

Catalytic hydrogenation of 2,4-dinitrotoluene over a Pd/C catalyst: identification of 2-(hydroxyamino)-4-nitrotoluene (2HA4NT) as reaction intermediate

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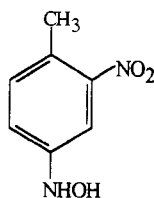
Abstract

The catalytic hydrogenation of 2,4-DNT over palladium supported on carbon catalysts is reported. The 2-(hydroxyamino)-4-nitrotoluene (2HA4NT) was identified as a reaction intermediate. The characterization of this compound and the reasons for its formation are discussed.

Keywords: Palladium; 2,4-Dinitrotoluene; Hydrogenation

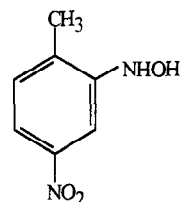
1. Introduction

The hydrogenation of 2,4-dinitrotoluene (2,4-DNT) can be carried out by using chemical, biological or catalytic methods. In previous papers we have investigated the mechanism of the catalytic reaction over a commercial Pd/C catalyst [1,2]. The reduction follows a complex reaction pathway involving several intermediates. The 4-(hydroxyamino)-2-nitrotoluene (4HA2NT) (1),



(1)

formed by the selective reduction of the *p*-NO₂ group into a -NHOH group, was the main reaction intermediate detected. Somewhat surprising is the lack of the isomer 2-(hydroxyamino)-4-nitrotoluene (2HA4NT) (2)



(2)

in the reaction products. This is however in agreement with the reports of other authors concerning with the 2,4-DNT catalytic hydrogenation [3–5]. The reasons of such a behaviour are not clear. The formation of 2HA4NT has

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been instead observed in the reduction of 2,4-DNT by Zn powder in NH_4Cl and by bacterial agents under anaerobic conditions [6].

In this communication we report the proof of the presence of 2HA4NT during the catalytic hydrogenation of 2,4-DNT over palladium supported on carbon catalysts.

2. Experimental

The hydrogenation of 2,4-DNT (Aldrich, purity 97%) was carried out in a batch type reactor at 323 K and at pressure of 0.1 MPa under H_2 flow. The catalyst MGPd1, containing 1 wt.-% Pd, was prepared by incipient wetness impregnation of carbon support (Chemviron, 1100 m^2/g BET surface area) with an aqueous solution of PdCl_2 . After drying at 393 K, the sample was reduced at 423 K in flowing H_2 for 1 h. As comparison, a commercial 5% Pd/C catalyst (supplied by Montecatini Tecnologie) was used. Before the reaction, the catalyst, suspended in 25 ml of EtOH (95%, analytical grade), was further reduced in situ at 323 K for 1 h under H_2 flow. In a typical run 25 ml of a solution, containing 1.154 g of 2,4-DNT (0.25 M) in EtOH was added and the reaction mixture was stirred at a rate of 500 rpm.

The progress of reaction was followed with a liquid chromatograph (Waters 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} , $3 \times 300 \text{ mm}$) using a mixture of solvents (acetonitrile–water).

In order to isolate the reaction intermediates the reaction was stopped at total conversion of the reagent. The catalyst was separated immediately from the reaction mixture by filtration and the solvent was removed by a rotavapor in order to avoid the oxidation of the arylhydroxylamines. The solid obtained was dissolved in CHCl_3 and the separation of 2HA4NT from the other reaction products was carried out by using a chromatography column of silica gel (70–230

mesh) and CHCl_3 as eluent. Reaction products were identified by MS, IR, ^1H and ^{13}C NMR.

The following spectroscopy data were collected for 2HA4NT: mp 108–112°C; IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3600 (NH), 3340 (OH), 1530 (NO_2). MS m/e : 168 (M^+), 151 ($\text{M}^+ - \text{OH}$). ^1H -NMR (300 MHz, CDCl_3) d: 2.209 (s, 3H), 5.28 (br s, 1H), 6.80 (br s, 1H), 7.200 (d, 1H, $J_{bc} = 8.2 \text{ Hz}$), 7.775 (dd, 1H, $J_{bc} = 8.2 \text{ Hz}$, $J_{ab} = 2.3 \text{ Hz}$), 8.116 (d, 1H, $J_{ab} = 2.3 \text{ Hz}$). ^{13}C $\{^1\text{H}\}$ NMR (75.47 MHz, CDCl_3) d: 17.2 (CH_3), 108.28 (C-3), 116.26 (C-5), 129.80 (C-1), 147.49 (C-4 or C-2), 148.60 (C-2 or C-4). ^{13}C assignment by $^{13}\text{C}/^1\text{H}$ heterocorrelated 2D spectra.

3. Results and discussion

Fig. 1 shows HPLC analysis of the reaction mixture, taken at an intermediate conversion, of the 2,4-DNT hydrogenation carried out over Pd/C catalysts. Analysis a is related to the reaction performed over the MGPd1 catalyst. A typical analysis of the reaction carried out over a commercial Pd/C sample is also shown for comparison in Fig. 1b. The analysis were performed immediately after sampling in order to avoid the decomposition of arylhydroxylamines [1]. In the analysis a, in addition to the compo-

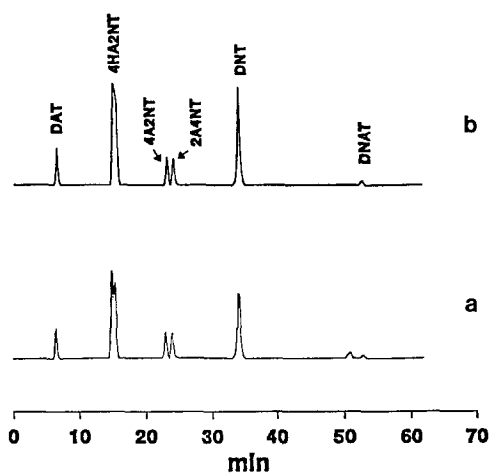


Fig. 1. Typical HPLC analysis of the reaction mixture of 2,4-DNT hydrogenation over: (a) MGPd1 catalyst; (b) commercial 5% Pd/C catalyst.

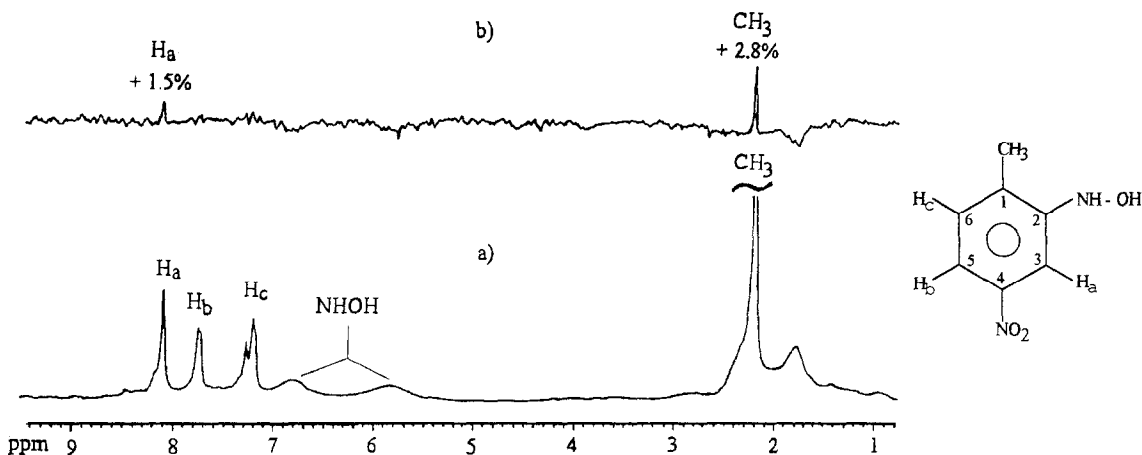


Fig. 2. (a) Standard ^1H NMR spectrum of compound (2) in CDCl_3 ; (b) NOED spectrum with increased intensity of H_a and CH_3 resonances ($-\text{NHOH}$ protons irradiated; line broadening = 8 Hz).

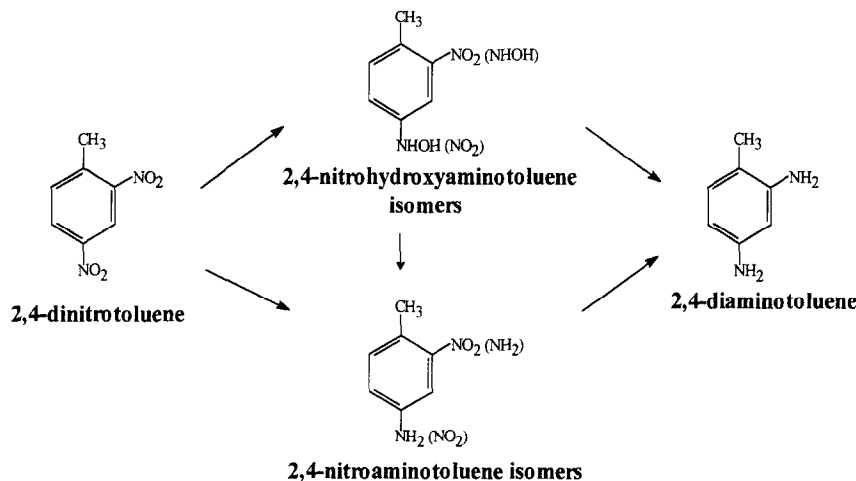
nents previously identified [1], a new peak present as a shoulder of the peak of 4HA2NT was revealed. This strongly suggests the presence of a compound with chemical behaviour and characteristics similar to 4HA2NT.

In order to identify this compound, the separation procedure described in detail in the Experimental section, was followed.

Two major fractions (A and B) were eluted from the chromatographic column and, after removal of the solvent, a residue of 0.112 g and

of 0.284 g was obtained. The 4HA2NT was identified as the main component of fraction B. Fraction A, dissolved and recrystallized in CHCl_3 , yields a pure crystalline compound characterised by MS, IR, ^1H and ^{13}C NMR spectroscopy. The spectroscopic data, reported in the Experimental section, are in good agreement with that known for 2HA4NT [6].

As additional proof, the relative position of the substituents on the aromatic ring of the isolated compound have been assigned by NOE



Scheme 1.

(Nuclear Overhauser Effect). An increase in the relative intensity of CH_3 ($\approx 2.8\%$) and H_a ($\approx 1.5\%$) was observed by irradiation of hydroxylamino protons, indicating a magnetization transfer between the nitrogen and the oxygen bonded protons whose frequencies are strongly concentration dependent (Fig. 2). This confirms the presence of a $-\text{NHOH}$ group surrounded by the $-\text{CH}_3$ and H_a groups, as shown in the molecular structure reported in Fig. 2.

The above results give new insight into the mechanism of 2,4-DNT catalytic hydrogenation over Pd catalysts. The reaction pathway up to now proposed [1,2,4] does not take in account the formation of 2HA4NT. However by analogy with the pathway leading to 4A2NT through 4HA2NT (see Scheme 1) a similar sequence is to be expected in the formation of 2A4NT. It has previously been observed that the hydrogenation rate of *p*- NO_2 group into $-\text{NHOH}$ is faster than the subsequent reduction of $-\text{NHOH}$ into $-\text{NH}_2$ [2]. Therefore the isomer 4HA2NT accumulates in the reaction mixture. To explain the absence of the isomer 2HA4NT in the reaction products we should assume that the rate of hydrogenation of the *o*- NO_2 group is similar or lower than that of the *o*- NHOH group. However, on the basis of the results reported in this note this seems do not be a general conclusion. In fact the relative rate of hydrogenation of the $-\text{NO}_2$ and $-\text{NHOH}$ groups seems to depend on the catalyst used. A detailed characterization of

the catalysts is necessary to correlate the formation of 2HA4NT with their physico-chemical properties.

A more general reaction scheme (Scheme 1), involving the presence of both 2,4-nitrohydroxylamino functions as intermediates of the reaction, is therefore proposed for the catalytic hydrogenation of 2,4-dinitrotoluene over Pd/C catalysts.

It is also interesting to note that, because the hydroxylamines can undergo rearrangement to yield a variety of important chemicals [7], the catalytic hydrogenation of 2,4-DNT over MGPd1-type catalysts can be regarded as a convenient route for the synthesis of 2HA4NT due to the a higher yield of product and to the lower cost of hydrogen as compared to other reducing agents.

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