

I. INTRODUCTION

Organic peroxides in the atmosphere are formed through the oxidation of volatile organic compounds (VOC) by hydroxyl (OH) and ozone (O₃) radicals. These species are reservoirs for OH, perhydroxyl (HO₂) and alkoxy (RO₂) radicals and in turn, reflect the radical levels of the troposphere.¹ The presence of these oxidants help determine the lifetime of many biogenic and anthropogenic pollutants such as methane.¹

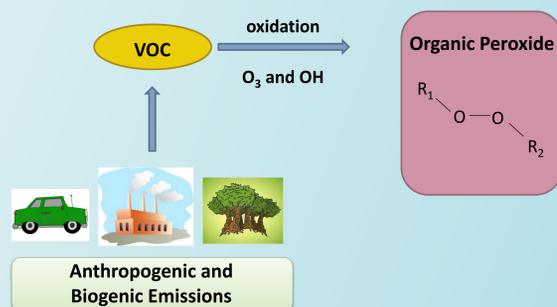


Figure 1: Formation of organic peroxide by oxidation of anthropogenic and biogenic emissions

Since organic peroxides are a potential product, numerous analytical methods have been employed for their detection. Most of these methods combine spectrophotometric and chromatographic techniques which require extensive treatment such as extraction, derivitization and/or separation before analysis.²⁻⁴ In this study, an atmospheric pressure chemical ionization mass spectrometer (APCI-MS) was used to determine its ability to detect organic peroxides. Unlike the spectrophotometric and chromatographic methods, APCI-MS allows for fast on-line measurements and chemical characterization without any kind of sample pre-treatments. The ultimate goal was to develop a universal method to detect different types of organic peroxides using the APCI-MS.

II. Methodology

The mass spectra of 5 commercially available organic peroxides were studied to evaluate the usefulness of an APCI-MS for their detection. Peroxide standards were continuously injected into an air stream entering the APCI-MS through the use of a syringe pump. In the APCI-MS, peroxides underwent chemical ionization with either protonated water or methanol clusters. Ionization products were detected by the mass spectrometer operating in the positive-ion mode.

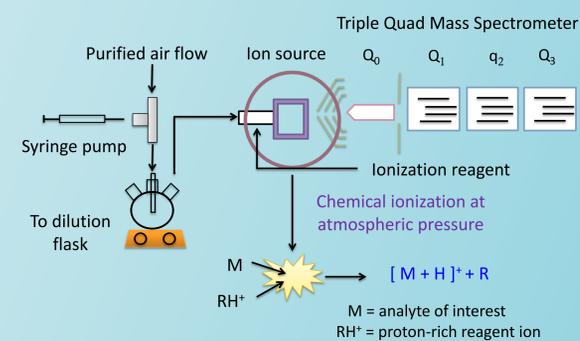


Figure 2: Experimental design for detecting organic peroxides using an APCI-MS

III. APCI-MS Analysis Modes

The APCI-MS is capable of analyzing in several different modes. Full scan (Q₁ MS), product ion, and neutral loss scan modes were utilized in this experiment to observe the gas phase ion-molecule chemistry of selected organic peroxides in the positive-ion mode. Initially for organic peroxide detection, the following reactions were believed to occur in the ion source:

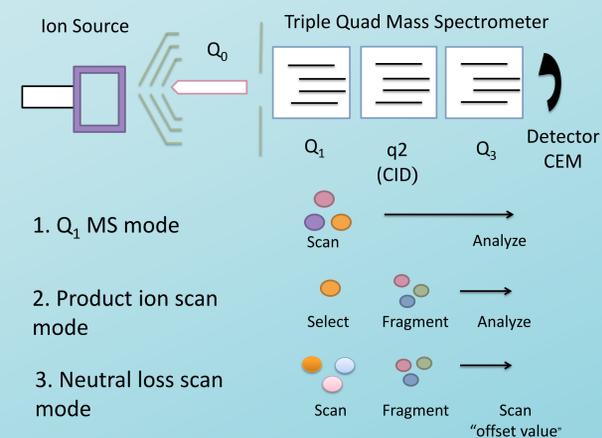
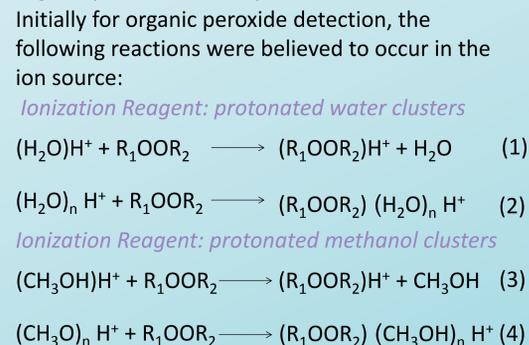


Figure 3: Summary of APCI-MS analysis modes used in this experiment

IV. Results

This experiment studied the mass spectra of 5 commercially available organic peroxides:

- tert-butyl hydroperoxide
- peracetic acid
- cumene hydroperoxide
- tert-butyl peroxyacetate
- di-tert-butyl peroxide

Q₁ MS scans for selected organic peroxides are presented below.

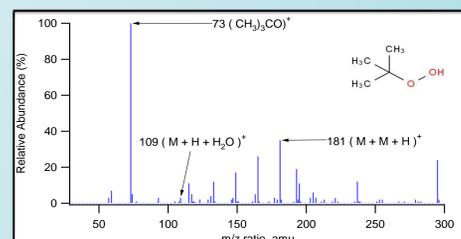


Figure 4: Q₁ MS scan of tert-butyl hydroperoxide

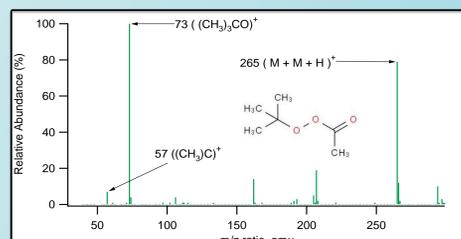


Figure 5: Q₁ MS scan of tert-butyl peroxyacetate

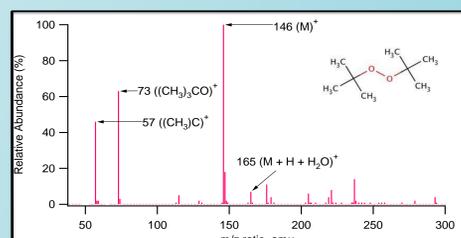


Figure 6: Q₁ MS scan of di-tert-butyl peroxide

V. Results

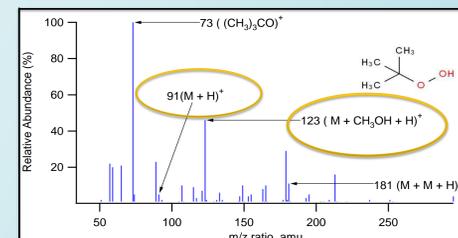


Figure 7: Q₁ MS scan of tert-butyl hydroperoxide using protonated methanol as an ionization reagent

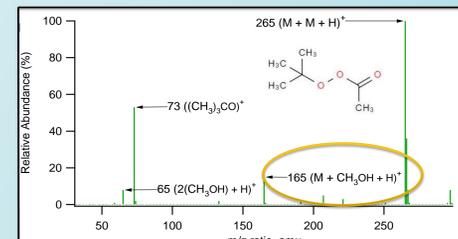


Figure 8: Q₁ MS scan of tert-butyl peroxyacetate using protonated methanol as an ionization reagent

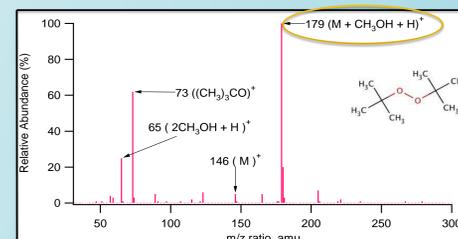


Figure 9: Q₁ MS scan of di-tert-butyl peroxide using protonated methanol as an ionization reagent

Compound	Water as Ionization Reagent	Methanol as Ionization Reagent
tert-butyl hydroperoxide	No	Yes
cumene hydroperoxide	No	No
peracetic acid	Yes	Yes

Table 1: Summary of neutral loss scans performed on selected organic peroxides. Organic peroxides containing a hydroperoxy group (O-O-H) exhibit a characteristic neutral loss of 34 amu (H₂O₂) after protonation and collision with CID gas during collision experiments.

VI. RESULTS & DISCUSSION

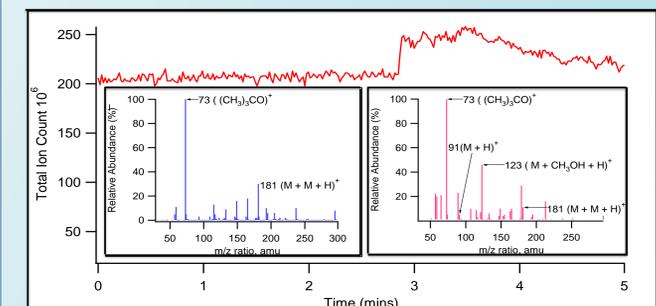


Figure 10: Q₁ MS scan of pre- and post-ionization of tert-butyl hydroperoxide with protonated methanol clusters.

Compound	Ionization with (H ₂ O) _n H ⁺	Ionization with (CH ₃ OH) _n H ⁺
tert-butyl hydroperoxide	[M + H ₂ O + H] ⁺ [M + M + H] ⁺	[M + H ₂ O + H] ⁺ [M + CH ₃ OH + H] ⁺
di-tert-butyl peroxide	[M] ⁺	[M + H ₂ O + H] ⁺ [M + CH ₃ OH + H] ⁺
cumene hydroperoxide	Fragment ions	Fragment ions
peracetic acid	[M + H ₂ O + H] ⁺	[M + CH ₃ OH + H] ⁺ [M + M + H] ⁺
tert-butyl peroxyacetate	[M + M + H] ⁺	[M + CH ₃ OH + H] ⁺

Table 2: Summary of Q₁ MS scans performed using protonated water or methanol clusters during ionization.

Ionization Reagent: protonated water clusters

- Organic peroxides analyzed by the APCI-MS using protonated water cluster as an ionization reagent yielded unexpected results (Figures 4 – 6)
- Mass spectra were dominated by fragment ions resulting from the cleavage of the weak peroxide (O – O) bond during ionization
- Furthermore, ionization with protonated water clusters did not produce [M + H]⁺ or [M + H + H₂O]⁺ consistently or in appreciable amounts (Figures 4 – 6)
- Neutral loss scan performed on organic peroxides capable of exhibiting a characteristic loss of 34 amu (H₂O₂) after protonation was only observed for peracetic acid (Table 1)

Ionization Reagent: protonated methanol clusters

- Methanol was selected as an ionization reagent since it has the ability to generate quasi-molecular ions in the gas phase⁵
- With the exception of cumene hydroperoxide, all organic peroxides spectra showed the formation of a stable adduct ion [M + CH₃OH + H]⁺ (Figures 7 – 9)
- Adduct ion structures were confirmed through CID experiments using the product ion analysis mode
- Peracetic acid and tert-butyl hydroperoxide showed a loss of 34 amu during neutral loss scan analysis (Table 1)

VII. Conclusions

- Table 2 shows a summary of organic peroxides analyzed using two different ionization reagents
- Results show that mostly fragment ions are observed when protonated water clusters are used as an ionization reagent
- Stable adducts are only observed when protonated methanol cluster were used as an ionization reagent