Multi-reagent ion chemical ionization mass spectrometry and *ab initio* calculations for peroxide measurements in DC3.

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I. Introduction

Hydrogen peroxide (HP, H_2O_2), and methylhydroperoxide (MHP, CH_3OOH) are important atmospheric compounds. H_2O_2 is formed through the self reaction of perhydroxyl radicals:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

Organic peroxides generally form via OH mediated oxidation of saturated hydrocarbons R-H,

$$R\text{-}H + {\bullet}OH \qquad R{\bullet} + H_2O$$
$$R{\bullet} + O_2 + M \qquad RO_2{\bullet} + M$$
$$RO_2{\bullet} + HO_2 \qquad ROOH + O_2$$
$$HO_x \text{ Family} = (H{\bullet} + HO{\bullet} + HO_2{\bullet} + RO_2{\bullet})$$

HP has a central role in the HO_x chemistry of the troposphere. HP and MHP impact ground level ozone formation.

In the Deep Convective Clouds and Chemistry (DC3) field campaign, multi-reagent ion chemical ionization mass spectroscopy was used to quantify MHP and HP. For the detection and quantification of MHP, O_2^- was used as the reagent ion. The reagent used for HP determination was CO_4^-, which is itself a cluster of $O_2^-{\bullet}CO_2$. These reagent ions produced ion-molecule adducts at mass 80 for MHP ($MHP{\bullet}O_2^-$) and at mass 110 for HP ($HP{\bullet}O_2^-{\bullet}CO_2$). The analytical viability of a particular ion-molecule adduct is related to the stability of the adduct. Advance ab-initio molecular orbital calculations were used to identify thermodynamically favorable ion-molecule adducts which were confirmed by experimentation.

II. Description of the Analytical Methods

Peroxide Chemical Ionization Mass Spectrometer (P-CIMS):

CIMS has been shown to be a versatile and fast measurement technique for a wide variety of atmospheric trace gases. A CIMS system was obtained from THS Instruments, and adapted for peroxide measurements. Peroxide inflight additions were performed using a microsyringe pump to inject an aqueous peroxide standard into a dry N_2 stream that was then introduced into the ambient gas stream. The reagent ions were generated by passing pure air with 400 ppm CO_2 through a Polonium-210 ionization source (Figure 1). A Carulite-200 trap was used to remove peroxides during DC3. *Ab-initio* calculations indicated that stable adducts would be formed with CO_3^-, $O_2^-{\bullet}CO_2$, NO_2^-, NO_3^-, and O_2^- reagent ions for either HP or MHP.

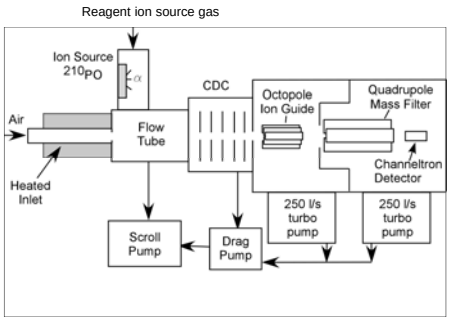


Figure 1. P-CIMS instrument schematic for DC3.

III. DC3 Reagent ion Chemistry, Sensitivity, and Blanks

III A: Reagent Ions

Reagent ions produced with the ionization scheme included, O_2^- (m/z 32), NO_2^- (m/z 46), CO_3^- (m/z 60), NO_3^- (m/z 62), and CO_4^- (m/z 76), shown in red on Figure 2, a mass spectrum from RF13. Also shown with a red line is m/z 50, $H_2O{\bullet}O_2^-$ adduct, the largest peak is at m/z 94, $H_2O{\bullet}CO_4^-$.

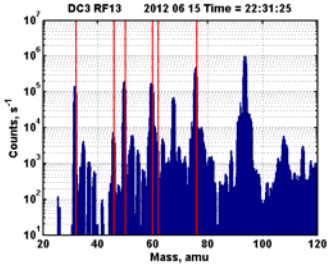


Figure 2. Ambient air mass spectrum at 35Kft.

- **CO_3^-, CO_4^-, NO_2^-, NO_3^- form relatively stable adducts with H_2O_2 however in our system the abundance of NO_2^- and NO_3^- were relatively low. The analytical mass used for H_2O_2 was mass 110.**

$$O_2^- {\bullet} CO_2 + H_2O_2 \rightarrow O_2^- {\bullet} CO_2 {\bullet} H_2O_2 \qquad 110 \text{ amu}$$

- **The most stable adduct for MHP was with O_2^- at mass 80.**

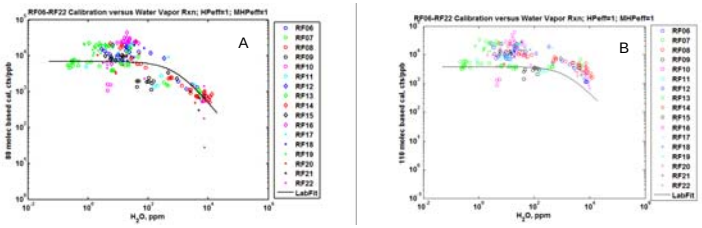
$$O_2^- + CH_3OOH \rightarrow O_2^- {\bullet} CH_3OOH \quad 80 \text{ amu} \qquad \Delta G = -230.8 \text{ kJ/mol}$$

- ***There are a number of possible interfering peaks.***

$$NO_2^- + H_2O_2 \rightarrow NO_2^- {\bullet} H_2O_2 \quad 80 \text{ amu} \qquad \Delta G = -67.3 \text{ kJ/mol}$$
$$CO_3^- + H_2{}^{18}O \rightarrow CO_3^- {\bullet} H_2{}^{18}O \quad 80 \text{ amu} \qquad \Delta G = -25.6 \text{ kJ/mol}$$
$$C^{18}O_3^- + H_2O \rightarrow C^{18}O_3^- {\bullet} H_2O \quad 80 \text{ amu} \qquad \Delta G = -26.9 \text{ kJ/mol}$$

IIIB. Responses with water vapor

Figure 3. Mass 80 (A) and Mass 110 (B) dependence on water vapor.



$$O_2^- + H_2O \rightarrow O_2^- {\bullet} H_2O \qquad \text{eq. 1}$$
$$O_2^- {\bullet} H_2O + CH_3OOH \rightarrow O_2^- {\bullet} CH_3OOH + H_2O \qquad \text{eq. 2}$$
$$O_2^- + CH_3OOH \rightarrow O_2^- {\bullet} CH_3OOH \qquad \text{eq. 3}$$

- Water vapor dependence at mass 80 indicates eq 3 leads to the adduct formation, and eq 1 competes for O_2^- at high water vapor.
- Water vapor dependence at mass 110 also reflects a competition with the analytical adduct for the $O_2^- {\bullet} CO_2$ portion of the cluster.

IV. Field HP and MHP Observations

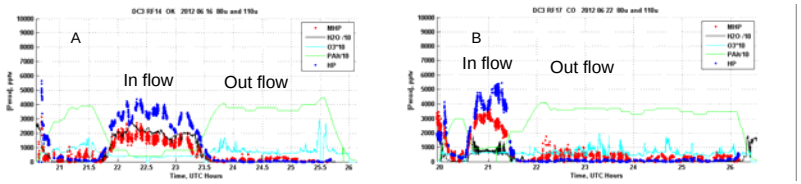


Figure 4. Flight data from storm sampling in Oklahoma, GV-RF14 (A) and Colorado GV-RF17(B)

IV. Computational Study

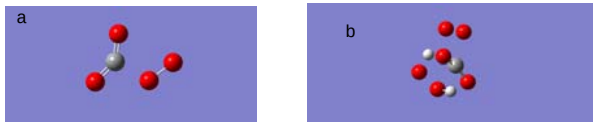


Figure 5: MP2 /6-31G (d) Optimized Structures of (a) CO_4^- which indicates it is a cluster of $O_2^- {\bullet} CO_2$; (b) $CO_4^- H_2O_2$ (m/z 110) which is also a complex with a probable structure of $O_2^- {\bullet} CO_2 {\bullet} H_2O_2$.

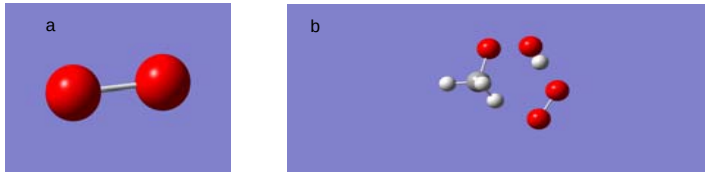


Figure 6: MP2 /6-31G (d) Optimized Structures of (a) O_2^- (b) $O_2^- {\bullet} CH_3OOH$ (m/z 80), the oxygen-oxygen bond in the peroxide is not depicted in the figure.

All calculations reported here were carried out using the Gaussian 09 program suite. *Ab-initio* molecular orbital calculations at the MP2/6-31G(d) level of theory were undertaken to find the most stable structures of the peroxide neutrals and their clusters with various anions. We used G2 level of theory to calculate the change in Gibbs free energy for all reactions which produce an adduct with a mass of 80 amu.

V. Conclusions

- **During DC3 the most promising masses for the analysis of H_2O_2 was found to be mass 110 with a $O_2^- {\bullet} CO_2 {\bullet} H_2O_2$ cluster ion.**
- **For CH_3OOH mass 80 was used with a $O_2^- {\bullet} CH_3OOH$ cluster ion.**
- **The formation of several other ionic clusters with a mass of 80 are also thermodynamically favorable, we have been investigating the background contributions from these species under the various atmospheric conditions encountered during DC3.**
- **Experiments to evaluate the sensitivity of the ion molecule reactions to water vapor, and background studies are nearly complete. We hope to submit revised data for HP and MHP in the near future.**