.0	26.1
45	700	1	16	90.0	1440.0	42.0
46	750	1	20	90.0	1800.0	50.4

TABLE XVII

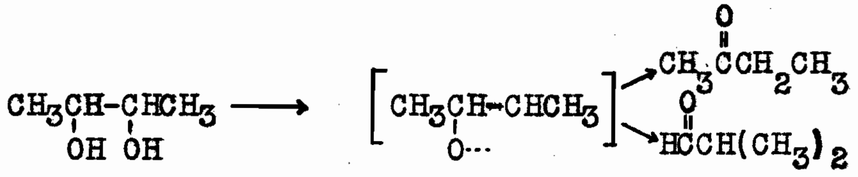
Analysis of Gaseous Products from Butanediol-2,3 Runs

General Gas Analysis in Volume Per Cent							Butadiene Analysis	
Run No.	CO_2	C_2H_4	Other Un-Saturates Including Butadiene	CO	H_2	Saturates	% Volume	% Yield
43	7.9	1.5	39.4	13.8	35.1	1.9	6.4	5.4
40	7.0	1.4	34.1	17.2	29.9	10.1	12.1	13.6
41	6.6	1.0	28.6	21.6	31.5	9.6	8.0	11.0
42	5.3	3.3	14.2	23.7	43.0	8.9	3.5	7.4
44	7.2	1.1	30.0	21.7	32.1	7.1	10.0	11.6
45	9.6	1.4	34.6	11.2	34.9	7.0	19.2	36.0
46	10.5	2.1	25.0	11.6	44.0	6.7	14.0	31.6

Discussion of Results

From an examination of the analyses of the gaseous products, it will be seen that the percentage yield of butadiene has been increased considerably over the yield from the dry runs and those employing only small volumes of water. The volume per cent of butadiene is still comparatively small, but the very rapid rate of gas formation at high temperatures results in a yield of butadiene of 36 per cent of the theoretical at 700°. The glycol is very sensitive to slight differences in temperature, and the effect of dilution by large volumes of water is even more marked than in the case of butanone. At 650°, if the amount of water used is raised from 8 to 12 cc. per minute, the volume of unsaturated gases goes from 14.2 to 30.0 per cent of the total volume, and the volume per cent of butadiene from 3.5 to 10.0. As in the butanone runs, with increasing temperature and at the same rate, the volume of carbon dioxide and saturates decreases, while carbon monoxide, ethylene, and hydrogen increases. The butadiene volume per cent decreases with increasing temperature and increases with decrease in the time of contact. Large volumes of hydrogen were produced, forming the largest single component of the gas. Considerable quantities of carbon were deposited on the catalyst, indicating that very severe cracking has occurred.

Turning to a consideration of the mechanism of the dehydration, it is evident that water can be eliminated from butanediol-2,3 in two ways. A molecule of water may be formed by the removal of a hydroxyl group and a hydrogen atom from either the second hydroxyl group or from the carbon atom containing the second hydroxyl group. In both these cases, a carbonyl type of compound will result. Secondly, water may be eliminated between a hydroxyl group and a hydrogen from the terminal methyl group. This results in the formation of methyl vinyl carbinol. At low temperatures, Bourns (3) obtained only carbonyl compounds, mainly butanone, with some isobutyraldehyde. These products may arise from the following reaction:



$$\underset{\mathrm{OH}}{\mathrm{CH_3CH}}-\underset{\mathrm{OH}}{\mathrm{CHCH_3}} \longrightarrow \left[\underset{\mathrm{O\cdots}}{\mathrm{CH_3CH}}-\mathrm{CHCH_3}\right] \begin{matrix} \nearrow \mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_2CH_3} \\ \searrow \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH(CH_3)_2} \end{matrix}$$

A water molecule is thus eliminated between one hydroxyl group and the hydrogen atom of the second hydroxyl group, followed by the migration of a hydrogen atom to form butanone, or by the migration of a methyl group to form isobutyraldehyde. The greater migration aptitude of hydrogen over the methyl radical explains the large proportion of ketone. Butanone may also arise from a vinyl type of dehydration, but this was considered unlikely from the results of Bourns and Wasson. It is possible that the free radical mechanism might be applied to the decomposition of the glycol as in the case of butanone, giving rise to carbon monoxide, ethylene, saturated hydrocarbons, and water. The concept of a slippage of atoms or groups without the existence of an independent radical may also apply to the rearrangement of butanediol-2,3. It would seem that the butadiene produced occurs largely through the preliminary formation of butanone, which dehydrates as previously discussed.

This work has shown that butadiene can be prepared in approximately 40 per cent from butanediol-2,3, with the advantage of cheap catalyst. The suitability of the process to industrial use would depend therefore on the availability of the glycol. Large quantities of the glycol can be made cheaply from wheat, which would suggest that when the world again has a surplus of wheat, some of it may be converted to butadiene.

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

High yields of butadiene have been obtained in this Department from the dehydration of butanediol-1,3 over Morden bentonite. These runs were carried out at slow rates and low temperatures. As high temperatures and fast rates increased the yield of butadiene from butanediol-2,3, the work has been extended to cover the 1,3-glycol under these conditions.

Source and Purification of Butanediol-1,3.

Butanediol-1,3 is not used in any industrial processes on this continent, and is therefore available in only limited quantities as a by-product in the manufacture of ethyl acetate from acetaldehyde. The material used was obtained from Shawinigan Chemicals Limited after fractionation through a Steadman column, and was used without further purification. The physical constants of this product were: b.p. 207.5-208°C., d_4^{20} 1.002 and n_D^{20} 1.4404.

Procedure

The procedure followed was essentially the same as in previous runs. Eighty grams of catalyst were again used. It was noted that overheating in the preheater greatly reduces the unsaturated content of the gases, while much hydrogen is produced. A good deal of carbon was deposited on the catalyst, necessitating careful reactivation. No attempt was made to analyse the the liquid products, owing to the large volumes of water employed. The gaseous products were analysed in the Bone and Wheeler apparatus, and a separate analysis made for butadiene. The conditions employed are reported in Table XVIII and the gas analysis in Table XIX.

Discussion of Results

The products of the high temperature dehydration of butanediol-1,3 are disappointing. Butadiene yields are low, even when very large volumes of water are used to decrease the contact time. Thus this glycol did not give results similar to those obtained from the 2,3-glycol. At 250°C. and a rate of 1 cc. per minute of glycol with no water, Bourns (3) obtained a volume per cent of butadiene of 65.9, the yield per cent being 18.4, as only 5.6 litres of gas were produced. A maximum yield of 28.3 per cent of theoretical was obtained in dry runs, and 29.0 per cent in runs with water as a diluent. These runs were all in the range of 250° to 350°C. and rates of 1 to 4 cc. per minute.

The glycol proved to be very easily decomposed at high temperatures. Very large volumes of gas were produced, the hydrogen content steadily increasing with increasing temperature. The amount of unsaturated gases correspondingly drops. The same trends were noticeable as before. Thus with increasing temperature, the volume per cent of ethylene, carbon monoxide and hydrogen increases, while carbon dioxide and unsaturates decrease. At the same temperature, with a faster rate, the percentage of carbon dioxide, and unsaturates increases, while carbon monoxide, ethylene, and hydrogen decrease. With increasing

TABLE XVIII

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

80.0 g. Bentonite

Run No.	Furnace °C.	Rate cc./min. Ketone	Rate cc./min. Water	Glycol g.	Water g.	Total Gas l.
68	500	1	4	90.0	360.0	21.2
69	550	1	8	90.0	720.0	27.0
73	600	1	8	90.0	720.0	40.5
70	600	1	12	90.0	1080.0	36.0
74	650	1	8	90.0	720.0	46.8
71	650	1	16	90.0	1440.0	38.7
75	700	1	8	90.0	720.0	51.2
72	700	1	16	90.0	1440.0	45.0

TABLE XIX

Analysis of Gaseous Products from Butanediol-1,3 Runs

	General Gas Analysis in Volume Per Cent							Butadiene Analysis	
Run No.	CO_2	Iso-butylene	C_2H_4	Other Un-Saturates Including Butadiene	CO	H_2	Saturates	% Volume	% Yield
68	5.6	2.5	3.0	61.0	3.8	11.3	11.1	12.2	11.5
69	12.5	2.0	1.8	43.4	2.6	29.4	8.0	10.4	12.5
73	11.5	1.7	2.8	35.4	7.0	32.6	8.0	10.8	19.5
70	12.5	2.3	1.4	40.0	4.5	30.0	8.1	11.3	18.1
74	9.2	1.3	3.7	32.2	7.6	36.2	9.1	8.6	17.9
71	11.0	1.9	2.1	34.6	5.4	34.6	7.5	11.5	19.9
75	8.6	1.0	5.2	19.3	9.2	46.0	10.1	6.8	15.5
72	10.5	1.4	3.1	27.4	7.1	39.6	9.0	9.8	19.7

temperature, the volume per cent of butadiene decreases along with the total unsaturates, but the greater evolution of gas brings the yield per cent to a maximum of 19.9 at 650° with a rate of 1cc. per minute of glycol and 16 cc. per minute of water. At the same temperature and a faster rate, the volume per cent of butadiene is raised, but the decreased evolution of gas prevents a corresponding increase in the yield per cent.

From a consideration of the low temperature runs, Bourns concluded that the dehydration of butanediol-1,3 proceeds by the elimination of a 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. Thus

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

Considerable quantities of 1-butenol-4 have been isolated. Propylene, formaldehyde and n-butyraldehyde are formed by a dehydration involving the elimination of a molecule of water from the two hydroxyl groups followed by a fission of the oxide ring, as well as from the breakdown of 1-butenol-4. Again, the free radical theory may well fit the reaction, especially in combination with the concept of slippage of groups or atoms.

The Pyrolysis of Octanone-2 over Activated Morden Bentonite

In an attempt to synthesize dienes higher than butadiene and to determine the specificity of the bentonites as dehydration catalysts for methyl ketones, octanone-2 was pyrolysed in the vertical type catalysis apparatus over activated Morden bentonite. The material used had the following physical constants: b.p. 173.0°, d_4^{20} 0.818, n_D^{20} 1.4155.

Gaseous products were found to occur over 500°C, and were analysed in the Bone and Wheeler apparatus with a separate analysis for diene content. These runs were done in the presence of water vapor. Dry runs were also carried out at lower temperatures and the liquid products analysed. The diene content of the gas was considered to be butadiene, as higher dienes are liquids at room temperature.

The gas was found to contain up to 45 per cent of unsaturates, of which the maximum butadiene content was 15.9 per cent, giving a yield per cent of 24.4. The other gases were carbon dioxide, carbon monoxide, hydrogen, and saturated hydrocarbons. Except at high temperature and very short contact time, no butadiene was produced.

The liquid products were first distilled in a Claisen flask and separated into three fractions. The first boiled below 150°C., the second from 150 to 180°C., leaving a high boiling tarry residue which amounted to as high as 30 per cent of the total. This indicated that a very large degree of polymerization of unsaturated products has occurred. The second fraction was unchanged octanone-2.

The low boiling fraction was then distilled through the small glass helices fractionation column, using octanone-2 as a booster and hydroquinone to decrease polymerization. Great difficulty was encountered in obtaining clear cut fractions, especially at higher temperatures. A very small fraction boiling from 35-40° was obtained and was thought to be a mixture of pentenes. A second fraction boiled between 62 and 68°C., also unsaturated, and was thought to be a mixture of hexenes. A certain amount of water was separated from the organic liquid prior to the distillation, and more water was obtained as an azeotrope with an organic liquid whose composition was not discovered. From 110° to 165° the liquid boiled over a continuous range, with the largest proportion boiling from 118° to 140°. This was thought to be a mixture of unsaturated compounds, probably containing octadienes. In all cases, in spite of the addition of hydroquinone, a considerable amount of polymerized residue was left in the distillation flask. From 0.3 to 0.5 moles of water were recovered per mole of ketone.

In an attempt to determine the constituents of the unsaturated gases other than butadiene, the gas from one of the high temperature runs was passed through liquid bromine. The resulting dibromides were washed with potassium hydroxide solution, dried, and distilled in vacuo. Successive boiling point and refractive index measurements were taken and plotted on a graph. A flat corresponding to 1,2-dibromoethane and a second flat corresponding to 1,2-dibromopropane were observed. This second flat extended over approximately one half of the graph. Beyond this both boiling point and refractive index curves rose rapidly until the limit of the heating device was reached.

As octadienes are not of industrial importance, the results obtained did not justify the continuance of this investigation.

SUMMARY

1. Activated bentonites have been investigated as catalysts for the vapor phase dehydration of butanone, butanediol-1,3, butanediol-2,3 and octanone-2.

2. The dehydration of butanone was carried out over a temperature range of 500 to 750° C. and a combined rate of organic compound and water of from 5 to 21 cc. per minute. The amount of butadiene produced increases with increasing temperature and decreasing contact time to a maximum of 38.4% at 750° and a rate of 1 cc. of ketone and 8 cc. of water per minute over activated Manitoba bentonite.

3. Bentonites from British Columbia, Alberta, and Saskatchewan were compared as to their efficiency as dehydration catalysts with the Manitoba clay. Of these, the British Columbia clay is least efficient, the Alberta clay is next, while the Saskatchewan bentonite most nearly approaches the Manitoba sample.

4. The effect of the addition of nitric oxide on the butanone decomposition was noted. It was found that the gaseous decomposition was considerably depressed by small amounts of nitric oxide, larger amounts having little effect.

5. The effect of the addition of methyl iodide on the butanone decomposition was also studied. In these runs, the gaseous decomposition was catalysed, an increasing amount of saturates

at the expense of unsaturates in the gas produced being apparent.

6. Possible mechanisms for the pyrolysis reactions were discussed. It appears that there is a competition between the dehydration of the ketone to butadiene and a decomposition to carbon monoxide, ethylene and saturated hydrocarbons involving a free radical chain mechanism.

7. Butanediol-2,3 was pyrolysed in order to determine the optimum conditions for butadiene production over activated Manitoba bentonite. At 700°, with a rate of 1 cc. of glycol and 16 cc. of water per minute, 36 per cent of butadiene was produced.

8. Butanediol-1,3 was studied under conditions of high temperature and rapid rate of throughput. The results were in the opposite direction to the butanediol-2,3 runs, less butadiene being produced than in low temperature runs.

9. Octanone-2 was pyrolysed over activated Morden bentonite. Gaseous decomposition occurs over 500°, with a yield of butadiene of up to 11.5 per cent. The liquid products of the reaction were found to consist mainly of polymerized unsaturated hydrocarbons, probably octadienes.

TABLE XX (concluded)

Sample	Compounds Identified	Long Spacing of Bentonite
Manitoba Bentonite Unactivated	Bentonite Quartz	14.6 A°
Manitoba Bentonite Activated	Bentonite Quartz	14.5 A°
Manitoba Bentonite Reactivated	Bentonite Quartz	...

From all samples, the pattern obtained was similar to Pattern No. 18 as listed in Dow Publication--Industrial and Engineering Chemistry, Analytical Edition <u>10</u>, 457 (1938). Silica is present in all samples, as cristobalite in the British Columbia and Alberta, and quartz in the Saskatchewan and Manitoba samples.

It will be noted that for the bentonites for which data are available, there is an increase from 9.8 A° to 14.5 A° in the long spacing of the crystal lattice of the activated bentonite. This dimension decreases on activation, and tends to decrease further on reactivation. It is suggested that this dimension represents the spacing of successive silicate layers which contract as water is removed from the hydrated silicate. As this spacing increases with increasing efficiency of the clay as a dehydration catalyst, these figures may account for the difference in activity of the four clays, and provide a means of estimating the efficiency of other clay samples.

From the spectrographic data, it is seen that silicon is the main constituent, aluminum, iron, calcium, and magnesium are major constituents, with sodium a major constituent in the Alberta bentonite. Other elements detected are copper, silver, nickel, manganese, lead, chromium, boron, barium and potassium. The data for the four samples are recorded in the following table.

TABLE XXI

British Columbia Bentonite			Alberta Bentonite			Saskatchewan Bentonite			Manitoba Bentonite (a)		
Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.
Main Constituent:											
Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si	Si
Major Constituents:											
Al	Al	Al	Al	Al	Al	Al	Al	Al	Al	Al	Al
Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe	Fe
Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca	Ca
Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg	Mg
			Na								
Detected Constituents:											
Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu			
Na	Na	Na	..	Na	Na	Na	Na	Na			
Ag	..	..	..	..	..	..	..	..			
Ni	..	Ni	..	..	..	..	..	..			

(continued on page 91)

TABLE XXI (concluded)

British Columbia Bentonite			Alberta Bentonite			Saskatchewan Bentonite			Manitoba Bentonite(a)		
Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.	Un-act.	Act.	Re-act.
Detected Constituents:											
Mn	Mn	Mn	Mn	..	..	Mn	..	Mn	Mn	Mn	Mn
Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb	Pb			
Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr	Cr			
..	..	..	..	..	..	B	B	B			
..	..	..	..	..	..	Ba	..	..			
..	..	..	..	..	..	..	..	K			

(a) The report on the Manitoba bentonite was earlier and less complete than that for the other three clays.

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