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# A study of Pd/C catalysts in the liquid-phase hydrogenation of 1,3,5-Trinitrobenzene and 2,4,6-Trinitrobenzoic acid. Selection of hydrogenation conditions for selective production of 1,3,5-Triaminobenzene

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## Abstract

The liquid-phase hydrogenation of aromatic trinitro compounds was studied at atmospheric and elevated pressure and a temperature of 50–70 °C. It was shown that at atmospheric pressure, irrespective of the solvent type (water or acetic anhydride), a complete reduction of the nitro groups of 2,4,6-trinitrobenzoic acid to amino groups does not occur; the intermediate products of hydrogenation and the products of secondary transformations are present in the solution. An increase in pressure to 5 bars ensures a complete hydrogenation of 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene with the formation of 1,3,5-triaminobenzene.

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## 1. Introduction

Catalytic hydrogenation of aromatic trinitro compounds is of interest for the development of theoretical bases of the liquid-phase hydrogenation of organic compounds and has practical value in utilization of explosives. Safe deactivation of one of the most widespread explosives, 2,4,6-trinitrotoluene (TNT), by this method has significant advantages over its utilization by blasting, burning or chemical reduction in terms of detrimental environmental outcome. So, the topical lines of investigation include optimization of the catalytic process conditions and development of more efficient catalysts. The reduction of all nitro groups can produce 2,4,6-triaminotoluene, which is an essential component for the synthesis of a wide range of civil products [1].

A scheme of TNT hydrogenation is a complex chain of consecutive and parallel reactions [2–4], which can hardly be described due to difficult identification of intermediate compounds. Along with TNT, among the most available and promising trinitro compounds are 1,3,5-trinitrobenzene (TNB) and 2,4,6-trinitrobenzoic acid (TNBA) [5–9]. TNB is a product of decarboxylation of TNBA, while TNBA can be obtained by oxidation of TNT. The direct use of TNBA as the substrate for aqueous-phase hydrogenation is limited by low solubility in water. However, as a component of a salt with alkaline metals this compound has a good solubility in water [7]. The performance of hydrogenation in aqueous solutions ensures environmental benefit for the synthesis of aromatic amines from TNBA. Information about the effect produced by conditions of the aqueous-phase hydrogenation on the process rate and depth is virtually absent in the literature.

The work was aimed at selecting such conditions (pressure, temperature and solvent) of the hydrogenation that would provide an exhaustive reduction of all nitro groups of TNB and TNBA with the use of the 6 % Pd/C catalyst.

## 2. Experimental

Ethanol (96 %) was employed as a solvent for hydrogenation of TNB. The hydrogenation of TNBA was carried out in an aqueous solution or in a mixture of acetic anhydride and acetic acid. The aqueous solution was prepared by suspending a dry TNBA powder in a specified volume of distilled water with the addition of a stoichiometric amount of sodium bicarbonate.

The catalyst was represented by the 6 % Pd/C sample, which was synthesized by the hydrolytic precipitation of palladium polyhydroxo complexes on the surface of carbon material Sibunit and the reduction of the complexes with sodium formate [10]. Moisture content of the catalyst was about 50 %.

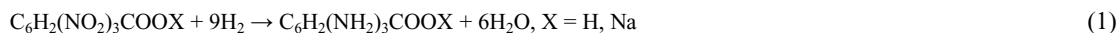
The catalytic hydrogenation at atmospheric pressure was performed in a setup consisting of a glass thermostatted reactor, a system for measuring of hydrogen consumption, and a vacuum unit. Mixing was carried out with a magnetic stirrer. Catalytic hydrogenation at elevated pressure was conducted in a 180 mL steel autoclave equipped with a controllable valve for hydrogen input, a sampler, and an external thermostatted jacket.

The reaction products were examined by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, IR spectroscopy and elemental analysis. NMR spectra were recorded on an Avance-400 (Bruker) spectrometer using standard ampoules with the diameter of 5 mm at a Larmor frequency of 400 MHz ( $^1\text{H}$  NMR) or 100.6 MHz ( $^{13}\text{C}$  NMR) at a temperature of 25 °C in a pulsed mode. Acetone- $d_6$  was used as the lock signal. Tetramethylsilane served as the external standard. The IR transmission spectrum was recorded on an IR Prestige-21 (Shimadzu) instrument in the region of 400–4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . The elemental composition of the product of TNB complete reduction was determined using a universal elemental analyzer Vario EL cube (Elementar Analysensysteme GmbH).

## 3. Results and discussion

### 3.1. Hydrogenation of TNBA at atmospheric pressure

TNBA was hydrogenated at atmospheric pressure as the sodium salt in an aqueous solution and in a medium of acidifying agent (mixture of acetic anhydride and acetic acid). The amounts of TNBA and sodium bicarbonate (for hydrogenation of sodium salt in an aqueous solution) were calculated from the stoichiometric consumption of 100 mL hydrogen (normal conditions) according to the equation of reaction (1). The reaction was run at a temperature of 50 °C, and the substrate to catalyst weight ratio was equal to 6 in all the experiments at atmospheric pressure.



The composition of solutions before and after hydrogenation was studied by NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of TNBA in an aqueous solution has a singlet at 9.25 ppm which is assigned to protons of the aromatic ring. The following signals ( $\delta$ , ppm) are observed in the  $^{13}\text{C}$  NMR spectrum of TNBA (Fig. 1): 167.4 (C-7), 146.9 (C-4), 146.6 (C-2, C-6), 136.4 (C-1), and 126.1 (C-3, C-5).

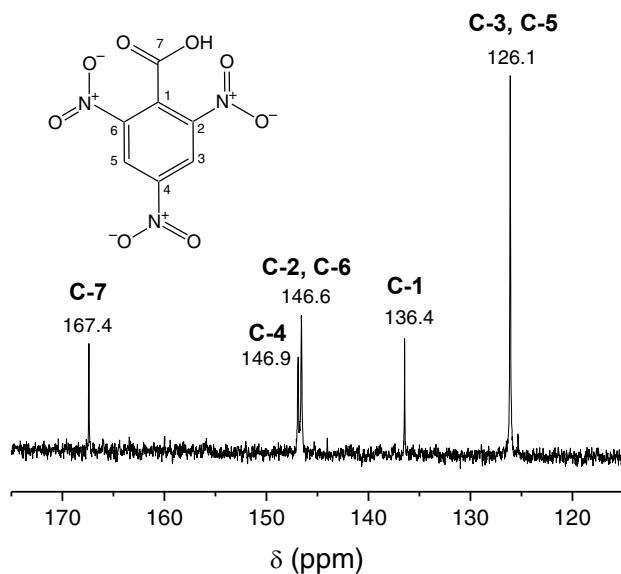


Fig. 1. The  $^{13}\text{C}$  NMR spectrum of an aqueous solution of TNBA (the concentration of 1 wt. %) with the addition of  $\text{NaHCO}_3$ .

The progress of TNBA hydrogenation was monitored by measuring the amount of consumed hydrogen. Although the amount of consumed hydrogen approximately corresponded to the stoichiometric amount for the target reaction, the analysis of reaction products showed that the formation of triamino compounds does not occur under the given conditions (Fig. 2).

The  $^1\text{H}$  NMR spectrum of hydrogenation products of TNBA sodium salt in an aqueous solution (Fig. 2a) shows an intense resonance from aromatic protons of TNBA (9.12 ppm) and signals from minor admixtures of non-identified reaction products in the region of 8.7–9.5 ppm. The  $^{13}\text{C}$  NMR spectrum ( $J$ -modulated (JMOD) pulse sequence was employed) of the same solution (Fig. 2b) shows only the signals from TNBA and acetone- $\text{d}_6$ , which was introduced upon recording.

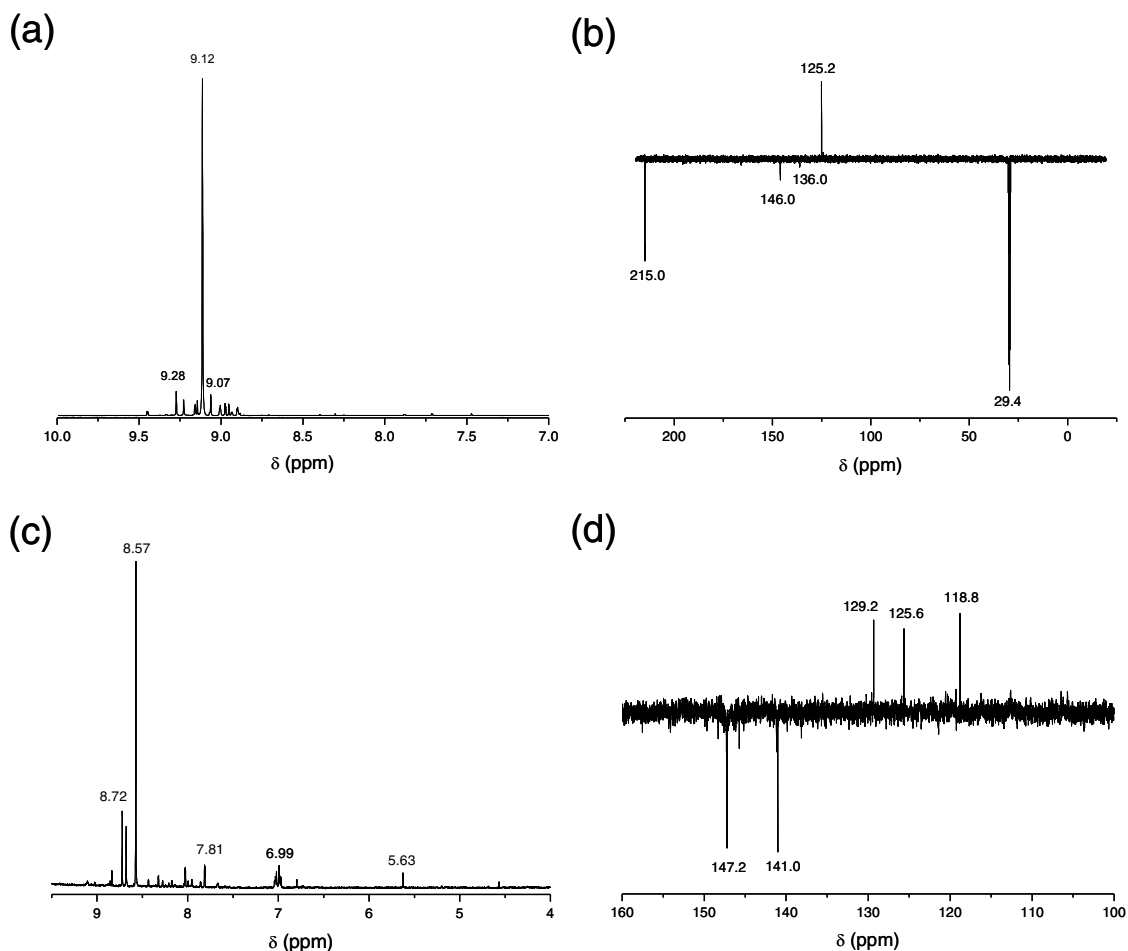


Fig. 2.  $^1\text{H}$  (a) and  $^{13}\text{C}\{^1\text{H}\}$  JMOD (b) NMR spectra of hydrogenation products of TNBA sodium salt in an aqueous solution;  $^1\text{H}$  (c) and  $^{13}\text{C}\{^1\text{H}\}$  JMOD (d) NMR spectra of hydrogenation products of TNBA dissolved in a mixture of acetic anhydride and acetic acid. Reaction conditions: the 6 % Pd/Sibunit catalyst, a temperature of 50 °C, and atmospheric pressure.

Hydrogenation of TNBA in a medium of mixture of acetic anhydride and acetic acid resulted in a complete conversion (signals corresponding to the initial substrate are absent in the NMR spectra) and a partial reduction of the TNBA nitro groups; however, a selective formation of triamino compounds was not observed (Fig. 2c, d). Taking into account parameters of the signals, the most intensive signals can be assigned to the acids that are formed via the reduction of one of TNBA nitro groups to hydroxyamino group.

### 3.2. Hydrogenation of TNBA and TNB at elevated pressure

To increase the hydrogenation depth and rate and to suppress polymerization (resinification) of intermediate products, the hydrogenation of aromatic trinitro compounds was performed at a pressure of 5 bars.

TNBA (as a sodium salt) was hydrogenated in aqueous solution (the concentration of 1 wt. %) at a temperature of 70 °C, while the hydrogenation of TNB was performed in ethanol medium (the concentration of 1 wt. %) at 50 °C.

The substrate to catalyst weight ratio was equal to 5. Under the chosen conditions, the reactions terminated 45–55 min after the onset of experiment, with the amount of consumed hydrogen being close to stoichiometric one (Fig. 3a). For both reactions, the  $^{13}\text{C}$  NMR study of the composition of solutions after the reaction showed the absence of TNBA, TNB and intermediate products of their reduction. Hydrogenations resulted in a selective formation of 1,3,5-triaminobenzene (TAB) (Fig. 3b).

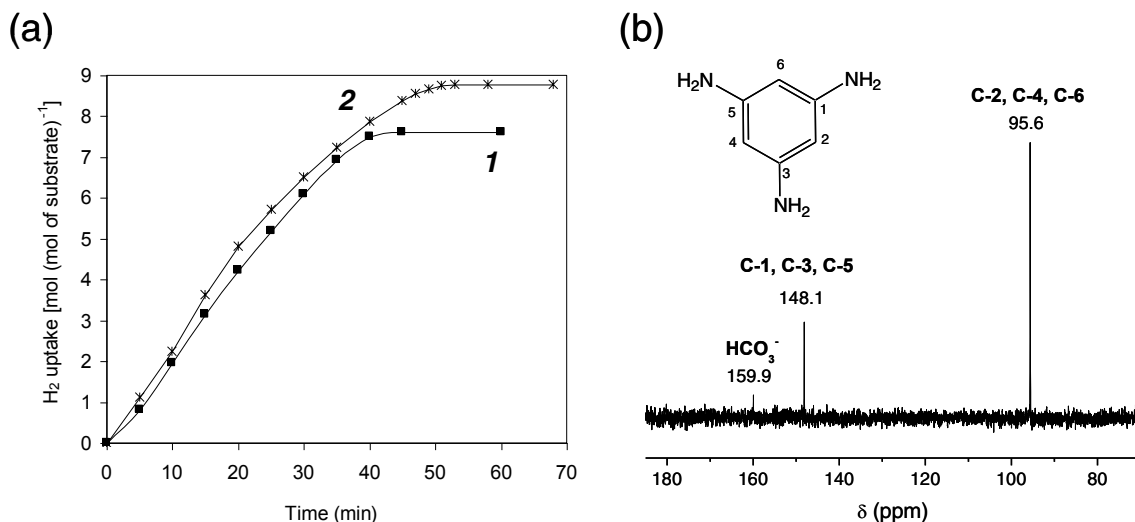


Fig. 3. (a) Hydrogen consumption during hydrogenation of TNBA as the sodium salt in an aqueous solution at a temperature of 70 °C and pressure of 5 bars (1) and hydrogenation of TNB in ethanol at 50 °C and 5 bars (2). (b) The  $^{13}\text{C}$  NMR spectrum of an aqueous solution after hydrogenation of TNBA as the sodium salt (the concentration of 1 wt. %).

The obtained product was precipitated from the ethanol solution as hydrochloride by adding an excess of concentrated hydrochloric acid. A light cream-colored powder was characterized by elemental analysis,  $^1\text{H}$  NMR, and IR spectroscopy. The following results were obtained (%): C, 31.70; H, 5.49; N, 15.94. Calculated for C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>·3HCl (%): C, 30.99; H, 5.21; N, 18.07. The  $^1\text{H}$  NMR spectrum (H<sub>2</sub>O,  $\delta$ , ppm): 6.72 (s, 3H, H-2, H-4, H-6). The IR spectrum (KBr, cm<sup>-1</sup>): 2800 (br.); 2593,  $\nu(\text{N}^+\text{H})$ ; 1533,  $\delta(\text{N}^+\text{H})$ ; 1126,  $\nu(\text{CN})$ ; 1102,  $\nu(\text{CN})$ ; 1043,  $\nu(\text{CN})$ ; 847,  $\delta(\text{CH})$ ; 662,  $\delta(\text{CH})$ . The obtained characteristics verify the formation of TAB upon hydrogenation of TNB under the chosen conditions.

#### 4. Conclusion

Thus, the study made it possible to suggest the conditions that ensure a selective formation of TAB from TNB and TNBA. With 0.2 g of the 6 % Pd/C catalyst at a substrate concentration of 1 wt. % and temperature of 50–70 °C, a rise of hydrogen pressure to 5 bars provides a hydrogenation of trinitro compounds with the formation of TAB.

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