

Isotopic fractionation of the O₃-nitric oxide reaction

Supriyo Chakraborty^{†,*} and
Subrata Chakraborty[‡]

Department of Chemistry, University of California, San Diego, CA 92093, USA.

[†]Present address: Birbal Sahni Institute of Paleobotany, Lucknow 226 007, India

[‡]Physical Research Laboratory, Navrangpura, Ahmedabad 380 009, India

Atmospheric ozone is known to possess mass-independent isotopic enrichment in both ¹⁸O and ¹⁷O (relative to ambient oxygen) and at the ground level it exhibits high regional variability, which is reflected through the different slope values in the three-isotope plot and is believed to be controlled by transport and chemical transformation processes. The fractionation factors associated with these processes are essential to model the observed distribution of isotopic composition. We show here that one of the important *in situ* ozone destruction processes, i.e. reaction with nitric oxide (NO), proceeds in a mass-dependent way with an instantaneous fractionation factor of 30.5‰.

THE isotopic composition of atmospheric ozone is found to be isotopically anomalous; it is enriched in both ¹⁸O and ¹⁷O (with respect to atmospheric oxygen) and their relative enrichment does not obey the conventional mass-dependent fractionation relationship ($\delta^{17}\text{O} = 0.52 \delta^{18}\text{O}$). The enrichments in stratospheric ozone are very high¹⁻³ and it increases with increase in altitude following a slope value of 0.62 in a three-isotope plot ($\Delta\delta^{17}\text{O}$ vs $\Delta\delta^{18}\text{O}$) (ref. 4). Unlike stratosphere, tropospheric ozone is not well constrained. The tropospheric ozone measurements were reported by Krankowsky *et al.*⁵ and Johnston and Thiemens⁶, which show that the tropospheric ozone possesses relatively lower enrichments compared to that of stratosphere. Interestingly, measurement of Johnston and Thiemens⁶ reflects the regional variation of isotopic composition. They sampled ozone from three different environments (two urban and one remote locations) and found that the enrichment in ¹⁸O for the three environments are comparable (La Jolla: 82.3 ± 6.7 ; Pasadena: 86.1 ± 5.6 ; White Sand Missile Range (WSMR): 89.7 ± 4.3) but having large variations in ¹⁷O enrichment within rural and urban environments (La Jolla: 69.1 ± 6.5 ; Pasadena: 66.0 ± 3.3 ; WSMR: 78.0 ± 5.4), which is reflected in the slope values in a three-isotope plot (La Jolla: 0.72; Pasadena: 0.54; WSMR: 1.1) for the three regions (see figure 5 of ref. 6). In addition to the observed regional variation, large range of values for $\delta^{18}\text{O}$ (27‰) and $\delta^{17}\text{O}$ (46‰) were also observed for a particular location due to seasonal variation⁵. Though some of the differ-

ences in isotopic signatures of stratospheric and troposphere ozone can be explained in terms of temperature and pressure dependence of the O + O₂ recombination reaction^{7,8}, many features still remain unaccounted for.

The tropospheric ozone has two major sources: (1) transport from stratosphere, and (2) *in situ* photochemical production. These two are balanced by two major decomposition pathways, (1) decomposition on the Earth's surface and (2) chemical destruction. Operation of these processes in differential temporal and spatial scales makes the tropospheric ozone budget complex. Each of the sources and sink processes have the potential to control the enrichment value of a region, nevertheless, all these processes may not have the potential to vary the slope values to any large extent. Among the two source processes, the transported component would only reflect the stratospheric composition and the *in situ* production would reflect nearly a slope of unity⁸, therefore, the observed variation in the slope values (sometimes close to the mass dependent slope of 0.52) might only be explained through the sink processes. Among the two sink processes; destruction at the Earth surface is very difficult to estimate. There is only one recent study, which shows dissociation of ozone on a glass or a quartz surface proceeds in a mass-independent way⁹. The other sink processes, i.e. *in-situ* chemical destruction may be of interest in this respect. The chemical chain reactions, which comes under this group can be represented simplistically by the pair of reactions



Several species have been suggested for the catalytic 'X' in the atmosphere. The most important of these are X = NO, Cl, Br, and possibly iodine. Moreover, among this group, NO is one of the major species contributing significantly particularly in the stratosphere¹⁰ and in polluted urban areas¹¹ through the reaction,



The ambient NO_x mixing ratio varies significantly in the above three-mentioned sample locations. The NO_x concentrations in WSMR is quite low about <1 ppbv and at La Jolla the concentration is highly variable with a mean value of 11 ± 15 ppbv. At Pasadena, the NO_x concentration is consistently high with an average of 55 ± 12 ppbv (ref. 6). Unfortunately, there is no direct correlation observed between the ozone and NO_x concentration⁶. At the same time it is evident from the data that with the increasing NO_x concentration, the slope value decreases.

In this context, it is important to evaluate the relative role of R2 in the isotopic fractionation in ozone as well as the associated fractionation factor of this reaction to

*For correspondence. (e-mail: subrata@prl.ernet.in)

decipher the variation in the slope values observed at different tropospheric environments. In this communication, we have determined the associated fractionation factor of the above reaction and the possible implications for tropospheric and stratospheric ozone are discussed.

The experiment initiates with the production of ozone via electrical (Tesla) discharge from an isotopically characterized O_2 gas (ultra high purity Matheson gas, UPHO hereafter) in a 85 cm^3 glass chamber at a pressure of 28 mbar. The formed ozone was continuously condensed at the bottom of the chamber with liquid nitrogen. At the end of the conversion process, the unreacted oxygen was pumped out. It was estimated that approximately 98% of initial oxygen gets converted to ozone. This process was repeated a number of times to ascertain the isotopic composition ($\delta^{18}O = -0.5\text{‰}$ and $\delta^{17}O = -0.6\text{‰}$ with respect to UPHO) and amount of ($\sim 67\text{ }\mu\text{mol}$) of product ozone. Following ozone formation an aliquot of purified NO ($9.2\text{ }\mu\text{mol}$) was admitted into the chamber with O_3/NO ratio of about 7. The chamber was warmed to room temperature initiating the $O_3 + \text{NO}$ reaction. After sufficient time ($\sim 20\text{ min}$), ensuring significant reaction extent, the chamber was frozen in liquid nitrogen and the non-condensable component, O_2 were separated from unreacted NO, product NO_2 , and left-over ozone. Subsequently, ozone was separated from NO and NO_2 mixture using -110°C slush. The oxygen and ozone were collected on a molecular sieve at liquid nitrogen temperature. Ozone was decomposed to oxygen by repeated freezing and thawing in the molecular sieve. The oxygen and ozone (as oxygen) pressures were measured by a Baratron capacitance manometer and their amounts were estimated. The oxygen and ozone (as oxygen) isotopic ratios were determined by using a Finnigan MAT 251 isotope ratio mass spectrometer with analytical uncertainties of ± 0.1 and $\pm 0.2\text{‰}$ for $\delta^{18}O$ and $\delta^{17}O$ respectively (all the measurements are carried out with respect to UPHO as machine standard). The experimental procedure was repeated, with various O_3/NO ratios ranging from >7 to about 7 in four other experiments.

The result shows that the dissociation of ozone through NO enriches the left-over ozone (with respect to initial ozone) in a mass-dependent way with a slope value of 0.52 ± 0.001 (Figure 1). The extent of enrichment increases with the decrease in O_3/NO as expected and attains a value of $\Delta\delta^{18}O = 96.6\text{‰}$ at a ratio of 1.8. Consequently, the product oxygen gets depleted (following a similar slope value as that of ozone). Since the isotopic composition of other species were not measured, the isotopic mass-balance was not possible to check.

In order to determine the fractionation factor α we assume a Rayleigh model of the form $R = R_0 f^{(\alpha-1)}$, where R_0 and R are the respective initial and final $^{18}O/^{16}O$ ratios of ozone and f is the fraction of ozone left after the reaction. Rewriting the Rayleigh equation in δ notation we obtain¹²,

$$\ln(1 + 0.001*\delta) = \ln(1 + 0.001*\delta_0) + (\alpha - 1)\ln f, \quad (R3)$$

where δ_0 and δ are the initial and final $\delta^{18}O$ respectively. Figure 2 shows the correlation diagram between $\Delta\ln(1 + 0.001*\delta)$ (i.e. $\ln(1 + 0.001*\delta) - \ln(1 + 0.001*\delta_0)$) and $\ln f$. The slope of this line was used to calculate the fractionation factor, and found to be $\alpha = 1.0305$, implying a single stage fractionation of 30.5%.

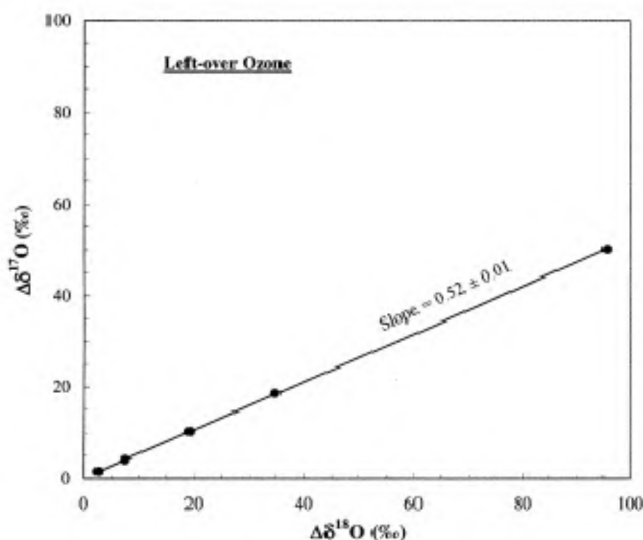


Figure 1. The three-isotope plot for the left-over ozone showing $\text{NO} + \text{O}_3$ reaction proceeds in a mass-dependent way (slope = 0.52 ± 0.1) enriching the left-over ozone compared to the initial ozone. The extent of reaction increases with the decrease of O_3/NO ratio and hence, the enrichment in left-over ozone increases (as described in the text).

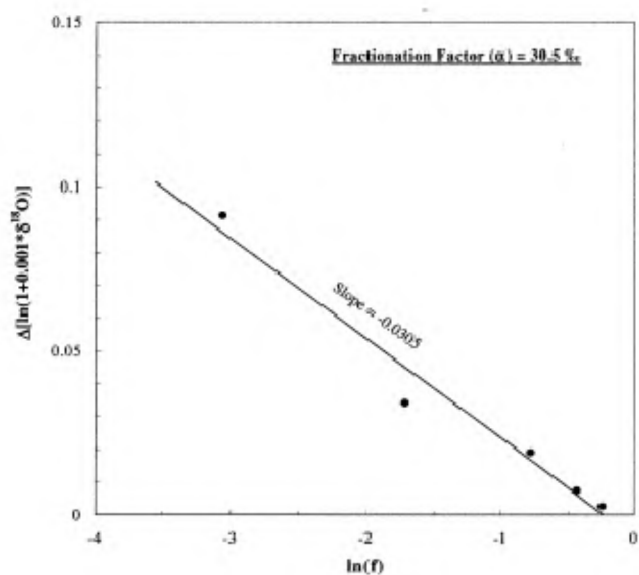


Figure 2. Correlation plot between $\Delta\ln(1 + 0.001*\delta)$ and $\ln(f)$ (the symbols are explained in the text) following a Rayleigh model to calculate the fractionation factor (α) associated with $\text{NO} + \text{O}_3$ reaction. From the slope value of the best fit line of this correlation diagram, the calculated α comes out to be 1.0305 (or 30.5%).

It is known that with the decrease of NO concentration from 50 to 1 ppbv, the lifetime of ozone increases from 42 s to 30 min⁶. Therefore, the recycling of ozone through NO is far more efficient for Pasadena compared to WSMR. Coupling of the above fact with this experimental finding (i.e. mass-dependent fractionation with large fractionation factor) leads us to conclude that more the recycling of ozone through NO, more is the enrichment (in $\delta^{18}\text{O}$) and less is the slope from its expected value (from $\text{O} + \text{O}_2$ recombination reaction) of unity. Hence, the slope values observed in the three environments were consistent with the NO_x concentrations of these three sampling locations. Though large enrichment variations in ^{18}O were not observed consistent with their corresponding slope values, that can be interpreted as effect of other source process controlling the enrichment as described earlier. Moreover, this fractionation factor may be a useful parameter for the mathematical modelling to construct the isotopic budget of tropospheric ozone.

It was recently proposed by Bhattacharya *et al.*¹³ that dissociation of ozone plays a significant role over the above temperature effect¹⁴ in deciding the isotopic enrichment in stratospheric ozone. Moreover, the observed slope ($\Delta\delta^{17}\text{O}/\Delta\delta^{18}\text{O}$) in lower stratosphere (up to 33 km) is 0.62⁴ instead of what was expected from $\text{O} + \text{O}_2$ recombination reaction (nearly unity). Additionally, it is also known that the observed stratospheric ozone concentration is half of that calculated from Chapman's cycle and is attributed to the catalytic destruction cycle. Therefore, the $\text{NO} + \text{O}_3$ reaction can be considered as a representative reaction for the catalytic cycles active in destroying ozone and hence, both the lowering of slope value as well as the increase in enrichment with altitudinal in stratospheric ozone can be accounted.

The $\text{NO} + \text{O}_3$ sink reaction follows a mass-dependent path with a significantly large associated fractionation factor ($\alpha=1.0305$, or 30.5‰) enriching the left-over ozone. This can be used as an important parameter to model the tropospheric ozone budget. This reaction has the potential to control the relative variations of oxygen isotopic enrichments in ozone at different tropospheric environments. Additionally, this reaction can be used as a representative reaction for catalytic cycles to explain the observed slope value and the altitudinal variation of enrichment in stratospheric ozone.

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Influence of methyl jasmonate and salicylic acid in the enhancement of capsaicin production in cell suspension cultures of *Capsicum frutescens* Mill

G. Sudha and G. A. Ravishankar*

Department of Plant Cell Biotechnology, Central Food Technological Research Institute, Mysore 570 013, India

The cell suspension cultures of *Capsicum frutescens* were treated with two signalling compounds, salicylic acid (SA) and methyl jasmonate (MeJA), individually, and in combination. SA and MeJA were found to individually enhance capsaicin production, but when administered in combination there was no further enhancement in capsaicin production. Both the signalling compounds were also found to result in higher leaching of capsaicin into the medium. The endogenous polyamine (PA) levels were higher in the treatments with SA and lower in the treatments with MeJA. The endogenous PA levels were found to be the highest on the sixth day of culture, after which the ethylene levels were found to increase. Maximum ethylene produc-

*For correspondence. (e-mail: pcbt@cscftri.res.nic.in)