

A New Platinum Catalyst for the Hydrogenation of Halonitroaromatics

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A platinum catalyst has been developed for the selective hydrogenation of halonitroaromatics. The catalyst performs favourably under a variety of operating conditions without the need for process additives. Satisfactory selectivities have been obtained with a wide variety of substrates and further product purification may be unnecessary.

The wide application of haloaromatic amines in the production of pesticides, herbicides, synthetic dyes, pharmaceutical preparations and other substances has resulted in considerable interest in their mode of preparation. The principal route to halogenated amines is from the nitro compound, either by reduction with iron-hydrochloric acid or by catalytic reduction with hydrogen over a noble metal catalyst. Until recently the preferred route in Europe, and to a certain extent in the United States of America, was the iron-hydrochloric acid reduction route. The reduction usually proceeds smoothly with a high yield of the haloamine, but requires that a steam distillation step be inserted into the preparation to separate the

haloamine from the iron oxide sludge. The high energy consumption by this process and the environmental problems associated with disposing of the iron oxide sludge have led haloamine producers to seriously consider the catalytic reduction of halonitroaromatics. However, the catalytic reduction of the corresponding halogen-substituted aromatic nitro compounds is complicated because the conversion to the amines is usually accompanied by simultaneous dehalogenation which thus lowers the yield of the desired product and promotes the formation of corrosive halogen acids:

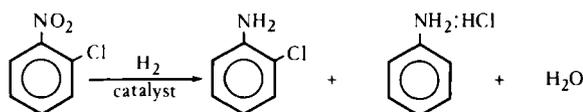


Table I				
Comparison of the Hydrogenation of 2-Chloronitrobenzene in the Cook and Baskerville Autoclaves				
Temperature: 90°C			Pressure: 1140 kPa	
Catalyst platinum/carbon	Catalyst loading: weight per cent of substrate	Reaction rate mol./min./g Pt	Conversion per cent	Selectivity to 2-chloroaniline per cent
Baskerville stirred autoclave, 1000 rpm				
Conventional	0.7	0.9	100	66.0
Modified	0.5	1.26	100	99.5
Cook hydrogenator, 250 cycles per minute				
Conventional	0.5	1.63	100	80.0
Modified	0.5	1.58	100	99.0

Table IV						
Effect of Catalyst Loading on the Hydrogenation of 2,5-Dichloronitrobenzene in the Cook Autoclave						
Temperature: 90°C		Pressure: 1140 kPa Agitation Rate: 250 cpm				
Catalyst loading: weight per cent of substrate	Reaction rate 10 ³ mol./min.	Product distribution, per cent				
		2,5-DCA	2,5-DCNB	o-CA	m-CA	A
0.25★	2.23	50.89	49.08	0.03	—	—
0.50	6.25	99.32	0	0.24	—	0.43
1.0	8.93	97.23	0	0.51	0.88	1.15
1.5	10.00	96.77	0	0.79	0.37	1.67
2.0	11.63	95.26	0	0.76	2.07	1.92

● This run was not taken to completion

2,5-DCA 2,5-dichloroaniline
2,5-DCNB 2,5-dichloronitrobenzene
o-CA ortho-chloroaniline

m-CA meta-chloroaniline
A aniline

these requirements and operate under conditions which relate to commercial processes, two types of high pressure autoclave were employed:

1. A Baskerville mini-glandless autoclave in which the reaction mixture is stirred.
2. A modified Cook autoclave which provides agitation by rocking.

The products of the reaction form a two phase system consisting of an organic and an aqueous layer. However an ionic organic halide formed by dehalogenation tends to reside in the aqueous layer. Consequently, to obtain a true analysis of the reaction mixture, the dehalogenated product was shifted to the organic layer by addition of sodium bicarbonate. The organic layer was then separated and diluted with diethyl ether and the catalyst removed by filtration. The resulting solution was analysed by gas-liquid chromatography and the selectivity of a catalyst for the completed reaction was defined as the following percentage:

$$\frac{[\text{Hydrogenation Product}] \times 100}{[\text{Hydrogenation Product}] + [\text{Hydrogenolysis Product}]}$$

Effect of Agitation

The results given in Table I demonstrate that for both of the autoclaves employed, with obviously different agitation characteristics, the new platinum on charcoal catalyst gives

selectivities greater than or equal to 99 per cent. In comparison, a conventional carbon supported platinum catalyst displays poor selectivity with both the Baskerville and the Cook autoclaves.

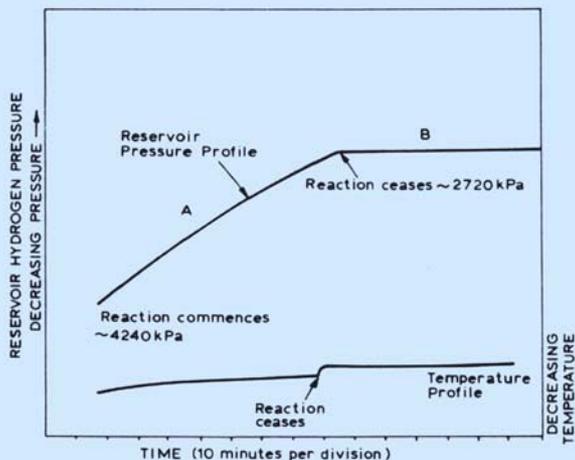
The results of a series of experiments using the Cook rocking autoclave, where the rate of agitation of the mixture was varied, are given in Table II.

Here, increased agitation is seen to increase the overall dehalogenation. Between 200 and 250 cycles per minute a rapid increase in the rate of hydrogenation occurs. A further increase in the rate of agitation has little effect on the rate, possibly indicating that the reaction is now under chemical kinetic control. This behaviour is similar to that observed previously by Acres and Cooper during the hydrogenation of nitrobenzene over charcoal-supported palladium metal catalysts (9).

Effect of Pressure

The effect on the selectivity of the new catalyst when operating the reaction at an elevated pressure of 2170kPa is illustrated in Table III. It is clear that increased dehalogenation occurs under such conditions, and therefore low pressures of the order of 1137kPa are recommended for use with this catalyst. However, it is worth noting that even at high pressures the catalyst remains superior to a

Fig. 1 During the hydrogenation of 0.5 moles of 2,5-dichloronitrobenzene hydrogen is stored in a reservoir. As the reaction proceeds, and the nitrobody is converted, the decline in hydrogen pressure within the reservoir is recorded. The reaction temperature is also simultaneously monitored and the end of a reaction is indicated by a sharp fall in temperature of about 10 to 15°C



conventional noble metal catalyst operating at the lower pressure normally employed.

Catalyst Loading

The variation in selectivity obtained with different catalyst loadings is given in Table IV. It is apparent that dehalogenation increases as greater amounts of the catalyst are used, which may be a consequence of increasing the number of sites active for haloamine hydrogenolysis.

A typical hydrogenation trace obtained with 2,5-dichloronitrobenzene is illustrated in Figure 1. The reaction proceeded continuously until the completion of region A. If no dehalogenation occurred no further hydrogen uptake was observed in region B. However, if catalyst loadings greater than 0.5 per cent were employed the hydrogen pressure drop did not abruptly cease at the completion of A, but continued after the reaction had entered B.

Effect of Temperature

As the reaction temperature is increased, while all other reaction conditions remain constant, there is an increase in the amount of dehalogenation. The results obtained for the hydrogenation of 2,5-dichloronitrobenzene are presented in Figure 2. An apparent activation energy of 13.1kJ/mol was observed at temperatures above 110°C, which indicates that the reaction suffers from mass transfer

restrictions. Below 110°C the effect of temperature on the rate of reaction is more pronounced and the apparent activation energy was 39.4kJ/mol.

Alternative Substrates

So far only those results obtained with the modified platinum catalyst for the hydrogenation of both 2-chloronitrobenzene and

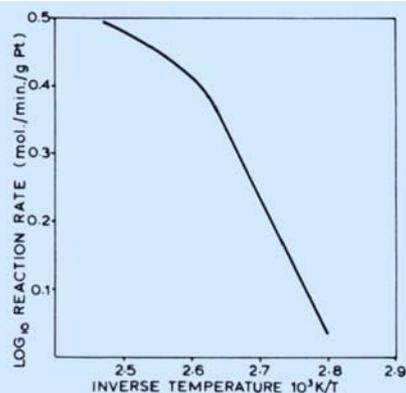


Fig. 2 The hydrogenation of 0.5 moles of 2,5-dichloronitrobenzene as represented here by an Arrhenius plot. Using a catalyst loading of 0.5 per cent of its substrate weight, it is evident that at temperatures above 110°C (reciprocal temperature $2.68 \times 10^{-3} \text{K}^{-1}$) the reaction rate begins to suffer from mass-transfer restrictions thus causing the Arrhenius plot to curve

Table V
Hydrogenation of a Variety of Chloro Substituted Compounds

Substrate	Autoclave	Catalyst loading: weight per cent of substrate	Temp. °C	Pressure kPa	Agitation rate cpm	Reaction rate mol./min./g Pt	Conversion per cent	Selectivity to desired products per cent
4-chloronitrobenzene	Baskerville	0.63	90	1205	1,000	1.01	100	98.8
3,4-dichloronitrobenzene	Baskerville	0.63	90	1205	1,000	1.65	100	97.2
2-chloro-6-nitrotoluene	Cook	0.63	80	1140	350	1.68	99.78	97.5
2-chloro-4-nitrotoluene (Batch 1)	Cook	1.88	80	1140	350	0.27	99.95	99.6
2-chloro-4-nitrotoluene (Batch 2)	Cook	0.63	80	1140	350	1.85	99.98	98.6

2,5-dichloronitrobenzene have been reported. However, the performance of the catalyst has also been assessed with a number of alternative haloaromatic substrates.

Chloro Substituted Compounds

The results obtained with several other chloro substituted compounds are summarised in Table V. The results show that the catalyst can hydrogenate a wide variety of substrates selectively to the desired products. It is likely that the selectivities quoted are lower than can actually be attained as the operating conditions were not optimised for each substrate.

Fluoro Substituted Compounds

Aromatic fluoro-amines offer great potential in the pharmaceutical industry. Since the strength of the carbon-fluorine bond is greater than that for the other halogens, the replacement of fluorine by hydrogen during a catalytic hydrogenation would not be expected to occur readily. However, hydrogenolyses of carbon-fluorine bonds have often been reported (10) and even fluorine species attached to an aromatic system can be replaced (11). Therefore, in view of their commercial importance, the performance of the modified catalyst with such compounds was evaluated.

The rate of hydrogenation of the fluoronitrobenzenes was lower than that observed with other halonitroaromatics and catalyst loadings of between 2 and 4 per cent were necessary with both 2- and 4-fluoronitrobenzene. However, 2,4-difluoronitrobenzene was hydrogenated rapidly with a loading of only 1 per cent at a reaction temperature of 110°C. Table VI describes the hydrogenation of 2- and 4-fluoronitrobenzene and also 2,4-difluoronitrobenzene. It is important to note that, as expected, very little dehalogenation took place.

Bromo Substituted Compounds

A brief examination was also made of the hydrogenation of 2-bromonitrobenzene on the Baskerville autoclave and a summary of the results obtained are presented in Table VII.

