

Chemical and environmental problems of utilization of trinitrotoluene

OLGA KOVALCHUKOVA & KONSTANTIN KOBRAKOV*

General Chemistry Department
Peoples' Friendship University of Russia
Miklukho-Maklaya street, 6, Moscow 117198
RUSSIAN FEDERATION

* Organic Chemistry Department
Moscow State University of Design and Technology
Malaya Kaluzhskaya street, 1, Moscow 119071
RUSSIAN FEDERATION

okovalchukova@mail.ru

Abstract: - The results of investigations of ecologically and economically efficient ways of chemical transformations of trinitrotoluene into products of civil needs are reviewed. The elaboration of a cheap and ecological way of transformation of nitro-aromatic compounds into non-explosive hydroxy-derivatives and their further chemical transformations are described. New hydroxyimino- and azo compounds and their metal complexes were synthesized and investigated by a set of spectroscopic and theoretical methods. They may be proposed as new effective azo-dyes and azo-pigments with high resistance to physical and chemical treatments and fungicide activity, as well as analytical reagents and extractors of ions of heavy metals from the waste waters.

Key-Words: - TNT; chemical transformation; azo- and hydroxyimino-compounds; synthesis; properties; applications

1 Introduction

Among various technogenic environmental problems, the recycling of explosives removed from ammunition of arms is of a great significance in now days. Blasting or burning methods of utilization are rejected by civilized countries as ecologically and economically barbarous. Major residue of ammunition manufactured until 1960-1970 are 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene (TNB) as a product of an oxidative demethylation of TNT.

As the technology of extraction of TNT from ammunition is effectively developed, the problem of edition of effective, ecologically and economically expedient technology of its transformation into chemical products of civil appointment is of a great significance.

In order to find new civil applications of products of transformation of TNT, new amino-, hydroxyimino- and azo compounds and their metal complexes were synthesized and investigated by a set of spectroscopic and theoretical methods.

2 Problems of transformation of trinitrotoluene into non-explosive compounds

In nowadays, 4 million tons of the ammunition, which is the subject to utilization, is accumulated on our Planet, and 350 thousand tons from them make the explosives (basically trinitrotoluene, TNT). Destruction of the ammunition is regarded as damage at least for two reasons. First, the results of the substantiated work of various sectors of society (scientists, engineers, designers, workers, testers) represent irrevocable losses, which lower and worsen welfare of big groups of the population of the countries and society as a whole. Second, the negative influence of the destruction of the ammunition is connected with violation (deterioration) of ecology of the environment, pollution of the soil, superficial (rivers, lakes, seas) and underground waters, vegetation and air pollution.

The transformation of explosive trinitrotoluene into non-explosive products is based upon reduction of highly energetic nitro-groups into ecologically

safe amino-groups and/or their substitution by hydroxy-groups.

2,4,6-Trihydroxytoluene (methylphloroglucinol, MPG) possesses strong and attractive synthetic potential because of its specific structure.

Unfortunately, until the last decade it practically has not been realized because of small yields of its isolation and, as a result, of its high cost. The ways of transformation of TNT into MPG are presented on the Fig. 1.

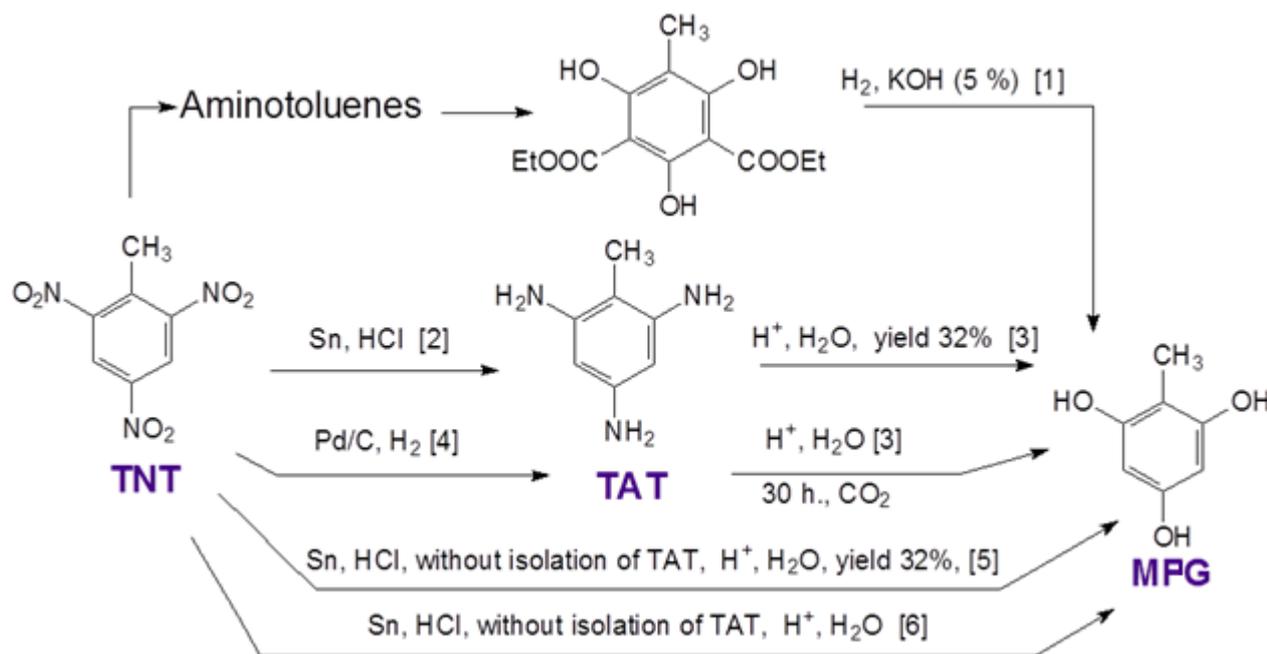
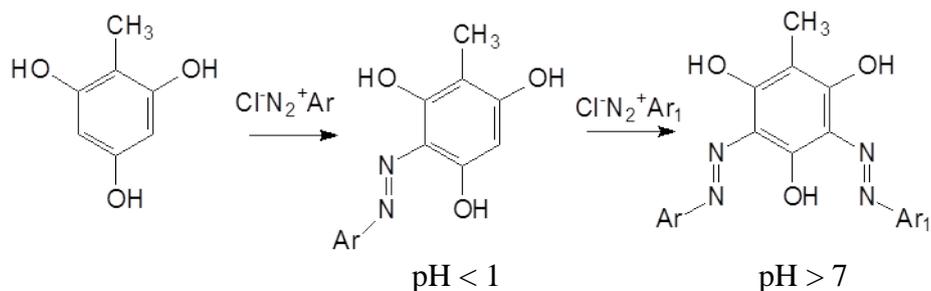


Fig. 1. Methods of transformation of TNT into MPG

Recently, the economically efficient method of isolation of MPG on base of 2,4,6-trinitrotoluene [7,8] was developed. The one pot reaction proceeds in acidic boiling aqueous media in presence of ammonium containing catalysts. The advantages of this method are high yields (more than 75%); high purity of the product (95 – 98% by NMR); possibility to use concentrated solutions; significantly decreased time of the reaction. In addition, it allows avoid corrosion by replacement of chlorides by sulfates, fluorides or other salts.

3 Transformation of MPG into azo dyes and azo pigments

The reactions of azo-coupling of MPG with a large variety of diazonium salts was studied in the temperature interval 0 ÷ 5 °C, in the pH range from 1 to 12. As a result, the methods of synthesis of mono- and diazo-compounds derived from MPG with high yields (70-90 %) were elaborated, and more than 100 new azo-compounds were isolated [9,10]:



All the obtained substances were tested as acid and disperse dyes for wool, polycapromamide and polyester fibres. Majority of them showed good coloristic characteristics with the intensive colors from yellow to blue depending upon substituent in the aryl-radical (Fig. 2).



Fig. 2. Coloristic triangle of azo dyes derived from MFG

It was shown that presence of MFG-fragments in the composition of azo dyes increases their resistance to physical and chemical treatments. Some of them possess high thermo stabilities (m.p. 230 – 360°C) and may be used for dyeing of polymers and wood.

It is well known that adhesion properties of azo dyes is related to their spatial structures. To correlate the spatial structures of the isolated azo-compounds with their coloristic characteristics, quantum-chemical modeling was performed which indicated the preference of the planar azo-tautomer [9].

As the coloristic characteristics of the substances are described by the changes in the electronic absorption spectra, the UV-VIS spectrophotometric titration was performed.

As it is evident from the Fig. 3, the addition of NaOH to the solutions of azo-derivatives of MPG provokes two stepwise equilibrium processes. In the pH interval 6.5 – 8.0 the long-wave band undergoes bathochrome shift to 471.0 nm ($lg\varepsilon = 4.32$), and the short-wave band appears at 264.4 nm ($lg\varepsilon = 3.70$). The further addition of NaOH leads to a strong bathochromic shift of both two bands: 533.3 nm ($lg\varepsilon = 4.12$) and 382.2 nm ($lg\varepsilon = 3.69$). This change in

the spectrum is explained by the transformation of the substance into hydrazo-form with its further dissociation.

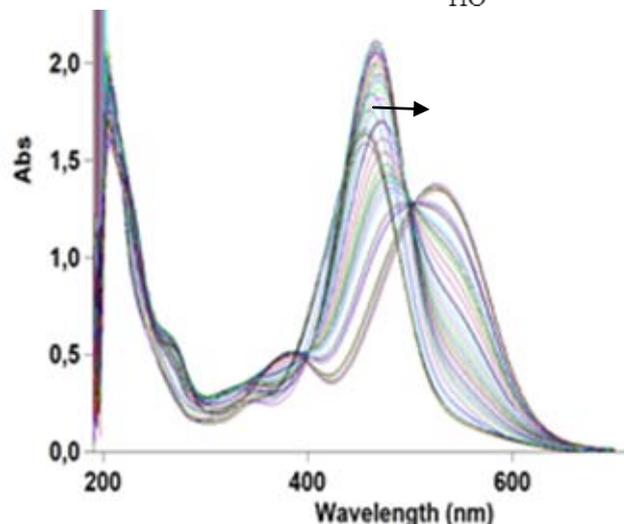
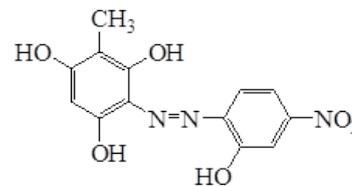


Fig. 3. Change in UV-VIS spectra of the azo-compound derived from MPG after stepwise addition of NaOH

The shift of the long-wave absorption band provokes the change in color of the solution, which depends upon pH, and concentration of the azo-dye (Table 1).

Table 1. The change in color of one of the azo dyes derived from MFG (for the formula see Fig. 3) depending on pH and concentration.

pH	%					
	10	6	4	2	1	0,5
0						
2,5						
4,5						
5						
5,5						
6						
6,5						
7						
7,25						
7,5						
8						
8,5						
10,5						

The change in color from red to violet in the pH range 8 – 8.5 allows proposing the substance as the acid-base indicator.

The calculated pKa values of the MPG azo derivatives lie in the interval from 10.16 ± 0.79 to 8.50 ± 0.61 . This is in a good accordance with the literal data on the acidities of azo-derivatives of MPG and other polyphenols.

The addition of the solutions of metal salts to the solutions of the described azo dyes provokes the same changes in the UV-VIS spectra as ionization of the compounds, i.e. bathochromic shift of the long wave band (see Fig. 3). This correlates with the behavior of traditional azo dyes. The evaporation of solutions provokes formation of varnish-like films of intense colors. The structure of metal complexes was concluded by the correlation of spectral data of the compounds and the theoretical modeling (Fig. 4) [11].

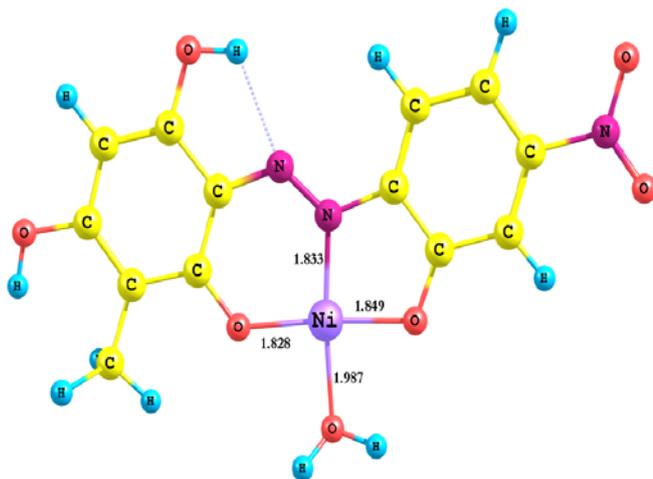


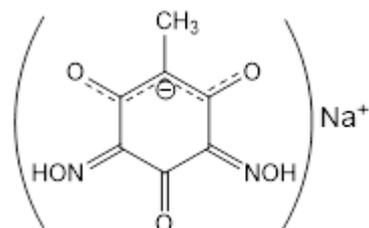
Fig. 4. Geometry optimization of the NiL·H₂O complex (DFT/B3LYP)

The *in vitro* tests showed high fungicide activity of the azo dyes derived from MPG and their metal complexes (*Aspergillus niger*, *Aspergillus flavus*, *Penicillium chrysogenum*, *Ulocladium atrum*, *Chaetomium globosum*). The above-mentioned micromycetes are often present on textile materials and cause both mechanical, and chemical destruction of fibres. The performed tests showed that the majority of the samples have an overwhelming effect on the development of test cultures, and some of them completely suppress growth or sporulation.

The correlation between the complex formation and fungicide ability of the substances was established for variety of samples.

4 Hydroxyimino-derivatives of MPG

Hydroxyimino-derivatives were isolated within the reaction of nitrosation of MPG. The structure was proved by X-Ray analysis as well as with the help of the chemical modeling [12]. As it was shown, the most stable form of the substance is the anionic form of a triketo-dihydroxyimino tautomer:



Dark-red plates of single crystals of the only product of MPG nitrosation in the form of the sodium salt were obtained by recrystallization from ethanolic aqueous solution. Their treatment by a strong mineral acid leads to the precipitation of the neutral form of the organic molecule which electronic spectrum coincide with that of the sodium salt. This fact indicates rather strong acidic properties of the substance. The potentiometric titration curve of the neutral dihydroxyimino-MPG with NaOH (Fig. 5) shows the existence of two equivalent points. The *substance-to-NaOH* mole ratio indicates the dissociation of one proton in the 4 - 7 pH interval. The $pH_{1/2}$ value of the 1st dissociation step is 5.6 ± 0.1 which correlates with the dissociation constant of benzoic acid ($K_a = 6.5 \cdot 10^{-5}$).

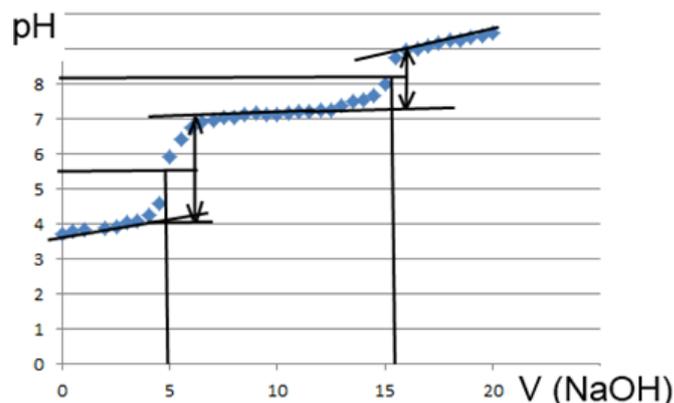


Fig. 5. The potentiometric titration curve of the aqueous solution of the neutral dihydroxyimino-MPG with NaOH

The dissociation of the two oxime protons occurs at once in the pH interval from 7.0 to 9.5 ($pH_{1/2} 8.15 \pm 0.12$). The pKa value correlates with that of aromatic oximes.

Addition of the dihydroxyimino-MPG aqueous solutions to the solutions containing cations of

The introduction of several electron donating fragments in the benzene ring leads to the multiplicity of the ionic and tautomeric equilibria as

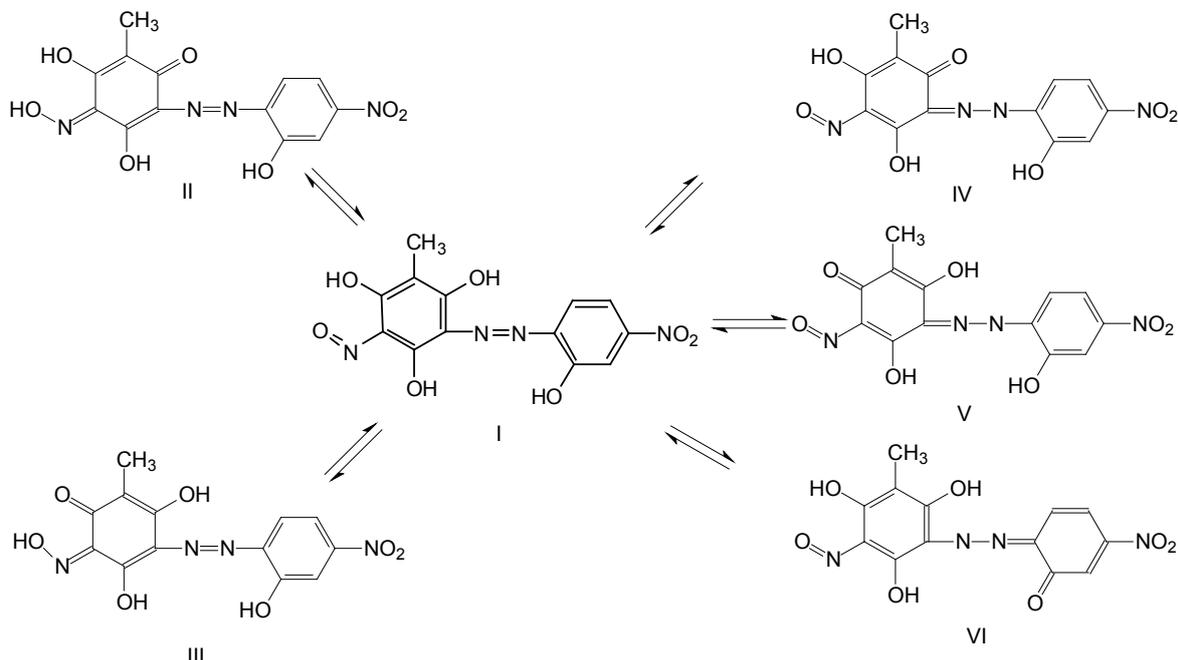


Fig. 8. Some possible tautomeric forms for azo-hydroxyimino derivatives of MPG

To describe the properties of the compounds, it is necessary to detect the dominant forms of the organic species.

The addition of alkalis or solutions of transition metals salts to the solutions of the hydroxyimino-azo derivatives of MPG provokes the same type of the change in the UV-VIS absorption spectra as for the dihydroxyimino-compounds (Fig. 9).

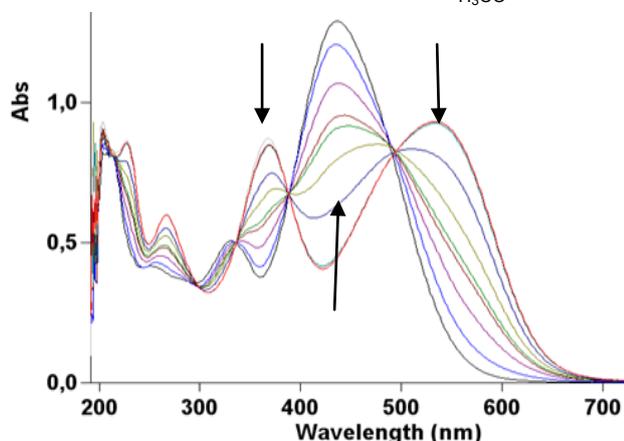
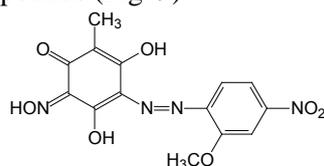


Fig. 9. Changes in the UV-VIS spectra of hydroxyimino-azo derivatives of MPG after stepwise addition of CuCl_2

well as coordination modes in reactions of complex formation (Fig. 8) [15].

This indicates that the substances exist in the solutions in the forms of azo-hydroxyimino tautomers II and III (see Fig. 8). The ability of the tautomer III to be stabilized by an intramolecular H-bond between the neighboring $=\text{NOH}$ and $\text{C}=\text{O}$ groups makes it more preferable. The ionization process involves nitroso-group better than hydroxy-groups [16].

The introduction of hydroxyimino groups to the composition of azo dyes derived from MPG increase their anti-fungal activity and formation constants of their metal complexes.

6 Conclusion

The proposed chemical ways of transformation of the explosive TNT wastes into the products of civil needs (azo-dyes and azo-pigments with high resistance to physical and chemical treatments and fungicide activity, as well as analytical reagents and extractors of ions of heavy metals from the waste waters) are attractive from the ecological and economical points of view. They do not demand expensive reactants, concentrated aggressive media and high temperatures. They aim to prevent the environmental pollution by technogenic wastes. They allow obtaining new materials and compounds

with a set of useful properties. At least, finding a way of converting TNT into civil products would allow the TNT production facilities to be kept up.

Methylphloroglucinol as a possible product of successive TNT conversion is can be used as the starting compound in the production of heat-resistant thermosetting resins; as a component of heat-resistant dips and insulation for electromotors, generators, and transformers; as a component of polyisocyanate compositions with a high polymerization rate; in the fabrication of photosensitive and lithographic plates; in the synthesis of antibacterial and antiviral drugs with a flavone or xanthone structure; etc. However, until now because of its low availability and expensiveness, MPG has not been considered as the starting compound for the above applications.

The technology suggested in the above paper provides a solution to the problem of utilizing expired ammunition in an environmentally friendly and economically efficient way.

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