An unusual reduction route of 2,4,6-trinitrobenzoic acid under conditions of aqueous-phase hydrogenation over Pd/Sibunit catalyst*

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For the first time it was established that the catalytic hydrogenation of 2,4,6-trinitrobenzoic acid to 1,3,5-triaminobenzene can proceed *via* the formation of aromatic hydroxyamines and cyclohexane-1,3,5-trione trioxime. As a result of aqueous-phase hydrogenation of sodium salt of 2,4,6-trinitrobenzoic acid in the presence of 5% Pd/Sibunit catalyst at a temperature of 323 K and pressure of 0.5 MPa, a trioxime in high yield (about 70 %) was obtained. Due to high selectivity to cyclohexane-1,3,5-trione trioxime the catalytic hydrogenation of sodium salt of 2,4,6-trinitrobenzoic acid can be considered as a new method for its synthesis.

Key words: 2,4,6-trinitrobenzoic acid, catalytic hydrogenation, palladium catalyst, cyclohexane-1,3,5-trione trioxime.

Catalytic hydrogenation of aromatic nitro compounds[1,2]** is one of the most effective synthetic approaches to aromatic amines both in laboratory practice and in the industry.[3—8] Aromatic amines as well as products of partial hydrogenation of nitro compounds are valuable intermediates for polymers, pharmaceutical drugs, dyes and pesticides.[8] Features of the nitro group reduction in the course of catalytic hydrogenation of mono- and dinitroarenes were thoroughly investigated,[4—7] whereas hydrogenation of aromatic nitro compounds received significantly less attention. At the same time, catalytic hydrogenation of trinitroarenes is of high practical value because it can be utilized for the disposal of explosives. Catalytic hydrogenation of one of the most common explosive agents, namely, 2,4,6-trinitrotoluene (TNT) can afford 2,4,6-triaminotoluene which is a precursor for a wide range of products.[9—12] Moreover, among the most available and promising for processing of trinitro compounds is a product of TNT oxidation, *i.e.* 2,4,6-trinitrobenzoic acid (**1a**), reduction of which can lead to such valuable chemical compounds as 1,3,5-triaminobenzene (**2**) and 1,3,5-trihydroxybenzene (phloroglucinol).[13—19]

So far only few reports describing[14—20] catalytic hydrogenation of the acid **1a** were published. It was shown that hydrogenation of the acid **1a**, usually in an organic solvent and using Pd/C or the Raney Ni catalysts involves decarboxylation and formation of the product **2**. Meanwhile, 2,4,6-triaminobenzoic acid, which is formed upon chemical or electrochemical reduction of the acid **1a**, was not found among the hydrogenation products.[21—23] Decrease in selectivity for the compound **2** and catalyst deactivation resulting apparently from the side reactions of polycondensation yielding resinous substances are generally observed for hydrogenation under atmospheric pressure.[19,20] The published works related to the reduction of

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** Discovered by M. M. Zaitsev in 1871.

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the acid **1a** are focused mainly on the search for ortimal conditions of the selective formation of the compound **2**, whereas they give no information about the intermediate reduction products. At the same time studying the features of hydrogenation of trinitroarenes is important not only from the theoretical viewpoint, but also is of practical value for developing the synthetic approaches to the products of partial reduction.[24—26]

The present study is a part of our investigations directed to elucidation of the transformation routes of the acid **1a** and its sodium salt (**1b**) during hydrogenation in the presence of Pd/Sibunit catalysts. The synthesis and application of such catalysts are widely reported in literature.[27] The choice of the catalysts is motivated by their high efficiency in hydrogenation of various organic compounds including aromatic nitro compounds. Previuosly,[28] using the NMR technique we found that aqueous-phase catalytic hydrogenation of the salt **1b** to the compound **2** presents a complex chain of reactions occurring *via* formation of intermediates with mixed-type functionalities. Moreover, as it turned out, the direction of transformations and consequently the product distribution depend on the conditions used to prepare Pd/Sibunit catalysts and to conduct the catalytic hydrogenation.

Experimental

Preparation of a catalyst. Catalyst 5 wt.% Pd/Sibunit was obtained by hydrolytic precipitation of palladium polyhydroxo complexes on the surface of the Sibunit carbon material[29—31] (synthesized in the Department of experimental technologies of the Institute of Hydrocarbons Processing of the Siberian Branch of RAS, S_{sp} = 422 $m^2\ g^{-1}$). Precipitation was followed by the reduction of palladium by sodium formate.[32,33] On precipitation, $NaHCO_3$ was used as a precipitant (pH 5.4). No additional treatment of the catalyst with humidity ~50 wt. % was performed.

Catalytic hydrogenation of the salt 1b. The parent acid **1a** (98% purity) was obtained by oxidation of TNT according to the previously reported procedure.[34] A solution of the salt **1b** was prepared by adding powdered $NaHCO_3$ (0.59 g) to the carefully stirred aqueous slurry of the acid **1a** (2.00 g) until complete dissolution of bicarbonate and complete release of CO_2.[15] The salt **1b** was hydrogenated in an aqueous solution (2 wt.%, 100 mL) using 5%Pd/Sibunit (100 mg) in a steel autoclave at a temperature of 323 K and pressure of 0.5 MPa. The reaction mass was stirred using a magnetic stirring bar (1400 min^{-1}). The reaction course was monitored by measuring the volume of hydrogen consumed over a particular period of time. When the reaction was completed (*i.e.* after termination of the hydrogen consumption) the autoclave was cooled and a sample of the reaction mixture was taked by a syringe.

Analysis of the reaction products. The products of hydrogenation were analysed by the ^1H and ^{13}C NMR techniques. Spectra were recorded on an «Avance-400» («Bruker») NMR spectrometer at Larmor frequency of 400 (^1H) or 100 MHz (^{13}C) in a pulse mode. Residual proton signals (δ_H 3.30, quintet) or carbon nuclei in the methyl group (δ_C 49.0, septet) of methanol-d_4 were used as internal standards. Signal of water in the ^1H NMR spectrum was suppressed by the zgpr pre-saturation («Bruker»). ^{13}C NMR spectra were recorded in a *J*-modulation mode (JMOD).[35] Quantitative composition of the reaction mixture was estimated from the ^1H NMR spectroscopy data based on the integral intensities of the corresponding signals of the individual components non-overlapping with the other ones.

Results and Discussion

It is known that liquid-phase hydrogenation of compound **1a** or **1b** when performed under mild reaction conditions, generally in an organic solvent or water at a temperature of 323—348 K and pressure of 0.5—1.0 MPa on the 5%Pd/C catalysts, selectively yields the product **2**.[15—18] In the course of hydrogenation only nitro groups are reduced, while aromaticity of a benzene ring is not disturbed. For three nitro groups to be completely reduced (*i.e.* to convert **1a**,**b** into **2**), 9 moles of H_2 per 1 mole of **1a**,**b** are required. However we have demonstrated that upon hydrogenation of the salt **1b** in an aqueous solution using the 5%Pd/Sibunit catalyst at a temperature of 323 K and pressure of 0.5 MPa, the amount of the consumed hydrogen is 6 moles of H_2 per 1 mole of **1b**, which is noticeably less than the amount of hydrogen required for the reaction stoichiometry. Initially, the rate of the hydrogen consumption reaches a maximum and then gradually decreases over time (Fig. 1), apparently due to the blockage of the active sites of the catalyst by the reaction products. Furthermore, on a hydrogen consumption curve obtained a noticeable step is observed the presence of which might be indicative of the change in the direction of transformations proceeding at different rates.

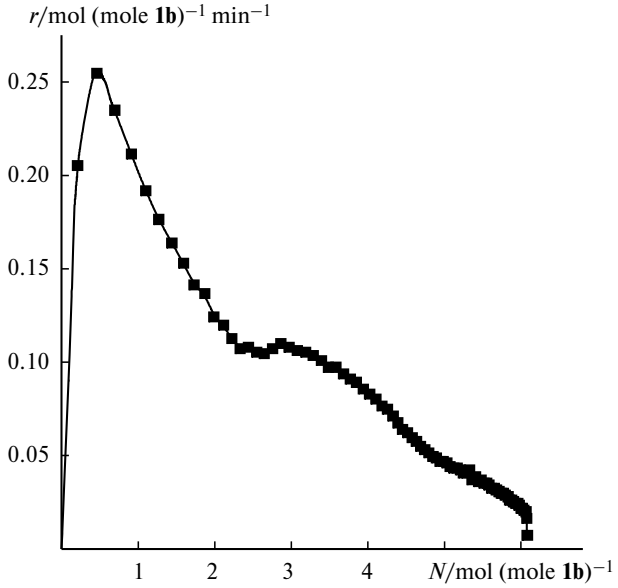


Fig. 1. Hydrogen consumption curve for the aqueous-phase hydrogenation of the salt **1b** over 5%Pd/Sibunit catalyst at a temperature of 323 K and pressure of 0.5 MPa; *r* is rate of H_2 absorption, *N* is an amount of consumed H_2.

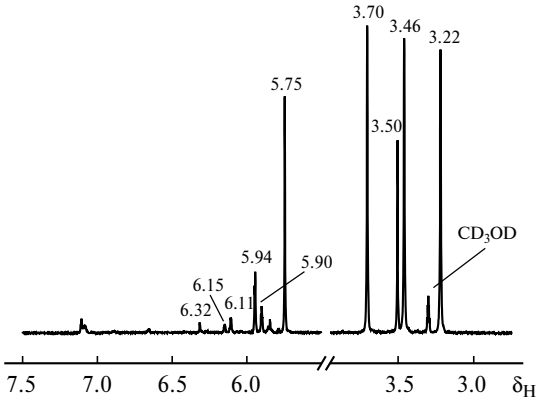


Fig. 2. ^{1}H NMR spectrum of the reaction mixture obtained by aqueous-phase hydrogenation of the salt **1b** over 5% Pd/Sibunit at a temperature of 323 K and pressure of 0.5 MPa (after consumption of 6 mole H_2 (mole **1b**)$^{-1}$). Suppression of signal from solvent (water) was performed by the zgpr pulse sequence.

The reaction products were identified and their content in the reaction mixture was estimated based on the NMR spectroscopy data. The efficacy of application of the NMR technique in analysing the products of hydrogenation of aromatic trinitrocompounds was reported earlier.[18,24,36,37] The choice of this method is explained mainly by its high informativity. Moreover, other analytical techniques are characterized by either low efficiency or application irrelevance. Thus, for example, GC/MS or HPLC methods should be considered unsuitable for this analytical task because of low stability of the compounds under investigation as well as the absence of reference compounds and published mass spectra for the majority of these compounds.

In the ^{1}H NMR spectrum of the reaction mixture (Fig. 2) signals were detected corresponding not only to aromatic but also to nonaromatic protons. An intensive signal of aromatic protons at δ_H 5.75 corresponds to the product **2**, other signals of lesser intensity in the range of δ_H 5.8—7.1 are related to aromatic protons in the products of partial reduction of nitro groups in the salt **1b**. Among these products 1,3,5-tris(hydroxyamino)benzene (**3**), 3,5-bis-(hydroxyamino)aniline (**4**) and 5-hydroxyamino-1,3-diaminobenzene (**5**) were identified (Table 1). Identification of the compounds **3**—**5**, which was not supported by the spectral information in literature, was confirmed by simulating their ^{1}H and ^{13}C NMR spectra using the software package ACD/Labs. The most intensive peaks in the ^{1}H NMR spectrum are located in the area characteristic of chemical shifts of nonaromatic protons. According to the published data[39—41] they were attributed to methylene protons of cyclohexane-1,3,5-trione trioxime (**6**). Three singlets of equal intensity at δ_H 3.22, 3.46, and 3.70 correspond to the unsymmetrical isomer (1*Z*)-**6**, and a singlet at δ_H 3.50 corresponds to the symmetrical isomer (1*E*,3*E*,5*E*)-**6**.

Identification of the compounds **2**, **5**, and **6** was confirmed by the analysis of the ^{13}C{^{1}H} NMR spectrum of the reaction mixture recorded in the *J*-modulation mode.[35] This method enables one to discriminate the carbon atoms according to the value of the ^{1}H—^{13}C interaction. Thus, signals at δ_C 96.8, and 149.1 are oppositely orientated and originate from the presence of methine and quaternary carbon atoms in the product **2**, respectively (Fig. 3). Signals having chemical shifts of 94.9, 99.3, 149.0, and 152.7 can be attributed to diamine **5**. To the carbon atoms of trioxime **6** the following signals (δ_C) were ascribed: 25.8, 31.0, 35.7 (CH_2-groups in (1*Z*)-**6**); 30.4 (CH_2 groups in (1*E*,3*E*,5*E*)-**6**); 154.1, 154.8 (quaternary carbon atoms of the both isomers of compound **6**).

Based on the NMR data on the composition of the reaction mixture, one may suggest the scheme of transformations describing the course of the aqueous-phase

Table 1. Signal assignments in the ^{1}H NMR spectrum and results of the quantitative assessment of the content of the products of hydrogenation of the salt **1b** in catalyzate

Compound	^{1}H NMR spectrum (δ_H, *J*/Hz)		Relative content according to the ^{1}H NMR data (%)
	Experiment (water, methanol-d_4)	Literature data	
2	5.75 (s, 3 H, H(2), H(4), H(6))	5.52 (s, 3 H, H(2), H(4), H(6)); 1.50 (br.s, 6 H, NH_2)[a]	14
3	6.32 (s, 3 H, H(2), H(4), H(6))	—	1
4	6.15 (t, 1 H, H(4), *J* = 2); 6.11 (d, 2 H, H(2), H(6), *J* = 2)	—	5
5	5.94 (d, 2 H, H(4), H(6), *J* = 2); 5.90 (t, 1 H, H(2), *J* = 2)	—	11
(1*Z*)-**6**	3.70, 3.46, 3.22 (all s, 2 H each, CH_2)	10.81, 10.74, 10.71 (all s, 1 H each, OH); 3.50, 3.24, 3.04 (all s, 2 H each, CH_2)[b]	60
(1*E*,3*E*,5*E*)-**6**	3.50 (s, 6 H, CH_2)	3.33 (s, 6 H, CH_2)[c]	9

[a] See Ref. 38, solvent is $CDCl_3$.
[b] See Ref. 39, solvent is DMSO-d_6.
[c] See Ref. 40, solvent is DMSO.

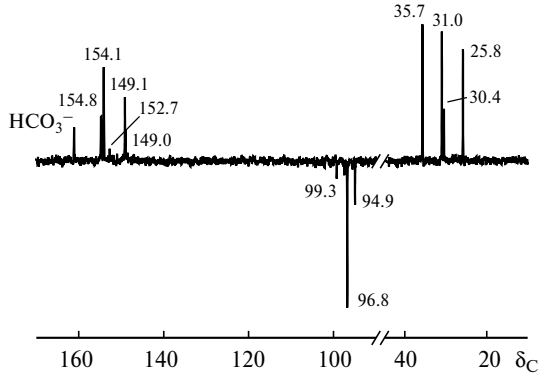


Fig. 3. $^{13}C\{^1H\}$ JMOD NMR spectrum of the reaction mixture obtained by aqueous-phase hydrogenation of the salt **1b** over 5%Pd/Sibunit catalyst at a temperature of 323 K and pressure of 0.5 MPa (after consumption of 6 mole H_2 (mole **1b**)$^{-1}$).

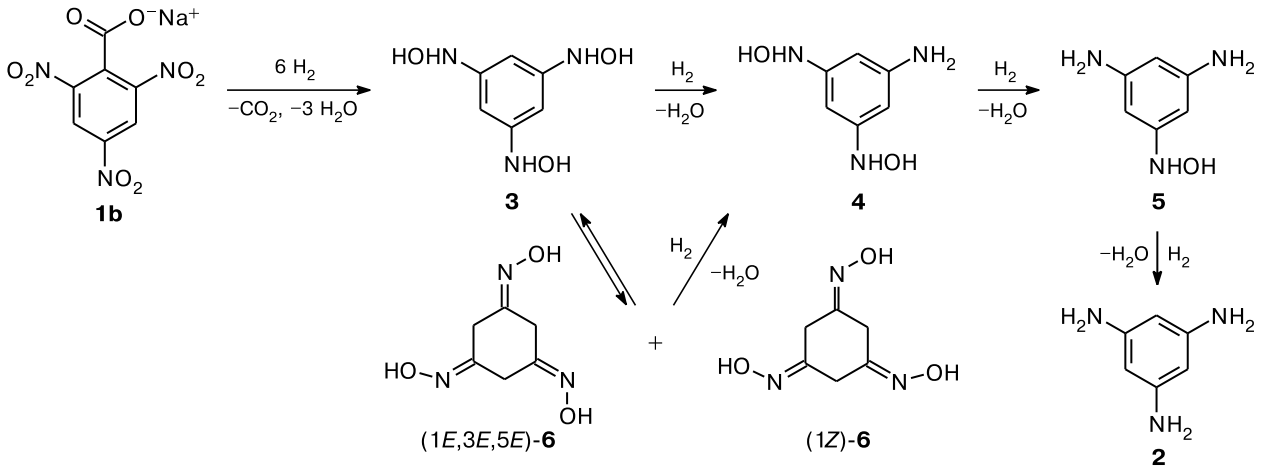
hydrogenation of salt **1b** in the presence of Pd/Sibunit catalyst (Scheme 1). It appears, decarboxylation and reduction of three nitro groups of salt **1b** to hydroxyamino groups is a necessary condition for trioxime **6** to be formed with treatment of hydrogen consumed of 6 mole (mole **1b**)$^{-1}$. Such transformation of the salt **1b** into compound **3** can in fact proceed *via* several steps of sequential reduction of nitro groups and will be the object of further investigations. At the same time it is known that the compound **3** is unstable and tautomerizes into more stable trioxime **6**.[39,40] During the further hydrogenation of trioxime **6** aromaticity is restored[39] and the compounds **4**, **5**, and **2** are consequently formed.

From the analysis of the ^1H NMR spectrum (see also Fig. 2) it follows that the major product of the reaction under investigation is trioxime **6**, the yield of which was about 70% (isomer mixture with (1*Z*)-**6** predominating, see Table 1). Such a high yield of trioxime **6** can be explained by the selective formation of compound **3** during hydrogenation of salt **1b** and low rate of accumulation of **4** (along the paths **3** → **4** or **6** → **4**). The reason can be sought not only in the catalyst nature and the hydrogenation conditions chosen but also in the substrate nature (the substituent effect). Formation of trioxime **6** resulted from catalytic hydrogenation has not been reported so far. Thus, when studying hydrogenation of TNT in the presence of supported platinum or palladium catalysts in the medium of aliphatic alcohols it was established that the reduction scheme for 2,4,6-triaminotoluene presents a complex chain of consecutive and parallel reactions. The products of these transformations are only aromatic compounds bearing nitro-, nitroso-, hydroxyamino- and amino groups in different ratios.[36,37,42,43] Apart from well characterized hydrogenation of TNT, there are almost no information in literature regarding the transformation paths of other trinitroarenes (including **1a**,**b**) under catalytic hydrogenation conditions. As cited above, the published articles concerning the reduction of **1a**,**b** deal mainly with optimizing the conditions of the selective formation of the compound **2**,[14–20] while features of the reactions and conditions of the intermediate product formation are not established as yet.

Trioxime **6** presents a practical interest as it can find application, *e.g.* in the synthesis of 1,3,5-triaminocyclohexane,[44] 1,3,5-trinitrobenzene[41] and 1,3,5-trinitrosobenzene.[45,46] A single synthetic procedure to obtain trioxime **6** is known based on oximation of phloroglucinol with hydroxylamine in the presence of K_2CO_3.[47] Based on results of the present study, catalytic hydrogenation of the salt **1b** can be considered as an alternative approach to trioxime **6**.

Isolation of the trioxime **6** from the catalyzate fraught with difficulties, as it crystallizes poorly from an aqueous solution[40] and has low solubility in organic solvents[47], which prevents the use of extraction. Moreover, aromatic

Scheme 1



amines presenting in the reaction mixture have propensity to polycondensation when contacted with air. However it is believed[40,47] that in the absence of aromatic by-products in the reaction mixture and on concentrating the solution trioxime **6** can be isolated in quantitative yield.

Thus, using ^{1}H and ^{13}C NMR spectroscopy technique it was established for the first time that catalytic hydrogenation of compound **1** affording compound **2** can proceed *via* the intermediate formation of aromatic hydroxyamines **3**—**5** and trioxime **6**. Violation of aromaticity of the benzene ring and formation of trioxime **6** in the course of reduction of trinitroarenes has not been reported so far. Aqueous-phase hydrogenation of the salt **1b** using the 5%Pd/Sibunit catalyst at 323 K and a pressure of 0.5 MPa produces trioxime **6** in a high yield (~70%). The reason can be sought in the catalyst nature, hydrogenation conditions chosen as well as in the substrate nature (a substituent effect). Selective formation of the trioxime **6** allows one to consider the catalytic hydrogenation of the salt **1b** as a novel synthetic approach to this compound. Therefore, further studies will be focused on elucidating the principles of trioxime **6** formation as well as on search for conditions which would prevent accumulation of aromatic amines in the reaction mixture. It can be expected that this information can be of use to obtain trioxime **6** with improved selectivity and also to isolate it from the reaction mixture.

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