CHAPTER 2

Mass-Independent Oxygen Isotope Fractionation in Selected Systems. Mechanistic Considerations

R.A. Marcus*

Contents

Abstract

Studies of the mass-independent effect on oxygen isotope fractionation (MIF) are summarized, focusing on the MIF in ozone formation in the laboratory, a similar effect being found in the atmosphere. (As used here the MIF for O isotopomers means that the usual three-isotope plot has a slope of about unity instead of the conventional 0.52.) The marked difference of results obtained with systems when there is extensive isotopic exchange ("scrambled") and experimental conditions where isotopic exchange is minimized ("unscrambled") is also discussed. Ratios of rate constants can be measured only in the latter and show large isotope effects. These large isotope effects were shown to cancel exactly when there is extensive isotopic exchange, and one then obtains instead an MIF for ozone. We also consider a possible role of the chaperon versus energy transfer mechanisms for ozone formation in influencing the temperature dependence of the MIF. MIF in other systems are noted. Separately we consider the $CO + OH \rightarrow CO_2 + H$ reaction, an isotopically anomalous reaction. It

* Noyes Laboratory of Chemical Physics, MC 127-72, California Institute of Technology, Pasadena, CA 91125-0072, USA

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has sometimes been called "mass-independent" but has no O atom symmetry for the HOCO* intermediate and so no MIF in the above sense (*ca.* unit slope) would be expected on theoretical grounds.

1. INTRODUCTION

The principal focus of the present article is on the "mass-independent isotope effect" (MIF) found in atmospheric and laboratory produced ozone. When this MIF occurs, a plot of the positive or negative "enrichment" $\delta^{17}O$ in samples versus that of $\delta^{18}O$ in those same samples has a slope of approximately unity, rather than its typical value of about 0.52. The 0.52 is the value expected using conventional transition state theory when nuclear tunneling effects are absent. For an isotope Q, δQ is defined in per mil as $1000\ [(Q/O)/(Q/O)_{std} - 1]$, where Q/O is the ratio of Q to ^{16}O in the sample and std refers to its value in some standard sample, standard mean ocean water. An example of a three-isotope plot showing a slope of 0.52 is given in Figure 2.1.

The MIF phenomenon was first observed by Clayton in 1973 for the isotopic oxygen content in the earliest solids in the solar system, the so-called calcium-aluminum-rich inclusions (CAIs) in carbonaceous chondritic meteorites [1]. The slope of $\delta^{17}O$ versus $\delta^{18}O$ plot for the CAIs was close to unity, the CAIs being equally deficient in the heavy O isotopes, deficient in the δ notation sense, while the ozone is equally enriched in those isotopes in that sense, as in Figure 2.2. Both are examples of an MIF. Interest in this striking phenomenon for the CAIs is motivated by what it may reveal about the formation of the early solar system. Standard reaction rate transition state theory [3], and behavior of oxygen an other isotope fractionation in many other systems, would have led, instead, to the slope

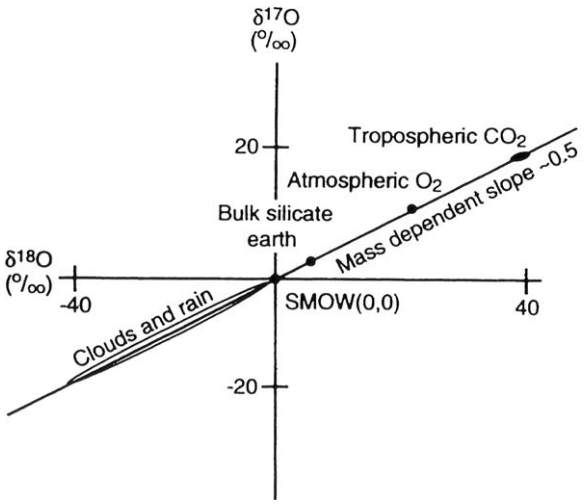

FIGURE 2.1 Three-isotope plot with a conventional slope [59].

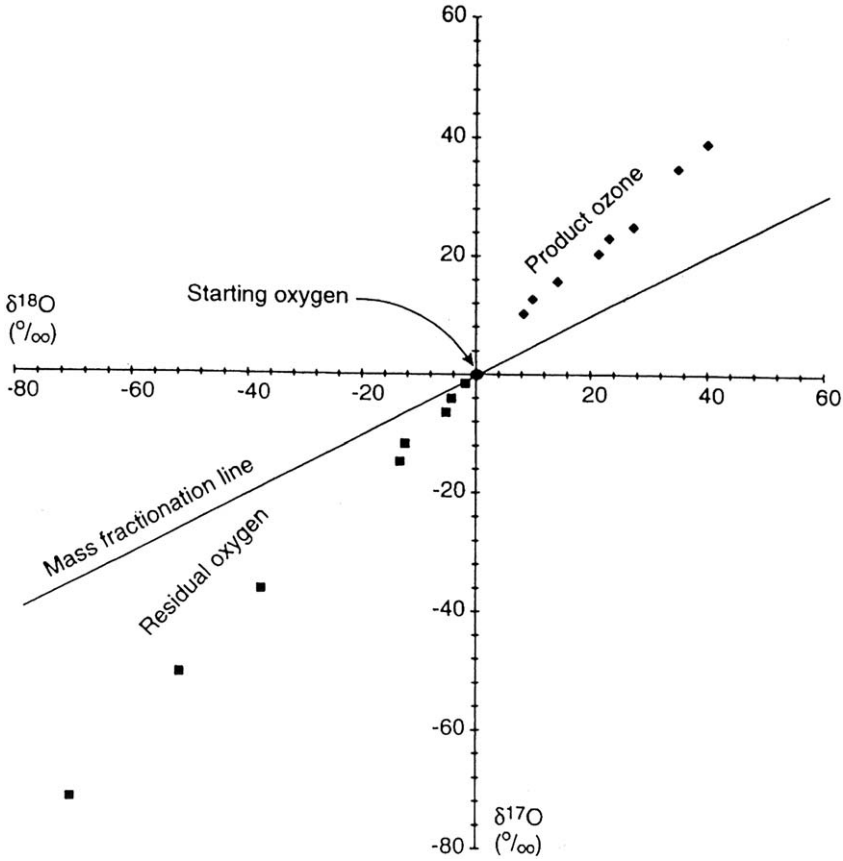

FIGURE 2.2 Three-isotope plot for ozone [5].

being about 0.52 [4]. This present chapter draws, in part, upon previous work in my group and on a recent contribution to a multi-authored chapter written for a quite different audience, one focused on the CAIs [2].

The MIF oxygen isotope effect in the gas phase was first discovered by Thiemens and Heidenreich in 1983 for ozone formation in the laboratory, the ozone being equally enriched in ^{17}O and ^{18}O relative to some standard [5], as in Figure 2.2. In these experiments the O_3 was produced by an electric discharge of O_2, followed by a reaction $O + O_2 \rightarrow O_3$, which proceeds via a vibrationally excited intermediate O_3^*, as in Eq. (1) below. Later, this MIF was also found by Yang and Epstein [6]. Anomalous oxygen isotope fractionation was found in the stratosphere by Mauersberger [7] and the anomaly has proven to be an important tracer in Earth's atmosphere (e.g., [8]). By studying both ^{17}O and ^{18}O the MIF was later found for O_3 in the stratosphere in 1990 by Morton *et al.* [9]. Studies have shown MIF effects in reactions involving CO and CO_2 [10,11].

Understanding the mass-independent isotope fractionation effect for ozone in the laboratory [5] and stratosphere [9] poses interesting challenges. These chal-

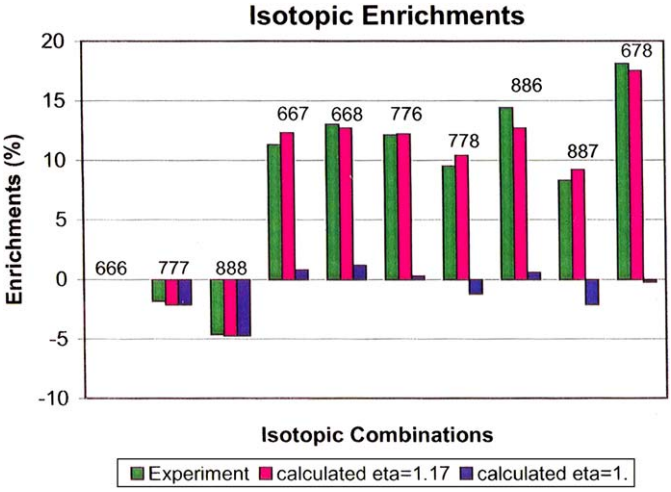

FIGURE 2.3 Heavy oxygen isotope enriched mass independent fractionation, experiment [59] and theory [13].

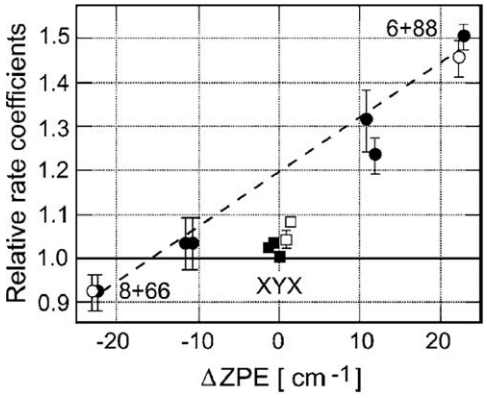

FIGURE 2.4 Ratios of rate constants ($k^r_{X+ZZ\rightarrow XYZ}/k^r_{6+66\rightarrow 666}$) vs. zero-point energy difference of exit channels [45]. The clustering of points for the symmetric isotopomers at $\Delta ZPE = 0$ is due to the points having been slightly displaced horizontally for clarity [45].

lenges are both in the stratospheric/atmospheric interest in the phenomenon itself and in understanding the new chemical physics responsible for the phenomenon. Much is now understood about the MIF in ozone formation in the gas phase [12–16], but there remain interesting questions, posed below, to be addressed. The experimental data themselves involve the effect of pressure [9,17] and temperature [9] on the MIF, and the observation of the MIF for all possible isotopomers in systems enriched in the heavy isotopes ^{17}O and ^{18}O, the latter depicted in Figure 2.3. There are also data that are interesting in their own right but are not relevant to the MIF, namely a large mass-dependent but anomalous isotope effect

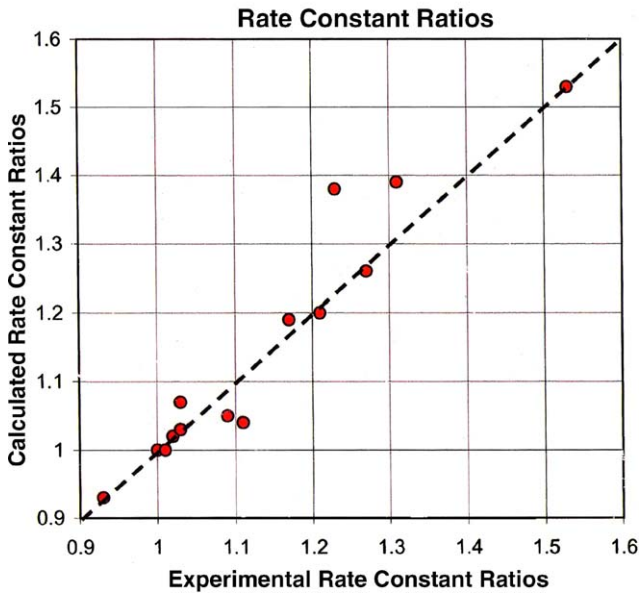

FIGURE 2.5 Experimental vs. calculated ratios of rate constants [13].

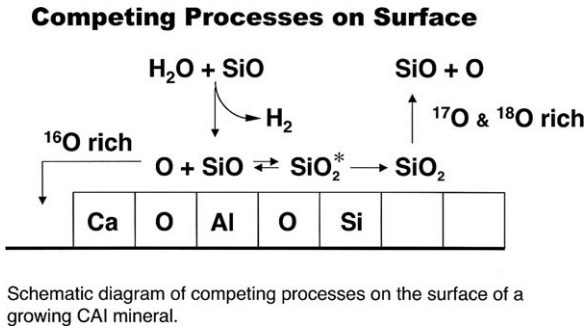

FIGURE 2.6 Theory for forming CAIs on dust surfaces at 1500–2000 K and separating oxygen isotopes in a mass-independent way [27].

for ozone formation observed under very special experimental conditions [18], as in Figures 2.4 and 2.5. We discuss it later. Recent review articles on MIF and related behavior in the atmosphere include [19–26].

While the main focus of the present article is on ozone, we note briefly in passing that several mechanisms have been postulated for the MIF in the CAIs, in particular an on-dust chemical mechanism [27] that is a surface reaction analog of the ozone formation mechanism discussed here, depicted schematically in Figure 2.6, and spectral self-shielding mechanisms [28–30]. In the latter, CO is dissociated photochemically in the early solar system, so producing a ^{16}O domain that is largely physically separated from that of the less abundant isotopes ^{17}O

and ^{18}O, because of spectral shielding (saturation). Subsequent mixing of the two domains in different proportions would yield gases that have a slope near unity for a plot of $\delta^{17}O$ versus $\delta^{18}O$. The details of how the separated O atom isotopes in the domains are transformed chemically into the MIF in CAIs remain to be described. We also note that unusual isotope effects have been reported for ionic systems [31–33].

2. THE MIF IN OZONE FORMATION

We first summarize a theory applied to the MIF effect in ozone formation [12–15]. The theory of the MIF in ozone formation involves several concepts, some of which are well established in the literature by many studies on the rates of unimolecular dissociation and bimolecular recombination reactions [34–39]. The main features of this analysis of the MIF in ozone formation are summarized below.

Oxygen atoms are typically formed in the stratosphere or laboratory by photodissociation of O_2 and in the laboratory also by electric discharge in O_2. The O and O_2 in the gas phase recombine on collision to form a vibrationally excited ozone molecule O_3^*:

$$O + O_2 \rightleftarrows O_3^*. \tag{1}$$

The O_3^* subsequently redissociates, as in the reverse of reaction (1), or is stabilized by collisions involving loss of vibrational energy to any molecule M:

$$O_3^* + M \rightarrow O_3 + M. \tag{2}$$

After formation of O_3^* an energy redistribution ("intramolecular energy randomization") occurs among the vibrations and rotations of the O_3^* molecule. This redistribution is typically assumed to provide on the average an equipartitioning of the excess energy among all the coordinates of this vibrationally hot O_3, subject to the constraint of the fixed total energy E and total angular momentum J of the O_3^* that exists prior to the next collision. The energy redistribution among the coordinates is due to anharmonic couplings of the molecular vibrations of O_3^* and to coriolis, centrifugal distortion, and other couplings of the vibrations and rotations. Similar remarks apply to other dissociating molecules.

The most common theory used to treat bimolecular recombination and unimolecular dissociation reactions in the literature is a statistical theory, "RRKM" theory (Rice, Ramsperger, Kassel, Marcus) [34–39]. However, symmetrical isotopomers such as $^{16}O^{16}O^{16}O$, $^{16}O^{17}O^{16}O$ and $^{16}O^{18}O^{16}O$ have fewer intramolecular dynamical couplings for an intramolecular energy redistribution (fewer "quantum mechanical coupling matrix elements"), because of symmetry restrictions, as compared with asymmetric O_3 isotopomers, such as $^{16}O^{16}O^{17}O$ and $^{16}O^{16}O^{18}O$ [15]. Because of the reduced number of coupling elements in the symmetric isotopomers, we have assumed that the symmetric isotopomers have less energy redistribution of the energy of the newly formed chemical bond among the other coordinates than do the asymmetric isotopomers ("less statistical") [15]. Thereby, this O_3^* occupies less "phase space" (as depicted schematically in Figure 2.7) and,

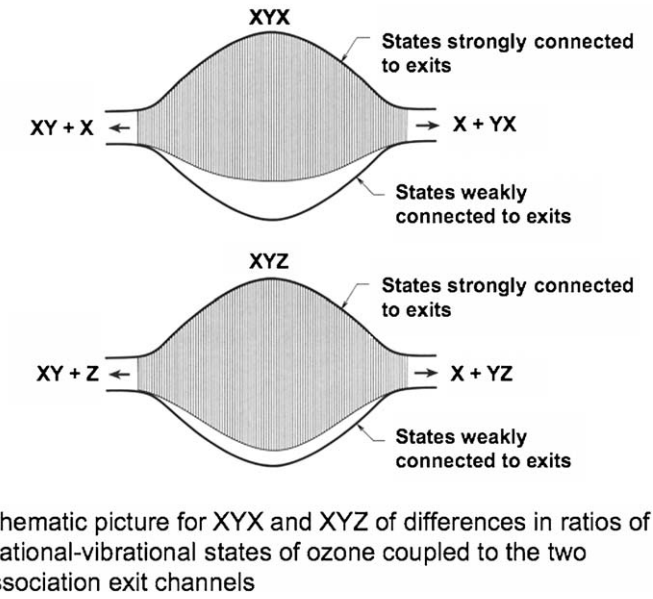

FIGURE 2.7 Schematic diagram illustrating the reduced effective phase space for a symmetric ozone isotopomer, so leading to an enhanced dissociation rate [12].

consequently, in terms of unimolecular reaction theory it has a shorter lifetime for redissociation. The shorter lifetime of an O_3^* isotopomer means that there is less chance of its being stabilized by loss of energy in a collision in reaction (2) and so the rate of formation of the stabilized O_3 molecule is less. For symmetric molecules the conventional expression for the density of states of the vibrationally excited molecule is divided by a factor η for symmetric isotopomers and by unity for asymmetric ones. In the calculations, to fit the experimental result on the MIF, η was chosen to be about 1.18 [13,14].

This assumption of less energy redistribution in the symmetric isotopomers, compared with asymmetric isotopomers, remains to be tested by *ab initio* quantum mechanical calculations, and as well as by a more direct experiment, as noted later. Such fundamental quantum mechanical calculations would yield an *a priori* value of η. In principle, η can also be inferred from the more direct but more difficult experiment.

This property of a reduced number of coupling elements for symmetric systems is the same for all symmetrical isotopomers regardless of isotopic masses, since all have the same common symmetry property. The formation of symmetric heavy atom isotopomers, $^{16}O^{17}O^{16}O$ and $^{16}O^{18}O^{16}O$ in the isotopically scrambled system dilutes the magnitude of the MIF by about 1/3 but doesn't eliminate it.

In summary, because of a dynamical consequence of symmetry in this model, the vibrationally excited asymmetric isotopomers, such as QOO*, have approximately equal lifetimes that are longer than that of the symmetric isotopomers, such as OOO* and OQO*, Q being ^{17}O or ^{18}O. At low pressures they have thereby

an improved chance of being deactivated by a collision and so of forming a stable ozone molecule, so leading to an equal (mass-independent) fractionation of the heavy isotopes in the ozone, relative to some standard.

This symmetry/asymmetry behavior is not restricted to O_3 but would apply to all triatomic or larger molecules that have the possibility of forming symmetric and asymmetric isotopomers, although its extent will depend on the molecule and the temperature, e.g., it can differ in magnitude for O_3^*, CO_2^*, SiO_2^*, and O_4^{+*}. Of course, when a highly vibrationally excited molecule such as O_3^* undergoes large amplitude vibrations, it will for short instants deviate from its simple symmetry (C_{2V} in the case of the symmetric isotopomer O_3 or OQO). Such effects could reduce the magnitude of the MIF, though not eliminate it.

Experimental studies permit some tests of these ideas. For example, the universality of the effect among all types of ozone isotopomers is seen in oxygen mixtures heavily enriched in ^{17}O and ^{18}O [18] and compared with theory in Figure 2.3 [12,13]. It is also seen in Figure 2.4, the points at $\Delta ZPE = 0$ being about 18% lower than those for the asymmetric cases. The effect of pressure on the MIF from 10^{-2} to 10^2 bar [16,17] has been measured and the theory tested by comparison with the data [12,13]. We note that higher pressures all of the O_3^* formed is collisionally deactivated to form O_3 and so the anomaly reflected in the differences in lifetimes of the symmetric and asymmetric isotopomers of O_3^* disappears and so the MIF disappears, experimentally and theoretically.

The effect of temperature on the MIF is found in experiments [16] to increase with increasing temperature. Thus, the observed MIF is not a "threshold energy effect". The origin of this temperature effect poses an interesting question: is it because the higher the temperature the higher the energy of the typical O_3^*, the shorter its lifetime, the less time there is for energy redistribution in the excited ozone, and so the greater the non-statistical effect and thereby a larger MIF? Or does it indicate another phenomenon? We return to this point in a discussion of a 'chaperon' versus energy transfer mechanism for ozone formation.

Missing is a very direct experiment on energy redistribution in ozone formation: The dissociative lifetime behavior of the vibrationally excited O_3^* has not been studied under well-defined collision-free conditions. Under suitable conditions O_3^* could be prepared with a known vibrational energy and its time-evolution could be studied using a two laser "pump-dump" method in a molecular beam. A single-exponential decay of the O_3^* would indicate full statistical intramolecular mixing of the energy, while a more complex time decay would indicate incomplete mixing ("non-RRKM" behavior), e.g., [40]. Different isotopomers of O_3^* could be similarly studied, together with the effect of increased energy on the distribution of lifetimes. An increased energy is expected to increase the difference in the lifetimes of the symmetric and asymmetric isotopomers, based on one interpretation of the observed effect of temperature one the MIF noted above.

3. QUANTUM DYNAMICAL COMPUTATIONS

There have been several preliminary quantum mechanical computations of some elementary steps in ozone formation [41–43]. In some studies the zero-point en-

ergy exit channel aspect has been addressed, and there has also been some study of Feshbach resonances for the collision, $O+O_2 \rightleftarrows O_3^*$. The fully quantum mechanical calculations are typically at $J = 0$. The complete scheme involves, in addition to these scattering resonances of $O + O_2 \rightleftarrows O_3^*$ at all J, the role of collisions with a third-body M in reaction (2) in forming the collisionally stabilized O_3 molecules. At present quantum mechanical calculations of these processes are still in a very early stage.

4. INDIVIDUALLY STUDIED RATIOS OF ISOTOPOMERIC REACTION RATE CONSTANTS

In the standard experiments on the MIF there is extensive isotopic exchange ("isotopic scrambling"), such as $Q + OO \rightleftarrows QOO^* \rightleftarrows QO + O$. However, there is also a body of experimental data on ozone formation obtained under very special experimental conditions [18] in which isotopic exchange is minor. In these experiments ratios of recombination rate constants, such as the $[^{16}O + {}^{18}O^{18}O]/[^{16}O + {}^{16}O^{16}O]$ ratio of ks are measured directly. (The unmeasured ^{16}O atom concentration cancels in this ratio of rates.) The results show very large isotope-specific effects, very different from the MIF. The new data are now well understood in terms of differences of zero-point energies of the transition states for the two competing modes of dissociation of an asymmetric ozone molecule, e.g., $OOQ \rightarrow O+OQ$ and $\rightarrow OO+Q$, e.g., [12–14]. Earlier, excellent correlations of these rates with a variety of molecular properties had been noted [44,45] but the argument showing that of these properties it was the zero-point energy difference of the two exit channels of the dissociating asymmetric isotopomers that was the origin was given in a detailed theoretical analysis [14].

As interesting as these special "exit-channel" effects are in their own right, it has been shown that because of a cancellation, they have no bearing on the MIF phenomenon [15]. We stress this point, since occasionally it is assumed in the literature that the special exit channel effect in the ratios is a key to understanding the MIF. Instead, the mass-independent effect of "scrambled" systems and the anomalously large mass-dependent effect for reactions of the type $Q + OO \rightleftarrows QOO^* \rightarrow QOO$ and $QO + O$, have very different origins and are unrelated. Perhaps these remarks may seem paradoxical. The various rate constants for these "isotopically unscrambled" reactions can be used to compute the observables for the isotopically scrambled system, and so compute $\delta^{17}O$ and $\delta^{18}O$. However, the detailed analysis [15] showed that there is much cancellation, summarized below, and that the theoretical expression for the MIF conditions is now simpler than would appear from the expression for the MIF in terms of the individual rate constants [15]. In particular, the zero-point energy effect, important for the individual isotope rate constants, disappears when the combination of them that determines the MIF is calculated.

Some physical insight into how this cancellation arises is considered next. In particular, we comment on why the dramatic and large exit channel mass-dependent isotope effect observed [18] under "unscrambled" experimental conditions is not relevant when the experimental conditions are, instead, the usual ones

typical for MIF observations, "scrambled". We first note that under scrambled conditions an intermediate such as OQQ* formed at *low enough* energies from O + QQ can only dissociate back into O + QQ and not into the other channel, OQ + Q, because OQ has a higher zero-point energy than QQ. In contrast, in the comparison reaction in the ratio, $O + OO \rightarrow O_3^*$, there are always two energetically accessible dissociation channels at all energies. So this OQQ* has a longer lifetime on the average than the O_3^* aside from any conventional isotope effects, and is therefore more likely to be stabilized by a deactivating collision. Thereby, the ratio of rates of formation of the stabilized OQQ compared with that of O_3 is larger than unity. The opposite is true for a reaction such as $Q + OO \rightarrow QOO$, in which the reactant, O_2, has a higher zero-point energy than does the product of the dissociation into QO + O. In this case the dissociation via QOO* is faster than if it didn't have this energy excess, and so the ratio of the product QOO to that of the product of the comparison reaction, $Q + QQ \rightarrow QQQ$ can be lower than unity.

The cancellation noted above occurs via the partitioning factors in the expression for each rate constant: These factors describe the relative numbers of quantum states in the transition states of the two dissociating channels of the vibrationally hot dissociating asymmetric isotopomer [15]. The difference is magnified by difference in the zero-point energy of the two competing dissociating channels and leads to the large differences in specific rate constants. For systems where isotopic exchange is extensive, these two partitioning factors sum to unity in the theoretical expression for the enrichment [15], and so the ΔZPE effect is now absent.

The situation when the gas is isotopically scrambled, however, is very different and indeed the experimentally observed measured quantity is also very different. When the gas is isotopically scrambled, one does not measure these specific ratios of rate constants. Instead, a statistical steady-state, such as $Q + OO \rightleftarrows QOO^* \rightleftarrows QO + O$ and in the above example $O + QQ \rightleftarrows OQQ^* \rightleftarrows OQ + Q$, exists at all energies, and now the energy distribution of the vibrationally excited intermediates is that which is dictated by the steady-state equations for the above reactions, and not by that of a vibrationally hot intermediate formed solely via one channel. Under such conditions all energies of the intermediate are statistically accessible, if not from one side of the reaction intermediate then from the other. Phrased differently, the isotopic composition of the collisionally stabilized product O_3 or QO_2 or will typically differ from that of the vibrationally excited species O_3^* or QO_2^*, since the intrinsic lifetime of the latter is isotope-dependent, as discussed in [15]. The usual RRKM-type pressure-dependent rate expression and conventional isotope effect results, modified by the nonstatistical effect discussed earlier [15].

Another interesting result obtained in experiments on these ratios of rate constants is the lack of the dependence of the ratio on the nature of the gas collisionally deactivating the vibrationally excited ozone isotopomer [46]. Different mechanisms have been postulated for the collisional deactivation, including the energy transfer mechanism used here and most commonly used elsewhere, and a 'chaperon' mechanism in which the third-body collision partner forms collision complex with the O or with the O_2 prior to the recombination step. Recently the chaperon mechanism was revisited for ozone formation, analyzing pressure and temperature dependent data on the recombination rate [47]. Since the ratios of rate

constants of formation of the different isotopomers are independent of the nature of the third body [46] for the ratios studied, any chaperon mechanism and indeed any mechanism needs to be consistent with that observation. These different gases do affect the rate of ozone formation [48].

In an interpretation of the data [46] and in a calculation [49] it has been proposed that the energy transfer mechanism (Eqs. (1) and (2)) is dominant at higher temperatures and the chaperon mechanism at lower temperatures. In that case we can explore the consequences for MIF: From a theoretical point of view the chaperon mechanism does not have the long-lived O_3^* and so does not have the isotopic symmetry effect present in the energy transfer mechanism of Eqs. (1) and (2), and so would not be expected to have an MIF. In this case, therefore, we have an alternative explanation of why the MIF is larger at higher temperatures. At higher temperatures the energy transfer mechanism dominates and so there would be an MIF for ozone formation. At lower temperatures the chaperon mechanism dominates and so the MIF for ozone would tend to disappear. If the relative importance of the two mechanisms depends on the nature of the colliding gas, then the MIF would also, a result that can be tested experimentally. The test would be least ambiguous at lower pressures, before the decrease of the MIF with increasing pressure becomes important.

5. RATE CONSTANT RATIOS AND ENRICHMENTS FOR OTHER REACTIONS

The ratio of rate constants and the pressure dependence of the MIF for other reactions have also been treated theoretically, reactions such as $CO + O \rightarrow CO_2$, $SO + O \rightarrow SO_2$, $O + NO \rightarrow NO_2$ [49]. In a calculation of the ratios of rates and of the MIF for these other reactions, some of which may be "spin-forbidden" we should consider whether the odd spin of ^{17}O would affect the reaction rate and hence affect other properties such as an MIF. At first glance a potential objection to observing an MIF in a reaction such as $CO + O \rightarrow CO_2^*$, an objection that is easily removed however, is that the desired reaction is electronically spin-forbidden (singlet CO + triplet O $\rightarrow$ singlet CO_2). The presence of an odd numbered nucleus ^{17}O in a reactant reduces the spin-forbidden impediment for this reaction, due to electron spin-nuclear spin coupling, and so catalyzes the recombination and destroys any mass-independence. However, this effect would occur both in the formation, $CO + O \rightarrow CO_2^*$, and in the redissociation, $CO_2^* \rightarrow CO + O$, of the CO_2^*. Since the redissociation of the CO_2^* dominates over collisional stabilization of the CO_2^* at low pressures this spin–spin effect favoring formation of CO_2^* containing ^{17}O also favors this reverse process and so the effect cancels at low pressures. At sufficiently high pressures, however, pressures not relevant here, there would be little redissociation of the CO_2^* because of collisional deactivation, and then the spin–spin coupling would indeed favor ^{17}O enrichment in the CO_2 or in any of the other reactions. An approximate formula for the ratios of rate constants and for the pressure dependence for such systems is given elsewhere [50].

There are also well known isotope effects associated with odd nuclear spin, spin-electron spin coupling, e.g., [10]. Such an effect that would favor ^{17}O formation over even spin nuclei absent in ozone formation, presumably because the ozone formation occurs on a singlet electronic state surface: While there are some 27 electronic states of an O/O_2 pair that in principle could be involved in ozone formation, only the lowest singlet state of O_3 is deep enough to be sufficiently long-lived to be collisionally stabilized to lead to O_3 formation at atmospheric pressure. Only it was assumed [12–15] to play a significant route to O_3 formation under those conditions. The "no reaction" posed by the other entrance channels reduced the calculated rate of O_3 formation accordingly [15].

6. OXYGEN ISOTOPIC FRACTIONATION FOR CO + OH → CO_2 + H

The CO + OH → CO_2 + H reaction has been reported as showing mass independent fractionation [11]. This term, in the strict sense of "mass-independence" used earlier means that the slope of a $^{17}O/^{16}O$ fractionation plotted versus the corresponding $^{18}O/^{16}O$ fractionation would be about unity, rather than having the conventional mass-dependent value of 0.52. However, what is frequently meant by MIF of oxygen instead is that the quantity $\Delta^{17}O = \delta^{17}O - 0.52\delta^{18}O$ is different from zero. The number of experiments needed to determine $\Delta^{17}O$ is only one, instead of the number needed to determine the slope of a 3-isotope and is commonly used in the literature. Indeed, sometimes the data are such that a three-isotope plot cannot be obtained from the available data. To avoid possible confusion one might term reactions that have a non zero value for $\Delta^{17}O$ but for which the $\delta^{17}O$ vs. $\delta^{18}O$ slope has not been measured, as being mass-anomalous fractionated, MAF. However, the term MIF is in widespread usage, and includes both the strictly MIF and any mass anomalous fractionation (MAF) reactions.

The reaction CO + OH → CO_2 + H is important for controlling the CO and OH concentration in the atmosphere and has an anomalous $\Delta^{17}O$ [11,51] and an ^{18}O isotope effect has also been measured in [52]. In theoretical studies on this reaction results have been obtained for C [53], H [53] and O [54] isotope effects. Inasmuch as the intermediate in this reaction, HOCO*, has no symmetry with respect to isotopes, the symmetry effect that appears in the ozone and the CAI problems is now absent. Any anomalies that appear in $\Delta^{17}O$ are then due to other reasons. Available three-isotope plots for this reaction are too sparse to define its slope reliably. The theory [53] provides an understanding of the H/D and $^{12}C/^{13}C$ data, and its pressure dependence, even though the C isotope effect is very small (−5 or so mil [11,55] at the lowest pressures). In calculations both nuclear tunneling of the H and complexity of mechanism can cause some deviation from the slope of a 3-isotope plot of 0.52 [54]. So they too can be a source of non-zero $\Delta^{17}O$ effect. Thus far, both the calculated [54] and the experimental O isotope effect are small, but unlike the C isotope data they do not agree. The problem in understanding the O-isotope behavior lies either in a sensitivity of the theoretical calculations of a small effect, though the calculation of the equally small ^{13}C effect agreed with the data, or it

lies in the experimental complexity of the reactions. In any case the effect is considerably smaller by more than an order of magnitude than the isotopic anomaly in ozone.

In one study of the HO + CO reaction there were many reaction steps, including the presence of ozone among the reactants [51]. In others the presence of vibrationally excited OH reactants is possible when the source of the OH is photochemical [11,51,56,57]. Isotopic exchange would also be one source of discrepancy between theory and experiment for the ^{18}O isotope effect [54], if it occurred: It was estimated [54] that an isotopic exchange rate constant of about 2 to 3×10^{-15} cm^3 molecule^{-1} s^{-1} could explain the difference between the calculated and experimentally observed O isotope effect. In one case an O isotopic exchange was reported [56] that disappeared at higher pressure. In another experiment, consistently no O isotopic exchange was reported at that higher pressure [57]. In another experiment showing no isotopic exchange the upper limit set for O isotopic exchange [58] was improved, being a factor of two or three smaller than the rough value given above needed to explain the observed discrepancy in the ^{18}O isotope effect. There are also results on $\Delta^{17}O$ for this reaction [11], and a nonzero $\Delta^{17}O$ was obtained in the theory [54].

An experiment that may be simpler in its reactions, more sensitive than the detection limit of O isotope exchange need to explain the discrepancy, and as free as possible from OH vibrational excitation, would be helpful to explore the issue further. On the other hand the isotope effect is very small and the system sufficiently complicated that the theoretical calculations themselves may be the source of the discrepancy. In either case we infer that the reaction itself is mass anomalous rather than mass-independent in the strict sense of the term, both experimentally and in terms of current theoretical insight. In concluding this section we comment in physical terms on the small isotope effects, about -5 to -10 per mil, observed for ^{13}C and ^{18}O in this system at low pressures.

At low pressures the collisional deactivation of the HOCO* can be neglected, so simplifying considerably the analysis since the reaction rate will no longer depend on the density of states of the intermediate HOCO*. There are two transition states for the reaction, one for the formation of HOCO* from HO + CO and the other for the formation of H + OCO from HOCO*. Judging from the significant H isotope effect, the second transition state dominates (is rate controlling) at low pressures. In any case we will assume it for simplicity in the present discussion. Increasing the mass of the C or O has two effects: from its small contribution to the reaction tunneling coordinate (dominantly an H coordinate) the effective mass of the H is also increased, resulting in a reduced tunneling rate, so making the reaction rate smaller for the heavier isotope. On the other hand the extra mass increases the number of states in the transition state for the dissociation of HOCO* to OCO + H, relative to increasing the statistically average number for the reactants [54], so increasing the reaction rate. Thus an increase of the C or O mass has two conflicting consequences for the reaction rate.

The C in HOCO* is coupled to several vibrations in the HOCO* and so this "number of states effect" can be dominant for C and cause $^{12}k < {}^{13}k$, in agreement with experiment. For the O in CO leading to HOCO* it is coupled to fewer

vibrations in the HOCO*, compared with the number coupled to the C and, in the theoretical calculation, did not dominate the tunneling contribution and so in the theoretical calculations we had ${}^{16}k > {}^{18}k$, in disagreement with experiment. In this way one can understand the ${}^{13}C$ isotope effect, but not the current discrepancy for the ${}^{18}O$ effect. Nevertheless the effect is small, the result of opposing tendencies, and further experiments and theory may be helpful.

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