Carbon dioxide in the atmosphere: Isotopic exchange with ozone and its use as a tracer in the middle atmosphere

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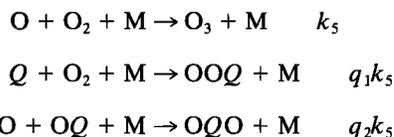
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Abstract. Atmospheric heavy ozone is enriched in the isotopes ^{18}O and ^{17}O. The magnitude of this enhancement, of the order of 100‰, is very large compared with that commonly known in atmospheric chemistry and geochemistry. The heavy oxygen atom in heavy ozone is therefore useful as a tracer of chemical species and pathways that involve ozone or its derived products. As a test of the isotopic exchange reactions, we successfully carry out a series of numerical experiments to simulate the results of the laboratory experiments performed by *Wen and Thiemens* [1993] on ozone and CO_2. A small discrepancy between the experimental and the model values for ^{17}O exchange is also revealed. The results are used to compute the magnitude of isotopic exchange between ozone and carbon dioxide via the excited atom $O(^1D)$ in the middle atmosphere. The model for ^{18}O is in good agreement with the observed values.

Introduction

More than a decade after the discovery of the anomalous heavy ozone fractionations in the atmosphere [*Mauersberger*, 1981] and in the laboratory [*Thiemens and Heidenreich*, 1983], the mechanism responsible for this effect was identified and quantified. It is now well established both in the atmosphere and in the laboratory that when ozone is formed from O and O_2 via the three-body (Chapman) reaction, there is a preference for the formation of heavy ozone. Let Q = heavy oxygen atom (^{18}O or ^{17}O). The Chapman reactions for ozone and heavy ozone are as follows:

$$O + O_2 + M \rightarrow O_3 + M \qquad k_5$$

$$Q + O_2 + M \rightarrow OOQ + M \qquad q_1 k_5$$

$$O + OQ + M \rightarrow OQO + M \qquad q_2 k_5$$

where M is the third body, q_1 and q_2 are enrichment factors, and k_5 is the rate coefficient in units of $cm^6 s^{-1}$ [*DeMore et al.*, 1994]. A series of laboratory experiments [*Heidenreich and Thiemens*, 1986; *Morton et al.*, 1989; *Thiemens and Jackson*, 1990] have demonstrated over a wide range of pressures and temperatures relevant to the stratosphere and the troposphere that q_1 and q_2 are of the order of magnitude of 1.10 to 1.15. These values are very large compared to what is expected from equilibrium statistical processes [*Kaye and Strobel*, 1983; *Kaye*, 1986, 1987]. Another important aspect of this fractionation is that the enrichments in ^{17}O and ^{18}O are related to each other with a slope of 1 [*Thiemens and Heidenreich*, 1983] rather than 0.5, a value that is characteristic of equilibrium processes

[*Kaye*, 1987]. Hence there remains a fundamental challenge to the physical chemist to explain the isotopic fractionation factors. The most likely explanation is that the formation of ozone goes through one or more of the weakly bound states [*Anderson and Mauersberger*, 1995] or that the formation reaction is subject to nuclear symmetry-based restrictions [*Gellene*, 1996]. However, as far as atmospheric applications are concerned, the laboratory values are adequate and appear to be consistent with the recent extensive data set obtained by the ATMOS experiment [*Irion et al.*, 1996]. In view of the new data set, the early high ozone fractionations reported by *Mauersberger* [1981] may not be typical of the stratosphere and could imply the existence of another source of ozone such as stratospheric lightning. *Boeck et al.* [1995] recently reported shuttle observations of lightning flashes and lightning strokes that extended 30 to 40 km above a thunderstorm. However, the amount of ozone that can be made in these events has not been quantitatively evaluated.

A notable recent advance in our knowledge of heavy ozone was obtained by *Johnston et al.* [1995] and *Krankowsky et al.* [1995], who measured the isotopic fractionation of tropospheric ozone. To first order, the measured fractionations are consistent with those in stratospheric ozone when scaled by appropriate pressures and temperatures according to *Morton et al.* [1989].

The existence of a large isotopic fractionation in a common and reactive molecule such as ozone provides atmospheric chemistry with exciting opportunities for tracing species and chemical pathways for reactions that involve ozone and its dissociation products. Let the fractional abundance of Q relative to O be f. From the above discussion and Table 1 we have

$$\frac{[OOQ]}{[O_3]} = 2E_1 f \qquad (1)$$

$$\frac{[OQO]}{[O_3]} = E_2 f \qquad (2)$$

Table 1. List of essential reactions used in the photochemical model

	Reaction	Rate Coefficient
(R1a)	$O_3 + h\nu \rightarrow O_2(^1\Delta) + O(^1D)$	$y_1 J_1$
(R1b)	$\rightarrow O_2 + O$	$y_2 J_1$
(R2a)	$OQO + h\nu \rightarrow O_2(^1\Delta) + Q(^1D)$	0
(R2b)	$\rightarrow O_2 + Q$	0
(R3a)	$OQO + h\nu \rightarrow OQ(^1\Delta) + O(^1D)$	$y_1 J_1$
(R3b)	$\rightarrow OQ + O$	$y_2 J_1$
(R4a)	$OOQ + h\nu \rightarrow OQ(^1\Delta) + O(^1D)$	$\frac{1}{2}y_1 J_1$
(R4b)	$\rightarrow O_2(^1\Delta) + Q(^1D)$	$\frac{1}{2}y_1 J_1$
(R4c)	$\rightarrow QO + O$	$\frac{1}{2}y_2 J_1$
(R4d)	$\rightarrow O_2 + Q$	$\frac{1}{2}y_2 J_1$
(R5)	$O + O_2 + M \rightarrow O_3 + M$	k_5
(R6)	$Q + O_2 + M \rightarrow OOQ + M$	$k_6 = q_1 k_5$
(R7a)	$O + OQ + M \rightarrow OOQ + M$	$k_{7a} = \frac{1}{2}q_1 k_5$
(R7b)	$\rightarrow OQO + M$	$k_{7b} = \frac{1}{2}q_2 k_5$
(R8)	$O(^1D) + CO_2 \rightarrow CO_2 + O$	$k_8 = 6.9 \times 10^{-11} e^{117/T}$
(R9a)	$Q(^1D) + CO_2 \rightarrow Q + CO_2$	$k_{9a} = \frac{1}{3}k_8$
(R9b)	$\rightarrow O + COQ$	$k_{9b} = \frac{2}{3}k_8$
(R10a)	$O(^1D) + COQ \rightarrow Q + CO_2$	$k_{10a} = \frac{1}{3}k_8$
(R10b)	$\rightarrow O + COQ$	$k_{10b} = \frac{2}{3}k_8$
(R11)	$Q + O_2 \rightarrow O + OQ$	$k_{11} = 2.90 \times 10^{-12}$
(R12)	$O + OQ \rightarrow Q + O_2$	$k_{12} = \frac{1}{2}q_3 k_{11}$
(R13a)	$O + O_3 \rightarrow 2O_2$	$k_{13a} = 8.0 \times 10^{-12} e^{-2060/T}$
(R13b)	$Q + O_3 \rightarrow OQ + O_2$	$k_{13b} = k_{13a}$
(R13c)	$O + OOQ \rightarrow OQ + O_2$	$k_{13c} = k_{13a}$
(R13d)	$O + OQO \rightarrow OQ + O_2$	$k_{13d} = k_{13a}$
(R14)	$P + O_2 \rightarrow O + OP$	$k_{14} = k_{11}$
(R15)	$O + OP \rightarrow P + O_2$	$k_{15} = \frac{1}{2}q_4 k_{11}$

The units for photodissociation, two-body and three-body rate coefficients are s^{-1}, $cm^3 s^{-1}$, and $cm^6 s^{-1}$, respectively. Unless otherwise stated, all kinetic data are taken from *DeMore et al.* [1994]. $Q = {}^{18}O$, $P = {}^{17}O$.

$$\frac{[Q(^1D)]}{[O(^1D)]} = E_1 f \qquad (3)$$

where the excited atoms $Q(^1D)$ and $O(^1D)$ are derived from

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$OOQ + h\nu \rightarrow O_2 + Q(^1D)$$
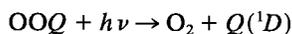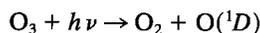
The enrichment values E_1 and E_2 are given by q_1 and q_2, respectively, for the Chapman process. There is little fractionation from photolysis itself. The isotopic enrichment in the above species will affect the isotopic composition of other stratospheric species. One such connection was proposed by *Yung et al.* [1991] to explain the isotopic fractionation in CO_2 in the stratosphere measured by *Gamo et al.* [1989] and confirmed by *Thiemens et al.* [1991], who also extended the measurements to ${}^{17}O$ fractionation [*Wen and Thiemens*, 1993; *Thiemens et al.*, 1995a, 1995b]. The latter work established that the enrichments of ${}^{18}O$ and ${}^{17}O$ obey a relation of slope 1 (characteristic of similar enrichments observed in heavy ozone). An

explanation of the observed fractionation was given by *Yung et al.* [1991], who proposed the exchange reactions

$$Q(^1D) + CO_2 \rightarrow (COOQ)^*$$

$$\rightarrow COQ + O$$

$$O(^1D) + COQ \rightarrow (COQO)^*$$

$$\rightarrow CO_2 + Q$$
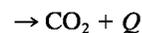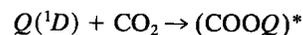
(see *Yung et al.* [1991] for details concerning the $(COOQ)^*$ and $(COQO)^*$ complexes). Note that the photolysis of OQO is not capable of producing a $Q(^1D)$. Since heavy ozone (OOQ) is enriched in Q, it follows that $Q(^1D)$ is enriched relative to $O(^1D)$. (See Table 1 for a complete listing of relevant reactions.) It can be shown that in photochemical equilibrium with the above reactions we have

$$\frac{[COQ]}{[CO_2]} = 2E_1 f \qquad (4)$$

Of course, atmospheric mixing (with the troposphere) will result in an isotopic dilution, and the resulting enrichment would be considerably less than the equilibrium value.

This paper is divided into two parts. We will apply the chemical scheme in Table 1 to simulate the laboratory measurements of *Wen and Thiemens* [1993] on the exchange of heavy oxygen atoms between O_3 and CO_2. Using the modeling results and more recent observations, we may now refine the atmospheric model of *Yung et al.* [1991]. The implications of the model for the use of isotopomers of CO_2 as tracers in the middle atmosphere are discussed.

Model Simulation of Laboratory Results for Isotopic Fractionations

As an application of the chemical scheme outlined in Table 1, we shall apply it to simulate the results of a series of laboratory experiments performed by *Wen and Thiemens* [1993, hereinafter referred to as WT93].

In the experiments of WT93, about 30 torr of O_3 of known initial isotopic composition was radiated by a Hg lamp in the presence of large amounts (600 torr) of CO_2. The details of the experiments are referred to J. Wen's Ph.D. thesis [*Wen*, 1991]. The Hg lamp emits light at 185 and 254 nm, and at these wavelengths O_3 is photolyzed in the Hartley band, producing an excited O atom in the ^1D state. The latter can undergo exchange with CO_2 but eventually turns into an O atom in the ground state that can react with O_3 to form O_2. Ultimately, all O_3 in the experiment was converted to O_2. The most interesting results of this work are summarized in Table 7 and Figure 5 of WT93. The most puzzling aspect of these experiments is that the isotopic fractionations of the end product (O_2) in ^{17}O and ^{18}O were always about $-55\%o$ and $-75\%o$, respectively, regardless of the initial isotopic fractionation of O_3. To date, these results have never been explained by a kinetic model.

We carried out a series of numerical experiments to understand the results of the laboratory experiments performed by *Wen and Thiemens* [1993] using the reactions and rate coefficients presented in Table 1.

The temperature, the initial concentrations in the experiments, and the reference value for the isotopic ratio are

Table 2a. Summary of Model Runs: From Baseline Model to Standard Model

Model Run	Model Assumptions	Isotopic Fractionation in OQ
1	baseline $q_1 = q_2 = q_3 = 1$ initial CO_2 and O_3 $\delta Q = 0$	$-0.1\%o$
2a	initial O_3 $\delta Q = 100\%o$	$6.9\%o$
2b	initial O_3 $\delta Q = -100\%o$	$-7.2\%o$
3	baseline + exchange reactions (R11) and (R12) with $q_3 = 1-76.5\%o$	$36.6\%o$
4	model 3 + Chapman reactions (R5), (R6), and (R7) with $q_1 = q_2 = 1 + 90\%o$	$-43.2\%o$

Table 2b. Summary of Model Runs: Testing Sensitivity of Standard Model to Rate Coefficients

Model Run	Model Assumptions	Isotopic Fractionation in OQ
4	standard model $q_1 = q_2 = 1 + 90\%o$ $q_3 = 1-76.5\%o$ $y_1 = 0.95, y_2 = 0.05$	$-43.2\%o$
5a	same as model 4 except $q_1 = q_2 = 1 + 120\%o$	$-66.6\%o$
5b	same as model 4 except $q_1 = q_2 = 1 + 60\%o$	$-17.4\%o$
5c	same as model 4 except $q_1 = 1 + 100\%o$	$-51.3\%o$
6	same as model 4 except $q_3 = 1-38.9\%o$	$-60.4\%o$
7a	same as model 4 except $y_1 = 1, y_2 = 0$	$-43.2\%o$
7b	same as model 4 except $y_1 = 0.9, y_2 = 0.1$	$-43.2\%o$
7c	same as model 4 except all photodissociation coefficients (R3a)–(R4d) are multiplied by 1.5	$-43.3\%o$
8	same as model 4 except $J_1 = 10^{-2}$	$-43.2\%o$

$$T = 296 \text{ K}$$

$$CO_2 = 600 \text{ torr} = 1.93 \times 10^{19} \text{ cm}^{-3}$$

$$O_3 = 30 \text{ torr} = 9.66 \times 10^{17} \text{ cm}^{-3}$$

$$f = Q/O = 1/500$$

Unless otherwise stated, this value of f is taken as the baseline for $Q(Q = {}^{18}O$ hereinafter) value. Any deviation from this value is expressed as a delta value per mil. The model was allowed to run for a sufficiently long time (of the order of days) so that 99% of O_3 was converted to O_2. We then examined the isotopic composition of O_2.

We carried out a total of 13 model runs. The key assumptions and principal results are summarized in Tables 2a, 2b, 2c, and 3. Models 1–4 (Table 2a) show the path from the baseline model to the standard model. Models 5–8 (Table 2b) test the sensitivity of the standard model to the rate coefficients used in the model. Models 9–10 (Table 2c) test the sensitivity of the standard model to the initial isotopic composition of CO_2 and

Table 2c. Summary of Model Runs: Testing of Sensitivity of Standard Model to Initial Isotopic Composition

Model Run	Model Assumptions	Isotopic Fractionation in OQ
4	standard model $\delta Q(CO_2) = 0$ $\delta Q(O_3) = 0$	$-43.2\%o$
9a	same as model 4 except $\delta Q(CO_2) = 100\%o$	$45.8\%o$
9b	same as model 4 except $\delta Q(CO_2) = -100\%o$	$-132.1\%o$
10a	standard model $\delta Q(O_3) = 100\%o$	$-36.5\%o$
10b	standard model $\delta Q(O_3) = -100\%o$	$-49.9\%o$

**Table 3.** Summary of Model Runs to Simulate the Laboratory Measurements of $Q = {}^{18}O$ and $P = {}^{17}O$

| Model Run	Model Assumptions	Isotopic Fractionation in O_2
4	standard model initial CO_2, O_3 $\delta Q = \delta P = 0$ $q_3 = 1-76.5\%o$ $q_4 = 1-38.9\%o$	$\delta Q = -43.2\%o$ $\delta P = -60.4\%o$
11 (WT93 EXP A64)	initial CO_2 $\delta Q = -34.6\%o$ $\delta P = -19.7\%o$ initial O_3 $\delta Q = 3.3\%o$ $\delta P = 1.7\%o$	$\delta Q = -73.7\%o$ $\delta P = -77.5\%o$
12 (WT93 EXP A67)	same as model 11 except initial O_3 $\delta Q = -15.4\%o$ $\delta P = -8.2\%o$	$\delta Q = -75.0\%o$ $\delta P = -78.2\%o$
13 (WT93 EXP A76)	same as model 11 except initial O_3 $\delta Q = -73\%o$ $\delta P = -54\%o$	$\delta Q = -78.9\%o$ $\delta P = -81.2\%o$
11a	same as model 11 except q_1 and q_2 in Chapman reactions (R5), (R6), and (R7) for $P = 1 + 60\%o$	$\delta Q = -73.7\%o$ $\delta P = -53.2\%o$
12a	same as model 12 as modified in model 11a	$\delta Q = -75.0\%o$ $\delta P = -53.8\%o$
13a	same as model 11 as modified in model 11a	$\delta Q = -78.9\%o$ $\delta P = -56.9\%o$
11b	same as model 11 except $q_3 = q_4 = 1-76.5\%o$	$\delta Q = -73.7\%o$ $\delta P = -60.6\%o$
12b	same as model 12 as modified in model 11b	$\delta Q = -75.0\%o$ $\delta P = -61.3\%o$
13b	same as model 13 as modified in model 11b	$\delta Q = -73.7\%o$ $\delta P = -64.3\%o$

O_3 in the model. Finally, models 11–13 (Table 3) employ the standard model to simulate the laboratory experiments of WT93. For the sake of convenience in comparison, we often repeat the results of some models in these tables.

Model 1 is the baseline model. We initialized the model to conditions as stated above, with a normal isotopic composition for CO_2 and O_3, $\delta Q = 0$. There was no fractionation in any of the chemical reaction pathways; that is, $q_1 = q_2 = q_3 = 1$ (q_3 is defined in model 3). As expected, the isotopic fractionation in the final product, O_2, was zero. The convergence criterion for the numerical code is 1 part in 10^4. Hence any isotopic fractionation in the range of $0.1\%o$ is not significant.

Model 2a is the same as the baseline model except that we initialized the ozone to be enriched in Q by $100\%o$. The result is a surprise in that there was only $6.9\%o$ enrichment in the final product (O_2). Most of the initial enrichment was "washed away." The reason, we believe, is in the exchange reaction between $O(^1D)$ and CO_2. Figures 1a and 1b present schematic diagrams of the essential chemical pathways in the experiment. The initial oxygen is in O_3, and the final oxygen is in O_2. However, the photolysis of O_3 produces $O(^1D)$ that will exchange with CO_2 via the CO_3 complex. The resulting product from CO_3 decay is O, which can react with O_3 to form O_2 via reaction (R13a) or react with O_2 to form O_3 back in (R5). Since (R5) exceeds (R13a) by orders of magnitude and CO_2 is

a very large reservoir of heavy oxygen, the recycling through CO_2 has the effect of "washing out" all the isotopic signature in the original O_3. We will return to this point later. Model 2b is the same as the baseline model except that we initialized the
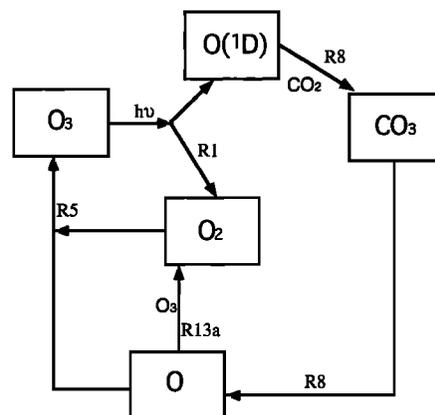
Figure 1a. Schematic diagram showing the principal chemical pathways for exchange of oxygen between O_2 and CO_2 reservoirs.
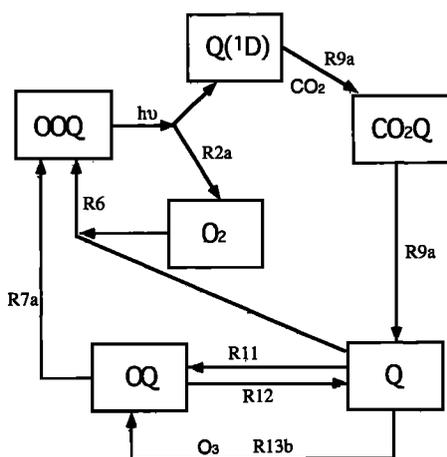
Figure 1b. Schematic diagram showing the principal chemical pathways for exchange of oxygen between OQ and COQ reservoirs.

Figure 2. Mixing ratios of oxygen species as function of time (in seconds) in the standard model (model 4; see Table 2a). The total pressure of CO_2 is 600 torr. The arrows indicate 1 s, 1 min, 1 hour, and 1 day, respectively.

ozone to be enriched in Q by $-100\%o$. The result, $-7.2\%o$, is a confirmation of what we would expect in light of model 2a.

Model 3 is the same as the baseline model except that we "activate" oxygen atom exchange reactions, (R11) and (R12), with measured and computed rate coefficients [*Anderson et al.*, 1985; *Kaye and Strobel*, 1983]
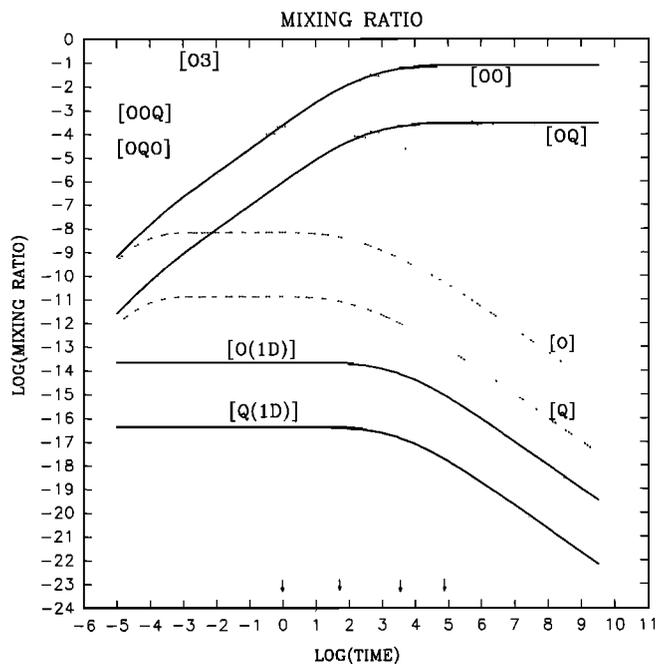
$$k_{11} = 2.9 \times 10^{-12}$$

$$k_{12} = 1.49 \times 10^{-12}e^{-31.6/T}$$

At $T = 296$, $k_{12} = 0.5q_3k_{11}$, where $q_3 = 1-76.5\%o = 0.9235$.

The result shows that these exchange reactions are responsible for an enrichment of $36.6\%o$. Note that the rate coefficients for the exchange reactions favor heavy O_2 by $76.5\%o$. Thus formation of heavy O_2 is favored.

Model 4 is the same as model 3 except that we introduced a fractionation of $90\%o$ in the Chapman reactions for the formation of ozone (reactions (R6) and (R7)); that is, $q_1 = q_2 = 1 + 90\%o$. (This choice of q_1 and q_2 is motivated by the laboratory measurements and what is roughly needed to account for the fractionation observed in atmospheric ozone.) The result is $-43.2\%o$. Note that comparing with model 3, the Chapman reactions are responsible for a total fractionation of $-79.8\%o$. For reasons that will become obvious later, we shall designate model 4 the standard model.

Since all subsequent model runs will be based on the standard model, it is of interest to examine in some detail the results of this model. The fascinating question is why should the Chapman reactions that favor the production of heavy ozone take heavy oxygen out of the oxygen reservoir ($O_3 + O_2$) and put that into the CO_2 reservoir? The reason is actually quite simple and is illustrated in Figures 1a, 1b, 2, 3, and 4. Figures 1a and 1b show the principal pathways by which the oxygen atoms, O and Q, in O_3, OOQ, and OQO are mobilized, recycled through CO_2 and COQ via the formation of $O(^1D)$ and $Q(^1D)$, and eventually form O_2 and OQ. The time history of the transformation of the major oxygen species in the standard model is shown in Figure 2. The decline of ozone is accompanied by the rise of molecular oxygen, with the crossover happening at about 1000 s (about 1/3 hour). The concentrations of O, Q, $O(^1D)$, and $Q(^1D)$ are given by photochem-

ical equilibrium with ozone. The important reaction rates are shown in Figure 3. Note that the net formation rate of O_2 and OQ, (R13a) and (R13b), are several orders of magnitude less than those for the recycling rates (R1) and (R2), respectively. This implies complete isotopic relaxation (in a kinetic sense) between the oxygen reservoir and the CO_2 reservoir.

The time history of $\delta Q(^1D)$ and δOQ is presented in Figure
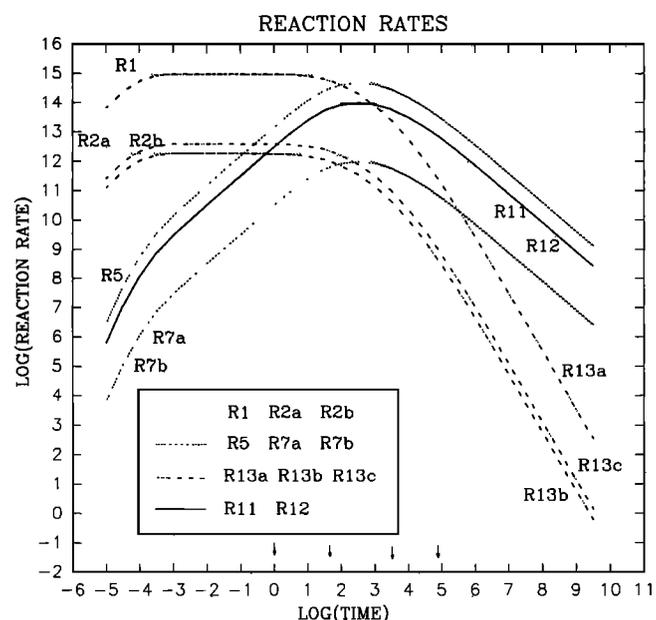
Figure 3. Reaction rates (in molecules cm^{-3} s^{-1}) of key reactions as a function of time (in seconds) in the standard model. The arrows indicate 1 s, 1 min, 1 hour, and 1 day, respectively.
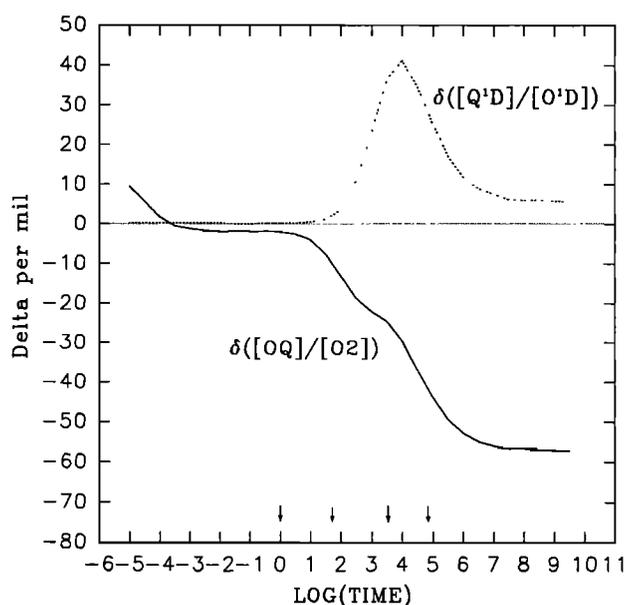
Figure 4. Isotopic fractionation in units of per mil for OQ and $Q(^1D)$ as a function of time (in seconds) in the standard model. The arrows indicate 1 s, 1 min, 1 hour, and 1 day, respectively.

4. The Chapman reactions favor the formation of heavy ozone. Upon photolysis this increases the $Q(^1D)$ yield. Thus $\delta Q(^1D)$ is positive, as shown in Figure 4. By the exchange reaction (R9b), COQ formation is therefore enhanced, and by conservation of mass, less OQ is formed. The gradual decrease of δQ in OQ is depicted in Figure 4 and is completed in about 10^5 s (about a day). We shall show later that the standard model has the essential ingredients to explain the results of WT93.

Having arrived at the standard model, we performed a series of model runs, summarized in Table 2b, on the sensitivity of the model to the assumed rate coefficients.

Models 5a and 5b are the same as the standard model except that the isotopic fractionation in the Chapman reactions is changed from $q_1 = q_2 = 1 + 90\%o$ to $1 + 120\%o$ and $1 + 60\%o$, respectively. The resulting δQ in OQ is $-66.6\%o$ and $-17.4\%o$, respectively. Model 5c is the same as the standard model except that $q_1 = 1 + 100\%o$ and $q_2 = 1 + 90\%o$. The reason for this choice is that the enrichment factor for the asymmetric ozone may be higher than that for the symmetric isotopomer. The resulting δQ in OQ is $-51.3\%o$. These results demonstrate the extreme sensitivity of the final results to the Chapman fractionation.

Model 6 is the same as the standard model except that in the exchange reaction (R12), q_3 has been changed from $1-76.5\%o$ to $1-38.9\%o$. The result is $-60.4\%o$. This model was chosen in anticipation of its application to ^{17}O.

Models 7a, 7b, 7c, and 8 are the same as the standard model except that the photolysis yields and dissociation coefficients are changed. The results are not sensitive at all to these changes.

Having tested the sensitivity of the standard model to kinetic rate coefficients, we performed a series of model runs, summarized in Table 2c, on the sensitivity of the model to the assumed initial isotopic fractionation in order to examine the underlying cause of the "washout" effect reported in WT93.

Models 9a and 9b are the same as the standard model except

that the isotopic composition of the reservoir CO_2 is changed from $\delta Q = 0$ to $\delta Q = 100\%o$ and $-100\%o$, respectively. The results are 45.8 and $-132.1\%o$, respectively. This demonstrates the extreme sensitivity to the reservoir CO_2.

Models 10a and 10b are the same as the standard model except that the isotopic composition of the initial ozone is changed from $\delta Q = 0$ to $\delta Q = 100$ and $-100\%o$, respectively. The results are -36.5 and $-49.9\%o$, respectively. Thus a hundred per mil change in initial ozone isotopic composition has a net effect that is less than $7\%o$ on the final product. This demonstrates the extreme insensitivity to the initial ozone, i.e., the "washout" effect.

It is clear from the above model runs that we have found a reasonable explanation for the laboratory experiments. They not only offer an independent confirmation of the "standard" Chapman chemistry, but because of the higher precision with which the isotopic composition is measured in the laboratory, we can use the model to deduce better isotopic fractionation factors for the key reactions responsible for the observed fractionation. This will be done in the following.

Having tested the major aspects of the standard model, we performed a series of model runs to simulate the results of experiments A64, A67, and A76 of WT93. These cases were chosen because of the long time duration of the experiments, guaranteeing that the asymptotic state has been reached (see Figure 4 for the time dependence of δOQ). In addition to simulating δQ, we also include δP, where $P = {}^{17}O$. We assume that all the chemistry for P is the same as that for Q, except for the exchange reaction (R15),

$$k_{15} = 1.47 \times 10^{-12}e^{-15.8/T}$$

At $T = 296$, $k_{15} = 0.5q_4k_{11}$, where $q_4 = 1-38.9\%o$.

Models 11, 12, and 13 are the same as the standard model except for the inclusion of P and setting the initial isotopic compositions of CO_2 and O_3 to those of experiments A64, A67, and A76 of WT93. The results show the remarkable independence of the initial isotopic composition of O_3. The values for δQ are close to those observed in the experiments, as shown in Figure 5. All δQ values cluster around $-75\%o$, despite the initial values that range from $3\%o$ to $-73\%o$. Experiments A64, A67, and A76 of WT93 are satisfactorily explained. However, the model predictions for δP are not correct. The model δP cluster around $-78\%o$, but the observed values in these experiments are around $-55\%o$. There is a discrepancy of about $20\%o$ for which the standard model offers no explanation.

Let us focus on a nonrigorous discussion of this discrepancy in order to formulate some hypotheses that should be tested by further experimentation. Take, for instance, WT93 EXP A67. We have shown that the initial isotopic composition of ozone is not important but that of CO_2 is. The initial δQ and δP for CO_2 are $-35\%o$ and $-20\%o$, respectively. The final δQ and δP for O_2 are $-75\%o$ and $-55\%o$, respectively. The net changes in δQ and δP in O_2 with reference to CO_2 are $-40\%o$ and $-35\%o$, respectively. Note the amazing similarity in the net delta values for Q and P.

Let us examine how the standard model explains the net delta value for Q. As summarized in Table 2a, the exchange reactions (R11) and (R12) with q_3 appropriate for Q contributes $37\%o$, the Chapman reaction with $q_1 = q_2 = 1.09$ contributes $-80\%o$, resulting in a net δQ of $-43\%o$. This is close to the observed value of $-40\%o$.

Let us examine how the standard model fails to explain the
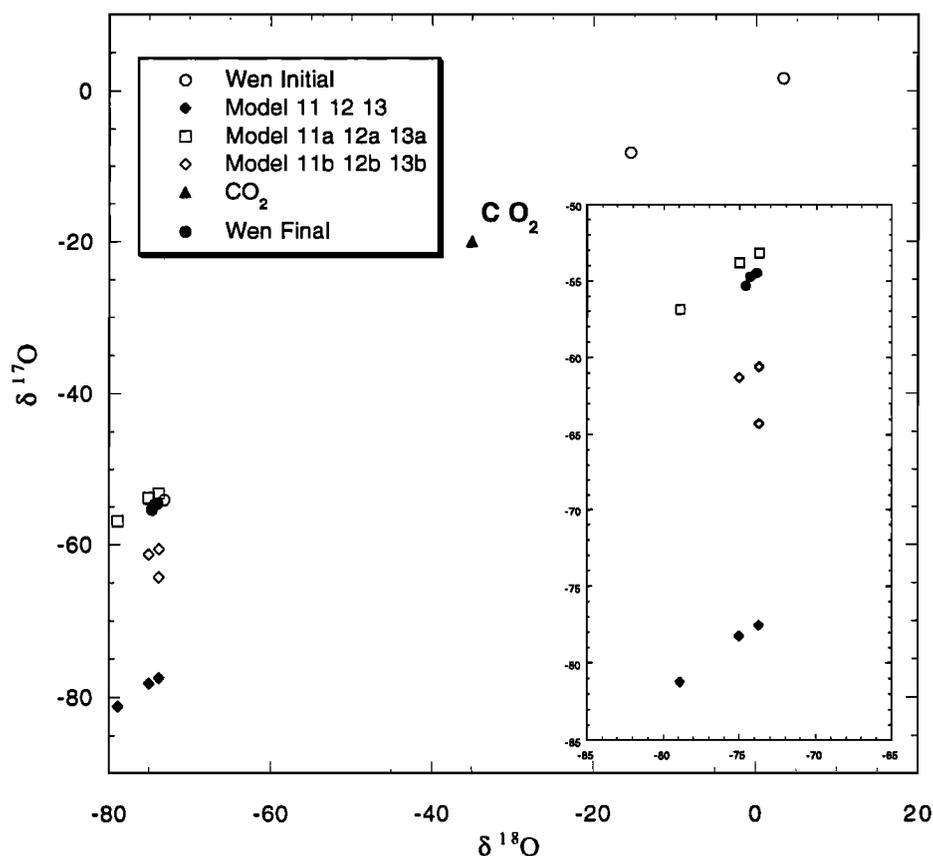
Figure 5. Two-isotope fractionation plot showing the isotopic composition of ozone, molecular oxygen, and carbon dioxide in WT93 and our models. Open circles, initial ozone in WT93 and model; solid circles, WT93 final O_2; solid triangle, CO_2 reservoir in WT93 and model; solid diamonds, final O_2 in models 11, 12, and 13; open squares, same for models 11a, 12a, and 13a; open diamonds, same for models 11b, 12b, and 13b. See summary in Table 3 and WT93 for details.

net delta value for P. Since exchange reactions (R14) and (R15) are mass dependent, they contribute only about half the effect as Q, or about 20‰. However, the Chapman reactions are mass independent, contributing the same −80‰ as in the case of Q. Thus the net δP is −60‰ (for a more rigorous value, see model 6 in Table 2b). This value is 25‰ too small compared with the value of −35‰ deduced from EXP A67.

A resolution of this puzzle is beyond the scope of this paper. However, we will propose some hypotheses that will be a useful guide to future experiments to settle this question. First, it is entirely possible that the set of reactions in Table 1 is incomplete. For instance, we have not included the chemistry of the excited state atoms and molecules other than $O(^1D)$, for example, $O_2(^1\Delta)$. However, assuming that the theory is correct, then there are two rate coefficients that we can adjust. The first possibility is that there is a mass dependence in the Chapman reactions, as suggested in the experiments of *Morton et al.* [1990]. The second possibility is that the fractionation factors computed for exchange reactions on the basis of classical harmonic oscillator model [*Kaye and Strobel*, 1983] may be incorrect. (See discussion of these factors by *Wen* [1991].) While there is no reason to distrust the theoretical fractionation factors in the Q and P exchange with O_2, we must emphasize that they have not been measured in the laboratory. To illustrate these possibilities, we carried out more model runs.

Models 11a, 12a, and 13a are the same as models 11, 12, and 13 except that the Chapman reaction forming P containing

ozone is enriched by $1 + 60‰$ instead of $1 + 90‰$. The results for δP are −53.2‰, −53.8‰, and −56.9‰, respectively. These values are close to the observed values (see Figure 5).

Models 11b, 12b, and 13b are the same as models 11, 12, and 13 except that the exchange reactions for P are the same as those for Q. The results for δP are −60.6‰, −61.3‰, and −64.3‰, respectively. These values are within 5‰ of the experiments, as shown in Figure 5.

We must emphasize that there is no experimental justification for the above hypotheses. In fact, the choice of fractionation factors in models 11a, 12a, and 13a is outside of the range of the measurements of *Morton et al.* [1990]. There is no experimental basis for the assumptions of models 11b, 12b, and 13b. Further laboratory experiments are needed to test these hypotheses.

Model Simulation of Observed Atmospheric CO₂ Isotopic Fractionation

In the model simulations described in the previous section, all experiments were carried out in a chemical environment in which CO_2 was greatly in excess. Therefore isotopic exchange with CO_2 was capable of "washing out" most of the initial O_3 isotopic signature. However, in the atmosphere, the chemical environment is quite different. Here O_2 is the principal reservoir of oxygen; CO_2 is a minor reservoir. Under this condition
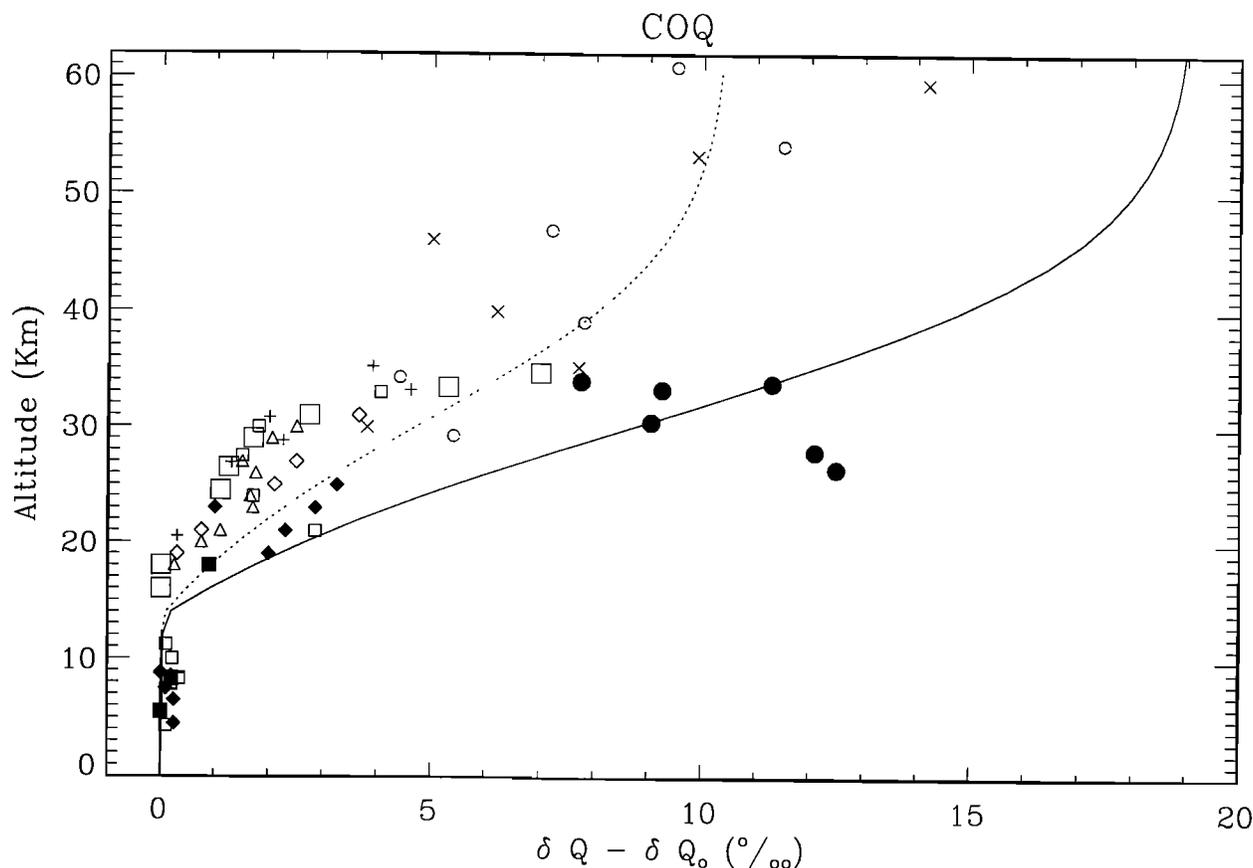
Figure 6. Isotopic fractionation in COQ computed using enrichment $E_1 = q_1 = 1 + 90\%o$ (standard model). The solid line is for a model with normal eddy diffusion coefficient (K); the dashed line is for a model with 2 × K. The data are from *Gamo et al.* [1989, 1995] taken in Japan from 1985 to 1991; the black dots are data taken by *Thiemens et al.* [1991] in the United States; δQ_0 in the troposphere $= 40.7\%o$. Points, small open squares, August 1985; solid diamonds, September 1985; solid squares, May 1986; open diamonds, May 1988; open triangles, September 1989; large open squares, June 1990; crosses, August 1991; solid circles, over United States. 1988–1989 measurement (the points above are taken from *Gamo et al.* [1995]); open circles, May 1992 (the points are taken from *Thiemens et al.* [1995]).

there is too little CO₂ to "wash out" the isotopic enrichment in O₃. The model of *Yung et al.* [1991] demonstrated that heavy ozone is capable of transferring its heavy oxygen atom to CO₂. Using Table 1 and the results of the previous section we have refined the models of *Yung et al.* [1991].

The results of the model calculations for the isotopic fractionation of CO₂ (relative to the surface) are presented in Figure 6, along with data obtained by *Gamo et al.* [1989, 1995] and *Thiemens et al.* [1991]. The exchange reaction is of the correct magnitude to account for the observed isotopic fractionations. However, there seems to be a discrepancy between the data of *Gamo et al.* [1995] and those of *Thiemens et al.* [1989]. Part of the disagreement between model and data in the lower stratosphere may be due to the unrealistic parameterization of atmospheric transport in the one-dimensional model.

The sensitivity of the enrichment values in Q to transport is illustrated by the dashed curve in Figure 6. A doubling of the eddy diffusion coefficient results in a large decrease in the predicted enrichment. The reason is very simple. In the troposphere the isotopic composition of COQ is determined by exchange with the ocean and the biosphere. Exchange with heavy ozone has relatively little impact. In the middle atmo-

sphere, exchange with ozone dominates and tends to drive the CO₂ toward isotopic equilibrium according to (4). Therefore the observed isotopic composition of CO₂ in the middle atmosphere represents the "age" of the CO₂ after it has entered the stratosphere. The "young" CO₂ near the tropopause is tropospheric, but as CO₂ is transported to the upper part of the stratosphere, it is subjected to isotopic exchange with heavy ozone. Thus "aged" CO₂ becomes increasingly enriched in Q. However, with enhanced transport, the "aged" CO₂ gets diluted by fresh CO₂ that has little enrichment, resulting in a lower net enrichment. The calculations may be improved using a two-dimensional model of the atmosphere. However, since the effects are of the order of 10^{-3}, there is the need to maintain an accuracy of 10^{-4} in the computations of the isotopic species. The sharp structure in the COQ enrichment observed by *Thiemens et al.* [1995] in March 1992 (see the crosses in Figure 6) is almost certainly due to mixing of tropical air that is depleted in COQ but enriched in CH₄ and N₂O (see Figure 2a of their paper). These data suggest that COQ is as good a tracer of air motion as CH₄ and N₂O in the stratosphere. However, COQ is more than a redundancy. As we go to the upper stratosphere and mesosphere, CH₄ and N₂O are no longer viable as tracers due to their destruction. The beauty

of COQ in the upper atmosphere is that its mixing ratio is roughly a constant until we come to the homopause, and its Q enrichment continues to increase (at least according to our model). Therefore this may be the only useful tracer of atmospheric motion in the upper stratosphere and mesosphere, especially for tracking descent of air into the winter poles. We should note that the usefulness of using the concentrations of CO_2 for deducing stratospheric transport rates has recently been demonstrated [*Boering et al.*, 1996]. The measurements of the isotopic composition of CO_2 will greatly enhance its usefulness.

Given that the stratosphere is the source of enriched COQ, we expect that COQ would serve as a tracer of stratosphere-troposphere exchange. Evidence of such COQ-enriched air from the stratosphere may have been found by *Friedli et al.* [1987], who analyzed samples of air from aircraft to altitudes of 7 km in Switzerland in 1982. Figure 5 of their paper shows the data for COQ fractionation. Most of the data points (7 out of 10) could fit a simple linear relation between fractionation and CO_2 abundance. However, 3 out of 10 data points are anomalously high, and the authors had no explanation for this unusual enrichment. We note that the anomaly in Q is about 1‰ and could be explained by transport of air from the lower stratosphere. A confirmation of this hypothesis will require a trajectory analysis of the air mass at the time of the observation.

Ultimately, the stratospheric source of enriched COQ will become diluted by exchange with the biosphere and the ocean. Precise measurements and detailed modeling could lead to better understanding of the nature of this exchange.

Conclusions

The anomalous heavy oxygen fractionation in atmospheric ozone (in the stratosphere and the troposphere) is now well understood with regard to its well-defined fractionation pattern and firm data base from atmospheric measurements and the laboratory experiments that provide the kinetic data. This opens up new opportunities for using the heavy oxygen atom in heavy ozone as a tracer for other atmospheric processes. It is as though atmospheric ozone and its derivative products, O, $O(^1D)$, and $O_2(^1\Delta)$ possess a quantity called "heaviness." The formation of ozone via the Chapman reaction is the principal source of this "heaviness." In all chemical reactions involving ozone and its derivatives, this "heaviness" is transmitted to the other species (e.g., oxygen containing molecules of carbon, hydrogen, nitrogen, chlorine, and sulfur) with various degrees of effectiveness.

In this paper we have presented results on the exchange of the heavy oxygen atom between ozone and CO_2. Much remains to be done to quantitatively test the model by simultaneous measurements of the isotopic species of CO_2 (both ^{18}O and ^{17}O) and O_3. We point out that those species should be isotopically enriched by the reactions that lead to their formation.

The usefulness of heavy oxygen derived from heavy ozone exists only useful if its chemical kinetics is completely understood. In this work we have demonstrated the ability of simple models to analyze laboratory data as well as atmospheric data. Further work needs to be done in elucidating the chemical fractionation factors in ^{17}O and in obtaining global patterns of COQ in the middle atmosphere as well the lower atmosphere.

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