Intermediate Compounds in the Catalytic Reduction of Aromatic Nitro Compounds with Raney Nickel Catalyst[1]

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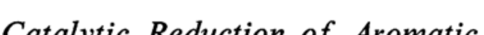
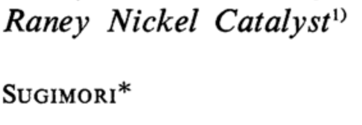
(Received June 21, 1960)

There have been some studies on the intermediate compounds in the catalytic reduction of nitro compounds with nickel catalysts. Scholnik, Reasenberg and Smith[2] reported that in the catalytic reduction of sodium *p*-nitrobenzoate with platinized Raney nickel hydrogen uptake stopped when 2 mol. of hydrogen was consumed (3 mol. of hydrogen is required for the complete reduction of a nitro compound to the corresponding primary amine). This would suggest the existence of an intermediate, but they found only the nitro compound and the *p*-aminobenzoate in the reduction product. Shmonina and Sokolski[3] reported that nitrosobenzene was formed as an intermediate in the catalytic reduction of nitrobenzene with Raney nickel.

The present author studied the partial reduction of aromatic nitro compounds with neutral Raney nickel. Contrary to the above reports, phenylhydroxylamine derivatives were identified as intermediates.

Nitrobenzene (0.01 mol.) was reduced in ethanol solution at 25°C under ordinary pressure with Raney nickel prepared by treating 1.00 g. of nickel-aluminum alloy (Ni, 40%) with 5 ml. of 20% aqueous sodium hydroxide at 50°C and by washing 10 times with cold water and twice with 20 ml. of ethanol. Shaking was stopped when 0.02 mol. of hydrogen was consumed, the catalyst was filtered off, and the filtrate was poured into 300 ml. of ice water. Light white crystals of phenylhydroxylamine were obtained and they were recrystallized from petroleum ether. The melting point was 76~78°C. Found: C, 66.20; H, 6.73. Calcd. for C_6H_7ON: C, 66.03; H, 6.47%. This unstable intermediate was easily converted into azoxybenzene on exposure to air according to the following equations:


(1)


(2)

Therefore, the yield of phenylhydroxylamine was calculated from that of azoxybenzene.

In the same way, the partial reduction of *p*-nitroanisole and of ethyl *p*-nitrobenzoate was carried out and the yields of hydroxylamines and amines were determined. The results are shown in Table I. Nitrobenzene and ethyl *p*-nitrobenzoate gave more hydroxylamines than *p*-nitroanisole.

This agrees with the analysis of the curves

TABLE I. THE PRODUCTS OF PARTIAL REDUCTION

Compound reduced	Yield of hydroxylamine, %	Yield of amine, %
Nitrobenzene	77	0
Ethyl *p*-nitrobenzoate	60	0
p-Nitroanisole	22	40

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[1] Cf. H. Debus and J. C. Jungers, *Bull. soc. chim. France*, **1959**, 785.

[2] S. Scholnik, J. R. Reasenberg, E. Lieber and G. Smith, *J. Am. Chem. Soc.*, **63**, 1192 (1941); J. R. Reasenberg, E. Lieber and G. Smith, ibid., **61**, 384 (1939).

[3] V. P. Shmonina and D. V. Sokolski, *Zhur. Obshchei Khim. S. S. S. R.*, **26**, 1759 (1956).

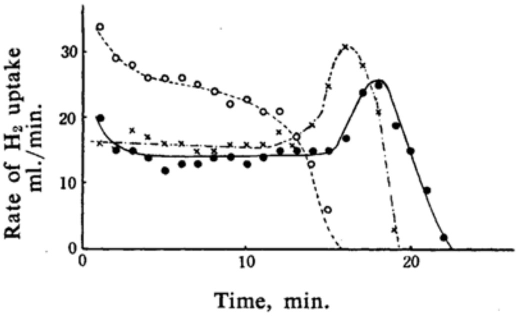

Fig. 1. Rate of Hydrogen uptake.
× Nitrobenzene.
○ *p*-Nitroanisole.
● Ethyl *p*-nitrobenzoate.

of the hydrogen consumption rates in the complete reduction to amines. As is shown in Fig. 1, the reduction rate of *p*-nitroanisole is monotonously decreasing, whereas those of nitrobenzene and ethyl *p*-nitrobenzoate have a remarkable increase towards the end of the reaction. It is likely that this increase in the rate takes place when the hydroxylamines are reduced to the amines. The fact that the hydroxylamines which have greater reduction rates than the parent nitro compounds were isolated as the intermediates in the partial reduction, can be understood from the difference in the affinities of the nitro compounds and hydroxylamines to the nickel catalyst. The nitro compounds with stronger affinities repel the hydroxylamines from the catalyst surface. And it can be said that the affinity difference is greater between nitrobenzene and phenylhydroxylamine and between ethyl *p*-nitrobenzoate (with an electron attracting group) and the corresponding hydroxylamine than between *p*-nitroanisole (with an electron repelling group) and its hydroxylamine. This agrees with the result[4] of the catalytic reduction of nitro compounds with a platinum catalyst.

Therefore, the following sequence of processes is presented:

$$\mathrm{ArNO_2} + \mathrm{Ni} \longrightarrow \mathrm{ArNO_2\text{-}Ni} \qquad (3)$$

$$\mathrm{ArNO_2\text{-}Ni} + 2\mathrm{H_2} \longrightarrow \mathrm{ArNHOH\text{-}Ni} + \mathrm{H_2O} \qquad (4)$$

$$\mathrm{ArNHOH\text{-}Ni}\ \begin{cases} \xrightarrow{\mathrm{H_2}} \mathrm{ArNH_2} + \mathrm{Ni} + \mathrm{H_2O} & (5) \\ \xrightarrow{\mathrm{ArNO_2}} \mathrm{ArNO_2\text{-}Ni} + \mathrm{ArNHOH} & (5') \end{cases}$$

$$\mathrm{ArNHOH} + \mathrm{Ni} \longrightarrow \mathrm{ArNHOH\text{-}Ni} \qquad (6)$$

$$\mathrm{ArNHOH\text{-}Ni} \xrightarrow{\mathrm{H_2}} \mathrm{ArNH_2} + \mathrm{Ni} + \mathrm{H_2O} \qquad (7)$$

where Ni means the active center of the nickel catalyst.

The author wishes to express his hearty thanks to Professor Y. Urushibara for his kind guidance and encouragement throughout this work. The author is also very grateful to Dr. M. Kobayashi and Dr. S. Nishimura for their kind discussion.

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[4] G. Cusmano, *Ann. chim. applicata*, **12**, 123 (1919), *Chem. Abstr.*, **14**, 1314 (1920).