[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

DEHYDRATION OF ALCOHOLS OVER ALUMINA

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It is believed that a precise knowledge of the relation of the structure of an alcohol or ether to its rate of dehydration and dehydrogenation, at various temperatures, is necessary for any worth-while formulation of the function of the catalyst in the causation of these fundamental reactions. Alumina produces only dehydration, zinc oxide dehydration and dehydrogenation, and copper only dehydrogenation. This paper is concerned with alumina as a catalyst. A second paper for which the experimental work is now complete, will deal with the relative rates of the two competing reactions over a zinc oxide catalyst. The compounds used in the experimental work were ethanol, propanol, *iso*propanol, butanol, *iso*butanol, *sec.*-butanol and diethyl and dibutyl ether.

Sabatier and Mailhe,[1] Brown and Reid,[2] and Pease and Yung,[3] have presented some data upon the effect of temperature upon the dehydration of alcohols. In all three cases the data bearing on this point are of doubtful value because they have not referred to, at all temperatures, a considerable excess of alcohol; hence, the increase in reaction was apparently less than it really is. Pease and Yung had such a large bulk of catalyst that it probably was not all at the same temperature, and hence when the temperature of the furnace was raised they brought into play a larger part of their catalyst so that the apparent effect of rise of temperature was much greater than it really is. It is essential for this work (and for many other catalytic studies) that the amount of catalyst be small, so that the whole of it may be at approximately the same temperature. It is necessary that at all times there be at least twice as much alcohol passed over the catalyst as is actually dehydrated.

If these precautions are taken, it may be seen from the figure that *over the temperature range studied* the increase in the formation of the alkene is a linear function of the temperature and that for the primary alcohols the slopes of the lines are approximately constant. The increase in rate of reaction with rise in temperature is apparently greater for the secondary alcohols than it is for the primary alcohols.

The rate of dehydration of the alcohols increases in the following order: butyl, propyl, *iso*butyl, ethyl, *iso*propyl and *sec.*-butyl alcohols. If, however, it is desired to state quantitatively the relative rates of reaction of the alcohols over alumina an interesting situation is encountered;

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[1] Sabatier and Mailhe, *Ann. chim. phys.*, [8] **20,** 325 (1910).

[2] Brown and Reid, *J. Phys. Chem.*, **28,** 1081 (1924).

[3] Pease and Yung, THIS JOURNAL, **46,** 402 (1924).

for while ethyl alcohol is 1.6 as reactive at 360° as is butyl alcohol, at 420° the former is only 1.2 as reactive as the latter. The relative stability is then a function of the temperature. If one wishes to compare quantitatively the relative reactivity of the alcohols it cannot then be expressed in terms of the amount reacting in unit time at a constant temperature, but may be stated in terms of the temperature interval for a constant amount of reaction. That is, to get the same volume of alkene one must use butyl alcohol 19° higher than in the case of ethyl alcohol. This value of 19° is approximately a constant (since the lines are nearly parallel) for comparison of the alcohols and is independent of the precise experimental conditions. The temperature intervals for equal activity are apparently in the vicinity of 5° from ethyl to *iso*butyl and 11° from propyl to butyl alcohols.

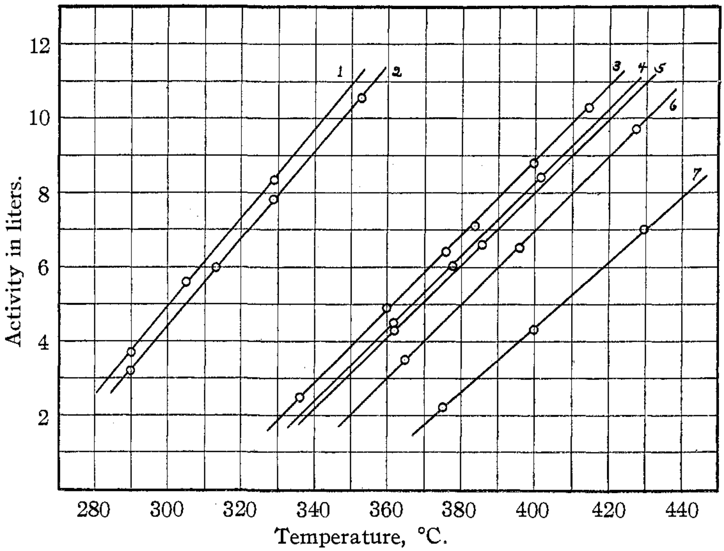

Fig. 1.—The volume in liters (22°, 740 mm.) of alkene formed during one hour by passing 50 g. of various alcohols over 1 g. of alumina (precipitated from the nitrate) is plotted as the ordinate against the temperature. The temperature was controlled by means of a thermocouple placed outside of the catalyst tube. The temperature reported is that recorded by a thermocouple head placed in the catalyst mass. 1, *sec.*-Butanol; 2, *iso*-propanol; 3, ethanol and diethyl ether; 4, *iso*butanol; 5, *n*-propanol; 6, *n*-butanol; 7, dibutyl ether.

The secondary alcohols, *iso*propyl and *sec.*-butyl form alkenes much more rapidly than the primary alcohols. Since the increase in reaction with rise in temperature is greater for these two alcohols than for the primary alcohols, one cannot assign a temperature interval that is a measure of their rapidity of dehydration. For an activity of 3 liters per hour the interval from ethyl to *iso*propyl is about 53°, and the interval from the latter to *sec.*-butyl about 5°. For a high activity of 10 liters per hour the interval between ethyl and *iso*propyl is in the neighborhood of 63°, the interval between the two secondary alcohols remaining approximately constant.

The increase in reaction with rise in temperature was also determined for certain of the alcohols over alumina from aluminum *iso*propoxide. The line so obtained was parallel with the line representing the increase in reaction over colloidal alumina, within approximately the limits of experimental error.

The method of experimentation which has been used is not satisfactory for the investigation of the reaction at lower temperatures where the production of the alkene is less than a liter or two per hour and where, as Pease and Yung have shown, considerable amounts of ether are formed, at least in the case of ethyl alcohol. Ether has been noted in certain of the distillates obtained in this work.

Pease and Yung[3] observed that their alumina catalyst produced a higher proportion of ethylene, and a lower proportion of ether from ethyl alcohol after it had been used for the dehydration of pure ether. They felt that this observation reflected upon the validity of the hypothesis[4] that the variation in the relative amounts of carbon dioxide and ethylene in the decomposition of ethyl acetate over various aluminas was due to the modification in the spacial relationships of the active points of the catalyst. Their criticism is not valid for at least two reasons. The first of these is that Pease and Yung did not mean the same thing by "relative efficiency" as did the present author; they meant relative efficiency for successive steps in the same reaction, while he meant relative efficiency for distinct reactions.

It is unfortunate if papers from this Laboratory have ever given the impression that the author believed that the method used in the work on selective activation was the *only one* that could be used to modify the spacial relationship of the catalyst, or that such modifications were the only ones that effected relative catalytic action. It is well known that in the oxidation of ammonia the *surface* of the catalyst is characteristically modified by certain impurities. Langmuir[5] pointed out various cases where changes in catalytic activity are apparently due to modification of the arrangements of the atoms on the surface of the catalyst. Sabatier long ago supposed that the relatively short life of alumina, as compared with some other oxide catalysts, was due to the fact that aluminum atoms had so low an atomic weight that they were more readily pushed out of the relationships in which they could function catalytically.

Pease and Yung have pointed out that there has been no real evidence

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[4] Adkins, This Journal, **44**, 2175 (1922); **46**, 130 (1924).

[5] Langmuir, *Trans. Faraday Soc.*, **17**, 618 (1922).

as to whether alkenes were formed directly from the alcohols or through the intermediate formation of the ether. They say that while the direct formation of ethylene from alcohol is possible, this is an unwarranted assumption. Their conclusion is supported by the observation made in this Laboratory and published only a month before their paper appeared, to the effect that ethyl alcohol and ethyl ether give the same volume of ethylene per hour when passed over alumina at 400°. This fact, which so effectively disposes of the theory of catalysis that presupposes that the causation of the reaction is dependent upon selective adsorption of the products of the reaction, indicates that the rate of formation of ethylene from alcohol may very well be dependent upon the rate at which ethyl ether is dehydrated. It is now certain that the above conclusion is incorrect. Butyl alcohol gives about 2.5 liters more of butylene per hour than does butyl ether. The "temperature interval" for equal activity is 25–30° from butyl alcohol to butyl ether. That is, butyl ether cannot be an intermediate in the formation of any considerable amount of the butylene. Apparently, it is purely fortuitous that ether and ethyl alcohol give the same volume of ethylene per hour, for Bischoff[6] has shown that ethyl ether is much more stable over titania than is ethyl alcohol. In other words, all alcohols and their ethers do not have the same stability over alumina, and ethyl alcohol and ethyl ether do not have the same stability over catalysts other than alumina. From this and from other experimental work, the conclusion is certain that alkenes are not formed through the ethers, but directly from the alcohols.

The relative rates of the formation of alkenes from the corresponding acetates is quite different from that indicated above for their formation from the alcohols. Ethyl acetate gives 2300 cc. of ethylene, *n*-propyl acetate gives 3000 cc. of propylene and *n*-butyl acetate 3000 cc. of butylene per hour at 445° over 1 g. of alumina. (There are also formed at the same time 720, 660 and 600 cc. of carbon dioxide, respectively.) Thus it may be seen that the substitution of the acetyl group for the hydrogen of the alcohol has decreased the rate of formation of the alkene very much more in the case of ethanol than it has in the case of *n*-propanol or *n*-butanol. These facts are of fundamental importance in a consideration of the mechanism of the reactions.

The experimental methods were those previously described,[7] except that the alkene dissolved in the distillate of excess alcohol, ether or ester was boiled out at the end of the hour's run, and this added to the alkene already collected. Numerous determinations were made with each alcohol to obtain the increase in the rate of the alkene formation with rise in temperature. The results so obtained gave the slope of the lines representing

[6] Bischoff and Adkins, THIS JOURNAL, **47**, 810 (1925).

[7] Adkins and Nissen, *ibid.*, **46**, 130 (1924).

the variation in rate of reaction with variation in temperature. The relation of the lines to one another was then determined. In general it is not possible to load two samples of the catalyst into the reaction tube so as to obtain identical results. For example, one charge of alumina may cause the formation of 5 liters of ethylene, while another charge of catalyst may give 4.7 liters. The procedure adopted was to run ethanol over a catalyst for an hour or two, noting the activity of the catalyst, then its activity against butanol was determined, and then ethanol was used again to see whether the catalyst had changed in activity. By the repetition of this procedure, using the same sample of catalyst and also different samples of catalyst, the difference in the amount of butylene and ethylene formed per hour could be determined and the result duplicated repeatedly. The activity of each alcohol was thus compared with ethanol. Butyl ether was compared with *n*-butanol. The points indicated in the graph were duplicated with an accuracy of from 100 to 200 cc. of alkene per hour. Precautions were taken against error because of change in activity of the catalyst caused by aging or fouling.

The alcohols were dried over quicklime. The *iso*propanol and *sec.*-butanol (from the cracking of petroleum) were then fractionated many times. The former boiled at 81° to 81.5°, the latter from 98° to 99°. The ethanol (77°) propanol (97°) and *iso*butanol (107°) were the products of alcoholic fermentation. The *n*-butanol (116.5–118°) was produced by the fermentation of starch.

Summary

The relative rates of dehydration of ethanol, propanol, *iso*propanol, butanol, *iso*butanol and *sec.*-butanol over alumina have been investigated. In order to obtain equal activity it is necessary to carry out the dehydration of *iso*butanol 5°, propanol 8°, and butanol 19° higher than in the case of ethanol. *iso*Propanol shows an activity equal to *sec.*-butano at a temperature about 5° lower than the latter. The temperature interval for equal activity between *iso*propanol and ethanol is a function of the activity and is from 50° to 65° higher.

Alkenes are not formed from the alcohols to any great extent through the intermediate formation of an ether.

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