

## Kinetics Approach for Hydrogenation of Nitrobenzene to *p*-Aminophenol in a Four-Phase System

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The kinetics of the catalytic hydrogenation of nitrobenzene (NB) on a Pt/carbon catalyst in an acid medium to *p*-aminophenol (PAP), with aniline (AN) as a byproduct, was investigated in a batch reactor. By the elimination of the external and internal diffusion effects by good mixing, use of a superfine catalyst and the maintenance of a constant nitrobenzene concentration, the exponential macro-kinetics with respect to hydrogen pressure and reaction temperature are reported.

$$r_{\text{PAP}} = k_0 \exp\left(-\frac{E_{\text{PAP}}}{RT}\right) p_{\text{H}}^{\alpha} = 1.912 \times 10^5 \exp\left(-\frac{2.874}{T}\right) p_{\text{H}}^{0.3251}$$

$$r_{\text{AN}} = k_0 \exp\left(-\frac{E_{\text{AN}}}{RT}\right) p_{\text{H}}^{\beta} = 7.083 \times 10^{33} \exp\left(-\frac{28.186}{T}\right) p_{\text{H}}^{2.8342}$$

$$\begin{aligned} -r_{\text{NB}} &\approx r_{\text{PAP}} + r_{\text{AN}} = k_0 \exp\left(-\frac{E_{\text{PAP}}}{RT}\right) p_{\text{H}}^{\alpha} + k_0 \exp\left(-\frac{28.186}{T}\right) p_{\text{H}}^{\beta} \\ &= 1.912 \times 10^5 \exp\left(-\frac{2.874}{T}\right) p_{\text{H}}^{0.3251} + 7.083 \times 10^{33} \exp\left(-\frac{28.186}{T}\right) p_{\text{H}}^{2.8342} \end{aligned}$$

In the kinetic equation, the reaction orders  $\alpha$ ,  $\beta$  for *p*-aminophenol (PAP) and aniline (AN) formation are 0.3251 and 2.8342, respectively, while the activation energies are  $E_{\text{PAP}}$  23.89 kJ/mol and  $E_{\text{AN}}$  234.34 kJ/mol, respectively. The reaction results correspond well with experimental data.

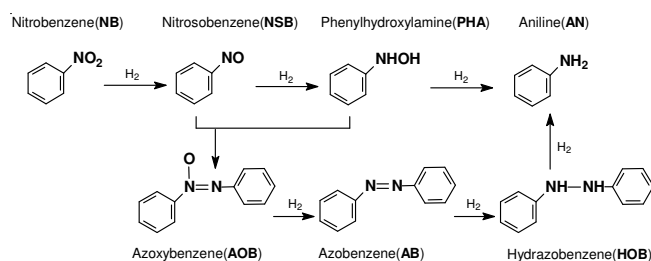
**Key Words:** Multi-phase flow, Catalysis, Reaction kinetics, Nitrobenzene, *p*-Aminophenol, Aniline.

### INTRODUCTION

*p*-Aminophenol is an important intermediate for synthesizing dyestuffs, antioxidants, photographic developers, urethanes, agrochemicals and pharmaceuticals. In 1874, Baeyer first prepared *p*-aminophenol (PAP) by reducing *p*-nitrosophenol with metallic tin in an acid medium<sup>1</sup>. Conventionally, *p*-aminophenol is prepared from chlorobenzene via the *p*-nitrochlorobenzene intermediate using iron powder (the Bechamp process) or by using molecular hydrogen reduction technology.

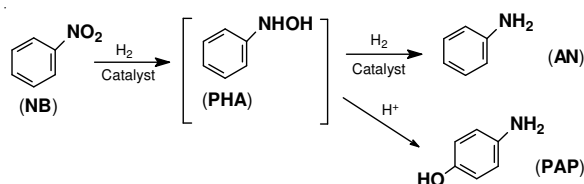
It is noted that Henke disclosed a more convenient process for the manufacture of *p*-aminophenol, which was by direct hydrogenation of nitrobenzene (NB) in the presence of Pt/C catalyst and a mineral acid<sup>2</sup>. Nitrobenzene reduction mechanism established by Haber, from his work on the electroche-

mical reduction of nitrobenzene, has been widely accepted<sup>3</sup>. The initial step was hydrogenolysis of the NO<sub>2</sub> functional group to form the key intermediate nitrosobenzene, followed by conversion to hydroxylamine, azoxy-, azo-, hydrazo- *etc.* (Scheme-I).



**Scheme-I:** Reaction pathway involved in nitrobenzene hydrogenation

Rylander and Ternary postulated that the hydrogenation of nitrobenzene to N-phenyl hydroxylamine (PHA) was followed by *in situ* a Bamberger rearrangement to *p*-aminophenol in the presence of an acid and the formation of aniline was the main competing side reaction in this process (**Scheme-II**)<sup>4,5</sup>.



**Scheme-II:** Hydrogenation reaction of nitrobenzene to *p*-aminophenol

The methodology concerning a one-pot preparation of *p*-aminophenol from nitrobenzene has received much attention because of the environmental economy and commercial potential compared with the *p*-nitrochlorobenzene route, especially the reaction behaviour with various metal catalysts such as Pt<sup>1,4,6-11</sup>, Pd<sup>1,12</sup>, Ni<sup>13</sup> and sulfides of Mo and W<sup>1,14</sup>. To enhance the efficiency and selectivity of the hydrogenation to *p*-aminophenol, various surfactants, such as octadecyl trimethyl ammonium chloride, dimethyldodecylamine sulfate, trimethylamine chloride, dimethyl alkylamine oxide<sup>7,12,15-17</sup> and some non-ionic surfactants<sup>8</sup>, have been investigated. The addition of morpholine, phosphorous acid<sup>18</sup> and dimethyl sulfoxide<sup>4,6,10-11</sup> favoured the formation of N-phenyl hydroxylamine. However, N-phenyl hydroxylamine separation was undesirable due to its carcinogenic and explosive properties<sup>19</sup>. The influences of catalysts and reaction conditions on the reaction activity and selectivity were also addressed in the references cited.

However, the rapid kinetics and exothermicity of nitrobenzene hydrogenation makes a detailed kinetic discussion difficult. Juang *et al.*<sup>20</sup> found that the rate-determining step for the catalytic hydrogenation of nitrobenzene to *p*-aminophenol was the process involving hydrogen atom adsorption on to the metal surface. A reaction kinetics model was set as reported by Juang *et al.*<sup>20</sup>

$$-\frac{d[\text{PhNO}_2]}{dt} = k[\text{H}_2]^{1/2} \quad (1)$$

Rode *et al.*<sup>21</sup> suggested a kinetic equation as in formula (2), giving an overall reaction rate in a four-phase system reactor with mass transfer effect.  $R_A$ , which is present on both sides of the equation, is a coupling or implicit function. Notations are given in the reference.

$$R_A = wk_1 + wk_2 \left[ \frac{A_{\text{NB}}^* - R_A/K_A a_B}{1 + K_A (A_{\text{NB}}^* - R_A/k_L a_B)} \right] \quad (2)$$

An exponential rate equation is rather convenient for auto-control chemistry, although a hyperbolic type equation from the Langmuir-Hinshelwood model can be obtained *via* complex deduction and computation. Therefore, the aim of this work is to discuss the macro kinetics of both *p*-aminophenol and aniline formation without any mass transfer effects on the reaction rate. An exponential expression for the reaction kinetics was found to fit the experimental data and the kinetic parameters have been obtained. This result is of importance as a guide for the engineering challenge of scaling up the reaction and characterizing the reactor.

## EXPERIMENTAL

Nitrobenzene, H<sub>2</sub>SO<sub>4</sub> (98 %), dodecyl trimethyl ammonium bromide and dimethyl sulfoxide were obtained commercially with chemical purity 99 % or over. Standard *p*-aminophenol was purchased from Sinopharm Chemicals Reagent Co. Ltd. Hydrogen with 99.999 % purity (GB/T7445-95) was supplied by Nanjing Special Gas Factory. Nitrogen, with more than 99.5 % purity (GB/T7445-95) from a commercial source was directly used from the compressed gas cylinder. 2-5 % Pt/C catalyst was prepared by impregnation of charcoal (U-101, Tangshan United Carbon Technology Co. Ltd., China) with chloroplatinic acid solution followed by formaldehyde reduction in basic conditions.

A 0.25 L Autoclave Hastelloy was supplied by Dalian Tongda Reactor Factory and a 500 L autoclave reactor obtained from Hangzhou Yuanzheng Chemical Engineering Equipment Co. Ltd., China.

**Procedure:** Two reactors were used for the hydrogenation experiment, one reactor of 0.25 L capacity, the other a 500 L autoclave reactor with gas-inducing turbine. The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor through a constant pressure regulator. Hydrogen was supplied from this reservoir to the reactor through a non-return valve. The gas consumed during the course of the reaction was monitored by the pressure drop in the reservoir vessel, measured using a transducer. Initial data were obtained at different temperatures, catalyst loading, agitation speed and partial pressure of hydrogen in a stirred high-pressure slurry reactor.

For a typical hydrogenation experiment the reactor was filled with nitrogen gas and charged with nitrobenzene, 2-5 % Pt/C catalyst, 14-18 % H<sub>2</sub>SO<sub>4</sub> solution, quaternary ammonium salt and dimethyl sulfoxide. The contents were flushed with hydrogen while stirring. After the desired temperature was attained, the system was pressurized with hydrogen to a defined level. The course of the reaction was monitored by the observed pressure drop in the reservoir vessel as a function of time. Samples were analyzed at intervals during the reaction. Upon completion, the solid catalyst was separated by filtration. The filtrate was kept at temperature of 30 °C and adjusted to pH 5.0-5.5 and then extracted with toluene in order to remove aniline, unconverted nitrobenzene and traces of impurities. The pH of the aqueous layer after extraction was adjusted to 7 by the addition of aqueous ammonia leading to the complete precipitation of *p*-aminophenol.

## RESULTS AND DISCUSSION

**Kinetics model fundamentals:** The hydrogenation reaction of nitrobenzene to *p*-aminophenol was conducted in a four-phase system, *i.e.*, gas phase-H<sub>2</sub>, inorganic phase-dilute sulfuric acid (which dissolves the aminophenol and aniline to form the corresponding salt), organic phase-nitrobenzene, solid phase-powdery Pt/C catalyst (which is distributed in the nitrobenzene). As the catalytic hydrogenation proceeded, the proportion of the nitrobenzene phase in the system decreased (for a defined amount of nitrobenzene) and the ratio of acid phase increased, with the subsequent formation of *p*-aminophenol, aniline and water. Accordingly, the reaction rate in each phase can be expressed in moles per unit mass of catalyst per unit time, *i.e.*,

$$-r_{NB} = -\frac{dn_{NB}}{wdt}, \quad r_{PAP} = \frac{dn_{PAP}}{wdt}, \quad r_{AN} = \frac{dn_{AN}}{wdt}$$

The reaction was influenced by many factors, such as surfactant, catalyst activity, reaction temperature and pressure, agitation strength and cooling capacity *etc.* In order to improve the reaction rate, a special device was employed to provide vigorous agitation and eliminate external diffusion resistance. It reduced the size of the H<sub>2</sub> gas bubbles and nitrobenzene and acid liquid droplets and mixed them well with the solid catalyst. The external diffusion resistance existed in two forms; one was the diffusion of gaseous H<sub>2</sub> into the solid catalyst *via* liquid nitrobenzene, the other was the diffusion of products (N-phenyl hydroxylamine, aniline and water) on catalyst surface to the acid phase *via* the nitrobenzene phase. Accordingly, the catalyst was finely grounded (to millimicron particle size) which was sufficient to eliminate the internal surface diffusion resistance to H<sub>2</sub>, nitrobenzene and intermediates or some formations existed in catalyst channels. Depending on the conditions, the macro-kinetics of the hydrogenation reaction at the active site of the catalyst can follow several reasonable hypotheses; (a) the reaction system could be pseudo-homogeneous; (b) the formation of *p*-aminophenol and aniline from nitrobenzene could be a parallel reaction; (c) the nitrobenzene concentration

in the system could be constant, giving  $C_{NB0} = C_{NB} = \frac{\rho_{NB}}{M_{NB}} = 9.786 \text{ kmol/m}^3$ .

Therefore, the differential equation for the complex reaction (**Scheme-II**) could be expressed as follows:

$$\begin{cases} -r_{NB} = r_{PAP} + r_{AN} \\ r_{PAP} = \frac{dn_{PAP}}{wdt} = k_{PAP} C_{NB}^{\alpha} P_H^{\alpha} = k P_H^{\alpha} \\ r_{AN} = \frac{dn_{AN}}{wdt} = k_{AN} C_{NB}^{\beta} P_H^{\beta} = k' P_H^{\beta} \end{cases}$$

The boundary conditions for the formulae above are:  $t = 0, \quad n_{BN0} \neq 0, \quad n_{AN} = 0, \quad n_{PAP} = 0; \quad t = t, \quad n_{NB0} = n_{NB} + n_{AN} + n_{PAP}$ .

**Estimation of the reaction order for the exponential macro-kinetics model:** Combining the finite difference expressions to give the reaction rate,

$$r_{PAP} = \frac{1}{w} \frac{dn_{PAP}}{dt} = \frac{1}{w} \frac{\Delta n_{PAP}}{\Delta t}$$

and

$$r_{AN} = \frac{1}{w} \frac{dn_{AN}}{dt} = \frac{1}{w} \frac{\Delta n_{AN}}{\Delta t}$$

and logarithm for the exponential kinetics model,

$$\ln r_{PAP} = \alpha \ln P_H + \ln k$$

and

$$\ln r_{AN} = \beta \ln P_H + \ln k'$$

Linear regression analysis using the Least Squares method or the linear equation in Excel 2003 for the experimental data at 90 °C (Fig. 1) gave the following formulae,

$$\alpha = \frac{n \sum (\ln r_{PAP} \ln P_H) - \sum \ln r_{PAP} \sum \ln P_H}{n \sum (\ln P_H)^2 - (\sum \ln P_H)^2} = 0.3251$$

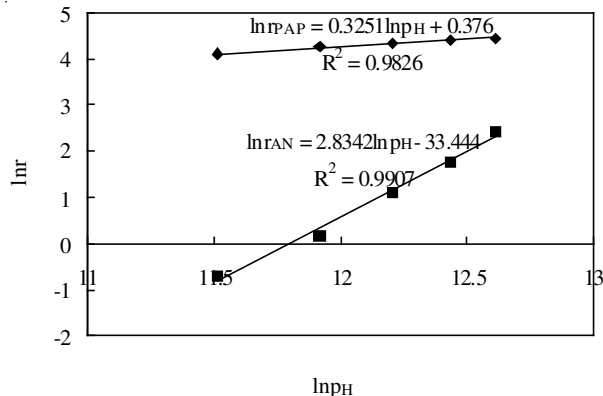


Fig. 1.  $\ln r - \ln p_H$  linear relation

and 
$$\ln k = \frac{\sum \ln r_{PAP} - \alpha \sum \ln p_H}{n} = 0.376$$

$\beta = 2.8342$  and  $\ln k' = -33.444$  were obtained in the same way. The rate equation effectively explains why low hydrogen pressure facilitated the *p*-aminophenol yield and a high hydrogen pressure accelerated aniline formation. Moreover, the selectivity of *p*-aminophenol with respect to aniline will decrease with increasing the hydrogen pressure.

**Estimation of the Arrhenius rate constant:** Since the reaction speed increases with increasing temperature and the rate of formation of aniline exceeds that of *p*-aminophenol, the activation energy of aniline must be higher than that of *p*-aminophenol. According to the Arrhenius equation

$$k = k_0 \exp\left(-\frac{E}{Rt}\right) \quad \text{or its linearized form}$$

$\ln k = -\frac{E}{RT} + \ln k_0$ , the linear regression analysis results using the Least Squares method for the experimental data or the linear equation using Excel 2003 for the experimental data from Fig. 2 could be

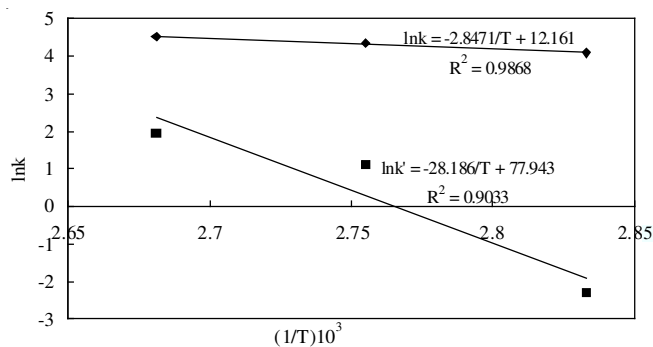


Fig. 2.  $\ln k - 1/T$  linear relation

$$\frac{E_{PAP}}{R} = \frac{\sum \frac{1}{T} \sum \ln k - n \sum \left(\frac{1}{T} \ln k\right)}{n \sum \frac{1}{T^2} - \left(\sum \frac{1}{T}\right)^2} = 2.847$$

so the activation energy of the *p*-aminophenol formation was  $E_{PAP} = 23.89 \text{ kJ/mol}$  and the rate constant  $k_0$  for the *p*-aminophenol formation was 191185.6, giving the equation

$$\ln k_0 = \frac{\sum \ln k + \frac{E_{\text{PAP}}}{R} \sum \frac{1}{T}}{n} = 12.161$$

Similarly, since  $\frac{E_{\text{AN}}}{R} = 28.186$ , the activation energy of aniline formation is  $E_{\text{AN}} = 234.34$  kJ/mol and  $k'_0 = 7.083 \times 10^{33}$ .

The results effectively explain a high *p*-aminophenol yield at low temperature as well as the corresponding aniline formation at high temperature. So, the selectivity of *p*-aminophenol with respect to aniline can be improved by employing a low reaction temperature. For *p*-aminophenol formation, the rate equation is

$$\begin{aligned} r_{\text{PAP}} &= k_0 \exp\left(-\frac{E_{\text{PAP}}}{RT}\right) p_{\text{H}}^\alpha \\ &= 1.912 \times 10^5 \exp\left(-\frac{2.874}{T}\right) p_{\text{H}}^{0.3251} \end{aligned} \quad (3)$$

and for aniline, 
$$\begin{aligned} r_{\text{AN}} &= k'_0 \exp\left(-\frac{E_{\text{AN}}}{RT}\right) p_{\text{H}}^\beta \\ &= 7.083 \times 10^{33} \exp\left(-\frac{28.186}{T}\right) p_{\text{H}}^{2.8342} \end{aligned} \quad (4)$$

Since conversion of most of the nitrobenzene gives *p*-aminophenol and aniline, the disappearance rate of nitrobenzene was approximately equal to the sum of the formation rates of *p*-aminophenol and aniline, *i.e.*,

$$\begin{aligned} -r_{\text{NB}} &\approx r_{\text{PAP}} + r_{\text{AN}} = k_0 \exp\left(-\frac{E_{\text{PAP}}}{RT}\right) p_{\text{H}}^\alpha \\ &\quad + k'_0 \exp\left(-\frac{E_{\text{AN}}}{RT}\right) p_{\text{H}}^\beta \\ &= 1.912 \times 10^5 \exp\left(-\frac{2.874}{T}\right) p_{\text{H}}^{0.3251} \\ &\quad + 7.083 \times 10^{33} \exp\left(-\frac{28.168}{T}\right) p_{\text{H}}^{2.8342} \end{aligned} \quad (5)$$

The rate of the hydrogenation and the selectivity for *p*-aminophenol or aniline, are significantly influenced by the catalyst, surfactant and mixing so that their influences are difficult to quantify. The catalyst is affected by the pore diameter and distribution, type of group at the surface of the activated carbon support and the method used for loading Pt. A catalyst with zero activity was found in present experiment using almost the same preparation method as one with high activity. The type and amount of the surfactant influenced the mass transport of H<sub>2</sub> from the gas phase to the nitrobenzene phase then to the catalyst surface and influenced the mass transport of N-phenyl hydroxylamine from the catalyst surface to the nitrobenzene phase then to the acid phase. As the mixing mode influences the mass transport in the four phase reaction system, scale-up effects may be significant.

The equation showed an excellent agreement with further experimental data, but an induced period of product formation was clearly observed. This was because of the initial hydrogen diffusion from the gas phase to the nitrobenzene phase and Pt/C catalyst active sites, after sequential adsorption, surface reaction and desorption, then product diffusion from the nitrobenzene phase to an acid phase. The induction period lasted about 10-30 min.

In this reaction system, considering the presence of a constant nitrobenzene concentration and a continuous decrease of the volume of the nitrobenzene phase as the hydrogenation processed (when some inert organic solvent such as benzene was added to the system), the reaction order for nitrobenzene was deduced by varying the nitrobenzene concentration.

The reaction temperature and pressure affected product selectivity. Although both factors could improve reaction rate and enhance the conversion of nitrobenzene, the selectivity for *p*-aminophenol formation could become poor because of faster aniline formation. The selectivity can be quantitatively expressed according to the following equation

$$\begin{aligned} S_{\text{PAP}} &= \frac{r_{\text{PAP}}}{r_{\text{AN}}} = \frac{k p_{\text{H}}^\alpha}{k' p_{\text{H}}^\beta} = \frac{k}{k'} p_{\text{H}}^{\alpha-\beta} \\ &= 2.699 \times 10^{-27} \exp\left(\frac{25.312}{T}\right) p_{\text{H}}^{-2.5091} \end{aligned} \quad (6)$$

When the temperature is increased, the disappearance rate of the nitrobenzene and the rate of *p*-aminophenol and aniline formation all increased, but aniline increases more than *p*-aminophenol, so low temperature favoured the selectivity to *p*-aminophenol and the activation energies are  $E_{\text{PAP}} < E_{\text{AN}}$ .

When the hydrogen pressure was increased, the disappearance rate of nitrobenzene and the rate of *p*-aminophenol and aniline formation, all increased, but aniline increased more than *p*-aminophenol, so low hydrogen pressure favoured the selectivity to *p*-aminophenol and the order for the reaction to *p*-aminophenol and aniline is  $\alpha < \beta$ .

The phenomenon of the induction period of about 20 min can be explained by the time required for hydrogen diffusion from the gas phase to the nitrobenzene phase then to the Pt/C catalyst active sites, followed by adsorption of the reactive species, surface reaction(s), desorption of the products N-phenyl hydroxylamine or aniline, then the product diffusion from the nitrobenzene phase to the acid phase.

## Conclusion

This first report on the macro-kinetics of the hydrogenation of nitrobenzene to *p*-aminophenol in a four-phase reactor provides an evaluation of a novel reaction sequence for *p*-aminophenol preparation. A rate equation is proposed depending on an exponential function of hydrogen pressure and temperature to quantitatively describe a selected result in the competitive formation of *p*-aminophenol and aniline.

## Notation

- $r_{\text{PAP}}$  : rate of hydrogenation for *p*-aminophenol (PAP) (kmol/m<sup>3</sup> s)  
 $r_{\text{AN}}$  : rate of hydrogenation for aniline (AN) (kmol/m<sup>3</sup> s)

- $-r_{NB}$  : overall rate of hydrogenation for nitrobenzene (NB) (kmol/m<sup>3</sup> s)
- $dn_{NB}$  : differential mole of nitrobenzene (kmol)
- $dn_{PAP}$  : differential mole of *p*-aminophenol (kmol)
- $dn_{AN}$  : differential mole of aniline (kmol)
- $w$  : catalyst loading (kg/m<sup>3</sup>)
- $dt$  : differential time (s)
- $E_{PAP}$  : activation energy for *p*-aminophenol formation (kJ/mol)
- $E_{AN}$  : activation energy for aniline formation (kJ/mol)
- $C_{NB0}$  : concentration for nitrobenzene at  $t = 0$  (kmol/m<sup>3</sup>)
- $C_{NB}$  : concentration for nitrobenzene (kmol/m<sup>3</sup>)
- $\rho_{NB}$  : density for nitrobenzene (kg/m<sup>3</sup>)
- $M_{NB}$  : mole weight (kg/kmol)
- $k_{PAP}$  : rate constant for *p*-aminophenol (kmol/kg s)
- $k_{AN}$  : rate constant for aniline (kmol/kg s)
- $k_0$  : specific rate constant for *p*-aminophenol
- $k'_0$  : specific rate constant for aniline
- $p_H$  : hydrogen pressure
- $\alpha$  : order for *p*-aminophenol formation
- $\beta$  : order for aniline formation
- $R$  : gas content, 8.314 kJ/kmol K
- $T$  : reaction temperature (K)
- $S_{PAP}$  : reaction selectivity for *p*-aminophenol to aniline
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