The rate of hydrogenation of acetone over copper chromite is very much more rapid at higher pressures. With an average pressure of 35 atmospheres the hydrogenation of 1.73 moles with 1 g. of catalyst had proceeded to the extent of only 17% in thirty minutes, while at a pressure of 148 atmospheres 60% of the acetone was hydrogenated, while at 212 atmospheres the reaction was 95% complete in the same length of time. At the end of one hour the percentage of hydrogenation was 22, 92 and 100% for the three pressures given above. The rate of hydrogenation at the lowest pressure was practically a linear function of the time.

Zinc chromite has also been used as a catalyst for hydrogenation but it is much less active than copper chromite and has been found to catalyze condensation. For example, 58 g. of acetone with zinc chromite required a temperature of 200° for a reasonable rate of hydrogenation (five and one-half hours) with 7.5 g. of catalyst and there was found almost one half as much mesityl oxide as propanol-2. Similarly, seven hours did not suffice for the complete hydrogenation of 75 g. of benzaldehyde and a condensation product, benzyl benzoate, was formed in considerable amount.

Summary

A new catalyst (copper chromite) has been tested in the hydrogenation of a group of twenty-one organic compounds in the liquid state. It has been shown to be quite superior in several respects to any catalyst hitherto used.

Madison, Wisconsin

[A Communication from the Laboratory of Organic Chemistry of the University of Wisconsin]

THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS

By Homer Adkins and Karl Folkers

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The only general method which has been used for the reduction of esters to the corresponding primary alcohols has been that involving the use of sodium and alcohol. This process was originated by Bouveault and Blanc[1] and in its various modifications has been used in the transformation of a large variety of acids, through their esters, to the corresponding primary alcohols. This reaction, however, leaves much to be desired in many cases because of low yields, difficulties of operation, and undesirable side reactions. In view of the importance of this reaction, a search for a catalyst and experimental conditions under which the reduction could be brought about by the use of hydrogen has been in progress for some time in this Laboratory. Recently this search has been successful and a method

[1] Bouveault and Blanc, *Bull. soc. chim.*, [3] **31**, 666 (1904).

is now available whereby various types of esters may be directly hydrogenated, as indicated in Equation 1, to the corresponding alcohols in excellent yields.

$$RCOOC_2H_5 + 2H_2 = RCH_2OH + C_2H_5OH \qquad (1)$$

The experimental methods and apparatus used in this study were the same as those previously described.[2] The catalyst, "copper chromite," was prepared as described in the preceding paper.[3]

The data on the hydrogenation of seven esters are recorded in Table I. The hydrogen pressure during the hydrogenations approximated 220 atmospheres and the temperature was 250°. The products from all the hydrogenations were subjected to fractional distillation through a Widmer column in order to separate the desired alcohol from the accompanying ethanol. In the case of ethyl valerate and ethyl cinnamate there was 1.4 and 4.5% of unreduced ester in the respective reaction mixture after hydrogenation, but in no other case was there any residual ester. The hydrogen absorption, as measured in each case, was from 0.03 to 0.07 mole of hydrogen above that required for the hydrogenation of the ester. This discrepancy was probably due to the diffusion of hydrogen through the walls of the bomb. The yields of alcohols given are those actually obtained, having the indicated boiling or melting point, except in the case of *n*-amyl alcohol, where two applications of catalyst were necessary and there was a mechanical loss. Allowance was made for the weight of product so lost in calculating the yield given in the table for this alcohol.

TABLE I

HYDROGENATION OF ESTERS

Ester		Catalyst,	Time,		
Name	Mole	g.	hrs.	Yield, %	Alcohol
Ethyl laurate	0.13	3	1.8	97.5	Lauryl (m. p. 24°)
Ethyl myristate	.15	5	2.0	98.5	Myristyl (m. p. 37.5–38°)
Ethyl valerate	.27	5	13.0	(94.1)	*n*-Amyl (b. p. 135–136.5°)
Ethyl cinnamate	.21	3	9	83.1	Phenylpropyl (b. p. 111–12, 8 mm.)
Ethyl trimethylacetate	.23	5	1.5	88.3	*Tert.*-butylcarbinol (b. p. 111–111.5, 738 mm.)
Ethyl succinate	.44	7	6.5	80.5	Tetramethyleneglycol (b. p. 106, 3.5 mm.)
Ethyl 2,2-dimethyl-3-hydroxybutyrate	.21	4	0.1	98.0	Isobutyl (b. p. 106–107.5°)

It seems unnecessary to add anything to the results given in the table for the seven esters except to point out that ethyl 2,2-dimethyl-3-hydroxybutyrate during hydrogenation underwent cleavage between the 2 and 3

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[2] Adkins and Cramer, THIS JOURNAL, **52,** 4349 (1930).

[3] Adkins and Connor, *ibid.*, **53,** 1091 (1931).

carbon atoms with the formation of two molecules of ethyl and one molecule of isobutyl alcohol as shown in Equation 2.

$$CH_3CHOHC(CH_3)_2COOC_2H_5 + 3H_2 = 2CH_3CH_2OH + (CH_3)_2CHCH_2OH \qquad (2)$$

Unsuccessful attempts were made to hydrogenate malonic and phenylacetic esters. Both of these esters reduced the catalyst so that it was inactive for the hydrogenation of esters. It is hoped that work now in progress will make it feasible to reduce such esters.

Other catalysts for the hydrogenation of esters have been used in this Laboratory but none of them have proved as effective as copper chromite. For example, the nickel catalyst obtained by reducing nickel chromite catalyzed the hydrogenation of ethyl laurate to the extent of only 40% after seven hours at 250°.

Summary

Ethyl laurate, myristate, valerate, cinnamate, trimethylacetate and succinate have been hydrogenated over a copper chromite catalyst with the formation of the corresponding alcohols in yields of from 80 to 98%. The carbethoxy group in 2,2-dimethyl-3-hydroxybutyrate was hydrogenated to a carbinol group, and in addition the molecule underwent cleavage between the 2 and 3 carbon atoms.

Madison, Wisconsin

[Contribution from the Chemical Laboratories of Columbia University, No. 651]

STUDIES ON π-CAMPHOR DERIVATIVES. II. THE IDENTITY OF DIHYDRO-TERESANTALIC ACID WITH 7-π-APOCAMPHAN-CARBOXYLIC ACID

By Torsten Hasselström

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In a previous paper the complete synthesis of 7-π-apocamphancarboxylic acid has been reported.[1] The present investigation was undertaken in order to prove the identity of this acid with dihydro-teresantalic acid. The preparation of dihydro-teresantalic acid itself was accomplished by new methods which furnish further evidence of the structure of the π-camphor derivatives.

By adding hydrogen chloride to teresantalic acid the trimethylene ring is opened and chlorodihydro-teresantalic acid formed.[2] This action of hydrogen chloride, however, does not yield a homogeneous product.[3] Rupe and Tomi[4] have investigated the action of hydrogen chloride on the methyl ester of teresantalic acid and found that two different chlorodi-

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[1] Hasselström, *Ann. Acad. Fenn.*, **30**, 12 (1929).

[2] Muller, *Arch. Pharm.*, **238**, 366 (1900).

[3] Semmler and Bartelt, *Ber.*, **40**, 3140 (1907).

[4] Rupe and Tomi, *ibid.*, **49**, 2563 (1916).