Explosive compounds and their implication in accidents and terrorist attacks

Abstract

Although most explosives detection equipment has been focused on explosives based on nitro- compounds because of their using in terrorist attacks interest in the chlorates and perchlorates as a base for explosives dates back to the 18^{th} century when Berthollet attempted to make a powerful gunpowder. Although the main focus has been put for many years for explosives within the group of black powder and mixtures alike it on nitrate as the bearer of oxygen that is required to trigger the explosive decomposition [1] Later it began to study also the possibility of replacing nitrate by other substances rich in oxygen, which would be also useful for the manufacture of explosives for civil or military use. This group of compounds includes, among others, chlorates, perchlorates, and esthers of hypochlorous, chloric, and perchloric acid. Today, unfortunately, it is not necessary to consider these compounds only in terms of official military or civilian uses, but also in the context of increasing frequency of terrorist attacks the question of the abuse possibility of mentioned salts and esters to such dangerous activities is pushed to the fore. The article deals with the production, physical - chemical properties and the possibility of misuse for terrorist purposes.

Introduction

The destabilization of the security environment not only in Europe but also worldwide has caused an increase in manifestations of aggressive enforcement of its own ideas.

Most of exposed manifestation are the terrorist attacks carried out for the purpose of causing as much harm to civilians. The most common way how to implement such actions has the common denominator and that is use of explosives. Despite the relatively sophisticated regulatory system are still easily accessible thanks to materials that do not belong to the primary inspection items. Such materials include the fireworks [8,9].

The majority of the terrorist attacks are done with homemade bombs. The first example is the attack attempt of Times Square in 2010. A car was discovered, filled to the brim with tanks of propane, two jugs of gasoline, dozens of M-88 firecrakers and a metal gun case holding 45kg of fertilizer (ammonium nitrate). By chance, the bomb did not explode because in a crowded place as Times Square, the consequences could have been atrocious. Unfortunately, in the second example, two homemade bombs exploded. The double terrorist attack of the marathon of Boston occured in 2013 at the finish line of the race. The pressure cooker bombs were filled with explosives nails and other improvised shrapnel (ball bearings). These eplosions killed three people and injured 264 others.

Many unfortunate incidents involving the detonation of explosives based on the presence of chlorates and perchlorates are the proof that these substances combined with some other substances are very dangerous and can result in huge material damage, loss of life or damaged health of many people who come into contact with them at explosion. Some of industrial accidents with the presents of not common explosives are listed in table 1.

Table 1: List of industrial accidents

Date	Localisation	Cause	Consequences
4 May 1988	Henderson, USA	Explosion of 4500 tons of ammonium perchlorate	2 deaths, 372 injured destruction of a part of the city
30 July 2004	Ghislenghien, Belgium	Explosion of a high natural gas pressure pipeline	24 deaths
1 January 2008	Gërdec, Albania	Explosion of an ex-military ammunition depot full of obsolete ammunation	29 deaths, destruction of hundreds of houses
9 September 2010	San Bruno, USA	Explosion of a high natural gas pressure pipeline	8 deaths, Shockwave as magnitude 1.1 earthquake
11 July 2011	Mari, Ciprus	Seld detonation of 98 containers of explosives stored for almost three years in the sun	13 deaths, Severely damaged hundreds of nearby buildings
12 August 2015	Tianjin, China	Explosion of an overheated container of dry nitrocellulose	Several explosions, 173 deaths, The first one with a magnitude of 2.3 earthquake, Severely damaged 304 buildings
11 August 2016	Dangyang, China	Explosion of a coal-fired power plant	22 deaths,

An explosion is a rapid expansion of matter into a much greater volume. The expansion is such that the energy is transferred almost completely into mass motion, and this is accompanied by loud noise and a great deal of heat. A detonation is a very special type of explosion. It is a rapid chemical reaction, initiated by the heat accompanying a shock compression which liberates sufficient energy, before any expansion occurs, to sustain the shock wave. To achieve maximum volume change, gas formation, and heat release, explosives are designed to be dense, to have high oxygen content, and to have positive heats of formation. [2]

Solid oxidant is the main carrier of oxygen that needed for combustion. Its thermal decomposition releases oxygen, which is used during combustion. Therefore, as such solid oxidants all substances can be used which contain in their molecules sufficient number of oxygen atoms and are capable of giving of free oxygen after decomposition. Peroxides, nitrates, chlorates and perchlorates can be such substances. The most commonly used solid oxidizer is sodium nitrate $NaNO_3$, potassium chlorate $KClO_3$, potassium perchlorate $KClO_4$ and ammonium perchlorate $NHClO_4$.

Properties of inorganic chlorates and perchlorates explosives

Among the oxides of chlorine, perchlorate is the most stable, but all are energetic and produce toxic fumes. Only chloric and perchloric acids can be isolated. Their reactivity follows that of tha salts. They violently react with combustibles, chloric acid being the more reactive.

ClO^-	<	ClO_2^-	<	ClO_3^-	<	ClO_4^-
hypochlorite		chlorite		chlorate		perchlorate

Among the oxidizers, chlorates ClO_3^- , are especially hazardous to handle. They decompose exothermically and are sensitive to heat, impact and friction. Chlorate explosives with aromatic nitro compounds have higher detonation velocities and are more brisant than those in which the carbonaceous material is merely combustible.

Mixtures of chlorate and fuel will spontaneously ignite with the addition of a drop of concentrated sulfuric acid. Spontaneous ignition or explosion can occur when alkali chlorates are combined with very reactive fuels such e.g. posphorus, sulfur, powdered arsenic, selenium, or with moist fuels. [2]

When discussing thermochemical point of view it is possible to observe the heat release of particular reactions of chlorates and perchlorates in the following chemical equations. It is clearly visible the exothermic and endothermic character of particular reactions.

$$2\ KClO_3 \leftrightarrow 2KCl + 3O_2 + 23{,}8\ cal$$

$$KClO_4 \leftrightarrow KCl + 2O_2 - 7{,}5\ cal$$

$$4NH_4CLO_4 \leftrightarrow 4HCl + 2N_2 + 5O_2 + 6H_2O + 30{,}8\ cal$$

Then it can be written next reaction how it is possible to get perchlorate from chlorate

$$2KClO_3 + O_2 \leftrightarrow 2KClO_4 + 34\ cal$$

$$4KClO_3 \leftrightarrow KCl + 3KClO_4 + 51{,}5\ cal$$

and one more thing is clear and that is exothermic decomposition of the chlorate. Oxygen in the chlorate is bounded just by weaker bound than e.g. in the nitre and that is why they are more labile.

Perchlorates have much stronger bonds and as a reaction of potassium chlorate to perchlorate with oxygen is exothermic, perchlorate is poorer in energy terms, although it is richer in the number of oxygen atoms. This results in the fact that it is less sensitive to impact. [1] Within explosives among the most commonly used chlorates and perchlorates includes potassium chlorate, sodium chlorate, potassium perchlorate, sodium perchlorate, ammonium perchlorate.

Potassium chlorate $KClO_3$

Potassium chlorate is also known as Bertholett´s salt, it is a white, crystalline, non-hygroscopic, toxic and environmentally harmful substance, which is relatively stable in air. However, when potassium chlorate is quickly overheated, it explodes. It is used for the manufacture of pyrotechnic articles and matches. It is industrially produced by electrolysis of potassium chloride.

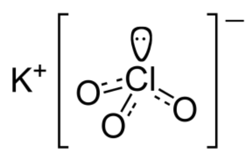

Figure - 1 Potassium chlorate structure [3]

Sodium chlorate $NaClO_3$

It is also a white, crystalline, toxic substance that is more hygroscopic than potassium chlorate. It is produced electrolytically, too, but for the decomposition sodium chloride is used.

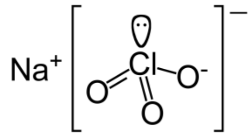

Figure – 2 Sodium chlorate structure [3]

Potassium perchlorate $KClO_4$

It is a colorless crystalline compound, slightly soluble in water, most often used as an oxidant in fireworks, detonators and sparklers. From the above mentioned equation it can be seen that potassium perchlorate is endothermic agent that holds oxygen quite strongly. From the thermochemical point of view it is therefore appropriate to mix potassium perchlorate e.g. with chlorate explosives, if it is necessary to achieve greater sensitivity.

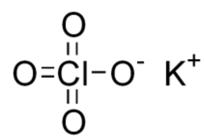

Figure – 3 Potassium perchlorate structure [3]

Sodium perchlorate $NaClO_4$

Sodium perchlorate is a white, crystalline, non-hygroscopic substance. It has the highest solubility in solvents such as water and ethanol within all the perchlorates. It serves as the precursor of many other perchlorates, in the area of explosives particular for the production of potassium perchlorate $KClO_4$ and ammonium NH_4ClO_4.

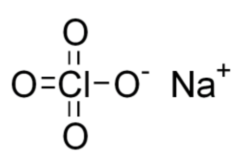

Figure - 4 Sodium perchlorate structure [3]

Ammonium perchlorate NH_4ClO_4

It is a white, crystalline, slightly hygroscopic substance, which is very little soluble in water. It is toxic to the human thyroid gland, to which it gradually causes loss of activity. E.g. in comparison to ammonium nitrate, which is used in explosives for the same purposes, the ammonium perchlorate is more sensitive and has also hogher efficiency. It serves as an ideal oxidizer for the rocket fuels. The main disadvantages are high exponent of burning and risk of pulsation during the engine operation, that may lead to an accident or explosion. It is not advisable and appropriate to combine it with nitrates, although it could appear that this is a perfect mix to achieve coloured flames. The reason is that there is a double exchange between ammonium perchlorate and particular nitrate competent at which it is produced highly hygroscopi ammonium nitrate and perchlorate of the particular cation, which may be even more hygroscopic. It helps and speeds up the degradation of the solid fuel. [4]

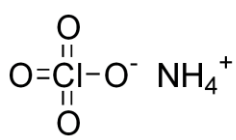

Figure – 5 Ammonium perchlorate [5]

Organic chlorates and perchlorates explosives

There are many instances of chlorate and perchlorate compounds exploding in the literature, including instances in which metal perchlorates or perchlorate complexes decomposed violently. Churchill [6] singles out tropylium perchlorate, 2 – dimethylaminomethylene – 1,3 – bis (dimethylimmonio) propane perchlorate, dipyridinesilver perchlorate and ferrocenium perchlorate as organic perchlorate compounds of potential hazard. There were studies some of the organic chlorates and perchlorates from the point of view of thermodynamics and thermochemistry. For example, there were studied isomers of methyl chlorate and concluded that O – bonded isomer, $H_3C - O - ClO_2$, was the most stable isomer, almost 105 kJ/mol lower in energy than the Cl – bonded isomer, $H_3C - ClO_3$, with $H_3C - O - O - Cl$ and $H_3C - O - O - O - Cl$ isomers in between these two etremes. [7]

Although there have been studied e.g. esters of hypochlorous, chloric and perchloric acid and it was found that they have explosive properties, for practical use in the area of explosives they are not suitable because they are very sensitive to friction and impact. This group includes e.g. ethyl and methylhypochlorates. For example methylperchlorate and ethylperchlorate have similar properties. Ethylperchlorate explodes already when it is poured from vessel to vessel. Explosive decomposition of methylperchlorate can be seen according to equation

$$CH_3ClO_4 \rightarrow CO_2 + H_2O + HCl + O_2 + 1529\ kcal/kg$$

Other chlorate explosives include, for example hydrazine chlorate, ethylenediamine chlorate, hydrazine perchlorate, methylamine perchlorate, guanidine perchlorate, aromatic amine perchlorate and heterocyclic bases perchlorates.

Hydrazine chlorate ($NH_2N^+H_3ClO_3^-$) violently explodes at 80 °C, while hydrazine perchlorate ($NH_2N^+H_3ClO_4^-$) is very sensitive to impact. Its monohydrate is more stable and thus more appropriate in this respect. Ethylenediamine chlorate (NH_2-CH_2-CH_2-$N^+H_3ClO_3^-$) is equally sensitive to impact that predetermines its unsuitability for practical usage.

Within organic chlorates and perchlorates guanidine perchlorate has considerable advantages, due to its stability, non-hygroscopicity and relatively small sensitivity to impact. Researches have shown that the presence of nitro group there in an aromatic core considerably increases sensitivity of perchlorates to shocks and simultaneously increases their strength [8]. Within the heterocyclic bases perchlorates pyridine perchlorate has been the most studied as it has the most interesting features.

Conclusion

Inorganic chlorates and perchlorates are quite well known for their oxidizing properties but organic chlorates and perchlorates has not been explored as appropriate substances for explosives. Those of them which have been studied are very sensitive for the bump and the most of them were never used. Their production is easy and the effects thanks to large is significant.

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