Effect of Isotopic Exchange upon Symmetry Dependent Fractionation in the $O + CO \rightarrow CO_2$ Reaction

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In a recent study, it was demonstrated that the mechanism associated with the O + CO reaction produces a large, mass independent isotopic fractionation in the product CO_2. A kinetic treatment of the data demonstrated that isotopic exchange between the O atom, produced by O_2 photolysis and CO, occurred prior to the O + CO recombination. It was concluded that the likely source of the mass independent fractionation was the O + CO recombination. The present paper includes a kinetic evaluation of the added role of $O + O_2$, along with O + CO, isotopic exchange. The new determinations provide a better fit of the experimental data.

Introduction

Bhattacharya and Thiemens [1] (hereafter, BT) demonstrated that a large mass independent isotopic fractionation component was present in the reaction of atomic oxygen with CO. These experiments are of particular interest for two reasons: 1) They extend the scope of reactions where mass independent isotopic fractionations are observed, which also include $O + O_2$ and $SF_5 + SF_5$; 2) The relative importance of the fractionation processes (both mass dependent and independent) may be quantitatively characterized. This is particularly important for the successful determination of the influence of different parameters, e.g. vibrational level densities of the transition state species, upon the fractionation process.

In BT it was suggested that, along with the mass independent fractionation component, at least one, and probably two mass dependent fractionation processes are likely to be present and influencing the final isotopic composition of the product CO_2. Since, ultimately, resolution of the mass independent process requires quantitative identification of all of the contributing factors towards the final isotopic product, it is equally important that other contributing fractionation processes be detailed as accurately as possible.

The exchange of atomic oxygen with CO was shown by BT, both on the basis of kinetics and isotopic results, to be a dominant process. Exchange of atomic oxygen with the modest amount of O_2 present in the experiments was kinetically shown to occur, but the consequence for the final isotopic composition of the carbon dioxide was not evaluated. In this paper, the effect of isotopie exchange between O and both CO and O_2 prior to the O + CO recombination is evaluated.

Formation and Exchange Reaction

In the experiments of BT [1], oxygen atoms were produced by UV light photolysis of O_2 in the presence of CO at pressures between 20 to 40 cm Hg. The relative amount of O_2 was small, e.g. ~ (180–630) micromoles of oxygen, which, in the volume of the photolysis chamber (5200 cm^3), corresponds to pressures of 0.5–2.1 mm at the experimental temperatures (~ 298 K). Continuous photolysis of oxygen produced a steady-state source of oxygen atoms which eventually reacted with CO to produce CO_2. The rate of CO_2 production was approximately 2–3 micromoles hr^{-1}. An important question in the interpretation of the experimental results is whether the oxygen atoms lifetime against exchange with the ambient CO and O_2 is sufficiently short to result in a significant isotopic fractionation in the product CO_2.

The possible fates of ground state oxygen atoms (O^3P) in the present experiments are:

$$^{18}O(^3P) + C\,^{16}O \quad \leftrightarrow \quad ^{16}O(^3P) + C\,^{18}O, \qquad (1)$$

$$^{18}O(^3P) + {}^{16}O^{16}O \leftrightarrow {}^{16}O(^3P) + {}^{16}O^{18}O, \qquad (2)$$

$$O(^3P) + CO + M \quad \rightarrow \quad OCO + M. \qquad (3)$$

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The rate constants for the reactions are:

$$k_1 = 8.3 \times 10^{-16}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}},$$

$$k_2 = 2.9 \times 10^{-12}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}},$$

$$k_3 = 3.9 \times 10^{-36}\ \mathrm{cm^6\ molec^{-2}\ s^{-1}}$$

(references [2–4], respectively).

For the experiments of BT, the rate of the isotope exchange of O with CO is faster than the O + CO + M recombination. For example, for a CO pressure of 20 cm the ratio of the rates of O – CO isotope exchange to recombination is simply: $k_1[\mathrm{O}]\,[\mathrm{CO}]/k_3[\mathrm{O}]\,[\mathrm{CO}]\,[\mathrm{M}] \approx 33$, with M, in this case, CO. The exchange of atomic oxygen with O_2 is faster yet, as may be seen by comparison of the rate of reactions (2) and (1). That ratio, R, is given by

$$R = k_2[\mathrm{O}]\,[\mathrm{O_2}]/k_1[\mathrm{O}]\,[\mathrm{CO}] \tag{4}$$

or $R \sim 3.5 \times 10^3\,[\mathrm{O_2}]/\mathrm{O_2}[\mathrm{CO}]$.

For the experiments of BT, $8 \leq R \leq 20$.

The evaluation of the two isotope exchange rates, compared to the rate of the O – CO recombination, demonstrates that the isotopic composition of the oxygen atoms is dynamically determined by the two exchange processes immediately subsequent to formation of the atoms by O_2 photolysis. This exchange-modified O-atom reservoir has the relevant isotopic composition for determining the fractionation which is ascribed to the O + CO + M step. Consequently, the net fractionation induced by the isotope exchange reactions (1) and (2) must be quantitatively evaluated to determine the end-member O-atom composition for reaction (3), where the CO isotopic composition is, of course, known.

The photodissociation of O_2 and subsequent oxygen isotope exchange reactions occur on short time scales. For the calculation of the resulting isotopic composition of O we use a combination of equilibrium constants and rate constants. One partner of the exchange reactions being monoatomic, the equilibrium constants are given by the reduced partition function ratios of the other, biatomic partner. (cf. Bigeleisen and Mayer [5]; Urey [6]). A recent, refined evaluation of the reduced partition function CO and O_2 will be used (Table 12 of [7]). At 25 °C they amount to 1.1064 and 1.077, for CO and O_2, respecticely [7]. These values compare to those of Urey [6] which are 1.1053 and 1.0818, respectively. These values indicate that, at equilibrium, exchange between oxygen atoms and CO produce isotopically fractionated oxygen atoms 106.4‰ lighter in δ^{18}O than the dominant CO reservoir. Similarly, exchange with O_2 produces oxygen atoms 77.2‰ lighter in δ^{18}O than the O_2 with which it exchanged.

In the experiments of BT, the initial isotopic compositions of CO and O_2 relative to our standard O_2 are $\delta^{18}\mathrm{O(CO)} = 16.1$, $\delta^{17}\mathrm{O(CO)} = 8.4$; $\delta^{18}\mathrm{O(O_2)} = 18.0$, $\delta^{17}\mathrm{O(O_2)} = 9.5$. Therefore, the two isotope exchange processes produce oxygen atoms whose isotopic composition may be calculated as follows.

Assuming that the net effect due to the two exchanges may be determined by statistically weighting each exchange according to its rate, the oxygen isotopic composition of O is then given by

$$\delta^{18}\mathrm{O(O\,net)} = (-59.2\,R - 90.3)/(R+1), \tag{5}$$

$$\delta^{17}\mathrm{O(O\,net)} = (-31.0\,R - 47.5)/(R+1). \tag{6}$$

The values of δ^{18}O(O net) and δ^{17}O(O net) calculated using the various values of R for the BT experiments show only small variations. The mean δ-values from calculations for both O_2 and CO exchange of the oxygen atom reservoir are

$$\delta^{18}\mathrm{O(O\,net)} = -61.7; \quad \delta^{17}\mathrm{O(O\,net)} = -32.4.$$

The oxygen atoms, with the steady state isotopic composition given above, subsequently react with CO ($\delta^{18}\mathrm{O(CO)} = 16.1$; $\delta^{17}\mathrm{O(CO)} = 8.4$) to form CO_2 whose composition, in the absence of any isotopic

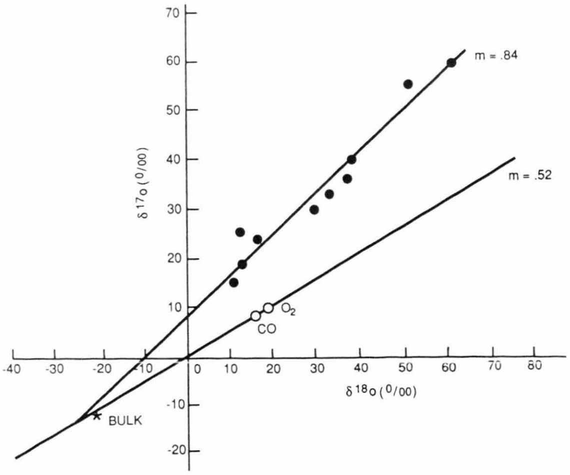

Fig. 1. The oxygen isotopic composition of CO_2 produced by reaction of atomic oxygen with carbon monoxide. The bulk isotopic composition is determined from equilibrium exchange between O and both CO and O_2, and the corresponding reaction rates.

fractionation, has the "bulk" value

$$\delta^{18}O(CO_2\ \text{bulk}) = -22.8;\quad \delta^{17}O = -12.0.$$

The data of BT are displayed in Fig. 1, along with the new "bulk" point calculated above. In the present work, the data have been fitted with an improved version of the least squares fitting [8], which takes into account the error associated with the individual data points ($\sim \pm 0.1‰$ for $\delta^{18}O(CO_2)$ and $\delta^{17}O(CO_2)$). The new best fit line has a slope (m) of 0.84 and differs slightly from the one given in Fig. 1 of BT ($m = 0.82$). The best fit line intersects the mass fractionation line ($m = 0.5 \cdot (17/16.5)^2 = 0.53$) at $\delta^{18}O = -25.7$, $\delta^{17}O = -13.5$, quite close to the calculated bulk point, and more so than for the original calculation of BT.

It is quite clear from the foregoing evaluation that oxygen atom isotope exchange with both CO and O_2 is significant. Although the O_2 concentration is quite low with respect to CO, the combined rapidity of the $O - O_2$, and slowness of $O - CO$ exchanges, render it a significant process. Finally, the observation that the data define a straight line, which touches so closely the bulk point calculated for isotopic exchanges, strongly suggests that isotopic exchange equilibria are attained. This also further supports the contention by BT that the source of the mass independent fractionation component is in the actual O + CO recombination process.

Conclusion

Formation of CO_2 by the reaction of O with CO produces a large mass independent isotopic fractionation. A best fit line of the data produces a slope of 0.84 in a $\delta^{17}O(CO_2)$ vs. $\delta^{18}O(CO_2)$ plot with an intercept of the mass fractionation line through the original CO and O_2 points, quite close to the "bulk CO_2" value calculated for the addition of an oxygen atom which has undergone equilibrium isotopic exchange with CO and O_2 in proportion to their relative rates.

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