BENTONITE as a VAPOR PHASE CATALYST

THE CONVERSION OF p-CYMENE INTO TOLUENE with ALUMINUM CHLORIDE

SYNTHESIS OF PROKNOCKS

A Thesis

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BENTONITE

as a

VAPOR PHASE CATALYST

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Chemistry

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SYNTHESIS OF PROKNOCKS

Activated Morden Bentonite was used as a vapor phase catalyst in the pyrolysis of alkyl aromatics, alcohols, ketones and acids. Ethylbenzene and cumene were dealkylated. Pentanol-1, pentanol-3 and dimethylethylcarbinol were dehydrated. Acetone, methyl isobutyl ketone and cyclohexanone were readily dehydrated to form allene, 4-methylpentadienel,3 and cyclohexanone respectively. The aliphatic ketones also formed methane, carbon monoxide and olefins. Cyclohexadiene-1,3 polymerized. Acetic acid formed methane and carbon dioxide as the chief products.

p-Cymene was converted into toluene at 185°C. in a yield of 63.8% by means of aluminum chloride and hydrogen chloride. A possible mechanism of the reaction was developed.

A number of organic compounds were synthesized for a study of their proknock activity. A method of preparing anhydrous nitrogen trioxide was developed. A study of the synthesis of nitrites by the use of nitrogen trioxide, nitrous acid, high boiling nitrites and nitrosyl chloride was made. 2-Nitrobutene-1 was synthesized from 2-nitrobutyl acetate-1.

INTRODUCTION

High-temperature catalysis as an essential step in the synthesis of organic compounds has become an important factor in our industrial development. Thus since the last war the cracking of high boiling petroleum constituents into gasoline has developed into an exact science. The polymerization of hydrocarbons (especially olefins) into liquid products suitable as motor fuel has been extensively utilized in recent years. Alcohols, esters, acids, ethers, resins and rubber-like materials are today made from light unsaturated hydrocarbons, which in turn may be produced from gasphase pyrolysis. Carbon black, hydrogen, and benzene are the direct products of pyrolysis. As early as 1928, B.T. Brookes (1) stated that the cracking of butane was carried out industrially for the production of ethylene and propylene for the manufacture of thirty tons of glycols and allied substances per day.

In industry there has been and 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; among these clays and claylike materials have already been used successfully, as catalysts for dehydration, polymerization, isomerization, condensation and dehydrogenation. This is also true of alumina and silica, which are the chief components of clays. A fairly comprehensive study of the use of clays as catalysts has already been made and the results of these researches will be described and interpreted in the historical section of this thesis. For purposes of comparison, some of the more important reactions catalyzed by alumina and silica will also be included.

Morden Bentonite has been used as a dealkylation agent by several workers both in this university and elsewhere and with considerable success (2,3). Morden Bentonite is a Canadian clay mined in Manitoba which is readily obtainable in considerable quantities at a relatively low cost (4). Thus it seemed possible that this clay could be used at this time to replace more expensive catalysts. With these considerations in mind, four classes of substances were chosen for a preliminary study of the catalytic effect of activated Morden Bentonite upon such substances when in the vapor phase and at relatively high temperatures.

The compounds studied by us are given in the following table:

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TABLE I

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Class	Type	Compound	Type of Reaction Expected			
alkyl aromatics	straight chain	ethylbenzene	dealkylation			
alkyl aromatics	branched chain	isopropylbenzene	dealkylation, dehydrogenation, and polymerization			
aliphatic alcohols	primary	n-amyl alcohol	dehydrogenation, polymerization, and isomerization			
aliphatic alcohols	secondary	diethyl carbinol	dehydrogenation, polymerization, and isomerization			
aliphatic alcohols	tertiary	dimethylethyl carbinol	dehydrogenation, polymerization, and isomerization			
ketones	symmetrical	acetone	dehydration, polymerization			
ketones	unsymmetrical	methyl isobutyl ketone	dehydration, polymerization			
ketones	alicyclic	cyclohexanone	dehydration, polymerization			
acids	mono	acetic acid	dehydration, decomposition			

It will be seen that the above table contains relatively simple molecules. Mixtures of compounds were avoided, due to the difficulties involved in separating and determining the identity of the products. Difficulties, both experimental and theoretical, would be too complex for a preliminary study such as this. Thus simple molecules were chosen so that the effect of such variables as temperature, rate of flow of reactants and quantity of catalyst could be studied. The products had to be anal-yzed adequately so that the types of reactions might be discovered.

It is hoped that this study of the catalytic activity of activated Morden Bentonite on organic compounds will serve as a basis for more extended research on its uses and finally for its industrial application. Clays such as kaolin, kieselguhr, Japanese acid earth already are widely used in industry. Until the present time these catalysts have been imported into Canada particularly by the petroleum industry as a drilling mud, for percolation and for filtration. Thus it would seem desirable to develop our own clays, such as Morden Bentonite, to replace these imported clays and to extend their use as catalysts.

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HISTORICAL

Clays and Claylike Substances as Catalysts

Commercial clays consist primarily of one or more hydrous aluminum silicates together with a varying proportion of other substances which are termed "impurities." Kaolin is the common constituent of clay. It is a compound analyzing for alumina (39.53 per cent), silica (46.52 per cent) and water (13.95 per cent) (5). Kaolinite is a hydrous aluminum silicate having the formula H₄Al₂Si₂O₉. Clays which contain essentially kaolinite are called primary clays; clays which contain impurities such as feldspar (from which kaolin is derived), iron oxides, calcium, carbonate are called secondary clays. Such impurities may greatly alter the properties of clays. When moist clays are plastic and tenacious; when dried they are hard or crumbly.

In the literature will be found numerous terms which are more or less synonymous with clay. Such terms have been used exactly the same as given in the original article or patent. Clays vary so greatly that their action as catalysts would in all probability differ for each locality from which the clay originated. Clay names have often been given to certain deposits and they have no connection with chemical constitution.

Aluminum silicates, aluminum hydrosilicates, bentonite, kaolin, earths, Fuller's earth, Florida earth, Floridin, natural earths, active earths, bleaching earths, active bleaching earths, Kambara earth, Japanese acid earth, attapulgus clay, "Superfiltrol" and Frankonite are the names commonly given in the literature to clays which are chiefly aluminum silicates. Some of the above names are synonymous but are used so loosely in the literature that an attempt to designate each one will not be made.

Dehydrated clays are reported to have a catalytic effect both in organic and inorganic catalytic reactions. According to Knote (6) clays when dehydrated change in actual composition.

Heat treatment of clays may drastically alter their physical characteristics, and in high temperature catalysis this factor should be carefully noted, especially when a catalytic reaction changes markedly, since the change may be due to an alteration in the structure of the catalyst. Many clays are quite plastic in nature and this plasticity is a function of particle size and shape.

Aluminum oxide and silica are the chief clay components and each one occurs naturally in large quantities. These substances, have been used as catalysts for organic reactions for some years with excellent results. Alumina, especially, has found wide industrial applications.

The catalytic effect of clays and claylike materials on organic compounds may be classified under

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types of reactions catalyzed. Nine types of reactions have received the attention of research workers. They are: polymerization, isomerization, hydration, dehydration, condensation, hydrogenation, dehydrogenation, reduction, and oxidation. Patents have been granted on work done on each of the above types of reactions; the yields are high and in many cases these reactions are applied in industry. Other reactions are catalyzed to a lesser extent by clays, such as: alkylation, dealkylation, cyclization, halogenation, dehalogenation, nitrogenation, denitrogenation, sulfurization, and desulfurization. It will be seen that such general terms as synthesis and decomposition may readily be associated with one or more of the types of reactions listed above.

In the following survey yields are mentioned whenever given by the original investigators. In many cases, however, the yields were not given. This was especially true of the numerous patents which have been included in this survey. Cases when pressures other than atmospheric were used were avoided, as a rule. In a few instances, when a particularly important reaction involved the use of pressure, it was included.

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Alkylation and Dealkylation

The alkylation of organic compounds using clays as catalysts has not been fully developed. However, some independent research has been done and a few patents granted. The alkylation of aromatic compounds today is still quite an expensive process, hence catalytic alkylation has possibilities of further research and development.

Aromatic hydrocarbons, such as benzene and naphthalene, when reacted with unsaturated hydrocarbons such as ethylene or propylene in the presence of activated hydrosilicates, or silica, are reported to form alkyl derivatives (7).

Aromatics, such as benzene, will condense with olefins, also cyclohexane and styrene (8). High yields of alkylated aromatics are obtained when aromatic hydrocarbons and acetylene are passed over Fuller's earth at 150-300°C(9).

0-, m- and p-cresols condense with propylene at 400° C. over kieselguhr to form mixtures of mono- or diisopropyleresols. The cresol isopropyl ethers are formed along with the isopropyl cresols (10). Phenols readily condense with olefins in the presence of earths or silicates to form phenyl ethers. Temperatures of 200-300° C. are favorable (8,11,12). Benzene and cyclohexanol combine when coming in contact with earths at 200° C. (13).

Carboxycyclic acids and olefinic hydrocarbons tend to form esters, thus benzoic acid and propylene form propyl benzoate. Alcohols with olefins form ethers, while

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ammonia, aliphatic and aromatic amines may be alkylated with olefins. In the latter case the alkyl group migrates to the benzene nucleus. Thus the reactions would be:

A French patent on catalytic alkylation dealt with the same types of compounds mentioned above, but other catalysts were used. Activated hydrosilicates or hydrates of silicic acid as: "Tonsil" or "Frankonite" were obtained by treatment with mineral acids (14).

Primary aromatic amines and aliphatic, cycloaliphatic olefins or the corresponding alcohol form alkylated products when passed over hydrosilicates such as "Tonsil," "Frankonite" or "Granisol." N-cyclohexyl-ptoluidine was prepared by this reaction (15). In many cases alcohols can replace olefins.

Aniline and methyl alcohol vapors passed over Japanese acid clay form monomethyl aniline as the main product, and p-toluidine as the byproduct. As the furnace temperature increases the yield of monomethyl aniline decreases and that of p-toluidine increases. The authors state that p-toluidine was formed by water splitting out directly and the methyl group replacing the hydrogen atom in the para position. Thus, it appears, there was no Hofmann rearrangement (16).

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The above alkylation reactions involve the creation of three types of linkages: carbon-carbon, carbon-oxygen and carbon-nitrogen. The linkages are direct unions. In those cases when an alcohol is used rather than an olefin, water is a product of the reaction.

Dealkylation of organic compounds using clays as catalysts has had few applications as yet. However, the recent work carried out with bentonite clay in this university and Mt. Allison University promises to pave the way for more extended research on the dealkylation of alkyl aromatics using clays as catalysts (2,3). It therefore appears that in alkylation reactions the clays may function as Friedel-Crefts catalysts such as AlCl₃, BF₃, etc., and in dealkylation reactions as Jacobsen reaction catalysts.

Alumina and silica have not been reported as alkylation or dealkylation catalysts.

Polymerization and Depolymerization

The polymerization of olefins using clays as catalysts is quite well known in industry. The literature contains a number of references on olefinic polymerization.

Active aluminosilicates polymerize olefins of the type $R.(R^{\bullet})C = CH_2$ at 150-250 °Cin all cases. In spite of deposition of carbon at higher temperatures the alumino-

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silicates show only a slight decrease in activity (17).

Much work has been done on the polymerization of olefins. Ethylene and butylene form isobutylene and isooctylene respectively when passed through earths at low temperatures (18). Propylene passed over floridin at 350° C. gives ninety percent polymerisate, which was a volatile, colorless fuel (octane No. 87) consisting chiefly of unsaturated hydrocarbons, C5-C9, chiefly C6 (19). Isobutylene passed over silicates such as "Trass," Fuller's earth, "kil" and "Glukhov Kaolin" readily polymerized at 300-325°G. Below 200° and above 600°C there is no polymerization. This depends upon the inner structural changes caused by heating (20).

When a mixture of amylenes (Meg C:CHMe and MeHC: CHEt) were heated with floridin the dimer, diamylene, was obtained, which, when heated at 150-160°Cover more floridin, formed gaseous and liquid products. The gaseous products consisted of methane and a mixture of iso and butylenes, indicating depolymerization and cracking. The liquid products ranged from pentenes to nonylene, indicating considerable polymerization (21).

The polymerisates formed from the conversion of methane and ethane to unsaturated compounds when passed over earths condense to form a product which is suitable for use as an antiknock motor fuel (22).

Olefinic hydrocarbon gases when passed through

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silicates at 100°C.(23) and Fuller's earth (24) form high boiling polymers which are suitable as motor fuels. Active acid clays of the Urals are considered to be equal to American floridin in their ability to polymerize unsaturated compounds. Indene, styrene, and cyclopentadiene, which are the tar forming compounds of crude benzene, are readily polymerized by this acid clay and thus are removed from benzene. Excellent results were obtained in the vapor phase (25). Floridin polymerized the asymmetrical di- and tri-substituted derivatives of RR'C:CH2 and RR'C:CHR" and not the mono and symmetrical di and tetra substituted derivatives. The same is true of diethylenic hydrocarbons. 2,5-dimethyl hexadiene-1,5 readily polymerizes when passed through floridin (26). Even in terpene chemistry, Fuller's earth is used as a catalyst to polymerize dipentene to a dimer when heated 175-550°C. Yields of ninety percent at 375° are reported (27).

Acetylene when passed over clays forms aliphatic and aromatic derivatives (28). Pure acetylene passed through pumice, clay or Japanese acid clay at 400-700 °C forms an 82 percent yield of tar. The tar contains benzene and other aromatic compounds. Much carbon is deposited on the catalyst and greatly affects the course of the reaction (29).

The above reactions involve polymerization of unsaturated olefins and acetylenes. They all involve the saturation of carbon-carbon linkages.

Depolymerization using clays as catalysts is not

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very well known. Depolymerization occurred when the diamylenes are passed over floridin at 150-160° C.(21). When trimeric, tetrameric and higher polymeric products are passed over "Tonsil" and Fuller's earth in the presence of water at 230-330° there is considerable depolymerization occurring. Monomeric and dimeric products are formed; i.e. Isobutylene (35 parts) and diisobutylene (30 parts) were obtained when triisobutylene (100 parts) was vaporized and passed through Tonsil at 230° with water vapor. (30).

Depolymerization involves the breaking of a carbon-carbon linkage.

In contrast with the silicates, alumina is not generally considered as a good polymerization catalyst. However, it has been used to polymerize butenes (31) and pinene (32). The yields of polymers are said to be high. Silica gel is also considered a poor polymerization catalyst. It was used to polymerize butylene at 650-700°C. to the required products (33) and to transform ethylene to paraffinic olefins and aromatic hydrocarbons at 700°C. (34).

It is the writer's belief that alumina and silica are not used as depolymerization catalysts in the industry.

Isomerization

Clays readily catalyze isomerization reactions. This type of reaction applies chiefly to unsaturated hydrocarbons but may also affect other types of compounds with

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multiple linkages.

Aluminosilicates tend to isomerize olefins of the type $R.(R^{\bullet})C = CH_2$ at 250-300°C. Paraffin hydrocarbons, however, do not readily isomerize. It has been suggested that adsorption of the olefins on silicates tends to deform the molecule so that the double bond loses its identity, and there is considerable change in the product from the starting material (17).

Diallyl when passed through floridin at 225°C. formed dipropenyl (yield 41.5 per cent) and diisobutylene in the presence of floridin at 205-210°C. gives diisocrotyl (70 per cent yield) (35).

Unsymmetrical dimethyl allene passed through floridin at 280 C forms isoprene in 20 per cent yield, but at 335 C a 60 per cent yield of isopropyl acetylene is obtained. The reaction is reversible. The isoprene formed tends to polymerize to the dimer (36). Methyl allene is more stable than the preceding compound and forms only 20.6 per cent bivinyl. At 205 C ethyl acetylene begins to form and increases to 3.9 per cent at 330 °C. Symmetrical dimethyl acetylene is not obtained and there is no evidence of polymerization (37). Pure tetramethyl allene partially isomerizes to 2,4-dimethyl-pentadiene-1,3 (38) which, unlike the methyl allene products, completely polymerizes as soon as it isomerizes. When allenewas passed through floridin at 325 °C there was partial isomerization to allylene. The product consisted of 38.5 per cent allene and 61.5 per

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cent allylene. Above 325°C. polymerization readily occurs (39).

1-Ethenyl-3-cyclohexene passed through floridin at 210-240° formed 1-ethylidene-2-cyclohexene (40) while 1-phenyl-1,3-butadiene passed at 250°Cover the same catalyst formed a mono-substituted acetylene, probably 1-phenyl-3-butyne (41). Allyl benzene isomerizes to propenylbenzene when treated with earths at 500°C. (42).

The literature contains one example of an acetylinic derivative isomerizing to an allene derivative. This is the reverse reaction of one mentioned above. Ethyl acetylene at 275°C. in vapor contact with floridin forms methyl allene. Some bivinyl is also formed but no dimethylacetylene was isolated from the product (43).

Oxides of cyclic olefins isomerize to cyclic ketones. The oxides of 1-menthane, 3-menthane, cyclohexene, and methylcyclohexene isomerize at 250°C to the corresponding ketones (44).

N-ethyl-o-toluidine when passed over kaolin, or ton at 220-230°C. isomerizes to 2-methyl-4-ethylaniline. The yield obtained was 80 per cent (45). It is interesting to note that Lebedev (16) reports a direct reaction rather than an addition and isomerization reaction. Many clays have been used as catalysts for the isomerization of terpenes in the liquid phase, but as yet there has been little work done on the vapor phase catalysis of terpenes. It would appear that rearrangement should be studied.

Practically all the cases cited above involve the

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shifting of unsaturated linkages. There is again revealed the great tendency for cumulated double bonds to shift to conjugated double bonds, or to triple bonds. Likewise acetylenic bonds shifted to adjacent or conjugated double bonds. Thus hydrogen atoms move from carbon atom to carbon atom and the only bond affected is the carbon-hydrogen linkage. The nitrogen-carbon linkage shifts to a carbon-carbon linkage.

Alumina has been used as an isomerization catalyst for some time. Ipatieff (46) cites examples of isomerization with ethylenes, acetylenes, and allenes. The same type of isomerization occurs as with the clays. Cyclohexane isomerizes to methyl cyclopentane. This is a highly important reaction since a six-membered ring is changed to a five-membered ring (47). Propionaldehyde may be prepared by isomerizing propylene oxide (48) or allyl alcohol (49) at 250-400°C. Goldmasser and Taylor (50) studied the stability of allenes in the vapor phase over alumina.

Silica has not been studied as a catalyst for isomerization. Levina (51) mentions passing 3-phenylpropene-1 over silica gel to get a 58 per cent yield of methyl styrene.

Cyclization

The literature contains little work on the catalytic effect of clays on cyclization of aliphatic compounds in the vapor phase. Steur and Grob (28) succeeded in forming aromatics by passing acetylene over clays and Fujio (29) obtained benzene, higher aromatics as well as naphthalene derivatives by passing acetylene over floridin at 400-700°C. Ammonia and acetylene passed over kaolin at 400-425°C. form a mixture of pyrrole and $\ll\&I$ picolenes (52).

The above reactions involve the formation of carbon-carbon linkages. In the last reaction there are also carbon-nitrogen linkages formed.

Alumina is not ordinarily used as cyclization catalyst but when ethylene and acetylene are passed over alumina at 600°C. a fair yield of benzene is formed (53). At 700°C. ethylene, over alumina, tends to form aromatics (34). When used as a carrier, alumina serves as a good catalyst in cyclization reactions (54,55).

Silica gel was used in the formation of aromatic compounds from acetylene at 250-500 °C.(56).

Since the products from cyclization reactions with clays contain so many compounds, it would seem that this type of reaction would not be very suitable for clay catalysis, especially when there are so many good cyclization catalysts already in use.

Hydration and Dehydration

It would seem that clays are not commonly used in hydration of olefin hydrocarbons. One good example, however, has appeared in the literature. One volume each of ethylene and water passed through clay in the vapor phase forms fair yields of ethyl alcohol (57).

Clays, especially the hydrous aluminosilicates, have been used as dehydration catalysts with excellent success; in fact there is a great tendency today to replace the more expensive dehydration catalysts with cheaper catalysts. The chief products of clay dehydrations are olefins, ethers and other condensates.

Ether formation from alcohols is readily accomplished at fairly low temperatures, while high temperatures tend to form olefins. Methanol passed over glowed kaolin forms methyl ether (58). Methyl, ethyl, propyl, butyl, isobutyl, amyl and isoamyl alcohols passed over Japanese acid clays readily form ethers at temperatures below 350°C. (59,60). Ethyl alcohol passed over kaolin or aluminum silicate (61) and active clay (62) formed ethyl ether in yields up to 60.2 per cent when treated in the vapor phase below 350°C. Phenol passed over earths at 350°C. gives a 15 per cent yield of diphenyl ether (63).

Two alcohols or hydroxy compounds may be dehydrated to form mixed ethers. Thus methyl alcohol and phenol passed over active bleaching earth form anisole (14).

Olefins are readily formed by passing alcohols over clays at temperatures above 300°C. Ethyl alcohol passed over kaolin formed excellent yields of ethylene and was employed at the Edgewood arsenal in the United States during World War I (64). Huff (65) decomposed ethyl alcohol over clay to form ethylene and water. Temp and Kudryash-

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ana (66) studied the effect of various clays on ethyl alcohol. White Chapon-ata clay, gray Chapon-ata clay and agalzk kaolinized formation gave yields of 88, 99 and 100 per cent respectively at 500°C. Isopropyl and isobutyl alcohols passed over agulyk kaolinites gave yields of 89 and 96 per cent respectively at 540-577°C. Isoamyl alcohol however gave yields of 10.7-40 per cent when passed over the same clay at 400-550°C. (67). Isoamyl alcohol passed over infusorial earth at 400°C, forms 3-methylbutene-1. Hence there was both dehydration and isomerization (68).

Cyclanols and aromatic alcohols may also be dehydrated. Thus methylphenylcarbinol passed through Japanese acid clay at 400-500°C. formed styrene in a very high degree of purity (69). o-Aminophenylethylalcohol passed over hydrosilicates at 250-400°C. forms o-aminostyrene (70). Cyclohexanol passed over clay at 300°C. forms cyclohexene but at 330°C. over Japanese acid clay methylcyclopentane was formed. Methylcyclohexanol over Japanese acid earth gave methylcyclohexene at 250°C. but at 350°C. dimethylcyclopentane was obtained (71).

Polyhydroxy substances may be readily dehydrated. 1,3-Butylene glycol passed over Japanese acid clay at 350°C. gave a 21.2 per cent yield of butadiene (72) but when passed over kaolin at 380-400°C. forms a number of diolefins (73). 2-Methylbutanediol-1,3 gives isoprene and 2,4-pentandiol gives piperylene (73). When the vapor of 1,3dihydroxy-2-methylbutane is passed over aluminum silicate at 400°C. a 70 per cent yield of isoprene is obtained (74). Glycerol vaporized and passed over kieselguhr first forms acrolein and then ethylene at 500°C.(75,76).

Diethyl ether when passed over aluminum silicate at 200°C. forms ethylene through loss of water (77). Isoa mylene oxide over aluminum silicate at 400-600°C.(78) or methyl isopropyl ketone vapors passed over the same catalyst (79) form isoprene. In the latter instance there is an intermediate step, as:

CH3.CO.CH (CH3) $2 \rightarrow$ H2O + CH2:C:C(CH3) $2 \rightarrow$ CH2:CH.C(CH3)=CH2

Methyl alcohol and ammonia passed over kaolin at 450-470°C. form methyl amine (80). Ammonia and acetic acid vapors passed over Japanese acid clay at 400°C. forms almost pure methyl cyanide in an over 90 per cent yield. The same yield can be obtained with a faster rate of flow of the gas at 500°C. Acetic anhydride reacts with ammonia at 350°C. Japanese acid clay loses its activity above 500°C.(81). This is also mentioned under nitrogenation.

The above reactions involve the removal of hydroxyl and hydrogen groups from carbon atoms. In the case of ether formation there is a carbon-oxygen linkage established and with formation of nitriles a carbon-nitrogen linkage is set up. The chief result of dehydration of hydroxy compounds is the establishment of a double bond.

Hydration is more readily accomplished with alumina than with clays. Thus ethylene and water at 250-300°C. form ethyl alcohol (82,83). Ethyl ether and water also form ethyl alcohol at 280-400°C. to give yields as high as 30 per cent (84,85). Mesityl oxide and water passed over alumina or silica gel at 200-300°C. forms acetone in yields of 19-32 per cent (86).

Alumina is considered today to be one of the best dehydration catalysts, especially in the dehydration of monohydroxy compounds. Ethyl (87), propyl (88), butyl (89), isobutyl (90), n-hexyl (91) and n-heptyl (92) alcohols passed over alumina at temperatures between 350-500°C. will give a yield of over 90 per cent of the corresponding olefin. Phenols tend to form hydrocarbons of undetermined structure at 450-500°C.(93).

Cyclic alcohols readily dehydrate. Good examples of this type of dehydration are: cyclohexanol to cyclohexene at 350°C.(94) and cyclopropylcarbinol to propylene at 300-400°C.(95). At 200-300°C. ethers are formed from the alcohols in yields as high as 90 per cent (96).

Polyhydroxy compounds such as ethylene glycol (97), butylene glycol (98) and isoamylene glycol (98) form acetaldehyde, erythrene and isoprene respectively at 300-450°C.

Ammonia and alcohols at 350-500°C. form amines, usually a mixture of primary, secondary and tertiary amines (99,100,101). Lower temperatures tend to form ethers and olefins (102).

Phenols and alcohols condense over alumina to give ethers (103) and they join with hydrogen sulfide to form thiophenol (3 per cent yield) (104). Acetic acid over

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alumina splits out water and carbon dioxide to form acetone (105).

Silica gel for the production of unsaturated hydrocarbons seems to be as good as alumina and superior to clay. With higher alcohols there are no stoppages or fouling. Isopropyl alcohol and cyclohexanol have been previously studied (106).

Hydrogenation, Dehydrogenation and Oxidation

Clays are seldom used as catalysts for the vapor phase hydrogenation of organic compounds. They have been used in liquid phase hydrogenation. Thus limonene may be hydrogenated to p-cymene and p-menthane over kieselguhr or earths (107). Organo-nitro compounds may be reduced in the presence of kieselguhr. Thus hitrobenzene and 3-nitropyridine are reduced to aniline and 3-aminopyridine (108,109). Furfural and hydrogen passed through earths formed furfural alcohol (110).

Clays, however, have been used for some time in industry as dehydrogenation catalysts. Many of the references in the literature are patents.

Methane passed over kaolin formed 16.9 per cent acetylene of the methane which reacted (111). Gaseous hydrocarbons passed over silicated at 600-800°C. dehydrogenate to form unsaturated compounds (112). Hydrocarbon gases when in contact with highly active clays such as the Montmorillionite type first form unsaturated gases which polymerize to form motor fuels. The temperature range was 300-600°C. with pressure (113). The octane no. of a heavy

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straight run naphtha may be increased by subjecting the naphtha to a dehydrogenating catalytic reformation for a limited time so that no appreciable increase of the light ends is obtained (114). Aluminum silicates show high cracking activity. Thus much dehydrogenation would be accomplished. Olefins, naphthene, and paraffin hydrocarbons are dehydrogenated in the order as given (17).

Trimethyl amine passed over aluminum silicate at 400-450°C. tends to reverse the ordinary method of forming the amines and gives lower aliphatic amines (115).

Unsaturated nitriles may be prepared by passing nitriles over dehydrogenation catalysts; i.e. Propiolic acid (HC:C.CN) and phenyl propiolic nitrile may be prepared this way at 400-800°C. over silicates (116).

Catalytic oxidation with clays is fairly well known, but as yet has only limited application. Ethyl alcohol and oxygen passed over earths forms acetaldehyde (117). Acetaldehyde and oxygen passed over kieselguhr forms acetic acid (118). The above are two steps that probably could be combined over some clay catalyst.

The above reactions involve carbon-hydrogen linkages in the case of dehydrogenation. In hydrogenation, nitrogen-oxygen, nitrogen-hydrogen, carbon-oxygen, and carbon-hydrogen linkages are affected. In oxidation the linkages affected are carbon-oxygen, oxygen-hydrogen and carbon-hydrogen.

Alumina has been used as a catalyst in the hydrogenation of carbon monoxide to form methane (118) and in the hydrogenation of nitrobenzene to aniline at 330-350°C.(119).

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Dehydrogenation with alumina is quite well known. Propane at 500-800°C. over alumina gives unsaturated compounds (120). Cyclohexane at 500°C. forms benzene as well as gaseous and liquid saturated and unsaturated hydrocarbons (121). Ethyl alcohol at 318-450°C. gives many gaseous and liquid products (122). Benzyl alcohol at 340°C. gives a 25.6 per cent yield of dibenzyl ether, 35 per cent toluene and 38 per cent benzaldehyde (123).

EtC(OEt)3 passed over alumina at 250°C. gives 73.6 per cent yield of ether and ethyl propionate (124). Terpenes such as pinene or dipinene may be transformed into cymene by passing over alumina at 420°C.(125). Alumina is not used as a catalyst for oxidation.

Silica gel is sometimes used as a reducing agent. Thus nitrobenzene is reduced to aniline (108), furfural to furfural alcohol (124) and diphenyl oxide to phenol (126). Silica is seldom used as an oxidation catalyst but acetaldehyde and oxygen at 145-160°C. gives high yields of acetic acid (127).

Halogenation and Dehalogenation

Clays are sometimes used as halogenation or dehalogenation agents but may very well be used more for the results obtained so far are very favorable.

Propylene and hydrochloric acid passed over floridin at temperatures below 200°C. tend to form isopropyl chloride in good yields (19). For the production of an alkyl halide such as propyl chloride, a gaseous mixture of the olefin and hydrochloric acid is caused to react in the presence of zeolite or glauconite which had been leached with a strong inorganic acid (128).

Catalytic dehalogenation of ethyl, propyl and isopropyl bromides at 280-300°C. readily occurs over kaolin. The decomposition temperature seems to increase with the number of carbon atoms and they are higher for bromides than for chlorides. The catalyst is unaffected over long periods of contact (129).

Carbon-halogen and carbon-hydrogen linkages are involved in the above reactions. The formation and removal of double bonds is involved. These are simple straightforward reactions.

Both alumina and silica have been used for halogenation and dehalogenation and appear as excellent catalysts for the work so far carried out.

Methyl or ethyl alcohol and hydrogen chloride passed over alumina heated at 150-350°C. give good yields of methyl or ethyl chloride (130). Methyl alcohol and chlorine in the presence of alumina tend to form methyl chloride in fair yields (131). Propylene and hydrogen chloride passed over alumina form isopropyl chloride at low temperatures. The alumina should be porous and adsorbent (132).

Pentane and chlorine passed over silica gel forms amyl chloride (133). Vinyl bromide and hydrogen bromide passed over silica gel formed some dibromomethane. Acety-

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lene and hydrogen bromide over silica gel give excellent yields (134) of dibromethane.

Nitrogenation and Denitrogenation

Clays have not been used very much for this type of reaction. Acetic acid and ammonia passed over Japanese acid clay at 400°C. gave 90 per cent yields of methyl cyanide. At 500°C. the same yield is obtained at a slower rate. With acetic anhydride the same yields are obtained at 350°C. The clay tends to lose its activity above 500°C. (81). Other nitrogenation reactions have been already mentioned under the headings of dehydration and condensation, and hence will not be written up here.

Alumina has been useful as a catalyst for the preparation of pyrroles, ~-methyl furan and primary amines at 475°C. to form 1-aryl-2-methyl-pyrrole. Yields of 10-12 per cent are reported (135). ~ -substituted tetrahydrofuran reacts with ammonia and primary aliphatic amines at 400-440°C. over alumina (136). Tetramethylene glycol and ammonia passed over alumina at 400°C. forms pyrrolidine in 35 per cent yield and 2 per cent tetrahydrofuran (137).

Silica gel is considered a good catalyst for the reaction of benzene and nitrogen dioxide at 310°C. to form 80 per cent nitrobenzene. Presence of air in the gas mixture tends to initiate side reactions. Toluene requires a lower temperature for nitration (138).

The above reaction involves carbon-nitrogen

linkage.

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Sulfurization and Desulfurization

Actual clays are not recommended for use as catalysts in the sulfurization of organic compounds.

Clays are extensively used in the petroleum industry for desulfurization. Thus a mixture of petroleum oils vaporized and passed over a clay tends to remove the sulfur from the oils (139). Light petroleum oil containing nonheterocyclic and heterocyclic organic sulfur compounds is vaporized and the vapor passed over a clay heated at 315-425°C., contact time being 2-10 seconds; nonheterocyclic sulfur compounds were removed, further treatment at 425-600°C. removed the heterocyclic compounds. The sulfur was removed as hydrogen sulfide (140).

Alumina is used both as a sulfurization catalyst and as a desulfurization catalyst. Tetrahydroethylene glycol and hydrogen sulfide passed over alumina gives a yield of 62.5 per cent tetrahydrothiophene at 400°C.(137).

Tetrahydrofuran and hydrogen sulfide form tetrahydrothiophene at 400°C. in yields of 95 per cent (141). Furan and hydrogen sulfide at 400°C. form thiophene (142).

Alumina is used in industry for desulfurization. The Virginian Gasoline and Oil Co. has installed a catalytic desulfurization unit at its natural gasoline plant. The petroleum vapors were passed over alumina at 750°E. (144).

Silica gel has seldom been used as a catalyst for sulfurization or desulfurization.

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Miscellaneous

There are a few reactions which do not readily fit into the previous classifications. Thus acetylene will condense with carbonic acid to form an ester of vinyl alcohol in the presence of kieselguhr (145) or silicates (146). High pressures are advantageous in this reaction.

Alumina serves as a catalyst for the condensation of acetone at high pressure to mesitylene, 1,3,5xylenol at 500-550°C. (147). Water is eliminated from acetone. Acetone in the presence of alumina condenses with itself at 300°C. to form mesityl oxide in excellent yields (148). Acetone and alcohols readily condense at 400°C.(149). Alumina is a strong condensation catalyst for acetone at 455°C. (150).

Ethylene and N-ethyl pyrrolidine form tetrahydrofuran and diethylamine in 29 and 9 per cent yields when passed over alumina (151). This is a complex reaction which involves the breaking of the pyrrolidine ring.

Bentonites

Bentonite was first described by W. C. Knight in 1898. It is a colloidal clay, whose particle size lies between 10-200 mu (152). Bentonite consists chiefly of montmorillonite, which resembles a colloidal solution when suspended in water, but it has a low binding strength and lacks adhesiveness and cohesion. P. G. Nutting (153) thinks that bentonite occupies an intermediate degradation stage between original igneous rock and active Fuller's earth and has been thoroughly weathered but not leached with water as much as is Fuller's earth. Bentonite occurs in abundance and can be readily handled.

Bentonites are deposited widely in the United States (154), Western Canada (155), Italy (156), Japan (157), Germany, Russia and Poland. Many of the deposits are too thin to be worked economically. Morden Bentonite occurs in a large bed with a total thickness of eight feet. A yield of 6000 tons may be recovered from one acre (4).

Bentonites consist chiefly of hydrous aluminum silicate and it usually contains oxides of alkalis or alkaline earths. They have no narrow chemical composition and their physical properties are not constant. A comparison of the analyses of various bentonites will show the wide differences in composition.

TABLE II

No.	Al203	Si02	Fe203	<u>Fe0</u>	Mg O	CaO	<u>L.O.I</u> .
A	24.2%	51.6%	trace	-	0.3%	0.5%	9.4%(partial)
в	20.0	70.5	trace	-	0.3	0.5	23.9
C	19.7	59.6	2.9	0.3	2.5	0.7	-
D	15.8	58.0	3.1	<u>-</u>	4.1	1.2	14.9
E	14.0	62.9	2.6	-	-	1.5	-
F	11.8	59.8	3.3	-	2.3	2.9	10.5
G	11-26	55-77	1-5	· -	1.3	0.5-10	23-9

L.O.I. means loss on ignition

A. Canadian Bentonite (Morden, analyzed by Gallay) (4)

B. Canadian Bentonite (Morden, analyzed by Pembina Mountain Clay Co. (158)

C. American Bentonite, Wyoming (159)

- D. American Bentonite, Wyoming, sample from another deposit (160)
- E. Italian Bentonite (156)

F. American Bentonite, California (154)

G. Soviet Bentonite, Urals (161)

From the above table it will be noted that the silica content varies much less proportionally than does alumina. The other constituents vary greatly; thus Russian bentonite varies from 0.5-10 per cent in calcium oxide.

A low silica to alumina ratio and high percentage of combined water are the outstanding characteristics of

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Morden bentonite in comparison with all other clays examined.

Bentonites are seldom used as catalysts in the raw state but are usually activated by boiling the clay with dilute sulfuric acid for several hours. Generally, twice as much weight of solution is used as clay. Upon filtering, the clay is broken up and passed through screens (161a).

Bentonites have been found to have important industrial uses in recent years (4), especially in the refining of petroleum distillates. Canadian bentonites do not swell as does the Wyoming bentonite, and they do not form stable colloids or emulsions with water; however, Canadian bentonites possess a much greater adsorbent power. Gallay (4) used bentonites to refine and bleach many petroleum and fatty oils and he found Morden bentonite to be superior to many of the earths being imported into this country.

Bentonites were found suitable for use in the vapor phase percolation treatment of cracked distillates.

Bentonite has been used by itself as a catalyst for the desulfurization of petroleum oils (162).

Bentonite has been recently used as a dealkylation catalyst with excellent results (2,3), cymene being transformed to toluene. Bentonite was activated with sulfuric acid, dried and placed in a glass or iron catalyst tube. The vaporized cymene was passed over the clay at

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various rates and temperatures. This work was the first important piece of research carried out on the catalytic effect of Canadian bentonite on organic compounds.

Bentonite has been used as a catalyst carrier for a few organic vapor phase reactions. Thus bentonite and nickel give a 22 per cent conversion of ethylene with hydrogen sulfide to mercaptan at $250^{\circ}C.(163)$. Aliphatic compounds may be cyclized at $400-700^{\circ}C.$ in the presence of bentonite and oxides of V, Nb, Ta (2-5%). The contact time is 6-50 sedonds (164). A number of metallized bentonites were studied for the catalytic decomposition of hydrogen peroxide and isopropyl alcohol and for the polymerization of pinene. Good yields were obtained in each case (165).

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EXPERIMENTAL

Materials

A fifty-pound sample of Morden Bentonite was obtained from the Pembina Mountain Clays Company of Winnipeg.* The sample consisted of a number of small lots taken from different sections of the clay deposit. This sample was finely powdered and it readily passed through a 200-mesh screen. The clay was a light brown color. It did not swell appreciably when treated with water.

The Morden Bentonite was activated according to the method outlined by Gallay (4). Concentrated sulfuric acid was diluted with water to form a twenty percent solution and added to the dry bentonite. A highly active clay was obtained by adding fifty percent by weight of concentrated sulfuric acid. The slurry was boiled gently for three hours, care being taken to have the mixture thoroughly dispersed, lumps were broken up and the whole mixture well shaken every few minutes. Upon cooling the mixture was diluted to three times its original volume. This was filtered, and well washed. The wet cake was then dried at 110°C. for twelve hours. The hard material was broken up and screened. All subsequent catalytic work involved the use of bentonite of The activated clay contained some mineral acid. 4-8 mesh. Gallay (4) emphasizes that the determination of the opti-

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

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mum procedure for the activation of a bentonite is purely empirical. Thus bentonite from each deposit would need a special study for determining the best method of activation.

The compounds used for the catalysis study were all purified before being passed through the catalyst. Each compound was dried and then fractionally distilled through a Whitmore column. The fractions used were those whose boiling points, densities and refractive indices agreed with the constants given in the literature as the correct values for the pure substances. The compounds which were purified and used in the catalytic experiments are: ethylbenzene, cumene, acetone, methyl isobutyl ketone, cyclohexanone, normal amyl alcohol, diethylcarbinol, dimethylethylcarbinol and acetic acid. Dimethylcarbinol tended to decompose into the corresponding pentene and water when fractionally distilled in a Whitmore column. Accordingly the alcohol was well dried and distilled through a column having about a five plate efficiency. The decomposition may be caused by the large surface of the glass helices coming in contact with the alcohol.

Apparatus

The pyrolysis apparatus consists of five principal parts. These are indicated by letters of the alphabet in Figure 1, and include a displacement gravity feed system consisting of a mercury reservoir (A) situated two feet

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Figure 1

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Pyrolysis Apparatus

above the furnace, a calibrated chamber (B), which is used to hold the liquid to be pyrolyzed and has a capacity of 250 c.c. A and B are connected by capillary tubing which has a stop-cock. The rate of flow of the liquid can be regulated by turning this stop-cock. Thus the mercury flowing through the capillary tubing and falling into vessel B displaces the liquid. The preheater (C) consists of a 250-c.c. glass bulb. The bulb is connected to B by means of a capillary tube and to the catalyst tube (D) by means of a glass tube having a diameter of 2.5 cm.. This tube is wound with asbestos and nichrome wire. It may be heated from 25° to 400°C. by means of a variable resistance. The preheater may be maintained at any temperature between 25 and 225°C. by immersing it in an oil bath. The catalyst tube (D) is made of No.172 Pyrex resistant glass. It is 100 cm. by 5 cm. The furnace (E) was especially designed for the purpose and consists of two No.7.470 Hoskins heating elements with wiring so arranged to permit operation in series or in parallel. The catalyst tube is connected to a Frederick condenser (F) by means of a short adapter 5 cm. in diameter. The condenser has a receiver (G) and an outlet (H) through which gaseous products pass to a gasometer (I). The metal junction was placed in the furnace and immediately outside of the pyrolysis tube. The construction of the apparatus was of such a nature that the pyrometer junction could not be placed inside the pyrolysis tube. The temperature of the preheater bath was measured by an ordinary 360°C. thermometer.

The gas analysis equipment consisted of a modified Hempel apparatus. A pipette containing fuming sulfuric acid for the determination of unsaturates and one containing a fifty percent potassium hydroxide solution for carbon dioxide analysis. An electric furnace containing copper oxide was used for the analysis of hydrogen and carbon monoxide. The temperature of the furnace was set at 290°C. so that saturated hydrocarbons such as methane, ethane, etc. would not be appreciably affected (166).

Two Whitmore-Fenske columns were used, one for the purification of all starting materials and one for the fractionation of the products. The columns were packed with 1/8" glass helices. They were wound with nichrome wire and surrounded by glass tubing to insure even heating. The still-heads used were of the total reflux partial take-off type. Calibrated receivers were used for the collection of the products. These columns had an efficiency of fifteen plates and they could readily be used for temperatures up to 200°C.

Procedure

Prior to making an experimental run a fifty-gram (approximate volume 130 c.c.) quantity of 4-8 mesh activated Morden Bentonite was placed in the catalyst tube. The catalyst was held in place by means of two glass wool plugs. The catalyst was heated to 500°C. and maintained at this

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temperature for one hour. This treatment removed some water and it was then ready for use.

The furnace was quickly adjusted to the desired temperature and then regulated so that the temperature was constant throughout the run. Cold water was then circulated in the Frederick condenser and the liquid placed in graduated vessel B. The liquid was displaced by running mercury into B from A at a fixed rate. The liquid flowed into the vaporizer which was maintained at thirty degrees above the boiling point of the liquid being used in the run. The liquid quickly vaporized and passed into the catalyst tube and through the activated Morden Bentonite. The liquid products were condensed in a Frederick condenser and collected in the receiver. The gaseous products were collected in a calibrated vessel (I) by displacement of water. The water was saturated with carbon dioxide. The rate of flow of the liquid material and the temperature were finally adjusted just before the actual run was made. After the run had been going for a short time the gases were collected from a 10-c.c. portion of the liquid. Samples for gas analysis were collected immediately after the rate of evolution of gaseous products was determined. The samples were collected in a 2-liter aspirator bottle. The gaseous products were transferred to a measuring burette and analyzed in the modified Hempel set-up previously described. The liquid products were distilled from a

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modified Claisen flask in order to determine the distillation range and to remove tars and high-boiling substances. The fractions with boiling points up to 200°C. were then fractionally distilled from a Whitmore column. When small samples were obtained an inert booster was used to keep losses at a minimum. The boiling points, refractive indices and densities were taken of the purified products. Thus the identity of the compounds was well established.

The catalyst usually carried some deposited carbon after a run. This carbon served to reduce the activity of the catalyst. The rejuvenation of the catalyst was accomplished by drawing air through it at 550°C. for three hours. The catalyst had precisely the same activity after reactivation as when originally prepared. This reactivation process was followed out after each experimental run.

THE CATALYTIC DECOMPOSITION

OF ALKYL AROMATICS

I THE PYROLYSIS OF ETHYLBENZENE OVER ACTIVATED MORDEN BENTONITE

Ethylbenzene was passed through activated Morden Bentonite at different temperatures and feed rates. The liquid and gaseous products were collected and analyzed. The conditions of the reaction and the analysis of products are given in Tables III and IV.

The liquid products were fractionally distilled through the Whitmore-Fenske column. Four liquid fractions were obtained together with a thick, oily dark-red residue which remained in the distillation flask after each distillation. The fractions consisted of four compounds. Fraction 1 was principally benzene, fraction 2, toluene, fraction 3 unchanged ethylbenzene and fraction 4, styrene. The presence of these compounds was proved by refractionation and comparison of the three principal physical constants with those reported in the literature. These physical constants were boiling point, density and refractive index, and are shown in Table V. The percentage of liquid fractions was calculated on the basis of ethylbenzene changed.

It will be seen from Table IV that when temperature increased there were higher yields of benzene and toluene. As temperature increased the ratio of benzene:toluene was reversed. Styrene was formed at 600°C. and was fairly constant for 600° and 650°C. The highest yield was at 650°C. The thick dark-red residual oil increased with an increase in temperature. An analysis of the residue was not considered necessary due to the low yields.

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TABLE	III
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	The Ca	talytic Lifec	t of Activa	ted Morden Be	ntonite	on Ethylber	izene
Run NO.	Ethylbenzene in g.	Furnace Temp.in °C.	Feed rate c.c./min.	Liquid pro- ducts in g.	Loss in g.	Total gas evolved in 1.	Gas evolved per g. of ethylbenzene in c.c.
60	43.4	400	0.4	40.3	3.1	0.20	4.6
61	43.4	400	1.0	40.2	3.2	0.05	1.1
62	43.4	600	1.0	36.7	6.7	3.50	80 .6
63	43.4	600	2.0	38 .9	4.5	3.00	69.1
6 4	43.4	650	1.0	29.5	13.9	7.00	161.3
65	43 . 4	650	2.0	34.7	8.7	6.50	149.7

Physical constants of ethylbenzene are b.p. 134-136 °C.; n_D^{20} 1.4983; D_4^{20} 0.867 The preheater temperature was maintained at 170 °C. The gas evolution rate was determined for a 10 c.c. quantity of ethylbenzene. The gas analysis sample was collected immediately after the determination of the gas evolution rate. Weight of catalyst used 50 g. with a volume of 130 c.c.

TABLE	IV
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Analysis of Products from Ethylbenzene

	Liqui	(Jas anal	ysi s				
Run No.	1. <u>75-85°C</u> .	2. 105-115°C.	3. <u>116-137°C</u> .	4. <u>138-150°C</u> .	Residue in g.	<u>Olef</u> .	Vol. %	of <u>Sat</u> .
60	-	-	90.3	-	1.1	-	-	-
61	-	-	89.9	-	1.2	-	-	-
62	24.5	25.2	31.3	10.5	1.3	6.5	84.2	9.3
63	21.6	21.5	49.5	2.8	1.2	12.6	81.4	6.0
64	35.1	23.4	6.9	9.7	2.8	4.5	92.2	3.3
65	29.8	24.4	17.2	13.8	2.3	6.5	89.3	4.2

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Compound	Boilin	g Point C.	Refractive	index	De	ensity 20
	given	found	given	found	given	found
Benzene	80	80	1.5016	1.5018	0.894	0.892
Toluene	110-1	110-1	1.4967	1.4966	0.866	0.866
Ethyl- benzene	134-6	134-6	1.4983	1.4980	0.867	0.866
Styrene	146	145-6	1.5449	1.5446	0.907	0.904

Feed rates markedly affect the yields of liquid products. The yields of benzene and toluene were always lower at the feed rate of 2 c.c./min. than the yields for the rate 1 c.c./min. There was always a greater recovery of unchanged ethylbenzene for the higher feed rates.

The analysis of the gaseous products indicated a high percentage of hydrogen and a small quantity of olefins and saturated hydrocarbons. The evolution of gas at 400°C. was so slight that analyses were not carried out due to the gas being mixed with air. The yields of hydrogen increased slowly with temperature increase. Thus between 600 and 650°C. there was an 8% change in hydrogen. The percentage of saturated and unsaturated compounds fell when the temperature was raised.

Feed rates also have marked effect on the gaseous products. Thus the percentage of hydrogen fell off when the feed rate was raised, while with olefins the amount of

TABLE V

olefin increased greatly for an advance in rate. Feed rate apparently had some effect on formation of saturated compounds but was not so evident as with the other gaseous products.

Temperature greatly affected the pyrolysis of ethylbenzene over bentonite. At 400°C. there was no reaction but at 600°C. a number of reactions were evidently taking place principally dehydrogenation and carbonization of the alkyl group. While at 650°C. the nucleus was attacked, much carbonization occurred and large losses of material were noted. The evolution of gas increased with higher temperatures. Feed rates also affected the reaction greatly. However, their chief action was to decrease the reaction.

The effect of bentonite on ethylbenzene has been described above. The literature contains references to the pyrolysis of ethylbenzene but these are chiefly carried out with metal oxides as catalysts. So far as we know, clay has not been used for the catalytic pyrolysis of ethylbenzene.

Zal'kind and Bulauskii (167) mixed ethylbenzene and nitrogen together and pyrolyzed the hydrocarbon over 90% alumina + 10% zinc oxide at 660-670°C. at a rate of 1 g./min. to yield 82.74% styrene. Thus with a metal oxide the chief product was styrene. It will be evident that bentonite differs greatly in its catalytic action compared to metal oxides. However the following year Ipatieff and Komarewsky (168) dehydrogenated ethylbenzene over alumina - nickel oxide at 350°C. and from 37 c.c. of ethylbenzene obtained 5 c.c. benzene, 6 c.c. toluene, 22.8% hydrogen, 38% methane and 38% ethane. A small quantity of naphthalene was also identified. These results differ widely Zal'kind and also from our work on benfrom those oftonite. Here the chief gas was saturated hydrocarbons while with bentonite the chief gas was hydrogen. However, their work was carried out at a much lower temperature. Oblod et al. (169) pyrolyzed ethylbenzene over chromic oxide at 480°C. at a space velocity of 0.5; 16% was converted to styrene. Only a small quantity of gas was evolved. They reported that a large amount of residue was formed and suggested that this was due to polymerized hydrocarbons. This work is comparable to that of Zal'kind but was by no means complete. Finally Sergienko (170) in 1940 dehydrogenated ethylbenzene over zinc chromate at 500-600°C. Styrene was formed in yields of 10.41 to 33.93%. Small quantities of benzene and toluene were reported. These were below 10%. Losses of material amounted to 30-35% in a single passage of ethylbenzene at a volume rate of passage of 0.1. Increasing the temperature to 650°C. sharply increased the loss, although the yields of benzene and toluene increased. The products and yields reported by Sergienko were quite similar to those obtained with bentonite.

From the experimental data it would appear that three reactions occur when ethylbenzene is pyrolyzed over activated Morden Bentonite. These are: (1) dehydrogenation

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of the ethyl group to form styrene; (2) a fission of the side chain resulting in the formation of toluene; and (3) the removal of the entire alkyl group to form benzene.

Since styrene was isolated in the analysis in yields as high as 13.8%, and high yields of hydrogen were noted, it was concluded that dehydrogenation was accomplished by the clay. Thus,

(1) $C_{6}H_{5}CH_{2}.CH_{3} \longrightarrow C_{6}H_{5}.CH = CH_{2} + H_{2}$ But the yields of styrene were low while the yields of benzene and toluene were relatively high, hence it appears bentonite preferentially splits C-C bonds rather than C-H bonds.

Metal oxides as used by Zal'kind (167) were therefore much better dehydrogenation catalysts, since yields of over 80% of styrene were obtained with them as compared with a maximum yield of 13.8% over bentonite.

The formation of benzene in good yields may be explained by simple cracking of ethylbenzene into benzene and ethylene:

(2) $C_6H_5.C_2H_5 \longrightarrow C_6H_6 + C_2H_4$ This was substantiated by the fact that appreciable quantitles of olefins were obtained. Thus at 600°C. a yield of 12.6% unsaturated hydrocarbons was detected.

The appearance of toluene in the liquid products indicated a break in the alkyl group. Just how this break occurs was not known and would be quite difficult to determine. One possible explanation was that the outer group consisting of CH_3^- was broken up into carbon and hydrogen. Thus:

(3) $C_{6}H_{5}CH_{2}.CH_{3} \longrightarrow C_{6}H_{5}.CH_{3} + C + H_{2}$ The deposition of carbon on the catalyst helped to support this reaction, also the large amount of hydrogen collected rather than methane was additional proof for the above reaction.

The above explanation is quite different from that of Ipatieff (168); since he obtained large quantities of methane and ethane, he concluded that ethylbenzene broke down in two ways: (1) completely, to form benzene and ethane, and (2) partially to form toluene and methane. He fails to mention where the hydrogen comes from to form benzene. Thus it would seem that metal oxides and bentonite catalyze different reactions. However, since small yields of hydrocarbon gases were detected, it was concluded that bentonite inhibited the formation of saturated hydrocarbons while metal oxides accelerated their formation. Thus the first step in the reactions would be:

(4) $C_{6}H_{5}.CH_{2}.CH_{3} \longrightarrow C_{6}H_{5}^{-} + C_{2}H_{5}^{-}$

(5) $C_{6}H_{5}$. CH_{2} . $CH_{3} \longrightarrow C_{6}H_{5}$. CH_{2}^{+} CH_{3}^{-} The unsaturated substances would react with the hydrogen formed from other reactions to give saturated compounds:

> (6) $C_6H_5^- + C_2H_5^- + 2H^- \rightarrow C_6H_6 + C_2H_6$ (7) $C_6H_5.CH_2^- + CH_3^- + 2H \rightarrow C_6H_6CH_3 + CH_4$

The above description of reactions serves to explain the high yields of hydrogen, toluene and benzene and the low yields of styrene, methane and ethane.

II CATALYTIC EFFECT OF ACTIVATED MORDEN BENTONITE ON ISOPROPYLBENZENE (CUMENE)

For this reaction purified cumene was vaporized and passed through activated Morden Bentonite. Temperature and feed rates were varied. The results are arranged in Tables VI and VII.

The liquid condensate upon fractional distillation gave four fractions along with a small emount of tarry residue. Three compounds were isolated and identified from these fractions. Fraction 1 consisted of mixed quantities of low-boiling substances which were not identified due to insufficient quantity for an exact purification. Fraction 2 was principally benzene. Fraction 3 contained some toluene but consisted chiefly of cumene. Fraction 4 consisted largely of unchanged cumene. Fraction 1 appeared only when the benzene nucleus started to break down. This was thought to consist of unsaturated hydrocarbons formed from the breaking of the benzene ring. The benzene fractions were combined and carefully distilled. The product had the properties of pure benzene. Fraction 3 upon further purification produced a small quantity of pure toluene. Fraction 4 upon purification consisted of unchanged cumene. A comparison of the physical constants of the isolated compounds with those given in the literature is indicated in Table VIII.

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TABLE VI

CATALYTIC EFFECT OF ACTIVATED MORDEN BENTONITE ON CUMENE

Run No.	Cumene in g.	Furnace Temp.°C.	Feed Rate c.c./min.	Liquid Prod. in g.	Loss in g.	Total gas evolved in 1.	<u>c.c.gas</u> / g.cumene
48	43.2	400	0.5	37.6	5.6	3.25	75.2
49	43.2	400	1.0	36.9	6.3	3.00	69.5
5 0	43.2	400	2.0	39 .2	4.0	1.75	40.6
51	43.2	450	0.5	34.4	8.8	5.25	121.5
52	43.2	450	1.0	33.2	10.0	3.65	84.5
53	43.2	450	2.0	36.1	7.1	2.00	46.3
54	43.2	500	0.5	32.5	10.7	6.00	152.8
55	43.2	500	1.0	31.6	11.6	5.50	127.3
56	43.2	500	2.0	33.4	9.8	2.75	63.6
57	43.2	550	0.5	29.0	14.2	7.50	173.6
58	43.2	550	1.0	30.5	12.7	9.75	225.7
59	43.2	600	1.0	28.0	15.2	7.50	173.6

Physical constants of purified cumene: b.p.152-3°C.; D_4^{20} 0.864; n_D^{20} 1.4930 The temperature of the preheater was maintained at 190°C. Weight of catalyst used was 50 g. and its volume was 130 c.c.

TABLE VII

PRODUCTS FROM THE CATALYSIS OF CUMENE

Liquid Analysis

Gas Analysis

Run	1.	2	•	3.	$\underline{4}$		Residue		٧o	1. % 0:	f	
No.	<u>25-75°C</u> <u>8</u> •	• <u>75-</u>	<u>90°C</u> . Z	<u>91-145°C</u> . <u>E</u> •	<u>146-</u>] <u>8</u> .	<u>160°C</u> .	in g.	<u>002</u>	<u>Olef</u> .	H ₂	<u>C0</u>	Sat.
48	-	15.7	55.8	6.8	13.6	31.4	1.5	1.4	77.5	10.8	1.7	8.5
49	-	12.7	45.1	7.5	15.2	35.4	1.5	2.0	72.6	10.1	1.4	13.7
50	-	8.2	29.2	8.2	21.3	49.3	1.5	1.2	85 .5	10.7	0.8	1.8
51	-	16.9	60.2	8.6	9.3	21.5	1.3	1.2	86.6	9.6	1.2	1.4
52	-	13.6	48.4	7.6	10.4	24.1	1.6	1.1	83.9	10.5	0.8	3.6
53	-	10.1	35.9	7.2	17.4	40.3	1.4	1.2	90.7	5.9	0.6	1.6
54	-	18.5	65.8	6.8	5.6	12.9	1.6	1.2	84.8	13.0	0.2	0.8
55	-	15.5	55.2	8.5	6.2	14.3	1.4	1.4	88.2	9.0	0.4	1.0
56	-	12.5	4 4. 5	6.5	13.4	31.0	1.0	1.2	86.3	11.1	0.4	1.0
57	0.5	23.1	82.2	3.0	0.8	1.8	1.6	0.5	73.9	23.5	0.5	1.6
58	1.2	19.1	67 .9	3.9	4.8	11.6	1.5	1.0	84.7	13.3	0.2	0.8
59	2.2	18.1	64.4	3.8	2.8	6.7	2.0	0.6	49.7	38.8	1.4	9.5

The gas evolution rate was determined for a 10 c.c. quantity of cumene.

The sample for gas analysis was collected after the determination of the gas evolution rate.



Compound	Boiling	g Point	Refractiv	ve index	$\frac{\text{Density}}{D_4^{20}}$		
	grven	round	given	found	given	found	
Benzene	80	80.2	1.5016	1.5016	0.894	0.893	
Toluene	110-1	110-12	1.4967	1.4969	0.866	0.867	
Cumene	152-3	152-3	1.4930	1.4932	0.864	0.864	
1,2-Di- bromop ropa ne	141-2 3	141-2	1.5203	1.5201	1.933	1.931	

T.	A	В	Ι	E	V	Ι	Ι	I
							-	_

The percentage of benzene was worked out on the basis of cumene reacted. The residues were small and hence were not distilled. There were probably traces of \propto -methyl styrene present in these residues but the quantities involved were not considered large enough to warrant further work upon them.

An increase in temperature caused an increase in yield of benzene. However at 650°C. due to cracking of the nucleus the yields of benzene dropped. These are shown in Graph 1. The amount of unchanged cumene naturally dropped when the temperature was increased. The intermediate fraction also dropped markedly as the temperature increased. This would indicate that little toluene was being formed and that this fraction was chiefly unchanged cumene. It is interesting to note that the residue remained fairly constant with temperature rise.

As would be expected, the yields of benzene dropped when the feed rate was increased. Thus at 400°C. the yield of benzene was 15.7% for 0.5 c.c./min., while the yield was 8.2% for a rate of 2 c.c./min. Therefore there was more unchanged cumene in the products from the higher feed rate than from the lower one.

An important feature of the results from the analysis of gaseous products was the high percentage of unsaturated gases formed. The unsaturated gases were passed through a solution of bromine in carbon tetrachloride. 1,2-Dibromopropane was obtained and identified by distillation and purification. The properties agreed with those given in the literature. These constants are given in Table VIII. Thus the reaction was essentially dealkylation. This will be discussed at greater length later on. The hydrogen content of the gaseous products was fairly constant until deep-seated pyrolysis occurred; thus at 600°C. 38.8% hydrogen was obtained but at lower temperatures the hydrogen evolved was about 10%. Thus during breaking of the benzene nucleus the yields of hydrogen greatly increased. The percentage of saturated hydrocarbons was quite high at first but dropped to a fairly constant value of 1 to 4%. Then when cracking occurred the yields were greatly increased. With temperature rise there was a fairly large increase in the percentage of olefins at first but between 450-550°C. the yields were fairly constant. Of course the percentage of olefins dropped sharply when the benzene ring was attacked. From 550° to 600°C, there was a drop of 35% in olefins. When feed rates were increased there was an increase in the yields of unsaturated hydrocarbons and

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a decrease in the saturated products. Changes in feed rates did not have the same effect on the formation of hydrogen, which remained fairly constant.

As was expected there were only small quantities of carbon monoxide and dioxide formed. This may be due to the presence of oxygen in the system or part of the water in the catalyst reaction with deposited carbon to give hydrogen and the oxides of carbon.

From the above results it would appear that increased temperature favored higher yields of benzene, and unsaturates, and decreased the quantity of unchanged cumene and saturated gases. The production of hydrogen was unaffected by temperature except at high temperatures. Likewise feed rates increased the formation of unsaturates and decreased the yields of benzene. The production of hydrogen and saturated gases was not materially affected by increased feed rates.

So far as we know the above work is the first experimental work carried out on the catalysis of cumene over clays. The literature seldom refers to the decomposition of cumene either by pyrolysis or by catalysis. The work reported in these papers will now be described and the results compared with those obtained with bentonite.

Herndon and Reid (171) pyrolyzed 100 g. of cumene at 450°C. and obtained 57 g. of changed material. A small volume of gas was evolved. These workers did not report identification of the products, hence it is not considered

sufficiently complete for any conclusions to be made. Dobrjanski (172) pyrolyzed cumene to yield 89.4%* liquid products and 18.6%* gaseous products. The liquid products consisted of 6% benzene, 0.5% toluene and 44% styrene. The gas contained 3.4% C3, 6.8% C2, 60% saturates and 28.8% hydrogen. This work was carried out at 600-650°C. Thus bentonite as a catalyst greatly altered the effect of heat on cumene. Apparently it inhibited the formation of styrene, ~-methylstyrene, hydrogen and saturated gases and accelerated the production of benzene and unsaturates. Stanley (173) has recently succeeded in forming *A*-methylstyrene when cumene was brought into contact with vanadium oxide at 450-700°C. This work was patented and as usual no yields are mentioned. This was the type of reaction which bentonite inhibited to such an extent that ~-methylstyrene could not be identified in the liquid products. Hence vanadium oxide and bentonite have an entirely different catalytic action on cumene.

From the above data it was concluded that the chief reaction occurring was the dealkylation of cumene in which the isopropyl group split off from the phenyl group to form benzene and propylene.

(1) $C_{6}H_{5}.CH(CH_{3})_{2} \longrightarrow C_{6}H_{6} + CH_{3}.CH = CH_{2}$ This was well substantiated by the high yields of benzene and propylene obtained.

The isolation of a small quantity of toluene would indicate a secondary reaction which had been strongly

* This is apparently a typographical error appearing in the abstract.

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inhibited by the clay catalyst. Thus the isopropyl group was partially broken up apparently to form toluene, hydrogen and carbon.

(2) $C_6H_5.CH(CH_3)_2 \longrightarrow C_6H_5.CH_3 + 2C + 2H_2$ The deposition of carbon on the catalyst and average yields of 10% hydrogen could readily account for this reaction. There was no evidence for the substance breaking up into toluene and ethylene since ethylene was not found in the unsaturates. However it could be an intermediate step.

There was no evidence for the occurrence of a simple clear-cut dehydrogenation reaction such as was obtained by Stanley (173) over vanadium oxide. A simple dehydrogenation would form \propto -methylstyrene and hydrogen.

(3) C₆H₅.CH(CH₃)₂ → C₆H₅.C(CH₃) = CH₂ + H₂
This reaction apparently was inhibited by the clay catalyst.
Therefore cumene was dealkylated by Morden Bentonite
to form benzene and propylene in high yields.

III THE ACTION OF ACTIVATED MORDEN BENTONITE ON ALKYL AROMATICS

Up to the present time only three alkyl aromatic substances have been subjected to the catalytic effect of activated Morden Bentonite. Two of these, ethylbenzene and cumene, have been described in this thesis, while p-cymene was examined by Deans (2). It has been shown that ethylbenzene was pyrolyzed into benzene, toluene and styrene, cumene into benzene and propylene in high yields and a small amount of toluene, and p-cymene into toluene in excellent yields, indicating the removal of the isopropyl group. Thus from this work several conclusions may be drawn.

(1) Hydrocarbons with phenyl group attached to the primary carbon atom of the chain tend to dealkylate, partially into toluene and completely into benzene and to dehydrogenate. Therefore three types of reactions were occurring.

(2) Hydrocarbons whose phenyl group was attached to a secondary carbon atom of the chain dealkylate to form benzene from cumene and toluene from p-cymene.

There was a definite tendency for dehydrogenation with ethylbenzene but only slight ability for cumene and p-cymene to dehydrogenate to form styrene or styrene derivatives.

Dobrjanski, Kanep and Katsman (174) pyrolyzed ethyl, propyl, isopropyl, butyl, tertiary butyl, amyl and isoamyl benzenes and they reached the following conclusions:

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(1) Hydrocarbons with phenyl attached to the primary carbon atom of the chain yield on pyrolysis mainly toluene; (2) those with phenyl attached to the secondary carbon atom yield mainly styrene; and (3) those with phenyl attached to the tertiary carbon atom yield mainly benzene. They claim that pyrolysis products may be postulated through the affinity theory. Therefore hydrocarbons of group (1) are ruptured mainly between the 1st and the 2nd carbon atom of the chain; those of (2) between the 2nd and the 3rd; and those of (3) are ruptured at the tertiary carbon atom.

A comparison of the conclusions of Dobrjanski et al. with those obtained by the effect of Morden Bentonite readily shows that this catalyst greatly alters the effect of heat on the alkyl aromatics. This clay accelerated the formation of benzene exclusively when a phenyl group was attached to a secondary carbon atom of the chain, whereas with pyrogenetic decomposition benzene was formed when the phenyl group was attached to a tertiary carbon atom of the chain. With a secondary carbon atom the yield was not benzene but styrene. Again ethylbenzene when pyrolyzed forms toluene as a chief product but with the catalyst benzene and toluene were formed. Thus bentonite serves as a catalyst more for the complete removal of the alkyl group than for the splitting up of the side chain to form such products as toluene and styrene.

This is a problem that requires much further

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work but as this was a preliminary survey of the use of Morden Bentonite as a catalyst for organic reactions, an intensive study was not made. However, another worker could readily fill in the gaps by studying toluene, propylbenzene, butyl, isobutyl and tertiary butyl benzene, etc.

THE CATALYTIC DEHYDRATION

OF ALCOHOLS

IV DEHYDRATION OF PENTANOL-1 (N-AMYL ALCOHOL) OVER ACTIVATED MORDEN BENTONITE

Purified pentanol-1 was passed over activated Morden Bentonite at 300, 350 and 400°C. at rates of 1 and 2 c.c./min. These conditions were found suitable for the formation of high yields of pentenes. The experimental data, yields of products and analyses are given in Table IX.

The liquid products were purified by distillation through a Whitmore-Fenske column. Three fractions were readily obtained. Fraction 1 had a boiling range of 30-40°C. A large part of this fraction distilled over at 30-32°C. and was apparently pentene-1. However, it was also mixed with other pentenes and could not be quantitatively separated by the distillation equipment at our disposal. Thus fraction 1 consisted of a mixture of pentenes with a boiling range of 30-40°C., density range of 0.6450 to 0.6555 and a refractive index range of 1.3720 - 1.3840. The yields reported in Table IX represent percentage pentenes obtained by dehydration of pentanol-1 and not for pure pentene-1 which theoretically should be formed.

Fraction 2 was water with physical constants: b.p. 100°C.; n_D^{20} 1.3333; D_4^{20} 0.998. The water and pentenes form two layers. The percentage of pentenes formed may be roughly calculated by the quantity of water obtained. Fraction 3 was unchanged n-amyl alcohol. The residues were relatively low, and may have contained polymerized pentenes.

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TABLE IX

ACTIVATED MORDEN BENTONITE AS A DEHYDRATION CATALYST FOR PENTANOL-1

Analysis of Liquid Products

$\frac{\text{Run}}{\text{NO}}$.	<u>l-Pentanol</u> <u>in g</u> .	<u>Furnace</u>	Feed Ra c.c./mi	<u>te</u> <u>n.</u> <u>30</u>	1. -40°C.	2. 99-101°C	• <u>135</u>	3. -1 <u>40°C</u> .	<u>Residue</u>	Total Recovery	Loss
				<u></u> .	10	<u>8</u> •	<u>g</u> .	20	<u>g</u> •	<u>8</u> •	<u>8</u> •
13	81.7	300	1.0	58.7	90.3	15.4	5.4	6.6	1.1	80.6	1.1
14	81.7	300	2.0	56.5	86.9	14.8	8.0	9.8	1.3	80.6	1.1
15	81.7	350	1.0	60.1	92.5	15.8	3.4	4.2	1.2	80.5	1.2
16	81.7	350	2.0	59.1	90 .9	15.6	4.4	5.4	1.5	80.6	1.1
17	81.7	400	1.0	60 .6	93.2	16.0	2.7	3.3	1.5	80.8	•9
18	81.7	40 0	2.0	59.9	92.2	15.8	3.6	4.4	1.5	80.8	•9

The physical properties of purified Pentanol-1 are: b.p. $137.9^{\circ}C.$; D_{20}^{20} 0.817; $n_D^{14.6}$ 1.4096. Sample of catalyst used was 50 g. with a volume of 130 c.c.

The temperature of the preheater was 170°C.

There was no indication of a diamyl ether being formed by the dehydration of two molecules of the alcohol.

It will be seen from Table IX that 300-400°C. was a maximum temperature range for the dehydration of n-amyl alcohol. Between these temperatures there was a slight increase in the yield of pentenes. Thus at 300°C. there was 90.3% pentenes formed and at 400°C. there was a yield of 93.2%. The residues gradually increased with an increase in temperature, while losses of material, gaseous and mechanical, were fairly constant for both temperature and feed rate change. An increase in feed rate tended to decrease dehydration. There were no gaseous products since the temperature of the furnace was kept below the regular pyrolysis conditions.

The pyrolysis of n-amyl alcohol led to the formation of many substances which were too difficult to separate and analyze. Hence this alcohol has not as yet been adequately studied, however much work has been done by using catalysts at lower temperatures. Kashima (60) reported that he catalyzed amyl alcohol over Japanese acid earth at 260-270°C. to form 32% amylene, water, some diamyl ether, oxygen and a trace of carbon monoxide. Thus Japanese acid earth apparently had a similar action to that of bentonite. However, his yields were much lower accordingly than those obtained with bentonite. Diamyl ether was formed at 260-270°C. quite readily, which is what may be expected. Kearby (175,176) obtained yields of amylene when subjecting

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n-amyl alcohol to catalysis over alumina aerogel, alumina xerogel, or precipitated alumina at 350°C. Yields from 41-91% were reported. Dehydrogenation was less than 1%. It would appear that precipitated alumina and bentonite at 350°C. produced similar catalytic effects. Alumina gave 91% yield while the yield from bentonite was 92.5%. The reaction over these catalysts was essentially dehydration. Ivannikov (177) formed esters at 220-310°C. by passing n-amyl alcohol over CuO + 10.8% UO₃. This catalyst was essentially a dehydrogenation catalyst and exerted little effect as a dehydration agent.

$2RCH_2OH \longrightarrow RCO_2CH_2R + 2H_2$ while at 575°-600°C. 5.5-12.5% piperylene and 49.6-40.6% olefins were formed. Alumina at 600°C. gave 73.1% olefin. Thus dehydration of the alcohol occurred first and the olefin was dehydrogenated to form piperylene. The dehydration of n-amyl alcohol over alumina activated by the

addition of small quantities of oxides of the heavy metals from groups 1,6,7 and 8 has been patented but the yields were not mentioned (178).

From the data given in Table IX it will be noted that two important reactions occur, first dehydration and then isomerization. Activated Morden Bentonite served as a powerful dehydration agent. Thus the results obtained in this laboratory were equal to or greater than the yields obtained with alumina, Japanese acid earth, or alumina gels.
(1) $CH_3.CH_2.CH_2.CH_2.CH_2OH \rightarrow CH_3.CH_2.CH_2.CH = CH_2 + H_2O$ at 300-400°C. The above reaction was the only one of any importance. The isomerization of the resulting pentene-1 is not so easily explained. There was a tendency for the double bond to shift in pentene-1 under these conditions. Undoubtedly the greater part of the pentene fraction was pentene-1, but a considerable portion had isomerized. This may have been due to heat or the presence of the catalyst. There was some evidence for polymerization of the pentenes. The temperature conditions, however, were not sufficiently high for polymers to form; on the other hand, the temperature range was too high for the formation of diamyl ether.

(2) $2C_{5H_{11}}.0H \rightarrow C_{5H_{11}}.0.C_{5H_{11}} + H_{2}O$ Apparently the formation of diamyl ether is an intermediate step in the preparation of pentene-1. Two molecules link together to eliminate a molecule of water, while the ether immediately dehydrates further to form two molecules of pentene-1 and one molecule of water.

There was no evidence for dehydrogenation to form esters, as explained by Ivannikov, or an aldehyde as carried out by Adkins, Kommes, Strauss and Dosler (179). Since a high boiling fraction was not obtained during the purification of the products, there was ample evidence that activated Morden Bentonite does not act as a dehydrogenation catalyst for n-amyl alcohol.

V DEHYDRATION OF PENTANOL-3 (DIETHYLCARBINOL) OVER ACTIVATED MORDEN BENTONITE

Purified pentanol-3 was decomposed over activated Morden Bentonite at 275, 325 and 375°C. at feed rates of 1 and 2 c.c./min. These conditions formed excellent yields of cis and trans pentene-2. The experimental data are given in Table X.

The liquid products were fractionally distilled. A dark, oily residue remained behind in the distillation flask. Four fractions were obtained. Fraction 1, b.p. 35-38°C., consisted essentially of a mixture of the cis and trans forms of pentene-2; fraction 2, water; fraction 3, unchanged diethylcarbinol; and fraction 4, the dimer of pentene-2. This fraction was considered to be a mixture of decenes formed by dimerization of pentene-2. Its b.p. was 150-160°C.; D_4^{20} 0.733 to 0.755; and n_D^{20} 1.4225 to 1.4285. These compounds were isolated by distillation of the fractions and identified by three physical properties, which were compared with the properties of pure compounds. See Table XI.

The yields were high for these temperatures. There was a slight increase in yield for an increase in temperature. However, for a range of 275-375°C. the yield of pentene-2 increased only 1.7%. There was no tendency for a diamyl ether to be formed at the lower temperature. The water formed during the reaction may readily be used as a proof of dehydration. Pentene-2 tended to polymerize

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TABLE X

DEHYDRATION OF DIETHYLCARBINOL OVER ACTIVATED MORDEN BENTONITE

Analysis of Liquid Products

Run No.	Alcohol	<u>°C</u> .	Feed Rate	1 35-3 <u>8</u> •	38°C.	2. 95-105°C <u>g</u> .	$\frac{3}{\frac{110-13}{g}}$	20°C. Z	4. <u>150-1</u> g.	<u>60°C</u> . ℤ	Residue	Total g.	Loss g.
7	81.5	275	1.0	60.1	92.7	15.9	1.0	1.2	1.0	1.5	1.0	79.0	2.5
8	81.5	275	2.0	60.6	93.5	15.8	1.2	1.5	0.5	0.8	0.9	79.0	2.5
9	81.5	325	1.0	60.4	93.1	16.3	0.0	0.0	1.2	1.9	1.8	79.7	1.8
10	81.5	325	2.0	61.1	94.2	15.9	0.8	1.1	0.7	1.1	1.3	79.8	1.7
11	81.5	375	1.0	59.7	92.1	15.9	0.0	0.0	2.1	3.2	1.3	79.0	2.5
12	81.5	375	2.0	61.3	94.6	16.3	0.0	0.0	1.1	1.7	1.1	79.8	1.7

Purified diethylcarbinol had the following physical constants: b.p. ll5.6°C.; D_4^{25} 0.815; n_D^{25} 1.4077.

A 50 g. quantity of catalyst was used, having a volume of 130 c.c. The temperature of the preheater was $150^{\circ}C$. to form a dimer with a boiling range of 150-160°C. This polymerization became more pronounced at 375°C. The quantity of residue formed was not affected greatly by temperature change. This was also true of the loss of material during the dehydration. An increase in feed rates tended to give a slight decrease in dehydration but did not affect residue and losses.

The dehydration was quite complete. Only very small quantities of unchanged diethylcarbinol were recovered at 375°C.

There was no gas formed. Hence there was no simple pyrogenic decomposition occurring.

Compound	Boiling	Point	Refractive	Index	Densit	ty
	<u>given</u>	found	given	found	<u>given</u>	found
Pentene-2	35-37	35-3 8	1.3780	1.3783	0.6485	0.653
Water	100	100	1.3333	1.3340	1.0000	0.998
Diethyl- carbinol	115.6	115-6	(25) 1.4077	(2) 1.4075	5) 0.815	0.817
Decenes	-	150-60	-	1.4225 to 1.4285	-	0.733 to 0.755

TABLE XI

Moncatalytic pyrolysis of diethylcarbinol has been carried out but has been unsatisfactory due to the complex mixture of substances. More accurate analytical methods are required before this problem will be adequately settled. However, some work has been carried out on the

effect of catalysts on diethylcarbinol at lower temperatures than are used for pyrogenic decomposition. Thus Leenderste, Tulleners and Waterman (180) dehydrated diethylcarbinol over alumina at 380-400°C. A yield of 81% pentene-2 was formed. A comparison of this yield with those of 92.7-94.6% for bentonite would indicate that this clay is as good a dehydration agent as alumina if not somewhat better. Diethylcarbinol ordinarily is dehydrated by using sulfuric acid. Sherrill and Matlock (181) obtained a 75% yield of the trans form of pentene-2 by this method. Their work was carried out in the liquid phase. Thus bentonite would appear to catalyze this reaction better than sulfuric acid. A further advantage of bentonite is that it is much cheaper than the catalysts mentioned above and is readily available.

It appears that activated Morden Bentonite catalyzes two reactions. The primary reaction is intramolecular dehydration of the alcohol and the secondary reaction is the polymerization of pentene-2 with the formation of dimers. The residue probably contains higher polymers of pentene-2 also. These reactions are:

(1) $(C_{2H5})_{2CHOH} \longrightarrow C_{H3}C_{H2}C_{H} = C_{H}C_{H3} + H_{2}O$

(2) 2CH3.CH2.CH = CH.CH3 \longrightarrow (CH3.CH2.CH = CH.CH3)2 The pentene formed is really a mixture of two pentenes, the cis and trans forms; these were in all probability evolved during the dehydration process and not by isomerization of cis to trans or vice versa. There was apparently no tendency for pentene-2 to isomerize to other pentenes.

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During this dehydration there was no tendency towards the formation of the ether. Hence bentonite eliminated the formation of an ether and gave only the end product which was pentene-2.

Since there were no gaseous products formed during the catalysis reaction, there was no evidence for dehydrogenation. The liquid products contained no carbonyl compounds, as shown by the absence of aldehydes.

VI DEHYDRATION OF DIMETHYLETHYLCARBINOL (TERTIARY AMYL ALCOHOL) OVER ACTIVATED MORDEN BENTONITE

Purified dimethylethylcarbinol was dehydrated by coming in contact with activated Morden Bentonite at 300, 350 and 400°C., and feed rates of 1 and 2 c.c./min. The data concerning the products and analysis are given in Table XII.

The products were carefully distilled. Three fractions were obtained: fraction 1, b.p.30-39°C., consisted of pentenes; fraction 2, b.p. 95-100°C., mostly water; and fraction 3, b.p.100-103°C., unchanged dimethylethylcarbinol. Fraction 1 was redistilled and apparently contained two pentenes: 2-methylbutene-1 and 2-methylbutene-2, the latter being in greater quantity. 2-Methylbutene-1 has a boiling point of 30-32°C. and 2-methylbutene-2 a boiling range of 36-39°C. Hence it would require a Steadman column to separate these substances quantitatively. The pentenes are reported as a total and not separately. The water and unchanged dimethylethylcarbinol were readily purified and identified by boiling point, refractive index and density.

In Table XIII the constants given for the pentenes were those obtained by repeated fractionation of the substances. Thus relatively pure substances were isolated, but only in small quantities. At 300-400°C. excellent dehydration of dimethylethylcarbinol was achieved. There was a slight increase in yield of pentenes for a 100° increase in temperature. Thus dehydration must start at a temperature

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TABLE XII

DEHYDRATION OF DIMETHYLETHYLCARBINOL OVER ACTIVATED MORDEN BENTONITE

Analysis of Liquid Products

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Run No.	T.amyl alcohol	<u>Furnace</u>	Feed rate c.c./min.	1 <u>30-</u>	<u>39°C</u> . %	2. 95-100°C.	3 100-1	103°C.	Residue	Total	Loss
10	80 9	300	1 0	<u>0</u> •	_ <u>_</u>	<u>9</u> .	<u>o</u> .	2 6	<u>9</u> • 1 5	<u>0</u> •	<u>2</u> •
T 2	00.5	500	1.0	59.0	96.0	10.7	~•⊥	~• U	Τ.Ο	10.9	2.0
20	80.9	300	2.0	59.2	92.0	15.5	3.0	3.7	1.2	78.9	2.0
21	80.9	350	1.0	60.2	93.6	15.8	1.1	1.4	1.4	78.5	2.4
22	80.9	350	2.0	60.1	93.4	15.8	1.7	2.1	1.3	78 .9	2.0
23	80.9	400	1.0	60.5	94.0	16.0	0.0	0.0	1.8	78 .3	2.6
24	80 . 9	400	2.0	60.5	94.0	16.0	0.6	0.7	1.4	78.5	2.4

The physical properties of purefied dimethylethylcarbinol are: b.p. 101-2°C.; n_D²⁰ 1.4050; 20 D4 0.810.

Sample of catalyst was 50 g. with a volume of 130 c.c.

The temperature of the preheater was 140°C.

below 300°C. The amount of water produced during this type of reaction may readily serve as a rough indication of the percentage of dehydration, since the pentenes and the alcohol are not very soluble in water at room temperature. The residue which was always formed and losses of materials were apparently unaffected by an increase in temperature from 300-400°C. An increase in feed rate caused a small drop in the yields of pentenes, but did not affect losses of materials; however, there was a slight decrease in formation of residues for a feed rate increase from 1 c.c. to 2 c.c./min. At 400°C. and a feed rate of 1 c.c./min., all of the alcohol had reacted. Only a small amount of carbonization occurred even at 400°C. The evolution of gas was very low. Insufficient gas was formed to warrant collecting it.

TABLE XIII

Compound	Boiling Point		Refractive	e Index	Density		
	given	found	given	found	given ²⁴	found	
2-Methylbutene-1	31	30-32	1.3785	1.3795	0.6504	0,652	
2-Methylbutene-2	38.6	38 -39	1.3876	1.3870	0.6578	0.660	
Water	100.0	100.0	1.3333	1.3340	1.0000	0.996	
Dimethylethyl- carbinol	101.8	101-2	1.4052	1.4050	0.809	0.810	

The above-mentioned dehydration of dimethylethylcarbinol proves that activated Morden Bentonite is an excellent catalyst for dehydration. As far as we know, the use of clays as catalysts for the dehydration of dimethylethylcarbinol has not been studied. In fact. the literature contains very little about the effect of catalysts on the reactions of this alcohol. The ordinary method of forming pentenes from dimethylethylcarbinol is by heating the alcohol with iodine. Excellent yields were obtained by Church, Whitmore and McGrew (182) when they dehydrated tertiary amyl alcohol by heating with iodine. The pyrogenic decomposition of this alcohol has not been adequately studied as yet due to the extreme difficulty of isolating and identifying the many products formed. More exact methods of analysis are required before this work may be successfully continued. However, catalyzed reactions at temperatures below those at which tertiary amyl alcohol decomposes may be very profitably studied.

From the data obtained in this study of the action of bentonite as a catalyst on dimethylethylcarbinol it will be noted that the essential reaction was that of dehydration. This alcohol may be dehydrated in two ways. Thus 2-methylbutene-2 is obtained when the hydrogen is removed from the ethyl group and joins with the hydroxyl group to form water.

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(1) $(CH_3)_2.C_2H_5.$ COH \longrightarrow $(CH_3)_2.C = CH.CH_3 + H_2O$ This was found to be the main reaction when the dehydration was catalyzed with bentonite; however, a second pentene was formed.

(2) $(CH_3)_2.C_2H_5.COH \longrightarrow CH_2 = C(CH_3).C_2H_5 + H_2O$ 2-Methylbutene-l was, however, obtained only in a small quantity. The high yields of pentenes would indicate that bentonite was a good catalyst for this reaction. This was more important when the absence of byproducts was noted. There was no ether isolated during the distillation of products. Hence the formation of ether does not occur, or the ether was instantaneously dehydrated further to form pentenes. Another interesting fact is that the pentenes were not polymerized to any extent. The residue formed during each experimental run may contain some polymers, but these residues were so small that in any event polymerization was only slight. Thus at 300-400°C. polymerization was not important.

Furthermore, there was no evidence that dehydrogenation occurred. Thus from the above conclusions the effect of bentonite on dimethylethylcarbinol is essentially that of dehydration.

VII EFFECT OF ACTIVATED MORDEN BENTONITE ON ALIPHATIC ALCOHOLS

Clays have not been used very widely for the dehydration of the amyl alcohols. Kashima (60) dehydrated normal amyl alcohol over Japanese acid earth but obtained only 32% amylene. Senderens (183) passed a mixture of Me₂CH.CH₂.CH₂OH and Me.CH.Et.CH₂OH over aluminum silicate at 340-350°C. and obtained 85% Et.Me.C:CH₂ and Me₂C:CH.Me and the rest was Me₂CH.CH:CH₂. Thus both isomerization and dehydration occurred. Alumina was mentioned in the previous sections as an excellent dehydration agent, but if bentonite gives as good yields as alumina, it should readily replace the alumina due to its comparative cheapness.

Bentonite was used as a catalyst for the dehydration of primary, secondary and tertiary alcohols. With the primary amyl alcohol, dehydration was the main reaction. The pentene so formed was isomerized and thus gave a mixture of pentenes.

Secondary amyl alcohol (diethylcarbinol) was easily dehydrated to form pentene-2. There was no isomerization but some polymerization was observed. Tertiary amyl alcohol dehydrated to form 2-methylbutene-2 predominantly and some 2methylbutene-1. Hence there was no evidence for isomerization. The highest yields obtained for these alcohols were 93.2, 94.6 and 94.0% respectively for primary, secondary and tertiary alcohols. As was expected, primary amyl alcohols

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gave the lowest yields, indicating that the primary alcohols are not as susceptible to dehydration as the secondary and tertiary alcohols.

Bentonite did not act as a dehydrogenation catalyst in the catalysis of alcohols. There was no evidence for the formation of aldehydes and hydrogen.

One of the surprising facts was the absence of ether formation. In all three cases there was no evidence of etherification. This may have been due to the fact that the reactions were carried out at too high a temperature or that ether formation was not an intermediate step in the dehydration of alcohols and that water was removed directly from one molecule of alcohol to form the pentene.

Polymerization was not very marked. Only in the case of a secondary alcohol was any polymerization noticed. There was little tendency for the pentenes from primary and tertiary alcohols to polymerize.

Isomerization occurred only in the case of the dehydration of a primary alcohol. This has been observed by other workers in the dehydration of n-amyl alcohol, and was apparently due to the difficulty of removing the water easily.

VIII THE DECOMPOSITION OF ACETONE OVER ACTIVATED MORDEN BENTONITE

Acetone was decomposed by passage over activated Morden Bentonite at 300, 350 and 450°C., at feed rates of 0.5 and 1 c.c./min. The details of products formed and analyses are given in Tables XIV and XV.

The liquid products were fractionally distilled and four fractions were obtained. Fraction 2 was unchanged acetone. Fractions 1 and 3 were the pre- and post-runs of acetone and apparently contained acetone. Upon refractionation no adequate quantity of any compound other than acetone was obtained from fractions 1 and 3. Fraction 4 consisted of water. The acetone and water were identified by boiling point, refractive index and density, and will be indicated in Table XVI. An increase in temperature greatly affected the quantity of acetone recovered. Thus at 300°C. there was little change: 38 g. of acetone was recovered from 39.6 of starting material, but at 450°C. and with a feed rate of 0.5 c.c./min., only 21 g. of liquid product was obtained, which was chiefly acetone. At 350°C. the yield of water was much higher than at 450 °C. The reason for this will be explained in the discussion. There was only a small residue left after the distillation of water and acetone. This increased as temperature rose. The feed rate also greatly affected the yields of recovered acetone at 450°C. A feed rate of 0.5 c.c./min. resulted in 21 g. of liquid

product, but a rate of 1 c.c./min. formed 24.5 g. of liquid product. Slight carbonization occurred at 350°C. but at 450°C. much carbon was deposited on the catalyst.

The gaseous products when analyzed consisted chiefly of olefins. Smaller quantities of carbon monoxide and saturated hydrocarbons, and only small quantities of carbon monoxide and hydrogen were formed during these reactions. The olefins were determined qualitatively. The gas was passed through potassium hydroxide to remove carbon dioxide and then through a trap cooled to -50°C. A water-white liquid was obtained which distilled at -36 to -33°C. The vapor was passed into concentrated sulfuric acid. The mixture was diluted with water and distilled. Some acetone was isolated and identified, thus indicating that the gas was allene. The gas from which the CO2 and allene had been removed was passed into a chloroformbromine solution. Ethylene dibromide was isolated and identified by its physical constants, hence there was also ethylene present in the unsaturated gas. Allene and ethylene were apparently the only unsaturated gases which were formed by decomposing acetone over bentonite. The saturated gas was passed through a trap cooled to -100°C. by means of liquid air. There was no condensation; hence the gas must have been methane, since the higher saturated hydrocarbons would have condensed.

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TABLE XIV

THE CATALYTIC EFFECT OF ACTIVATED MORDEN BENTONITE ON ACETONE

Run No.	Acetone g.	<u>Furnace</u>	Feed rate c.c./min.	Liquid yield g.	Loss g.	Total gas evolved <u>1</u> .	<u>c.c. of gas/</u> g. of acetone
36	39.6	300	1.0	38.0	l.6	0.00	0.0
37	39.6	350	1.0	31.0	8.6	3.25	82.1
38	39.6	450	0.5	21.0	18.6	8.25	208 .4
39	39.6	450	1.0	24.5	15 .1	7.50	189.5

The physical constants for purified acetone are: b.p.56-57°C.; n_D^{20} 1.3592; D_4^{20} 0.794. The temperature of the preheater was 90°C. The gas evolution rate was determined for a 10 c.c. quantity of acetone. The sample for gas analysis was collected immediately after the determination of the gas evolution rate. Weight of catalyst used was 50 g. with a volume of 130 c.c.

TABLE XV

PRODUCTS	FROM	THE	CATALYSIS	OF	ACETONE

		Liquid and	alysis	Gas analysis						
Run No.	<u>-50°C.</u> <u>g</u> .	2. <u>51-60°C</u> . <u>g</u> .	3. <u>61-95°C</u> . <u>£</u> .	4. <u>96-102°C</u> . <u>⊈</u> .	Residue	C02 %	<u>Olef</u> .	<u>нг</u>	<u>co</u> Z	Sat.
36	-	38.0	-	-	-	-	-	-	-	-
37	0.5	25.7	1.1	3.2	0.5	23.2	67.3	-	1.9	7.7
38	1.2	13.6	2.0	2.9	1.3	25.9	56.5	0.2	3.4	15.0
39	0.9	18.9	1.3	2.4	1.0	29.4	55.6	1.8	2.5	10.7

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The temperature greatly affected the proportion and amounts of gases formed. At 350°C. there was 67.3% olefins but at 450°C. only 55.6%. The amounts of carbon dioxide, saturated hydrocarbons, hydrogen and carbon monoxide increased with an increase in temperature. Rate of feed also affects the formation of gases. The olefin content remained about the same but there was a decrease in the saturated hydrocarbons formed and an increase in carbon dioxide, hydrogen and carbon monoxide.

TABLE XVI

Compound	mpound Boiling Point		Refractive	Refractive Index			
	°C		20 np		20 D4		
	given	found	given	found	given ⁴	found	
Acetone	56.5	56-57	1.3589	1.3593	.792	0.795	
Water	100.0	100.0	1.3333	1.3336	1.000	0.998	
Ethylene bromide	131.6	131-136	l.4465 ⁽²⁵⁾	پ 1.4462	5) 2.1701	2.170	
Allene	-34.4	-34 to -3	5 -	-	-	-	

Thus clay accelerates the decomposition of acetone into allene and water and also methane, carbon monoxide and ethylene. The pyrolysis of acetone has been quite well studied. Barbier and Roux (184) passed acetone through a 1-meter copper tube at 1000°C. and found that an almost quantitative reaction occurred in accordance with the equation

 $2CH_3.CO.CH_3 \longrightarrow 2CH_4 + 2CO + C_2H_4$

Thus bentonite greatly enhances this reaction at 350-450°C. compared to that at 1000°C. However, bentonite also affects another reaction, namely the formation of allene. This reaction was not observed during noncatalytic pyrogenic decomposition. Hurd and Tallyn (185) pyrolyzed acetone to ketene and concluded that for practical purposes the best conditions were at 700°C. at a rate of flow of 5 c.c./min. They obtained 35-45% yields of ketene. The pyrogenic decomposition of acetone into ketene was considered by Hurd to be the best synthetic method for ketene.

Catalysts tend to eliminate the formation of ketene. Thus Sabatier and Senderens (186) obtained methane, carbon monoxide, hydrogen and carbon by passing acetone over nickel at 270°C. Copper has no effect on ketones, at least below 400°C. The effect obtained indicates that nickel is much different from bentonite. Bentonite forms quantities of unsaturated gases and carbon monoxide, while nickel gives methane and carbon.

Eschenbach (187) patented a process for manufacturing ketene by passing acetone over carbon in a tube heated at 550-700°C. as recently as 1937.

Two reactions occurred when acetone was decomposed over bentonite. In the first reaction acetone was dehydrated to form allene and water. Both of these substances were isolated and identified.

(1) $CH_3.CO.CH_3 \longrightarrow CH_2 = C = CH_2 + H_2O$

From the quantity of water formed and the high percentage of olefins obtained, it would seem that this was the more important reaction, especially at 350°C. However, this reaction seemed to decrease with an increase in temperature.

The second reaction seemed to be the formation of ketene and methane.

(2) CH3.CO.CH3 \longrightarrow CH₂ = C = 0 + CH₄ This however was an intermediate step since only methane and ethylene were identified. Thus ketene decomposed into ethylene and carbon monoxide.

(3) $2CH_2 = C = 0 \longrightarrow CH_2 = CH_2 + 2CO$

This was substantiated by the work of Sabatier and Senderens (186).

The small quantity of carbon monoxide found upon analysis, and the large amount of carbon dioxide, would indicate that bentonite catalyzed a further reaction.

(4) $2CO \longrightarrow C + CO_2$

There was considerable carbon deposited on the catalyst. Thus it serves as a further check on this reaction. The small amount of hydrogen found indicates that there was little dehydrogenation occurring throughout the reaction. This is in contrast with the action of nickel as a catalyst, which yields CH_4 , CO, H_2 and C. The high olefin and carbon dioxide content would indicate that the catalytic effect of bentonite was different from that of nickel.

There was no tendency for two molecules of acetone

to dehydrate to form mesityl oxide. However, Mitchell and Reid (188) obtained mesityl oxide, phorone, isophorone and xyletone by passing acetone over silica gel at 460°C. A 65% conversion was mentioned. The gas consisted of 9% CO, 17% CH₄, 28% CO₂, 3% H₂ and 40% unsaturates. The results of the gas analysis compared quite favorably with the analysis carried out by us for bentonite at 450°C. However, the high boiling unsaturated ketones were not obtained.

OF KETONES

THE CATALYTIC DECOMPOSITION

IX THE CATALYSIS OF METHYL ISOBUTYL KETONE OVER ACTIVATED MORDEN BENTONITE

Methyl isobutyl ketone was decomposed over Morden Bentonite at 350, 400, 450 and 500°C. at rates of 0.5, 1.0 and 2 c.c./min. The liquid and gaseous fractions were isolated and identified. The data concerning these runs are given in Tables XVII and XVIII.

The liquid product was fractionally distilled and three fractions were obtained. Fraction 1, b.p. 70-80°C., consisted of 4-methylpentadiene-1,3; fraction 2, b.p. 98-102°C., water, and fraction 3, b.p. 110-120°C., unchanged methyl isobutyl ketone. There was a large residue. A small quantity of the residue was probably unchanged methyl isobutyl ketone, but the residual material was gummy and was considered to be polymers, chiefly high polymers of 4-methylpentadiene-1,3. From Graph II it will be seen that the residue increases uniformly between 400-500°C. This was what might have been expected since polymerization increases with heat.

Water, 4-methylpentadiene-1,3 and unchanged methyl isobutyl ketone were isolated by repeated distillation of their fractions. Only small quantities of pure 4-methylpentadiene-1,3 were obtained. This was due to the tendency of the diolefin to polymerize. These substances were identified by comparison with the physical constants of the pure substances as reported in the literature.

TABLE XVII

CATALYSIS OF METHYL ISOBUTYL KETONE OVER ACTIVATED MORDEN BENTONITE

Run No.	Ketone g.	<u>Furnace</u>	Feed Rate c.c./min.	<u>Total Liquid</u> product - g.	Vapor Products and loss - g.	<u>Total gas</u> <u>1</u> .
40	40.4	350	0.5	34.1	6.4	0.20
41	40.4	350	1.0	37.8	2.6	0.10
42	40.4	400	0.5	33.2	7.2	2.50
43	40.4	400	1.0	36.2	3.2	1.25
44	40.4	450	1.0	26.2	13.2	7.00
45	40.4	500	0.5	18.3	22.1	13.15
46	40.4	500	1.0	20.5	19.9	10.75
47	40.4	500	2.0	23,2	17.2	10.00

The physical constants for purified methyl isobutyl ketone are: 20 20 20 b.p. 115-118°C.; np 1.3940; D4 .802. The gas evolution rate was calculated by collecting a sample of gas from a 10 c.c. portion of the ketone after the temperature and feed rate had been constant for 10 minutes. The sample for gas analysis was collected after determination of the gas evolution rate. The catalysis sample weighed 50 g. and had a volume of 130 c.c.

TABLE XVIII

PRODUCTS FROM THE CATALYSIS OF METHYL ISOBUTYL KETONE

Liquid products in g.

Gas analysis in %

Run No.	1. <u>70-80°C.</u>	2. 98-102°C.	3. <u>110-120°C</u> .	Residue	<u>co</u> 2	Unsat.	H2	<u>co</u>	Sat.
40	5.3	1.0	23.8	4.0	-	-	-	-	-
41	4.2	0.8	29.5	3.1	-	-	-	-	-
42	7.7	1.5	19.5	4.5	15.4	44.0	16.3	4.4	19.9
43	7.1	1.5	24.0	3,6	14.5	38.3	17.8	7.7	11.7
44	9;8	2.0	8.2	6.2	11.4	59.2	10.2	5.0	14.2
45	3 .3	4.9	1.0	9.1	7.8	46.2	22.0	4.8	19.2
46	5.6	4.4	2.5	8.0	8.5	53 .2	18.4	3.6	16.3
47	4.3	5.2	6.5	7.2	8 .9	58 .9	6.8	4.4	21.0



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TABLE	XIX
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Compound	Boiling	Point	Refracti	ve Index	Density 20		
	°C.		n _T)	20 D4		
	given	found	given	found	given	found	
4-methylpenta- diene-1,3	76	75-77	1.4503	1.4500	0.7189	0 .720	
Water	100	100	1.3333	1.3330	1.0000	0.998	
Methyl isobutyl ketone	115-118	115-118	1.3935	1.3940	0.8017	0 .802	
Methylpropane-1	-6.6	-8-5	-	-	-	-	
Tertiary butyl alcohol	82.8	82-83	1.3878	1.3875	0.7887	.0.789	

The temperature effect may be readily noted from Graph II. The formation of 4-methylpentadiene-1,3 gradually increases to 450°C, but drops at 500°C. This was due to the increase of polymerization, which was removing much of the olefin when formed. The formation of water was gradual until at 500°C. 4.4 g. of water was formed. The curve indicating the amount of unchanged ketone shows that the reaction was quite rapid at 350-450°C. and then began to slacken at 500°C. The feed rate greatly affects the decomposition of this ketone. Thus at 500°C. the amount of unchanged ketone for rates of 0.5, 1.0 and 2.0 c.c./min. were 1.0 g., 2.5 g., and 6.5 g. respectively. At the higher feed rates there was insufficient contact time for the ketone to be completely decomposed. There was also a decrease in residue formation. This would indicate that there was less polymerization occurring. There

was considerable deposition of carbon on the catalyst at the higher temperatures. The analysis of the gaseous products indicated high percentages of olefins, saturated gases, hydrogen and carbon dioxide. The yields of carbon monoxide were much lower. A trap cooled to -100°C. failed to produce any liquid, hence the saturated gas must have been methane. The unsaturated gases were passed through a trap cooled to -15°C. A colorless liquid was obtained which distilled over at -8 to -5°C. This gas was collected in concentrated sulfuric acid. The mixture was diluted with water and distilled. Some tertiary butyl alcohol was isolated and identified. The physical properties obtained are given in Table XIX. There were other unsaturated hydrocarbons besides isobutylene but they were not identified due to the small amount of liquid products obtained when the gases were passed into a mixture of bromine and carbon tetra-There was no gas formed at 350°C, but at 500°C. chloride. and a feed rate of 0.5 c.c./min. there was a volume of 13.15 liters. Most of the unsaturated gas at this temperature was collected as isobutylene in a trap at -15°C.

The temperature changes greatly affected the percentage composition of the gas. The quantities of carbon dioxide and carbon monoxide decreased with temperature increase. Hydrogen also increased. Thus at 400°C. there was 15.6% but at 500°C. there was 18.0%. The yields of saturated gases increased quite uniformly at 400, 450, and 500°C.

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from 11.4% to 14.2 and 16.0% respectively. The yields of olefin, however, did not rise uniformly. Thus the olefin content of the gas was 37.6% at 400°C. but 58.9% at 450°C. and dropped to 52.6% at 500°C.

An increase in feed rate at 400°C. caused a decrease in the percentage of carbon dioxide, olefins and saturated hydrocarbons, but at 500°C. there was an increase in the yields of carbon monoxide, olefins and saturated hydrocarbons for an increase in feed rate. At 400°C. a feed rate change gave an increase in carbon monoxide content and did not affect the hydrogen content, but at 500°C. the hydrogen content decreased and the carbon monoxide content was unaffected with an increase in feed rate.

Thus bentonite served to decompose methyl isobutyl ketone into 4-methylpentadiene-1,3, high polymeric residues, isobutylene, methane, carbon dioxide, carbon monoxide and hydrogen. So far as we know this was the first work carried out on this ketone in the vapor phase over a clay catalyst. Maihle (189) in 1922 passed methyl isobutyl ketone over a Cu-Al₂O₃ catalyst at 590-600°C. and obtained isobutylene, methane, carbon monoxide and carbon. These products compare with those obtained by using bentonite except for the formation of water, 4-methylpentadiene-1,3 and carbon dioxide.

From the above results we may conclude that there were three important reactions occurring.

First: methyl isobutyl ketone was dehydrated to

form water and 4-methylpentadiene-1,3. Both substances were isolated and identified. This reaction was apparently the predominant one at the lower temperatures. Thus,

(1) CH₃.CO.CH₂.CH(CH₃)₂ \longrightarrow CH₂ = C = CH-CH(CH₃)₂ + H₂O

(2) $CH_2 = C = CH-CH(CH_3)_2 \longrightarrow CH_2 = CH-CH = C(CH_3)_2$ There was probably an intermediate stage in which the allene derivative was formed, which immediately rearranged to the diene structure, since there was none of the intermediate product isolated in the liquid fractions. However, as the temperature was increased another reaction became predominant - that of the formation of a ketone derivative and methane. However, the ketone was only intermediate since carbon monoxide and isobutylene were obtained.

(3) $CH_3.CO.CH_2.CH(CH_3)_2 \longrightarrow CH_4 + (CH_3)_2CH-CH = C = 0$

(4) $(CH_3)_2.CH-CH = C = 0 \longrightarrow (CH_3)_2.C = CH_2 + CO$ However, there were high yields of carbon dioxide, hence it would seem that this came from two sources: one decomposition of the molecule and the other decomposition of carbon monoxide. Thus:

(5) $2CO \longrightarrow C + CO_2$

The third reaction was apparently the polymerization of 2-methylpentadiene-1,3. This was thought probable due to the large quantity of residue even at the lower temperatures, which could not be accounted for in any other way.

Decomposition apparently occurs at the higher

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temperature since much carbon, hydrogen and water are formed. The low yields of carbon dioxide and carbon monoxide at 500°C. would indicate that the ketone decomposed to form water, carbon and hydrogen rather than carbon dioxide and hydrogen. This would readily account for the increase in the formation of water and carbon.

X VAPOR PHASE CATALYSIS OF CYCLOHEXANONE OVER ACTIVATED MORDEN BENTONITE

Cyclohexanone was passed over bentonite at 300, 350, 400 and 500°C.; feed rates of 0.25, 0.5, 1.0 and 2 c.c./min. were used. The liquid and gaseous products were collected, isolated and identified. The experimental conditions are given in Table XX and the results of the analyses in Table XXI.

The liquid products varied in color from a light yellow when formed at lower temperatures to a dark red when formed at higher temperatures. The liquids were fractionally distilled. Five fractions were obtained. Fraction 1, b.p. 25-80°C., appeared at 500°C. and apparently consisted of unsaturated hydrocarbons having 5 and 6 carbon atoms. The quantities were too small to isolate and identify. Fraction 2, b.p. 80-90°C., consisted largely of cyclohexadiene-1.3. This was identified by its physical constants and by its tetra-bromo derivative, m.p.140° C., which was prepared by adding cyclohexadiene-1,3 to a solution of bromine in carbon tetrachloride. The resulting solid was recrystallized several times and was considered to be 1,2,3,4-tetrabromocyclohexane. Fraction 3, b.p. 98-102, was water. Fraction 4 consisted of unreacted cyclohexanone and was readily identified. Fraction 5, b.p. 225-235°C. was fractionated repeatedly and a quantity of the dimer of cyclohexadiene-1,3 was obtained. Dicyclohexadiene

was identified by its physical constants. This substance added 2 moles of bromine in a chloroform solution, but the bromine addition product could not be identified. With a mixture of acetic and sulfuric acids it gave a violet color, whereas with alcoholic sulfuric acid there was a deep red color. These tests correspond to those for the dicyclohexadiene which Hofmann and Damm identified (190).

There was considerable residue. A small amount of liquid boiling at 270-278°C. with D²⁰ 1.004 and refractive index of 1.5068, was isolated. This compound was considered to be cyclohexylidene-cyclohexanone. The residue consisted of a viscous tarry material. This was thought to be high polymers of cyclohexadiene-1,3. It readily absorbed bromine but no crystalline product was isolated.

An increase in furnace temperature greatly affects the catalysis of cyclohexanone over bentonite. From Graph 3 it will be seen that the quantity of unchanged cyclohexanone drops linerally with temperature increase. At 500°C. the greater proportion of the original material had reacted. Even at 300°C. considerable dehydration had taken place. The quantity of water increased slowly with temperature increase. The formation of the dimer of cyclohexadiene-1,3 and of polymers was also slowly increasing with temperature increase. Only at 500°C. was there a decrease in residue. This was apparently due to decomposition of the molecule as a whole.

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TABLE XX

DEHYDRATION OF CYCLOHEXANONE OVER ACTIVATED MORDEN BENTONITE

Run No.	Cyclohexanone	<u>Furnace</u>	Feed Rate c.c./min.	<u>Total Liquid</u> Product - g.	Loss g.	Gas Evolved 1.	<u>c.c.gas</u> / <u>g.cyclo-</u> hexanone
25	47 .4	300	0.5	42.4	5.0	-	-
26	47.4	300	1.0	44.0	3.4	-	-
27	47.4	300	2.0	45.2	2.2	-	-
28	47.4	350	0.5	38.1	9.3	-	-
29	47.4	350	1.0	40.9	6.5	-	-
30	47.4	350	2.0	41.2	6.2	-	-
31	47.4	400	0.25	37.0	10.4	-	-
32	47.4	4 00	0.5	38.2	9.2	-	-
33	47.4	400	1.0	40.1	7.3	-	-
34	47.4	500	1.0	37.3	10.1	5,30	111.8
35	47.4	500	2.0	39.1	8 .3	3.75	79.1

The physical constants of purified cyclohexanone are: b.p. 156-157°C.; np 1.4506; 20 D₄ 0.9478. The rate of gas evolution was determined as soon as the experimental conditions became constant. The sample for gas analysis was collected immediately after the gas evolution rate was determined. Weight of the catalyst was 50 g. with a volume of 130 c.c.

TABLE XXI

PRODUCTS FROM THE CATALYSIS OF CYCLOHEXANONE

Liquid Products in g.

Gaseous Products in 🔏

Run No.	1. 25-80°C.	2. 80-90°C.	3. <u>98-102°C</u> .	4. 150-160°C.	5. 225-235°C.	Residue	C02	Unsat.	H2	<u>co</u>	Sat.
25	-	6.2	4.0	20.6	5.0	6.6	-	-	_	-	-
26	-	4.8	3.2	25.8	4.2	6.0	-	-	-	-	-
27	-	4.4	2.6	29.0	3.8	5.4	-	-	-	-	-
28	-	6.8	4.6	13.1	5.4	8.2	-	-	-	-	-
29	-	5.3	3.8	21.1	4.7	7.0	-	-	-	-	-
30	-	5.0	3.2	25.0	4.5	4.5	-	-	-	-	-
31	-	8.2	5.6	7.4	7.0	9.8	-	-	-	-	-
32	-	7.0	4.5	11.0	6.5	9.2	-	-	-	-	-
33	-	6.2	4.2	15.2	6.2	8.4	-	-	-	-	-
34	4.0	9.0	7.5	6.3	6.0	4.5	1.0	16.0	43.9	6.1	33.0
35	3.2	7.8	6.7	12.5	5.4	3.5	1.7	13.2	41.3	7.2	36.6

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The feed rate increases tended to lower the amount of dehydration and to increase the recovery of unchanged cyclohexanone. There was considerable difference in the results from different feed rates. Thus at 300°C. the amount of unchanged cyclohexanone was 20.6 g. for a feed rate of 0.5 c.c./min. but for a feed rate of 2 c.c./min. it was 29 g. Thus there was a difference of 8.4 g.,which indicates the importance of feed rate changes.

There was considerable deposition of carbon at 500°C., but not very much at lower temperatures. This was due to the fact that decomposition of the nucleus did not occur until 500°C. was reached.

Cyclohexanone was quite stable, and hence there were only gaseous products at 500°C. The predominant gas found was hydrogen. Some saturated and unsaturated gases were formed. An attempt to isolate the unsaturated gases by forming the bromides failed due to a mixture being formed which was too small for subsequent fractionation and analysis. The saturated gases were considered to be a mixture of methane, ethane, propane and butenes. One very important feature of the gas analysis was the absence of any quantity of CO₂ and CO. This indicated that the oxygen was removed as water and not as a carbon oxide. A study of these gaseous products, together with the deposition of carbon, indicated that there was considerable cracking. An increase in feed

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rate lowered the yields of hydrogen and olefins and increased the amount of saturated hydrocarbons and carbon oxides.

ጥል	R	T.	R	X	KT.	т
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Compound	<u>Boiling</u>	Point	<u>Densit</u> 20ת	ty	Refract	ive Index 20
	<u>°C</u> . given	found	given	found	given	D <u>found</u>
Cyclohexadiene-1,3	8 3-4	80-85	0.8404	0.843	1.4758	1.4762
Dicyclohexadiene	229-30	227-230	0.9951	4 0.994 ^{/4}	1.5288	1.5290 ¹⁴
Water	100	100	1.0000	0,998	1.3333	1.3330
Cyclohexanone	156-7	156-7	0,9478	0.9478	1.4507	1.4506
Cyclohexylidene- cyclohexanone	272-5	27 2-5	1.004	1.000	1.5062	1.5065

Considerable work has been carried out on the pyrolysis of cyclohexanone. Hurd (191) decomposed cyclohexanone vapor at 700°C. 4.71 liters of gas was obtained from 28 g. of the ketone. The gas consisted of 52% CO, 19% olefin, 27% hydrogen and 2% saturated hydrocarbons. No ketene was identified. Cyclohexadiene-1,3, water and unchanged cyclohexanone were identified from the liquid product,which amounted to 4 g. Thus the pyrolysis of cyclohexanone was somewhat similar to the effect of catalysis with bentonite. However the conditions were apparently unfavorable for polymerization.

Triebs (192) prepared cyclohexylidene-cyclohexanone from cyclohexanone by heating in an autoclave at 300°C. for 6 hrs. At 350°C. he obtained cyclohexene in considerable quantity, as well as carbon monoxide. This was quite different from the clay catalysis. The yield of carbon monoxide was low and there was little indication of cyclohexene being present.

Hurd, Greengard and Roe (193) pyrolyzed cyclohexanone in a "Pyrex" tube at 700-725°C. filled with porcelain. They obtained water, cyclohexadiene-1,3, and cyclohexanone. They identified cyclohexadiene-1,3 by forming the tetrabromide derivative, m.p. 140°C. Their work again corresponds somewhat to that with bentonite except that bentonite was more specific in its dehydrating action.

Activated Morden Bentonite at temperatures of 300-400°C. tends to dehydrate cyclohexanone to cyclohexadiene-1,3 and water. The cyclohexanone probably first forms cyclohexadiene-1,2, which is an allene, and this rearranges to form cyclohexadiene, which was isolated.



This was by far the more important reaction at 300-400°C. There was a strong tendency for the cyclohexadiene to polymerize to form a terpene (which is the dimer) and also higher polymers. There was always a large quantity

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of a red viscous liquid left in the still pot after distillation.

Hofmann and Damm (190) and Alder and Stein (194) considered that the reaction occurred as follows:



Both groups of workers ascribed the same formula to dicyclohexadiene.

At 500°C. another effect was observed. The ring was broken to give a wide variety of substances. Even when cracking occurred there was little tendency for CO and CO_2 to be formed. Most of the oxygen joined with hydrogen to form water. There was no evidence for the formation of any quantity of cyclopentane by the splitting out of CO as:



However Norrish (195) reported a 90% yield of cyclopentane from cyclohexanone by pyrolysis. If this had happened over bentonite there would have been high yields of carbon monoxide. This was not found to be the case.

A side reaction was noted which occurred during dehydration of one molecule of cyclohexanone. Two molecules of cyclohexanone condensed to eliminate one molecule of water and form cyclohexylidene-cyclohexanone.



This reaction was not surprising since cyclohexanone formed cyclohexylidene-cyclohexanone in good yields when refluxed for a long period.

Activated Morden Bentonite therefore acted as a strong dehydration cataylst for the formation of cyclohexadiene-1,3 and water from cyclohexanone. XI THE EFFECT OF ACTIVATED MORDEN BENTONITE ON KETONES

Three ketones were studied. Two were aliphatic ketones; as acetone was symmetrical while methyl isobutyl ketone was unsymmetrical. The third ketone, cyclohexanone, was an alicyclic ketone.

When acetone was catalyzed three reactions occurred. At the lower furnace temperatures acetone decomposed to form water and allene besides splitting to give methane and ketene, which immediately decomposed to form ethylene and carbon monoxide. The third reaction was decomposition of the ketone with deposition of carbon.

Methyl isobutyl ketone decomposed somewhat similarly. The three reactions were: (1) formation of methane, CO and isobutylene; (2) dehydration to give water and 4-methylpentadiene-1,3; (3) polymerization of the 4-methylpentadiene to high polymers.

Cyclohexanone passed over bentonite decomposed readily. Three important reactions were noted: (1) dehydration to give cyclohexadiene-1,3 and water; (2) polymerization of cyclohexadiene-1,3 to form the dimer and higher polymers; (3) cracking of the cyclic ring to give a mixture of unsaturated and saturated compounds.

Thus from the above results we may conclude that activated Morden Bentonite serves as an excellent catalyst for the dehydration of ketones. Polymerization occurred readily with each ketone but was more marked with cyclohexanone. The identification of the dimer indicates that cyclohexadiene-1,3 readily polymerizes over bentonite at 300-500°C. The breaking of carbon-carbon linkages occurred with each ketone. The aliphatic ketones exhibited a strong tendency to form the saturated hydrocarbon and ketene which decomposed immediately into carbon monoxide and an olefin. The cyclic ketone carbon-carbon linkage was broken with greater difficulty than with the aliphatic ketones. There was also a greater number of saturated and unsaturated hydrocarbons formed. The formation of water to the exclusion of carbon monoxide was especially important during the cracking of cyclohexanone. There was no tendency to form cyclic compounds having a lower number of carbon atoms.

There was no tendency for the aliphatic ketones to form keto-unsaturated compounds such as mesivel oxide, etc. However two molecules of cyclohexanone split out water to form cyclohexylidene-cyclohexanone.

THE CATALYTIC DECOMPOSITION

OF ACIDS

XII THE DECOMPOSITION OF ACETIC ACID OVER ACTIVATED MORDEN BENTONITE

Purified acetic acid was catalyzed over bentonite at 400, 450 and 500°C. at feed rates of 0.5, 1.0 and 2.0 c.c./min. The liquid and gaseous products were collected and identified. The experimental data are given in Tables XXIII and XXIV.

The liquid products were fractionally distilled. Most of the liquid condensate consisted of unchanged acetic acid. Fraction 1 contained small quantities of acetone and water, while acetic anhydride was obtained in small yields from fraction 3. There was no residue from the distillation. At 500°C. considerable carbon was deposited on the catalyst. A temperature rise greatly affects the decomposition of acetic acid. The amount of acetic acid at 450°C. was 34.6 g. while at 500°C. there was 28.0 g. Thus 6.6 g. more had reacted than at the lower temperature. An increase in feed rate caused a drop in the decomposition of the acid.

The gaseous products contained large percentages of carbon dioxide and saturated hydrocarbons. There were appreciable quantities of olefins, hydrogen and carbon dioxide. A liquid air trap at -100°C. failed to remove any hydrocarbons, hence the saturated gas was considered to be methane. The olefins were passed into a bromine solution and ethylene bromide was obtained. An increase in temperature decreased the amount of methane, and carbon dioxide found, and increased the production of olefin and hydrogen.

TABLE XXIII

DECOMPOSITION OF ACETIC ACID OVER ACTIVATED MORDEN BENTONITE

Run NO•	HOAC	<u>Furnace</u>	Feed Rate c.c./min.	Condensate g.	Loss + Gaseous Products - g.	Gas Evolved
2	52,5	400	2.0	40.0	12.5	3.0
3	52.5	450	1.0	34.6	17.9	7.0
4	52.5	500	0.5	22.1	30.4	17.5
5	52.5	500	1.0	28.0	24.5	8.5

The physical constants of redistilled acetic acid are: b.p. 118°C.; n_D^{20} 1.3900; D_4^{20} 1.080. The gas evolution rate was determined as soon as the experimental conditions became constant. The sample for gas analysis was collected after the determination of the gas evolution rate. Weight of the catalyst was 50 g. having a volume of 130 c.c. TABLE XXIV

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	Liqui	id Analysis		
Run No.	l. Pre-run g.	2. <u>Recovered</u> HOAc - g.	3. Post-run g.	
2	2.0	37.5	0.5	
3	3.1	30.1	1.4	
4	2.4	17.7	2.0	
5	22	24 8	10	

00 ₂	<u>Olef</u> .	H ₂	<u>co</u>	Sat.
35.4	4.8	8.0	11.2	40.6
33.6	9.0	11.4	7.8	38.2
30.0	12.4	14.5	6.4	36.7
34.0	8.2	14.0	7.4	36.4

<u>Gas Analysis - %</u>

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Carbon monoxide fluctuated too much to draw any satisfactory conclusion. A change in feed rate did not greatly alter the composition of the gaseous products.

TABLE XXV

Compound	Boiling Point		Refractive Index 20 nD		Density 20 D4	
°C						
	given	found	given	found	given	found
Acetone	56.5	56-57	1.3589	1.3590	0.792	0.796
Water	100	100	1.3333	1.3330	1.000	0.998
Acetic acid	118	118	1.3718	1.3720	1.049	1,050
Acetic anhydride	140	139-41	1.3904	1.3900	1.082	1.080
Ethylene bromide	131.6	131-2	1.5379	1.5376	2.170	2.178

The pyrolysis of acetic acid has been extentively studied. Oppenheim and Precht (196) pyrolyzed acetic acid to give carbon dioxide and methane, as well as acetone, carbon dioxide and water. Ethylene was also obtained when a lower temperature was used. The formation of carbon dioxide and methane compares readily with the action of bentonite, which forms considerable quantities of methane and carbon dioxide. However, this clay seems to inhibit the formation of acetone. Nef (197) passed acetic acid vapors over pumice at 500°C. and obtained much carbon dioxide and carbonization. 58.6% methane, 34% CO and 7.4% hydrogen were also reported by Nef. His work corresponds to Oppenheim's.

Meingast and Mugden (198) prepared acetic anhydride

by passing acetic acid over fireclay at 650°C.

Mlle. Peytral (199) pyrolyzed acetic acid in a platinum tube at 1150°C. 18.1 g. of acid gave 17.9 g. of liquid products, only 3.17 g. of which boil above 118.6°C. There was some anhydride. Analysis of gaseous products gave: methane,16%; ethylene,5.6%; CO2,34.8%; CO,16% and hydrogen,4.9%. It is interesting to note how closely this analysis compares with that obtained over bentonite at 450°C. and 1 c.c./min. rate.

Kearby and Swann (176) recently obtained acetone, carbon dioxide and water from acetic acid at 275°C. over thoria catalysts. 18.6 to 98.8% acid reacted.

Thus Morden Bentonite primarily decomposed acetic acid into methane and carbon dioxide.

(1) $CH_3.COOH \rightarrow CH_4 + CO_2$

A gas analysis indicated that at 500°C. up to 25% of the acid had decomposed into carbon dioxide and methane. A secondary reaction apparently occurred, but only to a small extent. Namely, acetic acid decomposed into ketene and water. However, the ketene was further decomposed into ethylene and carbon monoxide.

(2) $CH_3.COOH \longrightarrow CH_2 = C = 0 + H_2O$

(3) $2CH_2 = C = 0 \longrightarrow CH_2 = CH_2 + 2CO$

Water, carbon monoxide and ethylene were identified in the products from the catalysis of acetic acid, indicating that the above reaction occurred.

A small quantity of acetone was identified, in-

dicating that two molecules of acid had split out carbon dioxide and water thus:

(4) $2CH_3.COOH \longrightarrow CH_3.CO.CH_3 + CO_2 + H_2O$

This reaction has been studied by many investigators and in some cases excellent yields of acetone have been reported. A small quantity of acetic anhydride was also identified, indicating a simple dehydration reaction:

(5) $2CH_3.COOH \longrightarrow (CH_3.CO)_2O + H_2O$ This reaction was reported by Peytral (199); however the yields were also very small, 0.31 g. of anhydride being formed from 18.1 g. of acetic acid.

The high yields of hydrogen obtained would indicate that a portion of the acid was being decomposed into hydrogen, carbon, and carbon dioxide. No simple, accurate equation has been given for this, but it may be shown thus:

(6) $CH_3.COOH \longrightarrow C + CO_2 + 2H_2$

(7) CH3.COOH \longrightarrow 2CO + 2H₂

Equation 6 is the more plausible reaction, since a large quantity of carbon dioxide was obtained compared to the amount of carbon monoxide. Carbon was also deposited on the catalyst, to prove this equation further.

SUMMARY

1. Four groups of compounds were chosen for a vapor phase study of the catalytic effect of Activated Morden Bentonite. These groups were: alkylaromatics, aliphatic alcohols, ketones and acids. The compounds were chosen after an exhaustive literature survey of the catalytic effect of clays upon organic compounds in the vapor phase. Such catalysts as aluminum oxide and silica were also considered, since they bear a formal structural relationship to hydrous aluminum silicates (activated clays).

2. Ethylbenzene catalyzed by bentonite at 600-650°C. formed benzene, toluene and a small quantity of styrene. Thus the chief reactions were dealkylation and dehydrogenation. Yields as high as 35.1% of benzene and 23.4% of toluene were obtained. The chief gas constituent was hydrogen.

3. Cumene passed over bentonite at 400-600 °C. dealkylated to form benzene and propylene. The optimum conditions for this reaction were a temperature of 550 °C. and a feed rate of 0.5 c.c./min. Benzene to the extent of 82.2% was formed. Considerable dehydrogenation occurred at 550-600 °C. A secondary reaction forming small quantities of toluene was noted. There was no evidence of simple dehydrogenation to form \propto -methylstyrene or dealkylationdehydrogenation to give styrene.

4. Normal amyl alcohol dehydrates intramolecularly when passed over bentonite at 300-400°C. to form a

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mixture of pentenes in yields of 86.9-93.2%. Pentene-1 apparently isomerized. There was no indication of ether formation through intermolecular dehydration.

5. Diethylcarbinol was dehydrated at 275-375°C. over bentonite to form 92.1-94.6% yields of pentene-2. There was no evidence for isomerization or ether formation. Some polymerization of pentene-2 was noted.

6. The dehydration of dimethylethylcarbinol was readily accomplished at 300-400°C. Yields of 92-94% pentenes were obtained. The pentenes consisted chiefly of 2-methylbutene-2. Small quantities of 2-methylbutene-1 were isolated. Ether formation and polymerization did not occur.

7. Two important reactions occurred when acetone was passed over bentonite at 300-450°C.: (a) acetone dehydrated to form allene and water; (b) acetone decomposed to give methane, carbon monoxide and ethylene, indicating the intermediate formation of ketene. A high carbon dioxide content indicated the pyrogenic decomposition of carbon monoxide to carbon and carbon dioxide. Apparently there was no condensation to form mesityl oxide.

8. Methyl isobutyl ketone was catalyzed by bentonite at 350-500°C. to form in one case methane, carbon monoxide and isobutylene, and in another case 4-methylpentadiene-1,3 and water. The dehydration reaction was the predominant one.

9. Cyclohexanone was dehydrated at 350-500°C.

over bentonite to give cyclohexadiene and water. At 500°C., besides, dehydration there was considerable nuclear decomposition. A large proportion of the cyclohexadiene polymerized. The dimer, dicyclohexadiene, was isolated and identified. A small quantity of cyclohexanone dehydrated intermolecularly to give cyclohexylidene-cyclohexanone.

10. The catalysis of acetic acid over bentonite at 400-500°C. indicated two reactions were occurring. The chief reaction was the decomposition of acetic acid into methane and carbon dioxide. Acetic acid also decomposed into water, carbon monoxide and ethylene, indicating that ketene may have been formed as an intermediate. Some acid was dehydrated to form acetic anhydride. A further minor reaction was the formation of acetone, carbon dioxide and water from two molecules of acetic acid.

CLAIMS TO ORIGINAL WORK

- Activated Morden Bentonite has been used for the first time as a vapor phase catalyst for the pyrolysis of nine compounds over a wide range of temperatures and at various feed rates.
- 2. Two alkylated benzenes, ethylbenzene and isopropylbenzene, have been shown to undergo dealkylation and dehydrogenation over this catalyst.
- 3. Three aliphatic alcohols, pentanol-1, pentanol-3, and dimethylethylcarbinol have been dehydrated.
- 4. Three ketones, acetone, methyl isobutyl ketone and cyclohexanone, have been shown to undergo both dehydration and degradation.
- 5. One carboxylic acid, acetic acid, has been pyrolyzed.

6. Simple mechanisms have been advanced that will successfully account for the products obtained.

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THE CONVERSION OF p-CYMENE INTO TOLUENE

with

ALUMINUM CHLORIDE

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Sulfite turpentine is a by-product obtained from the pulping of certain softwoods by the sulfite process. About one and one-half to two million gallons of turpentine were produced in the mills of the United States and Canada (1918) using spruce pine for wood pulp (1). More modern methods of cooking havea tendency to reduce the production of turpentine so that at the present time a figure of 200,000-300,000 gallons per annum would be a more accurate estimate of the potential production. It is estimated that $\frac{1}{2}$ -l gallon of turpentine is produced per ton of sulfite pulp.

Spruce turpentine is from eighty to ninety per cent p-cymene, whereas the turpentine from other soft woods may contain only fifty to eighty per cent cymene.

Several methods for the purification of p-cymene have been developed. Schorger (2) obtained very pure p-cymene by shaking sulfite turpentine with concentrated sulfuric acid and distilling over sodium. The purified p-cymene had the following properties: b.p. 176-176.6°C., D_{15}^{20} 0.8575, n_D^{20} 1.4908, M 45.29. Wheeler (3) elected to purify p-cymene in much the same way. Mann, Montonna and Larian (4) removed sulfur dioxide by extracting with a 30% sodium hydroxide solution. Upon distillation, a low boiling fraction (b.p._{10 mm}. 55-62°C.) which represented about 75% of the total was obtained. Fure p-cymene was produced from this low boiling fraction by treating with concentrated sulfuric acid, washing, drying and fractionating (b.p.₇₄₇ 174.6°C., n_D^{20} 1.4902). It therefore appears that no beneficial results are obtained from the use of sodium. The method described by the author is a modification of that used by Mann, Montonna and Larian (4).

The information available on the action of aluminum chloride on p-cymene has been given by a handful of workers. In most cases the authors have not reported yields of material obtained and have not mentioned the physical properties of the products. Anschutz (5) heated p-cymene with one-third of its weight of aluminum chloride at 150°C. and remarked that the liquid product contained toluene. The percentage yield of toluene was not given. Boedtker and Halse (6) in their report mentioned four experiments which they had carried out, e.g.:

(1) One hundred and fifty g. of spruce turpentine (90% cymene), 1000 g. benzene and 30 g. aluminum chloride were boiled six hours on the water bath to yield 52 g. toluene and 75 g. cumene.

(2) One hundred g. pure cymene, 1000 g. benzene
and 20 g. aluminum chloride were boiled six hours to yield
41 g. toluene and 85 g. cumene.

(3) One hundred g. pure cymene, 1000 g. benzeneand 10 g. aluminum chloride were boiled eight hours to yield31 g. toluene and 67 g. cumene.

(4) Ninety g. pure cymene, 900 g. benzene and 4.5
g. aluminum chloride were boiled ten hours to yield 44 g.
toluene (71%. This is Wheeler's correction; the authors reported 80%), and 68 g. cumene. A Vigreux column was used by

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them for distilling. There was no statement concerning the number of fractionations or the boiling points of the fractions. The above-mentioned reaction is a true reversal of the Friedel-Crafts reaction.

Moore and Egloff (7) studied the action of aluminum chloride on pure aromatic hydrocarbons and they obtained a yield of 14.3 per cent of toluene from p-cymene. R. H. McKee (8) heated spruce turpentine with aluminum chloride and hydrogen chloride and distilled the products. He reported a yield of 50-60% toluene. Propane was the chief by-product. R.H.McKee (9) in his Canadian patent reports that the yield is approximately doubled by passing a current of hydrogen chloride through the liquid during distillation. Ruttan et al. (10) discussed the possible industrial utilization of p-cymene to form toluene. They thought that 100,000 gallons of toluene could be produced annually from the turpentine of the sulfite mills of Ontario, Quebec and New Brunswick. The crude sulfite turpentine containing 80-90% p-cymene would cost 10 cents per gallon and would yield 0.45 U.S. gallon toluene per gallon crude cymene. Aluminum chloride was suggested as the dealkylation catalyst. A.S. Wheeler (4) repeated Boedtker and Halse's work but he obtained much lower yields of toluene and cumene than they reported.

A.W. Schorger (2) heated 200-g. portions of p-cymene with 50 g. aluminum chloride in a slow current of hydrogen chloride, carbon dioxide or air at such a rate that 1-2 drops

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distilled over per second. He obtained 24-37 g. of a product, b.p. 80-105°C., and 46-55 g. of a product, b.p. 105-116°C. With 100 g. aluminum chloride 46 and 40 g. respectively were formed. He mentions that Brooks obtained a 40% yield of toluene by treating p-cymene with 7% aluminum chloride by removing the low boiling reaction products as rapidly as they were formed. The use of metallic aluminum with HgCl₂ or dry HCl, ZnCl₂ or fresh FeCl₃ gave poor results. He identified diisopropyl (b.p. 56-58°C.), benzene, toluene, m-xylene, and 1-methyl-3,5-diisopropylbenzene (b.p. 215-218°C., D_4^{20} 0.8668, n_D^{20} 1.4950, M. 58.66).

Mlle. A. Lacourt (15) treated pure p-cymene (b.p. $176.2-177.2^{\circ}C.; n_D^{20}$ 1.49083, D_4^{20} 0.8583) with aluminum chloride at room temperature. Benzene, toluene, xylene, unchanged cymene, 1,3,5-diisopropyltoluene and a high boiling residue were obtained.

In the author's judgment the most comprehensive study of the problem has been made by Schorger, and the purpose of the present investigation was to check his work and, if possible, to improve the yields of toluene obtained.

PURIFICATION OF SULFITE TURPENTINE

The sulfite turpentine used for this experimental work was obtained from the Anglo-Canadian Pulp and Paper Mills, Limited, Quebec City*. This consisted of a large turpentine layer, a bottom acid layer, some solid waste, and was saturated with sulfur dioxide. The liquid was filtered and the turpentine separated from the acid layer. No attempt was made to remove the sulfur dioxide although Wheeler (11) drew air through the crude turpentine and Mann, Montonna and Larian (4) treated it with sodium hydroxide solution to remove any sulfur dioxide present. The turpentine layer was distilled and the fraction (170-200°C. at 760 mm.) consisted chiefly of p-cymene. This was further purified by treating with concentrated sulfuric acid (1200 g. of acid per kilogram of crude cymene), washing, drying over calcium chloride and fractionating. The fraction between 176-190°C. was collected. This was considered sufficiently pure for subsequent work in that when a portion of the former was redistilled, it came over almost entirely between 176-177°C. Yields of p-cymene varied from 52 to 58 per cent. These yields are considerably lower than the yields reported by various workers. This result, however, is probably due to the fact that they used turpentine from spruce pulp, whereas the author used turpentine from ten per cent spruce and ninety per cent balsam (14).

* Acknowledgment with thanks is hereby made to Dr.Rowley of the Anglo-Canadian Pulp and Paper Mills for supplying the crude sulfite turpentine at no cost.

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The turpentine, purified as above, had a faint aromatic odor, gave a faint discoloration with concentrated sulfuric acid, n_D^{20} 1.4900-1.4910. The refractive index of pure p-cymene obtained from Finnish sulfite turpentine is given by Karvonen (12) as n_D^{20} 1.49051 and from American sources by Schorger (2) as n_D^{20} 1.4908. The author agrees with Mann, Montonna and Larian (4) that the use of metallic sodium after the acid treatment, either for refluxing or for fractioning, was not necessary because the same physical constants were obtained in either case. It is to be noted, however, that concentrated sulfuric acid gave a deep wine red coloration to crude p-cymene whereas Schorger (2) mentions a yellow coloration.

ACTION OF ALUMINUM CHLORIDE ON P-CYMENE

In Table I are given the results obtained by heating cymene with aluminum chloride at different concentrations and temperatures.

In each experiment 100 g. of cymene was heated with different percentages of aluminum chloride. The apparatus consisted of a 500-c.c. three-necked, round-bottomed flask fitted with a thermometer, a mechanical stirrer with a mercury seal and a 20 cm. stillhead connected to a downward condenser. The flask was placed in a paraffin wax bath heated with a bunsen burner. This apparatus was arranged so that the low boiling fractions would distill over during the course of the reaction. The aluminum chloride was added to the cymene in one portion except for experiment In this case five lots of five per cent aluminum chlor-13. ide were added at ten minute intervals. This method of addition, however, gives lower yields than a single addition. The best yields of toluene were obtained when the aluminum chloride was added just below the temperature at which the experiment was carried out.

The undistilled residue was treated with water and sodium hydroxide solution, dried with calcium chloride and distilled. It will be noted from this table that the optimum temperature is 165°C. with an optimum yield of toluene being obtained with 25% aluminum chloride. A considerable amount of charring occurred at higher temperatures and concentrations.

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TABLE I

EFFECT OF TEMPERATURE AND CONCENTRATION

Run	Cotolwet	Temp °C	Time in	Total liquid	Residue and	Toluene yield
<u>NO</u> •	Cataryst	remp. C.	<u>111 D •</u>	<u>111_8</u> •	<u>1099 11 8</u> .	<u>// 11001001001001</u>
l	5% AlC13	120	2	74.75	26.25	0
2	5% "	140	2	76.80	23.20	1
3	5% "	160	2	68.11	31.89	26.1
4	10% "	140	2	74.30	25.70	19.8
5	10% "	150	2	65.65	34,35	20.3
6	10% "	160	2	67.55	32,45	33,5
7	20% *	145	l	61.60	38,40	29.8
8	20% "	155	1	59.95	40.05	35,3
9	20% "	165	l	56,55	43.45	50.4
10	30% "	150	1	54.60	45.40	39.0
11	30% "	160	1	58.30	41.70	46.4
12	30% "	170	l	62.90	37.10	51.5

TABLE I (continued)

EFFECT OF TEMPERATURE AND CONCENTRATION

$\frac{\text{Run}}{\text{No}}$.	Catalyst	Temp.°C.	$\frac{\text{Time in}}{\text{hrs}}$.	<u>Total liquid</u> <u>in g.</u>	<u>Residue and</u> loss in g.	Toluene yield % Theoretical
13	5 X 5% AlCl;	3 165	1.5	59.65	40.35	42.7
14	25% "	165	l	60.15	39.85	48.3
24	40%Na Cl 25% "	165	l	81.40	18.60	39.8
25	5%NaCl 25% "	165	l	67.45	32,55	50.3
26	10%HgCl2 25% "	165	l	65.60	35.40	51.5
27	50% "	165	l	54.65	45.35	56 .3

In every run the liquid product was separated into two fractions by redistillation, one between $50-145^{\circ}C$. and the other between $145-220^{\circ}C$. The first fraction was redistilled several times and the fraction between $109-112^{\circ}C$. was taken as being quite pure toluene, n_D^{20} 1.4948. The residues from the fraction with a boiling point up to $145^{\circ}C$. were added to the fraction from $145-220^{\circ}C$. and this was given a thorough fractional distillation. The various fractions were examined for certain physical properties as shown in Table II:

B.P. °C.	2	n_D^{20}	Mol.Wt.	Probable Constituent
58-70	0.5	1.4788	92.2	Diisopropyl
71-109	1.0	1.4794	95.2)	
109-111	12.5	1.4945	92.3)	Toluene
112-130	1.5	1.4920	96.8)	
131-140	2.0	1.4909	105.0	m- and p-Xylenes
141-150	4.0	1.4895	109.4)	Cumono
151-160	4.5	1.4870	119.9)	oditerre
161-170	10.0	1.4872	130.1)	
171-175	21.0	1.4901	135.8	Unchanged cymene
175-180	22.5	1.4913	135.8)	
181-200	6.0	1.4937	140.5)	Methuldifsonronulhengene
201-220	11.5	1.4950	168.7)	Methy furisopropy foenzene
221-240	3.0	1.5018	179.3	

TABLE II

This table indicates the presence of toluene,p-cymene and probably methyl 2,5-diisopropylbenzene, xylene, and cumene.

The liquid products of the above experiments were closely studied. Time, so far, has not permitted the study of solid derivatives from the liquids. But from the various physical constants obtained and previous work done by Schorger, one may make a good estimate of the substances formed in the action of aluminum chloride on p-cymene.

<u>Diisopropyl</u> Only a few drops of liquid with a boiling point of 56-58°C. were obtained. This was probably diisopropyl, which Brooks (13) has already isolated and identified. <u>Benzene</u> There was no evidence for the presence of benzene. <u>Toluene</u> This fraction distilled almost entirely between 108-112°C. The refractive index and molecular weight determinations indicated comparatively pure toluene.

<u>Xylenes and Cumene</u> The fractions with boiling points of 135-145°C. and 145-170°C. had refractive indices and molecular weights which indicated the presence of m- and p-xylene and cumene.

<u>Methyldiisopropylbenzene</u> The higher boiling fractions distilled mainly between 200-220°C. This has a molecular weight of about 170 and a refractive index of n_D^{20} 1.4950. These data compare favorably with the data given by Schorger (2) for methyldiisopropylbenzene.

<u>High boiling oils</u> These oils distilled over as high as 380°C. at which temperature reddish colored solids began to appear. These oils had a blue fluorescence. Two runs were made in order to identify the gases given off during the reaction. The gas evolved was first passed through a silver nitrate solution to remove hydrogen chloride and chlorine and then it was collected over a saturated salt solution. Both runs were made with 100 g. of p-cymene and 25% aluminum chloride.

TABLE III

GAS ANALYSES

Experiment No.	15	16
Volume of gas evolved	3200 c.c.	3500 c.c.
Unsaturation	3.3%	4.5%
Saturated gases present	H_2 , C_3H_8	H_2 , C_3H_8
Percentage of AlCl ₃ decomposed to give off HCl	4.24%	3.40%
Molecular weight	38.6	32.5

The gas analysis indicated that the reaction was catalytic in nature since only a very small amount of aluminum chloride was decomposed to produce hydrogen chloride or chlorine. The slight amount of unsaturation is due to the decomposition of the isopropyl group. The molecular weight would indicate that most of the saturated gas is propane. The data are given in Table III.

Analysis of the liquid products for chloride. The liquid fractions obtained from various reactions in which aluminum chloride was employed were tested qualitatively for chloride by using sodium dissolved in ethyl alcohol to split out chlorine. The resulting products were treated with silver nitrate. There was no indication of a chloride.

ACTION OF ALUMINUM CHLORIDE ON P-CYMENE IN THE PRESENCE OF DRY HYDROGEN CHLORIDE

Since McKee (8,9) claimed that he doubled the yield of toluene by passing a current of hydrogen chloride through a mixture of p-cymene and aluminum chloride during distillation, it was decided to repeat his work.

Four experiments were carried out. In three experiments 100 g. of cymene was used in each case, but in experiment #32, 200 g. of p-cymene was used. In each experiment dry hydrogen chloride was continuously bubbled through the p-cymene. The temperature was kept at 165°C. for each experiment, while the quantity of aluminum chloride was different in each case. A 15 cm. stillhead was used so that the low boiling fractions could be distilled during the reaction. Data on these runs are given in Table IV.

ACTION OF DRY HYDROGEN CHLORIDE ON P-CYMENE IN THE PRESENCE OF ALUMINUM

The formation of toluene employing the above experimental conditions always resulted in a tarry residue due to the aluminum chloride and some of the p-cymene reacting to form a complex. It was thought that aluminum powder and dry hydrogen chloride might react with p-cymene to give high yields of toluene without forming the large tarry residues.

One hundred g. of p-cymene was heated with stirring to 100°C. with 15 g. of aluminum powder. Dry hydrogen chloride was passed in and the mixture was heated to 165°C. and maintained at this temperature for two hours. During this period no low boiling fraction had distilled. The aluminum was only slightly decomposed by the hydrogen chloride. Toluene was not produced by this method.

ACTION OF ALUMINUM CHLORIDE ON P-CYMENE, USING ANILINE AS A DILUENT

Since it was practically impossible to obtain an inert solvent to use as a diluent, a substance with a boiling point above the boiling point of p-cymene was chosen. Aniline should adequately serve this purpose.

A mixture of 100 g. of p-cymene and 200 g. of aniline was heated to 120°C. with mechanical stirring, and 25 g. of AlCl₃ was added. The mixture was then heated to 165°C. and maintained at this temperature for two hours with stirring. During this period no low boiling fraction was obtained. Upon cooling the residue solidified into a gummy mass. There was no indication that toluene was formed during the reaction.

OTHER CATALYSTS USED

Several experiments were made using metallic aluminum-mercury couple, anhydrous ferric chloride, sulfuric acid and anhydrous aluminum chloride and 85% phosphoric acid. These were poor catalysts since only small quantities of toluene were formed. The results with the first two of these substances confirm Schorger's (2) work.

TABLE IV

ACTION OF P-CYMENE WITH $AlCl_3$ WITH DRY HYDROGEN CHLORIDE

Expt. No.	% AlCl ₃	g. of dry HCl used	Time in hrs.	<u>AlCl</u> 3 Added_at	<u>Yield of</u> Toluene in g.	Total liquid yield in g.	<u>% Yield</u> of Toluene
30	15	14	2	140°C.	36.5	50.3	52 .9
29	25	10	2	140°C.	41.7	42.2	60.4
31	35	17	l	105°C.	44.0	51.4	63.8
32	35	17	11	105°C.	41.5	49.9	60.3

DISCUSSION

The fact that sulfite turpentine consists of about 50% p-cymene is accounted for by Komatsu and Nodzu (16) on the basis that the terpene existing in the wood is transformed, during the manufacturing of the pulp by the sulfite process, into p-cymene by catalytic dehydrogenation with sulfur which is liberated in a free state in the digestor. Thus pinene, for instance, is converted into pcymene:



The action of aluminum chloride on p-cymene is not a straightforward reaction but probably consists of at least seven different types of reactions; alkylation, Friedel-Crafts, polymerization, isomerization, hydrogenation, dehydrogenation, and cracking. The great variety of reactions is the real difficulty in obtaining good yields of toluene. The removal of the isopropyl group and the transfer of a hydrogen atom from the isopropyl group to the toluene structure is the essential reaction required. The purpose of the whole experimental procedure mentioned above was to reduce the possibility of the occurrence of other types of reactions. Mixed halides of an active type, e.g., AlCl₃ and an inactive type, e.g., NaCl or HgCl₂, were tried. When these were used in large quantities there was a decreased yield of toluene. When mixed halides were used in small quantities the reaction was not affected.

<u>A possible mechanism of the reaction</u>. The mechanism of this reaction is vitally important. Unfortunately the mechanism of the action of aluminum chloride on hydrocarbons remains uncertain.

Palmer and Elliott (17) investigated aluminum chloride by electron diffraction and postulated the structure as Al₂Cl₆, e.g.



thus the real catalyst may be a hydrohalogen acid HAlCl4; the HAlCl₄ probably acts in turn on p-cymene through intermediate compound formations to give toluene, some aluminum chloride, propane, hydrogen, etc. This mechanism as mentioned by Burk (20) sets up an analogy between the action of halides and the action of acids which is quite real and has been already recognized.

In contrast to the above mechanism Copisarow (18) suggested a function of HCl which may be expressed by the action of p-cymene and aluminum chloride as:

- (1) $CH_3.C_6H_4.C_3H_7 + Al_2Cl_6 \longrightarrow CH_3.C_6H_4.Al_2Cl_5 + C_3H_7Cl$
- (2) $CH_3.C_6H_4.C_3H_7 + C_3H_7C1 \longrightarrow CH_3.C_6H_3.(C_3H_7)_2 + HC1$
- (3) $CH_3.C_6H_4.Al_2Cl_5 + HCl \longrightarrow CH_3.C_6H_5 + Al_2Cl_6$

Thus p-cymene would give toluene and methyldiisopropylbenzene. But if the methyl group instead of the isopropyl group was affected, cumene and 1-methyl-2,5-diisopropylbenzene would be formed. There would also be a tendency for some toluene to yield xylene and benzene.

The above mechanism explains the presence of toluene, xylene, cumene, and methyldiisopropylbenzene as reported by Schorger (2) and found in the experimental work given in this thesis but there should be large yields of methyldiisopropylbenzene and xylene and small yields of toluene and cymene. However, we have definitely obtained only small yields of methyldiisopropylbenzene and relatively large yields of toluene. The reason for the formation of propane during the course of the reaction is not explained. One may anticipate a simple reaction because bromine water will react with ease with cymene to give isopropyl bromide and pentabromotoluene (19), which would indicate that the isopropyl group should be more easily split off than the accumulated experimental evidence shows. Since theories regarding activation are naturally vague, we have not mentioned this type of theory because it does not

explain the mechanism of the reaction being studied.

According to Hammett (21) the Friedel-Crafts reaction by which aromatic compounds are alkylated with alkyl halides, alcohols, ethers, esters or olefins involves the intermediate formation of carbonium ions, thus:

RCl + AlCl₃ \longrightarrow R⁺ + AlCl₄⁻ Step I The driving force of this reaction is the strongly electrophilic nature of aluminum chloride and of other metal halides. The second step in the reaction is:

 R^+ + C_6H_6 + $AlCl_4^- \longrightarrow RC_6H_5$ + HCl + $AlCl_3$ Step II

It may be assumed for sake of argument that the reverse reaction of dealkylation or Jacobsen reaction also goes through the formation of a carbonium. Such an assumption would receive support if it can be shown that the isolated products of dealkylation reactions are the normal products arising from the stabilization of carbonium ions.

The following products have been isolated as a result of the dealkylation of p-cymene: toluene, propene, diisopropyltoluene, propane, diisopropyl and tars. It is worthy of note that the presence of propyl chloride or pchlorotoluene has not been reported.

The toluene arises then from the cracking of p-cymene through a reversed Friedel-Crafts mechanism, thus:

+ (CH3)H:C. +

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The propyl anion, it may be assumed, can stabilize itself in a variety of ways, but it appears that it does so principally by loss of a proton to form propene, by combination with p-cymene to form diisopropyltoluene, and by combination with olefinic and paraffinic substances present (principally propene and propane) to form dimers and higher polymers (tars). The fact that it does not appear to combine with Cl⁻ ions, which are surely present, to form propyl chloride, seems difficult to explain. The tolyl cation stabilizes itself by reaction with protons (supplied from the HCl, when used, by the propyl ion, or as a result of deep seated cracking).

The appearance of appreciable quantities of diisopropyl is not explained so easily. The presence of a compound of this type seems to postulate the formation of isopropyl free radicals as intermediates. We are loath to suggest such a mechanism. However, the explanation of the formation of this compound may lie in the appearance of propyl cations and tolyl anions, thus:



The propyl cation would then react with the anion to form diisopropyl. The fate of the tolyl cation would be to react with hydrogen ions to form toluene. Apparently it does not react with the chloride ions present to form p-chlorotoluene. Such a carbonium mechanism for the Jacobsen reaction has the additional advantage that it offers a satisfactory explanation of the observation that hydrogen chloride (a source of protons) assists the dealkylation. It also helps to explain why the secondary propyl group is preferentially removed rather than the primary methyl. The reason lies in the fact that in the former case there is a lower energy of activation. Thus it has been reported that when benzene is alkylated with $CH_3.CH_2.CH(CH_3).C(CH_3)_3$ in the presence of AlCl3 and HCl the products are tert-butylbenzene and n-butane (22).

SUMMARY

- The isolation and purification of p-cymene has been quite thoroughly studied by previous workers. Their work was reviewed by us and was modified by eliminating the process of removing sulfur dioxide.
- 2. By the action of aluminum chloride on p-cymene a yield of 50% to 60% of toluene may be obtained. The optimum temperature was about 165°C. The optimum percentage of aluminum chloride was 25 to 30%.
- 3. The action of aluminum chloride on p-cymene in the presence of dry hydrogen chloride served to give a yield of toluene of about 65%, using 35% aluminum chloride. These yields were much higher than those with aluminum chloride and p-cymene alone. The highest yield of 56% with the latter was almost 10% lower than the yields using dry hydrogen chloride. It is to be noted that the passage of the hydrogen chloride diminished the tendency of the aluminum chloride to sublime.
- 4. P-cymene gave no yield of toluene when treated with aluminum chloride and diluted with aniline. Evidently the aluminum chloride reacts with aniline to give a solid derivative.
- 5. A steady increase in temperature served to increase the yield of toluene and to reduce that of the other liquid products, but the amount of charring was greatly increased.

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- P-cymene gave no yield of toluene when treated with aluminum powder and dry hydrogen chloride. The aluminum powder was not affected.
- 7. An inactive type of halide such as NaCl or HgClg mixed with AlCl₃ in small quantities did not affect the yield of toluene but large quantities retarded the formation of toluene.
- 8. Anhydrous ferric chloride, aluminum-mercury couple and sulfuric acid and aluminum chloride gave only small yields of toluene.
- 9. The analysis for chlorine in the liquid products indicated that chlorination had not occurred. Aluminum chloride was not decomposed. The aluminum chloride probably lost its activity due to clogging with organic matter.
- 10. It seems probable that in the main reaction the isopropyl group is removed from p-cymene. Some of this group is then decomposed to provide hydrogen for the toluene and carbon is left behind in the reaction mixture.

CLAIMS TO ORIGINAL WORK

- A reinvestigation of the dealkylation of p-cymene through the agency of aluminum chloride, alone and with hydrogen chloride, has been made.
- 2. Improvements in the experimental procedure have been introduced with a definite increase in the yield of toluene, to 63.8%.
- 3. A satisfactory mechanism for the Jacobson Reaction (reversed Friedel-Crafts Reaction) is presented.

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SYNTHESIS OF PROKNOCKS

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INTRODUCTION

Knock Phenomena in Internal-Combustion Engines

A normal combustion consists of admitting a mixture of a combustible hydrocarbon and air to the engine cylinder. This charge is compressed, and towards the end of the compression stroke a spark passes through a portion of the mixture. A rapid bluish flame burns the mixture; the burning occurs along a narrow flame front, the burnt product reaching a high temperature due to the heat of reaction, thus causing a very rapid rise in pressure. The energy was utilized during the expansion stroke. (1)

Knock may be defined as an abnormally rapid explosion of a certain portion of the charge which is the last to burn (2). The flame velocity and pressure rise of a knocking explosion are greater than those of a normal combustion, but are much less than for a true detonation. (1)

The tendency to knock depends not only on the physical factors of time and temperature but also on the chemical composition of the charge. Thus such factors as chemical nature, concentration, air-fuel ratio, presence of pro- or antiknock agents and heat of vaporization and combustion of the fuel greatly influence knocking.

An ordinary internal-combustion engine is not greatly damaged by knock, although efficiency falls off. An aircraft engine, however, rapidly suffers from knock and gumming. The limitation which the fuel sets on the performance of the engine is very definite.

Methods of Testing

The earliest work was based on the observation of knock in engines by the ear. Ricardo (3) determined the highest compression ratio at which the engine could be operated on the fuel in question without audible knocking. So many methods were soon devised that in 1928 a sub-committee of the Co-operative Fuel Research Committee was formed to develop a uniform knock-testing apparatus and procedure.

A standard engine was devised which determines knock rating by means of a knockmeter (4). This operates on the principle of the bouncing-pin indicator. It does not give an absolute measure of knock intensity; but merely a comparative indication of knock intensity between two fuels.

A second essential to a knock-testing method is a scale for measuring relative knocking tendency. Two hydrocarbons were selected as reference fuels, normal heptane having an octane number of zero and iso-octane of 100. Thus the octane number of a motor fuel is the whole number nearest to the octane number of that mixture of iso-octane and normal heptane which the motor fuel matches in knock characteristics (5).

In rating aviation fuels for knock, the tendency of the fuel to heat the cylinder and the piston is generally accepted as a more important criterion of the suitability of a fuel than the tendency to emit audible sounds recognized as knock (6).

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Proknocks

The literature contains many references to antiknock compounds. This is due to the constant demand for better automotive fuels. The wide application of tetraethyl lead as an antiknock is well known. By contrast the existing information on proknocks is very meagre.

Proknock compounds are substances which when added to automotive fuel in small quantities increase the knocking of the internal-combustion engine. Many proknocks were discovered during the intensive search made by the various oil companies for adequate antiknocks. Others were noted from a study of the intermediate products formed during the combustion of hydrocarbons. Yet for obvious reasons little data have been published.

A distinction must be made between knocking fuels and true proknock compounds. Ethers and aldehydes in general are considered as knocking fuels which, when added in fairly large quantities, will cause a decrease in the octane rating of a fuel (7).

Organic peroxides are considered as excellent proknock agents (2). Dimethyl (8), diethyl (8,9) and ethyl (2) hydrogen peroxides are among the most efficient. Ozone was considered the best proknock (10); ethylidene peroxide (8) and hydrogen peroxide (2) are slightly less effective. Acetyl (8), benzoyl (7,11), cetyl benzoyl (8), and diaceto peroxides (8) are quite good proknocks. Methyl and ethyl

-3-

ketone peroxides (12) and olefin peroxides are not of much value (1,2,8,11).

A number of organic compounds containing nitrogen are quite powerful proknock agents, especially ethyl (13), isopropyl (13,14), butyl (7,15), amyl (7,11) and isoamyl nitrites (7,11). The corresponding nitrates (16), nitro compounds and the oxides of nitrogen (1,2,8,11) are less effective, although a few show a marked proknock activity.

One of the most intensified studies of proknock agents was carried out by Stacey and Wasson (17). The following compounds were considered "inducers" of knock:

nitroso-isopropyl-p-toluidine petrolatum thiocarbanilide benzaldehyde allyl-iso-cyanate heptaldehyde allyl-iso-thiocyanate methyl nonyl ketone amyl salicylate zinc diethyl methyl sulphate lead triphenyl iodide ethyl nitrite phenyl mercuric iodide isopropyl nitrite cetyl alcohol stearic acid amyl nitrite cobalt oleate amyl ether cadmium bromide mercuric diphenyl ammonia (dry gas) tin tetraphenyl

silicon tetraphenyl

-4-

It was noted that nitrogen when present as an organic nitrite or nitrate was considered a proknock, and when present in the amine form, an antiknock or neutral. Iodine had both anti- and proknock properties, depending upon the conditions under which it was investigated.

Lapeyrouse and Lebo (18), when determining the octane blending improvement of over 300 compounds, found that some compounds had a high negative O.B.I., i.e., ali-phatic hydroxy amines -1000.

Thomas and Hockwalt Laboratories (19) found that small amounts of resins were effective in rendering automotive fuel unusable.

Sugden (20) listed phosphorus trichloride, phosphorus oxychloride and carbon tetrachloride as agents which caused stoppage of internal-combustion engines either by sticking the pistons, or by fouling the spark plugs.

It must be noted that both proknock and antiknock compounds are not catalysts since they are used up, and their effectiveness ends. Proknock compounds are known to decrease the self-ignition temperature of hydrocarbons. It was noted that nitrogen when present as an organic nitrite or nitrate was considered a proknock, and when present in the amine form, an antiknock or neutral. Iodine had both anti- and proknock properties, depending upon the conditions under which it was investigated.

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It must be noted that both proknock and antiknock compounds are not catalysts since they are used up, and their effectiveness ends. Proknock compounds are known to decrease the self-ignition temperature of hydrocarbons.

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Relation of Chemical Structure to Proknock Activity

Today there is no theory which adequately explains the reason for the anti- and proknock activity of compounds. Several theories have been advanced (12,21,22, 23,24) to explain the phenomena, but they are either untenable or incomplete. This is not at all difficult to understand since there are many factors governing the combustions occurring in internal-combustion engines. The theory of oxidation chain breaking or branching by the knock agent may be accepted for the present as the best explanation. (2,22,23)

The relation between anti- and proknock activity and ignition temperature has been studied (25). Those compounds which lower the ignition temperature tend to have proknock activity, while those which raise the ignition temperature tend to have antiknock activity. There are, however, many exceptions to this rule.

Lovell, Campbell and Boyd (26,27) published data on a series of pure paraffin and olefin hydrocarbons in fairly dilute solutions of gasoline, showing the number of consistent and regular relationships between the molecular configuration and the tendency of these fuels to knock.

Although there is very little information in the literature on the relationship of chemical constitution to proknock activity, a few generalizations, based on the literature and work done by Ogilvie (28) may be offered: 1. Proknock activity is associated with the nonmetallic elements, especially those of low atomic weight, as: boron, carbon, nitrogen, oxygen, sulfur, the halogens excluding iodine. Carbon is not essential to give proknock activity to a molecule. Its ability of chain formation may serve as a skeleton for other active elements to rest upon.

2. For nitrogen to be effective it must be present in the higher states of positive valence; nitrites and oxides were found to be more effective than nitrates, nitro compounds and diazo compounds in the above order. Amines are not proknocks and are even in some cases reported as antiknocks.

3. The halogens, excluding iodine, are good proknocks and they are apparently effective in order of decreasing atomic weight.

4. Molecular oxygen has no proknock activity, but it has some activity in ozone, peroxides and ozonides. Sulfur may be more effective than oxygen. Thus isoamyl sulfide gave a slight knock, while isomyl ether had no effect.

5. Branching of the hydrocarbon appears to cause an increase in the activity; e.g.,tertiary butyl nitrite is a stronger proknock than normal butyl nitrite.

6. The effect of unsaturation is not at all clear. Aromatics are reported in the literature as being antiknocks, and olefins appear to have the same function. Phenylcyclohexene is unique in being a proknock.

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The above information gave some indication to the author as to what compounds should be synthesized for further testing on the knock engine. These, however, are too limited to allow a prediction of the proknock strength of a certain organic or inorganic compound before it is synthesized. Further work may well broaden the field sufficiently for this type of prediction.

Preliminary Testing of Certain Compounds for their Proknock Rating

Qualitative and semi-quantitative work was carried out in these laboratories (28) using a Chevrolet engine and testing the effectiveness of a compound injected into the air intake, by the audibility of the resulting knock. Over 197 compounds, inorganic and organic, gases and liquids, were tested. From this list of substances a number of compounds were found to be valuable for further investigation on an Ethyl Knock-Testing Engine.

Previous to the above-mentioned research project, the following compounds and types of substances had been described in the literature as proknocks: ozone, peroxides, oxides of nitrogen, nitrites, nitro compounds, nitrates, the halogens (except iodine).

The results obtained may be indicated in the following manner:

1. Gases

Fourteen gaseous compounds were tested. The amounts used for testing were between ten and twenty parts per thousand of intake air. Oxygen caused bad knocking; nitrogen, carbon dioxide and paraffins caused uneven running; hydrogen, acetylene, ammonia, and olefins decreased knock and caused drop in load; ethylene, hydrogen sulfide, propylene and sulfur dioxide had no effect.
2. Liquids

(a) <u>Aliphatic and aromatic hydrocarbons</u>. Twenty-two compounds were studied. Phenylcyclohexene was the only compound to produce a definite knock.

(b) <u>Halides</u>. Twenty-nine compounds were studied, representing aliphatic and aromatic derivatives. Bromoform, chloroform and tetrachloroethylene produced slight knocking. Allyl bromide, fluorobenzene, methylene chloride and propylene bromide gave a drop in load.

(c) <u>Alcohols and Phenols</u>. Twenty-nine compounds were studied, representing aliphatic and aromatic, primary, secondary and tertiary, halo, amino and keto, hydroxy derivatives. No effect was noted.

(d) <u>Aldehydes and ketones</u>. Twenty-eight compounds were studied. Butyraldehyde was the only active compound and then gave but a slight knock.

(e) <u>Acids and anhydrides</u>. Eleven compounds were studied. No effect was noted.

(f) <u>Ethers</u>. Twenty-one compounds were studied. Diethyl ether produced a marked knock, diisopropyl and ethyl tert-amyl ethers gave a slight knock.

(g) <u>Esters</u>. Twenty-seven organic-acid esters and twelve inorganic acid esters were studied; halogenated, keto, nitrites, nitrates, borates, carbonates, phosphates and sulphates. Ethyl chloroacetate, ethyl valerate and methyl borate gave a slight knock. Acetoacetic ester produced a noticeable knock. Diazoacetic ester, n-butyl nitrite and

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tert-butyl nitrite gave a marked knock.

(h) <u>Sulfur derivatives</u>. Five compounds were studied. Isoamyl sulfide gave a slight knock, and carbon disulfide gave a decrease in load.

(i) <u>Acyl halides, amides and amines</u>. Twentythree compounds were studied. There was no effect.

(j) <u>Nitro compounds</u>. Seven compounds were studied. Nitromethane and 2-nitropropane gave a slight knock. Bromopicrin and chloropicrin gave a marked knock.

(k) <u>Nitriles, thiocyanates, azides</u>. Eleven compounds were studied. Phenyl azide gave a loss of load.

(1) <u>Miscellaneous</u>. Twelve compounds were studied, inorganic and organic. Bromine and nitrosyl chloride gave a marked knock, nitrogen peroxide gave a noticeable knock, phosphorus trichloride and thionyl chloride gave a slight knock and phosgene a drop in load.

3. Solids

Solids were not investigated by the above workers.

In summation of this work, the compounds which exhibited marked proknock activity were: chloropicrin, bromopicrin, isoamyl nitrite, n-butyl nitrite, tertiary butyl nitrite, thionyl chloride, nitromethane, acetoacetic ester, isopropyl ether, bromine, nitrosyl chloride, nitrogen peroxide and diazoacetic ester.

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Tentative Specifications for an Ideal Proknock

1. A compound of carbon, nitrogen, oxygen and halogen, and effective when present to the extent of a few parts per ten- or hundred-million parts of intake air by volume.

2. A liquid with a boiling point of about 100°C.

3. A compound if solid that would be soluble in gasoline.

4. A compound of sufficient stability to remain unaffected by the oxygen and moisture of the atmosphere, the tetraethyl leads of doped gasolines, and if dispersed by an explosive charge.

From the limited experimental data already known, the ideal proknock must draw elements from the first phase in IV, V, VI, VII of the periodic table. It is interesting to note that these substances are non-metals and are all of negative valency except carbon, which lies half way between negative and positive valency. An ideal proknock must not necessarily have all these elements in one molecule. A certain arrangement, however, of a number of these elements should lead to an exceptionally high proknock compound. Unfortunately, the relation of structure to knocking is not sufficiently developed to give any indication as to how these elements may be arranged. It would appear, however, that the molecular weight should not be very great. Certain compounds containing these elements in part or whole are not proknocks at all, while some are even antiknocks. Thus structure must play a definite part in a good proknock compound.

It should therefore be possible to develop some compound which may be used to damage enemy aeroplane or automotive engines. The logical place to render enemy aircraft useless would be at their bases. This may be accomplished either by spraying the airfields with the proknock substance, thus grounding their planes, or by sabotage of their gasoline supply. As a defensive weapon the proknock may be used in anti-aircraft shells.

For the first method a gas would be entirely unsatisfactory as it would be too easily dissipated. On the other hand a solid would not be satisfactory unless it could be used as a fine dust. Thus a liquid would be much better. A liquid boiling at 100°C. with a fair vapor pressure would be ideal for the above purpose. If it was too volatile, there would be great difficulty in obtaining sufficient concentration to cause effective damage.

Should a solid be used for the sabotage of gasoline supplies, certain properties are essential. The solid must dissolve in the gasoline, be colorless and odorless and nonreactive with the hydrocarbons and tetraethyl lead in doped gasolines. The work done on this phase of the problem (19) indicated that gumming materials would be quite satisfactory. Thus resins were used.

Stability of the proknock is by far the most dif-

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ficult factor in the choice of an ideal proknock. Most good proknocks are highly reactive compounds and tend to be greatly affected by oxygen of the air and water. Thus if such compounds were used their effectiveness would last only a comparatively short time. Thermal and concussion stability are also quite difficult properties to associate with an ideal proknock.

Theoretically it would be ideal to enclose some solid material in a shell which on bursting would give a number of compounds capable of giving marked proknock activity.

The limits of one part in one hundred million parts of intake air by volume seem to be outside the scope of chemical reactions, but it may be possible to find a substance which along with proknock activity may exhibit catalytic powers.

EXPERIMENTAL

Outline of the Problem

A number of organic compounds were required in the study of proknocks. Some of these could be readily purchased, but many had to be synthesized. Thus the purpose of this work was to synthesize some of these compounds. Certain elements were considered when these substances were synthesized. They were carbon, nitrogen, oxygen and halogen. A few organo-metallic substances were also synthesized. It was also decided to prepare liquids boiling around 100°C. or solids which would be soluble in the gasoline hydrocarbons. Some gaseous organic compounds were synthesized in order to complete a study of the effect of a group of compounds. The compounds to be prepared must necessarily be quite stable and not easily oxidized by the oxygen or moisture of the air.

Description of Results

Forty-four compounds were synthesized according to the specifications previously mentioned.

Many of these compounds have already been prepared by previous workers but as yet are not available commercially; accordingly, they were synthesized in this laboratory by procedures already well defined. These compounds will be mentioned in Table I, but a detailed account of the experimental

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procedures will not be given. The reference number will indicate the procedure which was followed in this work. These methods have been followed quite closely and with but few changes. Such changes as there were will be indicated in the notes.

Other preparations required definite modifications. For instance, a fairly complete study was made of nitrition and this will be reported fully. However, since the primary object of this project was to provide organic and organometallic compounds, so that they may be studied for their proknock properties, as expeditiously as possible, many interesting experiments were necessarily curtailed, and entangling hypotheses avoided.

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TABLE I

COMPOUNDS PREPARED FOR PROKNOCK STUDY

<u>No</u> .	Compound	Formula	Method of Prep.	Parts/million for a 10-octane drop
1.	Ammonium azide	NH4.N3	Frost,W.S.,Cothran, J.C. & Browne,A.W. (29)	no knock
2.	Nitrosyl bromide	NO.Br	Roozeboom, H.W. (30)	decomposed
3.	Nitrosyl chloride	NO.Cl	Mitchell,S. and Carson,S.C. (31)	7.0
4.	Nitrosyl cyanide	NO.CN	Original	no product
5.	Nitrogen trioxide	N203	Dox, A.W. (32)	fair
6.	Tertiary nitroso- butene	(CH3)3.C.NO	Original	no product
7.	2-Nitroso-2-nitropro- pane	$(CH_3)_2.C(NO).NO_2$	Meyer, V. (33)	not suitable
8.	Tertiary butyl nitrite	(CH3)3.CO.NO	Original	95.3
9.	Tertiary amyl nitrite	C2H5.(CH3)2.CO.NO	Original	yet to be done

<u>No</u> .	Compound	Formula	Method of Prep.	Parts/million for a 10-octane drop
10.	Allyl nitrite	CH2=CH.CH20.NO	Bertoni, G. (34)	decomposed
11.	Ethylene chloronitrite	CH2.C1.CH20.NO	Original	150
12.	Ethylene dinitrite	$C_{2}H_{4}(ONO)_{2}$	Original	decomposed
13.	Glycerine trinitrite	$C_{3}H_{5}$ (ONO) $_{3}$	Masson, 0. (35)	unstable
14.	Pentaerythritol tetra- nitrite	C(CH2ONO)4	Original	unstable
15.	Butyl thionitrite	C ₄ H ₉ SNO	Original	130
16.	Diacetylorthonitric acid	$(CH_3.COO)_2N(OH)_2$	Pictet, A. and Genequand, P. (36)	no knock at 12
17.	Acetyl nitrate	CH3.COONO2	Pictet,A. and Khotinsky,E. (37)	140
18.	2-Nitrobutanenitrite-1	C2H5.CHNO2.CH20.NO	Original	yet to be done
19.	2-Methyl-2-nitropro- panedinitrite-1,3	$CH_3.C(CH_2ONO)_2.NO_2$	Original	unstable

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<u>No</u> .	Compound	Formula	Method of Prep.	Parts/million for a 10-octane drop
20.	Nitro isobutyl tri- nitrite	0_2 N.C(CH ₂ ONO) ₃	Original	decomposed
21.	2-Nitrobutyl acetate-1	C2H5.CHNO2.CH200C.C	H ₃ Schmidt, E. and Rutz, G. (38)	310
22.	Nitroacetaldoxime	O2N.CH2.CH=NOH	Steinkopf,W. (84)	no knock
23.	Nitrobutene	CH3.CH2.CHO2:CH2	Wieland, H. and Sakellarias, E. (39) Schmidt, E. and Rutz, G. (38) Gal, H. (40) Haitinger, L. (41) Bouveault, L. and Wahl, W. (42) Loevenich, J.K., Koch, I. and Pucknots, U.	decomposed (43)
24.	Sodium bromonitrometha	ne Br.CH=NO ₂ Na	Scholl,R. (44) Tscherniak,J.(45)	intermediate
25.	Dibromonitromethyl cya	nide $O_2N.CBr_2.CN$	Steinkopf,W. and Bohrmann,L. (46)	intermediate

<u>No</u> .	Compound	Formula	Method of Prep.	Parts/million for a 10-octane drop
26.	2-Methyl-2-nitropro- panol-1	$(CH_3)_2C(NO_2).CH_2OH$	Henry, R. (47)	intermediate
27.	2-Methyl-2-nitropro- panediol-1,3	$CH_3.C(CH_2OH)_2.NO_2$	Henry, R. (47)	intermediate
28.	Tri(methylol)nitro- methane	$(HOCH_2)_3CNO_2$	Henry, R. (47)	intermediate
29.	ω -Nitrostyrene	C ₆ H ₅ .CH:CHNO ₂	Worrell, D.E. (48) Thiele,J. (49) Thiele,J. and Haeckel,S. (50)	insoluble in gasoline
30.	Phenylnitropropylene	C6H5.CH:C(CH3)NO2	Priebs, A. (51)	no product
31.	Phenylnitrobutadiene	C6H5.CH=CH.CH=CHNO2	Original	no product
32.	Phenylethylnitrobuta- diene	C ₆ H ₅ .CH=CH.CH=C(C ₂ H	$5).NO_2$ Original	no product
33.	Formamidoxime	NH2.CH=NOH	Nef, J. (52)	decomposed
34.	Diethyl chloramine	(C2H5)2N.Cl	Berg, T. (53)	164
35.	Ethyl dichloramine	C2H5.NCl2	Tscherniak, J. (54)	decomposed

<u>No</u> .	Compound	Formula	Method of Prep.	Parts/million for a 10-octane drop
36.	Ethyl hypochlorite	C2H5.0Cl	Sandmeyer,T.(55) Suknevich,I.F. and Chilingaryan,A.A.(56 Comastri Haracio,T.(5	135 57)
37.	Trichloromethylsul- fochloride	CC13.S02C1	Kolbe, H. (58)	not suitable
3 8.	Cacodyl	$(CH_3)_2As.As(CH_3)_2$	Bunsen, R. (59)	unstable
39.	Cacodyl chloride	(CH3)2AsCl	Bunsen, R. (60) Baeyer, A. (61)	4.2
40.	Methyl dichloroarsine	CH3.AsCl2	Nenitzescu, C.D.(62)	3.8
41.	Bromonitromethyl dichloroarsine	$O_2N.CHBr.AsCl_2$	Original	no product
42.	Mercury diethyl	$(C_2H_5)_2Hg$	Gilman,H. and Brown, R.E. (64) Gilman,H. and Brown, R.E. (65) Buckton,G.B. (63)	fair
43.	Cyanogen	(CN)2	Jacquemin,M.B.(66)	no effect at 600
44.	Hydrogen disulfide	H_2S_2	Butler,K.H. and Maass,O. (67)	not tried

The preparation of the nitrites and 2-nitrobutene -- 1 will be reported in full and discussed later in this thesis. The other compounds which have been prepared by methods already known will be discussed here and any changes in procedure, yields, etc. will be noted.

Pure ammonium azide, m.p. 160°C., was obtained in 80% yield. Extreme care was taken due to its unstability and its toxic properties.

Yields of 55% and 58% respectively were obtained in the preparation of nitrosyl chloride and nitrosyl bromide. An attempt to prepare nitrosyl cyanide by the dry distillation of a mixture of nitrosyl chloride and potassium cyanide was unsuccessful. A 37% yield of nitroxyl chloride was obtained by adding phosphorus.oxychloride to concentrated nitric acid.

Tertiary nitrosobutane could not be prepared by adding nitrosyl chloride to tertiary butyl magnesium chloride. 2-Nitroso-2-nitropropane was readily obtained in a 70% yield by adding a potassium nitrite solution to the sodium salt of 2-nitropropane.

Acetyl nitrate and diacetylorthonitric acid were formed in excellent yields. It is interesting to note that Pichtet and Genequand (36) obtained a refractive index of n_D^{23} 1.38432, whereas Bacharach and Breckstone (68) obtained a value of n_D^{23} 1.37542. Our determination of n_D^{23} 1.3754 confirmed the results of the latter workers.

2-Nitrobutyl acetate-1 was prepared by treating the

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nitro alcohol with acetic anhydride according to the method of Hass and Vanderbilt (69). However, in this laboratory we found that excellent yields were obtained by treating 2-nitrobutanol-1 with acetyl chloride. The only by-product was hydrogen chloride, which was eliminated in the gaseous form.

The preparation of nitroacetaldoxime was not considered to be entirely satisfactory. The yields reported by Steinkopf (84) were considered to be above the maximum. Certainly nitroacetaldoxime is quite unstable and it is difficult to purify.

Sodium bromonitromethane and dibromonitromethyl cyanide were prepared by existing procedures. However, the latter substance was quite unstable, and this should be stored as the ammonium salt.

Three nitro alcohols were readily formed by condensing the proper nitroparaffin with an aldehyde. These were 2-methyl-2-nitropropanol-1, 2-methyl-2-nitropropanediol-1,3, and tri(methylol)nitromethane. These compounds could not be vacuum distilled, since they tend to explode on heating. The explosion was ascribed to the presence of traces of metal organic compounds (70).

 ω -Nitrostyrene was prepared in 50% yields only despite the fact that Worrell in "Organic Syntheses" reports yields of 80-83%.

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An attempt to prepare phenyl nitropropylene by reacting the sodium salt of nitroethane with benzaldehyde was unsatisfactory. Two nitrodienes, phenylnitrobutadiene and phenylethylnitrobutadiene, could not be formed by condensing cinnamyldehyde with the corresponding nitroparaffin salt. Only tarry residues were formed. It was hoped to form a solid nitrodiene which would serve as a basis for a study of the series. So far as we know, nitrodienes have not been prepared to any extent.

Formamidoxime, diethyl chloramine and ethyl dichloramine were readily prepared. These were all very unstable and could not be stored for any length of time.

Trichloromethylsulfochloride was obtained in very small yield.

Three arsenic derivatives were synthesized: cacodyl, cacodyl chloride and methyldichloroarsine. These were highly toxic substances. An attempt to condense sodium bromonitromethane with arsenic tribromide failed to give the expected bromonitromethyldichloroarsine. Organo-arsenic compounds so far have proved to be the best proknocks.

Mercury diethyl, cyanogen and hydrogen disulfide were readily obtained by well-known procedures.

No direct correlation between structure and proknock activity has yet been established. However, it is important to consider the fact that many elements in groups V, VII of the periodic table possess proknock properties either alone or combined with other elements. Some of the best of these are: arsenic, the halogens, antimony, phosphorus and nitrogen derivatives.

Unfortunately, much of the present work followed the trial-and-error method. Thus as often as not compounds which before being synthesized were thought to possess good proknock qualities were found upon testing to give meagre results.

Syntheses of Nitrites

Five general methods were considered for the preparation of the organic nitrites, namely: (a) reacting nitrous acid with alcohols (71); (b) trans-esterifying alcohols with glycerine trinitrite (34,72); (c) a general method for preparing nitrites by the action of liquid nitrogen trioxide developed in this laboratory and a modification of Masson's method (35); (d) reacting an alkyl halide with silver nitrite (73); and (e) addition of a Grignard reagent to an aldehyde or ketone, followed by treatment with nitrosyl chloride (74).

The first method has the advantage of simplicity and has been generally employed in the case of aliphatic water-soluble alcohols whose nitrites were relatively stable. As the solubility decreases, the reaction is greatly hindered by the existence of a two-phase mixture. A number of monoaliphatic alcohols were nitrited in this laboratory by Orloff (75) using the nitrous acid method. The trans-esterification method is of value only when the desired nitrite has a lower boiling point than glycerine trinitrite. A further disadvantage is encountered in the relative instability of glycerine trinitrite and the difficulty of purifying the trinitrite. The third method was developed in this laboratory and hence will be discussed at length in this thesis. The fourth method was not considered very important in the present work and therefore has not been developed further. The fifth method seems to be a fruitful procedure for forming difficultly prepared nitrites.

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Synthesis of Nitrogen Trioxide

Methods of Preparation

The object of preparing anhydrous nitrogen trioxide was to use it as a nitriting agent in the synthesis of nitrites susceptible to hydrolysis.

Nitrogen trioxide has been prepared by dropping concentrated nitric acid on warm arsenious trioxide (32); by mixing nitric oxide and oxygen in any proportion below -100°C. (76); by the action of water on nitrosyl-sulfuric acid (77) by adding a small quantity of water to nitrogen tetroxide (78,79); by saturating liquid nitrogen dioxide with nitric oxide (80) and by the action of dilute nitric acid on copper (81). None of these methods seemed quite satisfactory for preparing anhydrous nitrogen trioxide. The first mentioned method was improved by repurification of the liquid nitrogen trioxide.

Experimental Details

One hundred and fifty grams of arsenious trioxide was placed in a three-necked flask fitted with a dropping funnel, thermometer and an outlet connected to a drying tube containing phosphorus pentoxide and glass wool. The tube led into a 250-c.c. trap which was fitted to a large test tube with a side-arm immersed in a freezing bath. The bath was maintained at -40°C. throughout the reaction. Concentrated nitric acid was added dropwise to the previously heated arsenious trioxide to a total of 150 c.c. The flask was heated until all the solid had reacted and a viscous solution remained in the flask. Seventy grams of a blue semi-solid was collected in the receiver. The contents of the tube were warmed to -20°C. and the liquid nitrogen trioxide removed by decantation.

The blue liquid when distilled in an atmosphere of nitrogen boiled at 3-5°C. The physical constants obtained for the anhydrous nitrogen trioxide are: b.p. 3-4°C., density at 0°C.,1.451. It was quite stable at ordinary temperature and pressure when placed in a sealed tube and stored in the dark. The yield was 70 g. or 91% of the theoretical amount.

Discussion

The above method gives excellent yields of anhydrous nitrogen trioxide. The purity of arsenious trioxide was found to be important. Thus c.p. grade was used. The experimental details varied from those of Ramsey and Cundall (82), as they suggested distilling nitrogen trioxide in an atmosphere of nitric oxide, whereas nitrogen was used, also a simplified drying tube. Nitrogen dioxide was readily removed by decantation.

There has been some controversy as to the existence of nitrogen trioxide due to the occurrence of an equilibrium

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reaction:

 $N_2O_3 \longrightarrow NO + NO_2$

The reaction to the right would be favored on heating, according to the law of Le Chatelier; however, if the substance is kept at low temperatures this should be prevented. Hence for the first purification from nitrogen dioxide the trioxide was decanted at -20 °C. Then the final purification was carried out by distilling in a nitrogen atmosphere. It was thought that the N_2O_3 dissociated into NO-NO₂ in the vapor phase but was collected as N_2O_3 .

The reaction was a relatively simple one:

4 HNO_3 + 2 $\text{As}_2\text{O}_3 \longrightarrow 2 \text{N}_2\text{O}_3$ + 4 HAsO_3 Thus only arsenious acid was left behind in the distillation vessel.

Synthesis of 2-Nitrobutyl Nitrite-1

Insofar as it is known, 2-nitrobutyl nitrite-1 has not been previously synthesized.

Fifty grams of sodium nitrite was dissolved in 300 c.c. of water. The solution was placed in a 1-liter, three-necked flask fitted with a mechanical stirrer, a separatory funnel and a thermometer. The solution was stirred vigorously and cooled to -5°C. with solid carbon dioxide. A mixture of 25 g. of water, 22 c.c. concentrated sulfuric acid and 60 g. of 2-nitrobutanol-1 was cooled to -5°C, and added dropwise to the sodium nitrite solution through the separatory funnel. Addition time was three hours. The temperature was kept at -5°C. to -2°C. The mixture was finally warmed up to 5°C, and was left for two minutes; during this period bubbles of gas were given off and a greenish-blue liquid settled out. The mixture was extracted with two 75-c.c. portions of ether. The ethereal solution was washed with a salt solution (50 g. sodium chloride in 100 g. of water), dried over 5 g. of anhydrous sodium sulphate and left overnight in a Dewar flask cooled to -50°C. The ether was distilled off. A product was obtained with a boiling range of 45-90°C./2mm. Upon redistillation a yield of 39.5 g. (53.4% of the theoretical amount) was obtained, b.p._{2mm} 65-67°C. This substance readily hydrolyzed to form nitrous acid and 2-nitrobutanol-1. Thus the compound was considered to be 2-nitrobutyl nitrite-1.

Decomposition of the compound was quite noticeable. This was undoubtedly due to the large amount of water used in this type of reaction. Nitrites should be as free of water as possible, hence the use of liquid nitrogen trioxide was attempted.

Nitroisobutyl trinitrite was prepared following the procedure mentioned above.

A twelve g. quantity of a light yellow oil was obtained upon extracting the reaction mixture with ether. The product could not be distilled due to decomposition occurring. The unreacted nitro alcohol was removed by freezing out the alcohol and decanting off the nitrite. The substance readily reacted with ethyl alcohol to give ethyl nitrite and tri(methylol)nitromethane. Due to the instability of the product and difficulty of purification, further work was suspended.

Synthesis of Ethylene Dinitrite

Ethylene dinitrite was prepared by Bertoni (34) by distilling glycerine trinitrite with glycol. In this laboratory liquid nitrogen trioxide was added to glycol and distilled. This method affords a relatively simple procedure for preparing ethylene dinitrite and eliminates the preparation of the somewhat unstable trinitrite.

Twenty grams (18 c.c.) of freshly distilled ethylene glycol (b.p. 197.5°C. n_D^{20} 1.4370) was added to 10 g. of anhydrous sodium sulphate in a small flask and cooled to -5°C. Thirty-two grams of liquid nitrogen trioxide was slowly added to the mixture accompanied by vigorous shaking. The deep-blue color of the nitrogen trioxide disappeared upon addition until towards the end, then a permanent greenishyellow color remained in the solution, indicating a slight excess of nitrogen trioxide. After standing several hours, the liquid was decanted from the sodium sulphate into a Claisen flask and vacuum distilled. A fraction collected between 33-37°C. amounted to 26 g., which was 67% of the theoretical 20mm. A further fraction of 6 g. contained chiefly ethyamount. lene dinitrite. Boiling point at room temperature was 96-97°C. with a density of 1.216 at 0°C.

Bertoni (34) reported a b.p. of 96-98°C. and a density of 1.2156 at 0°C. The ethylene dinitrite was further identified by distilling with ethyl alcohol to yield ethyl nitrite. An excess of nitrogen trioxide serves to give a

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more complete nitrition of glycol. The dinitrite was quite unstable, decomposing rapidly when exposed to direct sunlight, water or moist air.

Five more nitrites were prepared by the above method. Since the method used was essentially the same as in the above procedure, the data will be given in Table II and discussed.

TABLE II

Nitrites Prepared Using Nitrogen Trioxide

				Yield	
<u>No</u> .	Compound	B.P.	<u>Density</u>	in g.	in %
1.	Ethylene chloronitrite	96-97	1.220	35	59
2.	Glycerine trinitrite	150-154	1.290	20	57
З.	2-Methyl-2-nitropropane dinitrite-1,3	decomposed above 100°C	•	15.5	80
4.	Pentaerythritol tetra- nitrite	decomposed above 100°C	•	30	60
5.	Butyl thionitrite	45-60		2	8

From the above table it will be seen that nitrites in good yields may be obtained by using anhydrous nitrogen trioxide as the nitriting agent.

The yield reported for ethylene chloronitrite was an average value. Higher yields may be obtained using large excess of nitrogen trioxide. A satisfactory test for ethylene chloronitrite was to treat a sample with absolute ethyl alcohol. Only ethylene chlorohydrin and ethyl nitrite were obtained. These were readily identified by their physical properties. Glycerine trinitrite was readily obtained in good yields and identified. For a nitriting agent it was found unnecessary to purify glycerine trinitrite.

2-Methyl-2-nitropropane dinitrite-1,3 and pentaerythritol tetranitrite were readily formed but were very difficult to purify. Both compounds tended to decompose upon heating and at high temperatures were explosive. Even vacuum distillation at 6 mm. pressure failed to give stable products. Hence the nitrites were heated gently to 40°C. to remove excess nitrogen trioxide and the unchanged nitroalcohol was removed by freezing the product, and upon warming up, the liquid was decanted. In this way we obtained what may be considered rather pure nitronitrites. Their presence was proved by adding ethyl alcohol and distilling. Ethyl nitrite and the original nitro poly alcohol were obtained. The substances were not considered sufficiently pure to give densities.

The yield of butyl thionitrite was rather disappointing, since such good results were obtained in the case of the alcohols. Unfortunately, a number of other reactions occurred, chiefly the formation of dibutyl disulfide, as:

 $2 C_4H_9.SH + N_2O_3 \longrightarrow C_4H_9.S.S.C_4H_9 + H_2O + 2 NO$

The small amount of butyl thionitrite formed was a wine-red in color, very unstable. It readily formed the disulfide when exposed to the air. It was distilled in vacuo without decomposing.

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Synthesis of Allyl Nitrite

Allyl nitrite was prepared by the trans-esterification of glycerine trinitrite. This was similar to the work done by Bertoni (34).

Ten grams of glycerine trinitrite (prepared by adding anhydrous nitrogen trioxide to glycerine and distilling) was cooled to 0°C. and mixed with 10 g. of allyl alcohol cooled to -10°C. Two layers formed rapidly. The mixture was placed in a small distilling flask and distilled gently on a water bath. Twelve g. of a light yellowish-green liquid distilled over at 43.5-44.5°C. The product was redistilled and was found to be pure. A yield of 12 g. (74% of the theoretical amount) was obtained, with a density of 0.955. Bertoni (34) reported a b.p. of 43.5-44.5°C. and a density of 0.9546 at 0°C. The vapor tends to explode when heated above 100°C. It was found to be insoluble in water.

This procedure was very easy to carry out and the yield was exceptionally high for an unsaturated nitrite. One of the chief advantages of the above method was its simplicity. Allyl nitrite must be free of water and pure in order to be stored. With ethyl alcohol it gives ethyl nitrite.

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Synthesis of Tertiary Amyl Nitrite

Tertiary amyl nitrite is customarily prepared by the trans-esterification of tertiary amyl alcohol with glycerine trinitrite (34) or by adding dilute sulfuric acid to a sodium nitrite solution suspended in the alcohol (83). The trans-esterification method has the disadvantage of producing only nitrites which are more volatile than the substance being used as the source of the -NO group. Furthermore in the case of glycerine trinitrite the substance decomposes during distillation. The nitrous acid procedure does not give high yields of tertiary nitrites due to the common difficulty of esterification of tertiary alcohols and due to the well recognized instability of nitrites. We thought that by adding a Grignard reagent to a ketone, or aldehyde and then treating the intermediate alcoholate with nitrosyl chloride, a versatile method would be developed to produce a nitrite of a secondary or tertiary alcohol. If we carried this reaction out under anhydrous conditions good yields should be obtained, according to the following equations:

1. $C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$ 2. $C_2H_5MgBr + (CH_3)_2CO \longrightarrow (CH_3)_2.(C_2H_5) COMgBr$ 3. $(CH_3)_2(C_2H_5) COMgBr + NOCl \longrightarrow (CH_3)_2C_2H_5.CONO + Mg Br$

Fifty-five grams (38.5 c.c.) of ethyl bromide (dried over calcium chloride for some time and distilled) was mixed with 100 c.c. of anhydrous ether. Forty grams of this mixture was run into a flask fitted with a dropping funnel and a reflux condenser. The flask contained 12 g. of magnesium turnings. One hundred and forty grams of dry ether was added and the rest of the ethyl bromide solution added dropwise. Finally the contents of the flask were boiled on a water bath until all of the magnesium had reacted. The flask was cooled and placed in an ice bath. Twenty-eight grams (35 c.c.) of anhydrous acetone dissolved in 60 c.c. of anhydrous ether was slowly added to the contents of the flask. A white bulky precipitate of the intermediate product was thrown down. This product was left in suspension and the yield was not calculated.

The mixture of magnesium alcoholate was placed in a cooling bath and kept at 0°C. Thirty-five grams of nitrosyl chloride was added slowly in the gaseous form. The white solid was slowly dissolved and the mixture was colored a reddishbrown. Some of the magnesium alcoholate did not go into solution and was removed by filtering. The filtrate was distilled. Ether was first collected. The next fraction consisted of 21 g. of tertiary butyl nitrite. Upon redistillation, 16 g. was obtained with a boiling point range of 61-64°C./345 mm. (Wilson (83) reports b_{345} 62-63°C.); $n_D^{16.8}$ 1.3920 (Wilson (83) $n_D^{16.8}$ 1.3904). A 27 per cent yield of pure tertiary amyl nitrite was obtained.

Unfortunately the yield was too low for the method to have any wide application and no further attempt was made to improve it. Only in the synthesis of nitrites whose alco-

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hols are difficult to prepare would this method be useful. Care was taken to keep the mixture cool at all times. It is possible that other solvents may have a different effect upon the yield. However, even though the yield was small, this constitutes, we believe, a hitherto unreported method of synthesizing nitrites.

An attempt was made to prepare tertiary butyl nitrite by the above procedure but there was no yield.

Discussion on the Formation of Nitrites

2-Nitrobutyl nitrite-l was apparently formed in fair yields by reacting 2-nitrobutanol-l with nitrous acid. Thus:

 $2NaNO_2 + H_2SO_4 \longrightarrow 2HONO + Na_2SO_4$

 $CH_3.CH_2.CHN0_2.CH_2OH + HONO \rightarrow CH_3.CH_2.CHN0_2.CH_2ONO + H_2O$

Orloff (75) prepared a number of nitrites from mono hydroxy alcohols by this method and obtained excellent yields for those alcohols which were water soluble. This method was not as satisfactory when tri(methylol)nitromethane was nitrited. Poly nitrites tend to be quite unstable in the presence of water.

Nitrition with anhydrous nitrogen trioxide using a strong dehydration agent such as calcium chloride or sodium sulphate has been a fruitful method in this laboratory for preparing various types of nitrites, as:

 $\begin{array}{c} CH_2 \cdot OH \\ I \\ CH_2 OH \end{array} + N_2 O_3 \longrightarrow \begin{array}{c} CH_2 \cdot ONO \\ I \\ CH_2 \cdot ONO \end{array} + H_2 O$

Any nitrite which can be distilled either in vacuo or at atmospheric pressure may be readily prepared by this method in good yields and in a highly pure state. However, unstable nitrites like the poly nitrites are not so satisfactorily prepared. They may be obtained fairly pure by freezing out the unreacted acid. This does offer a good method for preparing agents for trans-esterification since their alcohols would be high boiling by-products. It is especially interesting note that butyl thionitrite was obtained in a very small yield. The tendency was apparently for the formation of dibutyl disulfide.

The trans-esterification method has the advantage of eliminating the formation of water. This is especially important in preparing the nitrites which decompose easily in the presence of small quantities of water. Allyl nitrite was readily obtained by reacting allyl alcohol with glycerine trinitrite:

 $\begin{array}{c} CH_2ONO \\ | \\ CHONO \\ | \\ CH_2ONO \end{array} + 3 CH_2 = CH.CH_2OH \longrightarrow \begin{array}{c} CH_2OH \\ CHOH + 3 CH_2: CH.CH_2ONO \\ | \\ CH_2OH \end{array}$

Thus the above reaction could be carried out under strictly anhydrous conditions.

The formation of nitrites by reacting nitrosyl chloride with a magnesium organic compound was attempted in this laboratory, but the yields obtained were not as high as hoped for. The reaction was relatively simple from the viewpoint of mechanism:

 $(CH_3)_2CO + C_2H_5MgBr \longrightarrow (CH_3)_2(C_2H_5).COMgBr$

 $(CH_3)_2(C_2H_5).COMgBr + NOCl \rightarrow (CH_3)_2(C_2H_5).CONO + MgBrCl$ However, in the preparation of nitrites which are difficult to prepare by the other methods, this method may be advantageous.

Synthesis of 2-Nitrobutene-1

General Introduction

The effect of nitro-olefins as proknocks was considered to be sufficiently important to prepare some nitro-olefin derivatives. As the literature contained no preparation for 2-nitrobutene-1, it was thought that this should be the first nitro-olefin to be prepared in this laboratory. The literature contains several methods for preparing nitro-olefins. Most of these methods depend upon the dehydration of nitro-alcohols and differ only in the dehydration agents used. Some of the most important of these procedures are: by reacting an olefinic halide with alcoholic potassium nitromethane (40); by dropping fuming nitric acid on an alcohol such as dimethyl carbinol and distilling the reaction mixture (41); by reacting a nitroalcohol with zinc chloride (42), anhydrous sodium bisulphate (39) and anhydrous potassium bicarbonate and ether (38); by heating a nitroalkyl acetate in an ethereal solution with potassium carbonate (38), crystalline sodium acetate (38), and anhydrous sodium carbonate (43).

Experimental

Thirty grams of 2-nitrobutyl acetate-1 was added to 150 c.c. of ethyl ether and 20 g. of sodium bicarbonate was added to the solution. The mixture was refluxed, in a

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500 c.c. three-necked flask, fitted with a mechanical stirrer and condenser. This was heated on a steam bath for three hours, with constant stirring. The liquid was filtered by suction and the residue washed with 50 c.c. of ether. The ethereal solution was distilled on a steam bath to remove ether. A vacuum distillation gave two fractions:

I b.p._{15 mm}.^{50-100°C}. ll g. II b.p._{15 mm}.^{100-124°C}. l5 g.

A redistillation of fraction I gave a yield of 5.7 g. (30.3% of the theoretical amount). This was a pale yellow oil, b.p. 60-63°C./10 mm., n_D^{20} 1.4545, D_4^{20} 1.035. It had a strong lachrymatory effect. This was undoubtedly 2-nitrobutene-1. It apparently was easily polymerized, since, on standing, a red gummy solid was formed. The liquid readily added one mole of bromine but the dibromide was not isolated as a check, since we were unable to find physical constants in the literature for 1,2-dibromo-2-nitrobutane.

Potassium carbonate and 2-nitrobutyl acetate-1 was treated in the above manner but only a small quantity of what was thought to be 2-nitrobutene-1 was obtained, which readily polymerized to a tarry mass.

Four further attempts were made to increase the yield of the butene but no product was obtained. These were: (1) sodium bisulphate, (2) acetic anhydride, (3) thionyl chloride and pyridine as a diluent, and (4) thionyl chloride were added to 2-nitrobutanol-1. Since thionyl chloride is a powerful dehydrating agent, it was hoped that sulfur dioxide, hydrogen chloride and 2-nitrobutene-1 would be formed. This however was not the case.

Discussion

Thus the reaction which produced 2-nitrobutene-1 was easy to understand.

 $C_{2}H_{5}$. $CHNO_{2}$. $CH_{2}OOC$. CH_{3} + $NaHCO_{3} \rightarrow C_{2}H_{5}$. CNO_{2} = CH_{2}

+ $CH_3.COONa + H_2O + CO_2$

It is interesting to note that Schmidt and Rutz (38) reported forming 1-nitrobutene-1 by reacting 1-nitrobutyl acetate-2 in ether with potassium bicarbonate in a 70% yield. Apparently when the nitro group is on the second carbon atom the yields are lower.

The low yield was apparently due to the ease with which 2-nitrobutene-l polymerizes. A certain proportion of polymerization was expected. Schmidt and Rutz (38) noted that 1-nitropropene-l entirely polymerized, when left standing over potassium bicarbonate solution overnight, to a yellow brown, odorless substance. Hence it would seem that in the attempts to prepare the nitro-olefin, the product had in most cases entirely polymerized.

SUMMARY

- A number of organic and organo-metallic substances were synthesized to be studied as proknock agents. Most of these were prepared by procedures already developed.
- 2. A method for preparing pure anhydrous nitrogen trioxide was devised.
- 3. So far as we know, 2-nitrobutyl nitrite-1 was synthesized for the first time, by treating the alcohol with nitrous acid. Nitroisobutyl trinitrite was also prepared by this method. The nitrites were identified by reacting with ethyl alcohol to give ethyl nitrite and the original alcohols which were readily identified.
- 4. Five nitrites were prepared by treating the alcohol with anhydrous liquid nitrogen trioxide over a drying agent. Ethylene dinitrite, ethylene chloronitrite, butyl thionitrite, 2-methyl-2-nitropropane dinitrite-1,3 and pentaerythritol tetranitrite were readily prepared by this method. This was an original method for the first two compounds, and as far as we know the last three substances had not been synthesized before. Good yields were obtained for all of these nitrites except butyl thionitrite. The reason for this was probably the formation of dibutyl disulfide.

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- Allyl nitrite was prepared in 74% yield from glycerine trinitrite by trans-esterification. This confirmed the previous work done by Bertoni (34).
- 6. Tertiary amyl nitrite was synthesized by reacting the product formed by condensing acetone and ethyl magnesium bromide with nitrosyl chloride. A 27% yield of pure tertiary amyl nitrite was obtained. A poor yield was obtained in forming tertiary butyl nitrite. The method was developed in this laboratory and gives a further method for preparing nitrites.
- 7. 2-Nitrobutene-1 was prepared by heating 2-nitrobutyl acetate-1 with sodium bicarbonate. It added one mole of bromine indicating an olefinic double bond. A number of other methods were tried but failed to give results, due to the ease with which 2-nitro-butene-1 polymerizes.
- 8. An attempt to prepare crystalline nitrobutadienes was unsuccessful. So far the field of nitro-dienes has barely been touched and should be a fruitful branch of chemistry for further research.
CLAIMS TO ORIGINAL WORK

- An investigation of the methods of preparing nitrites has been made.
- 2. A method for preparing pure anhydrous nitrogen trioxide was devised.
- 3. 2-Nitrobutyl nitrite-l and nitroisobutyl trinitrite were synthesized by the action of nitrous acid on the 2-nitrobutanol-l and tri(methylol)nitromethane respectively.
- 4. Ethylene dinitrite, ethylene chloronitrite, glycerine trinitrite, 2-methyl-2-nitropropyl dinitrite-1,3, pentaerythritol tetranitrite and butyl thionitrite were synthesized by adding anhydrous liquid nitrogen trioxide to the corresponding alcohol.
- 5. Tertiary amyl nitrite was synthesized by reacting the magnesium bromide of tertiary amyl alcohol with nitro-syl chloride.
- 6. An investigation of the synthesis of 2-nitrobutene-1 has been made.
- 7. 2-Nitrobutene-1 was synthesized by heating 2-nitrobutyl acetate-1 with sodium bicarbonate.

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