The hydrogenation of nitrobenzene to aniline: a new mechanism

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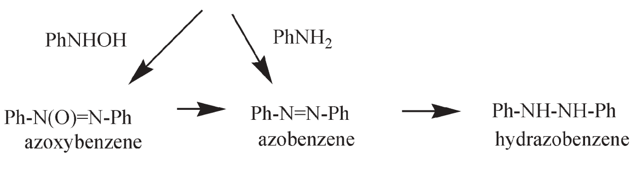
The Haber mechanism describing the process of hydrogenating nitrobenzene to aniline is shown to be incorrect and a new mechanism is proposed.

The catalytic hydrogenation of nitrobenzene is an industrially important reaction, utilised in the production of aniline for the plastics industry.[1] Commercially, the reaction is carried out in the gas phase over a nickel or copper based catalyst.[2] However, the transformation is extremely facile and is carried out under relatively mild conditions. For this reason, hydrogenation occurs rapidly over most metals and is commonly employed as a standard reference reaction for comparing the activities of other hydrogenation catalysts.[3–6] Despite the large volume of literature available citing the use of this reaction, very little has been published regarding actual mechanistic detail. Haber's initial scheme was published in 1898[7] and proposed that nitrobenzene was transformed to aniline in a three-step process involving nitrosobenzene and phenylhydroxylamine intermediates (Scheme 1). In addition, it was also proposed that azoxybenzene, azobenzene and hydrazobenzene by-products could be formed *via* reaction of the two intermediate species. This mechanism has been widely accepted since and a number of studies have reported the identification of the suggested reaction intermediates during hydrogenation.[8,9] In addition, Figueras and Coq[10] have reviewed the hydrogenation behaviour of these intermediates and by-products and found azobenzene to hydrogenate through to aniline. While these studies have appeared to provide further supporting evidence for Haber's reaction scheme, the mechanism is still not well understood and has never been fully delineated.

A palladium/carbon catalyst was used to study the hydrogenation of nitrobenzene and two of the proposed reaction intermediates, nitrosobenzene and azobenzene. The catalyst was prepared by impregnation of the powdered activated carbon support, Norit SX Ultra (surface area 1200 $m^2\ g^{-1}$), with sufficient palladium nitrate to produce a metal loading of 3%. The resulting suspension was dried and calcined at 423 K for 3 hours. The dispersion of the catalyst was measured using CO chemisorption. Taking a CO : Pd ratio of 1 : 2, the dispersion was calculated as 42.0%. Hydrogenation was carried out in a Buchi stirred autoclave. The catalyst (0.1 g) was added to the reactor with the reaction solvent (280 ml methanol) and reduced in a flow of hydrogen (30 $cm^3\ min^{-1}$) for 30 minutes with a stirring rate of 300 rpm. During reduction the reactor temperature was increased to 323 K. The reactant, nitrobenzene (0.08 mol), or nitrosobenzene (0.08 mol) was added and the hydrogen/deuterium pressure set at 3 bara and the stirrer speed at 1000 rpm. In reactions involving the addition of one of the intermediates along with nitrobenzene, the intermediate was added first and mixed with the solvent under nitrogen before nitrobenzene was added and reaction commenced. No variation in hydrogenation rate was observed over a range of stirrer speeds (800–1500 rpm) indicating the absence of mass transfer control. Analysis of the reaction mixture was performed by GC-MS using a Varian CP-3800 GC with a Varian Saturn 2000 Trace MS detector fitted with a 25 m DB-5 column. The rate of hydrogen uptake was measured independently, while the rate of aniline production was calculated using the GC-MS data.



Scheme 1 The Haber mechanism.

The hydrogenation of nitrobenzene by hydrogen and deuterium is shown in Fig. 1 following the hydrogen uptake. The hydrogenation of nitrobenzene progressed to aniline without any significant by-product formation (<1% azobenzene) as the reaction went to completion. From Fig. 1 it can be seen that there is a kinetic isotope effect.

The hydrogenation of nitrosobenzene by hydrogen and deuterium was also studied and the hydrogen uptake is shown in Fig. 2. There is no kinetic isotope effect over the first 15–20 min and thereafter there is an inverse kinetic isotope effect. The reaction profile is shown in Fig. 3 and is dramatically different from that observed with nitrobenzene.

Comparison of the reaction profiles of nitrobenzene hydrogenation and nitrosobenzene hydrogenation show distinct differences as do the hydrogen uptake curves. The two stage hydrogen uptake curve observed with nitrosobenzene (Fig. 2) has been described

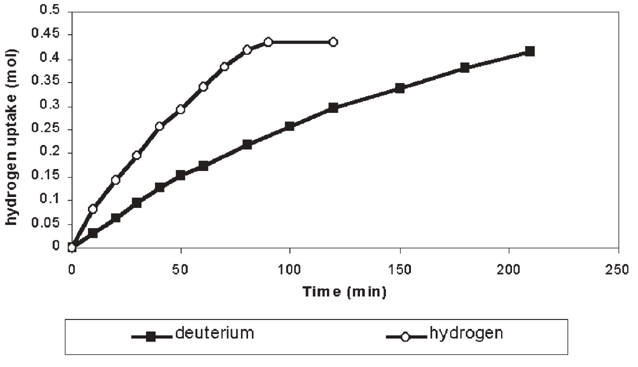


Fig. 1 Hydrogen/deuterium uptake during nitrobenzene hydrogenation.

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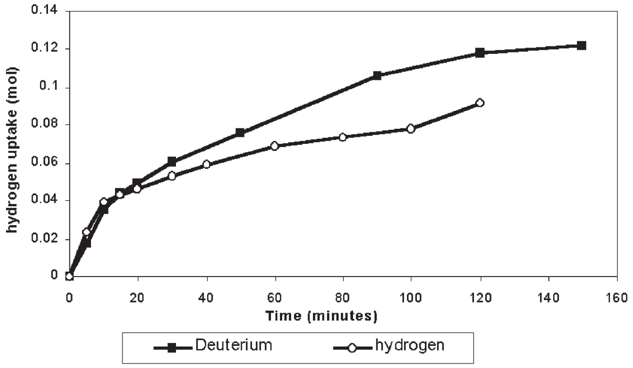


Fig. 2 Hydrogen/deuterium uptake during nitrosobenzene hydrogenation.

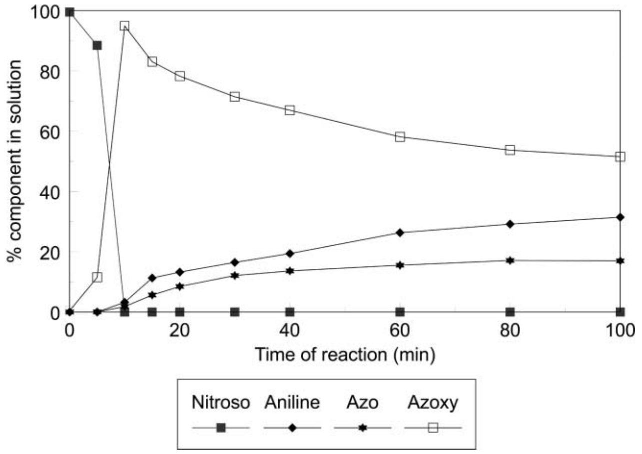
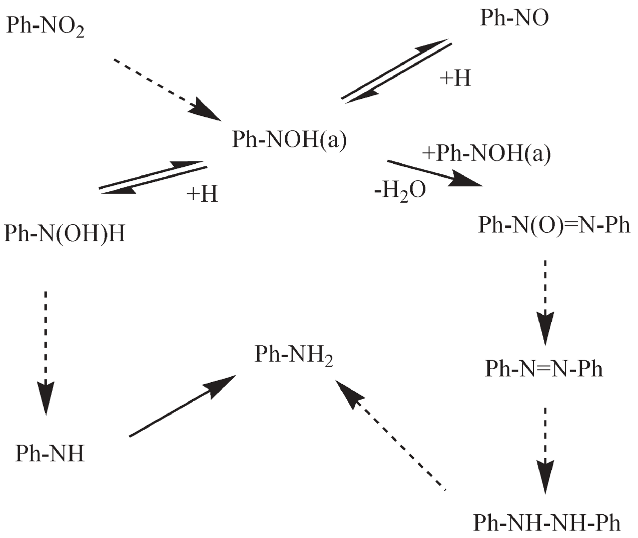


Fig. 3 Nitrosobenzene reaction profile.

over palladium/silica catalysts in a previous study by Smith *et al.*,[11] where they also report an identical reaction profile to the one presented in this study. The initial product of nitrosobenzene hydrogenation is azoxybenzene; aniline is not formed until after all the nitrosobenzene has been converted to azoxybenzene. The rate of aniline production was calculated at 15.5 mmol min^{-1} g^{-1} for nitrobenzene hydrogenation and 0.35 mmol min^{-1} g^{-1} for nitrosobenzene hydrogenation.

The lower rate of hydrogenation to aniline from nitrosobenzene and the different kinetic isotope effects make it clear that nitrosobenzene cannot be an intermediate in the hydrogenation of nitrobenzene. Therefore the Haber mechanism must be updated.

A detailed analysis of the surface reaction mechanisms for nitrobenzene and nitrosobenzene has led us to propose a new mechanism (Scheme 2). We are unable, due to the space limitations, to lay out the full detailed mechanism for both compounds, hence dotted arrows indicate multiple steps.



Scheme 2

The analysis suggests that there is a common surface intermediate, namely Ph–N(OH)(a). In the nitrobenzene mechanism, Ph–N(OH)(a) reacts with adsorbed hydrogen whereas in the nitrosobenzene mechanism, Ph–N(OH)(a) reacts with itself to eliminate water and produce azoxybenzene. In nitrobenzene hydrogenation each step involves the addition of hydrogen hence the kinetic isotope effect. However in the nitrosobenzene mechanism there is a coupling reaction and a hydrogenolysis reaction either of which could lead to an inverse kinetic isotope effect. The different processes occurring in the two mechanisms would be consistent with the different rates observed and the fact that nitrosobenzene has a slower rate of aniline formation.

The nitrobenzene and nitrosobenzene hydrogenation reactions were repeated with a pre-activated Raney Nickel catalyst (Aldrich) and similar reaction profiles were obtained. When the hydrogen pressure was reduced to 1 bara, trace levels of nitrosobenzene were detected in the reaction mix. This is predictable from Scheme 2, as under reaction conditions where hydrogen is limited it is possible for Ph–N(OH)(a) to dehydrogenate to give nitrosobenzene as a by-product of nitrobenzene hydrogenation.

This new understanding of the mechanism has implications for both catalyst and reactor design. To obtain a high activity and selectivity it is essential that the hydrogen flux at the surface is maintained, with good access to the reaction site and no diffusion limitations. Indeed the presence of typical by-products such as azobenzene and azoxybenzene may indicate that there are local regions on the catalyst surface where the hydrogen flux is insufficient to inhibit Ph–N(OH)(a) coupling, even though the system overall may not be in a diffusion controlled regime.

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