Organic Process Research & Development **2007**, *11*, 681–688

Hydrogenation of Nitrobenzene to 4-Aminophenol over Supported Platinum Catalysts

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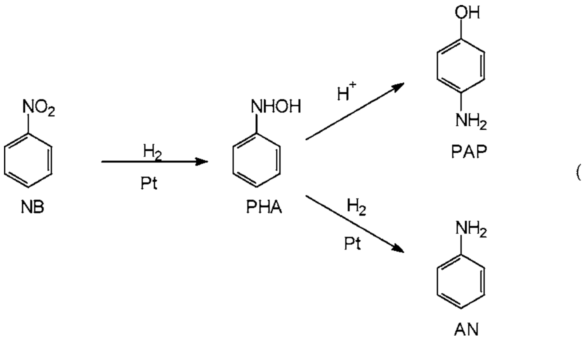
Abstract:

The conversion of nitrobenzene (NB) to *p*-aminophenol (PAP) takes place by way of an initial partial hydrogenation to produce phenylhydroxyl amine (PHA) which then undergoes an in situ acid-catalyzed rearrangement to PAP. This reaction is most commonly run using Pt/C catalysts in the presence of aqueous sulfuric acid and a surfactant to assist in dispersing the NB throughout the reaction medium. The yield of PAP is closely related to those reaction parameters which facilitate first the partial hydrogenation step and second the acid-promoted rearrangement before further hydrogenation to aniline can take place. The effect which a number of reaction parameters such as hydrogen pressure, reaction temperature, stirring rate, and the amounts of NB, the catalyst, and the surfactant present in the reaction mixture had on the rate and selectivity of the hydrogenation was examined. Optimization of these parameters led to the formation of PAP at a selectivity (PAP/AN) of 5.4 with a productivity of over 80,000 g PAP/g Pt/h.

Introduction

The catalytic hydrogenation of nitrobenzene (NB) to *p*-aminophenol (PAP) under phase transfer conditions is an industrially important process first reported by Henke and Vaughen in 1940.[1] PAP is an important intermediate which has been used in the production of analgesic drugs such as acetaminophen,[2] photographic developers, and dyes.[3] This hydrogenation is generally conducted in a four-phase system: an organic phase of the NB, an aqueous phase of dilute sulfuric acid, a supported platinum catalyst, and a hydrogen atmosphere. A significant rate enhancement and improvement in the selectivity to PAP was achieved when the hydrogenation was carried out in the presence of a phase transfer agent (PTA) such as a quaternary ammonium salt or a polyether polyol surfactant[4−9] which facilitated the dispersion of the NB throughout the aqueous reaction mixture.

While most of the information regarding the effect of the catalyst and catalyst modifiers, the nature of the surfactant, or specific process improvements are well documented in patent sources,[10−17] surprisingly little has been published in the open literature.[18−24] The commonly accepted reaction mechanism involves the initial hydrogenation of NB to give the intermediate PHA which desorbs from the catalyst surface into the aqueous phase and is further converted to PAP through an acid-catalyzed rearrangement[21,25,26] (eq 1). Some of the PHA. though, can be further hydrogenated to aniline (AN). The ratio of the products from these two pathways determines the reaction selectivity toward PAP.



(Eqn. 1)

Details regarding the influence of some reaction variables on the hydrogenation of NB to PAP in a multiphase system in the presence of a platinum catalyst and *N*,*N*-dimethyldodecylamine as a PTA are presented below. The variables

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10.1021/op700049p CCC: $37.00

Table 1. **Physical properties of the 1.5% Pt/C catalysts used for the hydrogenation of AN to PAP under standard reaction conditions**

cat. #	JM#	% metal dispersion[a]	metal surface area (m^2/g)	mean particle size (μm)	catalyst acidity/basicity
1	C-5105	53	1.96	36.0	acidic
2	C-5113	62	2.39	36.0	acidic
3	C-5118	73	2.71	36.0	acidic
4	C-5117	74	2.76	36.0	acidic
5	C-5109	79	2.94	36.0	acidic
6	C-5126	23	0.87	20.0	neutral
7	C-5112	25	0.91	20.0	neutral
8	C-5106	65	2.40	34.0	neutral
9	C-5114	79	2.94	34.0	neutral
10	C-5110	81	3.00	34.0	neutral

[a] (Number of metal atoms on the surface of the catalyst/total number of metal atoms) × 100.

studied were the hydrogen pressure, the stirring efficiency, the temperature, and the amounts of catalyst, NB, sulfuric acid, and the PTA. The effects of each of these variables on the initial rate of hydrogenation, the reaction productivity, and the selectivity to PAP formation were investigated.

Experimental Section

Materials. The materials used were all certified ACS grade. The nitrobenzene, aniline, *N*,*N*-dimethyldodecylamine, and *p*-aminophenol were obtained from Sigma-Aldrich and were used without further purification. Ten 1.5% Pt/carbon catalysts were received from Johnson Matthey, Precious Metals Division. Each had a uniform distribution of Pt on the support and was supplied in a wet form. The properties of these catalysts are listed in Table 1. In screening these catalysts the amount of each used corresponded to a dry weight of 13.5 mg of catalyst (1.04 μmol of Pt).

Apparatus. Experiments were carried out in a low-pressure glass volumetric system described elsewhere.[27] This apparatus allowed for the simultaneous running of four reactions with independent temperature and pressure control as well as the monitoring of the hydrogen uptake of each reaction separately. Each reactor was composed of an Ace Glass reaction flask capped with a Teflon plug which accommodated injection and thermocouple ports. The Teflon plug was additionally equipped with a suspended stirrer also made of Teflon.

Nitrobenzene Hydrogenation. In a representative hydrogenation the reactor was charged with sufficient wet catalyst equivalent to 13.5 mg on a dry basis (1.04 μmol Pt), 30 mL of 10% w/w aqueous H_2SO_4, 0.75 mL of the phase transfer agent (PTA) solution (0.145 M *N*,*N*-dimethyldodecylamine dissolved in 10% aqueous sulfuric acid) and 4.86 g (39.3 mmol) of freshly distilled NB. The reactor was connected to the system and was then alternately filled with nitrogen to 15 psig and purged five times. The reactor temperature was then slowly raised to the set value under constant stirring. The stirring rate, which appeared to be the most critical requirement for obtaining reproducible results, was accurately maintained at the desired value by using a microprocessor controlled magnetic stirrer (VWR brand model 400S). Once the desired temperature was reached the stirring was stopped, the nitrogen was replaced with hydrogen by multiple flush cycles, and the flask was pressurized to 10 psig with hydrogen. The stirring was reinitiated and computer monitoring of the reaction parameters begun. The progress of the reaction was followed by the hydrogen uptake, and once the required conversion level was reached, the reaction flask was cooled to ambient and a sample extracted for HPLC analysis. In some instances the reaction was run to full conversion with small portions of the reaction mixture extracted via gastight syringe at increments of 10% conversion, and the samples were analyzed.

Multiple Catalyst Use. As commonly done in most of commercial applications, the catalyst was separated after each reaction by terminating the hydrogenation when about 85−90% of the NB has reacted. The remaining NB was sufficient to hold the catalyst in a suspended form and allowed an easy extraction of the products dissolved in the aqueous phase. Recharging the reactor with a fresh portion of the starting reaction mixture permitted the multiple use of the catalyst without exposing it to air.

Analytical Methods. The analytical method used was similar to that reported.[19] A reversed phase Eclips XDB C18 column (150 mm × 4.6 mm ID), particle size 3.5 μk (Agilent Technologies) was used. The mobile phase A was a 0.084M NH_4OAc buffer at pH = 6.8 and mobile phase B was a 10:1 solution of acetonitrile/*i*-PrOH. The flow rate was set at 1 mL/min at 45% mobile phase A in isocratic mode. To prepare the sample solutions, 0.5 mL of the reaction mixture was pipetted into a 50 cm^3 volumetric flask, and the sample was diluted to the mark with a 0.5% H_2SO_4 solution of the internal standard, *N*-phenyl-1,2-phenylenediamine (0.5 mg/mL).

Data Processing and Analysis. At the end of each run the hydrogen uptake data were plotted against time, and the initial reaction rates were calculated from the slope of the initial linear portion of the hydrogen uptake curve. On the basis of this and on the results of the HPLC analysis of the aqueous phase, the following parameters were used to evaluate the efficiency of the reaction:

conversion of NB: ([PAP] + [AN]) × 100/([NB]), %
selectivity to PAP: g PAP/g AN
rate of H_2 uptake from the H_2 uptake curve to 30% conversion, mmol/min
productivity to PAP: g PAP/g Pt/

Results and Discussion

The reaction conditions described in previous reports concerning the partial hydrogenation of NB in acid media to form *p*-aminophenol are listed in Table 2. As seen from these data the platinum-catalyzed hydrogenation of NB in aqueous sulfuric acid has generally been carried out using relatively low concentrations of NB, a small amount of a Pt/C catalyst, temperatures of 80−90 °C, and low hydrogen pressures, generally below atmospheric. One publication[21]

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Table 2. **Conditions reported for the hydrogenation of nitrobenzene to PAP**

ref	4	7	8	9	12	21	this paper
H_2 (psig)	3.9	0.9[a]	0.4[b]	10	0.4[c]	400	10
T (°C)	88	85	85	80	90	80	90
Pt/C (%)	1	3	3	1.5	Pt/Al_2O_3	3	1.5
Pt (mg)	16	7.5	7.5	30	7.5	1	0.2
NB (g)	66.2	108	185	1200	108	23	4.86
H_2SO_4 (g)	28.2	80	110	665	80	11	3.84
H_2O (mL)	1,000	640	650	4,000	650	to 100	30
PTA	0.75 g	0.5 mL	2 mL	4 g	2 mL		23 mg
NB/Pt (w/w)	4100	14,400	25,000	40,000	14,400	22,000	24,000
NB/acid (w/w)	2.3	1.35	1.68	1.8	1.35	2.0	1.27
PAP/AN	7.5	5.4	4.1	6.6	5.5	1.4	6.7

[a] 6−25 in. of water (0.2−0.9 psig). [b] 10 in. of water (0.4 psig). [c] 6−10 in. of water.

reported the use of much higher hydrogen pressures, but the resulting reaction selectivity was very low. Since this is a four-phase system, an efficient and accurately controlled mixing of the two liquid phases is crucial for obtaining reproducible and meaningful results. On the basis of these published data the "standard" reaction conditions to be used in this study were selected as being fairly consistent with those listed in Table 1 while still allowing for a reasonable amount of variation when examining the effect which each parameter has on the outcome of the reaction. These standard conditions are listed in the last column of Table 2. As mentioned above, the degree and type of agitation of the reaction mixture is critical to the success of this hydrogenation. It is, however, difficult to compare stirring rates with the efficiency of agitation since the design and size of the reactor are also factors influencing mass transfer. On the basis of some preliminary studies it was determined that with our reactor system a stirring rate of 1700 rpm was sufficient in order to have a reaction reasonably free of diffusion limitations as shown by the data presented in Figure 4.

The Catalyst. The catalysts listed in Table 1 were each used for the hydrogenation of NB to PAP under our "standard" reaction conditions. Figure 1 shows the relationship between the metal surface areas of the catalyst and the product selectivity and productivity obtained with each. Most of these catalysts produced fairly high selectivities and productivities so the selection as to which one to use for the reaction parameter study was not straightforward. It was decided, though, that catalyst 1, which had only a moderate metal surface area (and dispersion) but still gave good selectivity and productivity, was the most reasonable to use in the further study. It was felt that with this moderate metal surface area this catalyst might be more influenced by changes in the various reaction parameters.

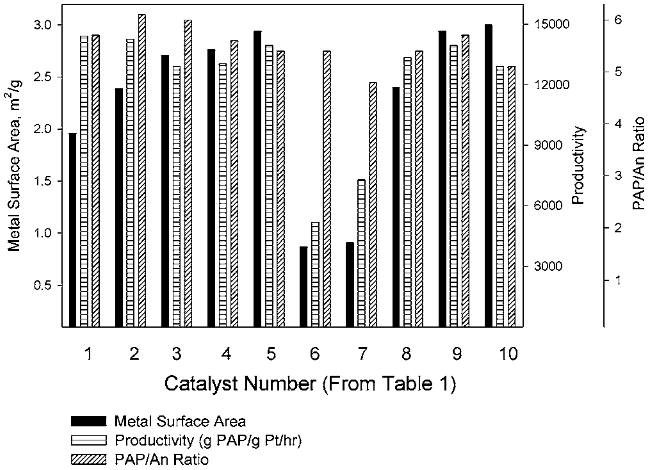

Figure 1. **Comparison between metal surface area and reaction productivity and selectivity in the hydrogenation of NB to PAP over the catalysts listed in Table 1.**

Table 3. **Initial hydrogenation rate, reaction productivity, and selectivity observed in the multiple use of catalyst 1 under the standard reaction conditions listed in the last column of Table 1**[a]

	rate mmol/min	productivity g PAP/g Pt /h	selectivity PAP/AN
first use	0.592	15,600	5.7
second use	0.592	15,300	5.7
third use	0.555	14,900	5.9
fourth use	0.533	15,000	5.9

[a] The hydrogenation was carried out at [NB] = 1.13 M, stir rate 1700 rpm, pressure 10 psi, catalyst 1 = 33.7 mg (wet), temperature 90 °C, [PTA] = 3.1×10^{-3} M.

In order to determine the stability of this catalyst under our standard reaction conditions it was used for four successive NB hydrogenations with the resultant initial rates, productivities, and selectivities listed in Table 3. These data show that the catalyst performance during these repeated cycles remained relatively stable as measured by the hydrogen uptake rate and the PAP selectivity and productivity. The cumulative turnover number for the catalyst after these four cycles was 132,000 mol PAP/mol Pt at an average selectivity to PAP in the 87−88% range and a productivity of about 15,000 g PAP/g Pt/h.

Reaction Details. The hydrogen uptake curve obtained from a hydrogenation run under our "standard" conditions using catalyst 1 is shown in Figure 2. Examination of this curve along with a careful observation of the reaction mixture shows that the hydrogenation is composed of four distinct regions. The first, A, is characterized by the linear rate of hydrogen uptake which continues to about the 70−75% conversion level. In the second region, B, the rate of hydrogen uptake slows, but the acid/NB/water emulsion is still intact (in these two regions it takes an average of 10−15 min after the stirring has stopped to see a phase separation with a bottom organic phase and a top aqueous phase with the catalyst being in the organic phase). During the third stage, C, when most of the NB has been consumed and there is not enough NB present to keep the catalyst in the dispersed state, the emulsion collapses, and the catalyst separates with the remaining NB into a few isolated organic droplets. The fourth stage, D, finishes the reaction with the disappearance of the remaining organic phase, redispersion of the catalyst

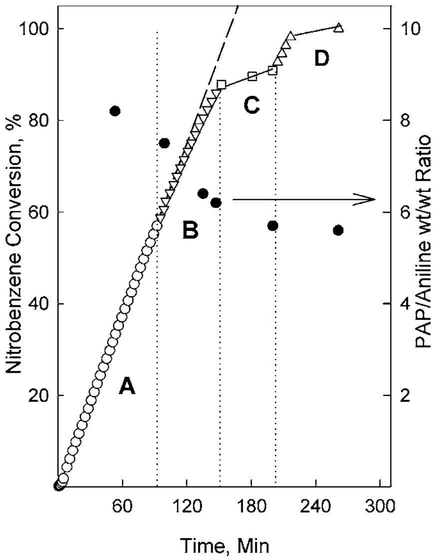

Figure 2. **Hydrogen uptake curve and reaction selectivity recorded during the hydrogenation of NB under the phase transfer conditions listed in the Experimental Section.**

into the aqueous phase, and the slow hydrogenation of the NB still remaining in the aqueous phase.

The PAP/AN ratios for samples withdrawn at different times in these four regions are also shown in Figure 2. The most interesting changes were taking place in the transition from region A to region B. Here the emulsion was still stable in appearance, and the hydrogenation was proceeding at a relatively constant rate, but the PAP selectivity showed a continuous deterioration. In regions C and D the hydrogenation took place at the expense of the NB dissolved in the aqueous phase. In these regions the system produced AN and PAP at relatively constant rates which led to a consistency in the PAP/AN ratios. In order to eliminate the effect of the variation in the selectivity to PAP and to have a reliable basis for comparison in all further experiments, all subsequent reactions were quickly quenched at the end of region B, and the product composition was analyzed after cooling to ambient.

Another observation from the analysis of the samples taken within the same run was that the only products formed during the hydrogenation were PAP and AN. No other intermediates or byproducts accumulated in measurable amounts, a fact which supports the idea that under this set of conditions the rate-determining step is probably the formation of the PHA intermediate.[6] Once this intermediate is formed, it can be hydrogenated further to produce AN or migrate to the acidic aqueous phase to rearrange to PAP (eq 1).

Since further hydrogenation requires a hydrogen-rich environment, all reaction variables which would increase the hydrogen availability to the platinum site should lead to the formation of more AN and a lower PAP selectivity. Alternately, creating a "hydrogen-poor" environment with a decreased hydrogen availability to the catalyst and an efficient transport of the PHA intermediate to the acidic phase will promote a higher PAP selectivity.

Figure 3 shows a cartoon depicting the various processes occurring during the hydrogenation of NB in presence of a PTA. The hydrophobic catalyst is contained exclusively within the NB droplets produced as a result of the stirring action and the presence of the PTA. The hydrogen migrates through the aqueous/organic interface into the droplet and onto a catalyst surface. Here, the initial hydrogenation of NB to PHA takes place. In an appropriate "hydrogen poor" environment, the PHA migrates out of the droplet and into the acidic aqueous phase to rearrange to PAP. However, as the reaction proceeds, the amount of NB present decreases, and most likely, the size of the NB droplets also decreases. Nevertheless, since the amount of catalyst remains the same, the catalyst concentration within each droplet increases, thus producing droplets such as that depicted by B in Figure 3. In such a "catalyst rich" environment the PHA will find it more difficult to migrate out of the droplet without encountering more catalyst with the potential for promoting further hydrogenation. This is apparently one reason why the PAP selectivity decreases during the course of the reaction, especially in the later stages of region A and throughout region B in Figure 1. There is, however, over 6 times more PAP formed than AN in regions C and D so that further hydrogenation of PHA is still slower than the rearrangement by an appreciable amount.

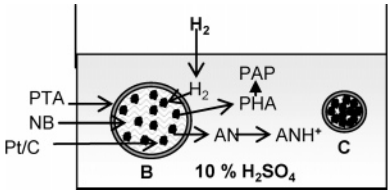

Figure 3. **Representation of the four-phase system in the NB hydrogenation over a Pt/C catalyst.**

Stirring Rate and Catalyst Quantity. One of the reaction parameters considered to be critical in achieving a rapid reaction and high PAP selectivity was the stirring rate. This should be sufficient to enhance the diffusion of the gaseous and liquid substrates to and from the catalyst but not too vigorous to keep an optimum "hydrogen-poor" environment so that high PAP selectivity can be attained.

Running the hydrogenations using the standard conditions listed in Table 2 but varying the stirring rate from 300 to 2000 rpm produced the results shown in Figure 4A. The most dramatic changes occurred when the stirring rate was varied between 300 and 1400 rpm during which the PAP selectivity declined to a PAP/AN ratio of 7 with the hydrogen uptake rate increasing and following a second-order relationship. When the stirring rate was increased from 1400 to 1800 rpm, the selectivity remained essentially constant, and the hydrogenation rate appeared to be leveling off, indicating that mass-transfer processes were becoming less important to the reaction with this range of agitation. All further reactions were run using 1700 rpm as the standard stirring rate.

The effect of the catalyst quantity on the rate of hydrogen uptake and the PAP selectivity was studied over the range of 10−60 mg of wet catalyst, corresponding to substrate-to-Pt mol ratios of 127,000:1 to 21,200:1. As shown in Figure 4B, varying the quantity of catalyst while maintaining the other standard conditions resulted in an initial rate increase with an increase in the amount of catalyst with a trend toward

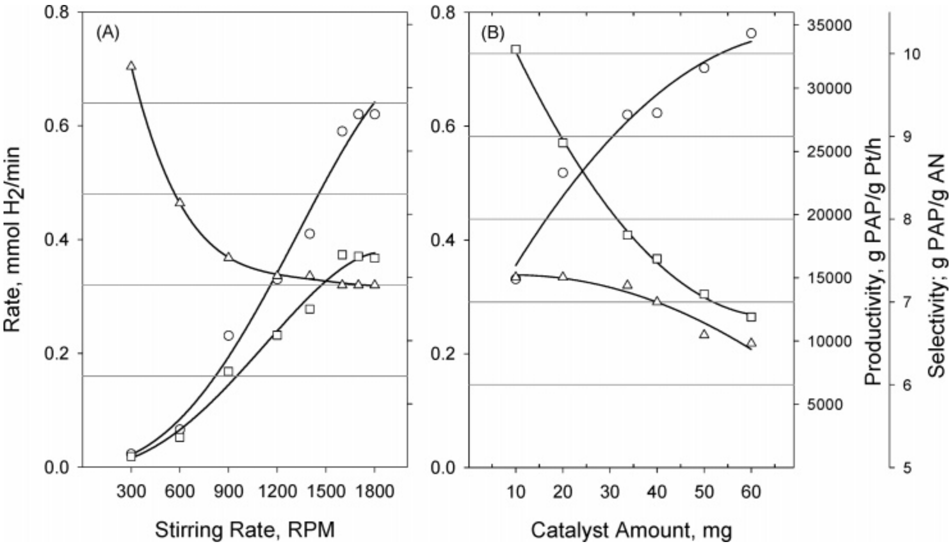

Figure 4. **Dependence of the hydrogen uptake rate (○), the selectivity to PAP (△), and the productivity (□) on the stirring rate (A) and on the catalyst quantity (B); other reaction parameters are as given in the Experimental Section.**

saturation observed using the higher catalyst amounts. This tendency of the hydrogen uptake to deviate from the first-order reaction kinetics indicated that some diffusion-related phenomenon may be taking place at the higher catalyst loadings within the limited space provided by the organic phase (Figure 2). The PAP selectivity and productivity both dropped off considerably at higher catalyst loadings.

The data shown in graphs A and B of Figure 4 complement each other and fit well into the model depicted in Figure 2 in which the PHA intermediate once formed in the organic phase will have to migrate from within the NB droplet towards the exterior acidic interface to rearrange or remain and be hydrogenated further to AN. According to this model, increasing the stirring rate at given substrate and PTA concentrations should lead to a reduction in the size of the NB particle and, respectively, to an increase in the contact area between the organic and the aqueous phases. The reduction in the size of the NB droplet is expected to act in two opposite directions. From one side, this will increase the contact area between the organic and the aqueous phase and will improve the rate at which the PHA can migrate out of the droplet and into the acidic aqueous phase. It will also increase the rate of hydrogen transport to the interior of the particle. Higher hydrogen availability will facilitate the PHA formation but will also enhance the rate of AN formation. This aspect is supported by the observed second-order relationship between the stirring rate and the hydrogen uptake rate and the reduction in the PAP selectivity for stirring rates in the 300−1400 rpm region. Above that value the rate of hydrogen diffusion likely remains constant, and the size of the NB particles probably does not change significantly, a factor which would also explain the independence of the hydrogenation rate and the PAP selectivity at stirring rates above 1400 rpm.

The drop in PAP productivity and selectivity observed at higher catalyst quantities (Figure 4B) is probably another example of the effect of having large amounts of catalyst present in the NB droplets. As discussed above (Figure 2B) after the initial formation of the PHA, if this species finds it difficult to migrate into the acidic aqueous phase because of the amount of catalyst present in the NB droplet, further hydrogenation of the PHA to AN has a high probability of taking place.

Temperature and Hydrogen Pressure Effect. The effect which the reaction temperature had on the hydrogenations is shown in Figure 5A in which a maximum in the reaction rate and PAP productivity is found at a reaction temperature of 90 °C. The relatively narrow temperature range studied (80−100 °C) was used because outside of this temperature interval the rate of hydrogenation was either too low or the reaction showed decreased selectivity.

The effect of the hydrogen pressure on the initial rate and on the selectivity under otherwise standard conditions is shown in Figure 5B. With an increase in the hydrogen pressure both the initial rate and productivity increased almost linearly up to about 30 psig beyond which point they reached constant levels of about 1.4 mmol/min and about 36,000 g PAP/g Pt/h respectively. The PAP productivity, which is a parameter relating the catalyst performance to the selectively in forming PAP, increased 2-fold in the hydrogen pressure range shown in Figure 5B. Increasing the hydrogen pressure and consequently the local hydrogen concentration in the interior of the organic droplets appears to affect primarily the rate of the first hydrogenation step to give PHA and to a lesser extent the further hydrogenation to give AN. This suggests that even under higher hydrogen availability conditions the further hydrogenation of PHA to AN remains relatively slow compared with the rearrangement of PHA to PAP. This is not too surprising given that the initial step involves the hydrogenation of an unsaturated species while the conversion of PHA to AN requires the hydrogenolytic cleavage of a N−O single bond.

Concentration of H_2SO_4 in the Aqueous Phase. The effect of the concentration of the H_2SO_4 in the aqueous phase was studied over the range of 5−15% w/w under the standard reaction conditions. The results are shown in Figure 6. Increasing the acid concentration over this range led to a slight reduction in the hydrogen uptake rate and, at the same

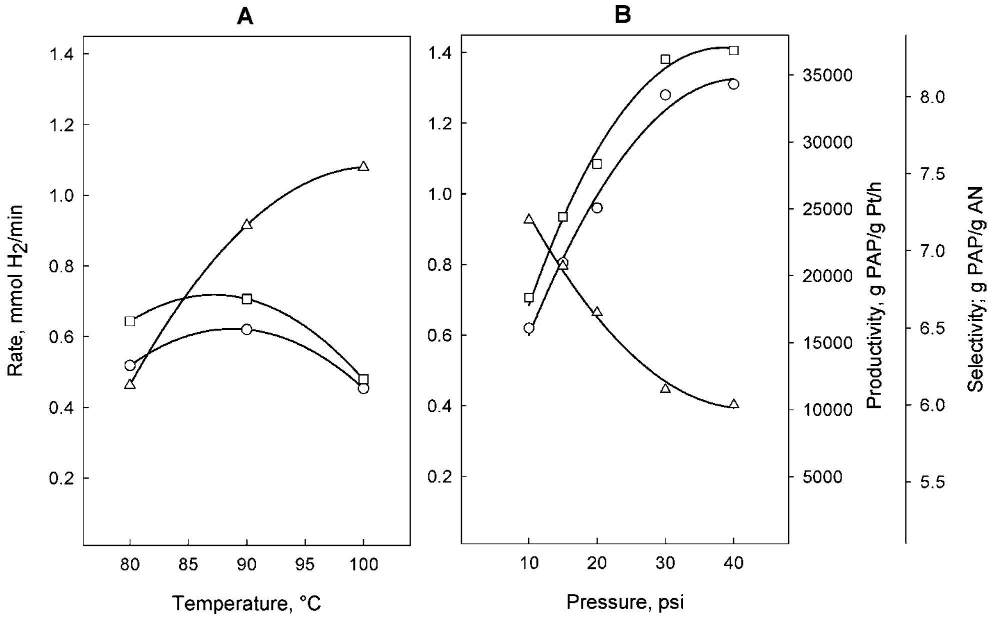

Figure 5. **Dependence of the hydrogen uptake rate (○), the selectivity to PAP (△), and the productivity (□) on the temperature (A) and on hydrogen pressure (B); other reaction parameters are as given in the Experimental Section.**

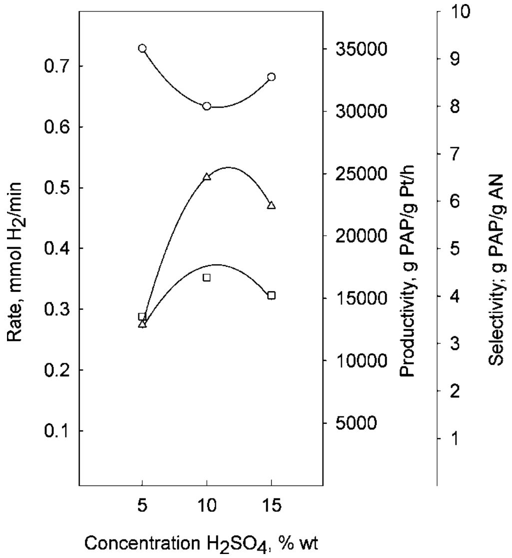

Figure 6. **Dependence of the hydrogen uptake rate (○), the selectivity to PAP (△), and the productivity (□) on the concentration of H_2SO_4 in the aqueous phase; other reaction parameters are as given in the Experimental Section.**

time, to an increase in the PAP selectivity. A further increase in the acid concentration did not produce significant changes in the reaction efficiency. The initial hydrogenation rate and the PAP selectivity remained fairly constant at the higher concentration of H_2SO_4. These findings are in agreement with the results reported earlier for the NB hydrogenation carried out under similar conditions but at higher hydrogen pressures.[18,21]

Nitrobenzene Concentration Effect. Figure 7 shows the effect of the initial NB concentration in 10% aqueous H_2SO_4 (A) and 15% aqueous H_2SO_4 (B) on the hydrogenation rate, PAP selectivity and reaction productivity. The [NB] was varied over the range 0.5−1.6M. A significant difference was found in the performance of the system under the "low" acid vs "high" acid regimes.

At the lower acid concentration increasing the substrate concentration over the range of interest resulted in a near linear increase in the initial hydrogen uptake which reached a saturation level at a substrate concentration of 1.14 M. The PAP productivity passed through a maximum at [NB] $\approx$ 1 M, while the selectivity to PAP deteriorated continuously to a PAP/AN ratio of 5 at high substrate concentrations (Figure 7A). The same trend in the PAP selectivity was observed under the "high" acid concentrations as well (Figure 7B). In contrast to the "low" acid system, in the presence of the more concentrated acid the initial rate of hydrogen uptake remained relatively constant, and as a result, the productivity showed a distinct deterioration with increasing [NB].

In general, an increase in the initial concentration of NB at constant PTA concentration should probably lead to the formation of a suspension in which the NB particles have a larger average particle size. The immediate result of such changes would be that the PHA intermediate will have to traverse longer distances to reach the exterior of the particle to form PAP while the probability for the secondary hydrogenation to form AN will be favored in the larger NB droplets. This can also explain the sharp decline in the PAP selectivity at high NB concentration under both acid concentrations.

Phase Transfer Agent Concentration Effect. The PTA concentration was also varied over the range of $1 - 5 \times 10^{-3}$ M with the results shown in Figure 8A−C. The effect of the [PTA] was studied at three different sets of conditions: (1) at low substrate and low acid concentrations (8A), (2) at low substrate and at high acid concentrations (8B), and (3) at high substrate and high acid concentrations (8C). As shown, the hydrogen uptake rate in the first case (8A) increased linearly with increasing PTA concentrations to about 4×10^{-3} M after which point the rate remained relatively constant. Surprisingly, the selectivity to PAP in this region was not affected. It is worth noting that the molar

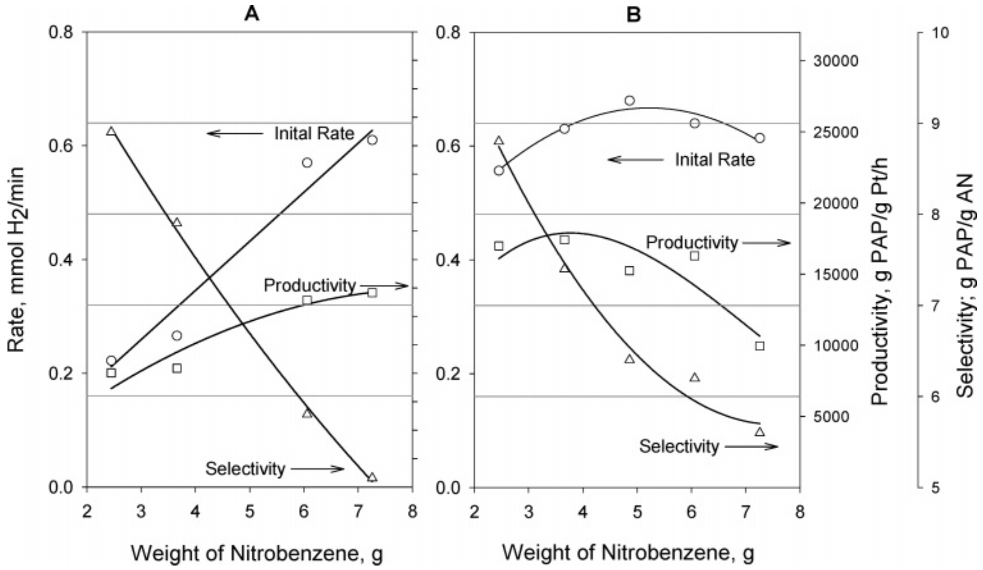

Figure 7. **Dependence of the hydrogen uptake rate (○), the selectivity to PAP (△), and the productivity (□) on the NB concentration using 10% aqueous H_2SO_4 (A) and 15% H_2SO_4 (B); other reaction parameters are as given in the Experimental Section.**

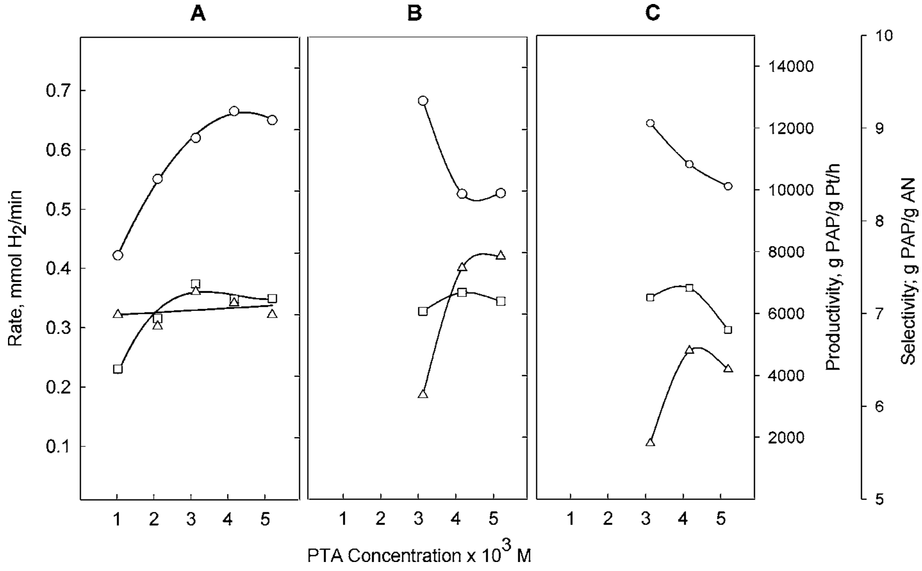

Figure 8. **Dependence of the hydrogen uptake rate (○), the selectivity to PAP (△), and the productivity (□) on the PTA concentration using 4.86 g of NB and 10% aqueous H_2SO_4 (A), 4.86 g of NB and 15% aqueous H_2SO_4 (B), and 6.06 g of NB and 15% aqueous H_2SO_4; other reaction parameters are as given in the Experimental Section.**

ratio of NB/PTA varied from 1000:1 at the low PTA concentration to 200:1 for the highest PTA concentration. In an attempt to further understand how the surfactant could affect the overall performance of this complex system one should consider the following simplified structure of small, water-immiscible organic droplets uniformly dispersed in the aqueous phase. In a model such as this a surfactant molecule interacts with the organic phase in the droplet with the alkyl chain being oriented towards the interior of the particle and the hydrophilic part forming a protective film around the dispersed phase.[28] It is also known that ionic surfactant molecules would form a more dense population on the surface of the particle than nonionic species due to electrostatic repulsion between their head groups. Such a particle forms a fairly immobile layer of ions that stick tightly to the surface and that may include water molecules. The densely charged particle attracts an oppositely charged ionic atmosphere. The inner shell of charge and the outer atmosphere are called the electric double layer the density of which is a function of the concentration of the surfactant.

With such a model in mind, one can hypothesize that an increase in the surfactant concentration could lead to a reduction in the size of the droplet and, as such, would lead to an increase in the rate of hydrogen transport into the interior of the particle. This, in turn, would bring about a reaction rate enhancement. When the PTA concentration is further increased above a certain level, the surface charge may become strong enough to hinder the hydrogen flow

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(28) Atkins, P. W. *Physical Chemistry, 4th ed.*; W.H. Freeman and Company: New York, 1990; p 708.

through the interface and cause a leveling off of the reaction rate. This surface charge, though, does not appear to affect the migration of the PHA into the acidic aqueous phase since the PAP selectivity remained constant over the whole range of PTA concentrations (Figure 8A).

Similar conclusions can be drawn for the reactions run with low NB and high acid concentration. Here, because of the higher proton concentration in the aqueous phase, the higher surface charge around the NB droplet may further hinder the hydrogen flow through the interface and cause an additional reduction in the reaction rate (Figure 8B). Increasing simultaneously the NB concentration and the acid concentration led to further deterioration in the PAP selectivity (Figure 8C).

Optimized Reaction Conditions. Examination of the data presented in Figures 3−7 shows that modification of our so-called “standard” reaction conditions can lead to an increase in PAP formation. The data indicate that such an increase could be accomplished by increasing the hydrogen pressure and the NB concentration while decreasing the amount of catalyst used. A small increase in the PTA concentration could also be of advantage. Changes in reaction temperature, agitation rate, and sulfuric acid concentration do not appear to result in a significant improvement in the reaction selectivity or productivity. As shown in Table 3, using the standard reaction conditions produces PAP with an initial hydrogen rate of 0.59 mmol/min, a productivity of 15,600 g PAP/g Pt/h and a selectivity of 5.7. To ascertain the extent to which the PAP productivity would increase when “optimized” reaction conditions were used, the hydrogenation was run with the amount of NB increased from 4.86 to 6.88 g, the hydrogen pressure increased from 10 to 35 psig, the PTA concentration increased from 3.1×10^{-3} to 3.5×10^{-3} M, and the amount of catalyst decreased from 33.5 to 20 mg (wet). This reaction proceeded at an initial rate of 1.73 mmol H_2/min with a productivity of 81,700 g PAP/g Pt/h and a selectivity of 5.4. Under these conditions the NB/Pt ratio increased to about 57,000, considerably higher than those ratios listed in Table 2. Granted, these particular reaction conditions apply only to the reactor used in this study, but these data do show that the hydrogen pressure and the NB/Pt ratio are the most important factors in this reaction. They also indicate that even though almost all of the previously reported NB to PAP hydrogenations (Table 2) were run under low hydrogen pressure the use of somewhat higher pressure, smaller amounts of catalyst, and a higher amount of NB appears to be of advantage in increasing the productivity of the reaction.

Acknowledgment

We acknowledge financial support for this project from Johnson Matthey.

Received for review February 27, 2007.

OP700049P