GEOPHYSICAL RESEARCH LETTERS, VOL. 18, NO. 1, PAGES 13-16, JANUARY 1991

ISOTOPIC EXCHANGE BETWEEN CARBON DIOXIDE AND OZONE VIA O(^{1}D) IN THE STRATOSPHERE

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Abstract. We propose a novel mechanism for isotopic exchange between CO_2 and O_3 via $O(^1D) + CO_2 \rightarrow CO_3^*$ followed by $CO_3^* \rightarrow CO_2 + O(^3P)$. A one-dimensional model calculation shows that this mechanism can account for the enrichment in ^{18}O in the stratospheric CO_2 observed by Gamo *et al.* [1989], using the heavy O_3 profile observed by Mauersberger [1981]. The implications of this mechanism for other stratospheric species and as a source of isotopically heavy CO_2 in the troposphere are briefly discussed.

Introduction

Recently Gamo *et al.* [1989] reported measurements of heavy isotopes of CO_2 in the stratosphere over Japan. Let O = ^{16}O and Q = ^{18}O. The δQ of stratospheric CO_2, as defined in Gamo *et al.*, was found to be 2‰ (two parts in a thousand) greater than that of tropospheric CO_2 at 19 km, and appears to continue to increase with altitude up to the highest altitude (25 km) where samples were taken. The data are reproduced in our Figure 2. The authors proposed two possible explanations, one dynamical and one chemical. The preferred mechanism was chemical and involved transferring a heavy oxygen atom from O_3, which was first measured to be isotopically enriched by Mauersberger [1981], to carbon dioxide. However, the authors did not propose a detailed chemical scheme. The direct thermal exchange reaction $CO_2 + O_2Q \rightarrow COQ + O_3$ is inefficient (J.-S. Wen, private communication, 1990).

We propose, instead, that the transfer of Q from O_3 to CO_2 is initiated by O(^{1}D) reactions. We will use a one-dimensional photochemical model incorporating reactions for exchange of Q to simulate the vertical profile of COQ observed by Gamo *et al.* The factors controlling the COQ/CO_2 ratio in the troposphere have been studied by Keeling [1961], Bottinga and Craig [1969], Francey and Tans [1987], and Friedli *et al.* [1987]. We will attempt to assess the importance of exchange with the stratosphere relative to these other factors.

Chemical Kinetics

Photolysis of O_3 below about 305 nm produces O(^{1}D), an excited state of the oxygen atom, by R1 (see listing and numbering of reactions in Table 1). The primary fate of O(^{1}D) in the atmosphere is quenching by the ambient atmospheric gases (R2a) Because of the efficiency of the quenching reactions, the abundance of O(^{1}D) in the atmosphere is very small and it has not been directly detected in the atmosphere. Nevertheless, this excited atom plays fundamental roles in the chemistry of HO_x radicals [Levy, 1971; Wofsy *et al.*, 1972] and NO_x species [McElroy and McConnell, 1971; Nicolet and Peetermans, 1972]. Figure 1 presents the O(^{1}D) concentration predicted by the Caltech-JPL model [Froidevaux *et al.*, 1985], a typical diurnally-averaged one-dimensional photochemical model, along with our O_3 profile.

Table 1

List of essential reactions used in the photochemical model. The units for photodissociation coefficients and two-body rate constants are s^{-1} and $cm^3\ s^{-1}$, respectively. The coefficients for photolysis refer to mid-latitude diurnally averaged values at 30 km. All molecular kinetic data are taken from DeMore *et al.* [1990], except otherwise stated. Rate constants for isotopic species are estimated by us. Q = ^{18}O.

R1a	$O_3 + h\nu \rightarrow O_2 + O(^1D)$	$J_{1a} = 7.4 \times 10^{-5}$	
R1b	$O_2Q + h\nu \rightarrow O_2 + Q(^1D)$	$J_{1b} = 1/2\ J_{1a}$	
R2a	$O(^1D) + M \rightarrow O + M$	$k_{2a} = 2.0 \times 10^{-11}\ e^{110/T}$	
R2b	$Q(^1D) + M \rightarrow Q + M$	$k_{2b} = k_{2a}$	
R3	$O(^1D) + CO_2 \rightarrow CO_2 + O$	$k_3 = 7.4 \times 10^{-11}\ e^{120/T}$	
R4a	$Q(^1D) + CO_2 \rightarrow COQ + O$	$k_{4a} = 2/3\ k_3$	
R4b	$O(^1D) + COQ \rightarrow CO_2 + Q$	$k_{4b} = 1/3\ k_3$	
R5	$O(^1D) + CO \rightarrow CO + O$	$k_5 = 4.6 \times 10^{-11}$	(a)
R6a	$Q(^1D) + CO \rightarrow CQ + O$	$k_{6a} = 1/2\ k_5$	
R6b	$O(^1D) + CQ \rightarrow CO + Q$	$k_{6b} = 1/2\ k_5$	
R7	$QH + CO_2 \rightarrow COQ + OH$	$k_7 < 1 \times 10^{-17}$	(b)
R8	$Q + CO_2 \rightarrow COQ + O$	$k_8 < 1 \times 10^{-18}$	(c)

(a) Cvetanovic [1975].
(b) Greenblatt and Howard [1989].
(c) Wen and Thiemens [1990].

Consider the reaction between O(^{1}D) and CO_2

$$O(^1D) + CO_2 \rightarrow CO_3^*$$
$$CO_3^* \rightarrow CO_2 + O$$

The existence of the CO_3^* complex was first proposed by Katakis and Taube [1962] in a study of the exchange between O(^{1}D) and CO_2. Jacox and Milligan [1971] favored a three-member ring structure with an O-C-O angle of 65°. The complex rapidly predissociates to CO_2 + O [DeMore

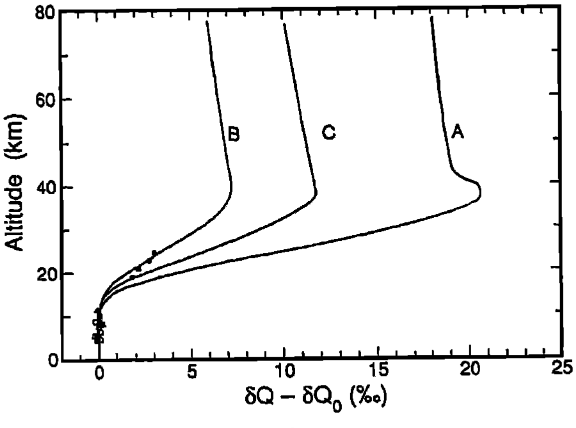

Fig. 1. Concentrations of O(^{1}D) and O_3 from the Caltech-JPL one-dimensional photochemical model [Froidevaux *et al.*, 1985].

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Paper number 90GL02478
0094-8534/90/90GL-02478$03.00

and Dede, 1970]. There has been great interest in CO_3^* in connection to the CO_2 stability problem on Mars [McElroy and Hunten, 1970; Noxon, 1970], which was subsequently solved by a different scheme [Parkinson and Hunten, 1972; McElroy and Donahue, 1972].

The rapid quenching of $O(^1D)$ by CO_2 [DeMore *et al.*, 1990] with rate coefficient, $k_3 = 1.1 \times 10^{-10}$ cm^3 s^{-1} at T = 298 K, undoubtedly proceeds via the CO_3^* intermediate [DeMore and Dede, 1970]. For comparison we note that the corresponding rate constants for quenching of $O(^1D)$ by Ar and Kr are 7×10^{-13} and 8×10^{-12} cm^3 s^{-1}, respectively [Cvetanovic, 1975]. The existence of CO_3^* would be expected to result in an exchange between the incident and emergent O atoms. Indeed, in an isotopically labelled study using CO_2 photolysis at 147 nm as the source of $O(^1D)$, Baulch and Breckenridge [1966] showed that the efficiency yield for isotopic exchange is 0.69, close to the expected value of 2/3 if the ejection of an O atom from CO_3^* were a purely statistical process. Other kinetic studies [Yamazaki and Cvetanovic, 1964; Weissberger *et al.*, 1967] have generally confirmed this result.

The startling discovery of an ^{18}O enrichment in stratospheric O_3 by Mauersberger [1981] has been confirmed [Carli *et al.*, 1982; de Zafra *et al.*, 1984; Mauersberger, 1983, 1987; Rinsland *et al.*, 1985; Goldman *et al.*, 1989], and studied in the laboratory [Heidenreich and Thiemens, 1986; Thiemens and Jackson, 1987; Yang and Epstein, 1987a,b; Morton *et al.*, 1989; Anderson *et al.*, 1989]. The theory of isotopic enrichment for O_3 was initiated even before the atmospheric observations [Cicerone and McCrumb, 1980], but this and all subsequent theories [Kaye and Strobel, 1983; Blake *et al.*, 1984; Kaye, 1986, 1987] completely fail to account for either the atmospheric or laboratory measurements. The suggestions of Valentini *et al.* [1987] and Bates [1986] are not widely accepted. It is not the purpose of this paper to enter this great debate. We accept as empirical fact that stratospheric O_3 is enhanced in ^{18}O and pursue its implications for the isotopic enrichment of CO_2 and other species.

Consider the following sequence of reactions initiated by the photolysis of a heavy ozone molecule,

$$\begin{aligned} O_2Q + h\nu &\rightarrow O_2 + Q(^1D) \\ Q(^1D) + CO_2 &\rightarrow CO_2Q^* \\ CO_2Q^* &\rightarrow COQ + O \end{aligned}$$

The net result is the transfer of Q from ozone to carbon dioxide. The reverse process can also readily occur via R4b, leading to the transfer of Q from carbon dioxide back to ozone. Therefore, ozone and carbon dioxide may set up some kind of kinetic isotopic equilibrium in the stratosphere. Under the assumptions of *photochemical equilibrium* and using the somewhat idealized chemical scheme summarized in Table 1, it can be shown that $[COQ]/[CO_2] = 2([Q(^1D)]/[O(^1D)]) = [O_2Q]/[O_3]$. On the other hand, this ratio would be equal to that at the ground if the atmosphere were well-mixed (i.e., transport time << chemical time). In other words, the ratio COQ/CO_2 in the atmosphere reflects a "tug-of-war" between photochemical equilibrium driven by UV radiation in the upper atmosphere, and reactions involving exchange with H_2O in the biosphere, the oceans, and clouds.

For our theory to be correct we must prove that other isotopic exchange reactions such as R7 with QH and R8 with Q are *not* important. Evidence for R7 was found by Kurylo and Laufer [1979], but Greenblatt and Howard [1989] reported an upper limit of $k < 1 \times 10^{-17}$ cm^3 s^{-1}, making it unimportant for the stratosphere. Jaffe and Klein [1966] reported $k_8 = 1.1 \times 10^{-12}$ $e^{-1750/T}$ cm^3 s^{-1} and this would suggest that R8 is fast enough to neutralize the isotopic enrichment produced by $Q(^1D)$. However, we believe that the results of Jaffe and Klein are in error. First, it is extremely improbable that $k_8 > 100$ k_7, since OH is generally more reactive than O. Second, a qualitative upper limit for k_8 may be obtained by modeling an experiment performed by Wen and Thiemens [1990]. Wen (1990, private communication) deduced $k_8 < 1.5 \times 10^{-17}$ cm^3 s^{-1} at T = 363 K. We conclude that $k_8 < 10^{-18}$ cm^3 s^{-1} at stratospheric temperatures, and hence R8 is not important.

Photochemical Modeling

The Caltech-JPL one-dimensional photochemical model is described elsewhere [Allen *et al.*, 1981; Froidevaux *et al.*, 1985; Michelangeli *et al.*, 1989]. In the present investigation we fix the concentrations of $O(^1D)$ and O_3 (see Figure 1) to the values in Froidevaux *et al.* [1985]. This is justified because CO_2 has negligible influence on oxygen photochemistry. The relevant photochemistry of O, $O(^1D)$, O_3, CO_2, CO, and their isotopes is summarized in Table 1. The rate coefficients for the isotopic species are for the most part unknown, and we have to make reasonable guesses to arrive at the preferred values given in Table 1. Vertical transport is parameterized by eddy diffusion.

Let the standard Q/O ratio be f. Since stratospheric O_3 is enriched in Q, we have $[O_2Q]/[O_3] = 2$ f E where E = enrichment factor. Since $O(^1D)$ is in photochemical equilibrium with O_3, we have, assuming the reactions of Table 1, $[Q(^1D)]/[O(^1D)] =$ f E. The choice of E in our model represents some difficulty. The observed enrichment factors are not reproducible, either due to uncertainties in the experiments or a possible dependence on the solar cycle (Mauersberger, 1990, private communication). It must be emphasized that there is no theoretical justification for a solar cycle dependence. In case A, we set the enrichment factor E_A to be the measurements of Mauersberger [1981]. To set a lower bound for E we also use the later measurements to derive another profile $E_B = 1 + (E_A - 1)/3$. All other uncertainties in the model are probably smaller than that of E.

The photochemical model was run to steady state in the diurnally averaged mode. We adopt f = 1/500 [Kaye, 1987] The lower boundary conditions at the ground are $[CO_2] =$ 340 ppm and [COQ] = 1.36 ppm. At the upper boundary (80 km), the fluxes of CO_2 and COQ are zero. In the standard run E = 1.0. In runs A and B we use as input the profiles E_A and E_B. The results for $\delta Q - \delta Q_o$ for CO_2 are shown in Figure 2 (δQ_o = tropospheric value = $40.7^{o}/_{oo}$ relative to SMOW at 24°C), along with Gamo *et al.*'s measurements. It is clear that our mechanism yields the correct trend with altitude as well as the magnitude of isotopic enrichment below 30 km. Model B appears to be closer to the observations of Gamo *et al.* [1989], although data in the higher regions were not available. The profile of $\delta Q - \delta Q_o$ is generally what we expected. The maximum effect occurs at 40 km where $O(^1D)$ concentrations are highest. In the troposphere the effect is overwhelmed by the ocean and the biosphere. The results above 60 km may not be reliable because we have completely ignored possible isotopic effects in CO_2 photolysis in the mesosphere [Allen *et al.*, 1981].

To test the sensitivity of our model to transport, we double the eddy diffusion coefficients in model C, which is otherwise the same as model A. This result, shown in Figure 2, demonstrates the greater influence of the troposphere when mixing is increased. Similar runs were made for CO. The source of CO is assumed to be isotopically normal. The exchange of Q between ozone and carbon monoxide is less efficient than the loss of CO via OH. We obtained an isotopic enrichment of CQ of the order of $1^{o}/_{oo}$. Unfortunately, there are no observations of CQ in the stratosphere to compare with.

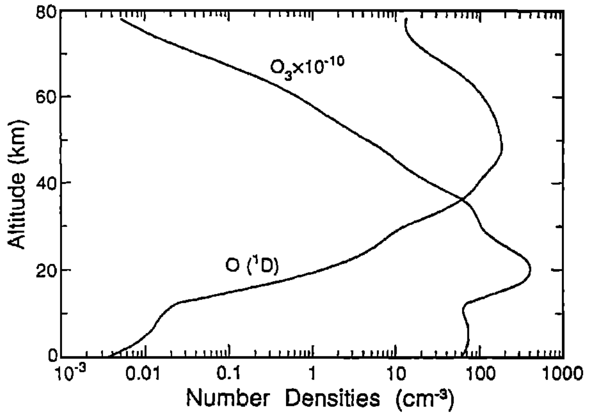

Fig. 2. Computed $\delta Q - \delta Q_0$. Cases A and B were computed using enrichment factors E_A and E_B for O_3 described in the text. Case C is same as case A, except that the eddy diffusivity profile is doubled. The data are from Gamo *et al.* [1989].

Discussion and Conclusion

The discovery of the $\delta^{18}O$ anomalies in stratospheric O_3 and CO_2 opens a new and exciting chapter in atmospheric chemistry. For the first time we encounter chemical phenomena that are the result of subtle quantum kinetic effects which are still not fully understood. We now have further evidence on how the "heaviness" in ozone is transmitted to another species, CO_2. We believe that similar transmissions of ^{18}O anomaly could occur to other stratospheric species that are connected to O_3, O, and $O(^1D)$. However, CO_2 is somewhat unique for enrichment by the present mechanism because of its rapid exchange with $O(^1D)$ and its long lifetime.

It is of interest to note that not all stratospheric species can communicate isotopically. In a perceptive analysis Kaye [1990] pointed out that the enhancement of ^{18}O in stratospheric O_3 is *not* expected to be reflected in stratospheric H_2O, thus casting doubts on the claims of observations of enhancements of ^{18}O in H_2O in the upper stratosphere [Guo *et al.*, 1989]. Recent accurate measurements of H_2Q in the stratosphere by the ATMOS experiment (M. Gunson, private communication 1990) have brilliantly confirmed Kaye's insight.

As shown in the modeling section, δQ of COQ is determined by transport and the abundance of $O(^1D)$. Thus, accurate simultaneous measurements of O_2Q and COQ, together with precise determination of appropriate rate constants may provide a reliable method for estimating the mean concentration of $O(^1D)$ in the stratosphere, a species that is otherwise exceedingly difficult to measure due to its low concentrations. This idea is similar to that of using methyl chloroform to estimate a mean global OH concentration in the troposphere [Singh, 1977; WMO 1986, Chapter 4]. The downward transport of COQ may have implications for the interpretation of its abundance and latitudinal gradient in the troposphere. CO_2 is observed to be heavier by a few tenths per mil at the South Pole, compared to the tropics and decreases even more rapidly towards the North Pole [Francey and Tans, 1987]. Assuming that stratospheric air entering the troposphere in tropopause folds in the Southern Hemisphere is enriched in ^{18}O by about $1^{0}/_{00}$ and scaling the downward transport of COQ to that for O_3 given by Mahlman *et al.* [1980], we calculate an enrichment in ^{18}O in CO_2 of 0.25 to $0.5^{0}/_{00}$, in going from the tropics to the South Pole. This calculation assumes that the isotopic equilibration time with the oceans and clouds is much longer than the intrahemispheric mixing time of about 3–6 months [Friedli *et al.*, 1987; Francey and Tans, 1987]. An even greater enhancement in COQ should result in the high latitude Northern Hemisphere by this mechanism since the stratosphere-troposphere exchange in the northern hemisphere is twice as large as in the Southern Hemisphere. However, COQ rapidly exchanges with liquid water in the terrestrial biosphere, resulting in even lower COQ abundances at high northern latitudes compared to the tropics. The effects of stratospheric intrusions therefore may not be visible in the troposphere of the northern hemisphere except for short periods following injection. Measurements of the decay of excess stratospheric COQ in the troposphere may give additional information regarding rates of exchange with the terrestrial biosphere compared with $^{13}CO_2$, which is currently used. In view of the importance of CO_2 in controlling climate, the presence of another isotopomer must be welcome.

Other stratospheric species such as CO and N_2O may also exchange Q with O_3. However, in the case of CO, the calculated enrichment by this mechanism is small. The isotopic composition of stratospheric CO may be determined mainly with reactions in the methane oxidation chain. $O(^1D)$ quenching by N_2O primarily results in a reaction. The upper limit for regenerating an oxygen atom is 4% [DeMore *et al.*, 1990]. Therefore, we expect negligible exchange of Q via this mechanism.

A number of important studies remain to be done. The chemical kinetics of isotopic species, summarized in Table 1, urgently needs to be refined by laboratory work. When properly modeled, the measurement of $CO^{18}O$ in the stratosphere may offer the best estimate for the average value of $O(^1D)$ concentrations in the stratosphere. Further laboratory studies are also required to clarify the mystery of ^{18}O enrichment in O_3 itself.

Acknowledgement. We thank M. Allen, S. Epstein, R. Friedl, K. Mauersberger, D. Michelangeli, and S. Sander for useful discussions, and M. Gunson and M. Thiemens for communication of results prior to publication. One of us (YLY) wishes to thank J.-S. Wen for drawing his attention to the work of Gamo *et al.*, and sharing with him his experimental insights. This research was supported by NASA grant NAGW–413 to California Institute of Technology and EPA grant 9D4 25 NALX to California Institute of Technology, and by the Jet Propulsion Laboratory, California Institute of Technology under contract with NASA. Contribution number 4889 from the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125.

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(Received August 6, 1990;
revised October 9, 1990;
accepted November 5, 1990.)