

Supplemental Information: An ion-neutral model to investigate chemical ionization mass spectrometry analysis of atmospheric molecules - application to a mixed reagent ion system for hydroperoxides and organic acids.

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1. Notes on mechanism development and adjustment of kinetic rates to resolve pressure and humidity trends in O_2^- (H_2O_2), O_2^- (CH_3OOH), O_2^- (CO_2)(H_2O_2), I^- (HFO) and I^- (HAc) sensitivities.

1.1 Base thermodynamic data for the $O_2^- - O_2 - CO_2 - H_2O$ – hydroperoxide system.

Formation enthalpy (ΔH_f^o), entropy (ΔS^o), and Gibb's formation energy (ΔG_f^o), data are published for some of the neutral, 15 ion and ion-cluster species involved in the $O_2^- - O_2 - CO_2 - H_2O$ – hydroperoxide system. Reaction enthalpy (ΔH_r^o), entropy (ΔS_r^o), and Gibb's energy (ΔG_r^o) data are also available for some of the reactions involved in this system. These thermodynamic data are summarized in Table A5 and Table A6. The NIST Chemistry WebBook (Bartmess, 2016) was used extensively in this analysis as it provides summary information from primary sources. In cases for which multiple values are available and without a recommended value, we have indicated which primary data set we adopted. Additional formation 20 and reaction energies were taken from *ab initio* calculations by Messer et al. (2000), Cappa and Elrod (2001), Goldsmith et al. (2012) and O'Sullivan et al. (2017). For ions and ion-cluster species and reactions, care must be exercised as to the notation used for the energy terms. Often, but not always, the ion and ion-neutral cluster species and reaction literature follows a negative sign convention with respect to the neutral species and neutral reaction literature. Here we have adopted a sign convention such that exothermic reactions have a negative reaction enthalpy and spontaneous reactions have a negative 25 Gibb's reaction energy.

The following thermodynamic relationship is used to calculate energy terms which were not previously available from the primary literature or the NIST Chemistry WebBook,

$$\Delta H_r^o - T_o \times \Delta S_r^o = \Delta G_r^o$$

30 where $T_o = 298.15$ K, ΔH_r^o is the stoichiometric sum of the formation enthalpies, ΔH_f^o , of the products (j index) minus the stoichiometric sum of the formation enthalpies of the reactants (i index),

$$\Delta H_r^o = \sum_j^J v_j H_{f,j}^o - \sum_i^I v_i H_{f,i}^o,$$

ΔS_r^o is the stoichiometric sum of the standard entropies, S^o , of the products minus the stoichiometric sum of the standard entropies of the reactants,

35 $\Delta S_r^o = \sum_j^J v_j S_j^o - \sum_i^I v_i S_i^o,$

and ΔG_r^o is the stoichiometric sum of the Gibb's formation energies, ΔG_f^o , of the products minus the stoichiometric sum of the Gibb's formation energies of the reactants,

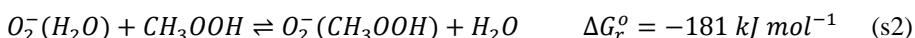
$$\Delta G_r^o = \sum_j^J v_j G_{f,j}^o - \sum_i^I v_i G_{f,i}^o,$$

where, v represents the stoichiometric coefficient for a species in a reaction. Formation energies for a reactant or product species are calculated using published ΔH_f^o and ΔG_f^o for that species as the sole product and the reactants are taken to be in their standard state and form with $\Delta G_f^o \equiv 0$ and $\Delta H_f^o \equiv 0$. In the case of the *ab initio* calculations, the Gibb's energy at 298.15 K and 1013.25 hPa, G^o , is calculated for each reactant and product and ΔG_r^o is calculated by stoichiometrically summing the *ab initio* Gibb's energies (Ochterski, 2000) of the products and then subtracting the stoichiometric sum of the reactants:

45 $\Delta G_r^o = \sum_j^J v_j G_j^o - \sum_i^I v_i G_i^o = \sum_j^J v_j G_{f,j}^o - \sum_i^I v_i G_{f,i}^o.$

The formation and reaction energies so calculated in this work are underlined and bold-faced in the Tables A5 and A6.

Goldsmith et al. (2012) estimated formation enthalpies, entropies and Gibb's formation energies for CH_3OOH and many other low molecular weight combustion related compounds. O'Sullivan et al. (2017) estimated Gibb's reaction energies at 298.15 K and 1013.25 hPa for:



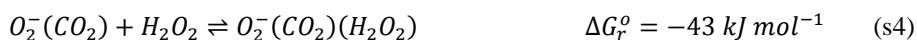
and



55 The Gibb's reaction energy given for (s2) has been modified from O'Sullivan's original value as outlined below. The ΔG_r^o value for (s3) compares favorably to that estimated using the linear correlation between ion-protonation energy and the Gibb's reaction energies for ion- H_2O_2 cluster formation (see main paper, $\Delta G_r^o = -94 \text{ kJ mol}^{-1}$). The O'Sullivan et al. calculated ΔG_r^o 's for ion-hydrates also agreed well (nominally within 7 kJ mol^{-1} ; sixth significant figure in the calculated Gibb's energy) with the NIST Chemistry WebBook tabulations. However, there was a large inconsistency between the

60 Gibb's reaction energies for (s1) and (s2) and the ΔG_f^o for $O_2^- (CH_3OOH)$ derived from their calculations using NIST or NIST
 derived reactant and product ΔG_f^o 's from Table A6. The ΔG_f^o of $O_2^- (CH_3OOH)$ calculated from either (s1) or (s2) was
 expected to be within 7 kJ mol⁻¹ but was found to be -340 or -521 kJ mol⁻¹, respectively, using O'Sullivan's original species
 specific Gibb's energies. The discrepancy was traced to a potential calculation issue for $O_2^- (H_2O)$. The Gibb's energy for
 65 $O_2^- (H_2O)$ was recalculated using the NIST Gibb's reaction energy for $O_2^- + H_2O \rightleftharpoons O_2^- (H_2O)$ (Table A6) and the O'Sullivan
 calculated Gibb's energies for O_2^- and H_2O . Applying this hybrid Gibb's energy for $O_2^- (H_2O)$ in (s2) rectified the ΔG_f^o of
 $O_2^- (CH_3OOH)$ between (s1) and (s2). The resultant ΔG_f^o of $O_2^- (CH_3OOH)$ was -340 kJ mol⁻¹ and the modified ΔG_r^o for
 reaction (s2) was -181 kJ mol⁻¹. These values are listed in Table A5 and Table A6, respectively.

70 A second issue exists between the derived NIST Gibb's formation energies and the O'Sullivan et al. (2017) Gibb's reaction
 energies for the formation of $O_2^- (CO_2)(H_2O_2)$. One pathway to $O_2^- (CO_2)(H_2O_2)$ formation is:



where the Gibb's reaction energy for (s4) is from O'Sullivan et al. A second pathway to $O_2^- (CO_2)(H_2O_2)$ is:



75 and was proposed by us to reconcile the sensitivity trends observed in $O_2^- (CO_2)(H_2O_2)$ as a function of sample flow rate
 (sample pressure) and humidity. The O'Sullivan et al. calculated Gibb's reaction energy for (s5) is shown. The Gibb's
 reaction energies suggest both reactions would be spontaneous and the equilibrium constants would strongly favor the
 products. The Gibb's formation energy of $O_2^- (CO_2)(H_2O_2)$ was determined to be -630 kJ mol⁻¹ using the Gibb's formation
 energies for $O_2^- (CO_2)$ and H_2O_2 derived from NIST data and the O'Sullivan et al. Gibb's reaction energy for (s4).

80 Alternatively using the Gibb's formation energies for $O_2^- (H_2O_2)$ and CO_2 derived from NIST data and the Gibb's reaction
 energy for (s5), the Gibb's formation energy for $O_2^- (CO_2)(H_2O_2)$ would be -721 kJ/mol⁻¹, a -91 kJ mol⁻¹ difference from that
 determined from (s4). At this point the reaction energies for (s4) and (s5) favored the production of $O_2^- (CO_2)(H_2O_2)$ by
 both reactions.

85 The Gibb's formation energies and Gibb's reaction energies for (s4) and (s5) were rectified similarly to the reconciliation of
 (s1) and (s2) thermodynamics above, but in so doing it reduces the argument for $O_2^- (CO_2)(H_2O_2)$ production by (s5). A key
 step in this reconciliation was a reanalysis of the energetics of $O_2^- (CO_2)$ production through reaction (s6)



where, the reaction energy is derived from NIST data alone. The O'Sullivan et al. *ab initio* calculated reaction energy for (s6) was -141 kJ mol⁻¹ or 92 kJ mol⁻¹ lower than the NIST derived value. Ascribing the difference fully to the calculated
 90 Gibb's energy of $O_2^- (CO_2)$ in O'Sullivan's calculation, reducing this quantity by 91 kJ mol⁻¹ while keeping the Gibb's
 reaction energies (s4) the same, necessitated reducing the calculated Gibb's energy for $O_2^- (CO_2)(H_2O_2)$ by the same amount.
 Propagating this change into the calculation of the Gibb's reaction energy for (s5), lead to $\Delta G_r^o = +7 \text{ kJ mol}^{-1}$ for this

reaction. Both (s4) and (s5) now yield the same Gibb's formation energy for $O_2^-(CO_2)(H_2O_2)$, which is equal to -630 kJ/mol⁻¹. The species Gibb's formation energies and the Gibb's reaction energies for (s4), (s5), and (s6) are thereby self-consistent but at the expense of the calculated reaction energy for (s5) which is now positive and suggestive of a non-spontaneous reaction with an equilibrium constant slightly favoring the reactants. This only partially weakened the case for reaction (s5) in the formation of $O_2^-(CO_2)(H_2O_2)$ because, while (s5) as revised is weakly endergonic, the reaction remains exothermic with an enthalpy of ~-20 kJ mol⁻¹ as its expected reduction in entropy is of order 10⁻² J mol⁻¹ K⁻¹ based upon analogy with other hydroperoxide clustering reaction data (i.e., Böhringer et al., 1984; Messer et al. 2000; Cappa and Elrod, 2001).

1.2 Modified kinetics data for the $O_2^- - O_2 - CO_2 - H_2O$ – hydroperoxide system with $I^- - H_2O - H_2O_2 - HFo - HAc$ chemistry.

After the ion-source tube, the reagent ion stream was assumed to instantaneously mix with ambient air. This air contains myriad other compounds most notably in terms of our reagent ion system: H_2O , O_2 , CO_2 and O_3 . The model mechanism with respect to O_2^- and its cluster ions with H_2O and additional CO_2 and O_2 follows Mohnen (1971), Kebarle et al. (1972), Fehsenfeld and Ferguson (1974) and Fahey et al. (1982). The full set of species considered and their reactions are listed in Tables A1 and A2, respectively. The species and reactions were developed in stages and the species and reaction indices (the number preceding the reaction) reflect that development. The main paper contains a list of reactions organized by the reacting ion.

Reagent ion hydration was critical. For the first hydrate, hydration can occur directly



or indirectly through $O_2^-(O_2)$ and possibly $O_2^-(CO_2)$



In these and subsequent reaction statements, M denotes a third molecule and the references by: Ada = Adams et al. (1970); Alb = Albritton (1978); Ike = Ikezoe et al. (1986); Fah = Fahey et al. (1982); FF = Fehsenfeld and Ferguson (1974); FFB = Fehsenfeld et al. (1969); Hue = Huertas et al. (1978); PK = Payzant and Kebarle (1972); PP = Pack and Phelps (1966). The reaction rate coefficient for (13), k_{13} , was set equal to 2.5×10^{-10} . This value of k_{13} was calculated assuming the switching reaction pair, (12) and (13),



$$K_{eq} = k_{12}/k_{13} = 2.3 \text{ (FF)}$$

could be combined to form a simple forward/reverse reaction sequence with the equilibrium constant equal to 2.3 (Fehsenfeld and Ferguson, 1974).

1.3 Mono-carbonate and poly-hydrates.

Payzant and Kebarle (1972) and Huertas et al. (1978) treated the formation of the second hydrate of O_2^- as a termolecular reaction,



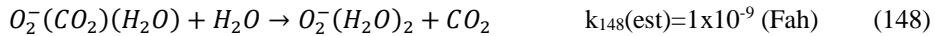
whereas, Kazil (2002) treated this as a bimolecular reaction at pressures above some high-pressure threshold (unstated), $k_f = 1.0 \times 10^{-9}$.



Kebarle et al. (1972) and Fehsenfeld and Ferguson (1974) further suggest a sequence involving $O_2^-(CO_2)$ as a hydration path to $O_2^-(H_2O)_2$ formation:



followed by:



$$k_{148}(\text{est}) = 1 \times 10^{-10} \text{ (Hue)}$$

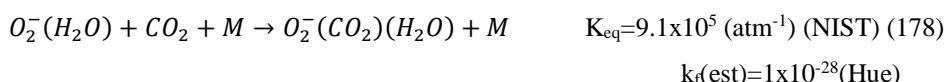
especially, when $P(CO_2) > P(H_2O)$ such as in the upper troposphere and above. Note, k_{148} presumed by Huertas et al. (1978) is an order of magnitude smaller than the assumed value used by Fahey et al. (1982) and is inconsistent with the reaction rate coefficient for reaction (147) measured by Fahey et al. and the equilibrium constants reported by Kebarle et al. (1972) and Fehsenfeld and Ferguson (1974). Kebarle et al. (1972) and Fehsenfeld and Ferguson (1974) gave equilibrium constants of 7 and 15, respectively, for the switching reaction pair (148) and (147),



Further, the reaction products of (147) were not explicitly stated in Fahey et al. (1982) and those shown here were inferred from their discussion and the discussion of Mohnen (1972). The $O_2^-(CO_2)(H_2O)$ cluster generated in reaction (147) provides an alternative $O_2^-(CO_2)$ generating mechanism, (147) followed by (14):

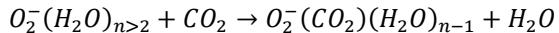


Huertas et al. (1978) attributed his presumed reaction rate coefficient for (14) to Mohnen (1974). Reaction (14) combined with reaction (21) yields a simple equilibrium constant of $9 \times 10^4 \text{ (atm}^{-1}\text{)}$; $K_{eq} = k_{21}/k_{14}$. The equilibrium constant for the combined equilibrium reactions K_{eq}(12,13) and K_{eq}(21,14) of 2.1×10^5 was within a factor of 5 of the NIST (2016) value for reaction (178)

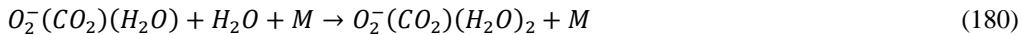


$$k_r(\text{est}) = 2.7 \times 10^{-15} = k_f / K_{\text{eq}}$$

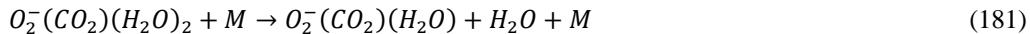
Kebarle et al. (1972) proposed reactions of the form:



in their preliminary mechanism. Mohnen (1972) indicated these reactions were unlikely for $n > 3$ and Fahey et al. (1982) indicated these reactions are endothermic and slow for $n > 1$. There is some evidence for $O_2^-(CO_2)$ hydrates up to $n=2$ in Mohnen (1972) and reactions:



and



were included in our mechanism. Mohnen (1971) and Kebarle et al. (1972) included these reactions in their O_2^- , CO_2 , and H_2O mechanisms and Kebarle et al. gave a measured reaction enthalpy. In one of the O_2^- , CO_2 , and H_2O drift-tube experiments of Mohnen (1972), Mohnen called out strong signals attributed to $O_2^-(CO_2)$ and $O_2^-(CO_2)(H_2O)$ and weaker signals attributed to $O_2^-(H_2O)_{n=4-7}$. While not specifically mentioned, weaker signals were also present in his data figure at masses of 50, 68, 86 and 112, which correspond to $O_2^-(H_2O)_{n=1-3}$ and $O_2^-(CO_2)(H_2O)_2$, respectively. Huertas et al. (1976) included the reaction pair, (180) and (181), in their mechanism following Kebarle et al. and assumed the reaction rate coefficients were 1×10^{-28} and 1×10^{-13} , respectively. The latter value for k_{181} was stated to be from Mohnen (1974), which in turn refers to Mohnen (1971; 1972) but was not explicitly found within these three references. Here, we have included only the first and second order hydrates of $O_2^-(CO_2)$ in our model scheme. Higher order O_2^- hydrates (up to $n=5$) are included (see reactions 70, 71, 192, 193, 194, and 195) as they comprise a significant fraction of O_2^- at higher ambient and laboratory humidities.

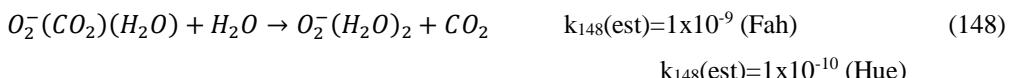
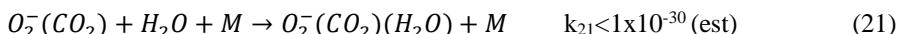
The sensitivity trends in ion-hydroperoxide chemistry were difficult to reproduce and additional reaction schemes were employed. First it was thought the problem lay within reaction rate coefficients for reactions (12), (13), (14), (21), (24), (147), and (148) describing the $O_2^- - (H_2O) - (CO_2)$ switching system as outlined below. Next, ozone, O_3 , present in the sample air could alter PCIMS hydroperoxide sensitivity as O_3 reacts with O_2^- reducing the O_2^- concentration and producing O_3^- and CO_3^- ions. Reactions capturing this chemistry were included. Also, a slower rate of reaction for (13) was required. Through systematic adjustment, we found k_{13} needed to be at or below 10^{-12} to leave sufficient O_2^- , $O_2^-(H_2O)$ and $O_2^-(CO_2)$ to fit our sensitivity data. This was approximately two orders of magnitude lower than predicted by the reaction (12)-(13) equilibrium. The following supported a potentially lower reaction rate coefficient for (13):

- 1) Banic and Iribarne (1985) argue $O_2^-(CO_2)$ is a “very stable” ion cluster in the troposphere and assumed it to be covalently bonded based upon Fehsenfeld and Ferguson (1974). In Fehsenfeld and Ferguson (1974) a covalently bonded $O_2^-(CO_2)$ cluster is not explicitly discussed although covalent bonding is discussed by them with respect to $HO^- + SO_2$ and $Cl^- + SO_2$ cluster reactions. They did, however, discuss reaction (13) indirectly, implying it

190

was “slow”. We infer this “slowness” is what lead to Banic and Iribarne’s suggestion of covalent bonding in the $O_2^- (CO_2)$ cluster ion, as stronger covalent bonding would be expected in a slowly reacting cluster ion such as (13).

- 195 2) Hiraoka and Yamabe (1992) discuss evidence of covalent bonding in the $O_2^- (CO_2)$ ion because of a noted jump in cluster reaction enthalpy for the addition of additional CO_2 to $O_2^- (CO_2)$ as compared to the reaction enthalpy changes noted with the addition of CO_2 to CO_3^- and NO_2^- ions. This was interpreted as an indication of covalent bonding in $O_2^- (CO_2)$.
- 200 3) Hayhurst et al. (1992) show $O_2^- (CO_2)$ to increase in dry or wet air “rich” in CO_2 (>100 ppm, and in keeping with our system) with a maximum in dry CO_2 rich air but to virtually disappear in wet air “deficient” in CO_2 (<2 ppm).
- 4) Fehsenfeld and Ferguson further stated hydrated $O_2^- (CO_2)$ [i.e., $O_2^- (CO_2)(H_2O)$] reacts with H_2O eliminating CO_2 thereby making $O_2^- (H_2O)_2$. In turn $O_2^- (H_2O)_2$ can undergo dehydration to $O_2^- (H_2O)$. Thus, the reaction sequence:



205 results in a reaction sequence with products identical to those in (13).

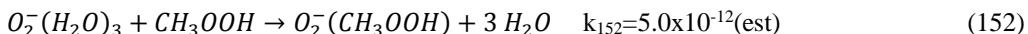
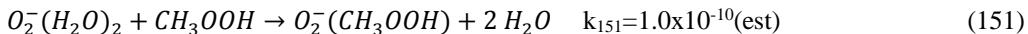
- 5) O’Sullivan et al. (2017) simulated the bonding in $O_2^- (CO_2)$ using an *ab initio* method and suggested it is an adduct with weak covalent bonding.

- 210 6) Last, the value shown for k_{21} fits our $O_2^- (CO_2)(H_2O_2)$ sensitivity trend with water vapor much better than the reaction rate coefficient of 1×10^{-28} estimated by Huertas et al. (1978) and subsequently cited by others (e.g., Popov, 2010). Mohnen (1971) also estimated a value of 1×10^{-29} and which was smaller than that in Huertas.

We hypothesize a reaction sequence like (21), (148) and (51) together with (12) could give rise to a steady-state system in which a reaction like (13) appears in the net but occurs slowly if at all directly.

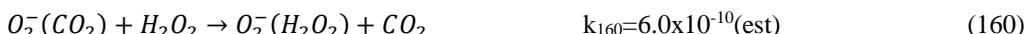
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Reactions or reaction sequences represented by (149)-(152)



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followed by (160) and (161):



were added to the mechanism. Their inclusion improved the pressure dependent sensitivity and water vapor trends for the O_2^- hydroperoxide clusters but did not significantly improve the pressure and water vapor sensitivity trends in

225 $O_2^-(CO_2)(H_2O_2)$.

Next ozone effects on the chemistry were included. O_3 present in the sample air could alter the peroxide chemical ionization mass spectrometer (PCIMS) hydroperoxide sensitivity as O_3 reacts with O_2^- reducing the O_2^- concentration and producing O_3^- and CO_3^- ions:



Additionally, O_3 reacts with $O_2^-(CO_2)$ and O_2^- hydrate clusters:



to produce additional O_3^- , CO_3^- and their hydrates. The O_3 reaction rate coefficients were assigned the same value regardless of the extent of O_2^- hydration and carbonation in keeping with Fahey et al. (1982) who pointed out the addition of CO_2 or H_2O did not significantly reduce the reaction rate coefficient between O_2^- or its cluster ions with O_3 . O_3 has the potential to shift the ion population from O_2^- , $O_2^-(H_2O)_n$ and $O_2^-(CO_2)_m$ to O_3^- and CO_3^- .

1.4 Iodide

Iyer et al. (2016) using *ab initio* methods estimated reaction rate coefficients and binding energies for I^- with HFO and HAc . They also calculated binding energies for I^- reactions with H_2O_2 and CH_3OOH using the same methodology (Iyer, Pers. Comm., 2016). The respective binding energies for $I^-(HFO)$, $I^-(HAc)$, $I^-(H_2O_2)$, and $I^-(CH_3OOH)$ are 100, 73, 70, and

245 60 kJ mol⁻¹. Iyer et al. predicted sensitivities for many organic compounds based on the correlation of their calculated binding energies and the experimental sensitivities for organic acids published in Lee et al. (2014) for a CIMS TOF I^- instrument. We have normalized their predicted sensitivities to $I^-(HFO)$ and the relative sensitivities are 1.000, 0.034, 0.007, and 0.001 for $I^-(HFO)$, $I^-(HAc)$, $I^-(H_2O_2)$, and $I^-(CH_3OOH)$, respectively. This ranking is consistent with the observations of O'Sullivan et al. (2017) in which they noted observing $I^-(H_2O_2)$ but not $I^-(CH_3OOH)$ clusters with the

250 PCIMS instrument and with Treadaway et al. (2017) in which they observed a weak standard addition calibration signal for $I^-(CH_3OOH)$ in the laboratory and during FRAPPE (Treadaway et al., 2017; Fig. 3). Fig. 8-10 (main paper) showed the sensitivity for $I^-(H_2O_2)$, $I^-(HFO)$, and $I^-(HAc)$ as a function of water vapor. The sensitivity of $I^-(CH_3OOH)$ appeared to be independent of water vapor from the laboratory work, although the FRAPPE field calibrations suggested (Treadaway et

al. 2017; Fig. 4) the sensitivity may increase with water like $I^-(HFO)$ whereas, $I^-(H_2O_2)$ and $I^-(HAc)$ decrease over the

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limited range in humidity encountered in FRAPPE.

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