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Mechanism of 2,4-dinitrotoluene hydrogenation over Pd/C

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Abstract

Hydrogenation of 2,4-dinitrotoluene (DNT) to 2,4-diaminotoluene (DAT) has been carried out over a 5% Pd/C catalyst. Gas chromatography and liquid chromatography have been used to detect the reaction intermediates. 4-Hydroxylamine,2-nitrotoluene (4HA2NT) is the main reaction intermediate. The two amino–nitro compounds 4-amino,2-nitrotoluene (4A2NT) and 2-amino,4-nitrotoluene (2A4NT) are the other relevant intermediates found. 4HA2NT decomposes by exposure to air and in the GC injector thus complicating the analysis of the reaction mixture. A simple procedure has been developed to perform the GC analysis without interference of the hydroxylamine. A kinetic study has been also carried out and a reaction pathway has been proposed. Intermediates are formed from DNT through three parallel reactions. They are then hydrogenated to the final product DAT by a series of consecutive reactions.

Keywords: 2,4-Dinitrotoluene; Hydrogenation; Palladium

1. Introduction

Catalytic hydrogenation of aromatic nitro-compounds is a process widely used for the production of large quantities of aromatic amines [1]. Amines are intermediates in the production of plastics, fine chemicals, pharmaceuticals, etc.

In this paper we have focused our attention on the catalytic hydrogenation of 2,4-dinitrotoluene (DNT) carried out in a batch slurry reactor over a 5% Pd/C catalyst.

Industrially this process is employed in the manufacture of the 2,4-toluenediamine (DAT) which is an intermediate in the formation of toluenediisocyanate used in the production of polyurethane [2].

Despite the great industrial interest, few studies have appeared in the literature on the hydrogenation of DNT [3–8]. Moreover, only in the recent papers of Janssen et al. [7,8] is there an extensive study of the reaction mechanism.

Hydrogenation of DNT shows a complex reaction mechanism which involves partial hydrogenation and/or condensation compounds, following the general scheme of the reduction of aromatic nitrocompounds first proposed for the reduction of nitrobenzene to aniline by Haber [9]. In studying the hydrogenation of DNT there are notable difficulties to detect all the reaction intermediates. In the previously published papers the gas chromatography has been widely used for analyzing the reaction mixture. This technique is however limited by the fact that some intermediate decom-

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poses in the GC apparatus because of the high temperatures used in the injector to volatilize the high boiling compounds. Therefore, to detect the intermediates involved in the reaction and to run the analysis in a relatively short time, a combination of different analytical techniques such as gas chromatography and liquid chromatography (HPLC) has to be used. In this paper a relatively simple analytical method to follow the reaction products is described.

A kinetic analysis has been also carried out with the aim of studying the reaction mechanism over a Pd catalyst. A comparison with mechanisms previously published in the literature is also reported.

2. Experimental

The hydrogenation of DNT was carried out in a 100 ml five necked flask, equipped with a reflux condenser and a thermocouple. Constant temperature ($\pm 0.5^\circ\text{C}$) was maintained by silicone oil circulation in an external jacket connected with a thermostat. The catalyst (5% Pd/C supplied by Montecatini Tecnologie) was added to 25 ml of ethanol (Fluka 95%, analytical grade) and reduced at 323 K for 1 h under H_2 flow. Then 25 ml of a 0.1 M solution of DNT (Aldrich, purity 97%) containing hexadecane as internal standard, was added through one arm of the flask. The reaction mixture was stirred with a stirrer head with permanent magnetic coupling at a stirring rate of 500 rpm and the reaction was carried out at atmospheric pressure under H_2 flow.

The progress of the reaction was followed by analyzing a sufficient number of samples withdrawn from the reaction mixture. Products analysis was performed with a gas chromatograph (Carlo Erba model 4200), equipped with a packed column (6 ft. \times 1/8 in., Tenax GC, 60–80 mesh) and a flame ionization detector. Quantitative analysis was carried out by calculating the area of the chromatographic peaks with an electronic integrator (HP 3396 Series II).

Chemical analysis of the reaction samples was also performed with a liquid chromatograph

(Waters model 510), equipped with a UV detector ($\lambda = 254 \text{ nm}$). The separation was carried out on a reverse-phase packed column (μ -Bondapak C_{18} , dimensions $3 \times 300 \text{ mm}$) using a mixture of solvents (acetonitrile–water).

3. Results and discussion

To identify the intermediates obtained in the hydrogenation of DNT over a 5% Pd/C catalyst, samples of the reaction mixture have been analyzed by GC and HPLC.

Fig. 1a shows the GC analysis of a sample of the reaction mixture, taken at a conversion of about 80%, and injected immediately after sampling in the gas chromatograph. Five major peaks have been detected. 2,4-diaminotoluene (DAT), 2,4-dinitrotoluene (DNT), 4-amino,2-nitrotoluene (4A2NT) and 2-amino,4-nitrotoluene (2A4NT) were identified by comparison with standard samples whereas the peak with retention time of 6.3 min was attributed (see below) to the decomposition of 4-hydroxylamine,2-nitrotoluene (4HA2NT) in the GC apparatus.

The quantitative analysis, carried out by using hexadecane as an internal standard, showed a neg-

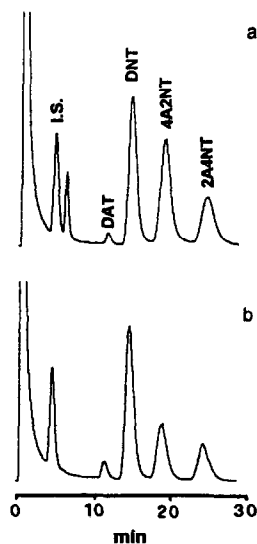


Fig. 1. Typical gas-chromatographic analysis: (a) sample injected immediately after sampling; (b) sample injected after one day. I.S. = internal standard.

ative mass balance likely due to products not revealed by the flame ionization detector of GC because strongly held by the chromatographic column.

The decomposition of 4HA2NT in the GC injector has been also reported by Janssen et al. [7]. They found that 4HA2NT decomposes giving 4A2NT and an unidentified peak corresponding to our peak at 6.3 min. In a previous paper we have found that, under conditions similar to those used in this work, hydroxylaminobenzene formed in the hydrogenation of nitrobenzene decomposes in the gas chromatographic apparatus into nitrosobenzene and aniline [10]. This could suggest that also in our case the unidentified peak is a nitroso compound. From the quantitative analysis it is also noted that these are not the only products. In fact, the negative material balance indicates that high molecular weight products, such as 2,2'-dinitro-4,4'-azoxytoluene (DNAT), are likely to be also formed. The formation of 4A2NT during the decomposition of 4HA2NT causes problems in the quantitative determination of the reaction products and a correction of the analytical results is necessary to find the real 4A2NT concentration. Janssen et al. [7] indeed have developed a complicated procedure to calculate the concentration of the components in the reaction mixture.

We have found that performing the analysis of the reaction samples after many hours (> 10 h), the peak with retention time of 6.3 min disappears and the 4A2NT/2A4NT ratio decreases (Fig. 1b). It is also noted that the amount of DNT, DAT and 2A4NT remains unchanged, whereas there is a further increase in the negative material balance. This can be explained by assuming that 4HA2NT is transformed to high molecular weight compounds which are not detected under the analytical conditions used. This is in agreement with the known decomposition of aromatic hydroxylamines during storage in air at room temperature [11].

On the basis of these results, we have carried out the gas chromatographic analysis after many hours to avoid the problems and errors due to hydroxylamine disproportion. The amount of

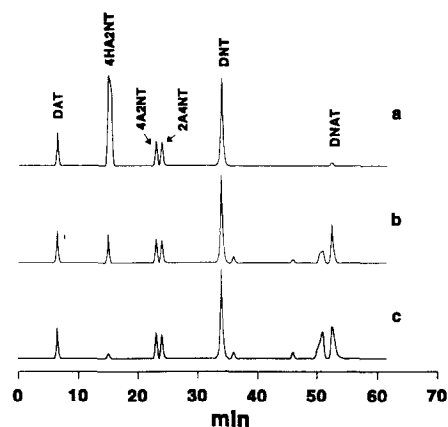


Fig. 2. HPLC analysis: (a) sample injected immediately after sampling; (b) after two hours; (c) after one day.

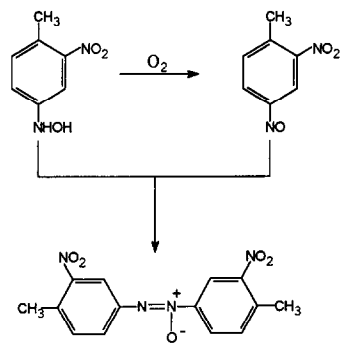
4HA2NT was estimated by the difference between the amount of DNT disappeared and the total products detected by gas chromatography.

In order to gain supplementary information on the intermediates involved in the reaction and to confirm the formation of 4HA2NT, analyses of reaction mixture with HPLC were also carried out. In addition to the components already identified with GC, other two compounds were revealed (Fig. 2a). The first was identified as 4HA2NT, whereas the two peaks at higher retention time were attributed to two geometric isomers (*cis* and *trans*) of DNAT. The *cis* and *trans*-azoxy compounds are well known in literature and the *cis* → *trans* isomerisation is reported to take place even at room temperature [12].

When the sample is immediately injected in the HPLC apparatus the amount of DNAT is very small (<1%), suggesting that it is not an intermediate in the 2,4-DNT hydrogenation under our conditions.

Performing the analysis of reaction mixture after exposure to air (Fig. 2a–c) we have observed with time a decrease in the concentration of 4HA2NT accompanied by an increase in the peaks of DNAT. Other minor peaks, likely due to decomposition of 4HA2NT and not identified, were also detected.

The mechanism of decomposition of 4HA2NT is not well known. Brand and Steiner [13] have



Scheme 1.

proposed two different routes. The first route involves the formation of DNAT only, whereas the second one occurs through the formation of DNAT and 4A2NT. The results of our HPLC analysis agree with the first route because no formation of 4A2NT was detected after oxidation of 4HA2NT. In this reaction pathway the primary compound of oxidation of 4HA2NT is likely a nitroso compound which cannot be isolated because it reacts immediately with the arylhydroxylamine to give DNAT (Scheme 1).

In the HPLC analysis the ratio of the two amino–nitro intermediates 4A2NT/2A4NT remains always constant with time confirming that a portion of 4A2NT revealed in the gas chromatograph is obtained by decomposition of 4HA2NT (Fig. 2a–c).

Following these indications we have carried out a reaction on a preparative scale to isolate these intermediates. If we stop the reaction at an intermediate conversion, after several hours a yellow precipitate can be separated from the solution. The obtained residue was dissolved in benzene and after cooling, crystals of DNAT and minor amount of 4HA2NT, have been isolated and purified by column chromatography as reported by Janssen [7]. These products were identified by IR, NMR and mass spectroscopy and were used as standard in the HPLC analysis.

The combination of HPLC and GC has shown that different mechanisms operate in the decomposition of 4HA2NT. At room temperature and in the presence of air, DNAT is the compound preferentially formed, whereas at high temperature, as

in the GC injector, uncontrolled reactions lead to DNAT, 4A2NT and likely to a nitroso compound. If great attention is observed in the interpretation of the analytical data, HPLC and GC give the same quantitative results. This is very important because the gas chromatography is a more routine technique in use in the catalysis laboratory than HPLC.

3.1. Kinetic experiments

A series of kinetic experiments have been performed to study the reaction mechanism over a 5% Pd/C catalyst. The reaction was carried out at temperatures between 283 and 323 K and at a constant pressure of 0.1 MPa. Experiments performed at different stirring rate and with samples of catalyst having a different grain size have shown the absence of mass-transfer limitations. In Fig. 3 is reported a plot composition versus time showing the course of reaction. The disappearance of DNT with time shows a zero-order behaviour up to high conversions (> 80%). This behaviour has been already observed in the catalytic hydrogenation of aromatic nitrocompounds [14]. The slight tailing at higher conversion can be explained by the competitive adsorption of the products on the catalyst surface.

In Fig. 4 the zero-order rate constant, K_{obs} , is plotted against the amount of catalyst. The rate increases linearly with increasing the amount of catalyst confirming the absence of external mass

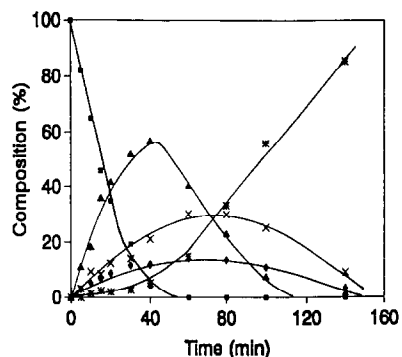


Fig. 3. Products composition as a function of the reaction time at 323 K and 0.1 MPa. (*) DAT, (■) DNT, (×) 4A2NT, (◆) 2A4NT, (▲) 4HA2NT.

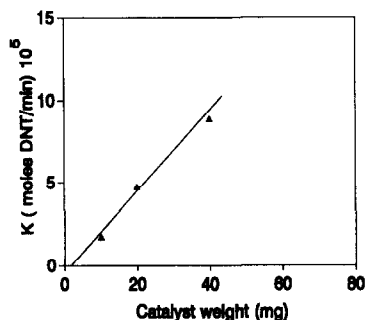


Fig. 4. Rate constant as a function of catalyst amount.

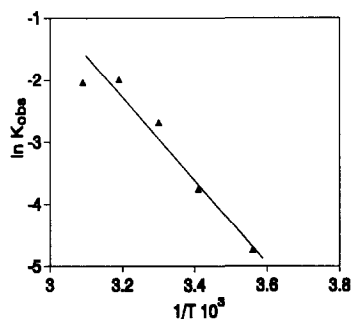


Fig. 5. Temperature effect on the rate constant.

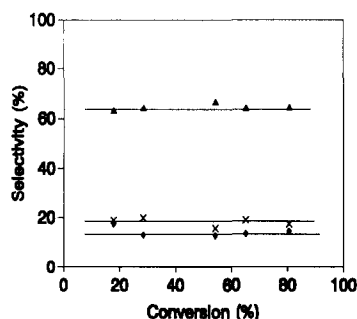


Fig. 6. Selectivity of reaction intermediates as a function of conversion: (\blacktriangle) 4HA2NT, (\times) 4A2NT, (\blacklozenge) 2A4NT.

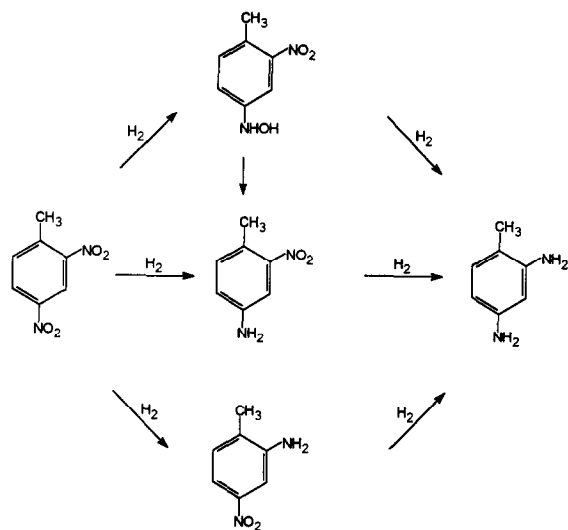
transfer limitations. However, the positive intercept with the X-axis revealed that the catalyst employed is poisoned by impurities present in the reaction mixture.

The temperature dependence of K_{obs} (expressed as moles of DNT converted per gram of Pd per minute) is shown in the Arrhenius plot reported in Fig. 5. The calculated activation energy was about 12.8 kcal/mol. This value is in agreement with the average activation energy reported in the literature for liquid phase hydro-

genations carried out under a kinetic regime. An activation energy of about 10.5 kcal/mol has been reported by Bird and Thompson for the hydrogenation of 2,4 DNT [6].

At 323 K 4HA2NT was the main product with a selectivity of about 65%. 4A2NT and 2A4NT were the other relevant intermediates (Fig. 3). The high amount of products obtained by hydrogenation of the 4-nitro group is in agreement with literature data which reports that the selectivity for reduction of the 4-nitro group increases with steric hindrance of the alkyl substituent [15]. Decreasing the reaction temperature the selectivity to 4HA2NT increases slightly (about 80% at 283 K) whereas that of the nitro-amino intermediates decreases. In all range of temperature investigated, the selectivity of the intermediates remains constant within a wide range of conversion (15–80%), indicating that they are formed from DNT through three parallel reactions (Fig. 6). DNAT and the other products of condensation were instead found to be negligible. The formation of condensation products has been reported in alkaline medium where the intermediates 4HA2NT and the nitroso compound can react to form DNAT and give, by subsequent hydrogenation, azo and hydrazo compounds [16]. In neutral or acidic condition, the formation of condensation products cannot take place because the 2,4-dinitrotoluene is directly hydrogenated to 4HA2NT without the intermediate step at nitroso compound. Hydrogenation of the intermediates to the final product (DAT) occurs only after almost all DNT has disappeared from the reaction vessel. This is likely a consequence of the strong adsorption of DNT on the active sites of the catalyst. From Fig. 3 it is also noted that the yield of 4A2NT increases further after the disappearance of DNT. This indicates that 4A2NT is also formed by hydrogenation of 4HA2NT. A reaction mechanism based on these observations is shown in Scheme 2.

A different mechanism of reaction has been reported by Janssen et al. [7,8]. They have suggested that DNT is converted to 4HA2NT and 2A4NT through two parallel reactions, whereas



4A2NT is formed consecutively from 4HA2NT. The direct route 4HA2NT → DAT has been ruled out. They developed also a kinetic model based on this reaction scheme which predicts the concentrations of DNT and DAT very well, but for the intermediate products, deviations between the predicted concentrations and the experimental data have been found [8]. There is, therefore, the possibility that the data treatment used is inadequate to describe the concentration of all intermediate products. A direct comparison with our data is not possible because their experiments were carried out under different conditions. To get more information on this complex reaction mechanism a kinetic modelling of the 2,4 DNT hydrogenation has been developed and will be presented in a forthcoming paper.

4. Conclusions

The main conclusions of this paper can be summarized as follow:

(1) The hydrogenation of 2,4-DNT to 2,4-DAT can be described by a complex reaction mechanism involving only three relevant intermediates, namely 4HA2NT, 4A2NT and 2A4NT.

(2) Condensation products (e.g. azoxy, azo and hydrazo compounds) were not formed during

the course of reaction. The azoxy compound DNAT was instead found during the decomposition of hydroxylamine in the GC apparatus and in the reaction samples after exposure to air.

(3) Decomposition of 4HA2NT in the gas chromatograph causes problems in the quantitative analysis of reaction products. The procedure which we have developed to perform the GC analysis without interference of 4HA2NT has been tested and verified by an independent analysis carried out with HPLC.

(4) On the basis of the obtained results, the reaction pathway reported in Scheme 2 is proposed for the hydrogenation of DNT to DAT.

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