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Development of the Technology of Phloroglucinol Production

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Abstract

Results of the works on the development of the technology of phloroglucinol production are presented. Phloroglucinol is a known multipurpose organic reactant that has gained wide and diverse applications, in particular as the starting compound for the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene. A review of the known methods of phloroglucinol synthesis is presented. The method which is most promising from the standpoint of commercialization is studied. The method is based on the reduction of nitroaromatic precursors – 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene – to 1,3,5-triaminobenzene, followed by its hydrolysis. Alternate approaches to the synthesis of 2,4,6-trinitrobenzoic acid from 2,4,6-trinitrotoluene are proposed. The catalytic hydrogenation of 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene over palladium-containing catalysts was studied in detail, and the effect of various process parameters on the yield of the reaction product 1,3,5-triaminobenzene was determined. Hydrolysis of triaminobenzene to form phloroglucinol is considered.

Keywords: phloroglucinol, 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzoic acid

INTRODUCTION

Phloroglucinol (PG, 1,3,5-trihydroxybenzene) has a broad range of applications in various areas of the chemical industry: as a starting component for the synthesis of epoxy resins, to obtain protective coatings, thermoreactive resins, semiproducts for the synthesis of dyes, antioxidation additives for fuel, as well as medicinal preparations against hepatitis C, HIV, *etc*. In addition, PG is an initial compound for the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a chemically stable explosive substance with low sensitivity. The compound possesses powerful energy characteristics and at the same time is stable to temperature and shock-wave action. The main area of TATB application is explosive for lower-risk munition.

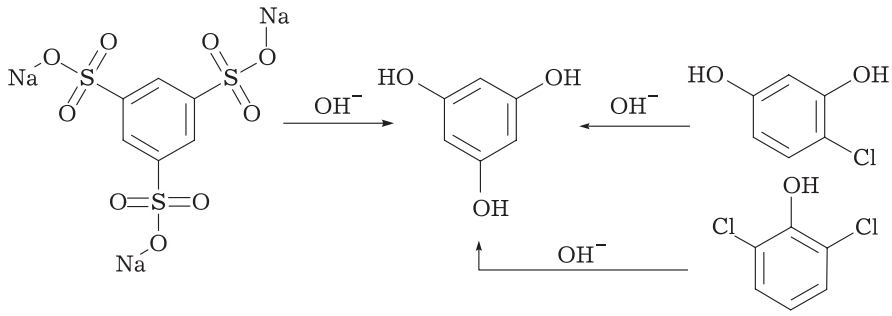
At present, PG is not manufactured in the Russian Federation, and the only source of this compound is importation. In view of the outlooks for industrial production of TATB, the development of homeland technology and construction of the facilities to manufacture with the necessary productivity becomes an urgent problem.

In the present work, a critical overview of laboratory and industrial methods of PG synthesis is described, along with the results of experimental studies aimed at the development of rational technology for its production.

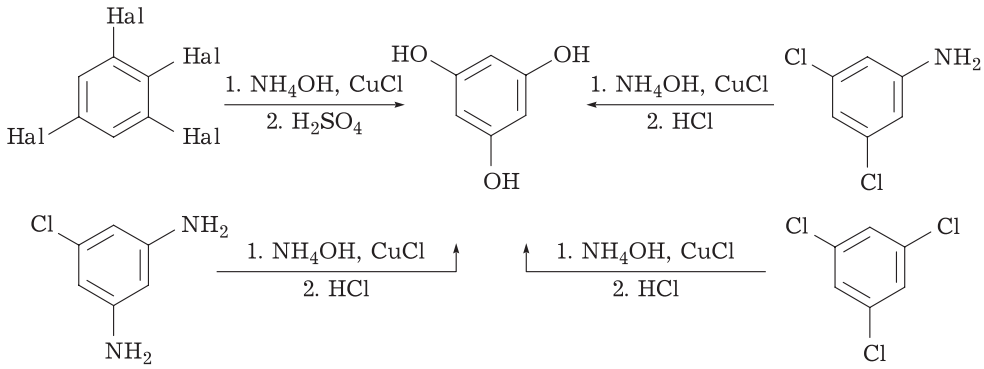
SYNTHESIS OF PHLOROGLUCINOL

Known laboratory procedures for the synthesis of phloroglucinol

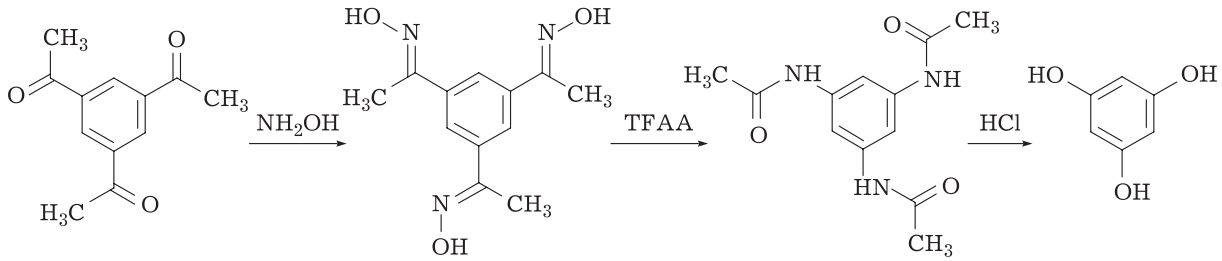
Analysis of the literature data shows that there are several approaches to the synthesis of PG. For instance, a known method involves PG synthesis through alkaline melting of the sodium salt



Scheme 1.



Scheme 2.



Scheme 3.

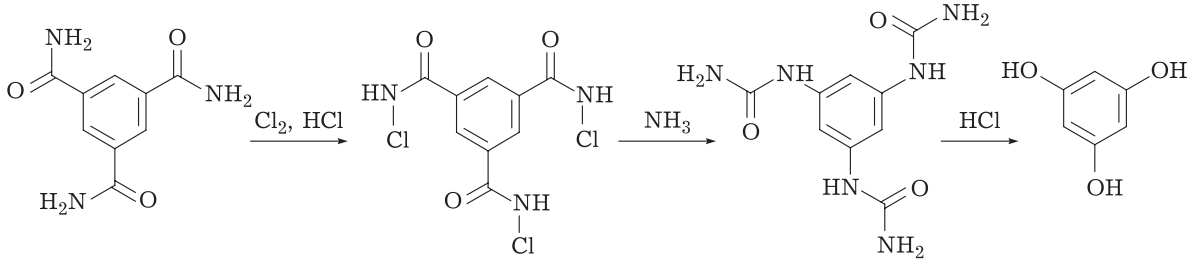
of benzene trisulphonic acid (PG yield 42.4 %) [1], 4-chloro-1,3-dihydroxybenzene (PG yield 60–66 %), and 2,6-dichlorophenol (PG yield 49 %) [2] (Scheme 1). In the case if the reaction is carried out in pseudo-cumene as reaction medium at its boiling point, PG yield increases (67 % with the use of 4-chloro-1,3-dihydroxybenzene and 55 % for 2,6-dichlorophenol) [3]. Phloroglucinol is extracted with ethylacetate of methyl ethyl ketone.

The indicated methods are characterized by several common disadvantages: the low yield of the target compound, high synthesis temperature, and the complicated procedure of PG isolation.

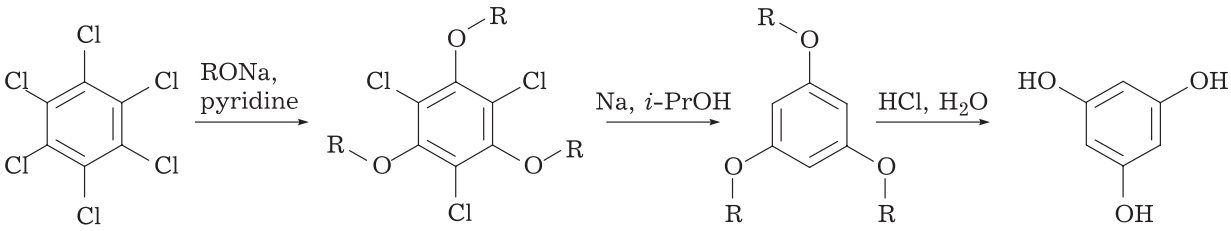
Another method of PG synthesis is connected with ammonolysis of 1,2,3,5-tetrahalogenobenzene by aqueous ammonia in the presence of catalytic amounts of copper(I). The process is carried out in an autoclave at a temperature of 200–240 °C, and then hydrolysis in the acid medium is performed [4]. PG is synthesised in a similar manner also from 3,5-diaminochlorobenzene [5] (PG yield 58.5 %), trichlorobenzene (PG yield 40 %) and 3,5-dichloroaniline (PG yield 60 %) (Scheme 2) [6, 7].

Along with rather low yield and the necessity of extraction, in some cases hydrochloric acid is used for hydrolysis, which implies higher requirements to the corrosion resistance of the equipment.

A method to synthesize PG from triacetylbenzene was described [8–10] (Scheme 3). At first,



Scheme 4.



Scheme 5.

triacetylbenzene is transformed into benzene-1,3,5-tris-acetoxime (yield 91 %) under the action of hydroxylamine. Then this compound is rearranged during long-term heating in trifluoroacetic acid (TFAA) into 1,3,5-triacetamidobenzene, which is then hydrolyzed into PG (yield up to 87 %) by boiling in a glass autoclave.

This method has a number of substantial disadvantages: the use of toxic ethylene glycol, expensive trifluoroacetic acid, corrosion-active hydrochloric acid, and a complicated procedure for the isolation of intermediates and PG.

A method to synthesize PG by means of hydrolysis of 1,3,5-triureidobenzene by boiling in the solutions of mineral acids in an autoclave within temperature range 140–200 °C is known. 1,3,5-Triureudobenzene, in turn, is synthesized by chlorination of 1,3,5-triamide of benzene tricarboxylic acid with gaseous chlorine, followed by amination of 1,3,5-tri-N-chloroamide of benzene tricarboxylic acid (Scheme 4) [11, 12].

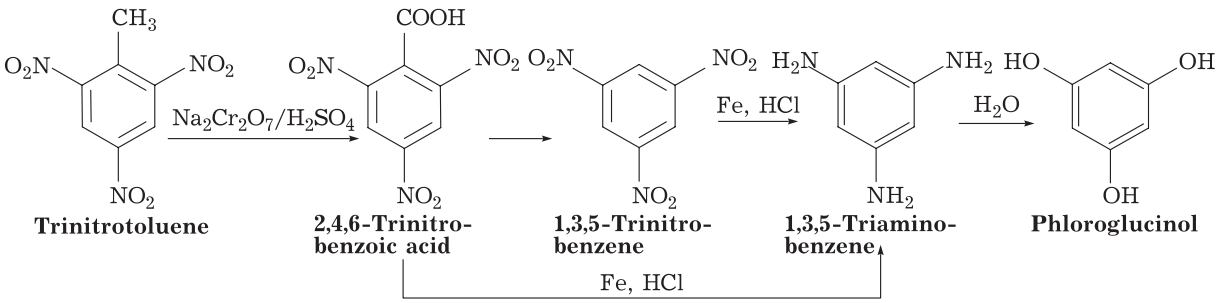
In spite of the high yields at all the stages of the process, this method has several disadvantages: the use of gaseous chlorine, hydrochloric acid, and the complicated procedure of PG isolation, which includes extraction and preparative chromatography.

A three-stage method to synthesize PG on the basis of hexachlorobenzene was also proposed (Scheme 5) [13]. However, this method implies the use of metal sodium at two stages, extraction of all intermediate products and PG, so it holds no commercial significance.

Industrial method to synthesize phloroglucinol from the products of trinitrotoluene processing

In fact, the only PG synthesis method that has won industrial application is the reduction of 1,3,5-trinitrobenzene (TNB) or 2,4,6-trinitrobenzoic acid (TNBA) into 1,3,5-triaminobenzene (TAB) and hydrolysis of the latter compound with the formation of PG (Scheme 6). The yield of the target compound is 75–85 % [14–16]. In turn, TNBA is obtained through the oxidation of trinitrotoluene with sodium dichromate [17–20] or potassium dichromate in sulphuric acid [21]. The yield is from 14 to 57 %.

This scheme is reasonably the most promising one because the raw material – trinitrotoluene (TNT) has been accumulated worldwide in great amounts, so the problem of processing aged munition into valuable and necessary products of organic synthesis is urgent. In addition, the method is characterized by the smallest number of stages and the simplicity of apparatus arrangement. However, at the same time, substantial disadvantages are the large amount of toxic wastes containing chromium and iron, and low process productivity. It is an interesting and promising task to solve the listed technological problem.



Scheme 6.

DEVELOPMENT OF THE METHOD OF OBTAINING PHLOROGLUCINOL

Search for a rational method of obtaining 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene

Alternative methods of TNT oxidation into TNBA are known from literature sources, but they do not have any potential for introduction into industry. For instance, the use of nitric acid (either diluted or concentrated) [22–24] at high temperature brings complications in view of its high corrosion activity; electrolytic method is characterized by the low yield of the target compound (12 %) [25]; the use of chlorates and perchlorates [26–32] is connected with the explosiveness of oxidizers themselves. Oxidation with the air requires the use of a catalyst – N,N′,N″-trihydroxyisocyanuric acid, which is synthesized through a four-stage process [33], while the application of more available cobalt salts as catalysts does not allow achieving an acceptable yield of TNBA [34].

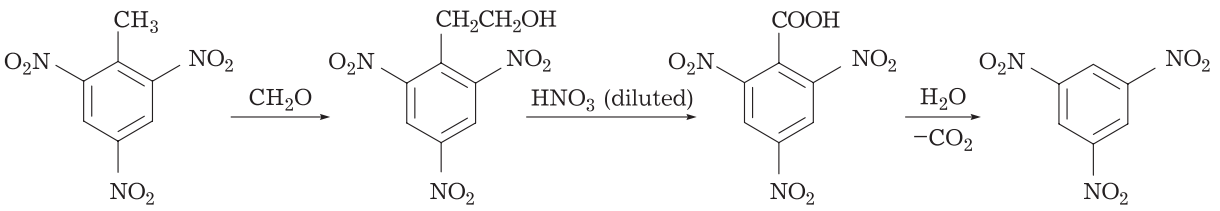
We studied the possibility to use potassium permanganate as an oxidizer in the alkaline, neutral, and acid medium. Since TNT is practically insoluble in water, oxidation does not proceed at a temperature below its melting point, so the reaction was carried out under the conditions of complete TNT melting, that is, at ~90 °C. It was demonstrated that the formed TNBA undergoes decarboxylation in the neutral and alkaline media. As a result, the major product of the reaction is TNB, but its yield is not high (28 and 45 %, respectively). The result of oxidation with potassium permanganate in sulphuric acid depends on the concentration of the acid; the acceptable yield of TNBA (61–65 %) is observed only for the concentration 65 % and higher. In spite of the fact that a minimal excess of the oxidizer is used, this method hold mainly laboratory significance [35].

Within the framework of the three-party interaction of Rosatom State Corporation, Biysk Oleum Plant, and the Institute for Problems of Chemical and Energetic Technologies SB RAS (IPCET SB RAS), an original technology for obtaining TNBA and TNB from TNT was developed. According to this method, TNT is hydroxymethylated by the action of formaldehyde, and then the formed 2,4,6-trinitrophenylethanol is subjected to destructive oxidation with diluted nitric acid. Then TNBA is readily decarboxylated during heating in water in the presence of the catalytic amount of alkali, which results in the formation of TNB with the yield above 95 %. Trinitrobenzene obtained according to this method is characterized by the high purity (the content of impurities is not more than 1 %) (Scheme 7).

The method was mastered at the facilities of the Biysk Oleum Plant, and larger-scale experimental lots of TNB were manufactured.

Development of the method to synthesize 1,3,5-triaminobenzene by the catalytic hydrogenation of trinitro derivatives of benzene

The development of catalytic hydrogenation methods using palladium-containing catalysts al-



Scheme 7.

lows one to do without chemical reduction of nitro groups, which is characterized by the large amount of iron-containing wastes, in favour of a more up-to-date and ecologically safe approach – heterogeneous catalysis.

Research work was carried out in two directions: hydrogenation of TNBA and TNB for the purpose of choosing the best method to obtain PG.

TNBA hydrogenation. Hydrogenation of TNBA appears to be more attractive method because in this case it is not necessary to carry out decarboxylation. However, until recently there have been only few data on this process in the literature. It is known that TNBA was hydrogenated over 5 % Pd/C in water with the addition of sodium dicarbonate (90–100 % of the stoichiometric amount) at 70 °C and a pressure of 0.6 MPa. Catalyst charge was 6 to 20 mass % depending on process version; quantitative hydrogen absorption was observed [36, 37].

In collaboration with the Centre for New Chemical Technologies of the IC SB RAS (SNCT IC SB RAS, Omsk), extensive integrated work was carried out to develop an optimal method to obtain palladium catalyst of aqueous-phase hydrogenation of TNBA; process mechanism was proposed, and technological modes were elaborated.

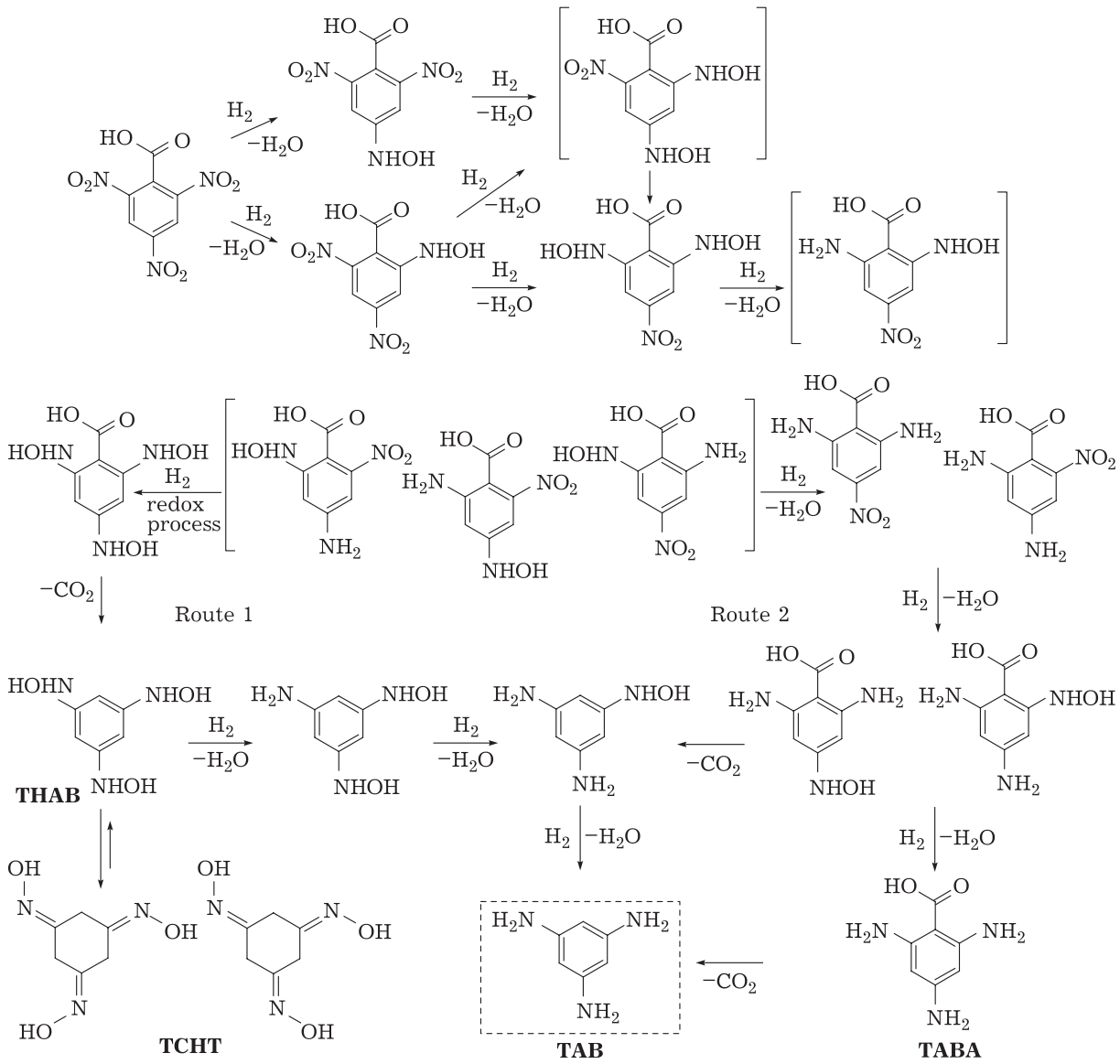
It was shown that complete reduction of all nitro groups in TNBA occurs only in the aqueous solution, while in organic solvents (acetone, ethylacetate, 96 % ethanol, isopropanol) a sharp decrease in hydrogenation rate during is observed the process, and many side products are formed. For selective synthesis of TAB through TNBA hydrogenation, it appears reasonable to minimize the electronic effect of carboxylic group, for example by transforming it into the salt form through the interaction of the aqueous solution of TNBA with $NaHCO_3$ (90 % of the stoichiometric amount necessary for the formation of sodium trinitrobenzoate) [37–39].

The effect of catalyst preparation conditions on its activity and selectivity in TNBA hydrogenation was studied in detail [40]. Sibunit was used as the substrate; its characteristics were: specific surface determined according to Brunauer–Emmett–Teller method (BET), 422 m^2/g; adsorption pore volume, 0.62 cm^3/g; average pore diameter, 5.9 nm. To provide comparative evaluation of the efficiency of palladium deposition conditions, catalysts with metal content 5 mass % were obtained in all cases.

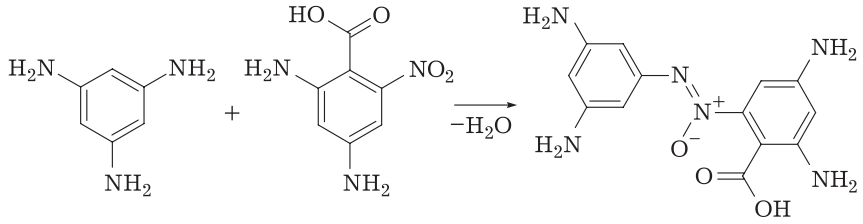
To carry out hydrolysis of H_2PdCl_4 through the formation of polyhydroxo complexes (PHC), authors used the aqueous solutions of precipitator compounds containing one of the cations K^+, Na^+, Li^+, and one of the anions CO_3^{2-}, HCO_3^-, OH^-. According to chemisorption data, the dispersity of palladium particles increases with an increase in cation size, independently of the nature of anion. At the same time, the formation of better dispersed palladium particles is promoted by the use of carbonate and hydrocarbonate anions; in the opinion of the authors, in the presence of these anions pH of solution changes slower, and the rate of H_2PdCl_4 hydrolysis decreases. Investigation showed that the dispersity of palladium particles is also dependent on solution pH during the hydrolysis of H_2PdCl_4. Independently of the nature of precipitating agent, the formation of PHC occurs within pH range 4–6. At the same time, the lower is pH, the higher is the dispersity of the formed particles. So, the best result was achieved at pH 4.43 with the use of $KHCO_3$ as a precipitating agent. Along with the high hydrogen absorption (0.85 equiv.) in hydrogenation, the highest selectivity with respect to TAB is also observed (72 %) [40].

Investigation of reaction mixtures by means of NMR spectroscopy allowed authors to establish the composition of the majority of intermediate products of hydrogenation and to propose a scheme of possible routes of TNBA hydrogenation (Scheme 8) [41–43].

The scheme depicts the reduction of TNBA to a mixture of the isomers of aminohydroxylaminonitrobenzoic acids, which are then transformed *via* two possible routes. The data of NMR spectra provide evidence that route No. 1 dominates under the conditions of hydrogenation. This route involves the formation of trihydroxylaminobenzoic acid and its decarboxylation. The formed *sim*-trihydroxylaminobenzene (THAB) may isomerize reversibly forming a mixture of 1,3,5-cyclohexanetrione trioximes (TCHT), which, depending on catalyst properties, may be either the major product of reduction or a minor admixture to TAB [40, 44]. In the case if a catalyst with finer dispersed palladium particles is used, a mixture of TCHT is involved in a further reduction to form TAB, with the concentration up to 85 %; about 1–2 % of TCHT remains in the form of admixtures, and 12–15 % admixtures are due to the side products of TAB condensation and its hydrolysis. In the case if the catalyst contains larger palladium particles, the interaction of TCHT with catalyst surface weakens, and a mixture of oximes gets desorbed, so these oximes become the major products



Scheme 8.



Scheme 9.

of synthesis (about 44 %), while the yield of TAB is only 23 % [43].

Separate experiments with deactivated catalyst showed that the reduction of a mixture of aminohydroxylaminonitrobenzoic acid isomers may follow route No. 2 (see Scheme 8), with decarboxylation taking place at the final stage. In addition, the formation of azoxybenzene (Scheme 9) is detected under these conditions. A detailed discussion of the hydrogenation mechanism and interpretation of the NMR spectra of intermediate and final products were considered in [42, 43].

TABLE 1

Effect of hydrogenation parameters on TNBA conversion

TNBA concentration, %	Catalyst charge, % with respect to TNBA	*T*, °C	*P*, MPa	Absorption time, min	Hydrogen absorption, %*
10	10	50	0.5	55	88
10	4	50	0.5	105	82
10	2	50	0.5	175	73
10	1	50	0.5	320	60
2.5	4	50	0.5	105	80
2.5	4	70	0.5	75	84
2.5	4	90	0.5	65	88
2.5	4	50	0.8	75	78

* With respect to the stoichiometric amount.

TABLE 2

Stability of catalyst performance in multicycle application

Cycle No.	Pd content in the catalyst, %	Catalyst charge, % with respect to TNBA	Absorption time, min	Hydrogen absorption, %*
1	5	5.0	100	95
2	5	–	160	86
3	5	–	170	70
1	2	12.5	100	92
2	2	–	115	92
3	2	–	130	91
4	2	–	220	85
1	1	25.0	90	95
2	1	–	100	95
3	1	–	120	95
4	1	–	180	92
5	1	–	220	80

* With respect to the stoichiometric amount.

The rate and selectivity of hydrogenation are strongly affected not only by catalyst properties but also by its amount with respect to the substrate, as well as by process temperature and hydrogen pressure [41, 45].

For the use of a 5 % catalyst as an example, it is shown in Table 1 that the highest hydrogenation rate and the maximal hydrogen absorption are achieved with 10 % catalyst added to the substrate, while a decrease in catalyst content leads to an increase in reaction time, decrease in hydrogenation extent, and the formation of size products. An increase in temperature from 50 to 90 °C has a positive effect on hydrogen absorption and therefore on the rate of TNBA hydrogenation; at the same time, the fraction of side products decreases. An increase in pressure from 0.5 to 0.8 MPa allows only an increase in the initial reaction rate; later on, hydrogen absorption decelerates sharply, and the reaction stops without achieving the transformation degree observed at a pressure of 0.5 MPa. The content of side products containing aliphatic fragments increases.

During the studies of multi-cycled catalyst operation, 5 %, 2 % and 1 % Pd/sibunit catalysts were tested (Table 2). It was established that for other conditions kept identical (10 % TNBA solution, temperature 70 °C, pressure 0.5 MPa) the most stable catalyst is 1 % Pd/sibunit conserving its activity during not less than four cycles. At the same time, complete and selective reduction for 5 % Pd/sibunit was observed only in the first cycle, while for the 2 % catalyst – only during the first two cycles, and after that hydrogenation showed down, and the presence of side products was recorded in the reaction mixture.

TABLE 3

Results of TNBA hydrogenation in the acid medium

Acid	Acid/TNBA molar ratio	T, °C	*P*, MPa	TAB yield, %
HCl	3.0	80	0.1	15.2
H_3PO_4	2.0	50	1.0	26.4
H_3PO_4	2.0	50	0.5	32.2
H_2SO_4	1.5	70	1.0	60.8
H_2SO_4	1.5	70	0.7	73.8
H_2SO_4	1.5	70	0.5	77.2
H_2SO_4	2.0	50	1.0	56.5
H_2SO_4	2.0	70	1.0	64.5
H_2SO_4	2.0	70	0.5	79.5
H_2SO_4	2.0	70	0.1	64.0
H_2SO_4	2.0	80	1.0	56.6
H_2SO_4	2.0	80	0.5	62.5

Note. The yield of TAB was determined quantitatively by means of HPLC using the characterized TAB trihydrochloride sample as a reference.

Isolation of TAB from aqueous solutions is unreasonable due to its high tendency to oxidation. For this reason, the aqueous solutions of TAB are acidified and hydrolyzed by long-term boiling to form PG.

Hydrogenation of TNBA in the presence of mineral acids appears to be a promising method. This allows obtaining TAB directly in the form of salts, which are more stable against oxidation than the base, which simplifies technological operations. We studied the effect of various factors on the yield of the target TAB, namely the composition of the acid and its amount, temperature, and pressure (Table 3). The catalyst was 5 % Pd/C in the amount of 10 % to the substrate mass [35].

It was determined that the maximal TAB yield does not exceed 80 % with complete conversion of the substrate, which is evidence of insufficiently selective catalyst performance in the acid medium.

So, aqueous-phase hydrogenation of TNBA, along with advantages (reaction carried out in water, direct hydrogenation without the necessity of decarboxylation), has some shortcomings: the catalyst conserves its activity only during four cycles, hydrogenation products are to be hydrolyzed immediately because TAB is readily oxidized, and it is undesirable to store it.

TNB hydrogenation. Hydrogenation of TNB may be carried out using NiRe as the catalyst [46, 47], as well as 5–6 % palladium on sibunit (or coal) [38, 48–52]. Reduction over nickel catalysts is carried out in ethylacetate or acetone under increased hydrogen pressure; the reaction takes a long time (up to 12 h), and its selectivity is insufficient, so the probability of the formation of side products of TAB interaction with intermediate products is high.

TNB hydrogenation over palladium catalysts was studied in detail by the research group headed by V. A. Kashaev [48]. The conditions for the multi-cycle catalyst performance were selected. Triaminobenzene was isolated in the form of stable salts with sulphuric, phosphoric and hydrochloric acids. The authors showed that hydrogenation in the medium of organic solvents is selective and allows obtaining and isolating the intermediate products of synthesis in high yields, if necessary. For instance, a method to obtain 1-hydroxylamino-3,5-dinitrobenzene in methanol and its mixture with toluene in the presence of 5 % Pd/C (2.3 % to substrate mass) was described. The reaction is carried out at a temperature of 20–30 °C until hydrogen is absorbed in the amount of 1.9–2.1 moles per one mole of TNB. The yield of 1-hydroxylamino-3,5-dinitrobenzene reaches 95 % [49]. In the case, if hydrogenation is stopped after the absorption of 6–6.05 moles of hydrogen per one mole of TNB, 1,3-diamino-5-nitrobenzene is formed selectively (yield 87–88 %) [50].

However, the main aim of TNB hydrogenation is its maximal transformation into TAB. The process is carried out either at atmospheric [48] or at an increased pressure of hydrogen [38, 51, 52] at a temperature of 50–60 °C until the stoichiometric amount of hydrogen is absorbed. The solvent used in the process has a substantial effect on the process (Table 4).

The cumulative data shown in Table 4 demonstrate that the best solvent is methanol, because it provides the achievement of the maximal TAB yield. In addition, the comparison between the experiments shows that pressure is not a critical parameter: the reaction goes on in a stable manner either at atmospheric or increased hydrogen pressure. It was demonstrated by V. A. Kashaev and co-workers that it is sufficient to add the catalyst in the amount of 3–5 mass % to achieve the maximal reduction of TNB into TAB; in addition, with other conditions kept identical, the yield of TAB trihydrochloride (TAB THC) is larger by 5 % on average than the yield of TAB disulphate (TAB DS). At the same time, taking into account the corrosion activity of the salts of hydrochloric acid, it appears more technological to use sulphate.

TABLE 4

Influence of the nature of the solvent and hydrogenation parameters on the TAB yield

No.	Catalyst	Amount of the catalyst, % with respect to TNB	Solvent (mg/g TNB)	*P*, MPa	*T*, °C	TAB yield, %	Reference
1	6 % Pd/sibunit	10.0	H_2O (20)	0.5	55–60	–	[52]
2	5 % Pd/C	4.7	EtOAc (24)	1.0	55–60	74.0 (hydrate)	[51]
3	6 % Pd/sibunit	10.0	EtOAc (10)	0.5	55–60	70.1 (hydrate)	[52]
4	6 % Pd/sibunit	10.0	EtOH (10)	0.5	55–60	18.7 (TAB DS)	[52]
5	6 % Pd/sibunit	10.0	*i*-PrOH (10)	0.5	55–60	–	[52]
6	6 % Pd/sibunit	10.0	*i*-PrOH/H_2O 9/1 (10)	0.5	55–60	77.7 (TAB DS)	[52]
7	5 % Pd/C	4.7	MeOH (24)	1.0	55–60	75.0 (TAB THC)	[51]
8	6 % Pd/sibunit	10.0	MeOH (5)	0.5	55–60	85.0 (TAB DS)	[52]
9	5 % Pd/C	2.0	MeOH (5)	0.1	57–59	83.4 (TAB DS)	[48]
10	5 % Pd/C	3.0	MeOH (5)	0.1	57–59	84.5 (TAB DS)	[48]
11	5 % Pd/C	4.0	MeOH (5)	0.1	57–59	84.3 (TAB DS)	[48]
12	5 % Pd/C	5.0	MeOH (5)	0.1	57–59	85.5 (TAB DS)	[48]
13	5 % Pd/C	5.7	MeOH (5)	0.1	57–59	85.5 (TAB DS)	[48]
14	5 % Pd/C	4.0	MeOH (5)	0.1	57–59	91.5 (TAB THC)	[48]

Note. The salts of TAB were isolated from alcohol solutions by acidifying the hydrogenizate with the corresponding acid. The isolation of TAB in the form of hydrate from ethylacetate was carried out by cooling the hydrogenizate to 0 °C.

The search for conditions under which the spent catalyst may be used repeatedly without any loss of activity is an essential task for the investigation of the reactions of Pd-catalyzed hydrogenation. This leads to a decrease in the average consumption of the precious metal and the cost of the final product, which is especially relevant if the industrial scale is considered.

We demonstrated that the activity of the spent catalyst decreases substantially during repeated use as a consequence of the adsorption of the side products of TAB hydrogenation and resinification on the catalyst support. For this reason, first of all, it was decided to introduce activated carbon as the adsorbent (1.25 % with respect to the mass of TNB in each cycle); second, a portion of the fresh catalyst is to be added (1 % with respect to TNB mass), starting from the second cycle. As a result, with the charged amount of 5 % Pd/sibunit accounting for 10 % with respect to the mass of TNB, the catalyst worked through 10 cycles with the average TAB DS yield equal to 82.5 %; the average catalyst consumption was 1.9 % [52].

A similar investigation was described in [48], where the initial catalyst charge (5 % Pd/C) was 4 %, the addition of the fresh portion was 1.33 %. The average yield of TAB THC was 88–90 %, and the average consumption of the catalyst was 1.6 %.

A possible method for further decrease in the average consumption of the catalyst is to decrease its initial load but conserve the amounts of fresh portions added, starting from the second cycle, or to provide the conditions under which the catalyst conserves its efficiency without the addition of a fresh portion. In both cases, catalyst regeneration is necessary, which is intended to recover its activity through desorption of admixtures.

Taking into account the basic nature of admixtures in TAB, we considered different versions of catalyst regeneration (Table 5). In all cases, 6 % palladium catalyst supported on sibunit was used, with the characteristics: specific surface according to BET – 360 m^2/g, total pore volume – 0.48 cm^3/g. TNB hydrogenation was carried out in methanol (with the ratio of methanol/TNB = 5) at a temperature of 55–60 °C and pressure 0.5 MPa, charging the catalyst in the amount of 10 mass %. After hydrogenation, the catalyst was separated, washed with methanol, and regenerated using the chosen method, then repeated hydrogenation was carried out.

With other conditions kept identical, only acetic acid among all organic solvents provides the most complete desorption of admixtures from the surface of the catalyst mixture, however, it is rather expensive to use it, and regeneration is hindered due to the high boiling temperature. Treatment with water vapour, most probably, leads to the blockage of the active centres of the catalyst by admixtures and results in a sharp decrease in TAB DS yield from the next cycle.

Among inorganic acids, the versions with the lowest corrosion activity were considered: 8 % solution of sulphuric acid, 5 % and 10 % solutions of orthophosphoric acid. Experiments showed that in all cases admixtures were well washed off the catalyst, however, in the case of sulphuric acid, the yield of TAB DS decreased in the second cycle (maybe because of catalyst poisoning by sulphurous admixtures), while the yield was at the same level in the case of orthophosphoric acid.

To decrease the load on the catalyst, the methanol/TNB ratio was increased because in this case, the solubility of admixtures in the reaction medium increases, while their adsorption on the catalyst support decreases. Other reaction conditions were kept the same, the catalyst was regenerated between the cycles with the help of the solution of orthophosphoric acid.

It was shown that the number of possible hydrogenation cycles that may be carried out with the reusable catalyst increases with an increase in the methanol/TNB ratio. Moreover, the yield of TAB DS increases by 5 %, which may be due to a decrease in its solubility in the mass in the case of isolation with sulphuric acid (see Fig. 1). Thus, for methanol/TNB = 5, a decrease in the yield of TAB DS below 80 % is observed after the third cycle, while for methanol/TNB = 10 – only after the sixth cycle. Taking into account a compromise between the positive effect of an increase in methanol amount and the process productivity, the ratio used in further studies was methanol/TNB = 7.

Taking into account the obtained results, three series of hydrogenation (see Fig. 2) were carried out. In the first series, the initial catalyst charge was decreased to 5 %, with the addition of a fresh portion in the amount of 1 % with respect to TNB mass, starting from the second cycle. The amount of sibunit added was 5 % in the first cycle and 0.5 % in each subsequent cycle.

In the second and the third series, initial sibunit charge was increased to 25 % and 40 %, respectively, and catalyst charge was increased up to 10 %, no additives were applied. The catalyst was regenerated after each cycle by the treatment with 10 % orthophosphoric acid.

In the first series (see Fig. 2, *a*) with the addition of the fresh portions, the catalyst operated during 10 cycles with the average yield of TAB DS about 85 %, and the duration of the process due to catalyst activity changed insignificantly. Due to a decrease in the initial catalyst charge, the average consumption was successfully decreased to 1.4 %, calculated for 10 operation cycles.

TABLE 5

Comparison of the efficiency of the methods of catalyst regeneration

Regeneration method	TAB DS yield, %	
	the 1st cycle	the 2nd cycle
Without regeneration	83.4	76.3
Treatment with water vapour	82.4	38.0
Washing with methanol	82.3	77.2
Washing with acetone	82.5	76.8
Washing with glacial CH_3COOH	82.5	81.9
Washing with 8 % H_2SO_4	82.6	77.6
Washing with 5 % H_3PO_4	83.7	83.1
Washing with 10 % H_3PO_4	82.9	82.5

In the series with an increased amount of sibunit (see Fig. 2, *b*, *c*) but without the addition of fresh catalyst portions, one can see that the activity of absorption decreases gradually as a consequence of the accumulation of admixtures, and it is necessary to add sibunit in the amount not less than 40 % with respect to TNB mass to provide 10 operation cycles. The average yield of TAB DS is about 84 %, and the average consumption of the catalyst is only 1 %, which is an advantage of this approach.

So, due to a small increase in methanol/TNB ratio, the introduction of sibunit as an adsorbent of admixtures, and regeneration of the catalyst with a solution of orthophosphoric acid, the average catalyst consumption was successfully decreased by a factor of about 1.5 in comparison with other methods described in the literature [48, 52].

As a result, during the development of the methods of TAB synthesis, two approaches were thoroughly studied: aqueous-phase hydrogenation of TNBA and the reduction of TNB in methanol.

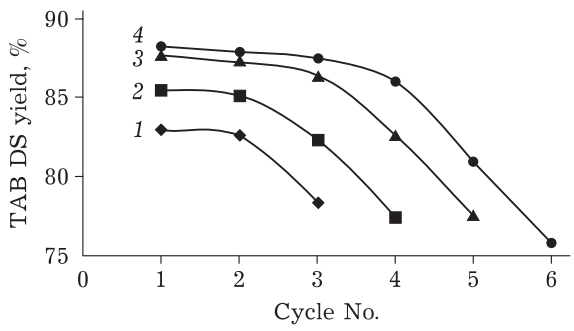


Fig. 1. Dependence of the yield of TAB DS on methanol/TNB ratio (M) and hydrogenation cycle with the reusable catalyst. M = 5 (*1*), 6 (*2*), 7 (*3*), 10 (*4*).

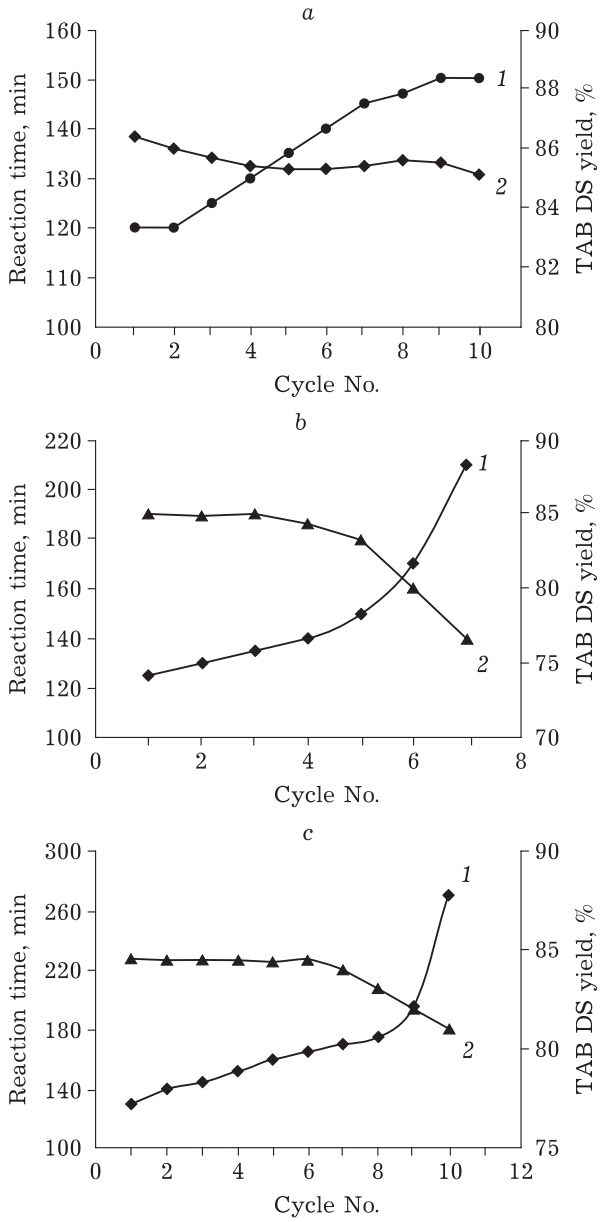


Fig. 2. Dependence of the yield of TAB DS and duration of TNB hydrogenation on catalyst and sibunit charge: series 1 (*a*), series 2 (*b*), series 3 (*c*). *1* – reaction time; *2* – the yield of TAB DS.

The comparative parameters of both processes in their optimal versions taking into account the multicycle use of the catalyst are shown in Table 6.

Hydrolysis of the salts of TAB

Isolation of TAB from alcohol solutions is carried out by treating with inorganic acids: hydrochloric (TAB THC), sulphuric (TAB DS), orthophosphoric (TAB diphosphate (DP)). The formed salts are rather stable during storage. Hydrolysis of the salts to PG is carried out by long-term boiling in water. The time necessary for complete conversion, and

TABLE 6

Comparative parameters of TNBA and TNB hydrogenation

Parameter	Value	
Substrate	TNBA	TNB
Solvent:	H_2O	MeOH
mL/g	10	7
Temperature, °C	70	55–60
Pressure, MPa	0.5	0.5
Catalyst:		
Pd content, %	1	6
amount, % with respect to the substrate	25	10
Sibunit, % with respect to the substrate	–	40
Number of cycles of catalyst performance without a decrease in the yield and quality of TAB	4	10
Average consumption of Pd, mg/g of the substrate	0.63	0.60
Average TAB yield, %	81	84

TABLE 7

Hydrolysis of the salts of 1,3,5-triaminobenzene (TAB)

Salt	Water volume, mL/g of salt	Reaction time, h	PG yield, %	Reference
TAB DS	1.75	12–15	79.9	[53]
TAB DP	1.75	12–15	64.1	[53]
TAB THC	8.6	15	80.1	[54]
TAB THC	6.3	15	75.1	[54]
TAB DS	5.3	11	85.7	[54]
TAB DS	4.8	11	85.1	[54]
TAB DS	3.5	13	80.0	[54]
TAB DS	2.4	13	73.7	[54]
TAB DS	2	12–14	78.2	[55]
TAB DS	3	12–14	77.4	[55]
TAB DS	5	12–14	87.1*	[55]

Note. TAB salts: DS - disulphate; DP – diphosphate; THC – trihydrochloride.

* Partial evaporation of the reaction mass.

PH yield vary depending on the anion. In addition, the yield of PG is affected by the ratio of water to TAB salt. The hydrolysis of TAB salts was studied in detail [53–55]. One can see (Table 7) that the maximal PG yield was obtained from the hydrolysis of TAB DS, while the minimal yield was that from the hydrolysis of TAB DP. Taking into account the fact that the yield of TAB DS is lower by 5 % on average than the yield of TAB THC, the total yield of PG in the case of chloride and sulphate is approximately the same. However, in view of the lower corrosion activity, TAB DS salt is preferable. It was established that the average yield of PG may be increased to 90 % if

the mother solution is used as the medium for TAB DS hydrolysis [55].

A method to obtain PG without intermediate isolation of TAB THC and TAB DS salts was proposed in [56]. This approach is characterized by the decreased consumption of the acid, and it is more reasonable from the technological point of view due to the elimination of salt filtration and methanol recovery operations. On the other hand, this method requires immediate processing of the water-methanol suspension of TAB salts, which is to be taken into account while designing the industrial installation. The yield of PG calculated for TNB is about 70 % for both salts, which is insignificantly lower than the total yield obtained in the case of the separation of stages.

So, comparing the parameters of hydrogenation of benzene nitro derivatives, taking into account the availability of raw material and specific features of TAB hydrolysis, we chose the method to obtain PG by TNB hydrogenation, followed by the isolation of TAB DS and its hydrolysis. This method was implemented on the basis of the industrial ground at the IPCET SB RAS, where the modes of technological stages were elaborated and corrected, and the experimental lots of phloroglucinol dihydrate were manufactured.

CONCLUSION

As a result of the collaboration of IPCET SB RAS, SNCT IC SB RAS, E. I. Zababakhin RFNC-VNIITF and the Biysk Oleum Plant – a branch of Ya. M. Sverdlov Plant, an integrated approach was developed to process 2,4,6-trinitrotoluene into phloroglucinol, a reagent in high demand for chemical synthesis. An original method of 2,4,6-trinitrotoluene oxidation to form 2,4,6-trinitrobenzoic acid and 1,3,5-trinitrobenzene was proposed. The methods of hydrogenation of trinitrobenzene derivatives into 1,3,5-triaminobenzene using palladium catalysts were studied in detail; the modes of efficient multi-cycle use of the spent catalysts were elaborated, which is undoubtedly important from the economical point of view. The obtained results were approved at the industrial facilities of the Biysk Oleum Plant and IPCET SB RAS.

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