

Tin Chloride Catalysed Oxidation of Acetone with Hydrogen Peroxide to Tetrameric Acetone Peroxide†

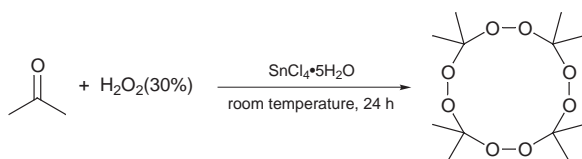
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$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ are efficient catalysts for the oxidation of acetone with 30% hydrogen peroxide at room temperature and produce tetrameric acetone peroxide which is identified by molecular weight determination, elemental analysis, FTIR, NMR and MS.

Hydrogen peroxide is one of the most attractive oxidation reagents because it is inexpensive and gives only water as a byproduct. In fact, an enormous amount of work has been carried out on the oxidation of alkanes, alkylaromatics and arenes by H_2O_2 in the presence of metal compounds.^{1–5} However, there are few reports of metal catalysed oxidation of acetone with hydrogen peroxide. It was reported that cycloalkanones can be oxidized by hydrogen peroxide to cyclic peroxides in the presence of inorganic acids.^{6–8} During the investigation of selective oxidation of olefins catalysed by metal compounds with hydrogen peroxide, we found that occasionally an unknown organic crystalline substance is obtained when acetone is used as cosolvent. Detailed research results show that $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ can catalyse the oxidation of acetone with 30% hydrogen peroxide (Scheme 1).



Scheme 1

Dimeric and trimeric acetone peroxide had been thoroughly studied many years ago.⁹ For example, dimeric acetone peroxide was obtained by treating acetone with solid H_2SO_5 in diethyl ether while trimeric acetone peroxide was prepared by reacting acetone with aqueous hydrogen peroxide in the absence or presence of concentrated HCl. Another method for the preparation of trimeric acetone peroxide is by autoxidation of diisopropyl ether with molecular oxygen.¹⁰ It can be seen from Table 1 that there is no reaction upon treating acetone with 30% hydrogen peroxide for 24 h. Upon the addition of a catalytic amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ or $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to the reaction system, a large amount of white solid is produced. It is found that this white solid is tetrameric acetone peroxide. The catalytic activity of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is lower than that of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ under the same reaction conditions. Table 1 also shows that the yield of tetrameric acetone peroxide increases with an increasing amount of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. In order to exclude the possibility of oxidation of acetone catalysed by HCl generated from the hydrolysis of SnCl_4 , 1 mmol HCl was added to the reaction system. It is found that the yield of tetrameric acetone peroxide was very low under such reaction conditions.

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Table 1 Oxidation of acetone with 30% hydrogen peroxide^a

Catalyst	Amount of catalyst/mmol	Acetone/mol	Tetrameric acetone peroxide yield(%)
—	0	0.27	0
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	0.5	0.27	19.5
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1	0.27	36.8
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	2	0.27	41.2
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1	0.41	15.9
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1	0.54	13.9
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1	0.14	44.7
$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$	1	0.27	19.4
HCl	1	0.27	8.9

^a Reaction conditions: 30% H_2O_2 , 20 ml; room temperature; 24 h. The yield of tetrameric acetone peroxide is the isolated yield based on acetone.

In the presence of chelating ligands (EDTA, BIPY) or radical inhibitor (hydroquinone, 2,6-di-*tert*-butyl-4-methylphenol) the yield of tetrameric acetone peroxide is 40.0–41.2%. These results show that the reaction is not *via* radical autoxidation or a coordination catalytic process. Thus, the oxidation of acetone with hydrogen peroxide catalysed by tin chloride appears to proceed *via* a Lewis acid-catalysed reaction.

Generally speaking, organic peroxides are dangerous because they readily decompose. Most organic peroxides such as *tert*-butyl hydroperoxide decompose rapidly in the presence of high valent metal oxides or complexes.¹¹ Under certain circumstances, tetrameric acetone peroxide is very stable and can be heated to 120 °C for 4 h or refluxed for 120 h in organic solvents such as benzene, chloroform and light petroleum. One of the salient features of tetrameric acetone peroxide is its stability in refluxing organic solvent in the presence of V_2O_5 , $\text{Co}(\text{acac})_3$ or $\text{Fe}(\text{acac})_3$. Although relatively safe to handle, tetrameric acetone peroxide, like almost all substances containing peroxidic bonds, should be handled cautiously; it is very explosive if it is struck firmly or fired.

In summary, we have shown that $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ are efficient catalysts for the oxidation of acetone with hydrogen peroxide to tetrameric acetone peroxide at room temperature.

Experimental

30% H_2O_2 aqueous solution is a guaranteed reagent, while acetone and SnCl_4 are analytical grade. The reagents were obtained from commercial sources and were used without further purification.

General Procedure for the Oxidation of Acetone.—Acetone was added to a solution of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ in 20 ml 30% hydrogen peroxide and the mixture was vigorously stirred with a magnetic stirrer at room temperature for 24 h. A white solid was produced gradually. After the reaction was stopped, the unreacted acetone was evaporated on rotary evaporator at 25–30 °C, then the solid was filtered

off, and washed with water. The solid thus obtained was recrystallized from a 50% acetone aqueous solution or benzene. Mp 93–94 °C.

Tetrameric acetone peroxide was identified by molecular weight determination, elemental analysis, FTIR (KBr), ^1H and ^{13}C NMR and MS. A molecular weight determination was performed on a Knauer Vapour Pressure OSMometer (Germany) and the molecular weight was 290 (calc. 296). Elemental analysis was performed on an Elementar Vario EL instrument (Germany). (Found: C, 48.76; H, 8.25. $\text{C}_{12}\text{H}_{24}\text{O}_8$ requires C, 48.64; H, 8.16%). The above analysis was repeated three times. A strong broad band for the carbon–oxygen stretching frequency is seen around 1195 cm^{-1} in the FTIR spectrum. NMR spectra were obtained on a Bruker MSL-90 NMR spectrometer (Germany). ^1H NMR shows only a methyl signal (δ 1.43, CDCl_3 solvent, TMS as internal standard). ^{13}C NMR determination shows two signals with the methyl carbon and carbon bound to the oxygen appearing at δ 21.3 and 107.4, respectively, which is analogous to trimeric acetone peroxide.¹² The major peaks in the mass spectrum are at m/z 74, 58 (base peak) and 43. The molecular ion is not observed in the mass spectrum, indicating that it is unstable.

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