

HOME

1,2,3-TRIAZOLES

1,2,4-TRIAZOLES

BASIC EXPLOSIVE

DADNE

DIAZO PRIMARIES

DPT

FURAZAN

NHN

NITROALKANES

NITROCUBANE

NITROGUANIDINE

NITROLIC ACIDS

**PERCHLORATES**

PYRAZOLE

TETRAZENE

TETRAZOLE

TRINITROMETHANE

SITEMAP

## perchlorates

Perchlorate esters are very unstable and dangerously sensitive to detonation. Even extremely small quantities are extremely brissant. When the perchlorate group is not in anionic form and does not have an extra electron resonating around the oxygen atoms, it loses much stability. As such, extreme caution and safety measures should be used.

A container of organic perchlorate ester, should never be turned to its side. This can wet the area around the lid so that when the lid is forcefully removed, there is a danger of friction that can cause detonation.

If working with perchlorate esters, use only small amounts at any one time, preferably use a test tube holder with rubber gripping to securely hold the tube. It would be a good idea use plastic containers and test tubes to handle the the compound right after it is made. Of course, during the actual synthesis a glass beaker might be required to resist the concentrated perchloric acid, but if possible, teflon be used to avoid scrapnel in case of an accident. There do exist plastic test tube holders. In the event that the compound was accidently detonated, this would prevent shredded bits of the metal tongs from being imparted into your body, but most likely if there was an accident it would be because the test tube fell out from the tongs, and so using a plastic test tube holder may be somewhat unnecessary. The test tube holder puts distance between the compound and your hands. Even a small ammount of distance offers much protection in case of accidental detonation. Make sure you have textured rubber gripping (you could superglue a piece of rubber onto the tongs); having a holder without good grip greatly increases the chance that it could slip out and fall to the floor, causing detonation. While the chance of accidental detonation may be greater than just using unprotected hands, it is much preferable to have an increased risk of detonation, rather than risk direct injury to a hand in the event of an accident. You should put a plush carpet mat or rug around the floor, in case of accidental dropping of the tube, provided it does not create a possibility of slipping on the mat. Always wear protective goggles around dangerously sensitive compounds, preferably thick plastic. If it goes off, it could launch fast moving bits of whatever container it was in toward your eyes. While all this may seem like a lot of unnecessary trouble, it should be mentioned that perchlorate esters are far more sensitive than nitroglycerin, and may go off with little provocation, or seemingly no reason at all. Experienced researchers have suffered irreversible injury, despite taking extreme safety measures and using what they thought was the utmost caution. An accident could cause severe personal injury, and all the trouble is worth mitigating the risk of potential injuries.

It is advised not to store perchlorate esters, especially for a prolonged length of time, as they can undergo spontaneous detonation. If they are stored, however, the compound should be highly diluted into a solvent, such as acetone or nitromethane. No more than 1g of ethyl perchlorate should be stored in any one tube, and if multiple tubes are present, they should be separated by at least 20cm with plastic separation between the tubes. It is advisable to store test tubes surrounded by foam to protect it from the possibility of accidental impact. The outside packaging should be clearly marked with the danger, in case a person unfamiliar with the compound happens to find it. Refrigeration could potentially help with stability, but the danger of freezing, and the subsequent thawing, is almost assuredly a guarantee of detonation. If a situation arises that the perchlorate ester has been stored of over sixty days, full safety precautions should be taken when removing it, and it should be assumed that it could detonate from the slightest movement at any time. The packaging should not be opened, and the whole thing should be remotely detonated in an appropriate area. Perchlorate esters become significantly more sensitive after time, far more so than even the extreme sensitivity they display when first prepared. Never open by hand or remove the stopper from a container or tube of perchlorate ester, even if diluted in solvent, that has been stored for more than two days.

While Ethyl Perchlorate is extremely sensitive, Methyl Perchlorate is virtually touch-sensitive, and as such unstorable in the pure or highly concentrated form. Trying to separate Methyl Perchlorate from its protective solvent is all but guaranteed to result in explosion. Perchlorate Esters slowly hydrolyze with water. Whereas ethyl perchlorate is stable under distilled water for 1-2 days, methyl perchlorate reacts within under an hour.

Another dangerous aspect of alkyl ether perchlorates, not commonly known of, and overshadowed by the sensitive explosive nature of the compounds, is *extreme toxicity*. **Methyl perchlorate is an alkylating agent, the vapors should be assumed to be deadly**. **Exposures that can lead to death can potentially occur prior to development of any warning signs**. Symptoms would appear within 4 to 6 hours after exposure, but could take up to 20 hours to become apparent. If the oil comes in contact with skin, assuming spontaneous detonation does not occur, severe blisters will quickly develop, with delayed secondary toxicity that may be fatal. However, a few amateur researchers have actually tasted drop sized quantities without ill effect (it is highly recommended that this not be attempted), likely owing to the fast hydrolysis of the ester with saliva. The ester has a very pleasant odour and a sweet taste that changes to a burning taste analogous to cinnamon.

There are at least five different routes to prepare Alkyl Perchlorates.

"Iodine(I) perchlorate can be made by reaction of I with silver perchlorate in a benzene solution:

12 + AgClO4 --> IClO4 + AgI; Iodine(III) perchlorate is obtained by reaction of the same substances in ether at -85C; 2I2 + 3AgClO4 --> I(ClO4)3 + 3AgI." Iodine (I) compounds can be stabilized by Lewis bases, such as pyridine, which forms [I Py2][ClO4]. "Concise encyclopedia chemistry" by Mary Eagleson. If the IClO4 is prepared in the solvent with an alkane present, such as dissolved propane, alkane perchlorates will be formed, the intermediate IClO4 attacking the hydrocarbon.

"The procedure involves addition of a secondary alcohol or unbranched olefin to a well-stirred emulsion of perchlorate acid, sulfuric acid, and an inert hydrocarbon or halocarbon. The acid reagent can be prepared by combining 70% perchloric acid, 96% sulfuric acid, and oleum, or by dissolving lithium perchlorate in 96% sulfuric acid. The formation of...alkyl perchlorates is...rapid and virtually quantitative. The ester products are found in the organic layer... the use of nonreactive organic <solvent> in combination with the <acids>...give either alkyl hydrogen sulfate or alkyl perchlorate. The alkyl perchlorate, being covalent in nature, moves quickly to the organic layer, where it is largely protected from further decomposition. The alkyl hydrogen sulfate remains in the acid layer until futher reaction produces alkyl perchlorate. However, prolonged <standing> of the emulsion leads to slow decomposition of the perchlorate, giving <undesired> products <typical of the reaction between> alcohols or olefins to sulfuric acid" The Preparation of sec-Alkyl Perchlorates in Strong Acid, J. Org. Chem. Vol. 36, #12, 1971, David M. Hoffman.

When ether perchlorates are being neutralized from their concentrated acid solution, explosion will result from straight addition of water. First, the solution must be diluted with 85% perchloric acid, and then successively diluted with ever more less concentrated solutions of perchloric acid (usually in four separate stages), until finally the solution is able to be mixed with a solution of bicarbonate.

Perhaps the most certain way for the researcher to meet with a swift demise would be the reaction of dissolved diazomethane with concentrated perchloric acid. <http://www.cdodgyd.heliohost.org/perchloric/ms5.jpg>

The reason for the run-away reaction is that over 70% concentrated HClO4 is a strong oxidizer, attacking the alcohol. If I can suggest, you might start with 65% perchloric acid in the Pentaerythritol, then very slowly drop-wise, while constantly stirring, add the more concentrated HClO4. This will avoid any significant ammount of perchloric acid from existing in the very concentrated, and thus oxidizing, form. Unfortunately there are not too many solvents that would be inert enough in this situation, to dilute the dangerous reactants. Possibly ethylamine perchlorate (the nitrate of ethylamine is an ionic liquid). Interestingly, 70% perchloric acid will not even oxidize hydrogen iodide! Neither will it be reduced by zinc. But 80% perchloric acid will slowly attack even the relatively inert benzene.

You might see <http://www.sciencemadness.org/talk/viewthread.php?tid=12475> , where

which can be used to turn Pentaerythritol into the associated tetrabromide, with the obvious appropriate modifications to the reaction.

Then react with a perchlorate that is soluble in some solvent without O-H bonds. For example, anhydrous silver perchlorate is soluble in benzene or toluene, the AgBr will precipitate. The product of the reaction between solid silver perchlorate and methyl iodide "explodes violently when struck" [M. F. Radies and T. Iredale, *J. Phys. Chem.*, **48**, 224 (1944)]. Handle the silver perchlorate very carefully, since it, too, detonates with disturbing frequency when struck or jarred. The reaction is rather slow. Assuming 0.7 M CH<sub>3</sub>I and 0.5 M AgClO<sub>4</sub> concentrations, at standard temperature, it is calculated that it will take forty-five hours to convert 98% of the silver perchlorate to methyl perchlorate. Note that anhydrous silver perchlorate cannot be made by heating the hydrate.

If you make the tetra iodide, instead, it can simply react with crushed solid sodium perchlorate added into (it will not dissolve) pure acetone. The sodium iodide formed will then be soluble in the acetone. This reaction requires constant disturbance to continually mix up the powder in the liquid, and again, the reaction will take much time. Fortunately the perchlorate ester will be safely diluted in the acetone.

### Iodomethane form Methanol

combine potassium iodide (66.4g, 400mmol), methanol (120ml, 3mol) and 85% phosphoric acid (175ml, 3mol) in a round bottom flask and optionally fill with an inert gas, such as carbon dioxide, to displace any air. Perform a simple distillation, slowly over a period of approximately 3 hours (condensor at -5°C). A clear product with a boiling point of 55-60°C distills over when the reaction mixture reached 90-100°C. - the potassium iodide was entirely dissolved and the reaction mixture was red. Continue heating until the distillate temperature rises to 70°C, at which point the reaction should be stopped. Dilute the distillate with 30ml of cold water and transfer it to a separatory funnel. This may optionally be washed with sodium thiosulfate and/or sodium bisulfite to remove free iodine from the product. Remove the lower layer and dry it with anhydrous calcium chloride. A small amount of copper may be added to help stabilize the product for storage, helping to absorb iodine resulting from spontaneous decomposition. As with other alkyl halides, iodomethane should be stored in the dark.

Phosphoric acid was employed to produce Hydrogen Iodide from Sodium Iodide. Sulfuric acid should be avoided in the preparation of hydrogen iodide because it can oxidize the iodide or bromide ion. "The hydrogen halide may be prepared in situ from its salt and a strong acid." Organic Syntheses, Coll. Vol. 4, p.323 (1963); Vol. 31, p.31 (1951).

## Amine Perchlorate Salts

“Organic perchlorates, in which the oxidant is already present in the same molecule, are in general much more violent in their explosive action than mechanical mixes in which the organic material and oxygen carrier are present as separate solid phases. Manuelli and Bernardini patented the use of perchlorates of biguanide and of guanidine for use as explosives, while Rintoul and Beckett covered the use of dicyanodiamine perchlorate as a blasting explosive. The compound is stated to have an explosive force equal to TNT, but to be insensitive to shock. When slowly heated, it begins to melt with slight decomposition at around 200C, completely melting at 300C, and finally exploding at 378C. It is relatively soluble in water, but less hygroscopic than potassium nitrate.

The perchlorates of aniline, phenylenediamine, aminoazobenzene, pyridine, and quinoline are supposedly suitable for use as explosives. patented methylaniline perchlorates, all of which are stated to be stable, and substantially insensitive to moisture, with the exception of (CH3)2NH2(ClO4). (Lungsgaard and Herbst)

The ammonium and hydrazine compounds of several bivalent metals have been investigated as possible initiating explosives for use in detonators. It was found that these compounds had explosive properties between primary, such as fulminate of mercury, and booster explosives,such as tetranitromethylalane. The chlorate salts were found to be deliquescent and to hydrolyze rapidly. They are much more sensitive than the corresponding perchlorate salts. (Friederich and Vervoorst)

Methylhydrazine perchlorate behaves as a high explosive, having good stability and low sensitivity to shock. Up to ten percent aluminum powder may be also be added. An explosive has been prepared from ethylenediamine perchlorate, by forming an addition compound with picric acid or other polynitro aromatic body containing hydroxyl groups. (Vogl) Such explosives have high detonating velocities, stated to be suitable for use in booster charges.”

CHAPTER: PERCHLORATES IN EXPLOSIVES AND PROPELLANTS p138, 139
"Perchlorates: Their Properties, Manufacture And Uses"

**Pyridineperchlorate** has a lead block rating of 95% TNT and is about as sensitive as PETN. It has a low solubility in ethanol so the salt may be precipitated from a water solution with ethanol.

Encyclopedia of explosives and related items, Vol. 9, PATR 2700, Seymour M. Kaye, article by Dr. W. Klöhn

This is in contrast to some of the more energetic perchlorates (ethylenediamine/phenylenediamine) which tend to be soluble in everything and hygroscopic so often not possible to extract and dry.

Amine perchlorates probably very slowly degrade after many years in storage.

### Preparation of Urea Perchlorate

606g of urea were added to 1040g of 35% hydrochloric acid and dissolved with stirring. Next, 1405 g of sodium perchlorate was added and the mixture stirred vigorously for ten minutes at 40degC. The mixture was then colled to 20degC. The sodium chlorides which precipitated was separated by filtration and discarded. The filtrate now contained about 65% urea perchlorate, still contaminated with remaining sodium chloride. Under reduced pressure (and keeping the temperature below 80degC) some of the water was boiled out to concentrate the solution. While still hot, the solution was filtered to remove the remaining sodium chloride, the crystals of which collected in the filter were again discarded. This last procedure was repeated again, the solution passing through the filter containing urea perchlorate, with almost all of the sodium chloride removed.

A mix of urea perchlorate (70%) and nitromethane (30%) has a detonation velocity of about 7070 m/sec, and a drop height sensitivity of 60cm

## Kommentare