

# Catalytic Action at High Temperatures and under High Pressure, II. Catalytic Hydrogenation of Aromatic Nitro-Compounds

By

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It is well known that aromatic nitro-compounds are reduced by Sabatier's method, in which reduced copper is used as catalyst, to the corresponding amino-compounds with almost theoretical yield.<sup>1</sup> By the use of reduced nickel instead of reduced copper in the Sabatier process, the aromatic nucleus is also hydrogenated in all cases, and nitrobenzene thus converted into cyclohexylamine with some dicyclohexylamine.<sup>2</sup> When, however, reduced nickel previously treated with thiophene, by which the catalyst is decreased in activity, is employed, nitrobenzene is reduced to aniline without hydrogenation of the nucleus.<sup>3</sup>

The fact that the nitro group in aromatic nitro-compounds is reduced to the amino group much more easily than the benzene nucleus suggests that partial reduction of aromatic nitro-compounds will take place in the presence of reduced nickel if the external conditions are regulated without changing the activity of the catalyst by the toxicity of a poison such as thiophene.

The authors thus considered that hydrogen at high temperature & under high pressure in the presence of the catalyst might be used effectively for reduction of the nitro group and also the hydrogenation

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1. C. R., 138, 226 (1902); 138, 457 (1904); Bull. Soc. Chim., 7, 270 (1910); Chem. Zent., I, 1926, 496; II, 1088; II (1927), 976.

2. P. Sabatier: La catalyse chimie organique (1920).

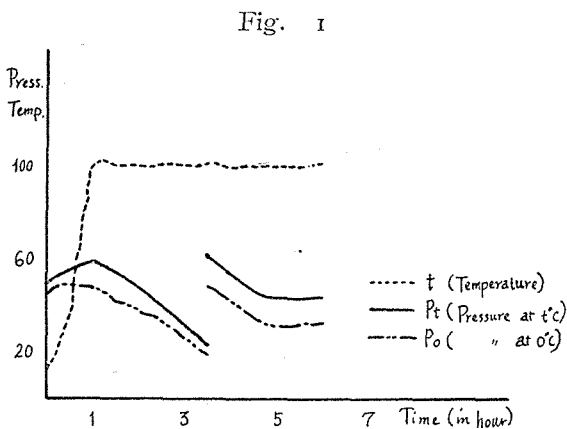
3. B. Kubota: Bull. Inst. phys. Chem. Res. Tokyo, 4, 356 (1925)

of the aromatic nucleus separately. The essential part of the process is similar to that of Ipatiew, and in the latter case, substances are hydrogenated in a liquid system, in the presence of nickel oxide with hydrogen under a pressure of at least 100 atmospheres.

In the experiments, pure nitro-compounds were treated in an autoclave of a capacity of 600 c.c., heated externally by electric resistance and mounted horizontally on a shaking machine, and the progress of the reaction was observed by watching the pressure change indicated on a manometer connected to the reaction vessel.

### 1. Nitro-benzene.

50 gms. of pure nitro benzene ( $d_4^{20} = 1.205$ ;  $n_D^{20} = 1.555$ ) with reduced nickel which had been previously reduced with hydrogen at  $280^\circ$  were placed with hydrogen in the autoclave & heated to  $100^\circ$  under a pressure of 50 atmospheres at  $15^\circ$ , and the reaction was completed with the absorption of 3.1 mols hydrogen in 3.5 hours. (Fig. 1) The product showed the constants ( $d_4^{20} = 1.019$ ;  $n_D^{20} = 1.579$ ) and was found to consist of aniline, which was confirmed after purification by distillation.



When the reduction was performed at a higher temperature, viz. at  $200^\circ$ , and a pressure of 100 atmospheres at  $15^\circ$ , the consumption of hydrogen was about 50 litres for 50 gms. of the sample, which corresponds to the theoretical value 6 mols for the complete reduction of nitrobenzene to cyclohexylamine. (Fig. 2)

The appearance and physical constants ( $d_4^{20} = 0.913$ ;  $n_D^{20} = 1.427$ ) of the reaction product being different from those of the former case, it was treated with  $\text{CO}_2$  first to separate cyclohexylamine B. p. ( $175-190$ )<sub>758</sub>,  $d_4^{20} = 1.023$ ;  $n_D^{20} = 1.585$  from dicyclohexylamine B. p. ( $145-148$ )<sub>30</sub>,  $d_4^{20} = 0.111$ ;  $n_D^{20} = 1.478$  and aniline, and the latter two substances were separated by fractional distillation. The purity of each of these substances,

separated in a pure state, was confirmed by determining the total nitrogen and the amino group by van Slyke's method.

The yield of aniline, cyclohexylamine and dicyclohexylamine was 5%, 78% and 7% respectively.

Fig. 2

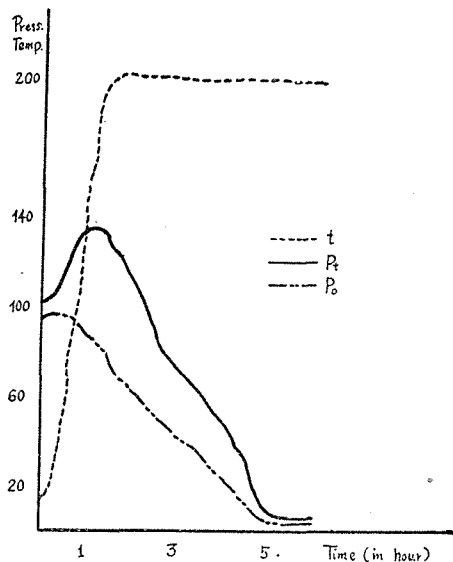
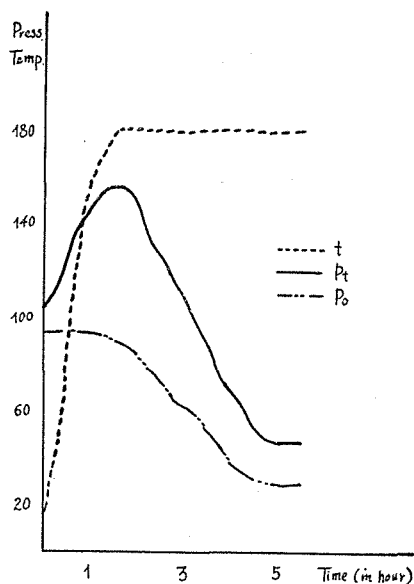
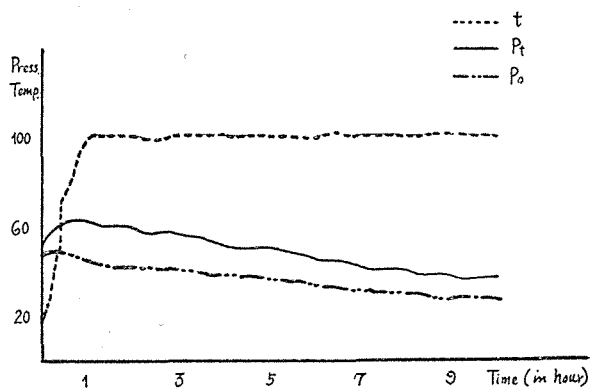


Fig. 3



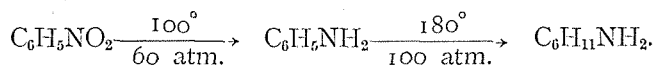
When aniline was treated in the presence of reduced nickel and hydrogen at  $180^\circ$  and 100 atmospheric pressures, the reaction was completed with absorption of 3 mols of hydrogen (Fig. 3) and the

Fig. 4



reaction product ( $d_4^{20}=0.864$ ;  $n_D^{20}=1.452$ ) consisted of aniline 4%, cyclohexylamine 81% & dicyclohexylamine 3%.

Thus, nitrobenzene, was converted by the catalytic reduction in the presence of reduced nickel at high temperature & pressure into aniline which was then converted into cyclohexylamine.



## 2. p-Nitro-phenol.

24 gms. of pure p-nitro-phenol (M.p.  $61^\circ$ ; B.p.  $304^\circ$ ) were heated to  $100^\circ$  under 50 (Fig. 4) and 100 atmospheric pressures (Fig. 5), the

Fig. 5

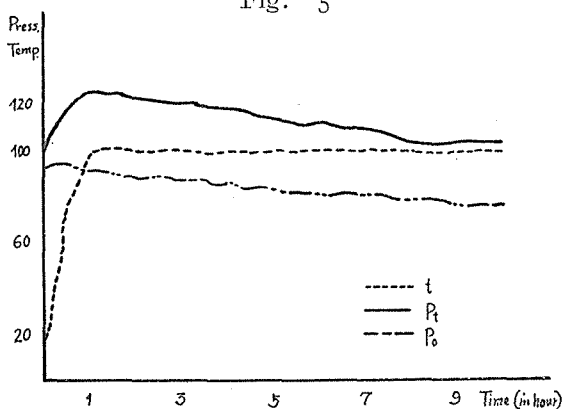
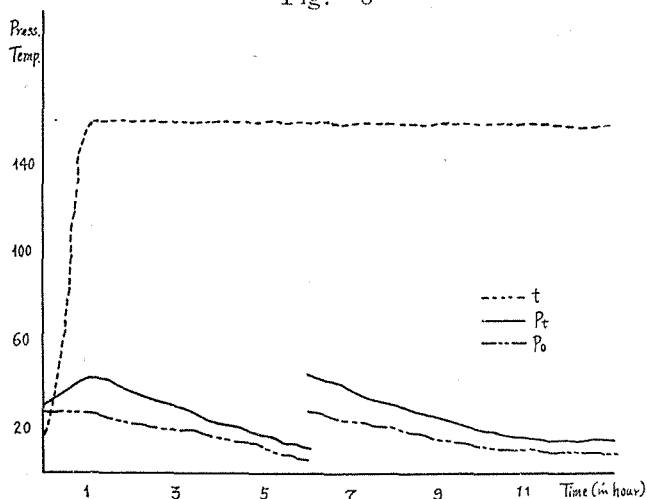


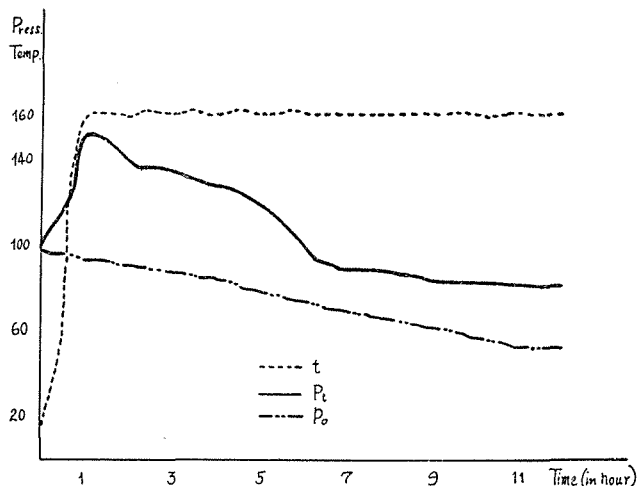
Fig. 6



nitro group was reduced completely with consumption of 3.1 mols of hydrogen, the theoretical value, and the product consisted of 14.2 gms. of p-aminophenol with about 5 gms. of water.

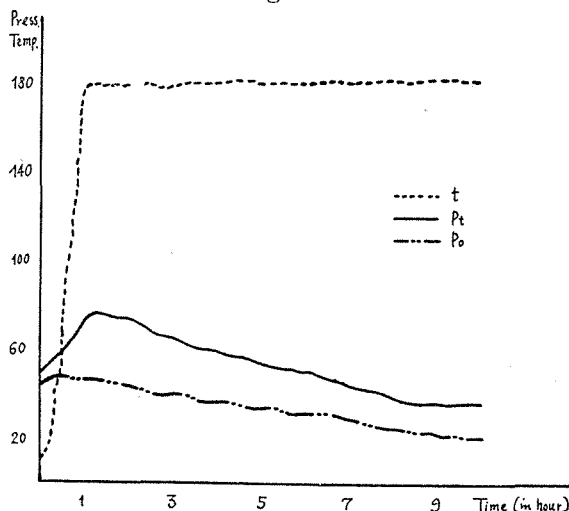
In the second experiment, 24 gms. of the sample were reduced at 160° and under 30 (Fig. 6) & 100 atmospheric pressures (Fig. 7)

Fig. 7



at 15°, the product being found to consist of 17.6 gms. p-oxy-cyclohexylamine, 0.7 gms. of p-aminophenol & 0.7 gms. of cyclohexanol

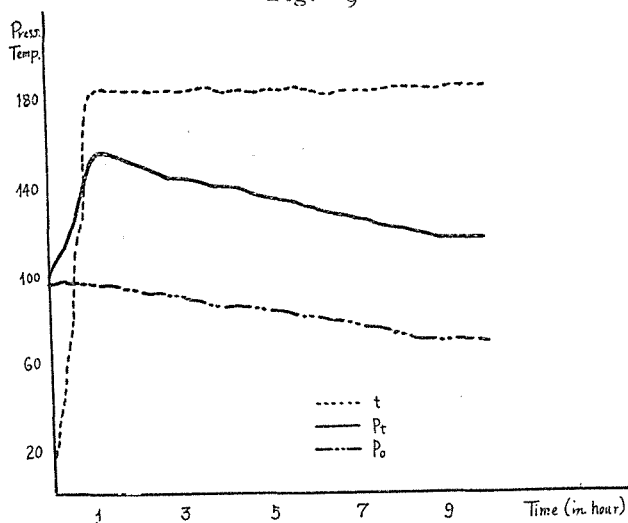
Fig. 8



with traces of cyclohexane and ammonia.

The reduction of p-amino-phenol to p-oxy-cyclohexylamine was performed under such conditions ( $180^{\circ}$ , 50 (Fig. 8) & 100 atmospheric pressures (Fig. 9) at  $15^{\circ}$ ), that the reaction products were similar

Fig. 9



qualitatively & quantitatively to those obtained in the second experiment.

## 2. $\alpha$ -Nitro-naphthalene.

The fact that the naphthalene ring is reduced with facility when compared with the benzene ring, is interesting in the partial reduction of  $\alpha$ -nitronaphthalene, since the gradient between the temperatures

Fig. 10

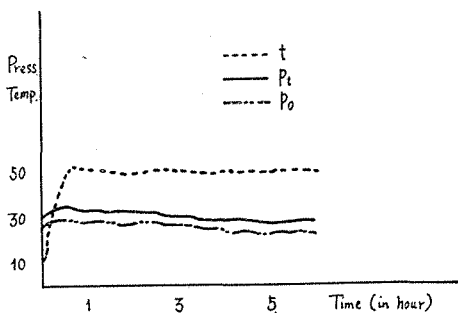
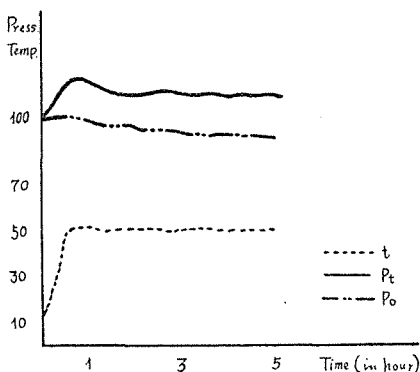


Fig. 11



required for reduction of the nitro group & the benzene nucleus in nitrobenzene should be diminished greatly in the case of nitronaphthalene.

9 gms. of pure nitronaphthalene, M.p.  $114^{\circ}$ , were reduced quantitatively at  $50^{\circ}$  & under 30 (Fig. 10) & 100 atmospheric pressures (Fig. 11) to naphthylamine, which was confirmed by its physical constants and determination of the total nitrogen by Kjeldahl's method.

When the reduction of nitronaphthalene was carried out at  $160^{\circ}$  and 30 (Fig. 12) or 78 atmospheric pressures (Fig. 13), the formation

Fig. 12

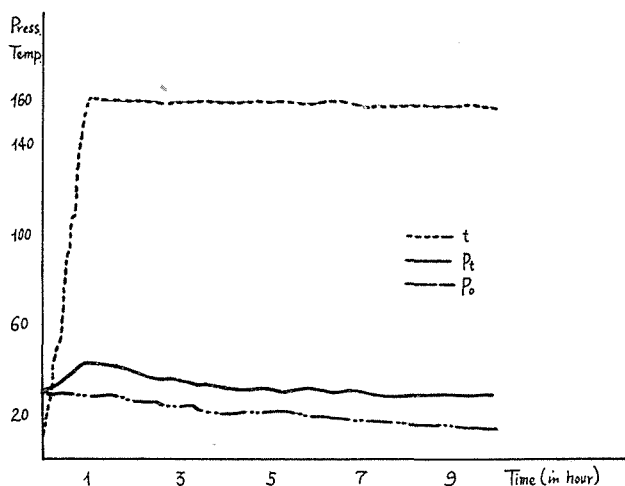
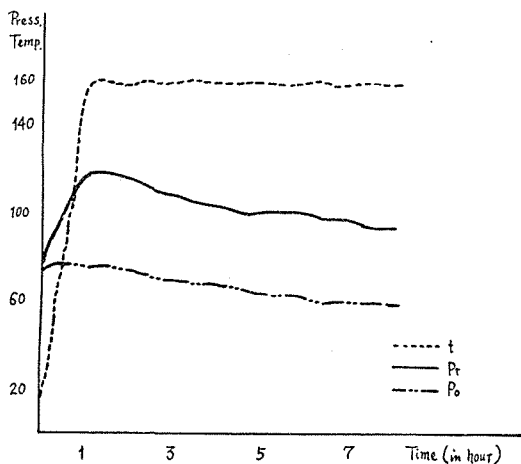


Fig. 13



of aci-tetra-hydronaphthylamine with some naphthylamine was confirmed.

The formation of aci-tetra-hydronaphthylamine from  $\alpha$ -naphthylamine by catalytic reduction at  $150^{\circ}$  and under 30 (Fig. 14) or 100 atmospheric pressures (Fig. 15) was confirmed experimentally.

It is noteworthy that  $\alpha$ -aci-tetra-hydronaphthylamine was only formed from  $\alpha$ -nitronaphthalene or

$\alpha$ -naphthylamine in the presence of reduced nickel & hydrogen under high pressure & temperature, while they are usually accompanied by

Fig. 14

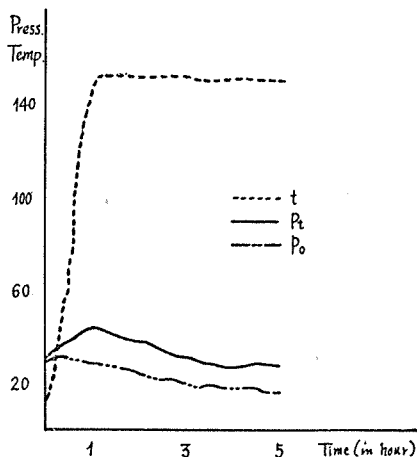
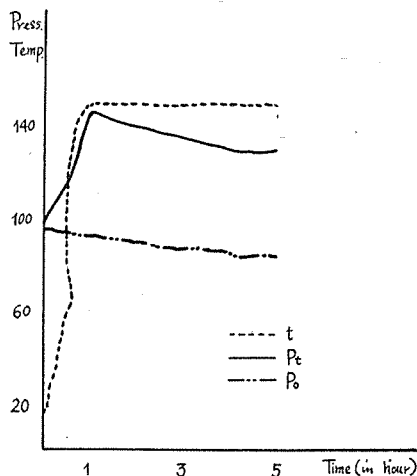
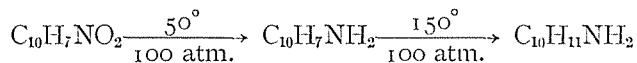
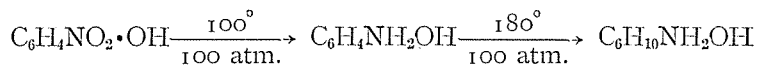


Fig. 15



the aro-isomer in the catalytic reduction by Sabatier's method, and also that ammonia is liberated in the course of the catalytic reduction of nitrophenol, due to separation of the nitrogen atom from the linked nitrogen and carbon by reduction, while the carbon & oxygen link remains unaffected by the process.

The partial reduction of nitro aromatic compounds was thus practically performed in the presence of reduced nickel and hydrogen under high pressure by controlling the activity by changing the reaction temperature.



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