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

DEHYDROGENATION AND DEHYDRATION OF ALCOHOLS OVER A ZINC OXIDE CATALYST

BY WILBUR A. LAZIER AND HOMER ADKINS

RECEIVED MARCH 16, 1925 PUBLISHED JUNE 5, 1925

The relation of the structure of six alcohols, and of the temperature to the rate of reaction over a purely dehydrating catalyst (alumina) has been considered in a previous paper.[1] These same variables have now been studied with a zinc oxide catalyst. Zinc oxide is both a dehydrating and dehydrogenating catalyst, the proportion of the two reactions being partially dependent upon the method of preparation of the catalyst.[2] The present paper has to do with the variation of the rates of the two competing reactions with changes in temperature and with the alcohol used.

The sums of the volumes of hydrogen and alkene formed in one hour from various alcohols over 1 g. of a zinc oxide catalyst are shown in Fig. 1. A comparison of the data here presented with those previously given for the rates of reaction of the alcohols over alumina shows that the relative rates are similar, although the rate of reaction at any given temperature over the alumina catalyst was several times as great as that over the zinc oxide catalyst. In both cases *n*-butanol is the least reactive, while *iso*butanol and *n*-propanol are more reactive than *n*-butanol but less reactive than ethanol. The temperature interval for equal activity between ethanol and *n*-butanol is about 22° in the case of the zinc oxide catalyst, while it is 19° over alumina. The secondary alcohols react much more rapidly than the primary alcohols. The temperature interval for equal activity between ethanol and *iso*propanol over the zinc oxide is from 50° to 70° depending upon the activity, while in the case of alumina it is from 50° to 65°. With both catalysts, rise in temperature causes a more rapid increase in rate of reaction in the case of the secondary alcohols than with the primary alcohols.

The chief point of interest in this work was the comparison of the effect of the structure of the alcohol upon the relative rates of dehydration and dehydrogenation. From these observations it is hoped that it will be possible to draw some conclusions with regard to the lability of hydroxyl groups and hydrogen atoms. The proportion of dehydration and dehydrogenation was constant over the whole temperature range studied in the case of the four primary alcohols. Ethanol gave 9.5% of ethylene and 90.5% of hydrogen, *n*-butanol 15% of butylene and 85% of hydrogen, *n*-propanol 16% of propylene and 84% of hydrogen and *iso*butanol 31.5% of butylene and 68.5% of hydrogen. The temperature of reaction has a

---

[1] Adkins and Perkins, THIS JOURNAL, **47**, 1163 (1925).

[2] Adkins and Lazier, *ibid.*, **46**, 2295 (1924).

marked effect upon the proportions of the two competing reactions in the case of the secondary alcohols. For *iso*propanol the values are: at 345°, 89% of propylene, 11% of hydrogen; at 394°, 80% of propylene, 20% of hydrogen; at 418°, 71% of propylene, 29% of hydrogen. For *sec*-butanol the percentages are: at 345°, 88% of butylene, 12% of hydrogen; at 377°, 79% of butylene, 21% of hydrogen; at 398°, 75% of butylene, 25% of hydrogen; at 418°, 73% of butylene and 27% of hydrogen.

An adequate discussion of the relation of the structure of an alcohol to its rates of dehydration and dehydrogenation would require precise information as to the rates of the reactions over a purely dehydrating catalyst (alumina), a mixed catalyst (zinc oxide) and a purely dehydrogenating catalyst (copper). The first two of these sets of data are now available to us and we intended to obtain the other data, but in consideration of the plans of W. G. Palmer,[3] we have postponed this work. Preliminary work indicated that the activity of *iso*propanol over a copper catalyst reduced by hydrogen was about as much more than that of ethanol over the same catalyst as it was when zinc oxide or alumina was used as catalyst.

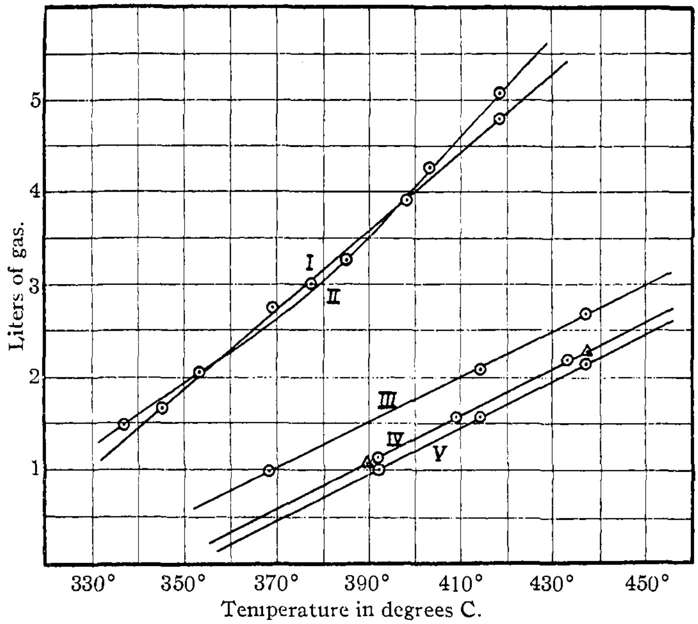

Fig. 1.—Reactivity of alcohols over zinc oxide. The liters of gas (hydrogen and alkene) at 740 mm. and 20° produced in one hour by 1 g. of a precipitated zinc oxide catalyst from various alcohols are plotted against the temperature of the catalyst. I, *sec*-Butanol: II. *iso*-Propanol: III. Ethanol; IV. *n*-Propanol. *iso*-Butanol; V. *n*-Butanol.

---

[3] Palmer and Constable, *Proc. Roy. Soc. London.* **106A,** 267 (1924).

It is evident from the data presented above that dehydration is slightly more rapid with respect to dehydrogenation in the case of propanol and butanol than it is in the case of ethanol. There is a very marked difference between *n*-butanol and *iso*butanol in the relative rates of dehydration and dehydrogenation over the zinc oxide catalyst. The reactivity is very similar but in the case of the straight-chain alcohol a little more than one-seventh of this is dehydration, while in the case of the branched-chain alcohol one-third of the amount of alcohol reacting goes to butylene. It is apparent that in the case of the two secondary alcohols, dehydration takes place with much greater speed with respect to dehydrogenation than it does in the ease of the corresponding primary alcohols. It has been demonstrated through the formation of the dibromides that the butylene formed from *n*-butanol is chiefly, at least, 1,2-butene, while that from *sec*-butanol is 2,3-butene.

The experimental method was essentially the same as previously described,[4] the alcohol vapors being passed through a heated Pyrex tube at such a rate that considerable excess condensed with the liquid products of reaction. A Gooch crucible disk was placed firmly in the catalyst tube and served as a permanent front boundary for the catalyst mass, thus insuring correct placing of successive charges. One g. of precipitated zinc hydroxide in the form of quartered tablets covered the disk in a single layer, and was held in place by a wad of glass wool. The method of preparation of the catalyst has already been described.[2]

The temperature of the furnace was controlled by a thermocouple placed in an indentation in the reaction tube while the temperatures recorded were determined by a couple imbedded in the catalyst mass. The cooling effect noted in this way varied from 5° to 30° and was greatest for the secondary alcohols. When a non-reactant such as benzene was passed over the catalyst, the inside temperature was the same as that outside the tube. The activity and percentage of alkene were found to be abnormally high during the first hour of use of the catalyst. but remained constant for several hours thereafter. All data reported were therefore taken after the catalyst had been in use at least an hour. Zinc oxide catalysts were found to age much more rapidly than alumina, and therefore frequent checks were made against previous runs to determine whether the catalyst had maintained its original activity. In one instance mercury was accidentally admitted to the reaction tube, but did not impair the activity of the catalyst. The gas produced in one hour was collected over salt water and the dissolved gases in the distillate were added by boiling the distillate under a reflux condenser. After mixing the gases, analyses of samples from the gas holder were made in duplicate. Although all zinc oxide catalysts thus far studied produce carbon dioxide from ethanol, less than 0.5% is produced by precipitated zinc oxide and it has been neglected in this work. An accuracy of 0.1 liter was attained in activity determinations and the gas analyses were easily checked to within 1%.

Summary

Ethanol, *n*-propanol, *iso*propanol, *n*-butanol, *sec*-butanol, and *iso*butanol show approximately the same relative reactivity over a zinc oxide catalyst that they do over an alumina catalyst.

The proportion of dehydration to dehydrogenation is apparently in-

---

[4] Adkins and Nissen, THIS JOURNAL, **46**, 140 (1924).

dependent of temperature in the case of the four primary alcohols, but is dependent upon the temperature in the case of the secondary alcohols.

Over the temperature range of about 340° to 440° the percentage of dehydration as compared to that of the total activity is as follows: ethanol, 10%; *n*-propanol, 16%; *iso*propanol, 88 to 73%; *n*-butanol, 15%; *iso*butanol, 31.5%; *sec*-butanol, 89 to 71%.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON HYDANTOINS. XLVI. NITROPYRUVIC UREIDE[1]

BY DAVID DAVIDSON

RECEIVED MARCH 16, 1925 PUBLISHED JUNE 5, 1925

In the course of the synthetic work in the hydantoin series now in progress in this Laboratory, one of the problems of immediate biochemical interest that has come up for solution is the development of a practical method of synthesizing the primary amine derivative of 5-methylhydantoin I. Nitropyruvic ureide II was suggested as a feasible starting point for the synthesis of this compound, but in order to determine the practicability of the method it was first necessary to acquire a better knowledge of the method of preparation, constitution, and properties of this nitro compound. This interesting substance was first prepared by Grimaux,[2] who has been the only investigator to study it, and who proposed for it the structure expressed by Formula III. The work of Fischer[3] and of Gabriel[4] on the bromopyruvic ureides has shown that these compounds are to be represented by Formulas IV and V and not by the tautomeric structures VI and VII. It is probable, therefore, that Formula II rather than Formula III represents the constitution of nitropyruvic ureide. Further evidence in support of this structure has been obtained by a study of its chemical behavior.

Nitropyruvic ureide II fails to give Victor Meyer's nitrolic acid test for primary nitro compounds.[5] This speaks against Grimaux's structure III which contains the primary nitro grouping —CH_2NO_2. When a solution of nitropyruvic ureide is boiled, the compound is rapidly hydrolyzed to nitromethane and parabanic acid VIII. This type of reaction is characteristic of the unsaturated grouping :$CHNO_2$, both in the aromatic and in

---

[1] Constructed from part of a dissertation presented by Mr. David Davidson to the Faculty of the Graduate School of Yale University, June, 1924, in candidacy for the degree of Doctor of Philosophy. (T. B. Johnson.)

[2] Grimaux, *Bull. soc. chim.*. (II) **23,** 49 (1875); *Ann. chim. phys.*, (V) **11,** 367 (1877).

[3] Fischer, *Ann.*, **239,** 185 (1887).

[4] Gabriel, *Ann.*, **348,** 50 (1906).

[5] Meyer and Jacobson, "Lehrbuch der Organischen Chemie," Veit and Co., Berlin and Leipzig, **1922,** I, part 1, p. 406.