

amounts of the hydrocarbon and picric acid according to the Beckmann method. The picrates were also prepared from a solution of the hydrocarbon and picric acid in boiling alcohol, and their physical properties were compared with the physical properties of the picrates prepared according to the Beckmann method. The colors and melting points of the corresponding picrates were found to be identical.

Although the melting points of the β -naphthalene derivatives are higher than those of the α -naphthalene derivatives, the β -naphthalene picrates have a lower melting point than the corresponding α -naphthalene picrates.

Summary

The addition of hydroxyl groups to benzene picrate lowers the melting point and deepens the color of the picrate formed. The addition of methyl groups to benzene picrate raises the melting point of the product and deepens the color of the picrate less than the hydroxyl group. The addition of methyl groups to a side chain of benzene picrate gradually increases the melting point and deepens the color of the picrate, and this increase is more rapid than when a corresponding number of methyl groups are substituted in the ring. The symmetrical trihydroxy- and trimethylbenzene picrates are the darkest, and the color of the picrates becomes lighter as we approach the 1,2,3-derivatives. The same deepening in color was obtained with the methyl derivatives of naphthalene. The β -naphthalene picrates possess lower melting points than the α -naphthalene picrates. Unsaturation in the side chain yields a very unstable picrate. The heavier the molecule the deeper the color of the picrate.

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

THE CATALYTIC HYDROGENATION OF ORGANIC COMPOUNDS OVER COPPER CHROMITE

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Nickel has been the only base metal catalyst which has offered much promise for the hydrogenation of pure organic compounds in the liquid phase, although several oxides and mixtures of oxides have been used for the hydrogenation of carbon monoxide in the gas phase at temperatures above 300°. In connection with a study of the action of some of these oxides in inducing the condensation of acetaldehyde at 360°,¹ it seemed advisable to investigate them with respect to their efficiency for catalyzing hydrogenations in the liquid phase. This latter study has resulted in the discovery that a combination of copper and chromium (oxides) is in many

¹ Adkins, Kinsey and Folkers, *Ind. Eng. Chem.*, 22, 1046 (1930).

ways very much superior to any catalyst known to the authors for the hydrogenation of several types of organic compounds.

The catalyst used in this investigation was prepared by decomposing copper ammonium chromate. This procedure is described for the preparation of catalysts containing a "hydrogenating metal" and chromium by Lazier.² The examples cited in the patents involve the use of the catalysts zinc and manganese chromite for the reaction of carbon monoxide and hydrogen in the vapor phase at 300 atmospheres and 400° to form methanol and higher alcohols.

Preparation of Catalyst.—Ammonium hydroxide was added to a solution of 126 g. (0.5 mole) of ammonium dichromate (Mallinckrodt) in 500 ml. of water until the color of the solution changed from orange to yellow. The volume of the solution was now 650 ml. The solution was allowed to come to room temperature and a solution of 241.6 g. (1.0 mole) of cupric nitrate trihydrate (Mallinckrodt) in 300 ml. of water was added with stirring. The red-brown precipitate was filtered with suction and dried overnight in an oven at 100–110°. It was then finely powdered, transferred to a porcelain casserole, and decomposed by heating the casserole in the flame of a Bunsen burner. After decomposition had begun, the heat of reaction was sufficient almost completely to decompose the chromate. When spontaneous decomposition had ceased, the casserole was heated with the free flame until fumes ceased to be evolved and the contents was black and so finely powdered as to be almost like a liquid. During this heating, care was taken to keep the material well stirred and to rotate the flame in order to avoid local superheating. The product was allowed to cool and then suspended in 200 ml. of a 10% solution of acetic acid. The suspension was filtered with suction, washed thoroughly with water, dried for twelve hours in an oven at 100–110°, and finely powdered. The yield of catalyst was 113 g.

Experimental Results.—There is recorded in Table I a summary of the data obtained in hydrogenating a representative list of 21 organic compounds. There are given in Columns 1, 2 and 3 the names and amounts of compound subjected to the action of hydrogen and the weight of catalyst. In five or six cases the amount of catalyst used (4 to 7 g.) is considerably in excess of that which it was necessary to use. These excessive amounts were used before the very great potency of the catalyst was realized. The temperature at which the temperature controller was set is given in the fourth column of the table. In the case of a majority of the compounds hydrogenation was so rapid and the reaction so exothermic that the temperature was for a few minutes as much as 15° above the recorded temperature. The time, if any, required for the hydrogenation after the contents of the bomb reached the designated temperature is given in column 5. The pressure of hydrogen during the hydrogenation was from 100 to 150 atmospheres. The yields of products given in the last column represent the amount of the indicated product when allowance was made for the mechanical losses in handling the reaction mixture. That is, a

² Lazier, British Patent 301,806, June 12, 1926; *Chem. Abstracts*, 23, 4306 (1929). U. S. Patent 1,746,783, Feb. 11, 1930; *Chem. Abstracts*, 24, 1649 (1930).

TABLE I
 HYDROGENATION OF VARIOUS COMPOUNDS OVER "COPPER CHROMITE"

Compound	Moles	Catalyst, g.	Temp., °C.	Time, hrs.	Product(s)	Yields, %
Acetone	1.73	1	150	0.7	Propanol-2	100
Pinacolone	2.05	5	150	1.3	2,2-Dimethylbutanol-3	100
Acetoacetic ester	0.77	4	175	0.3	Ethyl β -hydroxybutyrate	77
Acetoacetic ester	.38	1	150	3.0	Ethyl β -hydroxybutyrate	100
Ethyl α -methyl- β -ketovalerate	.18	1	175	2.0	Ethyl α -methyl- β -hydroxyvalerate	100
2-Methyl-2-hydroxypentanone-4	.41	3	150	0.1	2-Methyl-pentanediol-2,4	100
2-Methylpentanone-4	.39	1	150	2.5	2-Methylpentanol-4	100
Δ^2 -2-Methylpentanone-4	.51	2	175	7	2-Methylpentanol-4	100
Benzophenone	.27	7	175	1.0	Diphenylmethane	100
Benzoin	.18	1	175	2.0	Diphenylethane	100
Acetophenone	.42	1	150	0.5	Methylphenylcarbinol	100
Benzalacetone	.14	1	175	0.2	4-Phenylbutanol-2	100
Benzaldehyde	.71	7	180	0.0	Benzyl alcohol	92
Furfural	.78	3	150	2.0	Furfuryl alcohol	100
Furfuryl alcohol	.83	3	175	11.5	Pentane-diols-1,2 and -1,5	70
Nitrobenzene	.61	3	175	0.7	Aniline	100
<i>m</i> -Dinitrobenzene	.21	1	175	1.0	<i>m</i> -Phenylenediamine	70
Quinoline	.39	5	190	0.0	Tetrahydroquinoline	100
Pyridine	.63	5	220	9.0	Piperidine	50
Cinnamic acid	.24	2	175	0.3	β -Phenylpropionic acid	100
Cyclohexene	.50	3	165	0.0	Cyclohexane	100
N-Benzalaniline	.47	2	175	0.4	Phenylbenzylamine	100

100% yield means that no other product was formed in detectable amounts and that none of the original compound remained unhydrogenated. It has been demonstrated repeatedly that the mechanical losses can be reduced to 2% or less in this type of hydrogenation if precautions are taken to wash out the bomb, liner and filtered catalyst with a solvent.

Only five of the compounds referred to in Table I failed to give such quantitative hydrogenations. The yield of ethyl β -hydroxybutyrate was low (77%) when ethanol was not used as a solvent because of the formation of 16% of ethyl β -(β' -hydroxybutyryloxy)-butyrate and 7% of dehydroacetic acid.³ A hydrogenation of the acetoacetic ester in ethanol resulted in a quantitative formation of the corresponding β -hydroxy ester. Eight per cent. of toluene was formed in the hydrogenation of benzaldehyde, while there were some tar-like condensation products in the hydrogenation of *m*-nitrobenzene. Pyridine was completely hydrogenated, as indicated by the amount of hydrogen absorbed, but only 50% of it was recovered as piperidine, there being an equal amount of a condensation product b. p. 143.5–147.5° (3.5 mm.). Furfuryl alcohol gave only a 70% yield of pen-

³ Cf. Adkins, Connor and Cramer, THIS JOURNAL, 52, 5192 (1930).

tanediols, as there was a 10% yield of amyl alcohol along with some methyltetrahydrofuran and tetrahydrofurfuryl alcohol. The 70% yield of pentanediols was composed of 4 parts of the 1,2-glycol and 3 parts of the 1,5-glycol. Toluene, phenol, aniline, and furoic acid could not be hydrogenated under the conditions described in this paper for the hydrogenation of compounds referred to in Table I.

Discussion of Experimental Results.—Some of the characteristics of copper chromite in the catalysis of hydrogenation in the liquid phase may be described as follows. Numerous aldehydes and ketones may be quantitatively and rapidly hydrogenated to the corresponding alcohols. This holds true not only for aliphatic carbonyl compounds but also for aromatic ones, and for keto esters and a keto alcohol. A carbinol group adjacent to a benzenoid ring may be completely reduced. Nitro groups may be quantitatively converted to primary amines without the simultaneous formation of secondary amines. An alkene linkage in a hydrocarbon as well as in an acid or ketone may be hydrogenated without otherwise modifying the organic compound. Pyridinoid rings and carbon to nitrogen double bonds as in anils may be readily hydrogenated. The furanoid ring in furyl alcohol may be readily broken with the formation of 1,2- and 1,5-pentanediols in good yields. The copper chromite catalyst is not active toward cyanides or toward benzenoid nuclei and thus offers a means for the selective hydrogenation of compounds containing these groups which are so readily reducible over nickel catalysts.

The copper chromite catalyst possesses certain advantages over nickel catalysts. It is not nearly so sensitive as nickel to sulfur or halogen containing impurities in the compound to be hydrogenated. For example, the pinacolone, benzophenone, acetophenone and ethyl α -methyl- β -ketovalerate used for the hydrogenations referred to in Table I were of so poor a quality that they could not be hydrogenated over nickel. Its lesser sensitivity toward deactivation probably accounts for the fact that it is much more active after it has begun to act than is nickel despite the fact that nickel is active at lower temperatures. No special apparatus such as a reduction furnace is needed and the catalyst need not be freshly prepared before use. The catalyst ready for use does not change on standing in contact with air or moisture. In fact, it apparently need not be treated with any more care than would be accorded to such a reagent as sodium chloride. Less labor is involved in its preparation and smaller quantities may be used for reductions than is the case with the nickel catalyst. A sample of the catalyst may be used repeatedly, that is to say, it is not rapidly deactivated during use. The copper chromite catalyst is very much less active than is nickel toward carbinol groups adjacent to benzenoid rings so that it is more useful than nickel for the conversion of carbonyl groups adjacent to such a ring to the corresponding alcohol.

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.

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THE CATALYTIC HYDROGENATION OF ESTERS TO ALCOHOLS

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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 Blanc¹ 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).