

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY AND NORTHWESTERN UNIVERSITY]

Hydrogenation of Alkyl Phenyl Ketones in the Presence of Copper Alumina Catalysts

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The object of this investigation was to develop an active catalyst for the hydrogenation of ketones without hydrogenating the benzene nucleus, and to use this catalyst to compare the rates of hydrogenation of a number of *n*-alkyl phenyl ketones.

Copper-alumina catalysts were prepared by coprecipitation from the nitrates by ammonium carbonate followed by decomposition and reduction. The optimum copper-alumina concentrations were determined by measuring the time required for the complete hydrogenation of acetophenone to methylphenylcarbinol.

It was found that pure copper¹ prepared by the same method does not catalyze the hydrogenation of acetophenone below 260° under a hydrogen pressure of 164 atmospheres. However, a catalyst consisting of only 1% aluminum oxide and 99% copper oxide (on the unreduced basis) produces a rapid hydrogenation at 115° and 117 atmospheres pressure, yielding pure methylphenylcarbinol. The optimum alumina concentrations have been found to lie between 2.5 and 8% on the unreduced basis² (Fig. 1).

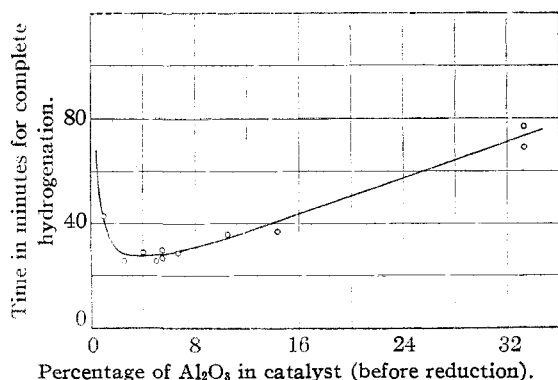
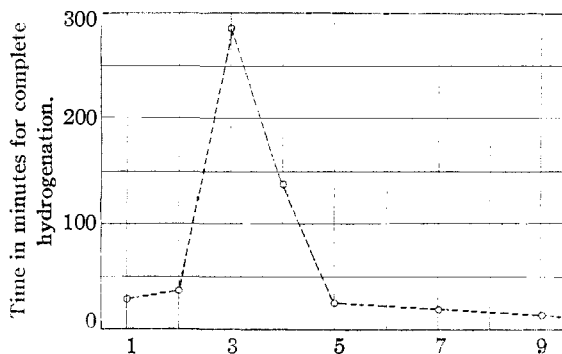


Fig. 1.—Hydrogenation of acetophenone to methylphenylcarbinol using copper-alumina catalysts: temp. 115–116°; initial hydrogen pressure 100 atm.; 50 cc. of acetophenone and 50 cc. of cyclohexane plus 5.3 g. of reduced catalyst.

(1) Ipatieff, Corson and Kurbatov [*J. Phys. Chem.*, **43**, 589 (1939)] showed that pure copper prepared by the above method does not hydrogenate benzene at ordinary pressure and 225°.

(2) Ipatieff and Corson, *ibid.*, **45**, 440 (1941), showed that the maximum activity for the hydrogenation of benzene by copper-alumina catalysts is exhibited when the alumina concentration is approximately 5% by weight.

A number of *n*-alkyl phenyl ketones were hydrogenated using a catalyst containing 4% alumina and 96% copper oxide prior to reduction. The product in all cases consisted of pure *n*-alkylphenylcarbinols with no trace of the cyclohexyl derivative. It was found that at a constant temperature of 115° and an initial hydrogen pressure of 100 atmospheres the rate of hydrogenation of various *n*-alkyl phenyl ketones depends to a considerable extent upon the number of carbon atoms in the alkyl chain (Table I and Fig. 2).



Number of carbon atoms in chain attached to C₆H₅CO—.

Fig. 2.—Rates of hydrogenation of *n*-alkyl phenyl ketones using a catalyst consisting of 4% Al₂O₃ and 96% CuO on the unreduced basis: temp. 115–116°; initial H₂ pressure 100 atm.; 50 cc. of ketone and 50 cc. of cyclohexane plus 5 g. of catalyst.

It will be observed that the hydrogenation becomes progressively more difficult from acetophenone to butyrophenone and less difficult from butyrophenone to nonyl phenyl ketone. The increased difficulty of hydrogenating butyrophenone and valerophenone may be explained to a certain extent by the possible existence of a hydrogen bond between the carbonyl oxygen and the terminal carbon atom. A similar hydrogen bonding effect has been used by Hurd and Blunck³ to explain variations in the decomposition characteristics of certain esters.

At higher temperatures (150–180°) the carbinols obtained at a lower temperature (115°) are readily hydrogenated in the presence of the copper-alumina catalysts to the corresponding *n*-alkylbenzenes. There was no indication of any

(3) Hurd and Blunck, *THIS JOURNAL*, **60**, 2419 (1938).

TABLE I
HYDROGENATION OF ALKYL ARYL KETONES IN THE PRESENCE OF 4% Al_2O_3 -96% CuO CATALYST
Temperature 115-116°. 100 Atms. Initial hydrogen pressure.

Expt.	Ketone	Temp. at which hydrogenation begins, °C.	Max. press. reached, atm.	Max. rate of press. drop, atm./min.	Time for drop from max. to const. press., min.	Product
1	$\text{C}_6\text{H}_5\text{COCH}_3$	90	116.5	0.89	29	$\text{C}_6\text{H}_5\text{CHOHCH}_3$
2	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$	101	118.0	.67	37	$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_3$
3	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_3$	110	122.5	.10	286	$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_2\text{CH}_3$
4	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	108	120.5	.13	138	$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
5	$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	92	117.5	.67	25	$\text{C}_6\text{H}_5\text{CHOHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
6	$\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_6\text{CH}_3$	94	116.0	.75	19	$\text{C}_6\text{H}_5\text{CHOH}(\text{CH}_2)_6\text{CH}_3$
7	$\text{C}_6\text{H}_5\text{CO}(\text{CH}_2)_8\text{CH}_3$	86	115.5	1.0	14	$\text{C}_6\text{H}_5\text{CHOH}(\text{CH}_2)_8\text{CH}_3$

TABLE II

Original compound	Formula	B. p., °C.	Hydrogenated product				
			n_D^{20}	C, calcd.	H, calcd.	C, found	H, found
$\text{C}_6\text{H}_5\text{COC}_2\text{H}_5$	$\text{C}_6\text{H}_5\text{CHOHC}_2\text{H}_5$	93 at 4 mm.	1.5208	79.37	8.89	78.90	8.55
$\text{C}_6\text{H}_5\text{COC}_4\text{H}_9$	$\text{C}_6\text{H}_5\text{CHOHC}_4\text{H}_9$	115 at 6 mm.	1.5078	80.45	9.80	81.00	9.80
$\text{C}_6\text{H}_5\text{COC}_6\text{H}_{11}$	$\text{C}_6\text{H}_5\text{CHOHC}_6\text{H}_{11}$	128 at 5 mm.	1.5105	80.86	10.18	81.14	9.71
$\text{C}_6\text{H}_5\text{COC}_7\text{H}_{15}$	$\text{C}_6\text{H}_5\text{CHOHC}_7\text{H}_{15}$	140 at 8 mm.	1.5010	81.48	10.75	82.17	10.18

hydrogenation of the benzene ring. The average yields of *n*-alkylbenzenes was 95-98%.

Experimental

All experiments were carried out in a glass liner in a rotating bomb of the Ipatieff type⁴ with a capacity of 850 cc. The hydrogenation was regarded as complete as soon as no further pressure drop was observed. All hydrogenations were carried out using an equal volume of cyclohexane as a solvent.

Catalyst Preparation.— $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in water and a solution of $(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$ was added rapidly to the agitated solution. After reaching the end-point, the precipitate was heated to 80° while stirred rapidly, following which the heating and stirring were discontinued. The cooled supernatant solution was decanted and the precipitate washed with water. This was followed by filtration and further washing. The catalyst was dried at 245° for ten hours. The catalyst was reduced in a stream of nitrogen and hydrogen (3:1) at 225° for one hour. Due to the high pyrophoricity of the catalyst it was transferred directly into a dish containing cyclohexane. The suspension in cyclohexane was then transferred into the bomb liner.

Determination of Catalyst Activity.—The rate of hydrogenation of acetophenone to methylphenylcarbinol was used to determine the catalyst activity. The reduced catalyst (5.3 g.), 50 cc. acetophenone (Eastman), and 50 cc. cyclohexane (Eastman) were used in these tests. Pres-

sure readings were taken every two minutes. The hydrogenated product was distilled and density measurements were made to determine the purity. In all cases it was found that no more than traces of ethylbenzene were obtained under the experimental conditions, 99% of the product being methylphenylcarbinol.

Hydrogenation of *n*-Alkyl Phenyl Ketones.—Acetophenone, propiophenone, butyrophenone and valerophenone were obtained from Eastman Kodak Co., while the higher *n*-alkyl phenyl ketones were kindly supplied by Dr. C. M. Suter of Northwestern University. The hydrogenations were carried out under the same conditions as those used for catalyst activity tests. At the low temperature of hydrogenation the products consisted almost completely of the corresponding *n*-alkylphenylcarbinols as determined by distillation. Table II shows the constants of the products.

Summary

Active copper-alumina catalysts have been prepared for the hydrogenation of ketones. The optimum catalyst composition is 2.5-8% Al_2O_3 and 97.5-92% CuO on the unreduced basis. Hydrogenation of a number of *n*-alkyl phenyl ketones at 115° showed that butyrophenone and valerophenone were more difficult to hydrogenate than any other *n*-alkyl phenyl ketone. At higher temperatures (150-180°) the carbinols can be converted readily to the corresponding alkyl benzenes using the same copper-alumina catalysts.

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(4) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, 1936, pp. 31-32 and p. 359(1).