As $Ti^{IV}/Ti^{II} = 10^{-6}$, it was clearly justifiable to disregard quadrivalent titanium in calculating the analyses.

We gratefully acknowledge a grant from the Du Pont Fund for the purchase of metallic titanium and of sundry apparatus.

Summary

A mixture of titanium trichloride and dichloride was obtained by heating the metal, presumably about 99.9% pure, in hydrogen chloride. Excluding air with carbon dioxide, it was dissolved and filtered into the cell
$$\overset{-}{Hg} \mid TiCl_3 \; TiCl_2 \; 0.05 \; M \; HCl \mid 4M \; KCl \mid HCl \; 0.1M \mid \overset{+}{Hg}.$$
All operations were at $0°$. The electromotive force gradually rose to a maximum, which was in general quite constant for a considerable time. Total titanium was determined gravimetrically and total reducing power by electrometric titration, giving the concentrations in both valences. Six cells when extrapolated to equal or molal concentrations of both valences at $0°$ averaged 0.700 volt with an extreme difference of 0.050 volt. The electromotive force at $0°$ of the chain, $H_2 \mid \overset{+}{H^+} M \mid 4M \; KCl \mid TiCl_3 \; TiCl_2 \mid \overset{-}{Hg}$, becomes -0.37 ± 0.01 when $Ti^{III} = Ti^{II}$, assuming zero potential for the normal hydrogen electrode at $0°$. Acid concentrations below $0.1 \; N$ had but little effect on the results, but the dichloride decomposed rapidly in more concentrated acid, and the electromotive force declined rapidly.

The electromotive force of the hypothetical chain, $H_2 \mid \overset{+}{H^+} M \mid 4 \; M \; KCl \mid Ti^{IV} \; Ti^{II} \mid \overset{-}{Hg}$, is calculated to be -0.16 ± 0.01 when $Ti^{IV} = Ti^{II}$.

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THE CATALYTIC DEHYDRATION OF ETHYL ALCOHOL AND ETHER BY ALUMINA

BY ROBERT N. PEASE AND CHI CHAO YUNG

The chief purpose of the investigation recorded in the following pages was to gain information as to the kinetics of the catalytic dehydration of alcohol in the vapor phase, with formation of ether and ethylene, by a more thorough study of the reactions involved than has yet been made. Much work of a qualitative nature has been done on catalytic vapor-phase organic reactions, especially by Sabatier and his students, and many hypotheses as to their mechanisms have been evolved. It would seem, however, that only by exhaustive study of particular examples from as many points of view as possible—and that of the simpler reactions first— can satisfactory explanations be arrived at.

Among such reactions, the dehydration of alcohol stands out as one of

the least complex, yet even in this case there is disagreement as to the mechanism. As ordinarily carried out at temperatures between 300° and 450°, ethyl alcohol is catalytically dehydrated by alumina yielding nearly pure ethylene. At lower temperatures, however, good yields of ethyl ether can be obtained, as Senderens[1] first showed. It is further known that ethyl ether is decomposed by alumina to give ethylene.[2] These facts would seem to indicate that the dehydration of alcohol might occur in two steps: $2C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$, $(C_2H_5)_2O \longrightarrow 2C_2H_4 + H_2O$, the second reaction predominating at the higher temperatures. From his own experiments, Ipatiev[2b] has concluded that this is in fact the mechanism. Senderens,[3] however, believes that the formation of ether and ethylene from alcohol are two independent reactions. He bases this belief on two pieces of evidence, namely, that at 250° the rate of decomposition of *pure* ether to give ethylene is many times greater than the rate of formation of ethylene from alcohol, and that with other catalysts and other alcohols the formation of ether is insignificant. Neither of these facts is really decisive, however. As to the first, it may be pointed out that the very fact that ether is present in the system when alcohol is passed through and yet does not decompose at the rate that pure ether would, as shown by the fact that the *total* ethylene is less than from pure ether, proves that the two cases are not directly comparable. An obvious explanation is that when alcohol is present the catalyst is engaged in other work, namely the decomposition of alcohol. One may say that the alcohol is more strongly adsorbed than the ether. As to the absence of ether with other catalysts and other alcohols, it would appear that this is simply a question of greater catalytic efficiency in ether decomposition on the one hand and greater instability of the ether on the other.

Senderens gives as the most probable mechanism the formation of a complex involving one molecule each of alumina and alcohol which may break down directly to give ethylene or which may react with another molecule of alcohol to give ether. This mechanism, Senderens points out, is exactly analogous to Williamson's mechanism for the same reactions in the sulfuric acid process. He also suggests as a possibility the formation of ether directly from a second type of complex containing two molecules of alcohol.

Two alternative mechanisms have, therefore, been suggested for the catalytic dehydration of alcohol, one of which assumes that the two possible reactions take place consecutively, the other, simultaneously. There would appear to be no reason to believe that the two are mutually exclu-

[1] Senderens, *Ann. chim. phys.*, [8] **25**, 505 (1912).

[2] (a) Grigorieff, *J. Russ. Phys. Chem. Soc.*, **33**, 173 (1901). (b) Ipatiev, *Ber.*, **37**, 2986 (1904). (c) Senderens, *Bull. soc. chim.*, [4] **3**, 824 (1908).

[3] Ref. 1, p. 524.

sive, however. Indeed, it would be very difficult, if not impossible, to prove that the ethylene is formed entirely either from the alcohol directly or through the intermediate formation of ether. Nevertheless, it was hoped that a more thorough study of the reactions in question than had previously been carried out might make it possible to judge the relative importance of the two mechanisms and yield further interesting information. This hope, it is believed, has been justified.

Apparatus and Procedure

The method adopted for the study of the reactions in question is essentially the flow method of Sabatier.[4]

The apparatus is shown in Fig. 1. A definite volume of liquid (40.0 cc. of alcohol or 20.0 cc. of ether) was allowed to drop at a controlled rate from a buret into the catalyst tube, the temperature of which was held constant in an electrically-heated glass tube furnace. The liquid products were condensed, using a short condenser just beyond the furnace, and collected in a distilling flask immersed in an ice-bath. Through the side arm of this flask the gaseous products were allowed to pass either to the air or to a gas buret, by means of which the rate of their formation was determined several times during a run. For compactness and convenience in manipulation, the furnace was mounted vertically instead of horizontally. The catalyst chamber was 2 cm. in diameter and 12 cm. long (volume, 35 cc.) and contained 24 g. of alumina, prepared as described below.

Before each run, the furnace was brought to the desired temperature and half the standard quantity of liquid run through at the rate at which the experiment was to be performed, in order to bring the system to its equilibrium state. The rate of addition of liquid was controlled by counting the number of drops falling from the buret tip per minute. Without stopping the flow, the receiver was then put in place and the definite volume of liquid allowed to pass through the apparatus. The amount of ether formed was determined by "salting out."
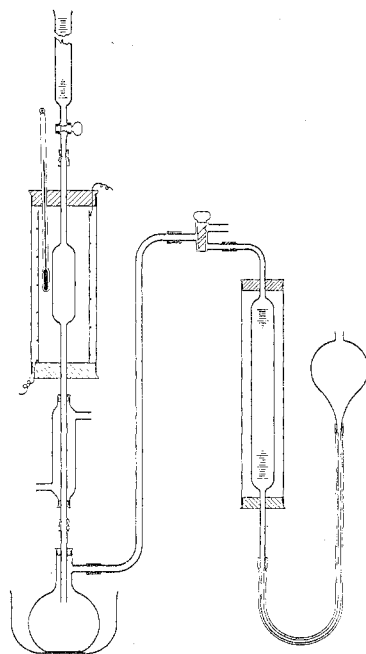
Fig. 1.—Apparatus.

The details of the method are given in the next section. The amount of ethylene formed was calculated from the average time required to generate 100 cc., and the time of the run. Samples of ethylene were analyzed from time to time by absorption in fuming sulfuric acid. Except in certain of the preliminary runs, the absorption was uniformly 99–100% complete.

Ether Determination.—The determination of the amount of ether in the recovered liquid offered some little difficulty. The method finally adopted is a simplification of

4 See Rideal and Taylor, "Catalysis in Theory and Practice," Macmillan Co., 1919, p. 70.

that described by Wolff.[5] The recovered liquid was shaken with about four times its volume of a saturated solution of sodium chloride and an excess of solid salt.   This causes separation of two layers, the upper being nearly pure ether.   Most of the lower layer was run off and the remainder, along with the ether layer, was run into a buret by means of which the volume of the latter was read off.   Experiments with ether-alcohol mixtures of known composition showed that this method was satisfactory as an approximate analysis, provided the volume of ether was not less than $1/3$ that of the alcohol.   With a smaller proportion than this, the recovered volume rapidly diminished until with a mixture containing only 10% of ether, no separation into layers occurred.   Fortunately, in all but a few experiments the proportion of ether to alcohol was greater than this limiting amount.   Except as just stated, the method is accurate to about 2%.

Preparation of Catalyst and Reagents

The alumina catalyst was prepared according to directions furnished by the Fixed Nitrogen Research Laboratory and due to A. T. Larsen and W. Hawkins.

Alumina was precipitated from hot, dil. (3–5%) solutions of aluminum nitrate and ammonium hydroxide.   The precipitate was washed several times by decantation with preliminary heating and was purified further by a method of dialysis assisted by an electrical potential.   The precipitate was then filtered on Büchner funnels and the filter cakes were dried overnight at 100°.   The resulting product consisted of hard, white, opaque granules.   These were reduced to about 10 mesh and filled into the catalyst bulb. The tube was plugged loosely with glass wool at both ends.

Before commencing the measurements the catalyst was heated to 200° while in place in the furnace and alcohol vapor passed slowly through it.   The purpose of this was to effect the decomposition of any ammonium nitrate remaining and to sweep out the air. Thereafter the catalyst was never exposed to air.   After each run, the catalyst tube was connected directly to the gas buret containing ethylene and allowed to cool in this gas. These precautions were taken because in certain preliminary runs the ethylene was found to contain appreciable quantities of carbon dioxide.[6]   It seemed that this must be due to the fortuitous presence of oxygen in the system.   Subsequent tests for carbon dioxide (using a solution of barium hydroxide)were consistently negative.

This one sample of catalyst was used in all the experiments recorded in this paper (about 70).   Its behavior was satisfactorily constant except for one curious activation that took place during the preliminary experiments with ether.   This is dealt with in a later section.

The alcohol was purified by treatment with calcium oxide and distillation; the ether by treatment first with calcium chloride, then with metallic sodium followed by distillation.

Calculations and Accuracy of Results.—The results of the experiments have been expressed in terms of the percentage conversions of the alcohol or ether employed.   In calculating the latter it has been assumed that complete conversion of the 40.0 cc. of alcohol to ether would yield 35.5 cc. of ether and to ethylene would yield 16.5 liters, measured at 20° and 760 mm.   Complete decomposition of the 20.0 cc. of ether used should yield 9.35 liters of ethylene at 20° and 760 mm.   The volume of ethylene

[5] Wolff, *Chem.-Ztg.*, **34**, 1193 (1910).

[6] Compare Reid, 1923 Spring Meeting of the American Chemical Society at New Haven, who reported large quantities of CO_2 in ethylene prepared in this way.

was not corrected for temperature and pressure, as the magnitude of the other corrections, which are to be considered presently, did not justify it; 20° and 760 mm. are taken as the average room temperature and pressure.

Except for those few experiments in which the yield of ether was too small to allow a satisfactory application of the method of analysis, the greatest source of error in the alcohol experiments is that introduced by the incomplete condensation of vapor from the ethylene stream. As the uncondensed vapor was probably largely ether, this makes the observed yield of ether too low and the yield of ethylene too high (because of the added volume of the vapors). That such losses did occur was shown by a comparison of the recovered volumes of liquid with those to be expected from the amounts of ether and ethylene formed. Making use of the ether-alcohol-water density tables of Sanfourche and Boutin,[7] it can be calculated that the volumes of such mixtures derived originally from alcohol are almost exactly the same as the volume of the original alcohol, provided there is no separation into layers—and there was not in these experiments—and that every liter of ethylene formed results in a diminution in volume of 1.9 cc. on the average. Any ether uncondensed decreases the liquid volume and increases the gas volume, and for every liter of ether vapor uncondensed (at 20° and 760 mm., assuming that the gas laws are obeyed) the liquid volume should decrease by 4.3 cc. Assuming that the volume of gas obtained is that of the ether vapor and ethylene together, it is possible to calculate the corrections to be applied. Thus if $V_{C_2H_4}$ represents the true volume of ethylene in liters and V_{Et} the gaseous volume in liters of ether uncondensed, $V_{C_2H_4} + V_{Et} = V_{gas}$, where V_{gas} is the observed volume of gas in liters. Also, if $\Delta V_{liq.}$ represents the difference between the original volume of alcohol (40.0 cc.) and the recovered liquid volume, then $\Delta V_{liq.} = 4.3\ V_{Et} + 1.9\ V_{C_2H_4}$, whence $V_{Et} = (\Delta V_{liq.} - 1.9\ V_{gas})/2.4$, and the liquid volume of ether vaporized $= 4.3\ V_{Et}$ cc. The true volume of ethylene is $V_{gas} - V_{Et}$.

Since the uncondensed vapors are not all ether and undoubtedly deviate markedly from the gas laws, the correction for ether is undoubtedly too large and the calculated ethylene volume too small. The averages of the observed and corrected ether volumes and of the observed and calculated volumes of ethylene have therefore been used in calculating the percentage conversions. It appears that the latter may be in error by as much as 5–10% in extreme cases.

As an example of the calculations, the following experiment, in which the corrections were large, is taken.

  Run 5.   40.0 cc. alcohol at 300°; time of run, 367 minutes.

  Av. time for the generation of 100 cc. of gas, 5 minutes and 40 seconds; extremes, 5 minutes and 23 seconds and 6 minutes and 9 seconds.

    [7] Sanfourche and Boutin, *Bull. soc. chim.*, [4] **31,** 546 (1922).

Total gas volume, 6.45 liters. Ether recovered, 7.9 cc. Total volume of recovered liquid, 24.8 cc. $\Delta V_{\text{liq.}} = 40.0 - 24.8 = 15.2$ cc. $V_{Et} = \dfrac{15.2 - 12.3}{2.4} = \dfrac{3.0}{2.4} = 1.2$ liters.

Liquid volume of ether vaporized, 5.2 cc. Corrected liquid volume of ether, 13.1 cc. Corrected volume of ethylene, $6.45 - 1.2 = 5.25$ liters.

Mean volume of ether, 10.5 cc. Mean volume of ethylene, 5.85 liters.

$$\begin{array}{lll} \text{Percentage conversion:} & \text{to ether} & 30\% \\ & \text{to ethylene} & 35\% \\ \hline & \text{Total} & 65\% \end{array}$$

A similar correction was made in the ether experiments.

Results and Discussion

Dehydration of Pure Alcohol and Ether at 275°, 300° and 350°.—The first experiments carried out dealt with the decomposition of pure alcohol and ether at 275°, 300° and 350°. The results are shown graphically in Figs. 2, 3, 4, and 5.

With respect to the dehydration of alcohol, it will be noted that at 300° (Fig. 2) the total percentage conversion of alcohol reaches a constant value
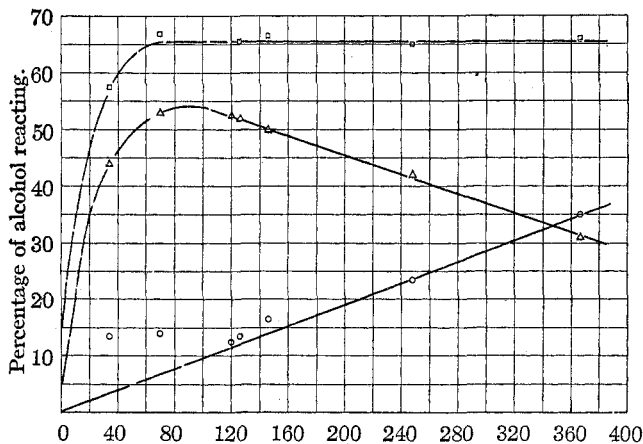

Fig. 2.—Dehydration of alcohol at 300°. Top curve, total percentage of alcohol reacting. Middle curve, percentage of alcohol converted to ether. Bottom curve, percentage of alcohol converted to ethylene.

as the time of run is increased but the fraction obtained as ether passes through a maximum, while that obtained as ethylene increases steadily, the decrease in the ether fraction after the maximum is passed being compensated for by a corresponding increase in the ethylene. At 275° (Fig. 3) the relations are probably the same but the amounts of ether and ethylene are changing so slowly that longer runs than could be successfully carried out would be necessary to demonstrate this conclusively. The

behavior at 350° (Fig. 4) differs from that at the lower temperatures in that the reaction proceeds rapidly to complete decomposition to ethylene. The yield of ether probably passes through a maximum as before.

The ether decomposition (Fig. 5) takes place readily enough at both 275° and 300°. It was too rapid at 350° to allow satisfactory measurement. The conversions to ethylene were calculated on the assumption that the reaction is $(C_2H_5)_2O \longrightarrow 2C_2H_4 + H_2O$. After the experiments had been completed it was realized that the reaction $(C_2H_5)_2O \longrightarrow C_2H_4 + C_2H_5OH$ might have taken place also. It was noted that the decomposition at 275° was approaching even 50% conversion (which might correspond to the second equation) only very slowly and that the curve for the results at 300° seemed to undergo a rather sharp change of slope at about 50% conversion.
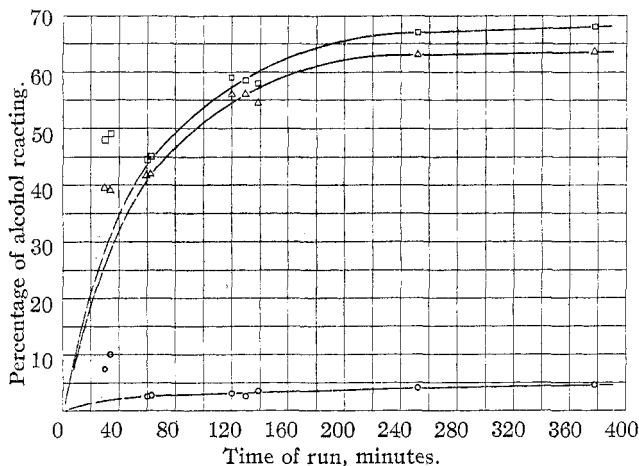

Fig. 3.—Dehydration of alcohol at 275°. Top curve, total percentage of alcohol reacting. Middle curve, percentage of alcohol converted to ether. Bottom curve, percentage of alcohol converted to ethylene.

In order to test this point, a run was carried out in which 160 cc. of ether was passed through at the (relatively rapid) rate of 20 cc. per hour with the catalyst at 275° and the recovered liquid fractionated. About 80 cc. came over between 35° and 75° and 9 cc. between 75° and 82°. The latter was unquestionably largely alcohol. These figures indicate that about half the ether was decomposed, of which about 20% went to ethylene and alcohol instead of ethylene and water. With slower rates of passage and higher temperatures it is reasonably certain that the conversion to alcohol would be less. This is shown by the fact that even when calculating on the basis of complete conversion, a 4-hour run showed 72% conversion and there was still ether undecomposed.

This finding obviously complicates matters, for in the decomposition of alcohol there are the following reactions to be taken into account. Alcohol

may first decompose in either one of the following ways: $C_2H_5OH \longrightarrow$ $C_2H_4 + H_2O$; $2C_2H_5OH \longrightarrow (C_2H_5)_2O + H_2O$. Then the ether may decompose: $(C_2H_5)_2O \longrightarrow C_2H_4 + C_2H_5OH$ or $(C_2H_5)_2O \longrightarrow 2C_2H_4 + H_2O$.

By the first of the latter two equations, one-half the original alcohol is regenerated and can react anew. In spite of these complications, certain experimental facts bearing on the mechanism stand out and these will be enumerated.
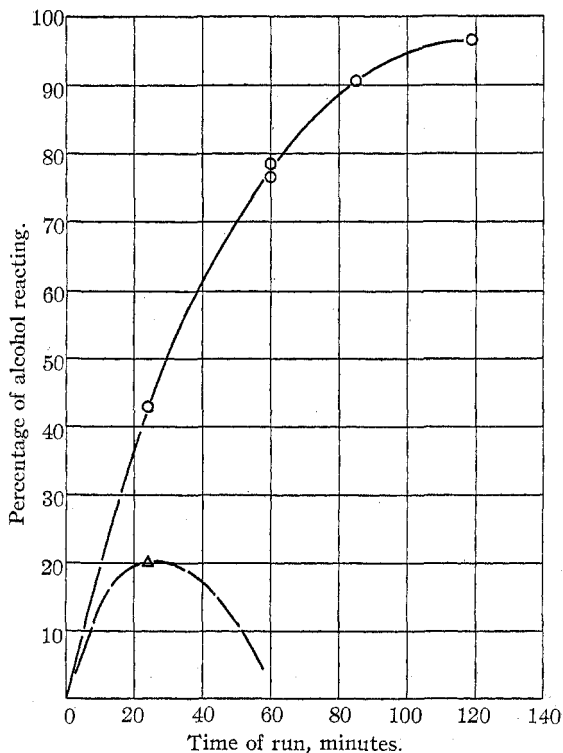

Fig. 4.—Dehydration of alcohol at 350°. Upper curve, percentage of alcohol converted to ethylene. Lower curve, percentage of alcohol converted to ether.

In the first place, it seems reasonable to believe that since ether is actually formed from alcohol in the presence of alumina and pure ether decomposes in the presence of alumina to give ethylene, part at least of the ethylene formed on passage of alcohol over alumina passes through the ether stage and that to this extent the mechanism is one of successive reactions as opposed to simultaneous reactions.

Second, there is good ground for the belief that the reaction, $2C_2H_5OH \rightleftarrows (C_2H_5)_2O + H_2O$, approaches equilibrium at about 60–70%

conversion. It will be noted that the decomposition of the alcohol stops at about this point both at 275° and 300°. At first sight, it appears improbable that at 300° this could be due to equilibrium since the proportion of ether is continuously decreasing. However, it must be remembered that at the same time the yield of ethylene is increasing and with it that of water, the other product of the above reaction (except in so far as the ethylene is derived from ether according to the equation $(C_2H_5)_2O \longrightarrow C_2H_5OH + C_2H_4$). The product of the concentrations of ether and water would therefore not necessarily alter greatly until the amount of ether became small. At 350° in the absence of measurable
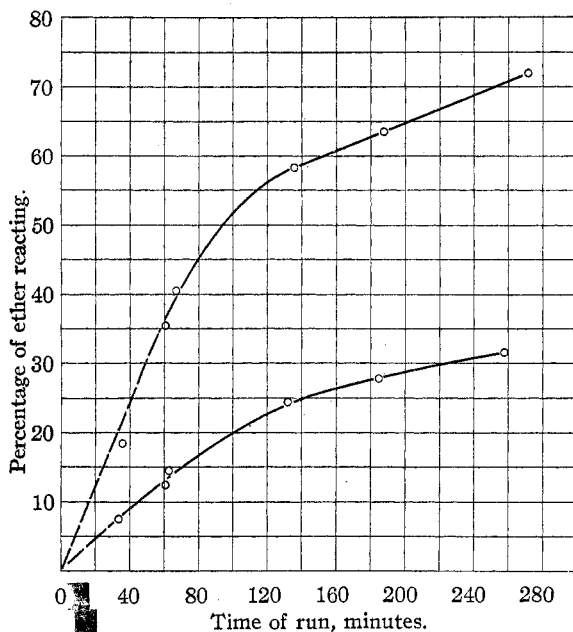

Fig. 5.—Dehydration of ether at 275° and 300°.
Upper curve, at 300°. Lower curve, at 275°.

amounts of ether, the complete decomposition of the alcohol was to have been expected on this view.

Another possible explanation of the incomplete decomposition of the alcohol at 275° and 300° is that one of the products is acting as a powerful poison for further alcohol decomposition, though not for ether decomposition, the additional ethylene in the long runs coming from the ether. It is difficult to believe that any third substance could act in such a way. The result would be explicable if ether itself were adsorbed by alumina preferentially to the exclusion of alcohol, but the properties of ether are such as to make it very doubtful that this can be the case. In addition, if it be admitted that the ether is itself decomposing, it follows that it

cannot act as a powerful poison because the fact of decomposition means the destruction of the hypothetical ether layer on the catalyst surface which would be responsible for the result.

The influence of water and ethylene, the other two products, on the decomposition of alcohol was determined. The results with water are shown graphically in Fig. 6. In each of these experiments, 40 cc. of alcohol plus the required amount of water were run through the system in
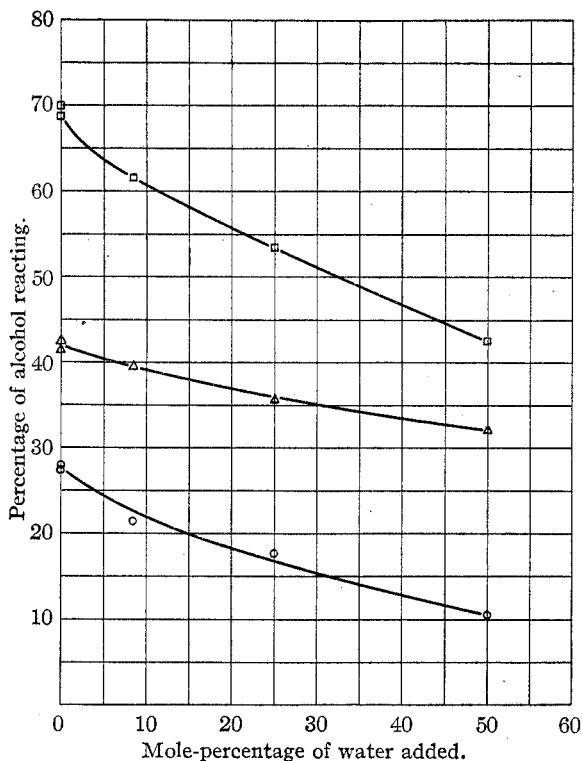

Fig. 6.—Effect of water on dehydration of alcohol at 300°.
Top curve, total percentage of alcohol decomposed. Middle curve, percentage of alcohol converted to ether. Bottom curve, percentage of alcohol converted to ethylene.

about 120 minutes. The yields are plotted against the mole percentage of water in the alcohol. It will be seen that the amount of reaction is effectively decreased by the water but to nothing like the necessary extent, if water were the powerful poison sought. The results with ethylene were not very satisfactory because of the excessive losses of vapors by entrainment in the ethylene stream. It is certain that the yield of ethylene from alcohol was effectively reduced by admixture of ethylene. The effect on the yield of ether was uncertain because of the large correction. The

amount of ether actually recovered decreased rapidly with increasing percentage of ethylene. The corrected yield of ether, however, remained substantially constant. In any event, the effect of ethylene does not seem to be sufficiently powerful to account for the result. It appears, therefore, that the incompleteness of the decomposition of the alcohol cannot be due to poisoning by the products and is therefore in all probability the result of an equilibrium condition in the ether reaction.

It does not seem at all improbable that the decomposition of alcohol to give ether at this temperature would be incomplete. It is known that at 130–140°, the equilibrium is well over on the ether side, though no quantitive measurements are available. Since the heat of reaction is positive and rather small ($Q = +11,000$ cal.), reaction should be less complete at the higher temperature but the equilibrium constant should not change greatly. Measurements of this equilibrium are at present in progress at 250°, at which temperature the formation of ethylene is negligible. Preliminary experiments have shown that the reaction is undoubtedly reversible, passage of ether and water over the catalyst resulting in the formation of an appreciable quantity of alcohol.

While the direct decomposition of alcohol to yield ethylene is not ruled out by these experiments, it appears unnecessary to assume it. All the results are explicable on the assumptions that the alcohol gives first, ether, which then decomposes to give ethylene, that the first (ether) reaction is incomplete in this temperature range and that the rate of ether decomposition increases more rapidly with the temperature than that of the initial alcohol decomposition so that with the catalyst used the former passes the latter somewhere between 300° and 350°.

These experiments give little evidence as to the more detailed mechanism of the reactions. For the formation of ether from alcohol, Senderens[1] has suggested two alternative mechanisms; the reaction may take place between two molecules of alcohol associated with the same alumina molecule or between one such molecule and another from the vapor phase. In the first, the alumina might split hydroxyl from one molecule and hydrogen from the other followed by combination of the ethyl and ethoxyl groups resulting; or it might split water from one molecule leaving an ethylidene group which then must combine with the other molecule of alcohol. By the second mechanism (the combination of a condensed molecule with a vapor-phase molecule) the reaction would of necessity be the latter. This recalls the speculations of Nef[8] on the formation of ether in the sulfuric acid process, in which it is assumed that the ethylsulfuric acid dissociates to give an ethylidene radical which then combines with a molecule of free alcohol to give ether, $CH_3\overset{/}{\underset{\backslash}{C}}H + C_2H_5OH \dashrightarrow C_2H_5OC_2H_5$. This gives

⁸ Nef, *Ann.*, **309**, 179 (1899).

really three different mechanisms, among which these experiments do not especially favor any one.   Possibly further investigation of reaction rate at lower temperatures may allow a choice between the explanation involving two condensed molecules and that involving one condensed molecule and one from the gas phase.

It may be mentioned that Nef[9] investigated the decomposition of ether and alcohol vapor, mainly at temperatures in the neighborhood of 500–600° but under conditions such that the dehydrogenation reactions, to form aldehyde, rather than the dehydration reactions were favored.   Some ethylene was formed under these conditions.   Nef assumed that this resulted from an ethylidene dissociation followed by rearrangement of the radical to give ethylene, $C_2H_5OH \longrightarrow H_2O + CH_3 - \overset{/}{\underset{\backslash}{C}}H \longrightarrow C_2H_4$; $(C_2H_5)_2O \longrightarrow$ $H_2O + 2CH_3\overset{/}{\underset{\backslash}{C}}H \longrightarrow 2C_2H_4$.   This seems to be a plausible view of the formation of ethylene from ether in the experiments here reported.

Effect of Temperature on Decomposition of Alcohol.—A series of 120-minute runs with alcohol was carried out between 200° and 350° to find how the yield of ether and ethylene varied with the temperature. The results are shown graphically in Fig. 7.   It will be seen that the yield of ether passes through a maximum at 250°, and that the formation of ethylene is negligible below 275°.

Activity of the Catalyst.—A marked change in the activity of the catalyst took place during the experiments on ether, which is of some interest.   Before the ether runs, the activity had remained satisfactorily constant as the following figures show.   For the 120-minute runs Nos. 2, 7 and 17 at 300°, the total decompositions were 66%, 65% and 64% of which 14%, 13% and 13%, respectively, went to ethylene and the remainder to ether.   After the ether runs, the total decomposition was about the same but a much larger proportion reacted to form ethylene.   Thus, for the 120-minute runs Nos. 43, 52 and 63 at 300° the total decompositions were 69%, 71% and 67% of which 26%, 25% and 24%, respectively, went to ethylene. Thus, the "ethylene efficiency" of the catalyst had about doubled.   It would appear that the training obtained in ether decomposition during the ether runs had thereafter served the catalyst in good stead.   It should be mentioned that after some preliminary runs with ether, the catalyst reached an approximately steady state with respect to this reaction. Thus, in the 60-minute runs Nos. 18, 29, 64 and 70 at 300°, the percentage decomposition was 36%, 40%, 38% and 46%, respectively.   If anything, the activity improved somewhat.   It is believed that the activation took place during the preliminary runs with ether, which showed considerable variation.

These observations are of special interest when considered in connection

[9] Nef, *Ann.*, **318**, 198 (1901).

with those of Adkins[10] on the variation in the relative efficiency of alumina as a dehydrating and decarboxylating agent in ester decomposition, depending upon the method of preparation and amount of use. Adkins accounts for this variation by assuming that the efficiency of the catalyst for one or the other reaction depends upon the size of pores of molecular dimensions on the catalyst surface which are supposed to be the active agents. Large pores, he assumes, favor the splitting off of carbon dioxide and small
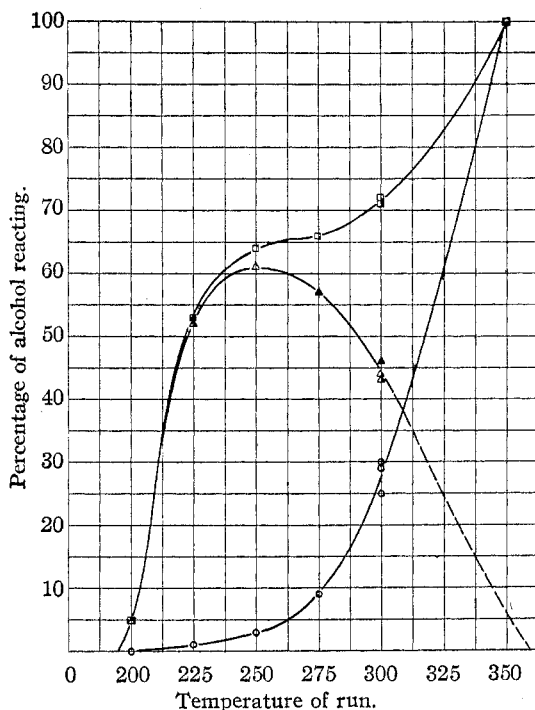
Fig. 7.—Effect of temperature on dehydration of alcohol. Top curve, total percentage of alcohol decomposed. Middle curve, percentage of alcohol converted to ether. Bottom curve, percentage of alcohol converted to ethylene. Standard 120-minute run.

pores the splitting off of ethylene. In the present case, a similar variation in relative efficiency took place. Since it is water which is split off in either reaction, however, this explanation would not seem to be valid as it stands.

Summary

1. A study of the catalytic dehydration of ethyl alcohol and ether vapors in presence of alumina mainly at 275° and 300° has been carried out by a flow method.

[10] Adkins, THIS JOURNAL, **44**, 2175 (1922).

2. It has been found that appreciable quantities of ether as well as ethylene are formed from alcohol and that at 275° and 300° the amount of alcohol decomposed attains a maximum corresponding to about 65% conversion, whereas at 350° the reaction goes to complete dehydration to form ethylene. The maximum yield of ether obtained was 60% at 250°. Ether decomposes readily from 275° up.

3. The results are shown to be explicable on the grounds that the dehydration of alcohol to yield ether is reversible, equilibrium corresponding to about 65% conversion, and that decomposition of alcohol occurs in steps. While the direct dehydration to yield ethylene is a possible mechanism, it is not necessary to assume it in order to account for the results.

4. Water vapor and ethylene diminish somewhat the efficiency of the catalyst toward alcohol dehydration.

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DEAMINIZATION OF ESTERS OF ALANINE AND OF AMINO-ISOBUTYRIC ACID

BY A. L. BARKER[1] WITH GLENN S. SKINNER

It has been shown by one of us[2] that *cis-trans* isomerism gives rise to very different products in the deaminization of esters of amino acids derived from cyclopentane, the most striking difference being the non-formation of the ether of a free hydroxy acid in the case of the *cis* compound. The silver salt[3] of this hydroxy acid by treatment with methyl iodide gives in part the same ether acid as that obtained in the nitrite decomposition. This reaction of a silver salt[4] to give an ether instead of an ester has been observed to take place in the case of the salt of the hydroxy acid corresponding to isocampholactone. Likewise the silver salts of lactic and malic acids[5] give ether acids as well as esters. The esters of the corresponding amino acids should be expected to give ethers and this has been found to be true in the case of alanine.

The deaminization of esters of α-amino-*iso*butyric acid has not been previously studied and no quantitative data are given with regard to the esters of alanine. Curtius and Koch[6] have decomposed the hydrochloride

¹ Abstract of a thesis presented by A. L. Barker in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Wisconsin.

² Skinner, THIS JOURNAL, **45**, 1498 (1923).

³ Noyes and Skinner, *ibid.*, **39**, 2692 (1917).

⁴ Noyes and Taveau, *Am. Chem. J.*, **35**, 381 (1906).

⁵ Purdie and Lander, *J. Chem. Soc.*, **73**, 296 (1898).

⁶ Curtius and Koch, *J. prakt Chem.*, [2] **38**, 472 (1888).