New Evidence for Symmetry Dependent Isotope Effects: O + CO Reaction

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This paper is dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday

The isotopic fractionation associated with the O + CO reaction has been studied using oxygen atoms produced by room temperature O_2 photolysis at two different wavelengths, 185 and 130 nm. A large mass-independent isotopic fractionation is observed in the product CO_2, extending the range of this type of reaction beyond $O + O_2$ and $SF_5 + SF_5$.

Kinetic evaluation of the data restricts the source of the mass-independent fractionation mechanism to the O + CO recombination step rather than O_2 photolysis, secondary ozone formation, or O_2 photodissociation. At least one, and most likely two other fractionation processes appear to occur in the experiments, and interpretation of the isotopic results is tentative at present. Based on the relevant reaction rates and the value for the reduced partition function for isotopic exchange between O and CO, it is suggested that this process may occur prior to the $\delta^{17}O \cong \delta^{18}O$ recombination process. Secondary CO_2 photolysis may superimpose an additional fractionation. The experimental data are also examined in the context of a model based upon energy randomization rates versus the lifetime of the activated complex.

Introduction

It has been more than 40 years since the classic papers by Bigeleisen and Mayer [1] and Urey [2] provided a quantitative framework for the determination of equilibrium constants in isotopic exchange reactions. The theoretical basis of these papers has led to an extraordinarily diverse range of applications, ranging from biochemistry to the evolution of the solar system (recent reviews are given in [3–5]. A basic premise of the Bigeleisen and Mayer [1] and Urey [2] formalism was that the chemical distinction of isotopically substituted molecules is a fundamental quantum mechanical process. The specific effect of isotopic substitution is to alter the internal energy of the particular molecule as a consequence of the vibrational frequencies differing for the substituted species. An important consequence is that isotopic exchange equilibria, along with kinetic and physical isotopic fractionation processes, all rely upon mass. This feature led Hulston and Thode [6] to suggest that measurement of multi-isotopic ratios in meteorites may provide a means by which nucleosynthetic or, in general, nuclear processes may be distinguished since they produce isotopic compositions which are not the result of isotopic fractionation. It was later demonstrated that the oxygen isotopic composition of mineral inclusions from the Allende meteorite is mass-independently fractionated [7]. This observation is quite important since oxygen is the major element in rocky planets and, consequently, may represent a significant component in the early history of the solar system. If oxygen isotopic composition is expressed in the conventional delta notation, where

$$\delta^{i}O\ (‰) = \left[\frac{\left(\frac{{}^{i}O}{{}^{16}O}\right)_{\text{sample}}}{\left(\frac{{}^{i}O}{{}^{16}O}\right)_{\text{standard}}} - 1\right] \times 1000 \qquad (1)$$

with ${}^{i}O$ representing a particular isotope of oxygen, the δ then expresses, in parts per thousand (or per mil), the deviation of a sample with respect to a specified standard. A mass-dependent fractionation then is one which has $\delta^{17}O \cong 0.5\ \delta^{18}O$ (see [3] for more detail). The Allende mineral inclusions, however, define a line with $\delta^{17}O/\delta^{18}O \cong 1$, which led to the suggestion that these anomalous isotopic components were derived from a nuclear process, specifically the injection into the early solar system of essentially pure ${}^{16}O$, possibly derived from a stellar explosive carbon or helium burning process [7]. The suggestion was based upon

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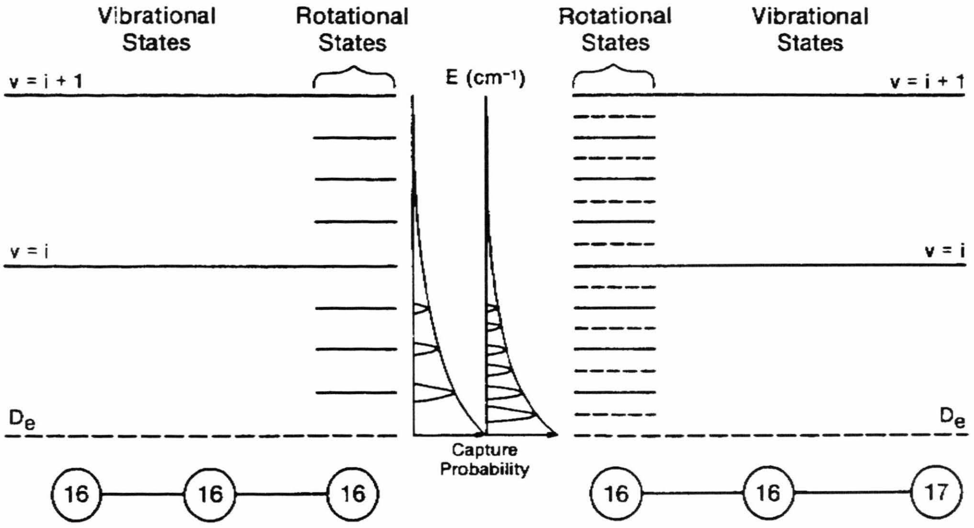

Fig. 1. Schematic diagram of the isotopic fractionation process during inverse predissociation. The asymmetric species is indicated as having twice as many rotational states from Reference [4].

the fundamental assumption that deviations from mass-dependent isotopic fractionations may only be due to a nuclear, rather than physical or chemical process. This assumption is now known to be incorrect. Thiemens and co-workers [8–12] have demonstrated that, in the process of ozone formation following O_2 dissociation, both with electrons and photons, a mass-independent isotopic fractionation occurs. In fact, the resulting isotopic composition is essentially identical to that observed in the Allende inclusions ($\delta^{17}O \cong \delta^{18}O$). This unusual fractionation process, aside from its inherent chemical-physical interest, may have a role as a process which occurs in the earliest history of the solar system and, as such, possesses information on the mechanism by which different solid objects were formed. In addition, it has recently been observed that stratospheric ozone possesses a large ($\sim 40\%$) heavy isotope enrichment with $\delta^{17}O \cong \delta^{18}O$ [13]; therefore, investigation of the mechanism by which this chemically-produced mass-independent fractionation occurs may be of use in understanding the process of ozone formation/destruction in the earth's stratosphere.

The fundamental mechanism which is responsible for the anomalous isotopic fractionation process is, as yet, not fully understood. Heidenreich and Thiemens [10] have suggested that the heavy isotope (^{17}O, ^{18}O) enrichment in O_3 formation, with $\delta^{17}O \cong \delta^{18}O$, occurs during the process of inverse predissociation shown schematically in Figure 1. During this particular type of reaction, a metastable collisional complex may be formed with an extended lifetime (with respect to a collisional time scale). If the energy of the $O-O_2$ pair overlaps one of the energy levels of the excited O_3, stabilization may ultimately occur, although the total number of successful stabilizations with respect to collisions is quite small. This probability, in part, is dependent upon the overlap between the energy levels within the diffuse bands and the energy of the collisional pair. As the number of levels within the diffuse bands increases, there is a concomitant increase in the lifetime of the O_3^* and an enhanced probability of stabilization to O_3 (cf. Herzberg [14]). In the specific case of ozone, C_s symmetric ozone ($^{16}O^{16}O^{17}O$, $^{16}O^{16}O^{18}O$) possesses twice the complement of rotational levels as C_{2v} symmetric ozone ($^{16}O^{16}O^{16}O$) due to the appearance of alternate rotational lines for the C_s species. As a consequence, asymmetric O_3 is preferentially produced which is enriched in ^{17}O, ^{18}O on a symmetry, rather than mass-dependent basis, with $\delta^{17}O \cong \delta^{18}O$, as is observed experimentally [8–12]. This particular model predicts that the fractionation process is, in part, dependent upon isotopic abundance since, at increased ^{17}O, ^{18}O abundances, significant quantities of the heavy isotopic species $^{17}O^{17}O^{17}O$, $^{18}O^{18}O^{18}O$, $^{17}O^{16}O^{17}O$, $^{18}O^{16}O^{18}O$, $^{18}O^{17}O^{18}O$ and $^{17}O^{18}O^{17}O$ are present; since these species are of C_{2v} symmetry, they have a decreased probability of stabilization. Thus the $\delta^{17}O \cong \delta^{18}O$ fractionation should be altered as a function of ^{17}O, ^{18}O abundance as discussed by Heidenreich and Thiemens [15] and experimentally demonstrated by Yang and Epstein [16, 17] and later, Morton et al. [18].

It has recently been suggested that the observed mass-independent fractionation may derive from symmetry number considerations in the association of atomic and molecular oxygen. The relative rate dependence of the energy randomization process and the activated complex lifetime are suggested as the factors which mitigate the mass-independent isotopic fractionation process [19]. As discussed in that paper, an interesting extention of the mass-independent mechanism studies would be the investigation of the isotopic fractionation resulting from the reaction of atomic oxygen with carbon monoxide to produce CO_2. In the $O + CO$ reaction, the relevant isotopic symmetries are the same as in $O + O_2$, since the central atom does not influence the relevant terminal symmetry. A second important consideration is the relative lifetime of CO_2 with respect to O_3; the lifetime of the excited CO_2 state will be greater than that of O_3, since the vibrational energy density of states of CO_2 is more than 200 times that of O_3 [19, 20]. A final important aspect is the possible role that chemically produced mass-independent isotopic fractionations may play in the early solar system. Thiemens [3] has suggested that since the central atom does not play a direct role in the fractionation process, reactions such as $O + CO$, $O + SiO$, $O + FeO$, and $O + AlO$, which plausibly may occur in the early solar system, would also produce a mass-independent isotopic fractionation. This premise is further supported by the recent demonstration of a chemically produced mass-independent isotopic fractionation in the sulfur isotopes ^{32}S, ^{33}S, ^{34}S [21, 22]. This paper reports the results of the isotopic fractionation during the reaction of atomic oxygen with carbon monoxide.

Experimental

Oxygen atoms were produced via O_2 photolysis with ultraviolet light photons from a Kr continuum (120–160 nm) or Hg (180–260 nm) lamp excited by a 120 watt, 2450 MHz microwave generator which drives an Evenson or Broida cavity. Further experimental details are provided in previous publications [11, 12, 23]. The $CO - O_2$ photolysis experiments were carried out in a 5.2 L pyrex reaction chamber with a 1 mm thick MgF_2 window ($\sim$2 cm diameter) situated at the top. A cylindrical cold trap at the bottom permitted condensation of the product CO_2 following cessation of the photolysis. Pressure of the admitted gases was measured with a mercury manometer, and ultimate vacuum was measured with a Sargent-Welch calibrated thermocouple gauge and a Granville-Phillips Convectron gauge. The experimental procedure employed for all experiments is as follows.

High purity oxygen gas (Matheson Gas) was admitted to the volumetrically calibrated reaction system to a known pressure. The amount of oxygen initially employed for the photolysis experiments was determined to be approximately 300 micromoles (the range was 180–630). Once the O_2 was admitted to the 5 liter photolysis chamber, the isolation stopcock was shut and the residual oxygen in the vacuum manifold evacuated. High purity carbon monoxide was then admitted to the evacuated manifold to a given pressure (>40 cm) and the stopcock to the photolysis system opened slightly to admit the high-pressure CO so as to minimize back flow of the O_2 to the vacuum manifold. The CO pressures employed ranged from 20–40 cm, at least 175 times in excess of the O_2. Mass spectrometric measurement of the residual manifold gas indicates that there is essentially no back diffusion of the low-pressure O_2 from the photolysis chamber. The procedure employed was necessary since isotopic integrity of both the CO and O_2 was an essential requirement.

The $O_2 - CO$ mixture was photolyzed with either a Hg or Kr lamp for periods of 10–15 hours, which dissociates O_2 into atoms which subsequently react with CO to produce CO_2. The ratio of CO/O_2 varied between 177.8 and 423. Since the $O + O_2$ reaction is significantly more rapid than that of $O + CO$, the high ratio was required to minimize ozone formation. Less O_2 could not be used because of the limited O_2 photolysis rate. At the lowest CO/O_2 ratio, the two reactions are approximately equally competitive; however, as conversion of O_2 to O atoms proceeds the CO/O_2 ratio increases, favoring O-atom reaction with CO. In addition, O_3 photolysis is rapid, and previous experiments in this system indicate that O_3 is rapidly photochemically decomposed [23]. Once the photolysis was terminated, the trap on the photolysis chamber was frozen with liquid nitrogen to condense the product carbon dioxide. The non-condensible CO and O_2

Table 1. Experimental results for the isotopic fractionation in the O+CO reaction.

Experiment number	O_2 Initial amount (micromoles)	CO Initial pressure (cm)	CO/O_2 Initial	CO_2 Yield (micromoles)	% Conversion of O_2	$\delta^{18}O$ (‰)	$\delta^{17}O$ (‰)	Photolysis time (min)
1.	185	28	423	16	4.3	12.2	25.5	1020
2.	353	31	246	58	8.2	38.2	39.2	2325
3.	282	30	298	50	8.9	33.1	33.0	960
4.	265	40	422	58	10.9	37.4	36.3	1060
5.	260	32	345	63	12.1	29.5	29.4	1330
6.	254	32	353	20	3.9	13.2	18.6	1020
7.	245	20	229	23	4.7	10.1	14.3	1320
8.	630	40	178	35	2.8	16.3	24.0	1110
9.*	253	31	343	41	8.1	60.6	59.3	1065
10.*	250	28	314	49	9.8	51.6	55.1	2660

* Indicates Photolysis of O_2 achieved with a Kr continuum lamp, all others are with a mercury lamp.

were pumped through three spiral traps maintained at liquid nitrogen temperature to insure that all product CO_2 was collected. The product CO_2 was then transferred to a calibrated manometer and the yield measured.

In order to determine both $\delta^{17}O$ and $\delta^{18}O$ of the product CO_2, it was necessary to perform the mass spectrometric analysis on O_2, rather than on CO_2, due to isobaric interferences from ^{13}C. Carbon dioxide was reacted with BrF_5 to convert CO_2 to CF_4 and O_2. The reaction was carried out in a nickel tube, essentially identical to that described by Clayton and Mayeda [24]. The carbon dioxide was transferred to a nickel reaction tube at liquid nitrogen temperature. An ~100-fold stoichiometric excess of BrF_5 was transferred to the nickel tube and the gases heated for ~48 hours at 800 °C. Following reaction, the nickel reaction tube was frozen at liquid nitrogen temperature and the product O_2 collected on a molecular sieve 13×(1/16″ pellets) trap at liquid nitrogen temperature after passage through three spiral traps maintained at liquid nitrogen temperature. Final purification of possible traces of CF_4, which interferes with the $\delta^{17}O$ measurement, was achieved by collecting the O_2 from the molecular sieve trap (originally −196 °C) in a Toepler pump after replacing the liquid nitrogen with ethanol at its melting point (measured as −120 °C); this process quantitatively releases O_2, but not CF_4. Background determinations were done mass spectrometrically to insure that no contaminants were present in the final O_2 product. Typical isotopic errors associated with the CO_2 fluorination procedure are $\sim \pm 0.1$‰ for $\delta^{18}O$.

The oxygen isotopic composition of the initial CO was determined by quantitative conversion of CO to CO_2 in an AC discharge between two platinum electrodes, with the product CO_2 continuously removed at liquid nitrogen temperature. The product CO_2 was then converted to O_2 by the described fluorination technique. The initial oxygen isotopic composition of the CO and O_2 for $\delta^{18}O$, $\delta^{17}O$ was 16.1 ± 0.1, 8.4 ± 0.15 for CO and 18.0 ± 0.08, 9.5 ± 0.1 per mil for O_2, respectively, as determined by multiple analysis. Blank experiments were performed where no molecular oxygen gas was added, and photolysis, using both Kr and Hg lamps, was performed on carbon monoxide. For irradiation periods in excess of any of those used for the $CO-O_2$ photolysis experiments, there was no measurable amount of product CO_2.

Oxygen isotopic measurements were performed on a triple collector mass spectrometer (Finnigan MAT 251). Typical errors associated with mass spectrometric analysis are $\sim \pm 0.05$‰ for $\delta^{17}O$ and $\delta^{18}O$.

Results

The results of the photolysis experiments are listed in Table 1 and plotted in Figure 2. The data define a straight line with a slope of 0.82, correlation coefficient r=0.97 and an intercept of the mass fractionation line, defined through the starting CO and O_2, at $\delta^{18}O = -31$, $\delta^{17}O = -16.2$‰. There is no trend in $\delta^{18}O$ with reaction time or initial O_2 or CO pressure observed in the present experiments. There is a weak association with per cent O_2 conversion to CO_2 or with amount

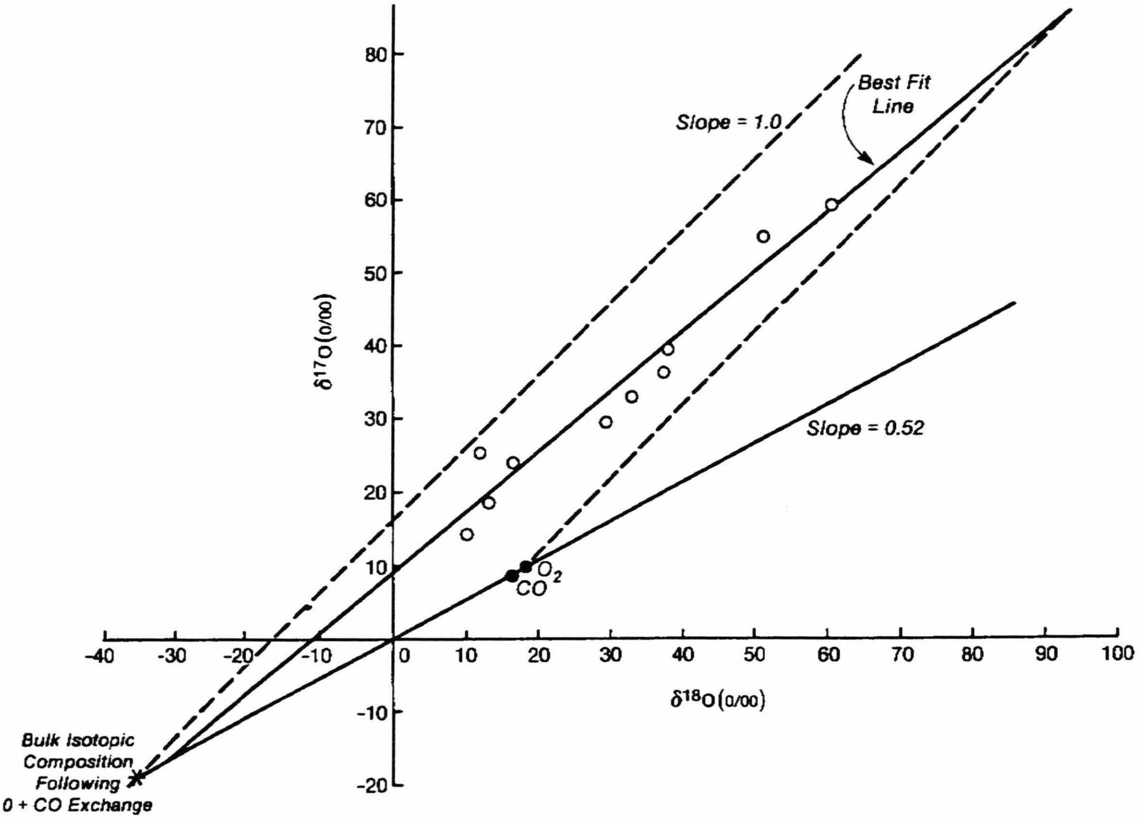

Fig. 2. Isotopic results of the O + CO experiments indicating the composition of the initial CO and O_2. The bulk point is that achieved by addition of one oxygen atom at $\delta^{18}O \cong -105$, $\delta^{17}O \cong -52.5$ and one at the CO point.

of product CO_2. The significance of each process will be discussed in the following section.

Discussion

It is clear from the data in Table 1 and Figure 2 that a mass-independent fractionation is observed in the CO_2 produced following O_2 photolysis in the presence of a large excess of carbon monoxide. The control experiments indicate that the source of the oxygen atoms is exclusively derived from O_2 photolysis since blank experiments demonstrate that no CO_2 is produced during irradiation of pure CO with either the Kr or Hg lamp. This also rules out isotopic contributions from processes such as

$$CO + CO^* \rightarrow CO_2 + C\,, \qquad (2)$$

where CO* is an excited vibrational or electronic state of CO. The best fit line of the data displayed in Figure 1 does not pass through the starting oxygen isotopic composition of either CO or O_2; this result requires that at least two distinct fractionation processes are necessary to account for the observed data.

The lightest isotopic composition of the product CO_2 is (experiment 7) $\delta^{18}O = 10.1$, $\delta^{17}O = 14.3$, which is lighter (for $\delta^{18}O$) than the starting CO or O_2 isotopic composition. Experiments 1, 6 and marginally 8 also possess $\delta^{18}O$ values smaller than the starting CO or O_2, which requires that at least one of the fractionation processes must produce a light isotopic component. If the relevant reactions are considered, the overall sequence is initiated by O_2 photolysis, which for the Schumann-Runge band region is represented by [25]

$$O_2 + h\nu\,(175\text{–}205\ \text{nm}) \rightarrow O(^3P) + O(^3P)\,. \qquad (3)$$

At wavelengths below ~175 nm to ~130 nm, O_2 dissociation results in a continuum, leading to dissociation of the O_2 B $^3\Sigma_u^-$ state to $O(^3P)$ and $O(^1D)$. Thus, for the present experiments, the Hg lamp produces nearly exclusively $O(^3P)$ atoms, while the Kr lamp produces equal amounts of $O(^3P)$ and $O(^1D)$, since the threshold wavelength for production of $O(^1D)$ is 175 nm [26]. For the $O(^1D)$ atom, the immediate fate is collisional quenching via

$$O(^1D) + CO \rightarrow O(^3P) + CO\,, \tag{4}$$

which has a rate constant of 7.3×10^{-11} cm^3 molecule^{-1} sec^{-1} [27]. Figure 2 indicates that the isotopic fractionation shows the same trend with Hg lamp photolysis, where only $O(^3P)$ atoms are produced, as with Kr lamp photolysis, where $O(^3P)$ and $O(^1D)$ are co-produced; therefore it appears as though the relevant fractionation processes must primarily involve $O(^3P)$. In the present experiments, the following reactions must be considered in accounting for the observed isotopic fractionation:

$$^{18}O(^3P) + C^{16}O \rightleftarrows {}^{16}O(^3P) + C^{18}O\,, \tag{5}$$

$$O(^3P) + CO + M \rightarrow OCO + M\,, \tag{6}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M\,, \tag{7}$$

$$O_3 + h\nu \rightarrow O_2 + O\,, \tag{8}$$

$$O + O_3 \rightarrow 2\,O_2\,. \tag{9}$$

The rate constants for reactions (5)–(8) are: $k_{(5)} = 8.3 \times 10^{-16}$ [28], $k_{(6)} = 3.9 \times 10^{-36}$ [29], $k_{(7)} = 6.0 \times 10^{-34}$ [30] and $k_{(9)} = 8.0 \times 10^{-12}$ with units of cm^3 molec^{-1} s^{-1} for 2-body reactions and cm^6 molec^{-2} s^{-1} for 3-body. For the reactions considered, the dominant kinetic fate of the ground state oxygen atom is to undergo isotopic exchange with CO. Although the rate constant for exchange between $O(^3P)$ and CO is quite small, recombination with CO is significantly slower [29, 31, 32]. For the present experiments, the rate of isotopic exchange, using the quoted rate constants and the relevant experimental pressures, exceeds recombination by factors ranging from 16.5 to 33 (experiments 4 and 7, respectively). Ozone formation following isotopic exchange is possible, at least initially; comparison of the ratio of the relative rates, reaction (6)/reaction (7), demonstrates a range of 1.16 (experiment 8) to 2.75 (experiment 1) favoring O + CO recombination. It is unlikely that O_3 formation significantly contributes to the observed fractionation, since 1) it is a minor branch, at most, and 2) it is photochemically decomposed quite rapidly in the present system [23]. The isotopic data also suggest that ozone formation is not a dominant process. It is known that the $O + O_2$ reaction produces O_3 enriched in ^{17}O, ^{18}O with $\delta^{17}O \cong \delta^{18}O \cong 85-90‰$ with respect to the initial O_2 isotopic composition. Secondary ozone decomposition may produce isotopically light O-atoms by $\sim 20-25‰$ in a mass-dependent process [23], though further clarification of this fractionation process is required. If the observed mass-independent fractionation was exclusively derived from the $O + O_2$ recombination, then one of the oxygen atoms in the product CO_2 would be derived from O_3 decomposition and the second from CO. Ozone produced from O_2 photolysis in this system should have an isotopic composition initially somewhere near $\delta^{18}O \cong 103‰$, $\delta^{17}O = 94.5$, assuming the single-stage fractionation factors measured in [12] of $\delta^{18}O \cong \delta^{17}O \cong 85‰$ and an initial O_2 isotopic composition of $\delta^{18}O = 18‰$ and $\delta^{17}O = 9.5‰$. If the photolysis of O_3 produces an O-atom isotopically lighter than the initial O_3, as expected from the isotopic vibrational frequencies and decomposition measurements [23], then the product O atom, assuming the fractionation factors measured in [23], would be $\delta^{18}O \cong 83-78‰$, $\delta^{17}O \cong 84.5-82‰$. If this atom reacts with CO at $\delta^{18}O = 16.1$, $\delta^{17}O = 8.5‰$, the product CO_2 would have a bulk isotopic composition mid-point between that of the O-atom and CO. At least 3 data points are, in fact, isotopically lighter than the starting CO isotopic composition, far removed from the calculated isotopic composition, which suggests that the O_3 formation process does not account for the observed mass-independent isotopic fractionation. A final constraint on the role of ozone formation is the apparent lack of a relation between the CO/O_2 initial ratio and the isotopic composition of product CO_2. Experiment (8) has the highest amount of O_2 initially, which is the most favorable kinetic situation for O_3 formation and enrichment of the heavy isotopes (though O + CO is still favored by a factor of 1.16), yet the CO_2 oxygen isotopic composition is similar to that observed in experiment (1), which has the highest CO/O_2 ratio and a similar reaction time. The observed isotopic fractionations in these two experiments are, in fact, among the lightest, rather than heaviest isotopic enrichments. Finally, for the ozone formation which does occur, photolysis of ozone rapidly re-produces atomic oxygen which subsequently undergoes isotopic exchange with CO. Thus, the kinetics suggest that the reactions which should dominate the isotopic fractionation process are isotopic exchange between the $O(^3P)$ atom and CO recombination between the same two species. Finally, in several experiments the condensed product was analyzed mass spectrometrically, and insignificant amounts of ozone were detected. Thus it is concluded that ozone does not play a significant role in the observed fractionation.

Further quantitative evidence for the significant intervention of isotopic exchange is provided from the reduced partition function ratios for isotopic exchange between O and CO. It is seen in Table 10 of Urey's paper [2] that the $^{18}O/^{16}O$ reduced partition function for CO at 298.1 K is 1.1053, which indicates that, at equilibrium, exchange between an oxygen atom and CO produces an isotopic composition for the atom which is 105.3‰ lighter in $\delta^{18}O$ than that for CO. In the present experiments, this atom would then acquire, at equilibrium, an isotopic composition of $\delta^{18}O \cong -89.2$, $\delta^{17}O \cong -44.6$ independent of the initial composition of the O-atom, since the exchange is dominated by the isotopic composition of the CO. If the exchanged atom then reacts without fractionation with CO, the calculated bulk isotopic composition of the CO_2 would be $\delta^{18}O \cong -36.6$, $\delta^{17}O \cong -18.3$, as indicated by the labelled point in Figure 2. If, in the subsequent O + CO recombination step, a symmetry dependent, mass-independent fractionation were to occur, the product CO_2 would lie along a $\delta^{17}O = \delta^{18}O$ ($m = 1$) fractionation line passing through the bulk point. If exchange were, however, incomplete, the mass-independent fractionation line would pass through a bulk CO_2 isotopic composition which lies somewhere along the mass-dependent fractionation line defined by the CO initial ↔ O − CO bulk line. The observation that the best fit of the data intersects the mass fractionation line at a point ($\delta^{18}O = -31$, $\delta^{17}O = -16.2$) close to the calculated bulk composition following O − CO exchange and subsequent CO addition (labeled with a star in Figure 2 at $\delta^{18}O = -36.6$, $\delta^{17}O = -18.3$) strongly suggests that exchange occurs. The kinetic data are also consistent with isotopic exchange occurring prior to O + CO recombination.

It is not immediately clear why the data define the observed trend rather than lie along the $m = 1$ line terminating at $^{18}O = -36.6$, $^{17}O = -17.9$, as shown in Figure 2. The first possibility, as discussed, is that O − CO exchange proceeds to varying degrees of completion. If this were the case, the extent of exchange would be a function of CO pressure. The ratio of exchange to recombination is

$$\frac{k_5\,(O)\,(CO)}{k_6\,(O)\,(CO)\,(m)} \tag{10}$$

or $2.13 \times 10^{20} \cdot 1/m$, where m, in this case, is [CO]. Exchange is then favored at the lowest CO pressure. Table 1 demonstrates, however, that there is no such trend in $\delta^{18}O$ with pressure. It also is unlikely that fractionation of the initial O_2 reservoir, due to conversion to CO_2 accounts for the deviation from $m = 1$, since the fractionation of the initial reservoir is small compared to the observed spread in $\delta^{18}O$ (50.5‰). The largest conversion extent of O_2 to CO_2 is 12.1%, since one of the oxygen atoms in the product CO_2 is derived from CO. The Rayleigh equation may be applied to determine the extent of initial reservoir fractionation:

$$\frac{R}{R_0} = f^{\,(\alpha-1)}, \tag{11}$$

where R is the isotope ratio at some extent of reaction f compared to the initial isotopic composition R_0, for a process having a fractionation factor α. For an assumed α of 100‰ (an unrealistically large value), a 12.1% reaction extent, with production of isotopically light O-atoms, only fractionates the initial O_2 reservoir by ~12.8‰, far short of that required to account for the observed 50.5‰ range. For an extent of reaction of 4.3% (experiment 1) and an $\alpha = 100$‰, the reservoir is fractionated by ~4.4‰. The total range in isotopic fractionation of the initial O_2 reservoir for the present experiments which would occur, even if there was a 100‰ fractionation associated with the O_2 dissociation, would be only ~10‰, clearly insufficient to account for the observed range in $\delta^{18}O$.

Isotopic exchange of the atom with O_2 must also be considered, since the rate is quite rapid. Anderson et al. [33] have performed a series of high precision experiments and have measured the rate constant for O − O_2 exchange to be 2.9×10^{-12} cm^3 molecule^{-1} s^{-1}. In the present experiments, even at low O_2 initial pressures, this particular exchange will be significant. For example, for experiment 8, which is the least favorable for O − O_2 exchange, due to the high initial CO/O_2 ratio, the ratio for the rate of O − O_2/O − CO exchange is ~20 : 1. However, once O − O_2 exchange occurs, the fate of the atom then is essentially as previously discussed, viz. it will undergo exchange with CO, thus eliminating the fractionation acquired during exchange with O_2.

A final process which has not been discussed is the secondary photolysis of carbon dioxide. In the emission region for the Hg lamp (~185 nm), CO_2 has an absorption coefficient of 1×10^{-2} atm^{-1} cm^{-1} and in the Kr lamp region ~16 atm^{-1} cm^{-1} [26]. If the CO_2 were photodissociated, the residual CO_2 should become enriched in the heavy isotopes in a mass-dependent fashion. The Hg lamp emits on the order of ~10^{16} photons · s^{-1} in the relevant CO_2 actinic region; which, for example in experiment 1, would only result in the photolysis of ~1.2×10^{16} molecules (or 2.0×10^{-8} moles), assuming that a pressure 7.7×10^{-5} atm. of CO_2 (16.0 micromoles in a 5200 cm^3 volume, as in experiment 1) was sustained. For a CO_2 pressure 2.98×10^{-4} atm (63 µmoles) photolyzed in the 5200 cm^3 over a period of 1330 min (experiment 5), ~6.0×10^{16} molecules (1.0×10^{-7} moles) of CO_2 would be photodissociated. If the deviation from the displayed $m = 1$ line is from CO_2 photolysis, the residual reservoir must be fractionated between ~2–32‰ in $\delta^{18}O$ to account for the data. If a fractionation factor of 100‰ in $\delta^{18}O$ is assumed, again probably an upper limit, a depletion of the CO_2 reservoir of ~26% would produce a ~30‰ fractionation of the residual CO_2. As demonstrated in experiment 5, if it is assumed as an upper limit that 63 µmoles of CO_2 are irradiated with the mercury lamp over a period of ~1330 minutes, approximately 1×10^{-7} moles of CO_2 are dissociated, or a conversion of only ~0.1%, several orders-of-magnitude less than that required to account for the data.

In the case of the Kr continuum lamp, however, with an emission peak at ~130 nm, the CO_2 absorption coefficient is ~16 atm^{-1} cm^{-1} [26]. For experiments 9 and 10, the average amount of CO_2 produced is 45 micromoles. For experiment 9, with a photolysis time of 1065 minutes, if we assumed that the average amount of CO_2 present was that at half photolysis time (e.g. 22.5 micromoles, or a pressure of 1.1×10^{-4} atm at 1065 minutes) then ~47 micromoles of CO_2 would have been photolyzed. The output of the lamp, however, may be more of the order of 5×10^{16}; regardless, this amount of CO_2 decomposition is sufficiently large to account for the observed departure from a pure symmetry dependent fractionation. It is also observed that, in experiment 10, the yield is nearly half that of experiment 9, while the photolysis time is nearly double. It should be noted, however, that the emission flux from the Kr lamp is variable. The observation that the isotopic data for the Kr continuum lamp exhibit the greatest departure from the slope 1 line which originates at $\delta^{18}O = -36$, $\delta^{17} = -16.2$ is consistent with the notion that secondary CO_2 photodissociation accounts for the departure from the pure $\delta^{17}O = \delta^{18}O$ fractionation line. Figure 3 is a plot of the CO_2 yield versus $\delta^{18}O$. The trend exhibited in Figure 3 is also consistent with the premise that secondary CO_2 photolysis, which is greatest at higher CO_2 pressures, accounts for a tertiary fractionation process. The main difficulty with this suggestion is, as stated, that for the Hg lamp experiments the combined small absorption coefficient at the relevant wavelength and the small CO_2 pressures do not result in a significant amount of CO_2 photolysis. It may only be qualitatively suggested that at the high pressures employed for the present experiments complete mixing does not occur, and the product CO_2, formed within the beam cylinder on a rapid time scale with respect to diffusion, has a significantly higher effective pressure than that determined from the CO_2 yield in a volume of 5200 cm^3. Although it would be desirable and possible to collect the product CO_2 immediately following its photolysis using a liquid nitrogen trap, it may not result in unambiguous results. Ozone formation becomes more favorable at low temperatures due to its negative activation energy and would, subsequently, be trapped along with the product CO_2, rather than undergo essentially immediate photolysis, thus introducing an unknown amount of isotopic fractionation.

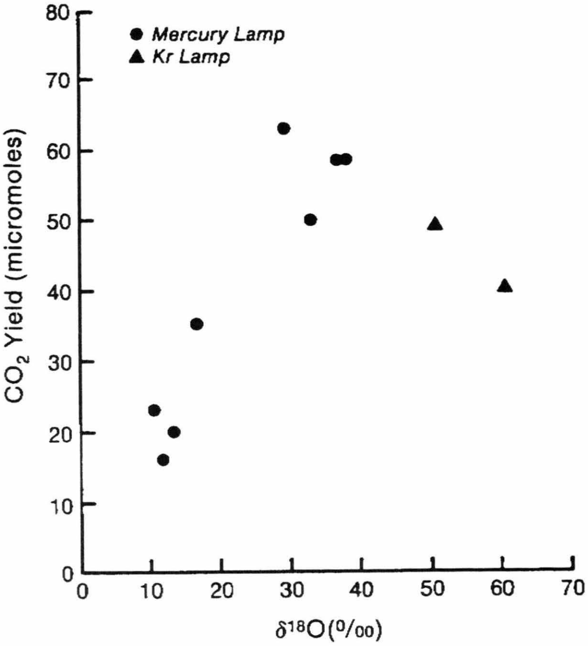

Fig. 3. The relation between $\delta^{18}O$ of the product CO_2 and CO_2 yield.

At present, it may be suggested that a tertiary isotopic fractionation of CO_2 is present due to its photodissociation. This is suggested partly based on the observation that the Kr continuum lamp, with an emission peak in the CO_2 actinic region where the absorption coefficient is relatively large (16 atm^{-1} cm^{-1}) produces the highest $\delta^{18}O$, with respect to the Hg lamp, with an absorption coefficient ~ 3 orders-of-magnitude smaller than for Kr. The apparent correlation of CO_2 yield with $\delta^{18}O$ is also qualitatively consistent with this suggestion. Future experiments employing a new photolysis vessel with a decreased volume (e.g. 2 cm diameter) will provide further tests of this suggestion. In addition, measurement of the fractionation factor associated with CO_2 photolysis is needed to quantitatively determine the role of CO_2 photolysis.

For the sake of discussion, the best fit line may be thought of as a mixing line. To account for the data, two end members in isotopic composition would then be required; one at the point labelled as the bulk CO_2 following $O-CO$ exchange and recombination, and a second which might be at the intersection of the best fit line with a slope-one line ($\delta^{18}O \cong 94$, $\delta^{17}O \cong 86‰$), terminating at the CO initial isotopic composition. If this were the case, it would require, for example in experiment 5, that approximately equal amounts of each end member be provided (exactly equal amounts would result in a final isotopic composition $\delta^{18}O = 28.7$, $\delta^{17}O = 33.85‰$). This would also imply that to produce the end member at $\delta^{18}O = 94$, $\delta^{17}O = 86‰$, a single-stage fractionation factor of $\delta^{18}O = \delta^{17}O = 78‰$ occurs, as compared to ~85‰ for $O+O_2$ [12] and 2–5‰ for SF_5+SF_5 [22]. While this is reasonable, in terms of the magnitude of the required fractionation, the kinetics do not support this contention. In order to account for the observed data by a twofold mixing of processes, the measured rate constant for exchange would need to be slower, or the reaction of $O+CO+M$ faster, by at least an order-of-magnitude, both of which almost certainly are not wrong by anywhere near that amount. A possibility may be that there is a dependency upon energy, particularly for the $O+CO$ reaction. It is seen that the Kr lamp produces a significantly greater fractionation than the Hg lamp. The average photon energies are 9.5 and 6.7 ev for the Kr and Hg lamps, respectively, qualitatively suggesting that the energy of the atom may be of importance. Bates [19] has suggested that the mass-independent fractionation observed in ozone formation derives from the termolecular association of $O+O_2$ and consideration of the specific symmetry numbers associated with the reaction. The magnitude of the fractionation is mediated by the energy randomization process and its time scale (τ_R). The isotopic enrichment is suggested as directly relating to the rates at which the species $O \sim OQ^*$ and $Q \sim OO^*$ are formed, where Q represents ^{17}O or ^{18}O and O is ^{16}O; the * denotes the activated ozone complex and ~ represents a bond possessing an average energy in excess of the randomized energy. The ultimate magnitude of the enrichment is controlled by the ratio of the energy randomization time (τ_R) to the lifetime of the activated complex (τ_D). The term $\bar{\Delta}$, given by Bates as

$$\bar{\Delta} = \{\tau(R)/\tau(D)\}\,\{1-\exp[-\tau(D)/\tau(R)]\}\,, \qquad (11)$$

ultimately defines the magnitude of isotopic enrichment. For ozone formation, a magnitude of 230‰ for a single-stage fractionation is calculated when $\tau(R)/\tau(D)$ is about one-third. An increase in the ratio $\tau(D)/\tau(R)$ would thus alter the magnitude of fractionation. As Bates states, $\tau(R)$ for CO_2 should be approximately the same as for ozone, while $\tau(D)$ should be ~200 times greater for CO_2, based upon calculations by Troe [20]. The relative lifetime difference suggests that the magnitude of fractionation should be significantly different from 85‰, the measured ^{18}O enrichment in O_3 formation. This clearly is not the case for the present experiments. As discussed by Bates [19], there are large uncertainties in $\tau(R)$ and $\tau(D)$, and caution in interpretation is warranted. In addition, the lifetime of the CO_2 activated complex may be influenced in an undetermined fashion by the forbidden spin change which must occur during the curve crossing [19]. Thus, at present, the mechanism prescribed by Bates [19] may not be ruled out, and future theoretical models based on the present experiments and those involving ozone formation [8–12] and decomposition [23] will be of importance. Spectroscopic studies of the role of symmetry in the reaction mechanism, such as those recently done by Anderson et al. [34] for ozone, would also be valuable.

Conclusions

Experiments involving the reaction of $O+CO$ have been performed to study the role of symmetry in isotopic fractionation processes. It is found that a large mass-independent fractionation, associated with the

$O + CO$ reaction, does occur; however, at least two other fractionation processes occur. Isotopic exchange between O and CO is suggested as occurring, based upon quantitative kinetic arguments and the calculated reduced partition functions for the exchange process. Following exchange, a symmetry dependent fractionation in the recombination step, with $\delta^{17}O \cong \delta^{18}O$, may occur, however, secondary CO_2 photodissociation may modify the pure effect. A model based on the relative lifetimes of the CO_2 activated complex and the energy randomization process is considered; however, the measured rates for the process and the observed magnitude of the fractionation place constraints on the model.

The general role of symmetry in isotopic fractionation processes for gas phase reactions, first measured at this laboratory in $O + O_2$, and later in $SF_5 + SF_5$, is now extended to $O + CO$. This further supports the suggestion that reactions such as $O + CO$, $O + SiO$, $O + MgO$, $O + AlO$ and $O + FeO$ may play a role in the early history of the solar system and produce the mass-independent oxygen isotope distribution observed in meteoritic material.

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