

Anal. Calcd. for $C_2N_3Cl_2$: Cl, 37.2. Found: 37.7.

Cyanurdichloridazide is sparingly soluble in alcohol and insoluble in water. The usual tests showed the presence of an azide group.

In conclusion, the author wishes to extend his sincere thanks to Dr. Edward Curtis Franklin under whose guidance this work progressed.

Summary

1. The product previously known as cyanogen azide or carbon pernitride is shown to be dicyandiazide.

2. The azides studied are shown to be derived from the ammonio carbonic acid, cyanamide and its polymers.

3. Two general tests, which show the distinction between compounds containing azide groups and their isomeric tetrazoles are described and their application demonstrated.

4. The structure of cyanurtriazide containing three azide groups is confirmed, thus eliminating the tetrazole structures which the original investigator considered.

5. A tetrazole ring is opened, revealing the free azide group from which the original tetrazole was derived.

6. The following new compounds are described: (1) dicyanamidazide, (2) dicyanamidazide hydrochloride, (3) dicyanphenylamidazide, (4) sodium dicyanphenylamidazide, (5) phenyldicyandiamide, (6) dicyan- α -naphthylamidazide, (7) sodium dicyan- α -naphthylamidazide, (8) cyanuricamididazide and (9) cyanuridichloridazide.

BERKELEY, CALIFORNIA

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

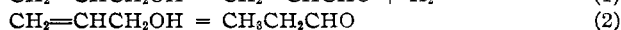
CATALYSIS IN THE CONVERSION OF ALLYL ALCOHOL AND ACROLEIN INTO PROPIONALDEHYDE

BY PAUL E. WESTON AND HOMER ADKINS

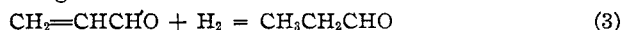
RECEIVED FEBRUARY 16, 1928

PUBLISHED JULY 6, 1928

F. H. Constable¹ concluded from a study of the rates of the reactions at different temperatures that allyl alcohol over copper showed two primary reactions



He demonstrated that propionaldehyde was not formed, as had previously been assumed, according to the reaction



For some time one of us has been greatly interested in those properties of oxide catalysts which determine the proportion of simultaneous and

¹ Constable, *Proc. Roy. Soc. (London)*, **A113**, 254 (1926).

competing reactions. In almost all of the cases previously studied in this Laboratory one of the competing reactions involved dehydration of the organic compound. It was therefore a matter of considerable interest to investigate the proportions of two reactions, one of which involved dehydrogenation and the other intramolecular rearrangement, over various catalysts whose characteristics had been previously studied for the reactions of saturated alcohols, esters, etc. The results of this investigation will shortly be submitted for publication, but in this communication we wish to present certain data bearing on the conversion of allyl alcohol and acrolein into propionaldehyde over a zinc oxide and an aluminum oxide catalyst.

The apparatus used in the experimental work is shown in Fig. 1. The method of introducing the alcohol was a modification of that designed by Paul E. Millington in this Laboratory. A constant head of water A, equivalent to 35 cm. of mercury, compressed air in the bottle B. The rate of flow of alcohol from the reservoir, G, through the fine

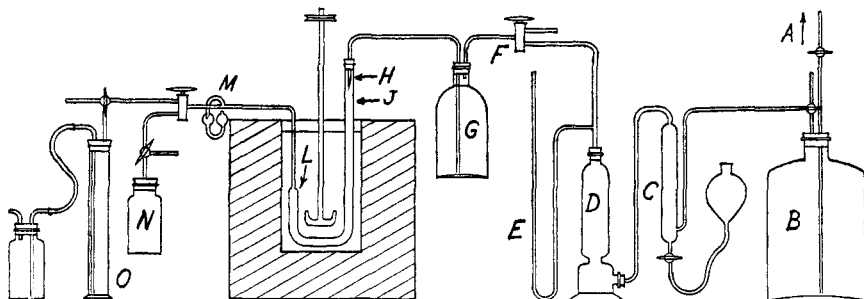


Fig. 1.—Apparatus for the study of the reactions of alcohols over solid catalysts.

capillary, H, could be varied slightly by regulating the pressure of the air by changing the depth of the mercury in C. D is a calcium chloride tower to dry the air and E is a manometer. The flow of alcohol could be stopped instantly by releasing the air pressure in the reservoir, G, through the stopcock, F. The limb, J, of the catalyst tube was 2 cm. in diameter and 33 cm. long. The exit tube was a capillary of 2 mm. bore. Six tenths of a cc. of the catalyst in the form of fragments of small pills was placed in a thin layer at L, on top of glass beads which filled the tube to the point J. The catalyst tube was immersed in an electrically heated bath of sodium and potassium nitrates, the temperature of which was kept constant at $330 \pm 3^\circ$ by means of a Leeds and Northrup potentiometer controller. At 400° considerable charring and side reactions took place but at 330° the amount of side reactions was small, as shown by the composition of the gaseous products.

The gaseous products of the reaction were collected over an aqueous solution of sodium bromide in the cylinder, O. Sufficient oxygen was added to make the volume 100 cc., and the gas was analyzed over water in an Orsat apparatus. The portion absorbed by potassium hydroxide is reported as carbon dioxide; that removed by bromine as unsaturated hydrocarbons. The hydrogen and carbon monoxide were determined by exploding the residue and measuring the contraction and subsequent absorption by potassium hydroxide. The composition of the gas was approximately 9% carbon dioxide, 6% unsaturated hydrocarbons, 80% hydrogen and 5% carbon monoxide.

The aldehydes formed in the reaction were determined by precipitation as the *p*-nitrophenyl hydrazones. Seventy cc. of a saturated solution of *p*-nitrophenyl hydrazine in normal hydrochloric acid was placed in a 250cc. wide-mouthed bottle, N, closed by a rubber stopper bearing a stopcock. Air was removed from the bottle till a pressure of 30 mm. of mercury was reached. The bottle was then attached to the exit of the catalyst tube and the stopcock opened enough to reduce the pressure in the tube (as indicated by the manometer, M) slightly below atmospheric pressure. After a sample had been collected, the stopcock was closed, the bottle shaken occasionally and allowed to stand for four hours. The hydrazone was collected in a Gooch crucible containing an asbestos mat, dried in a calcium chloride desiccator at 50° under reduced pressure and weighed.

The loaded catalyst tube was put in place in the bath and dry air was allowed to pass through it for one and one-half hours before admitting alcohol. Thirty minutes after the flow of alcohol had begun, an aldehyde sample was collected, then a gas sample which in turn was followed by another aldehyde sample, and so on till three gas samples and four aldehyde samples had been collected. Enough aldehyde was collected to give about 0.3 g. of hydrazone, which took from three to six minutes. Enough gas was collected to give about 15 cc. of hydrogen, which required from fifteen to thirty minutes. The allyl alcohol was prepared from formic acid and glycerin and dried by refluxing with potassium carbonate; b. p. 95.5–96.5° (corr.) at 745 mm.²

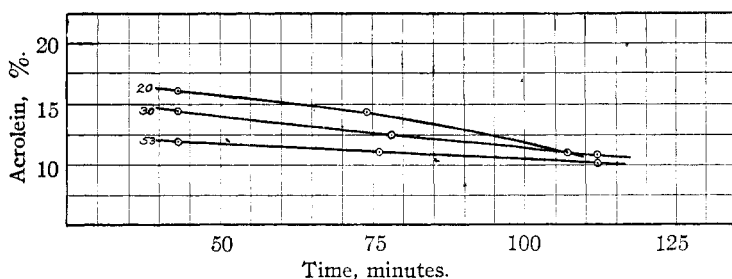


Fig. 2.—Variation in percentage of acrolein with rate of alcohol flow. The percentage of acrolein (ordinates) in the aldehydes produced is plotted against the time of sampling in minutes (abscissas) for three rates of allyl alcohol flow, namely, 20, 30 and 53 cc. per hour. The zinc oxide catalyst was formed by the thermal decomposition of zinc oxalate.

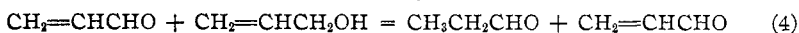
From the length of the interval for sampling the aldehyde and the weight of the hydrazone produced, the amount of hydrazone that would be formed per hour was calculated. This was plotted against the mean time during which the sample was collected, giving an activity curve as shown in Fig. 3. The weight of the hydrogen was calculated from the volume of hydrogen found in the gas analysis. Assuming a 96% conversion of acrolein to the hydrazone,¹ the weight of hydrazone formed was calculated and then the weight per hour. This value divided by the activity (from Fig. 3) at the mean time of collecting the gas sample gave the percentage of acrolein produced at that time. The three values obtained in one experiment were plotted as in Fig. 2.

It was observed in connection with other experiments that the pro-

² "Organic Syntheses," John Wiley and Sons, Inc., New York, 1921, Vol. I, p. 15.

portion of acrolein, as compared to propionaldehyde, was increased by decreasing the rate of passage of allyl alcohol over the catalyst. For example, in an experiment where the percentage of acrolein should have been about 14% with 30 cc. of alcohol per hour, the percentage of acrolein found was actually about 19% when the rate of alcohol flow had decreased to perhaps 15 cc. per hour. (A similar effect is of course produced by increasing the volume of the catalyst.) Following this casual observation, experiments were carried out in order to measure this effect. The results of these experiments are summarized in Fig. 2.

The decrease in proportion of acrolein with increased rate of passage of allyl alcohol suggested the possibility that propionaldehyde is formed through the reaction of acrolein and allyl alcohol



This possibility was not considered by Constable in his discussion of the reactions of allyl alcohol over copper. It cannot be eliminated as was the possibility that propionaldehyde resulted from the reaction of acrolein and hydrogen, for in this scheme acrolein is reproduced at exactly the same rate that it is consumed.

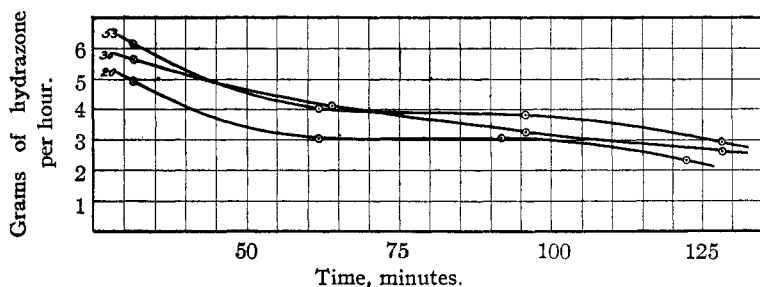


Fig. 3.—Variation of activity with rate of alcohol flow. The rate of hydrazone formation in g. per hour (ordinates) is plotted against the time of sampling expressed in minutes (abscissas) for three rates of alcohol flow.

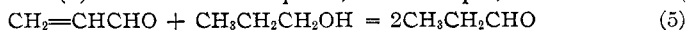
An increase in the rate of passage of the alcohol over the catalyst would favor reaction (4) because it would increase the probability that an allyl alcohol molecule would be adsorbed by the catalyst on a "point" or area adjacent to an adsorbed acrolein molecule *before* the latter was desorbed.

If propionaldehyde is formed according to reaction (4) then while the *proportion* of acrolein to propionaldehyde decreases with increasing rate of passage of allyl alcohol, the *amount* should remain constant and there should be an increased formation of propionaldehyde, that is, there should be an increase in activity as measured by the amount of hydrazone formation. This is seen to be true from a consideration of Fig. 3, where the highest rate of flow of alcohol gives the highest activity and the lowest rate of flow gives the lowest activity.

That the rate of formation of acrolein is approximately constant and is independent of the rate of flow of alcohol may be readily shown by a consideration of the data given in Figs. 2 and 3. In Fig. 3, the area under the curve between 40 and 110 minutes gives the total weight of hydrazone formed during that time interval at that rate of flow of alcohol. Thus at 53, 30 and 20 cc. per hour, the amounts of hydrazone formed are, respectively, 4.82 g., 4.58 g. and 3.67 g. In like manner the area under a curve in Fig. 2 divided by the length of time gives the mean percentage of acrolein formed during that interval. At rates of flow of allyl alcohol of 53, 30 and 20 cc. per hour, the mean percentages of acrolein are, respectively, 11.0, 12.8 and 14.0%. The product of the weight of hydrazone and the mean percentage of acrolein is the weight of hydrazone equivalent to acrolein. Since 96% of the hydrazone is precipitated, the weights of acrolein formed at rates of flow of alcohol of 53, 30 and 20 cc. per hour are, respectively, 0.16 g., 0.18 g. and 0.16 g. These values are identical within the limit of experimental error.

Furthermore, if reaction (4) takes place, then increasing the concentration of acrolein (as by adding it to the allyl alcohol passed over the catalyst) should increase the amount of propionaldehyde formed and should decrease the amount of acrolein formed over the catalyst. This point was tested experimentally by using allyl alcohol containing 5 cc. of acrolein per 100 cc. of alcohol at a rate of 53 cc. per hour. The weight of hydrazone equivalent to the weight of acrolein already present in the alcohol was subtracted from the total hydrazone found. The remainder was then used in the customary calculations. The percentage of acrolein with pure alcohol would be about 12% at forty-five minutes but with this allyl alcohol-acrolein solution it was only 6.7%. A second determination was made in which the value 6.7% was checked; then over the same catalyst pure alcohol was used and 9.3% of acrolein was obtained. At this time (117 minutes), using pure alcohol throughout, the acrolein would have been 10% of the total aldehyde formed. In another experiment in which a solution of 15 cc. of acrolein in 85 cc. of alcohol was used, 1.5% of acrolein was obtained at the end of forty-five minutes instead of the normal proportion of 12%. The activity in this case was abnormally high, 6.8 g. per hour. This indicated that an abnormally large amount of propionaldehyde was being produced.

The experimental evidence that propionaldehyde is formed through the reaction of acrolein and allyl alcohol would be strengthened if propionaldehyde could be formed under conditions in which the intramolecular rearrangement of reaction (2) could not take place, for example, as in reaction (5)



but *n*-propyl alcohol cannot be used over zinc oxide because it itself is dehydrogenated to propionaldehyde. However, over alumina this latter

reaction does not take place. Only traces of aldehyde were formed when *n*-propyl alcohol was passed over 0.6 cc. of an alumina at 330°. The flow of alcohol was then stopped and in its place over the same catalyst an approximately 10% solution of acrolein in *n*-propyl alcohol was used. The amount of aldehyde passed over the catalyst was equivalent to 8.7 g. of hydrazone per hour. At the end of seven minutes hydrazone was being produced at the rate of 12.0 g. per hour, at the end of twenty-five minutes the rate was 14.1 g. and at the end of forty-five minutes hydrazone was being produced at the rate of 13.4 g. per hour. There was thus being produced by the reaction of acrolein and *n*-propyl alcohol, aldehyde equivalent to 3.3 g., 5.4 g. and 4.7 g. of hydrazone per hour. These values correspond to a conversion of acrolein to propionaldehyde of 38, 62 and 54%, respectively. It is thus clearly established that *n*-propyl as well as allyl alcohol will reduce acrolein to propionaldehyde, and that the reaction takes place over alumina as well as over zinc oxide.

Constable showed that the hydrogenation of acrolein did not occur over copper, so it seems improbable that it should occur over the less active oxide catalysts. In the case of the reaction of acrolein and *n*-propyl alcohol over alumina there is no possibility of the hydrogenation of acrolein taking place, for alumina does not catalyze the formation of hydrogen from propyl alcohol. It is of course *possible* that a *part* of the propionaldehyde formed over zinc oxide from allyl alcohol results from intramolecular rearrangement or through some other mechanism.

Constable found that sintered copper gave a lower proportion of acrolein than did copper which was not sintered. He suggested that there were two sets of active points, one for each reaction, and that one set was destroyed to a greater extent than the other in the sintering. It is possible that sintering the copper simply reduced its activity, which is similar in effect to increasing the rate of flow of alcohol, and thus reduced the proportion of acrolein.

Summary

The behavior over a zinc oxide catalyst of allyl alcohol and mixtures of it with acrolein has been investigated as has also the reaction over alumina of acrolein and *n*-propyl alcohol. All of the experimental results indicate that the formation of propionaldehyde from allyl alcohol over zinc oxide results at least in part from the reaction of allyl alcohol with acrolein and not through the hydrogenation of acrolein nor through the intramolecular rearrangement of allyl alcohol.