# *The Competitive Reduction of Nitrobenzene and para-Substituted Nitrobenzenes with Nickel Catalysts*

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Several approaches to the elucidation of the mechanism of catalytic reduction may be possible. The present paper describes the competitive reduction of nitrobenzene and substituted nitrobenzenes with nickel catalysts. In all the cases examined, the nitro compounds with an electron attracting group in para position were reduced preferentially to those with an electron repelling group in the same position.

## Experimental

**Materials.** — Nitro compounds were purified by recrystallization or redistillation. The melting points and boiling points are listed in Table I.

TABLE I

| Compound | M. p. | B. p. |
|---|---|---|
| Nitrobenzene | | 95.5∼97°C/<br>17∼18 mmHg |
| *p*-Nitrophenol | 113°C | |
| *p*-Nitroanisole | 52 ∼ 53°C | |
| *p*-Nitroaniline | 145.5∼146.5°C | |
| Ethyl *p*-nitrobenzoate | 55 ∼ 56°C | |
| *p*-Nitrobenzaldehyde | 105 ∼105.5°C | |

**Preparation of Catalysts.** — a) Raney nickel catalyst. The method of Adkins and Billica[1] was modified in order to obtain stable catalytic activity. One gram of nickel-aluminum alloy (Ni 40%) was treated with 7 ml. cf. 20% aqueous sodium hydroxide at 50°C for 50 min. Then the catalyst was washed ten times by decantation with 20 ml. of cold water. The pH of the last washing wad 8.5∼9.0. The catalyst was then washed twice with 20 ml. of 95% ethanol.

b) Urushibara nickel A (U-Ni-A) was prepared according to Urushibara, Nishimura and Uehara[2].

**Catalytic Reduction.**—A suspension of the Raney nickel (0.4 g.) from 1 g. of the alloy in 30 ml. of 95% ethanol was shaken with hydrogen under ordinary pressure in a shaking type catalytic reduction apparatus until the catalyst absorbed no more hydrogen. Then 5 mM of a nitro compounds in 30 ml. of ethanol was added to the catalyst suspension, hydrogen was charged, and the reaction was started by shaking the reaction vessel. The temperature was maintained at 25°C, and the rate of hydrogen absorption was measured. In the reduction with U-Ni-A catalyst, 1.67 mM of a nitro compound, 1.0 g. of the catalyst and 20 ml. of 95% ethanol were used.

**Competitive Reduction.**—An equimolar mixture of two nitro compounds (each 5 mM) was reduced under the condition described above until 8∼13 mM of hydrogen was absorbed, whereas complete reduction to amines requires 30 mM of hydrogen. The catalyst was removed by filtration and was washed several times with ether. The products in the filtrate and washings were analysed. In the reduction with U-Ni-A, 6.67 mM each of two nitro compounds, 1.0 g. of the catalyst and 80 ml. of 95% ethanol were used.

**Analysis of Products.**—*Competitive Reduction of Nitrobenzene and p-Nitrophenol.* — Amines were removed from the ethereal solution of the products by shaking with dilute hydrochloric acid. Then the ethereal solution was extracted with dilute aqueous sodium hydroxide, the alkaline solution was acidified with hydrochloric acid and extracted with ether, and *p*-nitrophenol, m. p. 113°C, was obtained after removal of ether from the extract. The quantity of unchanged nitrobenzene was estimated from the volume of absorbed hydrogen in the catalytic reduction of the ethereal mother liquor of the alkaline extraction.

*Competitive Reduction of Nitrobenzene and p-Nitroaniline.* — *p*-Nitroaniline, *p*-phenylenediamine and aniline were separated from unchanged nitrobenzene by extracting ten times the ethereal solution of the reaction products with hydrochloric acid. Then the ethereal solution containing the unchanged nitrobenzene was evaporated in vacuum and the residue was catalytically reduced in alcoholic solution. The quantity of absorbed hydrogen was the same as that of unchanged nitrobenzene. The acidic extract was basified with aqueous sodium hydroxide and shaken with ether. The residue from the ethereal extract was catalytically reduced in alcoholic solution to know the quantity of unchanged *p*-nitroaniline.

*Competitive Reduction of Ethyl p-Nitrobenzoate and Nitrobenzene.*—After the solvent was distilled off from the reaction products, the residue was dissolved in a mixture of 30 ml. of dioxan and 40 ml. of concentrated hydrochloric acid. The solution was heated under reflux for 5 hr. The solution was made alkaline with aqueous sodium carbonate. Then nitrobenzene was steam-distilled, and the distillate was extracted with ether. After removal of ether from the extract, the residue was dissolved in alcohol and catalytically reduced to estimate the

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[1] H. Adkins and H. R. Billica, "Organic Syntheses" Vol., 29, John Wiley & Sons, Inc., New York (1949), p. 24.

[2] Y. Urushibara, S. Nishimura and H. Uehara. This Bulletin, 28, 446 (1955).

quantity of nitrobenzene. The quantity of reduced ethyl *p*-nitrobenzoate was estimated by weighing *p, p'*-diethoxycarbonylazoxy-benzene which precipitated on exposure of the reaction mixture to air.

*Competitive Reduction of p-Nitrobenzaldehyde and Nitrobenzene.*—The unchanged nitrobenzene and *p*-nitrobenzaldehyde were steam-distilled from the mixture produced, and the nitro compounds were extracted from the distillate with ether. The ethereal solution was divided into two portions of known volume. The total molar quantity of the nitro compounds was calculated from the quantity of absorbed hydrogen in catalytic reduction of one portion. An acidic solution of 2,4-dinitrophenylhydrazine was added to another portion. The quantity of *p*-nitrobenzaldehyde in the unchanged nitro compounds was obtained from that of the 2,4-dinitrophenylhydrazone. The quantity of nitrobenzene was given by the difference of the quantities of the total nitro compounds and *p*-nitrobenzaldehyde.

*Competitive Reduction of Ethyl p-Nitrobenzoate and p-Nitroanisole.*—The solution resulting from the competitive reduction was left under exposure to air for two days, and ethyl *p*-hydroxylaminobenzoate was changed to the corresponding azoxy compound[3]. After the precipitated *p, p'*-diethoxycarbonylazoxybenzene was collected by filtration, the solution was analysed chromatographically, and *p*-nitroanisole was obtained in white crystals. The quantity of *p, p'*-diethoxycarbonylaxoxybenzene gave the quantity of reduced ethyl *p*-nitrobenzoate, and the unchanged *p*-nitroanisole was directly weighed.

## Results and Discussion

**Separate Reduction Rates of Nitro Compounds.** — The hydrogenation curves of several nitro compounds were given in the preceding paper[3]. The increasing rates towards the end of the hydrogenation of nitrobenzene and of ethyl *p*-nitrobenzoate with Raney nickel catalyst are due to stepwise hydrogenation. Namely, the nitro compounds are reduced first to the hydroxylamines with $2H_2$, and then the hydroxylamines to amines with $H_2$, the latter process being faster than the former. In the hydrogenation of *p*-nitrobenzaldehyde and of ethyl *p*-nitrobenzoate with U-Ni-A the hydrogenation rates go down, making a break after 2 mol. of hydrogen has been consumed. This is also due to stepwise hydrogenation and here hydroxylamines are reduced more slowly than the parent compounds.

**Competitive Reduction.** — In the competitive catalytic reduction, a more reactive substance is not necessarily reduced in a greater quantity than a less reactive competitor. For example, in separate reduction nitrobenzene is reduced three times as quickly as ethyl *p*-nitrobenzoate with Raney nickel. But, when a mixture of nitrobenzene and ethyl *p*-nitrobenzoate was catalytically reduced, more ethyl *p*-nitrobenzoate was reduced than nitrobenzene. While nitrobenzene and *p*-nitrophenol are almost equally reactive in separate reduction with U-Ni-A catalyst, nitrobenzene was reduced exclusively at first in the competition with *p*-nitrophenol.

These phenomena can be explained by the difference in the affinities of substrates to nickel catalysts. In the above example, ethyl *p*-nitrobenzoate must be adsorbed, and thus reduced, preferentially to nitrobenzene. The same interpretation applies to the competitive reduction of nitrobenzene and *p*-nitrophenol with U-Ni-A catalyst.

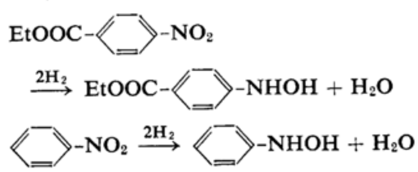
In order to find out the sequence, if any exists, in the strengths of affinities of nitrobenzene and substituted nitrobenzenes, the following considerations will be made:

To make the matter simple, any difference in the adsorption areas of the molecules of a pair of nitro compounds is neglected until later discussion.

If it is assumed that there was no selectivity in the adsorption of the nitro compounds, each component being adsorbed with equal ease, the rates of separate hydrogenation of the two compounds will give the quantities of both compounds to be reduced in a partial hydrogenation of their mixture, and comparison of the false values calculated in this way with observed ones will give a suggestion regarding the different affinities of the two nitro compounds to the nickel catalyst.

One or two examples will be illustrated below:

A mixture of 5 mM each of ethyl *p*-nitrobenzoate and nitrobenzene was hydrogenated with Raney nickel until 251 ml. of hydrogen was absorbed, and 2.60 mM of the former was reduced and 3.15 mM of the latter remained unchanged. Both ethyl *p*-nitrobenzoate and nitrobenzene are hydrogenated stepwise and, therefore, the competing reactions are:



As the initial rates of separate hydrogenation of ethyl *p*-nitrobenzoate and nitrobenzene are 73 ml./5 min. and 216 ml./5 min., respectively, the quantity of hydrogen to be consumed for the hydrogenation of ethyl *p*-nitrobenzoate would be from the above assumption:

$$H_1=\frac{73}{73+216}\times 251=63 \text{ ml.}$$

that for nitrobenzene:

$$H_2=\frac{216}{73+216}\times 251=188 \text{ ml.}$$

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3) A. Sugimori, submitted to this Bulletin.

The quantities of the nitro compounds to be hydrogenated would respectively be:

$$R_1=\frac{63}{2\times22.4}=1.41\ \text{mM}$$

$$R_2=\frac{188}{2\times22.4}=4.19\ \text{mM}$$

Accordingly, the quantities of the nitro compounds left unchanged would be:

$$L_1=5.00-1.41=3.59\ \text{mM}$$

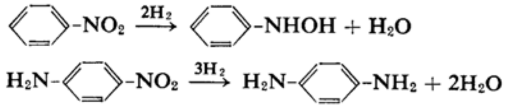
$$L_2=5.00-4.19=0.81\ \text{mM}$$

The calculated values are compared with the observed values in Table II, which is interpreted as showing that ethyl *p*-nitrobenzoate has a stronger affinity with the nickel catalyst than nitrobenzene has.

TABLE II

| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Ethyl *p*-nitrobenzoate | reduced | 1.41 | 2.60 |
| | unchanged | 3.59 | — |
| Nitrobenzene | reduced | 4.19 | — |
| | unchanged | 0.81 | 3.15 |

The competitive hydrogenation of nitrobenzene and *p*-nitroaniline with Raney nickel catalyst is more complicated, because the former gives phenylhydroxylamine while the latter is reduced to *p*-phenylenediamine:



The separate hydrogenation rates of nitrobenzene and *p*-nitroaniline are 216 ml./5 min. and 134 ml./5 min., respectively. The hydrogenation of a mixture of 5 mM each of nitrobenzene and *p*-nitroaniline was stopped when 291 ml. of hydrogen was absorbed, and 4.10 mM of *p*-nitroaniline remained unchanged. From the above assumption, the quantities of hydrogen to be consumed by nitrobenzene and *p*-nitroaniline would respectively be:

$$H_1=\frac{216}{216+134}\times291=180\ \text{ml.}$$

$$H_2=\frac{134}{216+134}\times291=111\ \text{ml.}$$

The quantity of nitrobenzene to be hydrogenated to phenylhydroxylamine with 180 ml. of hydrogen is:

$$R_1=\frac{180}{2\times22.4}=4.24\ \text{mM}$$

and the quantity of *p*-nitroaniline to be hydrogenated to *p*-phenylenediamine with 111 ml. of hydrogen is:

$$R_2=\frac{111}{3\times22.4}=1.65\ \text{mM}$$

Table III gives the comparison, which shows that nitrobenzene has a stronger affinity to the nickel catalyst than *p*-nitroaniline.

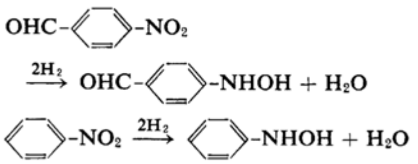
TABLE III

| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Nitrobenzene | reduced | 4.24 | |
| | unchanged | 0.76 | |
| *p*-Nitroaniline | reduced | 1.65 | |
| | unchanged | 3.35 | 4.10 |

Similar treatments of the other competitions are shown in Table IV.

TABLE IV

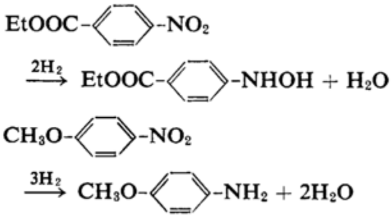
i) Nitrobenzene and *p*-nitrobenzaldehyde with Raney nickel.



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| *p*-Nitrobenzaldehyde | reduced | 1.18 | |
| | unchanged | 3.82 | 0.52 |
| Nitrobenzene | reduced | 4.78 | |
| | unchanged | 0.22 | 3.10 |

Affinity to the catalyst: *p*-Nitrobenzaldehyde > Nitrobenzene

ii) Ethyl *p*-nitrobenzoate and *p*-nitroanisole with Raney nickel.



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Ethyl *p*-nitrobenzoate | reduced | 1.83 | 3.15 |
| | unchanged | 3.17 | |
| *p*-Nitroanisole | reduced | 2.54 | |
| | unchanged | 2.46 | 2.85 |

Affinity to the catalyst: Ethyl *p*-nitrobenzoate > *p*-Nitroanisole

Separate and competitive hydrogenation of the nitro compounds were also studied with U-Ni-A catalyst. Results are shown in Table V.

TABLE V

(A) Initial hydrogenation rates of separate hydrogenations.

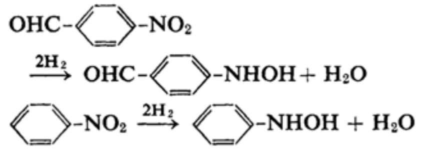
| | |
|---|---|
| Nitro compound | 1.67 mM |
| U-Ni-A | 1.0 g. |

| Compound | Rate of hydrogen absorption |
|---|---|
| Nitrobenzene | 126 ml./5 min. |
| *p*-Nitrobenzaldehyde | 126 ml./2.5 min. |
| Ethyl *p*-nitrobenzoate | 141 ml./5 min. |
| *p*-Nitrophenol | 138 ml./5 min. |
| *p*-Nitroaniline | 68 ml./5 min. |

(B) Competitive reduction

| | |
|---|---|
| Nitro compounds | 6.67 mM each |
| U-Ni-A | 1.0 g. |

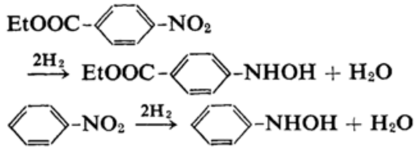
i) *p*-Nitrobenzaldehyde and nitrobenzene.



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| *p*-Nitrobenzaldehyde | reduced | 4.74 | |
| | unchanged | 1.93 | |
| Nitrobenzene | reduced | 2.37 | |
| | unchanged | 4.30 | 5.60 |

Affinity to the catalyst: *p*-Nitrobenzaldehyde >Nitrobenzene

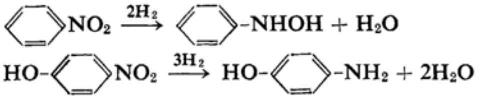
ii) Nitrobenzene and ethyl *p*-nitrobenzoate.



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Ethyl *p*-nitrobenzoate | reduced | 3.82 | |
| | unchanged | 2.85 | |
| Nitrobenzene | reduced | 3.37 | |
| | unchanged | 3.30 | 5.13 |

Affinity to the catalyst: Ethyl *p*-nitrobenzoate >Nitrobenzene

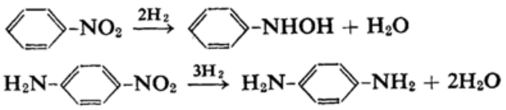
iii) Nitrobenzene and *p*-Nitrophenol



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Nitrobenzene | reduced | 4.80 | |
| | unchanged | 1.87 | 0.34 |
| *p*-Nitrophenol | reduced | 3.47 | |
| | unchanged | 3.20 | 5.10 |

Affinity to the catalyst: Nitrobenzene >*p*-Nitrophenol

iv) Nitrobenzene and *p*-nitroaniline.



| Compound | | Calcd. mM | Obs. mM |
|---|---|---|---|
| Nitrobenzene | reduced | 5.47 | |
| | unchanged | 1.20 | 0.47 |
| *p*-Nitroaniline | reduced | 1.92 | |
| | unchanged | 4.70 | 6.10 |

Affiinity to the catalyst: Nitrobenzene >*p*-Nitroaniline

To examine further the selectivity in adsorption, the initial rates of hydrogenation of mixtures were measured and compared with the initial rates of separate reduction in Table VI.

TABLE VI

| Compound | Initial rate of separate reduction (ml. of H$_2$/ 5 min.) | Initial rate of the reduction of mixture (ml. of H$_2$/ 5 min.) |
|---|---|---|
| Nitrobenzene | 216 | 54 |
| Ethyl *p*-nitrobenzoate | 73 | |
| Nitrobenzene | 216 | 63 |
| *p*-Nitrobenzaldehyde | 52 | |
| Nitrobenzene | 216 | 208 |
| *p*-Nitroaniline | 134 | |

Table VI shows that the reduction rate of a mixture is almost the same as that of the component which is considered to have a stronger affinity to the catalyst. These data also indicate that the difference in affinities of the two components of each combination is great enough to cause completely selective adsorption.

The comparisons of the affinities of the nitro compounds to the nickel catalysts are summarized in Table VII.

TABLE VII

| Raney nickel | U-Ni-A |
|---|---|
| Ethyl *p*-nitrobenzoate >Nitrobenzene | Ethyl *p*-nitrobenzoate >Nitrobenzene |
| *p*-Nitrobenzaldehyde >Nitrobenzene | *p*-Nitrobenzaldehyde >Nitrobenzene |
| Nitrobenzene >*p*-Nitroaniline | Nitrobenzene >*p*-Nitrophenol |
| Ethyl *p*-Nitrobenzoate >*p*-Nitroanisole | Nitrobenzene >*p*-Nitroaniline |

In all the systems studied, an aromatic nitro compound with an electron attracting group in para position has a stronger affinity to the nickel catalysts than the compound with an electron repelling group in the same position.

Other factors that might have effects on the affinities of nitro compounds to the nickel catalysts must also be examined.

*Cross Section in Adsorption.*—The cross section in adsorption has been neglected in the above discussion but it might affect the apparent affinity of the nitro compound to the nickel catalysts. The molecule with a larger cross section in adsorption may be adsorbed in a smaller number than the molecule with a smaller cross section. Therefore, the same observed rate of separate hydrogenation with U-Ni-A catalyst may suggest that the hydrogenation of one molecule of *p*-nitrophenol is more rapid than that of nitrobenzene. Thus, if there were no selectivity in adsorption, *p*-nitrophenol might be reduced to a greater extent than nitrobenzene in the competitive reduction, but this was not true, and so the selectivity in adsorption rather than the molecular cross section governs the results.

Carbonyl group in ethyl *p*-nitrobenzoate and *p*-nitrobenzaldehyde can attack the active centers of the nickel catalysts, and the strong affinity of *p*-nitrobenzaldehyde and ethyl *p*-nitrobenzoate to the catalyst might be attributed to the adsorption of the carbonyl group. But this is denied, because the partial reduction of *p*-nitrobenzaldehyde gave *p*-hydroxylaminobenzaldehyde, and nitro group is preferentially adsorbed to carbonyl group by the catalysts.

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