76. *Catalytic Reduction by Formic Acid under Pressure. Part II. A Comparison of Copper and Nickel as Catalysts.*

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Copper, when used as catalyst in conjunction with formic acid, promotes non-nuclear reduction exclusively; *e.g.*, benzaldehyde, benzoic acid, and nitrobenzene are reduced to benzyl alcohol and toluene, to benzene, and to aniline, respectively. Nickel, however, promotes nuclear reduction, *e.g.*, nitrobenzene and phenol are reduced to *cyclo*hexylamine and *cyclo*hexanol, respectively.

Sabatier and Mailhe (*Compt. rend.*, 1910, **151**, 492) found that reduced copper and nickel promoted the decomposition of formic acid into hydrogen and carbon dioxide, and we have adapted this discovery to reductions by formic acid in conjunction with copper or nickel in a sealed tube, and by means of the apparatus described in Part I (this vol., p. 85). *The method has proved of particular service for small-scale hydrogenations*, inasmuch as under sealed-tube conditions the exact amount of hydrogen for any individual hydrogenation may be included in the system as formic acid. It has been found, however, that by the use of copper as catalyst, the reductions of aromatic compounds appear to be exclusively non-nuclear for such typical substances as benzaldehyde, benzoic acid, and nitrobenzene, whereas with nickel as catalyst nuclear hydrogenation is promoted. The results are summarised below. Under identical conditions, benzaldehyde retains its side-chain carbon atom and is reduced to benzyl alcohol and toluene, whereas benzoic acid loses carbon dioxide to afford benzene. The method failed with 1 : 8-dinitronaphthalene, and with the dehydration of phenol to diphenyl ether with thoria as catalyst. Sabatier and Mailhe (*loc. cit.*) were probably successful with the latter dehydration because the water would be removed from the reaction zone as formed.

Compound hydrogenated.	Catalyst.	Maximum temp. of sealed tube.	Main product.
Benzaldehyde	Copper	200°	Benzyl alcohol and toluene
Benzoic acid	Copper	200	Benzene
Nitrobenzene	Copper	200	Aniline
Nitrobenzene	Nickel	200—220	*cycle*Hexylamine
Phenol	Nickel	200—220	*cyclo*Hexanol

Experimental.

Preparation of Catalysts.—Copper on kieselguhr. Kieselguhr (50 g.) was treated with boiling nitric acid (*d* 1·42), washed with boiling water, and impregnated with 10% aqueous cupric nitrate, followed by immersion in aqueous 2N-sodium hydroxide in amount just sufficient to give final alkalinity to brilliant-yellow paper. The kieselguhr was then removed, washed free from alkali, and dried at 100°. For the subsequent reduction with hydrogen at 300—360°, it was convenient to use the apparatus described in Part I (*loc. cit.*), with the plugs removed, and to pass the gas for an hour. The catalyst was prepared immediately before use.

Nickel catalyst. Kieselguhr (20 g.), pre-treated with nitric acid as above, was shaken for 15 mins. with a 10% aqueous solution of nickel sulphate (200 c.c.), filtered off, and immersed in water (200 c.c.), which was then rendered alkaline to brilliant-yellow paper with sodium carbonate. The kieselguhr was removed, washed free from sulphate and alkali with boiling water, dried at 100°, and reduced immediately before use by heating in a hard-glass tube at 300° for 3 hours in a stream of hydrogen.

Reduction Data.—Copper as catalyst. (i) Benzaldehyde (0·01 g.-mol.), formic acid (0·01 g.-mol.), and the copper-kieselguhr catalyst (1g .) were heated to 200° during 2 hours and maintained at 200° for 1 hour. The product was extracted with ether, washed with water, and dried, and the ether removed; the residual oil (0·92 g.) was redissolved in ether (50 c.c.) and then found to contain benzyl alcohol (*ca.* 56%, estimated by conversion into benzyl acetate), unchanged benzaldehyde (*ca.* 26%, estimated by titration with hydroxylamine hydrochloride; cf. Stillmann and Reed, *Perfume and Essential Oil Record*, 1932, 279), and toluene (*ca.* 18%).

(ii) Benzoic acid (0·01 g.-mol.), formic acid (0·02 g.-mol.), and the copper–kieselguhr catalyst (1 g.) were heated as above, all the aldehyde having then reacted and the product (0·82 g.) being mainly benzene.

(iii) Nitrobenzene (0·01 g.-mol.), formic acid (0·033 g.-mol.), and the copper–kieselguhr catalyst (1 g.) were heated as before. The contents of the tube were washed out with hot 2N-hydrochloric acid, and the solution analysed for aniline both by titration with standard sodium nitrite (Found : 0·0104 g.-mol.) and by diazotisation and coupling with R-salt, the excess of R-salt being estimated by titration with standard benzenediazonium chloride (Found : 0·0101 g.-mol.). The close correspondence between the two results indicated a yield of *ca.* 100% of aniline, with no hydrogenation of the ring. A repeat experiment with double the amount of formic acid gave identical results.

Nickel as catalyst. (i) Nitrobenzene (0·01 g.-mol.), formic acid (0·066 g.-mol.), and the freshly prepared nickel–kieselguhr catalyst (1 g.) were heated as in the foregoing experiments. After extraction of the tube contents with 2N-hydrochloric acid, the filtered extract was made alkaline to brilliant-yellow paper by aqueous sodium hydroxide, and the mixture extracted with ether. The products of two such experiments were combined, the ethereal extracts washed with water and dried with calcium chloride, and the ether removed; the residue of pale yellow oil (1·64 g.) had b. p. 135—137°/760 mm., $n_D^{20°}$ 1·4318 (Found : N, 14·2. Calc. for $C_6H_{13}N$: N, 14·1%). *cyclo*Hexylamine has b. p. 135—138° (Wallach, *Annalen*, 1905, **343**, 46), $n_D^{20°}$ 1·43176.

(ii) Phenol (0·1 g.-mol.), formic acid (0·33 g.-mol.), and the nickel catalyst (3 g.) were heated as above, and the apparatus allowed to cool to room temperature overnight. The contents of the tube were extracted with carbon tetrachloride (100 c.c.), the extract filtered, dried (calcium chloride), and distilled under 765 mm. After the carbon tetrachloride had passed over, the following fractions were collected : up to 155° (2·3 g.), 155—165° (5·2 g.), and 165—190° (3·4 g.). The middle fraction (Found : C, 71·8; H, 11·9. Calc. for $C_6H_{12}O$: C, 72·0; H, 12·0%) was mainly *cyclo*hexanol, and had $d_{4°}^{20°}$ 0·9568, $n_D^{26°}$ 1·4645 (*cyclo*hexanol has b. p. 161°, $d_{4°}^{20°}$ 0·9624, $n_D^{22°}$ 1·4650).

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