

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## THE REACTIONS OF ACETALDEHYDE OVER ZINC CHROMITE UNDER A PRESSURE OF 210 ATMOSPHERES

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The formation of esters and the higher alcohols by the hydrogenation of carbon monoxide or from the lower alcohols under similar conditions may well depend upon the behavior of aldehydes which are first formed. It was thus of interest to ascertain the nature and ratio of products formed from acetaldehyde under the experimental conditions used for the reactions referred to above. A rather extensive study of the condensation of acetaldehyde over a zinc chromite catalyst at  $360^{\circ}$  under a pressure of 200 atmospheres of hydrogen has therefore been made.<sup>1</sup>

The zinc chromite catalyst used in this work was prepared in the same way as has been previously described for copper chromite,<sup>2</sup> except that a mole of zinc nitrate was substituted for a mole of copper nitrate. The general process used in preparing the zinc chromite catalyst was first described by Lazier.<sup>3</sup>

The liquid product from the reactions of acetaldehyde over the zinc chromite catalyst is a mixture of water and saturated and unsaturated alcohols, esters, aldehydes, lactones, hydrocarbons and acids. All attempts to separate this mixture into its components by fractionation were unsuccessful. On this account and because of the tendency for the unsaturated compounds to condense it was necessary to reduce the carbonyl and alkene linkages and to saponify the esters prior to further attempts for the isolation of pure compounds.

All of the significant findings in connection with these attempts to isolate, identify and estimate the products from the condensation of acetaldehyde over a zinc chromite catalyst may be illustrated by describing the results of a single experiment in which the methods used were the resultant of the experience in many similar experiments carried out on a smaller scale. In this experiment a mixture of two parts of acetaldehyde and one part of ethanol was pumped at the rate of 270 cc. per hour over 30 cc. (30 g.) of

<sup>1</sup> A paper having to do in part with material herewith presented was published in *Industrial and Engineering Chemistry*, **22**, 1046 (1930). The previous paper was prepared as an outline of an oral report given before a symposium at the Cincinnati (1930) meeting of the Society, and was not intended for publication. It was in proof before the authors were aware that it had been submitted to the Editor by the Secretary of the Symposium.

<sup>2</sup> Adkins and Connor, *THIS JOURNAL*, **53**, 1091 (1931).

<sup>3</sup> Lazier, British Patent 301,806, June 12, 1926; *Chem. Abstracts*, **23**, 4306 (1929); U. S. Patent 1,746,783, February 11, 1930; *Chem. Abstracts*, **24**, 1649 (1930).

pellets of zinc chromite in a steel bomb held at  $360 \pm 5^\circ$ , under a pressure of  $210 \pm 10$  atmospheres of hydrogen. The apparatus and procedure used for this purpose have been previously described.<sup>1</sup>

The general scheme followed in working up the reaction product was as follows. The reaction product weighing 4732 g. was fractionated giving fraction A (2941 g.), b. p. from 21 to  $85^\circ$ ; fraction B (762 g.), b. p. from  $85$  to  $170^\circ$ ; fraction C (519 g.), b. p.  $50$ – $160^\circ$  (2 mm.); and fraction D (419 g.), which was not distilled. Widmer fractionating columns with glass spirals were used for all fractionations except that a Claisen flask was used in obtaining fraction C. One of the Widmer columns had a spiral 50 cm. in length while the other contained a spiral 15 cm. in length. When necessary the columns were heated externally in a shield containing spirals of nichrome wire.

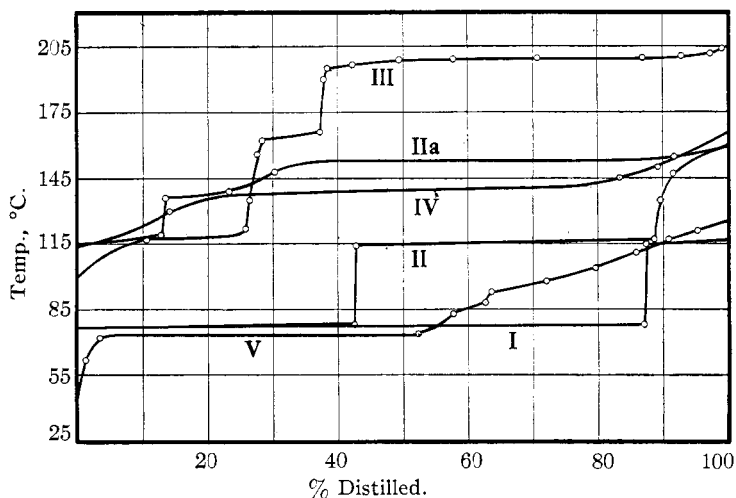


Fig. 1.—Distillation curves obtained in the fractionation of products from the condensation of acetaldehyde.

**Fraction A** contained 6 millimoles of aldehyde per gram according to the sodium sulfite method of analysis. An aliquot of 260 g. was hydrogenated at  $150$ – $175^\circ$  under a pressure of 150 atmospheres over a nickel catalyst by the method previously described.<sup>4</sup> Six millimoles of hydrogen per gram of fraction A was absorbed and the hydrogenated product contained 1.34 millimoles of ester per gram. The hydrogenated aliquot was saponified and the alcohols dried. These alcohols (203.7 g.) were fractionated with the result shown in Curve I of Fig. 1.

**Fraction B** was washed with a 5% sodium hydroxide solution in order to remove acids. The neutral compounds were recovered from the wash water by distillation and salting them out from the distillate. The neutral compounds so obtained were returned to fraction B which was hydrogenated after being partially dried over magnesium sulfate. The hydrogen absorption was 6.7 millimoles per gram and the ester content was

<sup>4</sup> Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

2.23 millimoles per gram. The fraction was then saponified and 246.7 g. of neutral compounds obtained. The fractionation of 211 g. of this material is shown in Curve II, there being a residue of 35.7 g. The portion boiling at 117–160° was refractionated as shown in Curve IIa. The acids originally washed out of fraction B were added to the acids obtained from the saponification and after drying over magnesium sulfate 117.6 g. of acids was obtained. The fractionation of 104.8 g. of acids is shown in Curve III, there being 12.8 g. of residue.

**Fraction C** upon hydrogenation absorbed 7.6 millimoles of hydrogen per gram. It had an average molecular weight of 195 as determined by the depression of the freezing point of benzene and contained 0.5 millimole of acids, 2.9 millimoles of esters and 1.3 millimoles of alcohols per gram. This latter value was calculated from the saponification value of the fraction as compared with the value after it had been acetylated through the use of acetic anhydride. Fraction C after hydrogenation was saponified and there was obtained after drying 237.7 g. of neutral compounds, and 112 g. of acids. The fractionation of 24.2 g. of the neutral compounds is shown in Curve IV of Fig. 1. The residue weighed 213.4 g. Ninety per cent. of the acids was taken for fractionation at 3 mm. Forty-six grams distilled as shown in Curve V, leaving a residue of 54.7 g.

**The Identification of Products.**—*Curve I.* This fraction was made up exclusively of ethanol and *n*-butanol, which were identified by the boiling points and by the preparation of the 3,5-dinitrobenzoates.

*Curve II.* The fractions boiling 77–78° and 115–116° were identified as ethanol and butanol as above. The fraction 117–160° was a mixture of butanol and hexanol which were refractionated as indicated below.

*Curve IIa.* The fraction 115–119° was butanol and that from 136–148° contained *p*-xylene and is referred to again under Curve IV. The main portion of this fraction (b. p. 148–154°) was identified as *n*-hexanol by comparing the melting point of its 3,5-dinitrobenzoate with that from an authentic sample of *n*-hexanol.

*Curve III.* The lower fraction was acetic acid, the middle one was butyric acid and the highest and chief fraction was caproic acid. These were identified by their boiling points and also by the preparation of the *p*-toluidide of acetic acid and *p*-bromoanilides of butyric and caproic acids, and the determination of mixed melting points with authentic specimens. However, the caproic acid was not pure, since a 1.000-g. sample at 25° required 8.26 ml. of 1 *N* alkali for its neutralization but when refluxed with an excess of alcoholic alkali 8.63 ml. of alkali reacted. From these data it may be calculated that the sample was 95.8% caproic acid and 4.2% a lactone having a saponification equivalent of 113.3. This value is almost identical (114) with that for caprolactone. The caproic acid fraction was shown to contain none of the isomeric diethylacetic acid by the following experiment. The *p*-bromoanilide of caproic acid, m. p. 103–104°, was obtained in a 60% yield from a sample of caproic acid of known purity, while a 61% yield of the derivative of m. p. 104–105° was obtained from the sample of acid referred to above. Recrystallization of these two preparations of the *p*-bromoanilide of caproic acid raised the melting points to 105–105.5° and reduced the yields to 55 and 58%, respectively.

*Curve IV.* The lower-boiling portions of this material was *n*-butanol while the highest was *n*-hexanol with perhaps some octyl alcohol. The chief fraction of 136–145° was identical with that indicated on Curve IIa and was shown to be *p*-xylene. This fraction after treatment with sodium and distillation had the following physical characteristics: b. p. 137–138°,  $n_D^{25}$  1.4910,  $d_4^{25}$  0.8595, mol. wt. by lowering of freezing point of benzene, 105.9, 100.5. The trinitro derivative after two recrystallizations melted at 138–140°, which was not changed when the unknown substance was mixed with the trinitro derivative of an authentic sample of *p*-xylene supplied by Dr. Carl S. Marvel.

*p*-Xylene has a molecular weight of 106 and has been described<sup>5</sup> as boiling at 137.5° and as having  $d_{20}^{25}$  0.8593. The trinitro-*p*-xylene is reported to melt at 138.5–139°. The identification of *p*-xylene in the reaction mixture was so unexpected that the whole experiment on the condensation of acetaldehyde was repeated on the same scale as before. *p*-Xylene was again obtained in a similar quantity, so that there can be no doubt as to its formation in these experiments. The fact that *p*-xylene did not undergo hydrogenation when fraction C was subjected to the action of nickel and hydrogen is due no doubt to the effect of water in the reaction mixture inhibiting the hydrogenation of the benzenoid ring.<sup>7</sup>

*Curve V.* About 79% of the material boiling 72–74° (3 mm.) was caproic acid as identified by its *p*-bromoanilide, mixed melting points being taken.

There remained to be identified the neutral compound boiling above 160° and the acids boiling above 205°. No specific compound except perhaps octyl alcohol has been identified among these mixtures so it is possible only to describe their general character. The neutral compounds boiling above 160° are mixtures of alcohols and hydrocarbons. This is indicated by the fact that the acetylation values are always greater than the average molecular weight as determined cryoscopically. Further, by the treatment of the mixtures with phthalic anhydride a residue was obtained which apparently contained no more than 4% of any alcohol, yet which had a boiling point of 55–75° (8 mm.), approximately the same as the alcohol mixture from which it was separated and an average molecular weight of 144. This residue was not entirely soluble in cold concentrated sulfuric acid. Attempts to separate these inert compounds completely from the alcohols by means of metallic sodium were uniformly unsuccessful. However, an alcohol boiling in the temperature range (190–191.5°) for *n*-octyl alcohol was obtained by the hydrolysis of the sodium alkoxides so obtained. The 3,5-dinitrobenzoate ester of this alcohol melted 4–7° lower than the ester of an authentic sample of *n*-octyl alcohol. The saponification equivalent of the acetate of this alcohol indicated a molecular weight of 184 as compared with a value of 172 for octyl acetate. Glycols were apparently absent from the neutral compounds for the saponification equivalent from the acetylated neutral compounds was always considerably more than the average molecular weight as determined by the cryoscopic method. A comparison of acetylation values obtained before and after hydrogenation indicated no increase in hydroxyl groups, so that aldehydes and ketones must have been absent from fraction C.

The acids of fraction C from the saponification of the esters always contained lactones or acyloxy acids after they had been subjected to distillation. This is evidenced by the fact that 25 to 50% more alkali was required for the neutralization of a sample of these fractions at 100° than was required at 25°. Further, it was found that after acetylation twice as much alkali was required to saponify a fraction at 100° as was required to titrate the sample at 25°.

There are given in Table I the weights of products calculated to be present in the reaction mixture after hydrogenation. For convenience in calculation and tabulation the assumption is made that acetic, butyric and caproic acids were in the form of ethyl esters, while the butyl, hexyl and higher alcohols were present as such. This assumption ignores the fact that in a mixture of acids, esters and alcohols, alcoholysis will occur so

<sup>5</sup> Perkin, *J. Chem. Soc.*, 69, 1193 (1876).

<sup>6</sup> Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, 1904, Vol. I, p. 202.

<sup>7</sup> Cf. Adkins, Zartman and Cramer, *THIS JOURNAL*, 53, 1425 (1931).

that all possible esters will be formed. The figures in Table I are calculated for the data given in Fig. 1, and elsewhere in this paper.

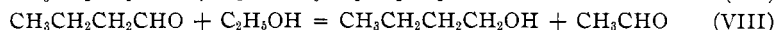
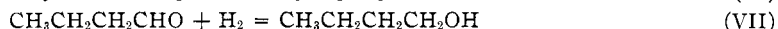
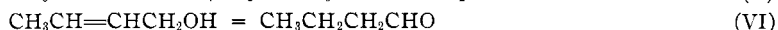
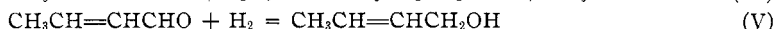
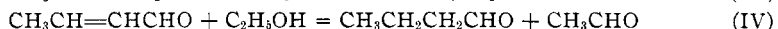
TABLE I  
THE WEIGHT OF THE PRODUCTS (G.) AFTER HYDROGENATION

Ethyl alcohol	1800	Higher alcohols	180
Ethyl alcohol (from acet- aldehyde)	593	Inerts (hydrocarbons)	77
Ethyl acetate	420	Ethyl butyrate	17
<i>n</i> -Butyl alcohol	456	Ethyl caproate	143
<i>n</i> -Hexyl alcohol	14	Higher acids and lactones	127
<i>p</i> -Xylene	19	Residue	419

**Hypothesis Concerning the Formation of Alcohols and Esters from Acetaldehyde.**—We are now in a position to consider the reactions by which alcohols and esters of higher molecular weight may be synthesized from acetaldehyde. The formation of ethyl acetate can hardly be explained except as a result of an autoxidation-reduction reaction (equation I) in which the zinc chromite plays the same role as the metallic alkoxide in the well-known Tischtschenko reaction.



The similar autoxidation-reduction of alcohols over oxide catalysts has recently been observed.<sup>8</sup> The formation of butanol and its possible precursors crotonyl alcohol, crotonic aldehyde and butyraldehyde, would result from a combination of the reactions shown in equations II to VIII, inclusive.



There is no direct evidence that reaction II occurs over oxide catalysts, but the aldol reaction is known to occur under such a wide variety of conditions that its tentative assumption seems justifiable. G. T. Morgan<sup>9</sup> has formulated the formation of the higher alcohols from carbon monoxide as depending upon the aldol reaction. The dehydration of an alcohol (equation III) has long been known to occur over a variety of oxide catalysts. Reaction IV was recently shown to take place over oxide catalysts<sup>10</sup> while reactions V and VII are hydrogenations of a type for which zinc

<sup>8</sup> Adkins and Folkers, *THIS JOURNAL*, **53**, 1420 (1931).

<sup>9</sup> Morgan, *Proc. Roy. Soc. (London)*, **127A**, 247 (1930).

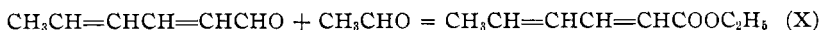
<sup>10</sup> Adkins and Weston, *THIS JOURNAL*, **51**, 2430 (1929).

chromite is quite active.<sup>11</sup> The occurrence of reaction VI in the case of allyl alcohol was also recently observed.<sup>12</sup>

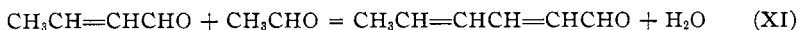
The formation of small amounts of butyrates (or crotonates) would be expected as the result of a reaction similar to equation I except that butyraldehyde or crotonic aldehyde played the role of acetaldehyde



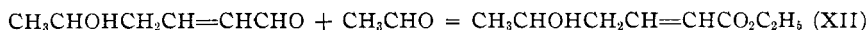
The formation of caproates (or their unsaturated precursors) can hardly occur exclusively as a result of a similar reaction, for the amount of hexyl alcohol in the reaction mixture is very much less than molecularly equivalent to the acid. This is not surprising in view of the great excess of acetaldehyde which would be present at any reaction surface and thus favor a reaction of the type indicated in equation X.



The formation of the hexadienal represented in equation X would result from a repetition of the aldol reaction followed by dehydration in which crotonaldehyde reacted with acetaldehyde as in equation XI.



Hydroxy acids as esters would result if a partly undehydrated aldol would react as in equation XII in a fashion similar to that indicated in equation X.



Esters of such hydroxy acids would readily give lactones as indicated in equation XIII.



Morgan in a discussion of the formation of higher alcohols and aldehydes from carbon monoxide and hydrogen states that "the aldolization hypothesis accounts for the products hitherto isolated, but it also postulates the transitory existence of intermediate hydroxyaldehydes and glycols which have not so far been detected." The detection in the present investigation of esters of hydroxy acids which would be derived from such hydroxy aldehydes thus lends strong support to the aldolization hypothesis.

The xylene was chiefly obtained from fraction C of the hydrogenated and saponified reaction mixture which boiled above 170°. It could not have been there as such because its boiling range (136–139°) is too low and *n*-hexanol, which boils higher (151–154°), was readily obtained from the fraction B boiling below 170°. That it was chiefly formed during the distillation of fraction C is further evidenced by the fact that water, which was not originally present in the mixture undergoing distillation, appeared

<sup>11</sup> Adkins and Connor, *THIS JOURNAL*, **53**, 1091 (1931).

<sup>12</sup> Constable, *Proc. Roy. Soc. (London)*, **113A**, 254 (1926); Adkins and Weston, *THIS JOURNAL*, **51**, 2430 (1929).

in the distillate. It is probable then that xylene resulted from the dehydration accompanied by cyclization of an unsaturated octyl alcohol or aldehyde.

### Summary

The reactions of acetaldehyde over a zinc chromite catalyst at  $360^{\circ}$  under a pressure of 210 atmospheres of hydrogen resulted in the formation of a complex mixture of saturated and unsaturated alcohols, aldehydes and esters. After hydrogenation of this product over nickel the following products were identified and estimated: *n*-butanol, *p*-xylene, *n*-hexanol and the esters of acetic, butyric and caproic acids. The chief components of the mixture were ethyl acetate, butyl acetate and ethyl caproate. There were also produced in considerable amounts higher alcohols, lactones, hydrocarbons and acids. The synthesis of these products may be accounted for as the result of aldol and Tischtschenko-like reactions accompanied by such dehydrations, hydrogenations, autoxidation-reductions and intramolecular rearrangements as have been demonstrated previously to occur over oxide catalysts.

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[CONTRIBUTION No. 71 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

## THE PREPARATION OF FLUORENONE FROM FLUORENE AND FROM DIPHENIC ACID

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In the extension of various studies in progress in this Laboratory<sup>1</sup> it became necessary to secure an adequate supply of fluorenone. Of the numerous reactions in which the formation of fluorenone has been noted, the most promising seemed to be the oxidation of fluorene. Since the published methods do not indicate the best results, we have studied the process in detail. Our results are expressed in the specific directions and accompanying notes in the Experimental Part.

During the course of the work, however, it was observed that fluorenone could be obtained in substantially quantitative yield merely by the action of heat upon diphenic acid. Since the latter is readily preparable from commercial anthranilic acid, this mode of formation of fluorenone has the advantage of starting with conventional intermediates. Careful search of the literature yielded no reference to the action of heat alone upon diphenic acid save the statement<sup>2</sup> that when heated  $10^{\circ}$  above its melting point, (*i. e.*, at  $238^{\circ}$ ) for half an hour, no diphenic anhydride was isolated. The

<sup>1</sup> Moore and Huntress, *THIS JOURNAL*, **49**, 1324-1334, 2618-2624 (1927).

<sup>2</sup> Underwood and Kochmann, *ibid.*, **45**, 3071-7 (1923).