

ABSTRACT

In my PhD thesis, I investigated the importance of singlet oxygen and hydrotrioxy radicals in the chemical transformation of aerosols. Chemical transformations involving singlet oxygen were studied experimentally and transformations involving hydrotrioxy radicals were studied theoretically, using semiempirical quantum mechanical methods and methods based on density functional theory. α -pinene was chosen as a model compound because it is very abundant in the atmosphere and important for the formation of secondary organic aerosols.

I have developed a simple procedure for liquid phase oxidation with singlet oxygen using a light bulb with tungsten filament and an acetonitrile solution of methylene blue. For the oxidation products, four α -pinene hydroperoxides, I have developed a liquid chromatography and a gas chromatography separation with an ultraviolet (UV), flame-ionization (FID), and mass spectrometry (MS) detection. The quantitative NMR technique, as an absolute technique, allows the determination of absorption coefficients, and was used to identify the hydroperoxide isomers of α -pinene. The analytes had low absorption coefficients, weak MS ionization, and low thermal stability. To overcome these limitations, I proposed a GC-FID approach involving pre-column silylation and quantification via the effective carbon number approach. The linearity of the method was confirmed between 1 and 90 mg/L, with correlation coefficients above 0.99. The method is reproducible with relative standard deviations below 5%. The entire process, from the synthesis of the hydroperoxides to their quantification, is transferable to other terpene hydroperoxides.

The validated method was applied to study the aging of turpentine in which the mass fraction of α -pinene hydroperoxides increased to 5%. It was found that the differences in abundance of each hydroperoxide were due to radical oxidation or a singlet oxygen oxidation mechanism. Furthermore, I was able to show that hydroperoxides are also formed by photochemical reactions with PM₁₀ particles. In solution, the dimerization of α -pinene hydroperoxides was observed by LC-MS and GC-MS and the mechanism was explained by the PM6 semiempirical quantum mechanical method.

So far, determinations of $^1\text{O}_2$ in the air have been very rare. Only one determination using the chemical trap α -terpinene was published in a scientific article. Since high concentrations may result from reactions with oxidants that react in a similar manner to $^1\text{O}_2$, the development of new methods is needed to confirm the accuracy of determinations. In developing the new method, I tested three $^1\text{O}_2$ chemical traps: *N,N*-dimethyl-4-nitrosoaniline, uric acid, and furfuryl alcohol. Furfuryl alcohol proved to be the most suitable reagent and was used to determine concentrations of singlet oxygen in solution, ranging from 2×10^{-12} to 4.5×10^{-12} mol/L. Further improvements to the method are required for air measurements.

The importance of the hydrotrioxy radical ($\bullet\text{OOOH}$) was investigated *in silico*. It was shown that $\bullet\text{OOOH}$ is not formed by the reaction of α -pinene with the radical form of ozone. The addition of $\bullet\text{OOOH}$ occurs at the double bond because the allylic hydrogen abstraction is thermodynamically and kinetically unfavorable. The hydrotrioxy radical is less reactive than the hydroxyl and hydroperoxy radicals and has very low stability, so it is unlikely to play a significant role in atmospheric chemistry.

Keywords: secondary organic aerosols, singlet oxygen, organic peroxides, mass spectrometry.