The Improvement of Picric Acid Synthesis Methodology

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Abstract. Explosives have the greatest importance in human practical activities, not only at time of war, but at tranquility as well. Nowadays, huge amount different type of explosives is synthesized, and fabricated for military and civilian applications. Nevertheless, this fact doesn’t exclude necessity of synthesis of new explosives for optimization of their characteristics, such as prime cost, power, safety during production, storage, transfer and etc. Picric acid is a fairly strong and energetic explosive, at the same time, beside to its explosive properties, it is characterized with antibacterial nature and it is the best yellow dye, especially for dyeing animal and plant tissues. The synthesis of picric acid structural analogues, is the main purpose of the research. One of the reasons of synthesis picric acid and further preparation of its structural analogues is safe nature of substances of this group, which makes them safe to various manipulations. On the other hand, it is well known that the synthesis and production of explosives is classified as high risk and costly technology. Therefore, even a small increase of their production productivity, is interesting from the economic effect point of view. During an investigation, changing of reaction conditions (temperature, concentrations and dosage of reagents) the improved method for syntheses of picric acid was developed. As result the significant increase of practical yield of picric acid, from 46% to 86% was achieved. Synthesized picric acid was placed in steel tube and tested on initiation of detonation in explosive camera. The description of modified method, comparisons to conventional technology, as well as explosion testing results is described in the paper.

1. Introduction
A vast majority of explosives are produced by the chemical synthesis, including picric acid, trotil, octogone, nitroglycerine and other well-known explosives. At the end of XX century in the USA powerful explosives with highest technical characteristics – octanitrocubane and Hexanitrohexaazaisowurzitane - CL-20 were synthesized [1-2]:

Octanitrocubane

Hexanitrohexaazaisowurzitane (CL-20)
Despite of their powerful explosive nature, these substances have a serious drawback – their high prime cost. Picric acid is a well-known, quite powerful and relatively cheap explosive. During the XX century, the millions of shells, charged with this explosive, were used in World wars and other conflicts.

Choice of picric acid as the main „working substance” is conditioned by the fact, that phenol and its chemical analogues (anisole, cresols, resorcin…) are cheap and at the same time, valuable „row materials” for the synthesis of numerous products, including well-known explosives – picric acid, isomeric dinitrophenols, methyl picrate, cresolite, styphnic acid … Besides, we have some experience in the synthesis of various alkyl phenols [3-5], which may be considered as interesting substrates for the synthesis of structural analogues of picric acid, presumably, by maintaining of explosive nature.

Because of acidic nature, picric acid reacts with metal casing of shell. This is its serious drawback. In this respect, trotil has an undeniable advantage. In spite of this, at war, the importance of picric acid may be increased. In this case, of course, before charging the shell with picric acid it’s necessary to place explosive in non-metal casing.

For avoidance of negative acidic nature of picric acid, a chemical method may also be used: changing of molecular structure or, synthesis its structural analogues.

At the same time, the world experience considers such changing as the most successful methodology for synthesis of new explosives. On the other-hand, chemical avoidance of mentioned acidity may become stimulant for synthesis of new explosives on the base of picric acid.

Such avoidance concerns exclusively hydroxyl, as an acid group and may be realized by corresponding reactions - alkylation, acylation, etc. In early period, we used similar transformations of acetylene phenols, synthesized by us [3-5], which already was mentioned above.

2. Theoretical part of phenol’s nitration

Usually, picric acid may be synthesized by nitration of phenol according to scheme:

\[
\text{OH} + 3\text{HNO}_3 \xrightarrow{(\text{H}_2\text{SO}_4)\ -3\text{H}_2\text{O}} \text{Picric acid}
\]

The role of the sulphuric acid is easy formation of 2,4 - disulphophenol – the first intermediate product of nitration (I). At the following step of reaction, two sulpho groups of I are easily changed to nitro groups of nitric acid and form 2,4 - dinitrophenol – the second intermediate product (II). At last, substitution of nitro group from third molecule of nitric acid, at 6-st carbon atom of phenol, leads to picric acid:
In the reaction mixture the ionic fragment is formed, which is called nitronium NO$_2^+$. This particle attacks the aromatic ring of phenol and replaces hydrogen atom, which removes as H$^+$ ion. This is electrophilic substitution in aromatic ring which consists of intermediate formation of $\pi$- and $\sigma$-complexes, and ended by formation of reaction products.

Here is the mechanism of this process, for benzene nitration:

\[
\text{Benzene} + \text{Nitronium} \rightarrow \text{Complex} \rightarrow \text{Nitrobenzene}
\]

3. Methodology of picric acid synthesis

3.1. The well-known methodology [6] of picric acid synthesis

In the porcelain basin 12.5 g of phenol is mixed with 34 ml of concentrated sulphuric acid and the mixture is heated on the water bath, till a formation of a limpid solution of phenol-sulphuric acid. Formation of phenol-sulphuric acid ends, usually, in 30-40 min.

Phenol-sulphuric acid solution is poured with stirring in to a 1L flask, contained 50 ml of cool water. The flask is cooled by water. With stirring, 25 ml of concentrated (d=1,4) nitric acid is added dropwise. Reaction mixture becomes red, temperature increases and red steam appears (inhaling is forbidden! Conduct work in suction cupboard!).

After, flask is placed on the water bath, add residual 10 ml of nitric acid and heated the mixture for 1.5-2 h.

After cooling, yellow crystals of picric acid are precipitated. Then, pour water into the flask, mix, filter crystals and wash. Picric acid is crystallized from 50% ethyl alcohol: m. p. 122$^\circ$C, yield – 14 g.

3.2. The improved methodology of picric acid synthesis

20 g of phenol is placed in to a flat-bottomed flask, carefully melt on the water bath, and at 50$^\circ$C dropwise add 33 ml of concentrated (d=1,84) sulphuric acid. Rise temperature till 96-97$^\circ$C and continue heating the mixture for 1 hour.

After cooling, rise temperature to 50$^\circ$C and start addition of 35 ml of nitric acid (d=1.42). Self-heating (till 76-77$^\circ$C) and darkening of the mixture, is caused by nitrous gases. After addition, reaction was continued at the same temperature, till elimination of nitrous gases emission. Then the temperature was diminished till 50$^\circ$C, add 24 ml of nitric acid, in drops and begin heating of the reaction mixture. At 70$^\circ$C gas emission is intensive; at 85$^\circ$C intensity is at maximum. Than the mixture is boiled for 1.5 h. After cooling, picric acid crystals appeared, which are removed by filtration. Crystals are washed with cool, diluted nitric acid and dried. 27 g yellowish crystals are received.

Dark red filtrate was returned in to a flask, added 12 ml of nitric acid in drops and heated to 96-97$^\circ$C for 1.0 h. After cooling, 300 ml of ice cold water is poured in to a flask, temperature is diminished till 0$^\circ$C, and crystals are filtrated and washed. 15 g of picric acid is obtained. After this, the total amount is equal to 42g, practical yield = 86%.

3.3. Comparison of two methodologies
According to “well-known methodology”, from 12.5g phenol 14g of picric acid is received (46%). Let’s try to explain such an low yield. “Well-known methodology” describes, that phenol and sulphuric acid are mixed together, at the same time, not in drops, and heated for 30-40 min.

In our method phenol is melted and then, at 50°C, sulphuric acid is added in drop, with stirring. After addition, reaction mixture is heated on steam bath (96-97°C), for minimum 1 h. So, formation of disulphophenol is almost accomplished.

In “well-known methodology”: before addition of nitric acid, 50 ml of cool water is added to the flask, which dilutes disulphophenol. It may diminish the concentration of added nitric acid, which is not desirable.

Before nitric acid addition, the temperature of mixture is risen to 50°C. During addition of the first portion of nitric acid temperature, usually, self-increases till 76-77°C and active emission of nitrous gases starts, which intensity is synchronized with temperature increase.

At the end of the reaction, after filtration of crystals, the consistence of filtrate, shows, that it isn’t the mixture of only unreacted acids, but, probably, consists of unreacted dinitrophenol too. It is noteworthy, that, at high temperatures, nitric acid evaporates. So, it needs compensation. Consequently, filtrate is poured back in to the flask and 1 portion of nitric acid is added – 15-20% of its reaction dosage. After heating, renewed emission of nitrous gases, confirms continuation of reaction.

Often, at the end of the reaction, nearly 1/3 of full amount of synthesized picric acid is formed additionally.

4. Testing of synthesized picric acid on blast conversion

Blast testing of picric acid was carried out in a camera integrated into the tunnel system of an underground experimental explosive base of Georgian G. Tsulukidze Mining Institute.

The views of the base’s portal and camera are shown on the figure 1.

![Figure 1. The portal of the underground tunnel system (a) The blasting camera (b)](image_url)

Synthesized picric acid were obtained in the form of brilliant, yellowish crystalline powder in which the granulometric consist of the particles varies in the range 0-0.5 mm. Its microphotograph is shown in figure 2(a).
To test the ability to induce detonation, a standard test scheme localized in a solid state of charge was used. In particular, to obtain longitudinal charges, 15 g of picric acid was loaded into a low-carbon steel tube. One end of the tube is closed with a stopper of the same material, while the other side (in the area of the detonator) is not charged and is in a free state. The pipe diameter was selected conditionally, according to the analogy of the tests of brisant explosives. A capsule detonator KD-8 with a fuse was used to initiate the detonation. The diagram (b) and the view (c) of testing tube also are shown in figure 2.

![Figure 2.](image)

**Figure 2.** The crystalline powder of synthesized picric acid (a). The diagram of testing tube (b): 1 – testing tube; 2 – picric acid; 3 – fuse; 4 – capsule-detonerator KD-8; 5 – testing tube stopper; The view of testing tube (c).

The explosion of picric acid occurred in full, without a waste. It caused complete fragmentation of the casing, which is typical for explosives with high brisant and working capacity. The results of blasting are shown in figure 3.

![Figure 3.](image)
Figure 3. Fragmentation of testing tube after explosion.

5. Conclusions

- The temperature conditions of reaction were almost completely changed.
- More concentrated (d=1.42) nitric acid was used.
- Considering the evaporation of nitric acid, at high temperatures, its reaction dosage was increased.
- All of this has increased a practical yield of picric acid till 86%.

In the future, the data of improved methodology, for increasing of practical yields, described in this article, will be used in the synthesis, of other analogues of picric acid – methylpicrate (from anisole), ethylpicrate (from phenetole), styphnic acid (from resorcine), etc.

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