ISSN 2720-8710 (Print)
ISSN 2960-9658 (Online)

APPLICATION OF CHEMICAL ANALYSIS, SYNTHESIS AND PURIFICATION METHODSIN THE PROCESS OF UTILIZATION OF EXPIRED TNT

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DOI: https://doi.org/10.61446/ds.3.2024.8471

Article History:

Received	15 September 2024
Accepted	20 October 2024
Published	25 December 2024

ABSTRACT

In the modern world, the scale of the use of explosives and explosion processes is immeasurable. Based on the current realities in Georgia, the study of the processes of utilization and recycling of expired TNT and other explosive substances released from ammunition is of great importance. The issue is doubly urgent, as these substances represent the greatest danger to the environment. Burning or destroying them is tantamount to an ecological disaster. For the same reason, keeping them for a long time is also dangerous. Instead, utilization will raise the prospect of recycling them into industrial explosives, which we consider the best way to solve the problem.

There are several key processes to be carried out for the utilization of TNT: chemical analysis of TNT, its purification by crystallization, synthesis of CT compounds, inclusion of the synthesis process in the analysis.

The article discusses a brief overview of the above processes, brings the results of our experiments in this direction, as well as brief conclusions.

Keywords: TNT, utilization, analysis, chromatography, spectroscopy, synthesis, explosives...

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ISSN 2720-8710 (Print)
ISSN 2960-9658 (Online)

INTRODUCTION

In general, the creation, research and use of substances are completely connected with the two main methods of chemistry - synthesis and analysis. The vast majority of explosives are created through organic synthesis. It is impossible to determine the chemical structure of any newly created substance, including explosives, without analysis. The same can be said for research and utilization processes of expired explosives.

The scope of analytical chemistry often goes beyond the boundaries of chemistry and reaches such important areas of human activity as criminalistics, food production, mineralogy, pharmacy, military affairs...

Chemical analysis of expired TNT includes both simple and instrumental methods. Below, a brief characterization of infrared - IR spectroscopy and HPLC chromatography methods is discussed.

As for the utilization of TNT, picric acid, tri nitro benzene and other poly nitro aromatic or PNA compounds, the cheapest and most effective way, we consider - the synthesis of such products of their chemical transformation, which will have the ability to explode back... First of all, are so-called CT compounds (Charge Transfer Compounds).

MAIN PART

1. Basic methods of chemical analysis

1.1. The essence of chemical analysis

Analytical chemistry includes two directions. Determining the content of individual elements, ions, and groups of atoms in molecules is the task of qualitative analysis. The goal of quantitative analysis is to determine the percentage content of components. Before determining the quantity of a component, it is necessary to determine its presence in the sample. Therefore, qualitative analysis always precedes quantitative analysis.[2,3]

The analysis of an individual substance is reduced to the determination of individual components. As for a mixture of substances, here two circumstances can be considered: 1. The mixture contains a commercially interesting substance and a small amount of impurities. Analytical methods must be found that will confirm the identity of this substance. After that, an appropriate purification method must be found. 2. It is more difficult to study a mixture of substances. This requires systematic analysis...

1.2. Infrared - IR spectroscopy. When IR rays are passed through a substance, part of the energy of the radiation is absorbed. Each chemical bond is characterized by only a specific

[2] A. P. Kreshkov fundamentals of analytical chemistry, book 1, Ed. „ Chemistry", Moscow, 1976 (in Russian).
[3] V. N. Alekseev Qualitative analysis, „Goskhimizdat’ Moscow, 1953 (in Russian).

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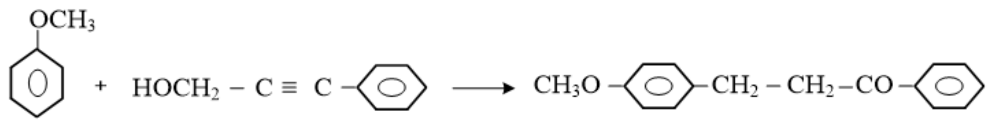
absorption band.[4] Based on the location of absorption minima in the IR spectrum, we can accurately determine the nature of a particular chemical bond. Previously, we synthesized more than 60 alkylphenols by alkylation of phenols with phenylacetylenic alcohols.[5,6] Below, the alkylation reaction of anisole with 3-phenylpropyn-2-ol-1 is presented, as well as the IR spectra of the alcohol and alkylanisole. Their comparison indicates an anomalous course of the alkylation reactions: not the acetylenic alcohol fragment, but its hydrated variation is replaced in the aromatic nucleus:[7]



Anisole 3-Phenylpropyn-2-ol-1 Alkylanisole

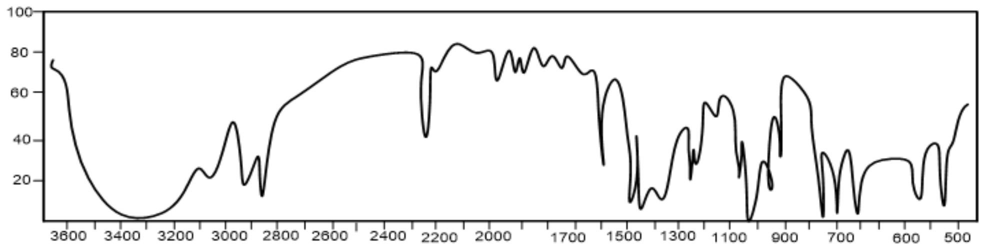


Fig. 1. IR spectra of 3-phenyl propyn-2-ol-1

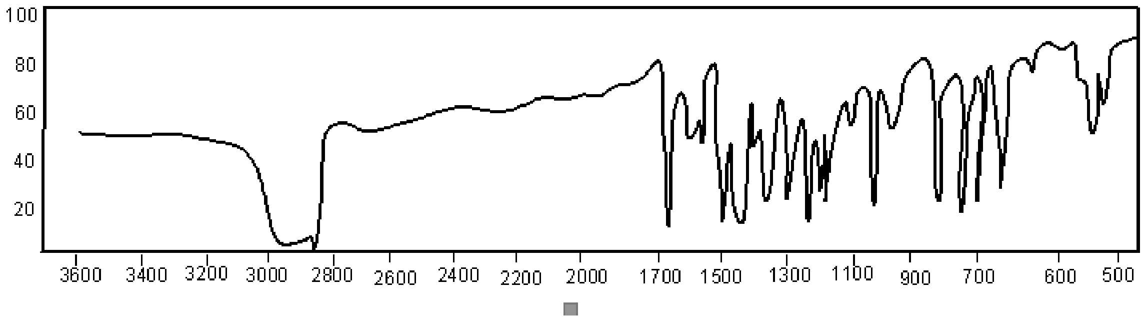


Fig. 2. IR spectra of alkyl anisole

Unlike phenylacetylenic alcohol, the IR spectrum of alkylanisole does not have a triple bond absorption band (γ C ≡ C, 2240 cm^{-1}), but instead, a band appears at 1679 cm^{-1}, which is characteristic of the carbonyl group (γ C = O). This clearly indicates that the acetylenic alcohol undergoes a change (hydration) during the reaction. The spectrum of alkylanisole, as expected,

[4] J. Brand, G. Eglinton Application of spectroscopy in organic chemistry, publishing house, Mir' Moscow, 1967.
[5] A.I. Kakhniasvili, D.Sh. Ioramash¬vili, M.D.Nadirashvili - "Synthesis and transformations of organogermanium and organosilicon unsaturated phenols"-VIIIth Inter¬national Conference on Organome¬tal¬lic Chemistry, JAPAN. Kyoto, 1977, Abstr., 5 A12.
[6] Nikoloz Chikhradze, Merab Nadirashvili, Sergo Khomeriki, Iasha Varshanidze „The Synthesis of Phenyl Acetylene Phenols for Development of New Explosives", World Multidisciplinary Earth Sciences Symposium WMESS, IOP Conf. Series: Earth and Environmental Science 95 (2017) 042030, Prague (Czech Republic).
[7] D. S. Ioramashvili, A. I. Kakhniashvili, M. D. Nadirashvili Interaction of 3-phenyl-2-propene-1-ol with phenols, Zhorkh 13, 804, 1978 (in Russian).

ISSN 2720-8710 (Print)
ISSN 2960-9658 (Online)

does not show the absorption bands of alcohol and phenolic hydroxyl. This example clearly demonstrates the importance of IR spectroscopy for the identification of chemical bonds.

1.3. High-performance liquid chromatography - HPLC. This is one of the most modern methods for the qualitative and quantitative analysis of organic compounds,[8] including explosives. Relevant - HPLC chromatograph is used for the analysis of solutions. Fig. 3 and Fig. 4 show its general scheme and chromatographic peaks a and b:

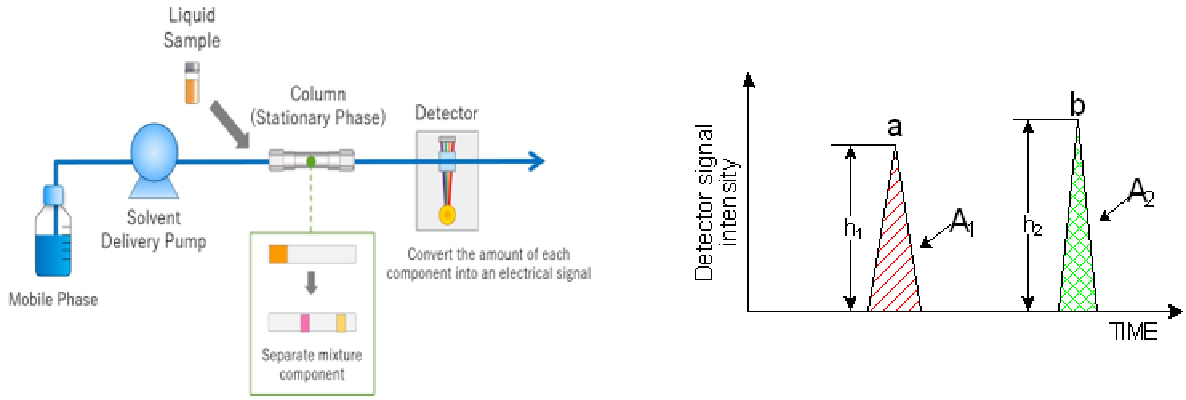


Fig. 4 General scheme of HPLC
Chromatographic peaks, a and b chromatograph

The solvent, or mobile phase, is delivered by a special pump to the adsorption column (stationary phase) and then to the detector. A certain amount of the sample enters the column and the substances present in it are separated, which is recorded by the detector. The results, in the form of peaks, appear on the chromatogram. It is a two-dimensional graph, where the vertical axis represents the **concentrations** of components, and the horizontal axis represents the **time** of analysis. Based on the height (h) and area (A) of the peaks on the graph, one can judge about qualitative and quantitative content of components.

We use HPLC chromatography to analyze of expired TNT.

2. Purification of expired TNT by crystallization

We use two different crystallization methods to purify expired TNT that is u-TNT. The first involves dissolving u-TNT in a heated solvent (toluene, ethanol, etc.) until a saturated solution is formed. Crystallization occurs as a result of gradual or rapid cooling of the solution.

The second variation is to dissolve the u-TNT in one solvent and crystallize it in a second solvent that dissolves the first solvent but does not dissolve crystals. Several variations of this method can be developed.

[8] What is HPLC (High Performance Liquid Chromatography)? https://www.shimadzu.com/an/service-support/technical-support/analysis- basics/basic/what_is_hplc.html

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In both cases, whitish crystals are obtained from the brownish u-TNT, which are visually quite different from the initial crystals (Photos 1, 2).

These methods are based on a well-known rule of chemistry: during crystallization, as crystals mature and grow, impurity molecules practically do not enter the growing crystal matrix, but instead mix with the solvent and are filtered out of the purified crystals.

For the purpose of initial testing, we detonated expired and purified TNT in low-carbon steel tubes. The experiment shows that in the case of u-TNT, the tube breaks into several fragments (photo 4), while when purified TNT is detonated, the tube is completely fragmented (photo 3). In other words, in the latter case, the explosion power is significantly increased:


Photo 1

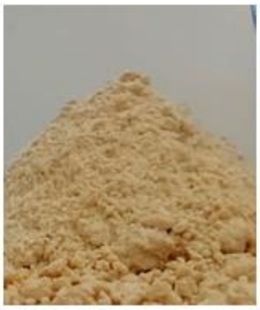


Photo 2


Photo 3

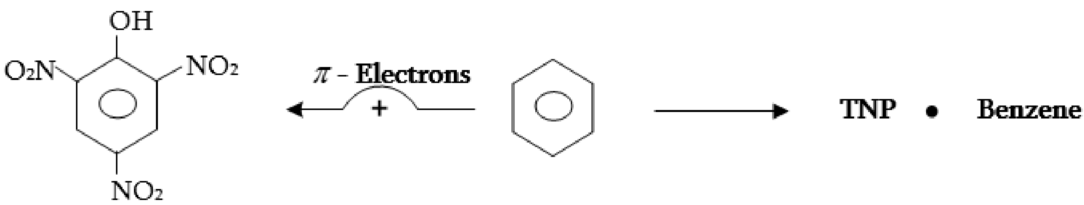

Photo 4

We determine the purity of the crystals using TLC that is thin layer chromatography.

After the experiments conducted by us at this stage and the confirmation of their results, it will be possible **to propose crystallization from solvents as one of the methods for utilizing expired TNT.**

3. CT compounds

3.1. Mechanism of synthesis of CT compounds. The presence of three nitro groups in the explosives molecule significantly impoverishes the π-electron system of the aromatic nucleus and gives the mentioned substances a strong electron acceptor property. Accordingly, their molecules acquire the ability to transfer π-electrons from electron donor molecules to themselves. At this time, there is no redistribution of chemical bonds and no formation of new bonds between the reacting molecules. Only electrostatic attraction occurs, resulting in



Picric acid, TNP

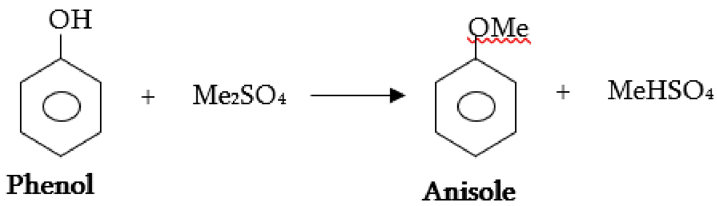
ISSN 2720-8710 (Print)
ISSN 2960-9658 (Online)

bimolecular aggregates - CT compounds [9], with a molar ratio of components of 1:1, which is expressed as follows in the example of picric acid and benzene:

The general scheme for the synthesis of CT compounds can be represented as follows:

EL.ACCEPTOR COMP. + EL. DONOR COMP. ⟶ EL. ACCEPTOR COMP. • EL. DONOR COMP.

3.2. Inclusion of the synthesis process of CT compounds in the analysis. In general, the inclusion of synthesis processes in the analysis of an unknown substance is one of the well-known and at the same time effective methods. For example, the content of the hydroxyl functional group(OH) can be determined by methylation with dimethyl sulfate:



For the quantitative analysis of aldehydes and ketones, their reactions with hydroxylamine are used:

$$R-CH=O+H_2NOH \xrightarrow[-H_2O]{} R-CH=NOH$$
Aldoxime

$$\begin{matrix}R\\R\end{matrix}>C=O+H_2NOH \xrightarrow[-H_2O]{} \begin{matrix}R\\R\end{matrix}>C=NOH$$
Ketoxime

The interaction of picric acid with alkaloids (morphine, nicotine, codeine, heroin...) is used for the analysis of the latter. The mechanisms of this process and the formation of CT compounds are close to each other.

Based on the above, we considered it necessary to include the synthesis reactions of CT compounds of various structures in the analysis of expired TNT and other explosive PNA compounds. Such PNA compounds, as a rule, contain impurities. For example, during the synthesis of CT compounds from u-TNP, we use easily volatile furan (tbp = +32°C) and ammonium nitrate as electron-donor components, which we introduce into the reaction in a threefold excess:

ISSN 2720-8710 (Print)
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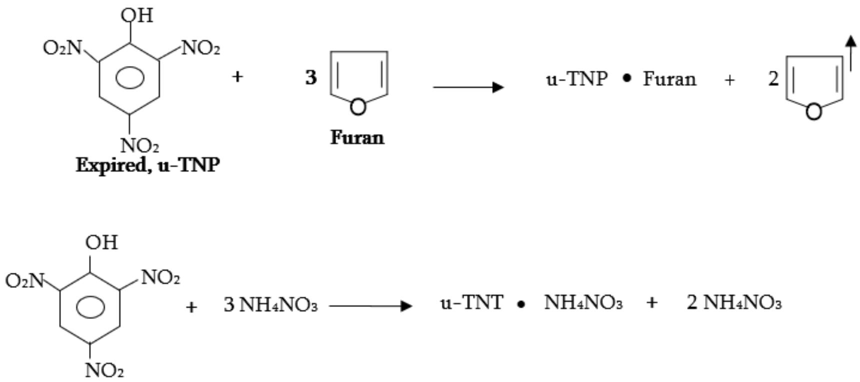

At the end of the reaction, after evaporation of excess furan and removal of excess nitrate by dissolution in water, CT compounds are obtained, in which all u-TNP is bound to furan and nitrate in a 1:1 ratio. The impurities present in the sample are also dispersed in the CT compounds thus obtained. The latter can be removed by crystallization or other methods. After that, quantitative calculations that will give us the percentage content of the PNA compound are not difficult.

3.3. CT compounds synthesized from u-TNT. Lately, two dozen CT compounds have been obtained from TNP synthesized by us [10], as well as from pure TNT. Their explosive power significantly exceeds the same power of the original explosives.

This fact became the prerequisite for the synthesis of CT compounds from u-TNT, and then - for comparing their explosive ability with the same ability of u-TNT. A total of 7 CT compounds have been synthesized:

u-TNT • $NaNO_2$ u-TNT • KNO_3 u-TNT • Toluene u-TNT • $NaNO_3$

u-TNT • Furan u-TNT • $Ba(NO_3)_2$ u-TNT • $K_2Cr_2O_7$

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All seven CT compounds have been tested in an explosion. In all cases, there was intensive fragmentation of steel reels occurred. Photos of the four samples (5-8) are presented below:


Photo 5

u-TNT • $NaNO_3$


Photo 6

u-TNT • KNO_3


Photo 7

u-TNT • Toluene


Photo 8

u-TNT • Furan

These results allow us to draw an initial conclusion. **By synthesizing CT compounds, the explosive ability of not only pure PNA compounds increases significantly, but also of expired, utilized TNT too.**

3.4. Priorities of synthesis of CT compounds. The use of CT compound synthesis in the utilization of expired explosives has certain advantages:

1. **The working capacity of the TNP • NH_4NO_3 exceeds the same characteristic of the PNA compound (TNP). We expect similar results in other cases;**
2. **The synthesis of CT compounds proceeds without energy-intensive costs, with a maximum solution (output) of cheap and practically pure targeted products;**
3. **Synthesis of CT compounds, allows to regulate the sharply negative oxygen balance of PNA compounds towards zero;**
4. **By synthesizing CT compounds, the percentage of impurities (which prevent explosion) in the expired explosive is reduced;**
5. **The mass of synthesized CT compound increases, and even more so the greater the molecular mass of the electron donor component.**

CONCLUSION

1. From an expired PNA compound, such as TNT, it is possible to obtain more power, with more mass, cheap and practically pure explosive CT compounds with maximum output.
2. We consider it possible to offer the processes of synthesis of CT compounds and crystallization from solvents as cheap and effective methods of utilization of expired TNT.
3. The same processes, after proper examination, can be offered as a general method of utilization of expired TNT and other explosive PNA compounds.

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