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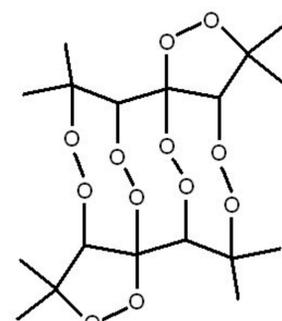
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Diphoronepentaperoxide (DPPP)

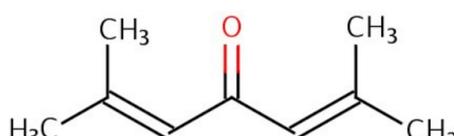


DPPP

This site tries to avoid organic peroxides because of their higher sensitivities, but DPPP is of interest because of lack of knowledge about the chemistry of its formation, as well as a debate about whether it even actually exists. See the attachment at the bottom of the page for more pictures. The exact molecular structure of DPPP is not known, it is likely that there are actually six peroxide groups.

Diphoronepentaperoxide has a formula of C₁₈H₂₆O₁₂. It is significantly more powerful than acetone peroxide. The patent says that it has a detonation velocity of 9 km/sec, but this should be viewed with some skepticism. Amateur experimenters have generally confirmed that DPPP seems to be more powerful than acetone peroxide. DPPP generates only a small amount of heat when it detonates. The temperature of the explosion is only around 200 degC. This is consistent with other organic peroxides being regarded as an entropic explosives, meaning most of the force of the explosion is due to formation of gaseous products rather than release of heat. For several possible reaction mechanisms, see the attachments.

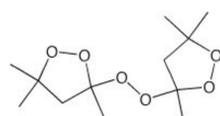
The reactants for preparing DPPP are similar to those for acetone peroxide, except more concentrated acid is used. It is not currently known whether hydrochloric acid must be employed, or if moderately concentrated sulfuric acid can suffice as the acid in the reaction for DPPP.



Phorone

Three molecules of acetone can condense into "phorone". Phorone is diisopropylidene acetone, or 2,6-Dimethyl-2,5-heptadiene-4-one. A yellow crystalline substance, having a geranium-like odor. It can be considered a trimerization product of acetone, obtained from mixing equal parts of acetone and HCl. Phorone has a mp of 28°C.

Mesityl Peroxide



mesityl peroxide

Condensation products of acetone, such as mesityl oxide can also condense with hydrogen peroxide to form peroxides. Mesityl peroxide has a melting point of 122-123 degC. Mesityl oxide is formed from only two molecules of acetone condensing, and smells strongly of peppermint.

"Hydrogen peroxide in dilute solution (1%) has no action on acetone. When hydrogen peroxide (10% solution) is allowed to remain in contact with mesityl oxide for several months at ordinary temperature, a crystalline substance (C₆H₁₁O₃)₂ is obtained. It is quite neutral, melts without decomposition at 123 degrees and is insoluble in dilute acids and alkalis. OH.CMe₂.CAc(OH).CAc(OH).CMe₂OH"

Journal of the Chemical Society, Volume 68, Part 1
 Royal Chemical Society (Great Britain)

In other words, the formula that they gave is HOC(CH₃)₂-C[C(=O)CH₃](OH)-C[C(=O)CH₃](OH)-C(CH₃)₂OH. This structure is likely incorrect, since modern instrumentation that could show the exact structure was not yet available. There are many examples of compounds with correct formulas, but false structures, in early chemistry encyclopedias.

"The presence of mesityl oxide peroxide dimer was established" patent 4233462

"Mesityl oxide peroxide, obtained in only 3% yield as by-product from the alkaline epoxidation of mesityl oxide at high pH, could be secured in 20% yield by carrying out the epoxidation at pH 7.5-8."

"Treatment of mesityl oxide with peroxyacetic acid gave the epoxy ester, 3,3-dimethyl-2- acetoxoxyirane."

Hydrogen Peroxide: New Techniques for its Utilization

G. Payne 5th World Petroleum Congress

Peroxyacetic acid (11%) is used to wash the oranges in many fresh-made Juice stores.

Wolffenstein, R (1895). "Über die Einwirkung von Wasserstoffsperoxyd auf Aceton und Mesityloxyd (On the effect of hydrogen peroxide on acetone and mesityl oxide)". *Chemische Berichte* 28: 2265

"Mesityl oxide and hydrogen peroxide react initially to form the cyclic hydroxyalkyl alkyl peroxide, a 1,2-dioxolane. Prolonged equilibration results in formation of the cyclic di(alkylperoxyalkyl) peroxide, 3,30 -dioxylbis(3,5,5-trimethyl-1, 2-dioxolane)" Ger. Pat. 1,100,033 (Februar 23, 1961), A. Rieche, E. Schmitz, and E. Grundemann.

Preparation of DPPP and Suggested Reactions

The idea for DPPP stems from German patent DE 1951660 (1969)

The exact reaction mechanism suggested in the patent is doubtful, however.

1 part of acetone are added to 1 part concentrated hydrochloric acid, through which acetone polymerizes to phorone.

Then 2 parts of 30% concentrated hydrogen peroxide are added, through which two molecules of HCl bond with the two C-double-bonds of the phorone.

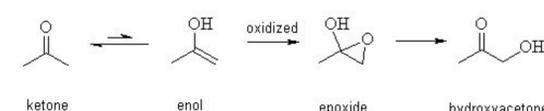
In the course of the reaction free chlorine develops, which bonds with 3 hydrogen atoms of the phorone to give 3 HCl(see drawing) and bonds itself with phorone.

"Hydrogen peroxide causes the chlorine atoms to split off the phorone and the peroxide itself bonds with the phorone. Because of the fact that one peroxy-bond stays half-opened, one also open phoroneperoxide adds to give diphoronepentaperoxide, which precipitates from the solution in crystalline form."

"Matsumoto Hideki" recommends that the phorone should first be made separately before being reacted to form the DPPP. "The black red liquid should be distilled and concentrated as much as possible, and should then be about as viscous as oil. DPPP has a plate-like pentagram crystal structure and is (dark yellow orange) almost amber coloured. It deflagrates at an amazing speed as well. at least 3x faster than TCAP does in a small amount."

Oxidation Reaction on Acetone

The peroxide groups may be added to acetone before acetone molecules condense with eachother. Under acidic conditions, the ketone turns into the unsaturated tautomer, which probably then gets oxidized by either singlet oxygen or the H₂O₂ in the highly acidic and reactive solution. Plain dilute H₂O₂ will not oxidize double bonds, however.



30% concentrated hydrochloric acid mixed with some 30% hydrogen peroxide can rapidly oxidize and dissolve metallic copper. Since concentrated H₂O₂/HCl can attack copper, it is quite possible that, when similarly concentrated, they react with acetone to form hydroxyacetone HOCH₂C(=O)CH₃, and various other oxidation byproducts. Because of the unsaturated tautomer, those hydroxy groups can likely be replaced by peroxide groups.

The whole reaction is complex, and it is likely that DPPP, if it exists, is not a single compound, but rather has a complex mixed structure, basically peroxidated acetone that is condensed to varying degrees. This also suggests that for optimum synthesis of DPPP, a small amount acetone and excess H₂O₂ should be mixed first, and then 30% concentrated HCl should be added.

Peracetic acid can oxidize enols.

"*Organic Peracid Oxidation of some Enol esters involving rearrangement*" *Pete D. Gardner (1956)*

Enol esters may be converted to ketols through an epoxide intermediate.

T. Kritchevsky, T. F. Gallagher, Journal of Biological Chemistry, volume 179 , p505 (1949)

Singlet oxygen is generated by decomposition of the hydrogen peroxide, this excited state of molecular oxygen having an unusually long 72 minute half life in the gas phase, although in solvents singlet oxygen quickly decays back to the ground state in a fraction of a second. Singlet oxygen reacts with an alkene -C=C-CH- by abstraction of the allylic proton (in an "ene" type reaction) to the allyl hydroperoxide. *H.H. Wasserman, J. L. Ives, Tetrahedron volume 37, p1825-1852, (1981).*

Formation of Chlorine

"The catalytic decomposition of hydrogen peroxide in either hydrogen chloride solution or with chlorine has been shown to be closely related to the two chemical reactions



and is believed to be due to the occurrence of these two competing reactions at equal rates."

Livingston and Bray, J. American Chem. Society, Volume 47, p2069 (1925)

In this reaction no net generation of chlorine results from the action of dilute solutions of hydrogen peroxide on hydrogen chloride, but there does exist an elemental chlorine intermediate in the reaction, which could potentially chlorinate enols.

When 30% concentrated HCl and 30% H₂O₂ is used then there develops a slight greenish yellow color and a faint but distinctive odor of chlorine, yet the gas from the bubbles is still mostly O₂. This site conducted this experiment and observed only moderate steady bubbling that persisted for several hours.

It is mentioned in the literature that chlorine gas is evolved from 30% solutions of HCl and H₂O₂, although in more dilute solutions, only oxygen is generated.

"*Oxidation of Hydrogen chloride with hydrogen peroxide in aqueous solution*" *V.I. Skudaev, A.B. Solomonov*

It is therefore possible that chlorine may be involved in the reaction, or at least forming some chlorinated byproducts.

However, an adequate theoretic explanation of the reaction mechanism does not necessitate the involvement of chlorine, besides its function to cause the decomposition of the hydrogen peroxide.

Controversy

The peroxidated product of condensed acetone, which is the alleged compound known as "DPPP" has been the subject of intense investigation over several years in the non-professional online community. Brissance tests comparing TATP to DPPP have generally failed to yield reproducible results. Even MIR spectroscopy on the intermediates and final product of the procedure has not given clear results. Some have even suggested that the alleged "DPPP" is only acetone peroxide, pointing to an MIR test done on a sample of "DPPP". This specific test, however, had several potential flaws, and the results should be viewed with skepticism. It is well known that acetone can condense to mesityl oxide or phorone under strongly acidic conditions. The formation of mesityl peroxide is already well established. The fact the "DPPP" was identical to the TATP under MIR spectroscopy in the test strongly suggests that the researcher did not properly prepare the phorone. The suggested reaction mechanism and molecular structure proposed in the original german patent seems very doubtful, causing further confusion, and casting doubt about the actual existence of DPPP. While the original inventors did not have access to modern equipment, chemists of the time had the ability to determine molecular formulas with good accuracy, and so the given formula of C₁₈H₂₆O₁₂ should not be doubted as much as the unlikely molecular structure given in the patent. It is also quite possible that the relevant reaction mechanisms for the formation of their experimental compound had not yet appeared in the chemical literature of their time. Thus they were likely at a loss to understand the correct reaction mechanism.

It is the opinion of this site that the substance regarded as "DPPP" is different from acetone peroxide, and if properly prepared, is slightly greater in brissance. It is not known whether "DPPP" has a single molecular structure, or exists as a mix of several isomers. Further, it has not been established whether "DPPP" contains five or six peroxide groups, although this should not be too difficult to determine using iodide titration. It may also be possible that the "DPPP" prepared from this simple procedure contains a substantial amount of peroxy-substituted impurities that cannot be separated out. As for the correct molecular structure, this site favors something similar to that shown at the top of this page, and thinks it likely that several other isomers similar to the depicted structure exist. It seems somewhat less likely that any peroxide groups will be added to the side methyl groups on the phorone. If this did occur it would require the action of singlet O₂ in an "ene" reaction, which would shift the double bond onto a methyl group (see appropriate attachment below). It also seems improbable that any methylene --CH₂-- groups would exist in any of the "DPPP" isomer molecules, despite the fact that they are probably present in mesityl peroxide.

It is suggested that the second attachment below be downloaded and opened rather than simply viewed, since otherwise the formatting will not be correct.

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Ĉ DPPPisomers.PNG (28k)	Anders Hoveland, Nov 30, 2010, 4:41 PM	v.1	Ď
Ĉ DPPPpictures.doc (284k)	Anders Hoveland, Nov 29, 2010, 6:25 PM	v.1	Ď
Ĉ DPPPReactionspec.bmp (1468k)	Anders Hoveland, Nov 30, 2010, 1:13 PM	v.1	Ď
Ĉ DPPPvsTATP.pdf (220k)	Anders Hoveland, Nov 30, 2010, 3:00 PM	v.1	Ď
Ĉ alkeneradicaloxidation.bmp (472k)	Anders Hoveland, Nov 30, 2010, 1:25 PM	v.1	Ď
Ĉ singletoxygenereaction.PNG (7k)	Anders Hoveland, Nov 30, 2010, 1:39 PM	v.1	Ď

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