# CATALYTIC PREPARATION OF ETHER FROM ALCOHOL

## BY MEANS OF

# ALUMINUM OXIDE

by

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# THE CATALYTIC PREPARATION OF ETHER FROM ALCOHOL
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## INTRODUCTION.

Considerable work has been done on the dehydration of alcohol in the gaseous phase by means of solid catalysts. The catalysts which have been used have been of many types, but metallic oxides have found the greatest favor, and of these alumina appears to be the most efficient and the most widely employed.

In the dehydration of ethyl alcohol alumina becomes active at temperatures above $300^{\circ}$C.,[1] giving increasing amounts of ether with increase of temperature. At $250^{\circ}$ the yield of ether is high and reaches a maximum value, for as the temperature is raised still further, increasing amounts of ethylene begin to be formed and the yield of ether is cut down accordingly. Above $300^{\circ}$ the product of dehydration is mainly ethylene.[1,2] Pure ether is, also, dehydrated readily to ethylene at, and above $250^{\circ}$. There is some difference of opinion among the different workers as to the mechanism of these reactions. The dehydration of alcohol to ether and ethylene may occur in two independent steps: $2\ C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O$, and $C_2H_5OH \rightarrow C_2H_4 + H_2O$. This, Senderens considers to be the mechanism. The dehydration to ethylene

1 Senderens, Ann.Chim.Phys.,(8) 25,505 (1912).
2 Ipatiew,Ber.,37, 2986 (1904).

may occur in two successive steps however : $2 C_2H_5OH \rightarrow$
$(C_2H_5)_2O + H_2O$, and $(C_2H_5)_2O \rightarrow C_2H_4 + H_2O$. Ipatiew[2] concludes
that the latter is the mechanism. Pease and Yung[5] consider
that it is not necessary to postulate either of the two
mechanisms to the exclusion of the other. From this investi-
gation reported herewith it would seem quite probable that
the reaction proceeds according to both mechanisms simul-
taneously.

Ipatiew, working at high temperatures and pressures,
with aluminum oxide has dehydrated alcohol to ether and
ethylene and furthermore has shown the reaction to be re-
versible, having obtained an appreciable amount of alcohol
from equimolecular quantities of ether and water. Senderens,
as result of considerable work, has reported a good yield of
ether from alcohol by means of aluminum oxide prepared
by dehydrating the hydroxide precipitated from solutions
of sodium aluminate by means of sulphuric acid. He considers
this form of alumina better than that obtained by preci-
pitating the hydroxide from solutions of aluminum salts
by means of ammonia. Mailhe and de Godon[4] were able to get
a 71% yield of ether at $190^0$ using anhydrous aluminum
sulphate as catalyst. They showed the influence of increasing
the amount of catalyst by obtaining higher and higher
yields. Pease and Yung report a 60% yield of ether at $250^0$
with alumina prepared from aluminum nitrate and ammonia.

It is generally accepted, in fact almost established,

3 Pease and Yung, J.Am.Chem.Soc.,46,390 (1924)
4 Mailhe & de Godon, Bull.soc.chim.,35,565 (1916)

that the results of catalysis are due to reactions taking

place at surface of the catalyst   material in the case of

heteregeneous systems.Older theory postulated the formation

of definite intermediate chemical compounds which are un_

stable and break down to give the reaction products.This,

Senderens considers to be the case in this reaction, a

complex involving one molecule each of alumina and alcohol

being formed which may break down directly to give ethy-

lene or which may react with another molecule of alcohol

to give ether.The more recent explanation is that cataly_

sis is the result of the molecules being brought into posi-

tion for reaction as a result of adsorption on the surface

of the catalyst.Molecular attraction of every degree between

that of distinct chemical combination and that of loose

adhesion is considered to exist.In either case it is easily

believed that the extent of the surface of the catalyst will

play a considerable part in the activation of the reaction.

The idea that the spacing of atoms or molecules would be

a factor in catalytic reactions at surfaces was first spoken

of by Langmuir[5]. Experimental evidence of this has later

been given by Adkins[6] who has been able to selectively

activate alumina for specific reactions by regulating the

size of the interstices in the molecules, or pores of mole-

cular dimensions in the oxide.Senderens considers the

alumina prepared from sodium aluminate more active than

dehydrated colloidal alumina.This difference may be explain_

ed as due to a difference in structure,as the former preci_

5Langmuir,Trans.Far.Soc.,17,617 (1922) through C.A.16,7(1923)
6 Adkins,J.Am.Chem.Soc.,44.385,2175 (1922);46, 130 (1924)

pitate is definitely crystalline and the latter amorphous.
From a consideration of the above it would seem highly
possible to obtain a catalyst more active in ether formation
than any hitherto prepared. The purpose of this investigation
was to determine the catalyst most efficient in the
production of ether. Different catalysts have been prepared
in ways which would give precipitates of differing nature.
The investigation is considered to have been quite success-
ful.

It has been mentioned that work on this problem has
been done by Pease and Yung.During the course of this
investigation two papers[5,6]on this reaction appeared by
them.In the former they reported a maximum yield of 60%
dehydration to ether at $250^{\circ}$C.In the latter paper were
given data for an equilibrium in the ether-alcohol-water
reaction showing a maximum possible conversion of alcohol
to ether of 62% at $375^{\circ}$.Calculations from the data given
by them show the equilibrium to correspond to a maximum
conversion of less than 66% at $350^{\circ}$.The results of our
work show yields considerably higher than this with several
catalysts as will be fully demonstrated later: we have
obtained yields of over 80% at $250^{\circ}$.The results of Senderens
work undoubtedly show yields higher than 66 % but Senderens
is indefinite as regards details. This fact is indicated by
a separation of the product into layers and Pease and Yung
state that the products they obtained did not separate into

7 (a) van Bremmelen,Rec.trav.chim.,7,75(1888);
- (b) Martin,Mon.Sci.,(5) 5,225 (1915) through Ch.Abst.10,571.
8Pease and Yung,J.Am.Chem.Soc.,46,2897 (1924)/

layers.These facts indicate that the equilibrium in the reaction cannot be where Pease and Yung have placed it.That the reaction is,however,reversible is undoubtedly the case. It was first shown by Ipatiew and has also been shown in this investigation.

As an explanation for the disagreement in equilibrium values such as is shown here the idea has been presented that a shift in equilibrium may be brought about by a solid catalyst.The idea has been mentioned by Bancroft[9] and Edgar and Schuyler[10] state that this explanation was offered at the Rochester meeting of the American Chemical Society in April 1921 to account for certain anomalies in esterification equilibria presented in a paper by Reid and Mulliken.There is no good evidence for such a viewpoint,however.

In determining their equilibrium data Pease and Yung have made determinations at $130^{\circ}$ using sulphuric acid as a catalyst and at $275^{\circ}$ using alumina.The work of Edgar and Schuyler on esterification equilibria show that the equilibrium in the gaseous phase may be higher than in the liquid phase and they conclude that the equilibria are in general not the same.From this it is open to question whether the data of Pease and Yung are comparable in the two cases.

Another point worth notice is that we have always obtained small amounts of ethylene,and the fact that this reaction is also catalyzed complicates the case.Pease and Yung claim that in their equilibria determinations no appre-ciable amounts of ethylene were formed.This would indicate

9 Bancroft,J.Phys.Chem.,21,603,(1917)
10 Edgar and Schuyler,J.Amer.Chem.Soc.,46,64 (1924).

that the alumina catalyst used in that case was not very
active,as at $275^{\circ}$ the ethylene reaction is ordinarily cata-
lyzed strongly. They state that this catalyst was not as
active as that used in the kinetic measurements of their
first paper. With the method of analysis available it would
be rather unsatisfactory to attempt to determine the
equilibrium point of the reaction other than approximately.

## APPARATUS AND PROCEEDURE.

In carrying out the experiments a flow method has been
used throughout. The arrangement of the apparatus is shown in
Fig.1 with the furnace in position and in Fig.2 with the
furnace removed.

The proceedure consisted in passing a definite volume
of liquid alcohol into a hot tube filled with the catalyst.
The alcohol vaporized on contact with the hot surface of the
tube. The vapors then passed on over the catalyst and out
through a condenser,the liquified products being retained in a
bulb attached to the condenser and the gases passing over to
an aspirator containing a saturated sodium chloride solution.

Before a run was made for analysis about 15 cc. of
alcohol were passed over the catalyst to make sure the latter
was in a steady state during the run.

Several methods were tried for introducing the
alcohol into the reaction tube. The method used must be such
that the alcohol can be passed over the catalyst at a con-
trolled steady rate. Sealed connections were used wherever
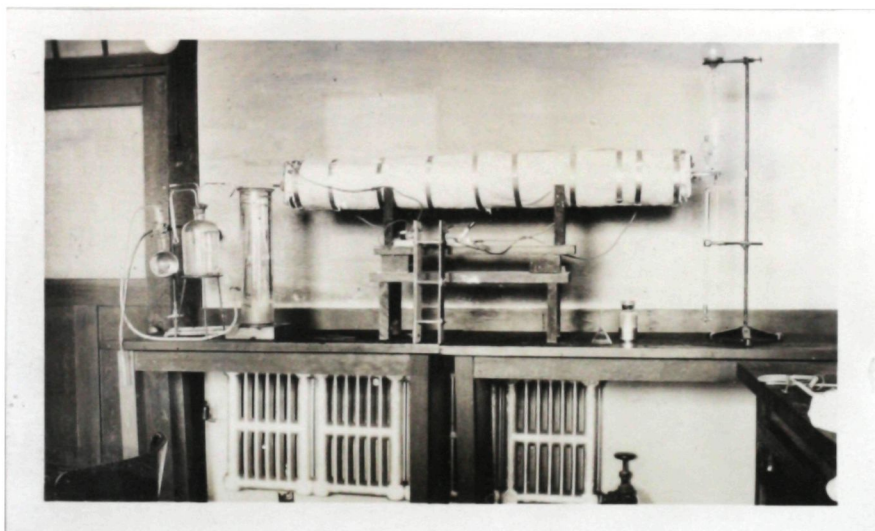possible and in other cases corks were used instead of
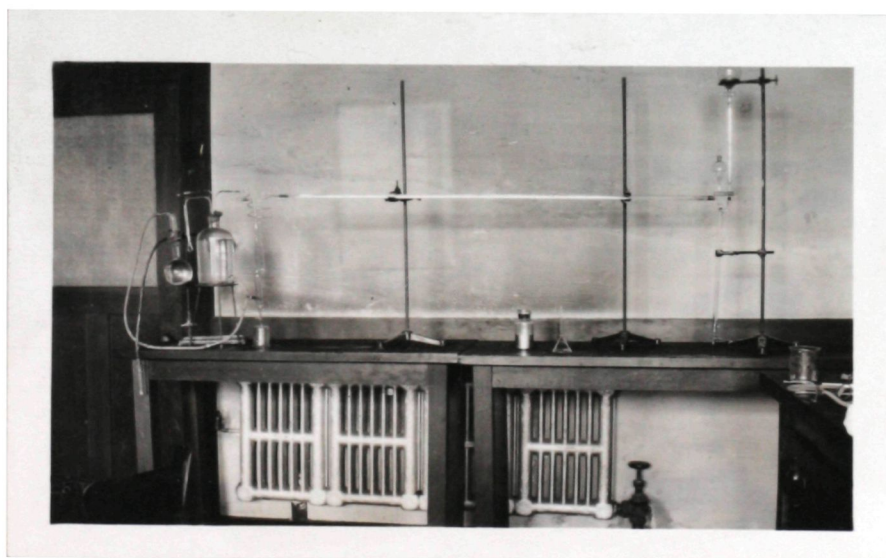
Fig.1 - Apparatus with furnace in position.



Fig.2 - Apparatus with furnace removed, showing connections with catalyst tube.

rubber connections on account of the sulphur content of the latter.

In the first experiments a heating element was used to pass alcohol vapor into the tube.The final form of this vaporizer consisted of a glass bulb with platinum heating coil with leads sealed through the glass,and deli_ very and filling tubes sealed on.The vaporizer method has the following disadvantages: The apparatus must be discon- nected after every run,with possible loss of alcohol vapors; the rate of vaporization is not easily controlled;consider- able time is required in heating the alcohol to boiling and the vaporizer must be cooled after each run for weighing.

It was decided to try a method of introducing the alcohol from a graduated vessel and allowing the vaporiza- tion to take place in the hot catalyst tube.Adkins considers that vaporization of the reactants by dropping on hot sur- faces unsatisfactory but we have found it to be quite suitable for a volatile substance like ethyl alcohol.The apparatus was arranged as follows: A capillary tube bent at right angles was sealed on to the top of a burette; a side tube bent upward at right angles was sealed into the burette near the top; a dropping funnel with a capillary tube stop- cock sealed on at the end of its stem was inserted into the side tube of the burette through a cork;a second dropping funnel was sealed into the burette near the top for refilling with alcohol.The capillary tube was introduced into the furnace.Mercury was allowed to drop at a controlled rate

from the dropping funnel into the burette forcing the alcohol into the catalyst chamber.The length of mercury column was about 45 cm.and the rate of flow was easily controlled by regulating the stop-cock.The flow is easier to control if the edges of the hole in the stopper are scraped back a little.The rate of flow for a short column of mercury was found to be difficult to control.The amount of alcohol passed over the catalyst was read off from the burette. This apparatus could be left connected to the furnace for several runs,fresh alcohol being introduced into the burette by drawing off the mercury at the bottom and allowing fresh alcohol to run in at the top.This method was very easily controlled and quite satisfactory.

The catalyst mass was ground up and spread along a pyrex tube about 1.6 cm.in diameter,almost filling it for a length of 120 cm.A small outlet tube was sealed on one end.The catalyst tube was slightly longer than the heating furnace and was placed inside the heating element of the latter.

The furnace was electrically heated.It consisted of a 1 1/4" iron pipe insulated with a thin sheet of asbestos and wound with nichrome resistance wire.The early experiments were carried out in a 30" furnace,but later a 54" furnace was constructed to permit the use of more catalyst.Concentric with the iron pipe was a 5" stove pipe jacket,the two pipes being held in place by means of two asbestos board plates with convenient grooves turned in

them to fit over the pipes,and a hole in the centre of each
to allow the insertion of the reaction tube.The temperature
was measured by a thermometer placed between the reaction
tube and the iron pipe.This was more convenient than one in
the catalyst tube and on test was found to register sensibly
the same temperature,particularly so when the furnace was
in a steady state.With a large furnace such as this,tem-
perature regulation was quite easy.

On account of the volatility of ether an efficient
condenser was a prime requisite.To get the most accurate
results in weighing the condensed products,the condenser
and receiving vessel were made in one piece and as light
as possible.A spiral of glass tubing was sealed into a
bulb; a straight vertical tube was sealed on to allow the
escape of ethylene to the aspirator and act as a reflux
condenser for any entrained ether vapor.The expansion of
the gas into the bulb helped to condense the ether and
only negligible amounts escaped.The condensate was removed
through a stop-cock at the bottom.The ethylene was collected
over saturated sodium chloride solution which was soon
saturated with the gas and served quite well.The pressure
was kept almost at atmospheric.The condenser was kept in
a cold bath and only in exceptional cases when the ethylene
yield was high was any appreciable amount of ether carried
over with the gas.

## METHOD OF ANALYSIS.

Considerable difficulty was encountered in getting
a suitable method of analysis.The literature on the subject
was of little avail.Some work was done on a method of
differential oxidation of ether and alcohol with unsatis_
factory results.

Pease and Yung in their papers on this reaction
made use of a salting out method of determining ether in
mixtures of ether,alcohol and water.They show a curve
for the correction which it is necessary to apply to the
observed volume of ether separating out from the mixture
when the latter is shaken up with saturated solution of
sodium chloride in the presence of an excess of the solid
salt.It was found impossible to get results to check with
the half of their curve corresponding to lower percentages
of ether.It was found that the amount of ether separating
depended on the ratio of ether to alcohol and on the ratio
of volumes of the sample analyzed and that of salt solution.
The disagreement with their curve may have been due to the
composition of the mixtures dealt with,and since Pease and
Yung used larger amounts of alcohol in their runs than it
was desired to use here,or than were necessary for accuracy,
it was found necessary to compile data based on mixtures of
the same total volume and containing ether,alcohol and
water in nearly the same proportions as would be obtained
from the catalyst tube.This was all the more necessary

since with the most active catalysts the products
separated into two layers in which case the entire product
would have to be taken in the analysis.This latter fact
eliminated altogether a method of analysis by specific
gravity determination.

A method of analysis based on the above was
worked out in this laboratory by Miss A.G.Winter.[11] The
problem was attacked as follows: A series of determinations
with mixtures of known composition corresponding to
different percentages of conversion of an original volume
of 20 cc.of alcohol was made and a curve plotted showing
the correction necessary to be applied to the volume
separating when the mixtures were shaken up with 100 cc.
of saturated salt solution.An excess of solid salt was
always present as some was always displaced by the alcohol
in the mixture. These mixtures were made up by volume at
15°C.and contained ether,alcohol and water in the propor-
tions in which they would occur in the products from the
dehydration of alcohol.Since the volumes of ether,alcohol
and water mixtures are very nearly the same as the volume
of the alcohol equivalent as shown by the specific gravity
tables of Sanfourche and Boutin[12]the method could be
directly applied to this work.To allow for a slight conver-
sion to ethylene a small excess of alcohol was passed over
the catalyst.The resulting product would contain a little
more water than the equivalent of the ether.Test determina-

11 Miss Winter,Thesis submitted for the degree of B.A.,at
   The University of British Columbia,April 1925.
12 Sanfourche and Boutin,Bull.Soc.Chim.(4) 31,456,(1922)
   through Pease and Yung,ref.3.

tions were therefore made with mixtures containing small
amounts of added water but showed no difference in the
amount of ether separating. Mixtures in which the volume
of ether was kept constant and that of the alcohol varied
gave no appreciable relative change in the necessary
correction.The method is accurate to 1% for mixtures having
the composition of those for which the data were compiled.

The mixture to be analyzed (30 cc.in volume) was
shaken up with a saturated sodium chloride solution in a
100 cc.volumetric flask to which a burette stem had been
sealed close to the bulb.The mixture was kept in a bath at
10° and repeatedly shaken until the volume separating
became constant. A curve is given (Fig.3) from the data
tabulated (Table 1) showing the observed volume separating
at 10° against the true volume at 15°.There was no loss of
ether when the flask was well corked and kept in the cold
bath.The design of the condenser enabled transfer of the
products to the flask to be made with a minimum escape
of vapors.The method is very convenient owing to the short
time required for a determination.

The method may be used as a rapid approximate
method for the determination of ether in mixtures of
composition differing from those for which the data are
given.The error is considered to be within 3% in the extreme
for such cases and for the most part within 2 %. The method
becomes inexact however,in all cases,when the volume of the
ether becomes less than 30% of that of the alcohol.

## Table 1.

| Composition of mixture, 15° | | | Volume | Correction |
|---|---|---|---|---|
| Ether cc. | Alcohol cc. | Water cc. | separating cc. | cc. |
| 17.8 | 0.00 | 3.1 | 16.5 | 1.5 |
| 16.3 | 2.00 | 2.8 | 15.05 | 1.25 |
| 14.3 | 4.00 | 2.5 | 13.1 | 1.2 |
| 12.8 | 5.7 | 2.2 | 11.7 | 1.1 |
| 10.7 | 8.0 | 1.8 | 9.6 | 1.1 |
| 8.9 | 10.0 | 1.5 | 7.9 | 1.0 |
| 6.9 | 12.0 | 1.25 | 6.0 | 0.9 |
| 5.3 | 13.8 | 0.9 | 4.3 | 0.9 |
| 3.3 | 15.8 | 0.6 | 1.2 | 2.1 |

PREPARATION OF CATALYSTS AND REAGENTS.

ALCOHOL: 95% alcohol was refluxed over lime and distilled and was in all cases practically absolute. In some of the earlier work absolute alcohol as purchased from Mallinckrodt Chemical Works was used.

Ether: The ether used was Merck's absolute ether distilled over sodium .

The specific gravities of the ether and alcohol were determined at 15° and calculations made from these values. Specific gravity of the alcohol was .795 and of the ether .719.

CATALYSTS: In the early part of this investigation it was found quite easy to prepare a catalyst active in ethylene formation but which was not nearly so active in ether
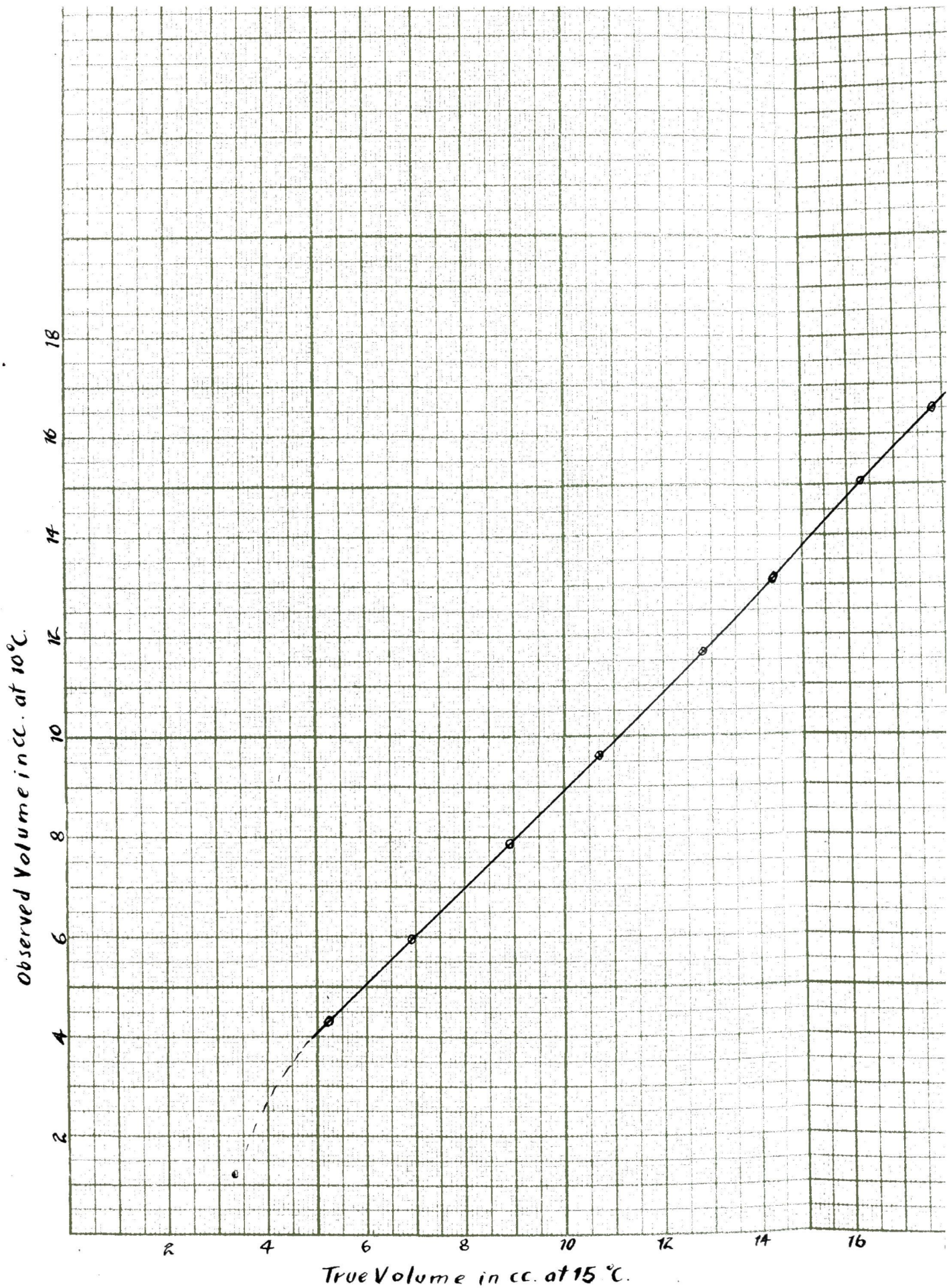
Fig. 3.— Correction Chart for Ether Determination.

formation.Since the purpose of this work was to determine
the best catalyst for ether,catalysts which gave large
yields of ethylene at relatively low temperatures- as
under 360° _ were discarded and few quantitative measure-
ments made with them.Since all previous work shows the
products of alcohol decomposition over alumina at this
temperature to be almost entirely ether or ethylene this
was considered a justifiable proceedure and much time was
saved thereby.

Of the alumina catalysts used in alcohol dehydration
that prepared by precipitation from a solution of an
aluminum salt with ammonia seems to have been used most
often.Senderens has however, shown that alumina prepared
from sodium aluminate by precipitation with sulphuric acid
is more active in ether formation.The precipitate in the
former case is quite amorphous while that in the latter
case is considered to be crystalline[7] Both are readily
soluble in acids and alkalies.The hydroxides formed in
these precipitations were dehydrated by heating to tempera-
tures not over 400°.

In this investigation the first catalysts made were
obtained by following the rather indefinite data given by
Senderens as closely as possible.It was thought that the
most active catalyst would be obtained by increasing the
surface of the particles of the precipitate.Accordingly the
precipitation was carried out in solutions of varying
dilution.An attempt was made to spread the precipitate out

on a support such as glass wool from very dilute solutions.
It was further thought that the use of a very weak acid
such as carbonic acid would give a much finer precipitate
than sulphuric.Some catalysts were prepared by bubbling
$CO_2$ through solutions of sodium aluminate.It is also known
that solutions of sodium aluminate in which the ratio of
$Al_2O_3$ : $Na_2O$ is under 1:2 will decompose slowly on standing,
due to hydrolysis, giving a crystalline precipitate of
aluminum hydroxide.[13] Catalysts were prepared in this
manner.The precipitate obtained by means of $CO_2$ from a 5%,
or stronger,solution of sodium aluminate is also of the same
crystalline nature.These precipitates were very insoluble
in acids and alkalies.The precipitates with sulphuric acid,
while they may be crystalline are evidently of a different
structure as they are readily soluble in acids.

The following general information was gained in
regard to the preparation of the catalysts.The precipitates
adsorb impurities such as sodium salts very strongly.Washing
with hot water helps to remove the impurities but the
precipitate must not be boiled as this coagulates the
particles.Washing is best carried out by means of decantation
as filtration is apt to contaminate the precipitate with
filter paper . Where filtering is necessary a layer next to
the paper must be scraped off and discarded.Pure water must
be used and in this work distilled water was used through-
out .Precipitation from concentrated solutions with sulphuric

13(a) Ditte, Compt.Rend.,116,183 (1893)
 (b) Russ , Zt.Anorg.Chem.41,216 (1904)

acid gives a lumpy precipitate,hard to wash.It was thought
that purification by means of dialysis might introduce some
impurity from the membrane though such a method might have
hastened washing.The temperature to which the catalyst is
heated in dehydration has considerable effect:the best
results were obtained by heating the precipitate to $400^{o}$C.
Heating to higher temperatures is apt to be injurious as
it tends to cinter the oxide.The precipitates on glass wool
were not very active,possibly owing to contamination from
the glass wool.These precipitates were not of the structure
found to be the best for the reaction.

The preparation of the best catalysts is described
in detail. Two different lots of sodium aluminate were
used which will be referred to as I and II.Lot I contained
10% moisture and considerable excess alkali.Lot II contained
18% moisture and little excess alkali.

**Catalyst A :** 800 grams of sodium aluminate I were dissolved
in 10 litres of water.An equivalent amount of sulphuric acid
in the same volume was allowed to drop slowly into the
alkaline solution with constant agitation.The precipitate
was washed by decantation until the wash water failed to
give a test for sulphate and then filtered.The filter cake
was then stirred up in nearly boiling water,decanted two or
three times and filtered again.The precipitate was then
dried in an oven at $120^{o}$ for about 24 hours,ground up and
heated in the furnace to about $350^{o}$.It was then considered
ready for use. This catalyst was successfully duplicated.
The maximum yield obtained with it was 74.5%.

Catalyst B :     1000 grams of aluminate I were dissolved in
18 litres of water and $CO_2$ bubbled through the solution at
a moderate rate until all the aluminum was precipitated as
hydroxide.This point was determined by filtering a little
of the suspension and testing the filtrate for aluminum.
This precipitate was crystalline and washed readily.
It was washed in cold water until it failed to give a test
for alkali with phenolphthalein and then filtered and
washed once with hot water.On drying at $120^\circ$ it became very
powdery.The best yield with this catalyst was 77.5%.

One attempt to duplicate this catalyst gave a
precipitate less crystalline and much more soluble in acid.
This is attributed to a difference in the composition of
the sodium aluminate which is known to vary.The precipitation
is governed somewhat by the composition of the aluminate.
It could not be washed free from alkali and was considerably
less active.The catalyst was however duplicated in other
attempts.

Catalyst C :  This catalyst was sensibly the same in
appearance,properties and activity as catalyst B.   500 grams
of aluminate I were dissolved in 4 litres of water and
precipitated and otherwise treated the same as B. The best
yield obtained was 79%.

Catalyst D:  This is not in the same class as the best
catalysts but is included here as an interesting case.

Tests were made with a sample of Merck's aluminum

hydroxide or precipitated oxide,which was dried for the
first run at 350° and later at 400°. No other treatment was
given this catalyst. This catalyst contained a small amount
of free alkali but gave a fair yield of ether.The best yield
was 69 %.

Catalyst E:  600 grams of aluminate II were dissolved in
4 litres of water. The solution began to decompose at once
precipitating aluminum hydroxide. The precipitate was washed
as before but after drying was found to contain a trace of
free alkali.The precipitate was therefore dried at 350° and
washed several times in nearly boiling water,by which means
the alkali was readily removed.On drying,a trace of alkali
was still present which was neutralized with dilute hydro-
chloric acid and the alumina washed until no test for
chloride was given in the wash water. In these washings it
was found necessary to filter as the suspension did not
settle.On drying this time no test for alkali was obtained.
The best yield with this catalyst was 81 %.

Catalyst F :  The preparation of this catalyst was similar
to that of E. 600 grams of aluminate II were dissolved in
1.8 litres of water. The specific gravity of the solution
at 20° was 1.18, very nearly the optimum condition for the
spontaneous decomposition of sodium aluminate solutions
given by Russ.[13(b)] After washing several times the precipi-
tate was dried at 350° and washed again in hot water.It was
thought possible to displace the adsorbed alkali by adding

acid.The suspension was made slightly acid and the alumina
washed until the wash water gave no test for chloride.Hot
water was used. The precipitate was dried again. The best
yield with this catalyst was 80.5 %.

Note on the Washing of Aluminum Hydroxide Precipitates:

An interesting point was observed in connection with
the crystalline precipitates such as catalyst E and F.This
has to do with the adsorption of sodium hydroxide by the
precipitate.The precipitate was washed until the wash
water gave no test for alkali with phenolphthalein and
only a very faint test was observed in the presence of the
precipitate. On drying and moistening the precipitate a
strong alkaline reaction was given with the indicator.
Successive washings with hot water now removed the alkali
quite rapidly. The alumina appeared to hydrate again to a
certain extent and finally ,as before,no test was given
for alkali in the wash water. On drying again more alkali
could be removed and this time the removal was so complete
that no further test was given with the indicator.

With another sample,before drying,an attempt was
made to displace the alkali by adding hydrochloric acid.
The suspension was made slightly acid and the precipitate
filtered out and dried. On drying a test for alkali was
still given.This precipitate was washed as above.It was
found possible however ,to completely remove the free
alkali from a dried precipitate. The precipitate was
washed until the water gave no test for alkali ,and flame

tests showed only a trace of sodium in the precipitate.

On several occasions other precipitates,which after long washing still settled rapidly,suddenly on one change of water failed to settle,indicating the acquiring of a charge.This might be explained on the basis of the more complete removal of one of two adsorbed ions than of the other.These phenomena would seem to offer an interesting field for investigation of ion adsorption both by the hydroxide and the anhydrous oxide.As this was a side line of this research pressure of time made investigation impossible.

CALCULATION AND ACCURACY OF RESULTS.

The results of the experiments reported in this paper are calculated on the basis of the percentage conversion of the alcohol introduced into the reaction tube into the products collected.The data given here are all for cases where the dropping method of alcohol feed was used.

In the standard runs by this method about 21 cc. of alcohol were passed into the tube. This was convenient and sufficient to permit accurate measurements as mentioned in connection with the method of analysis.After allowing for a slight conversion to ethylene of not over 5 % the unconverted alcohol,ether and its water equivalent were present in a total volume of about 30 cc.The method of analysis dould be applied directly.The ethylene was

measured at room temperature and atmospheric pressure in a
carefully graduated aspirator.Corrections were not made to
standard conditions as these were deemed negligible.

A check was made on all possible loss of alcohol or
products by weighing the condenser and contents and calcula-
ting the weight of ethylene.The sum of these weights checked
with the weight of the alcohol used in all cases.Only when
the ethylene yield was high was any appreciable quantity
of ether carried into the gas receiver and this did not
occur in the runs here reported.

As a check on the conversions determined, mixtures
containing ether,alcohol and water in the amounts calculated
for a standard run were made up. The amount of ether
separating out on analysis from these mixtures was the same
as that separating for the products of the runs.The cal-
culations are considered accurate to 1 %.

A further indication of high yields of ether was
afforded by the fact that for the/ best catalysts here mentioned
the liquid products separated out into two layers in the
receiving vessel.A separation in such mixtures only occurs
when the components are present in proportions corresponding
to approximately 80 % conversion. Excess water such as
would correspond to ethylene formation causes a separation
at slightly lower conversions to ether.In this work the
ethylene formed,and,consequently,the excess water were
very little.

## RESULTS AND DISCUSSION.

DEHYDRATION OF ALCOHOL TO ETHER: These experiments have shown that 250$^o$ is the best temperature for ether formation. The results show that the total alcohol dehydrated approaches a maximum value as the length of time of the run is increased. The best rate of flow varied with the different catalysts slightly,ranging from 15 to 20 cc.per hour.At rapid rates of flow the total dehydration falls off and at slower rates the relative amounts of ethylene formed increase at the expense of the ether.This has also been shown by Pease and Yung.

Results with the different catalysts are shown in tabular form.The column headed drying temperature refers to the temperature to which the catalyst was heated in drying.In some cases a catalyst was used after heating to one temperature and then heated to a higher temperature and further tests made. Heating up to 400$^o$ increased the activity. The reactants and products were measured by volume throughout and their weights calculated.

CATALYST A:    Table 2.

| Time of run, inmmins. | Drying Temp. °C | Temp of run. °C | Weight of Alc. used. grams | Ether coll. | Vol. of $C_2H_4$ cc | % conversion to Ether | % conversion to $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| 86 | 300$^o$ | 250±2 | 16.70 | 8.2 | 210cc | 61.5 | 2.6 |
| 125 | " | " | 16.55 | 9.35 | 220 | 70.2 | 2.7 |
| 95 | 400 | " | 16.80 | 9.50 | 750 | 70.5 | 9.2 |
| 63 | " | " | 17.15 | 9.80 | 590 | 71.0 | 7.1 |
| 57 | | " | 16.65 | 9.85 | 480 | 74.3 | 5.9 |
| 49 | | " | 16.40 | 9.50 | 320 | 70.0 | 3.9 |

CATALYST B: Table 3.

| Time of run in mins. | Drying Temp. °C | Temp. of run Deg.C | Weight of Alo. used grams | Ether coll. | Vol.of $C_2H_4$ cc. | % conversion to Ether | to $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| 360 | 300 | 250±2 | 25.75 | 14.8 | 900 | 72.3 | 7.1 |
| 65 | | " | 14.40 | 7.9 | 300 | 69.0 | 4.2 |
| 150 | 400 | " | 16.34 | 10.2 | 450 | 77.5 | 6.2 |
| 70 | | " | 16.34 | 10.2 | 240 | 77.5 | 3.0 |
| 75 | | " | 16.60 | 10.3 | 240 | 77.5 | 2.9 |

CATALYST C : Table 4.

| Time of run in mins. | Drying Temp. Deg.C. | Temp. of run Deg.C. | Weight of Alo. used grams | Ether coll. | Vol.of $C_2H_4$ cc. | % conversion to Ether | to $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| 95 | 350 | 250±2 | 16.64 | 10.35 | 200 | 77.2 | 2.5 |
| 110 | | " | 16.62 | 10.65 | 210 | 79.4 | 2.6 |
| 205 | | " | 16.40 | 10.30 | 340 | 78.0 | 4.2 |
| 95 | 400 | " | 16.50 | 10.20 | 360 | 78.0 | 4.7 |
| 64 | | " | 16.50 | 10.35 | 240 | 78.0 | 2.9 |
| 71 | | " | 16.50 | 10.35 | 260 | 78.0 | 3.2 |

CATALYST D: Table 5

| Time of run in Mins. | Drying Temp. Deg.C. | Temp. of run Deg.C. | Weight of Alo. used in grams. | Ether coll. | Vol.of $C_2H_4$ cc. | % conversion to Ether | to $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| 73 | 350 | 250±2 | 16.65 | 6.4 | 60 | 47.7 | 0.6 |
| 108 | 400 | " | 16.65 | 9.3 | 110 | 69.0 | 1.4 |

CATALYST E:  Table 6.

| Time of run in mins. | Drying Temp. Deg.C. | Temp. of run Deg.C. | Weight of Alo. used in grams | Ether coll. | Vol. $C_2H_4$ cc | % conversion to Ether | $C_2H_4$. |
|---|---|---|---|---|---|---|---|
| 95 | 400 | 250±2 | 16.50 | 10.72 | 370 | 80.6 | 4.5 |
| 69 | | " | 16.60 | 10.80 | 180 | 80.8 | 2.2 |
| 107 | | " | 16.60 | 10.60 | 220 | 80.6 | 2.7 |

CATALYST F: This catalyst was heated a little above 400$^o$ which appears to have decreased its activity a little, as it was prepared the same as catalyst E. The activity appears to have been recovered with use as is shown in Table 7. Indications were given in the case of other catalysts that the activity increased with use to a certain point. The ethylene is higher with this catalyst than with

Table 7.

| Time of run in mins. | Drying Temp. Deg.C. | Temp of run Deg.C. | Weight of Alo used in grams | Ether coll. | Vol $C_2H_4$ cc | % conversion to Ether | $C_2H_4$ |
|---|---|---|---|---|---|---|---|
| 96 | 430 | 250±2 | 16.55 | 10.55 | 400 | 78.0 | 3.0 |
| 67 | | " | 16.55 | 10.43 | 300 | 76.5 | 3.7 |
| 65 | | " | 16.50 | 10.73 | 340 | 80.5 | 4.2 |

catalyst E which is attributed to the drying temperature being too high.

EFFECT OF RE-RUNNING THE PRODUCTS: An attempt was made to find the effect of use of more catalyst but owing to inability to control the temperature in the long furnace which had to be used the idea was abandonned. As an alternative the effect of re-running the products was determined. About

100 cc. of alcohol were passed over the catalyst and
proportionate amounts of the two layers giving a total volume
of 30 cc.were analyzed.The amount of ether in the whole
product and in the balance was calculated.The remaining
product was then passed over the catalyst again.The two
layers were introduced in rates proportionate to their amounts
by means of two droppers united into a common delivery tube.
Again a sample containing the two layers in proportionate
amounts and having a total volume of 30 cc.was analyzed.The
amount of ether in the whole product was calculated and was
found to be slightly lower than before.This decrease was due
to the formation of a little ethylene and corresponded to
the equivalent of the ethylene closely.The products were
obtained in two burettes,graduated from the bottom up,
between the runs.This enabled equivalent amounts to be taken
out when desired.

EFFECT OF TEMPERATURE ON THE REACTION: The temperature effect
is shown by Table 8.The runs were made with catalyst C.

Table 8.

| Temp. of run Deg.C. | Time of run in mins. | Weight of Alc. used in grams | Ether collected | Vol. $C_2H_4$ cc | % conversion to Ether | $C_2H_4$ |
|---|---|---|---|---|---|---|
| 235±2 | 148 | 16.50 | 9.12 | 50 | 69.0 | 0.6 |
| 240±2 | 93 | 16.55 | 10.00 | 130 | 75.0 | 1.5 |
| 250±2 | 64 | 16.50 | 10.55 | 240 | 78.0 | 2.9 |
| 265±2 | 66 | 17.00 | 9.87 | 600 | 73.0 | 7.5 |

EFFECT OF TRACES OF ALKALI ON THE CATALYTIC ACTIVITY:

The effect of traces of impurities such as sodium hydroxide,and no doubt that of salts as well,is shown by the data in Table 9. A catalyst was prepared by the spontaneous decomposition of sodium aluminate and should have been in all respects the same as catalyst E. On drying it was found that traces of free alkali still remained in the precipitate . The catalyst was tried out in the furnace and a very poor yield resulted. The catalyst was then further washed and a much greater activity resulted. While the activity was not as great as for the best catalyst it is quite probable that since the catalyst was used before rewashing the impurities were not later all removed.The effect of better washing is, however, shown in no unmistakable manner.

### Table 9.

| Time of run in mins | Drying Temp. Temp. Deg.C. | Temp. of run. Deg.C. | Weight of Alc. used grams | Ether coll. | Vol. C$_2$H$_4$ cc | % conversion to Ether | C$_2$H$_4$ |
|---|---|---|---|---|---|---|---|
| Before rewashing: | | | | | | | |
| 75 | 400 | 250±2 | 16.60 | 5.83 | 60 | 45.0 | 0.8 |
| After rewashing: | | | | | | | |
| 69 | " | " | 17.10 | 9.50 | 120 | 71.0 | 5.0 |

DURATION OF CATALYST LIFE: That the catalysts will remain active for a considerable length of time is shown by Table 10 for a run with catalyst C after more than 1000 cc. of alcohol had been passed over it. The activity shows no sign of impairment.

## Table 10

| Temp. of run $^oC$ | Time of run in mins. | Weight of Alc. grams Ether | | Vol of $C_2H_4$ c.c. | % conversion to Ether to $C_2H_4$ | |
|---|---|---|---|---|---|---|
| 250±3 | 96 | 16.55 | 10.56 | 300 | 79.4 | 3.7 |

In some cases the alcohol tended to deposit car-
bonaceous matter on the catalyst which was evidenced by a
blackening of the latter but in the case of the best
catalysts this did not appear to happen. While this may be
due to impurities in the alcohol in some of the cases, for
the most part it is considered to have been due to the
nature of the side reactions taking place with the catalyst
in question. When carbon was deposited on a catalyst the
nature of the reaction appeared to be modified somewhat as
more ethylene was obtained.

## FORMATION OF ALCOHOL FROM ETHER AND WATER:

The reversibility of the reaction was previously
shown by Ipatiew[2] and later by Pease and Yung[5,8]. Some runs
were made in which ether and water in equal molecular
amounts were passed over catalyst C. The amount of ether
and water used in the runs were equivalent to a little
over 20 cc. of alcohol. The products were analyzed and the
amount of ether was found to have been decreased by an
amount considerably greater than the equivalent of the
ethylene formed. The latter was the same as would have been
formed if a standard run with alcohol had been made. The
decrease in the amount of ether was undoubtedly due to
the formation of alcohol according the equation

$C_2H_5OC_2H_5 + H_2O \rightarrow 2\ C_2H_5OH$. The results of these experiments are shown in Table 11. The column headed percent

### Table 11.

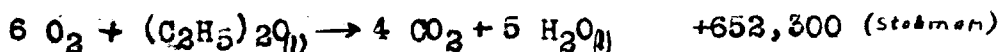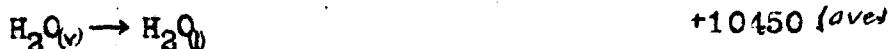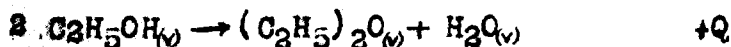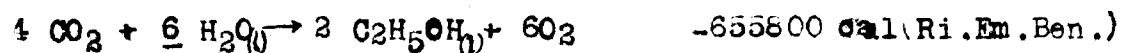| Temp. of run Deg.C. | Time of run mins. | Weights used Ether grams | Water | Alcohol Equivalent grams | Weight Ether Recovered grams | Vol. C$_2$H$_4$ cc | Alcohol formed gms | % | Conversion to C$_2$H$_4$ % |
|---|---|---|---|---|---|---|---|---|---|
| 250±2 | 63 | 13.40 | 3.30 | 16.65 | 11.57 | 200 | 2.03 | 12.2 | 2.4 |
| " | 56 | 13.60 | 3.40 | 16.90 | 11.95 | 150 | 1.84 | 11.0 | 1.8 |

alcohol formed is based on the total alcohol equivalent of the mixtures passed over the furnace. The iodoform test was made to determine the presence of alcohol in the products and a decided reaction was given. It is seen that approaching from the ether side about 12 % of the alcohol equivalent of the mixture is obtained as alcohol, the time of the run being about that of a standard run with alcohol.

The apparatus used to introduce ether and water into the catalyst tube at rates of flow proportional to their equivalents was the double dropper mentioned in connection with re-running the products (page 25).The two were joined with a common delivery tube and mercury dropped into each independently.

From the above it is seen that from the ether side, the ether recovered is equivalent to nearly an 88% conversion to ether.From the alcohol side yields of about 81 % have been obtained.The formation of ethylene complicates the case somewhat but for the purpose of an approximate calcula- tion may be neglected.Thus from these values the yield corresponding to the equilibrium may be estimated to be 85%.

This would mean a mixture containing 42.5 mol percent of each ether and water and 15 mol percent of alcohol.The equilibrium constant calculated from these values is given by $K = \dfrac{.425 \times .425}{(.15)^2}$ $= 8.0$ .

HEAT OF REACTION AND THERMAL DATA: The thermal data given are the most reliable values obtainable[14] and are as quoted by Pease and Yung.The heats of vaporization are for $30°C$ and have been obtained by Pease and Yung by plotting values for different temperatures and interpolating for $30°$.

$4\ CO_2 + 6\ H_2O_{(l)} \rightarrow 2\ C_2H_5OH_{(l)} + 6O_2$　　　$-655800$ cal(Ri.Em.Ben.)

$2\ C_2H_5OH_{(l)} \rightarrow 2\ C_2H_5OH_{(v)}$　　　$-20600$ (ave.)

$2\ C_2H_5OH_{(v)} \rightarrow (C_2H_5)_2O_{(v)} + H_2O_{(v)}$　　　$+Q$

$H_2O_{(v)} \rightarrow H_2O_{(l)}$　　　$+10450$ (ave.)

$(C_2H_5)_2O_{(v)} \rightarrow (C_2H_5)_2O_{(l)}$　　　$+6500$ (ave.)

$6\ O_2 + (C_2H_5)_2O_{(l)} \rightarrow 4\ CO_2 + 5\ H_2O_{(l)}$　　　$+653,300$ (Swatman)

Hence $Q_p = 655800 + 20600 - 10450 - 6500 - 653300 = 7100$ cal.

Adopting Lewis' notation $\Delta H = -Q_p = -7100$ cal.

From the heat of the reaction and the above value of the equilibrium constant the standard free energy of the reaction may be calculated. $\Delta F = -RT \ln K$ where ln stands for the logarithm to the base e,or $\Delta F = -2.303\ RT \log_{10}K$. $\Delta F$ comes out to be $-1360$.The standard free energy change varies with the temperature according to the equation $\Delta F = \Delta H + IT$. From this the integration constant I may be calculated and comes out to be 4.86.Considering $\Delta H$ to be constant over this temperature range the equilibrium constant at $275°$ may be calculated. $\Delta F_{548} = -7100 + 548 \times 4.86 = -4440$.From this

14 Landolt_Bornstein, "Tabellen",J.Springer,Berlin 1923

$$\log K = \frac{4440}{1.988 \times 548 \times 2.503}$$ ,whence $K_{548} = 5.88$. This corresponds to a maximum possible conversion at $275^{\circ}$ of $82.8\%$ which is much higher than the value given by Pease and Yung. It is certain that the equilibrium at $275^{C}$ is not where Pease and Yung have placed it.

Calculations of the standard free energy of ether are scarcely justified on the data available. In addition to the possible reactions already mentioned, another reaction $(C_2H_5)_2 O \rightarrow C_2H_4 + C_2H_5OH$ is also possible. Since the method of analysis determines one product only and the others may vary in several ways, a determination of the exact equilibrium point is hardly possible.

DISCUSSION OF THE VARIOUS CATALYSTS FOR ETHER FORMATION.

With alumina prepared by dehydration of the precipitate from aluminum salts with ammonia only low yields have been reported by those who have used this catalyst. This precipitate is very soluble in acids and alkalies. With the hydroxide prepared from solutions of sodium aluminate with sulphuric acid a yield of 74 % has been obtained in this investigation. This precipitate is considered to be crystalline[7] but it is readily soluble in acids. The precipitate produced by $CO_2$ from a 5% or stronger solution of sodium aluminate is decidedly crystalline and very insoluble in acids and alkalies. This precipitate gave a catalyst yielding 78 -79% ether. The precipitate obtained by

the spontaneous decomposition of sodium aluminate gave the most difficultly soluble precipitate of all and was the best catalyst giving a yield of 80-81% ether.

The distinction between colloidal aluminum hydroxide and the true crystalline aluminum hydroxide obtained by precipitation from solutions of sodium aluminate was made by van Bremmelen and substantiated by Martin.Milligan[15] has shown that the compound $Al(OH)_3$ loses most of its water on heating to $200^{\circ}C$ and after being heated above $275^{\circ}$ and then allowed to rehydrate, the water is adsorbed and not chemically combined in the true sense.The hydroxide itself furnishes a distinct crystalline X-ray pattern but on heating above $325^{\circ}$ gives another pattern which is that of a crystalline state according to Mead as quoted by Milligan,but different from the first.It would be interesting to observe whether the different precipitates from solutions of sodium aluminate which have been used as catalysts in this work have different patterns. The marked difference in their solubility in acids indicates a difference in their structure.Until the exact nature of each precipitate is determined it is not possible to develope a definite theory of the mechanism of the reaction.

SUMMARY.

1. A study of the catalytic dehydration of ethyl alcohol to ether has been made in the gaseous phase in the presence of alumina at $350^{\circ}$.

2. The maximum amount of ether was obtained with the

15 Milligan, J.Phys.Chem.,26,247 (1922)

product obtained by dehydration of the crystalline aluminum
hydroxide resulting from the spontaneous decomposition of
solutions of sodium aluminate.The highest yields were
obtained at 350° and amounted to 80.5% % of the theoretical
conversion to ether.

3. Alcohol was obtained from equimolecular quantities of
ether and water,showing the reaction to be reversible.The
position of equilibrium has been determined at 350° to
correspond to a maximum possible conversion to ether of
about 85 %.The corresponding equilibrium constant is 8.0 .

4. It has been shown that absolute purity of the catalyst
is essential. Impurities may be more quickly and completely
removed by drying the precipitate and washing again.

5. Heating the catalyst to about 400° but not higher,in
drying,gives the most active product.

6. The catalysts prepared as described retain their
activity,unimpaired,after long use.

## CONCLUSION

The catalytic preparation of ether by means of
aluminum oxide by the method developed in this investigation
has exceptional commercial advantages.The possible uses for
ether are increasing rapidly,not only as a solvent but also
in mixtures as a motor fuel,particularly in cold regions.
A very valuable application of this use of ether will be to
make possible the use of alcohol as a fuel.

The present method of manufacture,by dehydrating
alcohol with sulphuric acid is not only costly but troublesome.

The loss of alcohol is considerable,usually about 50% and the activity of the sulphuric acid quickly diminishes. In the method above described the catalyst is easily prepared and can be exactly duplicated and gives yields higher than are commercially feasible by the sulphuric acid method. In view of the large scale upon which this investigation was carried out,approaching semi-commercial size,it is safe to consider the high yields obtained can be duplicated commercially.The catalysts have been shown to retain their high activity with long use. The mechanical side of the operation is extremely simple and could be carried out with little cost.

oOo

I wish to take this opportunity of expressing my heartiest appreciation to Dr.R.H.Clark,Professor of Organic Chemistry,for his kind advice and assistance in connection with the work.

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