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Regulation of Oxygen Balance in The Process of Synthesis of Explosives

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Abstract

The role of explosives in the modern world is immeasurable, both in wartime and in peacetime. Accordingly, the optimization of their main blasting characteristics is of great importance, such as, detonation speed, workability, brisance, etc. They include the quantitative ratio of the chemical elements that make up these substances and its influence on the energy and ecology of the explosion, which It is defined by ,,oxygen balance''.

Generally, the elemental composition and ,,architecture'' of the molecules of substances, i.e. chemical structure, are the main determining factors of their physico-chemical characteristics. The same reasoning applies to explosives: basically, these two factors are the determinants of the energy of the explosion.

The article is about the possibilities of approaching zero oxygen balance in the process of synthesis of explosives. Examples of well-known poly nitro aromatic compounds and transformation products synthesized by us from them – CT compounds are discussed, as well as formulas of compounds with zero oxygen balance unknown in the literature and the procedure for their composition. It can be said with convinction that the specificity of organic synthesis and a wide scope of operation allow purposeful creation of explosive substances with zero oxygen balance. The article proposes the possibility of creating two such real methodologies.

Keywords:
explosives, oxidation, oxygen balance, ,,fuel'' elements, endogenous oxygen, CT compounds, nitrates...

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Introduction

Explosion is an exclusive property of a certain group of substances, which is accompanied by the instantaneous release of ,,time-concentrated'' energy. The main attribute of one of the types of this complex physical-chemical process - **chemical explosion**, is the fastest transformation of an **explosive** into gas products with high temperature and pressure, capable of performing certain work...

The elemental composition of explosive molecules and theirs ,,architecture”, that is, **chemical structure**, largely determines the peculiarities of the explosion course and its energy. These molecules usually contain carbon, hydrogen, nitrogen and oxygen atoms. It is established that when blasting, the “fuel” elements - **carbon** and **hydrogen** are oxidized without interference of the atmospheric oxygen, by the “oxidizing element” - the **endogenous oxygen** contained in the explosive molecule. The quantitative ratio of the elements mentioned has the greatest impact on the economic and ecological sides of the explosion processes**. When this ratio is stoichiometric, then the energy of the explosion is maximum, and the ecology of the environment - protected**. At this time, **higher oxides** are obtained from the ,,fuel'' elements - **carbon dioxide** and **water** (CO_2 and H_2O), and nitrogen is released in free form (N_2). None of them are poisonous[3].The criterion for evaluating the above ratio is one of the most important parameters of the explosion - Oxygen Balance[4].

Main Part

Essence of Oxygen Balance

Oxygen Balance (OB) generally is the **sufficient, excess** or **loss** amounts of endogenous oxygen required for complete oxidation of ,,fuel elements'' in explosive molecules. It can be mathematically calculated for explosive of the CcHhNnOo composition by the formula:

$$OB = \frac{\left[o - (2c + \frac{h}{2})\right]\cdot 16}{12c + h + 14n + 16o}\cdot 100\%$$

Where, c, h, n, o are the number of carbon, hydrogen, nitrogen, and oxygen atoms in the explosive molecule. Accordingly, 2c is the number of oxygen atoms in CO_2, h/2 - the same number in H_2O, 16 is the molar mass of atomic oxygen in g/moles. The denominator of the fraction figures the molar mass of explosive in g/mol.

In the stoichiometric content of elements in the explosive molecule, the image in round brackets is equal to the amount of endogenous oxygen. Because of this, the numerator of the fraction, and therefore OB, becomes zero. When the endogenous oxygen is more **(positive OB)** or less **(negative OB)** than the stoichiometric amount, the explosion is accompanied by the release of poisonous gases such as NO_2, NO, N_2O_4, CO, etc.

Only a small species of explosive are found in nature. They are produced by **chemical synthesis.** The vast majority of synthetic explosive are characterized by **highly negative OB** values. Therefore, when used in industry, they try to prepare such **mixture compositions**, the total OB of which will be close to zero. Earlier, we described in quite detail the mathematical methods of calculating OB, both for individual explosives and for mixtures[5].

Currently, we want to ask a question: Is there a possibility that the regulation of OB, its approach to zero, will occur purposefully, not in the mixture explosive compositions, but in concrete, individual explosives, in the process of their synthesis? Let's consider this problem, on the example, using well-known explosive poly nitro aromatic compounds i.e. **PNA compounds,** and synthesized from them ”Charge Transfer Compounds” i.e. **CT compounds.**

PNA compounds

As examples of PNA compounds, we give the well-known explosives: trotyl, picric acid, styphnic acid, hexa nitrobenzene, etc. Let's compare trotyl (TNT) and picric acid (TNP):

3 E.O. Mindeli, “Destruction of rocks”, Moscow, “NEDRA”, 1974, pp. 130-134 (in Russian).

4 B.N. Kutuzov, “Blasting works”, Moscow, “NEDRA”, 1980, pp. 75-80 (in Russian).

5 M. Nadirashvili, S. Khomeriki, N. Chikhradze, A. In other words, G. Ahhh, i.e. Varshanidze” role of endogenous oxygen in explosive substances”,” Mining Journal”, №2 (39), Tbilisi, 2017, PG. 52-59 (in Georgian).

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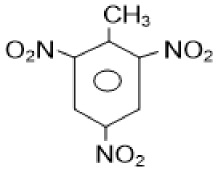
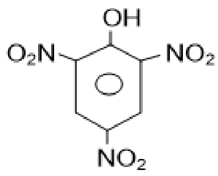


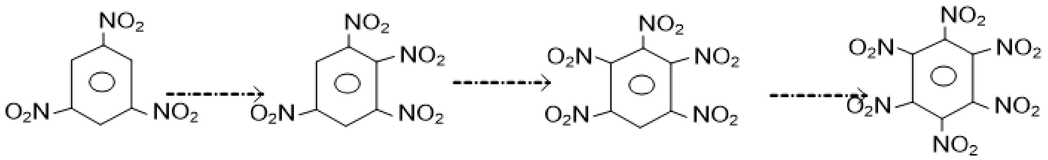
Trotyl (TNT)



Picric acid (TNP)

A fairly high negative OB of TNT (-74,0), in picric acid (-45,4), decreases by about 30 units, which is due to the only difference between the molecules: These are groups with the first carbon atom of the benzene nucleus (C-atoms are attached on the vertices of the hexagon), methyl (CH_3) – in TNT and hydroxyl (OH) – in picric acid. For synthesize of picric acid from TNT, we need to ,,remove” methylene (CH_2) from the methyl group and ,,insert” oxygen (O) instead, i.e., replace CH_2 with O. Only the CH_2 group of TNT requires three endogenous oxygen atoms to oxidize: Carbon - two (C+O_2 CO_2) and two hydrogens - one (H_2 + O H_2O). Picric acid, not only does not need these three oxygen, on the contrary, its molecule has one more oxygen than TNT. Differently, if compare, the picric acid molecule, with TNT, due to the peculiarity of its structure, the last one has a four-oxygen ,,deficiency”, which leads to its rather high negative OB.

Now, consider three rows of other known explosives that show two various **gradational increase** in endogenous oxygen. In the first row, adding each nitro group gives us a **two-oxygen** increase:



I

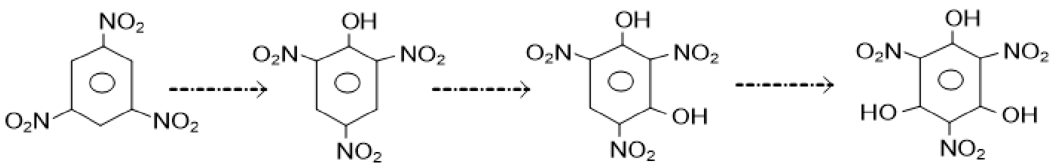
I — **1,3,5-Trinitrobenzene (-56,3)**

II — **1,2,3,5-Tetranitrobenzene (-31,0)**

III — **Pentanitro-Benzene (-15,7)**

IV — **Hexanitro-Benzene (0)**

The second and third rows reflect single-oxygen gradational growth. In I-V-VI-VII, this occurs by adding one hydroxyl (OH) group each, and then, in VII-VIII-IX-IV, hydroxyls are replaced by nitro groups:



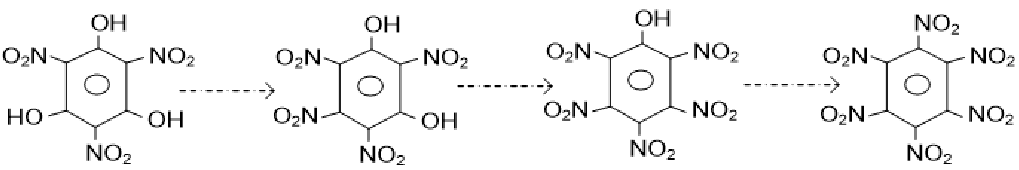
II

I — **1,3,5-trinitro-benzene (-56.3)**

V — **Picric acid, 2,4,6-trinitro-phenol (-45,4)**

VI — **Styphnic acid, 1,3-di-oxy-2,4,6-trinitro-benzene (-36.0)**

VII — **1,3,5-Triox-trinitroben-zene (-27,6)**



VII — **1,3,5-Triox-trinitroben-zene(-27,6)**

VIII — **1,3-dioxy-Tetranitroben-zene (-16,6)**

IX — **Monooxy-pentanitroben-zene (-7,5)**

IV — **Hexanitro-benzene (0)**

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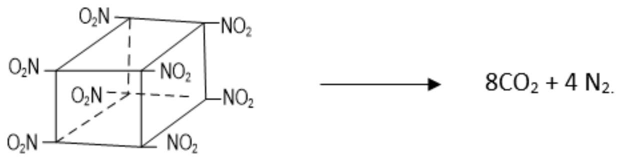
The values of OB are given in parentheses.

The first and third rows end in a hexanitrobenzene with zero OB, which is the strongest and at the same time environmentally pure explosive, as can be seen from its conversion reaction:

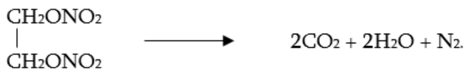
Hexanitrobenzene



Octanitrocubane

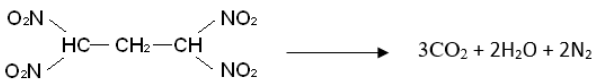
Zero OB has one of the strongest explosive - octanitrocubane, synthesized in the USA at the end of the XX century[6]:

Here are some more examples of explosives with zero OB and their explosive transformations:



Dinitroglycol

Di nitro acetaldehyde



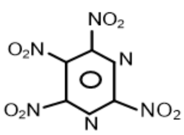
1,1,3,3, - tetranitropropane

None of the five explosive conversion products are poisonous.

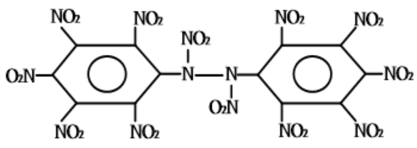
Similar examples give a positive answer to the question asked above. Also, the possibility of purposeful synthesis of new explosives with zero oxygen balance is clearly confirmed, specifically:

A chemist can draw up a molecular formula in which there will be two oxygen atoms for every carbon atom, and only one for a pair of hydrogen atoms. After, is required „only" successful synthesis…

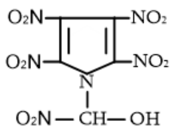
Here are some chemical formulas compiled by the above principle:



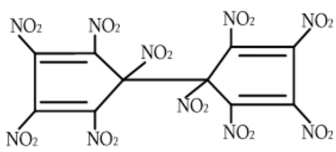
Tetra nitro pyrimidine



Dodeca nitro diphenylhydrazine



N-(nitro oxymethyl-
Tetra nitropyrol



Deca nitro dycyclopentadienyl

6 A.M. Astakhov, R.S. Stepanov and A.Yu. Babushkin, On the detonation parameters of octanitrocubane, Combustion, Explosion and Shock Waves, Volume 34, pages 85-87(1998).

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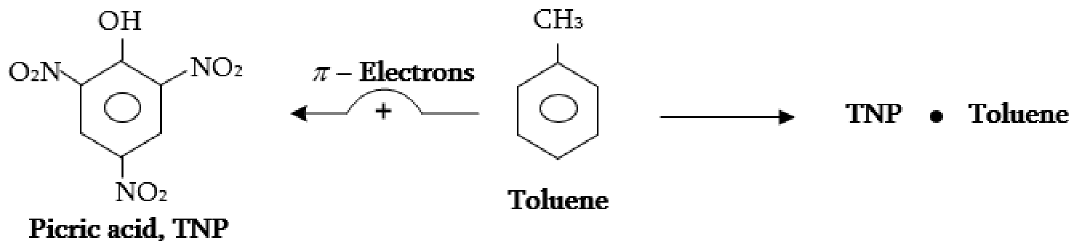
If we can synthesize these and other substances of similar structure, due to the „ordered" ratio of C, H, O, N-elements, we will get high-energy and ecologically pure explosives with zero OB...

CT compounds

Regulation of oxygen balance, "adjusting" it to zero, is relatively easy when synthesizing CT compounds from PNA compounds. The mechanism of this process is as follows: the presence of nitro groups in the molecule of PNA compounds impoverishes the π-electronic system of the aromatic nucleus and gives these substances a strong **electron-acceptor** property. Consequently, their molecules develop the ability to push the electrons of **electron-donor** molecules towards themselves. Electrostatic attraction appears, resulting in bimolecular chemical structures - CT compounds with molar ratio of components 1:1[7]. This, on the example of picric acid and toluene, can be expressed as follows:

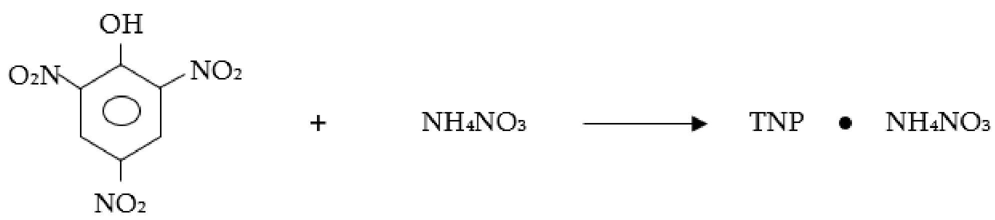


As for the formula's „morphology", it is similar in appearance to the formula of some other chemical compounds. Such are, double salts, for example, silvinite - KCl • NaCl, a compound of electron-donor ammonia with electron-acceptor boron tri fluoride H_3N • BF_3.

The synthesis reactions of CT compounds take place under rather "soft" conditions, with a high yield of practically pure products of the reaction. These substances usually retain a fairly strong explosive ability[8], and often, even surpass the initial reagents - PNA compounds in this characteristic[9].

From picric acid and TNT, more than 20 CT compounds have been synthesized by US. Organic as well as mineral compounds are used as electron-donor „visavi " substances. Of the first, toluene turned out to be the most effective. The testing of the corresponding CT compounds (TNP • Toluene and TNT • Toluene) on the explosion is **complete**, accompanied by maximum fragmentation of the steel tube with explosive.

As for mineral compounds (NH_4NO_3, $NaNO_3$, $K_2Cr_2O_7$, KNO_3, etc.), for synthesized CT compounds, the results of theirs explosion are similar. Give us a synthesis reaction of one of them:



Picric acid, TNP

The so-called „ Trautzl sampling " proved that the **working capacity (fugacity)** of this CT compound is 39% higher than the same one of picric acid.

The use of aromatic compounds with high negative OB (such as benzene, toluene, naphthalene) as electron-donor „visavi" substances in CT compounds will obviously not balance the strongly negative OB of electron-acceptor PNA compounds towards zero. Therefore, for this purpose, it is better to use oxygen-containing mineral salts with positive OB, such as nitrates, chlorates, sulfates, phosphates...

7 A.N. Nesmeyanov, N.A. Nesmeyanov, The beginnings of organic chemistry. Book II, ed.„Chemistry', Moscow, 1970. pp.94, 120-121 (in Russian).

8 M. Nadirashvili, A. Apriashvili, G. beinashvili, T. Iashvili "Synthesis and research of "Molecular Compounds" from some explosives „The Development of Mining and Geology is the Precondition for the Revival of Economy", 6th International Scientific-Practical Conference on Up-to-date Problems of Mining and Geology BOOK OF ABSTRACTS, p.70, Tbilisi, 2020.

9 M. Nadirashvili, T. Iashvili, G. Tkhelidze. Synthesis of new explosive „molecular compounds" and determination of workability, 8th International Scientific –Practical Conference on Up-to-date Problems of Mining and Geology, p. 104, Tbilisi 2022.

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Based on what has been said, we give OB-s of six inorganic nitrates and five well-known explosive PNA compounds (OB-s of CT compounds are given above in rows I-III):

Inorganic nitrates

NH_4NO_3	$NaNO_3$	KNO_3	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$Ba(NO_3)_2$
+20,0	+47,0	+39,6	+54,1	+48,1	+30,7

PNA compounds

TNT	Picric acid	Styphnic acid	Trinitrofloroglucin	Hexanitrobenzene
-74,0	-45,4	-36,0	-27,6	0

As already is mentioned, the regulation of oxygen balance is relatively easy in the synthesis of CT compounds from PNA compounds. **Both components of these bimolecular structures, must be chosen in such a way that the negative OB of one and the positive OB of the other, will be as close to each other as possible in absolute values.** OB of synthesized CT compounds, will be received by the algebraic sum of the OB-s of the components. For example, the oxygen balances of CT compounds synthesized from picric acid and sodium nitrate, picric acid and calcium nitrate, 1,3,5-trinitrobenzene and magnesium nitrate, tetra nitrobenzene and barium nitrate are, respectively: +1,6; +2,7; -2,2; and -0,3:

TNP • $NaNO_3$
OB = + 1,6

TNP • $Ca(NO_3)_2$
OB = + 2,7

1,3,5-Tri nitrobenzene • $Mg(NO_3)_2$

1,2,3,5-Tetra nitrobenzene • $Ba(NO_3)_2$
OB = -0,3

When testing on explosion, of all possible variants of CT compounds, the majority exhibit considerable power. The gases released of them, during the explosion of the last four CT compounds will necessarily turn out to be environmentally friendly.

Conclusion

Thus, our targeted synthesis of explosive PNA compounds, as well as CT compounds from them, is to offer two real methods of obtaining explosives with OB-s close to zero. Obviously, in the synthetic chemistry diversity, other methods, also, can be found...

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