The role of symmetry in the mass independent isotope effect in ozone

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Understanding the internal distribution of ''anomalous'' isotope enrichments has important implications for validating theoretical postulates on the origin of these enrichments in molecules such as ozone and for understanding the transfer of these enrichments to other compounds in the atmosphere via mass transfer. Here, we present an approach, using the reaction $NO_2^- + O_{3,}$ for assessing the internal distribution of the $\Delta^{17}O$ anomaly and the $\delta^{18}O$ enrichment in ozone produced by electric discharge. The $\Delta^{17}O$ results strongly support the symmetry mechanism for generating mass independent fractionations, and the $\delta^{18}O$ results are consistent with published data. Positional $\Delta^{17}O$ and $\delta^{18}O$ enrichments in ozone can now be more effectively used in photochemical models that use mass balance oxygen atom transfer mechanisms to infer atmospheric oxidation chemistry.

oxygen | nitrate | nitrite | oxidation

Recently, there has been considerable interest in using oxygen isotopes found in photochemically active compounds to trace chemical reactions in the atmosphere (see reviews in refs.1–3). This includes the use of traditional approaches that utilize kinetic and equilibrium isotope effects that occur during chemical reactions and phase changes. But there are also some promising new advances using "anomalous" oxygen isotope signatures (2): anomalous meaning isotope distributions that cannot be predicted by means of the usual statistical and quantum mechanical techniques (4). For oxygen, the anomaly is defined as the excess ^{17}O over what is expected based on ^{18}O isotopic abundances. This excess ^{17}O is quantified by $\Delta^{17}O \approx \delta^{17}O - 0.52\delta^{18}O$ or more precisely using natural log scales (5). The process, or processes, that generate $\Delta^{17}O$ signals have been termed mass-independent fractionations (MIF) (2, 6) because the enrichments appear to scale irrespective of the relative mass differences of ^{17}O with respect to ^{18}O when referenced to ^{16}O. They have also been referred to as "strange isotope effects" (7) and non-mass-dependent (NOMAD) (8, 9).

The most thoroughly studied MIF system is that of ozone formation. Ozone generated by electric discharge or UV photolysis can produce $\Delta^{17}O$ values of 30–40‰ (‰ = parts per thousand). There have also been numerous studies that have experimentally quantified the pressure and temperature dependence of the isotopic enrichments (10, 11). Most recently, the transfer of the $\Delta^{17}O$ anomaly from ozone to other compounds during oxidation reactions (via atom transfer, e.g., mass balance) has been used to elucidate chemical oxidation pathways in modern atmospheres (16–21). These include $\Delta^{17}O$ observations in atmospheric nitrate, sulfate, CO_2, and N_2O. $\Delta^{17}O$ variations in atmospheric nitrate and sulfate are intriguing because they have opened the possibility of using these $\Delta^{17}O$ variations in ice cores as a proxy for paleo-oxidation chemistry (22, 23). Modeling such transfer reactions, however, requires knowledge of the internal distribution of the $\Delta^{17}O$ anomaly, i.e., how much is contained in the central versus terminal atoms of ozone, because many atmospheric oxidations are thought to occur through terminal-only transition states.

Theories as to the origin of the MIF effect have taken many turns (7, 8, 24, 25), and some theories seem more adept at handling specific experimental cases than others. Most have symmetry as the main, albeit ad hoc, causal mechanism for producing MIF. Recent work by Marcus and coworkers (26–28) is perhaps the most thorough treatment, and they have suggested that nonstatistical RRKM effects arise because of differences in the rovibronic coupling efficiency of the asymmetric molecule when compared with the symmetric isomer. Recent NO_2 spectroscopic data appear to bear the theory out (29), but the uncertainties in that study remain significant, and no mass spectrometer isotope data on the unimolecular decay of NO_2 are available. Because the basis of the ozone MIF theory is symmetry driven, it is implied that the anomalous enrichment must be contained in the terminal atoms of ozone. To be clear, there maybe overall isotopic enrichment ($\delta^{18}O$, $\delta^{17}O$) distributed throughout the molecule based on isotopologue zero-point energy differences (30), but the ^{17}O excess ($\Delta^{17}O$) is expected to be only in the terminal position. Others, however, have argued against the symmetry theory (31–33) and have placed anomalous enrichments, even negative $\Delta^{17}O$ values (34), throughout ozone in an attempt to reconcile experimental observations. Precise and accurate measurements of ozone's $\Delta^{17}O$ internal distribution is therefore needed to test the symmetry hypothesis and for accurate modeling of transfer reactions in the atmosphere. Here, we present these measurements using a relatively simple analytical technique.

The internal distribution of oxygen isotopes in ozone was determined by taking advantage of an isotope transfer reaction. The challenge in using this approach is that the reaction must be quantitative (go to completion), there can be no isotopic exchange with spectator compounds or reaction intermediates, and there must be some experimental or theoretical evidence of the transition state structure or the branching ratios of the reaction. Recent works examining $\Delta^{17}O$ transfer reactions were limited in that they did not meet all of these criteria (35, 36). The aqueous phase oxidation reaction $NO_2^- + O_3 \rightarrow NO_3{}^- + O_2$ was used in the present work. This is a very rapid reaction (5.83×10^5 $M^{-1}s^{-1}$) that quickly goes to completion, and previous studies by Liu et al. showed that this was a oxygen atom transfer reaction (37). In addition, their ab initio calculations showed that the reaction pathway proceeded through an adduct conformation where the NO_2^- only abstracted the terminal atom (37) from the ozone molecule (Fig. 1). Control experiments carried out in this work using NO_2^- solutions mixed with isotopically unique waters showed that no water molecules were incorporated into the product $NO_3{}^-$ or O_2 at the conclusion of the experiments. Furthermore, both of the products (O_2 and $NO_3{}^-$) are resilient to water exchange in solution over 1,000-year time scales. The

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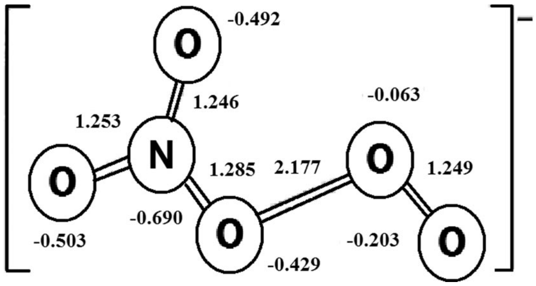

Fig. 1. Transition state of the O_3 + NO_2^- reaction showing terminal atom extraction. From Liu et al. (37).

terminal-only transition state, rapid reactivity, and lack of isotopic exchange make the NO_2^- + O_3 an ideal system to probe ozone's internal isotopic distribution.

Results and Discussion

To test the symmetry hypothesis, the isotopic composition of the O_2 product is measured with respect to the initial ozone for each experiment. If the $\Delta^{17}O$ anomaly is statistically distributed throughout the molecule, then the product O_2 would have the same $\Delta^{17}O$ value as the initial ozone. If, however, the anomaly is located only in the terminal atom, then the product O_2 $\Delta^{17}O$ value will be 3/4 of the O_3 $\Delta^{17}O$ value (see *Methods*). Fig. 2 shows the $\Delta^{17}O$ correlation plot of the measured O_2 relative to that predicted based on the measured bulk O_3 $\Delta^{17}O$ value and assuming $\Delta^{17}O$ resides only in the terminal atom. The regression of 0.86 and $r^2 = 0.98$ value is close to a 1:1 correspondence between the terminal only hypothesis and the O_2 $\Delta^{17}O$ observations. If 2 of the data points are excluded, then the regression improves to 0.95. The average difference between the terminal atom hypothesis and the observed O_2 $\Delta^{17}O$ value is 0.55‰ with a standard deviation of ±0.88‰ ($n = 14$). The negligible scatter in the data and the offset is likely due to a small percentage of the ozone breaking down on the reaction chamber walls, which would lead to an increase in the O_2 $\Delta^{17}O$ value. In contrast, assuming an approximately statistical distribution of $\Delta^{17}O$ among all atoms the O_2 generated would be 33% more enriched than our observations. This strongly suggests that the terminal atom possesses the $\Delta^{17}O$ anomaly in agreement with recent spectroscopic studies (38) and is similar to conclusions based on studies of oxidation of silver by ozone (35), and the mechanism suggested in the non-RRKM model (7, 26). We note that when trying to produce small $\Delta^{17}O$ values by manipulation at very low pressures and prolonged discharge times part of the $\Delta^{17}O$ begins to shift to the central position. Such extreme conditions are not realized in the atmosphere and would not be of relevance for modeling of $\Delta^{17}O$ transfer during oxidation reactions in the stratosphere or troposphere.

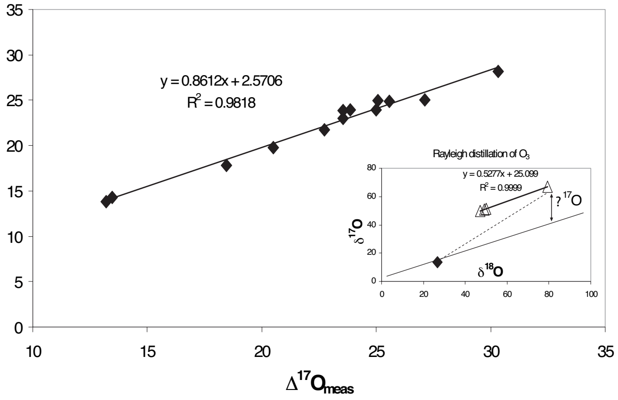

Fig. 2. Measured $\Delta^{17}O$ in product O_3 versus $\Delta^{17}O$ model (solid diamonds) assuming only the terminal atom contains the anomaly (i.e., $O_2 = \frac{3}{4} O_3$). (*Inset*) Rayleigh distillation of O_3 (open triangle) produced using O_2 (filled diamond) then distilled at 77 K and collected in 4 separate fractions (open triangles). The 2 largest $\Delta^{17}O$ values are ≈2‰ enriched over the modeled value which, if excluded, would improve the correlation to $R^2 = 0.95$.

Evaluation of the positional dependence of the ^{18}O enrichments is more complex because one must distinguish between the $\delta^{18}O$ generated during the O_3 formation process and the changes in the $\delta^{18}O$ via kinetic or equilibrium effects arising during the oxidation experiment. For example, there may be a mass-dependent alteration in the ozone $\delta^{18}O$ values by incomplete trapping in the flow system at 77 K. This can be seen in the Fig. 2 *Inset*. The data show a control experiment where the initial O_2 (solid diamond) is partially converted to O_3 (product O_3 is connected to O_2 via the dashed line). The vapor pressure of O_3 at 77 K is ≈3 millitorr, and this small gaseous component of the total O_3 was collected in 4 stages as a function of time onto a molecular sieve. The resulting fractionation gives a $\delta^{17}O$ vs. $\delta^{18}O$ slope of 0.5277, showing that the ozone evaporative process follows a normal, isotopic mass-dependant equilibrium vapor pressure law. This means that although the $\delta^{18}O$ may be altered by incomplete trapping, the process is mass dependent, and the $\Delta^{17}O$ value is conserved (Fig. 2). However, this should be a small $\delta^{18}O$ effect because O_3 production rate, based on a function of the flow rates and times of collection, suggests that the partial pressure of O_3 was ≈300 millitorr (99% trapping efficiency). Similarly, in the reaction between O_3 and NO_2^-, there will be different mass-dependent kinetic isotope effects (KIE) during each of the bond-breaking reaction pathways: O—O—^{18}O (asym-1), ^{18}O—O—O (asym-2), and O—^{18}O—O (sym). As a result of the small isotope effects associated with the O_3 collection and KIE of the reaction, the $\delta^{18}O$ value of our product O_2 is a function of both the initial isotopic distribution in ozone and these processes. These isotope effects, however, are typically much smaller than the high isotopic enrichments observed during ozone formation, so it is still informative to examine the results of ^{18}O in these experiments given these limitations.

Recent work by Janssen (30) examined the isotopic branching ratio for the symmetric and asymmetric isotopologues, called the r_{50} (ratio of mass 50), which statistically should be equal to 2. We used a quadratic fit of Janssen's r_{50} data relative to his measured O_3 bulk enrichment, then used that equation to calculate r_{50} using our bulk ozone $\delta^{18}O$ values, and from that the expected $\delta^{18}O$ value of O_2 in our experiments. The measured O_2 $\delta^{18}O$ values in this work were offset by −3.9‰ ± 2.7‰ relative to the quadratic fit. This is in fairly good agreement with spectroscopic evaluations of the positional dependence of the ^{18}O enrichment considering the experimental uncertainty in those experiments is on the order of ≈6‰ (38). From a kinetic perspective, the ^{18}O is more likely to be incorporated into the more strongly bonded NO_3^- (symmetric 2 pathway) leaving product O_2 depleted in ^{18}O, which may explain the −3.9‰ offset. Such a small KIE would not be surprising. One of the most important KIE mass-dependent factors, collisional frequency, is the same for the single isotopic substituted isomers (doubly substituted are statistically negligible). Second, the ground state zero point energy of the asymmetric isotopologue is the same for either pathway (asym-1, asym-2), so this important factor is negated in the branching ratio rates. Therefore, only a small contribution of the transition state vibrational frequencies and the zero point energy difference in the symmetric isotopologue will contribute to the KIE of the reaction. After correcting the O_2 $\delta^{18}O$ data by using this −3.9‰ KIE, the $\delta^{18}O$ values in the present work agree with Janssen's review to within ±3‰. Using these results, we have formulated an empirical linear fit of the $\delta^{18}O$ terminal and

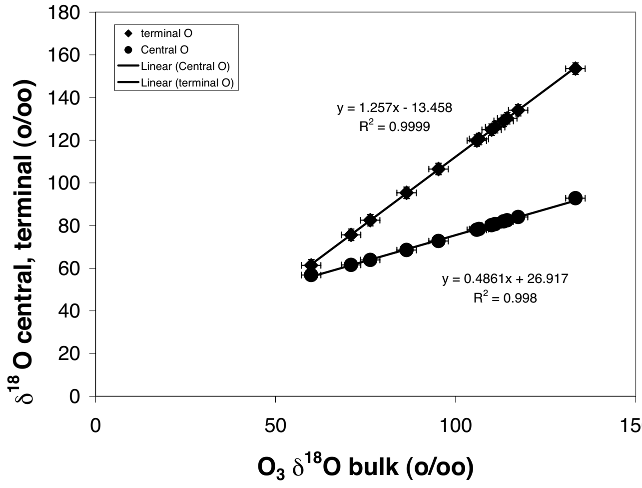

Fig. 3. Empirical relationship between the δ^{18}O value of the terminal and central atoms of the ozone molecule with respect to the bulk O_3 δ^{18}O values expected under tropospheric/stratospheric conditions.

δ^{18}O central for O_3 relative to the bulk ozone enrichment by using Janssen's r_{50} values and our corrected O_2 δ^{18}O enrichments values (Fig. 3; see *Methods*). When we compare terminal atom δ^{18}O values using our linear fit relative to those derived with the quadratic fit given by Janssen, the correlation between the 2 values are essentially identical with a $R^2 = 0.9999$ (related by $0.7955x + 10.714$, where x is our δ^{18}O value).

The reaction $NO_2^- + O_3$ was used to determine the internal distribution of the Δ^{17}O anomaly and the δ^{18}O partitioning within the ozone molecule. The data show that the Δ^{17}O anomaly is indeed found in the terminal position in agreement with the most recent theoretical assertions (26–28). Our estimates of the positional dependence of the ^{18}O enrichments are also in good agreement with other investigators (39). We conclude that although the overall isotopic enrichment is distributed throughout the ozone molecule, there is an anomalous excess in the terminal atoms. These findings should improve the photochemical modeling of Δ^{17}O transfer reactions such as $CO_2 + O^1D$ exchange (40, 41) and NO_x conversion to HNO_3 (16, 36). We note, however, that most of the Δ^{17}O values measured in tropospheric O_3 (12,14) fall outside their expected values based on temperature and pressure dependencies of formation (11, 30, 39, 42). Using quadratic fits of Morton et al.'s data, and using temperature and pressures typical of conditions during the tropospheric ozone measurements of Johnston and Thiemens, we derive expected δ^{18}O values of 75–85‰ (relative to air O_2), which are similar to, but offset from, the observed 70–97‰ values. Using the same approach, the expected ozone Δ^{17}O values are 33–37‰, significantly different from the observed Δ^{17}O values of 26 ± 4‰ (12). This is a serious limitation and needs to be resolved before any climatic or chemical interpretation of Δ^{17}O transfer models can be considered valid. We note that the Δ^{17}O signal is transferred to NO_3^- during the $NO_2^- + O_3$ reaction and that this may be an experimental approach for assessing tropospheric Δ^{17}O variations.

Methods

Ozone was produced by electric discharge in a flow system where the Δ^{17}O anomaly and δ^{18}O composition was varied by altering the O_2 pressure and temperature at the discharge interface. The ozone was collected downstream by using a liquid nitrogen trap. The system was then evacuated (10^{-4} torr) and the ozone thawed to room temperature. An aliquot of O_3 was collected on a molecular sieve for isotopic analysis. The remaining ozone (≈100 μmol) was transferred to a reaction tube containing 1 mL of a 1 M NO_2^- solution that had been previously degassed of dissolved O_2 (no O_2 could be detected after degassing step). The 10:1 NO_2^-/O_3 ratio ensures a rapid, complete reaction ($\tau \approx 0.02$ s) and limits O_3 breakdown on reaction vessel walls. Yields based on product O_2 pressure were always >95%. The product O_2 was collected for isotopic analysis, which was conducted at the Purdue Stable Isotope (PSI) facility by using a Thermo DeltaV isotope ratio mass spectrometer. The ln form of the Δ^{17}O equation $[\ln(1{,}000 + \delta^{17}O) - 0.52(\ln(1{,}000 + \delta^{18}O)]$ was used for all data.

The derivation of the Δ^{17}O of O_2 being 3/4 of O_3 bulk Δ^{17}O rule is as follows: Assuming the Δ^{17}O enrichment is statistically distributed the isotope mass balance dictates that $\Delta^{17}O_{bulk} = 1/3\ \Delta^{17}O_{central} + 2/3\Delta^{17}O_{terminal}$ (1). The use of the model that the Δ^{17}O is only in the terminal position means the $\Delta^{17}O_{central}$ term is equal to zero and solving for $\Delta^{17}O_{terminal}$ yields $\Delta^{17}O_{terminal} = 3/2\Delta^{17}O_{bulk}$. Because the O_2 formed by the transition state in Fig. 1 acquires 1 oxygen atom from the central position and 1 from the terminal position then $\Delta^{17}O_{O2} = ½(3/2\Delta^{17}O_{bulk}) + ½(\Delta^{17}O_{central}) = 3/4\Delta^{17}O_{bulk}$, because $\Delta^{17}O_{central}$ is taken to be zero in ref. 1. For determining ozone's δ^{18}O terminal and central enrichment we also start with statistical isotopic mass balance: $\delta^{18}O_{bulk} = 1/3(\delta^{18}O_{cent}) + 2/3(\delta^{18}O_{terminal})$ (2) and deviation from this statistical assumption by $r_{50} = 2(\delta^{18}O_{term} + 1)/(\delta^{18}O_{cent} + 1)$ (3). Using bulk ozone δ^{18}O values and Janssen's r_{50} values, one can solve for the expected $\delta^{18}O_{terminal}$ and $\delta^{18}O_{central}$. Again using the Fig. 1 transition state, the product O_2 δ^{18}O value can be derived from $½\ \delta^{18}O_{terminal} + ½\ \delta^{18}O_{central}$] and compared with our data. The −3.9‰ offset is corrected in the data as the reaction KIE and Fig. 3 is generated by plotting $\delta^{18}O_{terminal}$ and $\delta^{18}O_{central}$ versus the measured ozone $\delta^{18}O_{bulk}$ with the error bars being the observed deviation in the O_2 δ^{18}O data from the expected values.

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