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Oxygen Isotope Effects in the Oxidation of Methane to Carbon Monoxide[†]

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A significant fraction (estimated to be as large as 30%) of the carbon monoxide in the atmosphere is produced by the oxidation of methane. One of the approaches that has been used to determine this fraction is an inversion of observed carbon and oxygen isotopic abundance ratios, $^{13}C/^{12}C$ and $^{18}O/^{16}O$, together with estimates of the magnitudes of other sources of carbon monoxide, and isotope effects in each source. For this purpose, values of the kinetic isotope effects in the methane oxidation are required, and although these have been determined experimentally for ^{13}C, they have not been measured for ^{18}O. This article examines the kinetic mechanism of methane oxidation and shows that an oxygen isotope effect could take place in the addition reaction of methyl radicals with molecular oxygen to form methylperoxy. Subsequent reactions in the complicated mechanism for methane oxidation do not lead to isotopic fractionation of oxygen. The expected kinetic isotope effect is calculated using variational transition state theory for the dissociation of methylperoxy, and combining the rate coefficient ratio with the ratio of equilibrium constants to obtain the ratio of recombination rate coefficients. The calculated kinetic isotope effects enrich ^{18}O in the methylperoxy adduct relative to molecular oxygen. The atmospheric implications of this are briefly discussed.

1. Introduction

Carbon monoxide is an important constituent of the troposphere; the average mixing ratio is 70−100 ppbv, with a substantial latitude gradient and higher values in the Northern Hemisphere. Its importance in the atmosphere depends especially on the fact that the oxidation of carbon monoxide to carbon dioxide by hydroxyl radical is the penultimate step in the complicated oxidation mechanism of many hydrocarbon species in the atmosphere. A number of sources are known to contribute to the CO budget of the atmosphere, the more important being fossil fuel combustion, savanna burning, ocean emission, and oxidation of both methane and non-methane hydrocarbons (NMHC). Several estimates have compared the relative importance of the methane oxidation channel with total methane sinks and with total CO sources (Table 1). Hanst et al.[1] base their results on estimates of methane oxidation, ocean emission, anthropogenic emissions, and oxidation of both natural and anthropogenic NMHC. Their calculations assumed three different OH radical concentrations, all of them lower than present estimates of global averages, and their methane source values are correspondingly low. Methane oxidation as a CO source has also been estimated by Logan[2] and by Seiler and Conrad.[3]

The determination of the abundances of stable isotopes in atmospheric gases has become an important tool in unraveling the chemical processes involving these species. For example, the methane oxidation source for CO has been determined by an inversion of observed carbon and oxygen isotopic abundances ratios, $^{13}C/^{12}C$ and $^{18}O/^{16}O$, together with estimates of the magnitudes of other sources of carbon monoxide, and isotope effects in each source. For this purpose, values of the kinetic isotope effects in the methane oxidation are required, and although these have been determined experimentally for ^{13}C, they have not been measured for ^{18}O. Thus, Manning et al.[4] arrive at their estimates by using a model to fit observed CO mixing ratios and $^{13}C/^{12}C$ isotopic ratios. Bergamaschi et al.[5] based their estimates on observed CO mixing ratios at five observation stations ranging in latitude from 82.5° N to 77.8° S throughout the year, and also on $^{13}C/^{12}C$ and $^{18}O/^{16}O$ isotopic ratios. Brenninkmeijer and Röckmann[6] give estimates for the Southern Hemisphere based on $^{18}O/^{16}O$ isotopic ratios; it should be noted that the methane oxidation source in the Southern Hemisphere is relatively larger than it is in the Northern Hemisphere because anthropogenic contributions to CO are smaller. Another factor to consider in estimating the extent to which methane contributes as a CO source is the observation that the yield of CO formed per CH_4 removed by OH oxidation is not unity; values of 0.74−0.9 have been cited.[4,7−9] Tie et al.[9] have carried out two-dimensional atmospheric modeling calculations showing that for the Northern Hemisphere at an altitude corresponding to 500 mbar the yield ranges from ∼0.5 in the summer to ∼0.7−0.8 in the winter. Higher values are found at lower altitudes. In any case, it is clear that the methane

TABLE 1: CO Production from Methane Oxidation

total CO source, Tg yr^{-1}	CH_4 oxidation, Tg yr^{-1}	fraction	reference
1080−2120[a]	132−400[a]	0.12−0.18[a]	Hanst et al.[1]
2736	810	0.30	Logan et al.[2]
3300	580	0.17	Seiler and Conrad[3]
2099−2588[a]	474−624[a]	0.23−0.24[a]	Manning et al.[4]
		0.43[b]	Brenninkmeijer and Röckmann[6]
		0.28[c]	Brenninkmeijer and Röckmann[6]
2912 ± 35	678 ± 62	$0.28 \pm 0.00_4$	Bergamaschi et al.[5]
2873 ± 12	777 ± 47	0.26 ± 0.02	Bergamaschi et al.[7]

[a] This value depends on the assumed OH radical concentration [b] SH, March [c] SH, October.

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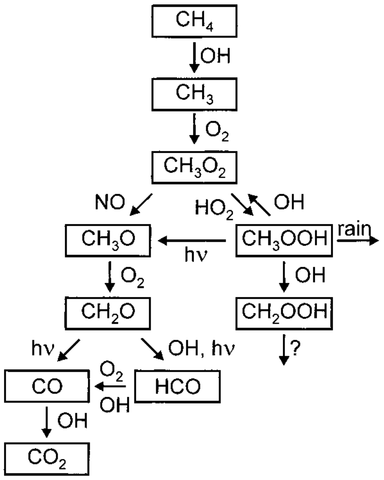

Figure 1. Flow diagram of the mechanism for the oxidation of methane to carbon monoxide.

oxidation source of carbon monoxide is important in the chemistry of the atmosphere.

As indicated in the preceding paragraph, a number of observations have been devoted to the measurement of the oxygen isotope ratios in atmospheric carbon monoxide.[6,7,10−17] Recently, interest has been sparked by the observation of “mass-independent” oxygen isotope effects in atmospheric reactions, in which the enrichment of the ^{18}O isotope with respect to ^{16}O is approximately the same as that of ^{17}O, contrary to the usual theory of equilibrium and kinetic isotope effects.[18,19] Röckmann et al.[20] have shown in laboratory experiments that such a mass-independent effect is produced in the reaction $CO + OH \rightarrow H + CO_2$. A comparison of k_{18}/k_{16} gives rate coefficient ratios that agree with earlier measurements by Stevens et al.[21]

The goal of this paper is to examine the mechanism of carbon monoxide formation from methane oxidation in order to determine the step(s) in which isotopic fractionation could occur, and having identified such step(s) to use currently available rate coefficient theory to calculate the kinetic isotope effect(s).

2. Mechanism of CH_4 Oxidation

The mechanism of methane oxidation has been discussed by a number of authors. In particular, a critical review of this topic was given by Ravishankara,[22] although many of the specific rate coefficients have been more recently evaluated. Johnston and Kinnison[23] have examined the photooxidation of methane in the atmosphere, although their calculations focused on the question of ozone formation. Similar two-dimensional modeling was carried out by Tie et al.[9] The sequence of reactions leading from methane to carbon monoxide is shown schematically in Figure 1, and rate coefficients at 300 K and one atmosphere are collected in Table 2. With typical atmospheric concentrations of reactive species (OH, O_2, NO, HO_2), the rate-determining step for the removal of methane is the reaction with OH. This fact has long been recognized and is the basis for the calculation of an atmospheric methane lifetime of about 9 years.[28] While it is not obvious that this should be the case, modeling calculations with the mechanism of Figure 1 and the rate coefficients of Table 2 indicate that the production rate for CO is equal to the removal rate for CH_4. This step is the source of the $^{13}C-^{12}C$ isotopic fractionation in methane or CO. Once formed, the methyl radical reacts with molecular oxygen in a termolecular reaction with a rate that is pressure dependent. At a pressure of 1 atm, this reaction is still in the falloff region, and the rate coefficient is about 65% of its limiting high-pressure value. This is the step that can introduce isotopic fractionation in the final CO product. The methylperoxy (or methyldioxy) radical thus formed can react either with NO or with HO_2. As the two rate coefficients are nearly equal, the relative contribution of these two branches will depend on the relative concentrations of NO and HO_2. The atmospheric abundance of both of these reactants is subject to wide temporal and spatial variation, which would be considered in a realistic and detailed model of atmospheric methane oxidation. Johnston and Kinnison[23] give values as a function of altitude for the ratio of rates $R(CH_3O_2 + NO)/[R(CH_3O_2 + NO)+R(CH_3OOH + h\nu)$, where the photolysis of CH_3OOH represents a possible next step in the HO_2 reaction sequence. They find this ratio to be between 0.7 and 1.0 up to 35 km. Tie et al.,[9] using two-dimensional modeling for the Northern Hemisphere at an altitude of 5 km, find that the ratio $R(CH_3O_2 + NO)/R(CH_3O_2 + HO_2)$ varies from about 0.3 in summer to values as large as 13 in winter. (The photochemical reactions leading to HO_2 are more important in the summer, and the concentration of NO_x is highest in winter due to industrial pollution.) The reaction $CH_3O_2 + NO$ leads fairly directly to CO through the CH_3O radical, which reacts rapidly with molecular oxygen in the atmosphere to form H_2CO, formaldehyde. Photodissociation rate coefficients (J) for the two pathways for formaldehyde reaction have been determined by Jenkin.[26] Photolysis competes with OH reaction and at a zenith angle of 40° and with an average OH concentration of $\sim 1 \times 10^6$ cm^{-3}, photolysis is about 5 times faster. The two photolysis branches are roughly comparable at this zenith angle; one leads directly to CO while the other branch forms HCO, most of which will form CO by reaction with O_2, since the molecular oxygen concentration is much greater than that of OH. The $HO_2 + CH_3O_2$ branch leads to a relatively stable species, methyl peroxide (CH_3OOH), which may be removed by precipitation. Alternatively, there are four possible reaction paths. The rate coefficients for the two possible H-atom abstraction reactions differ by only a factor of ~2; one reaction regenerates a CH_3O_2 radical while destroying one OH and one HO_2 radical, whereas the alternative path produces a new species, CH_2COOH. Vaghjiani and Ravishankara[29] report a lifetime for this radical of 20 μs at 205 K, without indicating what the products might be. The O−O bond is probably the weakest bond in the radical, and dissociation at this point will lead to the OH radical and

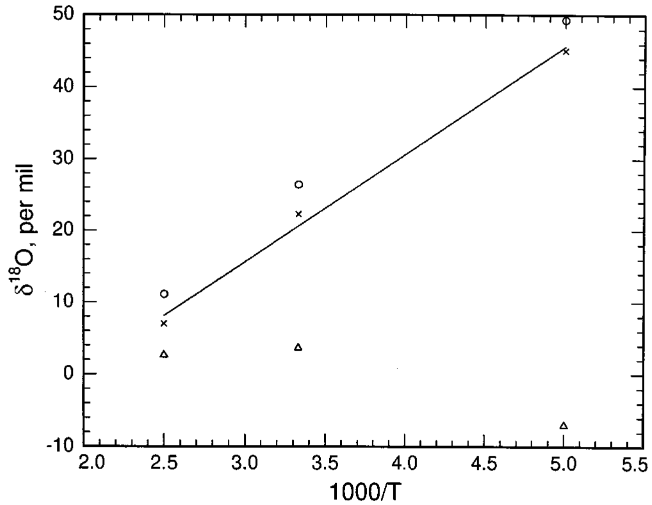

Figure 2. Calculated equilibrium isotope effects and ^{18}O enrichment for the reaction of CH_3 with O_2 as a function of the reciprocal temperature: (○) $\delta^{18}O = (K_{18}/K_{16}) - 1$; (Δ) $\delta^{18}O = (K'_{18}/K_{16})$-1; (×) $\delta^{18}O$ (per mil) $= 10^3\{({}^{18}k_r/{}^{16}k_r)_{CH_3{}^{18}O^{16}O}[1 - ({}^{18}k_r/{}^{16}k_r)_{CH_3{}^{16}O^{18}O})([{}^{18}O]/[{}^{16}O])_{O_2}]\}$

TABLE 2: Rate Coefficients

	reaction	k, cm^3 molecule^{-1} s^{-1} (300 K, 1 atm)	reference
(1)	$CH_4 + OH \rightarrow CH_3 + H_2O$	6.34(−15)[a]	DeMore et al.[24]
(2)	$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$	7.9(−13)	Baulch[25] et al.
(3)	$CH_3O_2 + NO \rightarrow CH_3O + NO_2$	7.63(−12)	DeMore et al.[24]
(4)	$CH_3O + O_2 \rightarrow H_2CO + HO_2$	1.94(−15)	DeMore et al.[24]
(5)	$H_2CO + OH \rightarrow HCO + H_2O$	1.0(−11)	DeMore et al.[24]
(6)	$H_2CO + h\nu \rightarrow H_2 + CO$	J = 4.1(−5)[b]	Jenkin[26]
(7)	$H_2CO + h\nu \rightarrow H + HCO$	J = 2.5(−5)	Jenkin[26]
(8)	$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$	5.47(−12)	DeMore et al.[24]
(9)	$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$	3.60(−12)	Atkinson[27] et al.
(10)	$CH_3OOH + OH \rightarrow CH_2OOH + H_2O$	1.90(−12)	Atkinson[27] et al.
(11)	$CH_2OOH + M \rightarrow H_2CO + OH + M$		See text
(12)	$CH_3OOH + h\nu \rightarrow CH_3O + OH$	J = 3.4(−6)	Jenkin[26]
(13)	$HCO + O_2 \rightarrow CO + HO_2$	5.58(−12)	DeMore et al.[24]
(14)	$HCO + OH \rightarrow CO + H_2O$	1.70(−10)	Baulch[25] et al.
(15)	$CO + OH$	2.40(−13)	DeMore et al.[24]

[a] $x.yz(m) = x.yz \times 10^m$. [b] Units of s^{-1}.

CH_2CO, ketene, which may have enough energy to dissociate, forming CO and methylene. In any case, no other data are available on reaction rate coefficients for CH_2COOH. Methyl peroxide may also be removed by photolysis,[26] with an estimated rate that is comparable to the rate of reaction with OH. The photodissociation also regenerates a methylperoxy radical.

3. Oxygen Isotope Effects in the Formation of Carbon Monoxide from Methane

Although the rate-determining reaction in this sequence is the first step, which will not lead to isotopic fractionation of oxygen, a possible kinetic isotope effect in the formation of CO is provided by the reaction of methyl with molecular oxygen, as suggested by Brenninkmeijer and Röckmann.[6] In effect this leads to branching such that

$$\frac{([^{18}O]/[^{16}O])_{CO}}{([^{18}O]/[^{16}O])_{O_2}} = \frac{k'_2}{k_2 + k''_2([^{18}O]/[^{16}O])_{O_2}} \qquad (E1)$$

where

$$CH_3 + {}^{16}O_2 \rightarrow CH_3{}^{16}O_2, \quad k_2 \qquad (2)$$

$$CH_3 + {}^{18}O^{16}O \rightarrow CH_3{}^{18}O^{16}O, \quad k_2' \qquad (2')$$

$$CH_3 + {}^{16}O^{18}O \rightarrow CH_3{}^{16}O^{18}O, \quad k_2'' \qquad (2'')$$

Note that, in the absence of oxygen atom scrambling in any of the subsequent reactions, only reaction 2′ leads to $C^{18}O$. The fact that this is the only step leading to isotope effects on the CO product formation has been verified by modeling calculations in which the rate coefficient for each subsequent step of the mechanism is changed, and it is observed that the CO product has the same isotopic composition as that assumed for the initial oxygen. At the natural abundance level of oxygen isotopes, and with the reasonable assumption that the rate coefficient ratios are all close to unity, (E1) can be written:

$$\frac{([^{18}O]/[^{16}O])_{CO}}{([^{18}O]/[^{16}O])_{O_2}} = (k_2'/k_2)[1 - (k_2''/k_2)([^{18}O]/[^{16}O])_{O_2}] \qquad (E2)$$

Thus, it is evident that in the absence of any isotope effects carbon monoxide containing the ^{18}O isotope will be depleted with respect to molecular oxygen containing ^{18}O at the natural abundance level, to the extent of approximately 4‰. If we define $\delta^{18}O$ in the usual way as the enrichment of ^{18}O in carbon monoxide with respect to molecular oxygen, then

$$\delta^{18}O\ (\text{per mil}) = 10^3\{(k_2'/k_2)[1 - (k_2''/k_2)([^{18}O]/[^{16}O])_{O_2}] - 1\} \qquad (E3)$$

4. Theoretical Estimates of Rate Coefficient Ratios

The mechanism given above indicates that an experimental determination of the rate coefficient ratios k_2'/k_2 and k_2''/k_2 would provide the information needed to predict the isotopic composition of carbon monoxide produced in the oxidation of methane, provided other aspects of the atmospheric chemistry, such as the concentrations of NO and of HO_2, are also known. Unfortunately, such experimental information is not available. The typical method for determining the rate coefficient of reaction 2 is to follow the pseudo-first-order disappearance of CH_3 in the presence of an excess of O_2, so no information is obtained about the isotopic composition of the oxygen or the adduct. It should not be impossible to do this, using appropriate spectrometric or mass spectrometric methods to observe the oxygen isotope distribution in the CH_3OO product, or to monitor the change in the isotopic composition of the molecular oxygen reactant.

The alternative approach to be followed here is to estimate the appropriate isotope effects on the rate coefficients using transition state theory. The reaction under consideration here is a radical recombination reaction with no barrier separating reactants and products other than the centrifugal barrier. Such reactions have usually been discussed in terms of a very loose activated complex, in which both reactants have rotational degrees of freedom that do not exist in the product molecule. The customary approach toward calculating a rate coefficient for such a reaction is to calculate the rate coefficient for the reverse reaction, i.e., the unimolecular dissociation, and to combine this with the calculated equilibrium constant to obtain the rate coefficient for recombination. This approach has been followed here for the $CH_3 + O_2$ reaction, with models chosen to give a calculated rate coefficient in agreement with the experimental value for $CH_3 + {}^{16}O_2$.[24,25] The rate coefficient ratios for dissociation of $CH_3{}^{16}O_2$ and $CH_3{}^{18}O^{16}O$ or $CH_3{}^{16}O^{18}O$ can be combined with equilibrium constant ratios calculated using standard methods[30,31] to obtain the ratio of rate coefficients for the recombination. The unimolecular rate coefficient is given by

$$k(E) = \frac{\int_0^{E-E_0} \rho^{\ddagger}(E^{\ddagger})\, dE^{\ddagger}}{h\rho(E)} \tag{E4}$$

where E_0 is the threshold energy, E is the energy of the molecule, $E^{\ddagger}$ the energy of the activated complex, and ρ and $\rho^{\ddagger}$ are the corresponding densities of states. The limiting high-pressure rate coefficient is then

$$k_{\mathrm{uni}}^{\infty}(T) = \frac{\int_{E_0}^{\infty} k(E)\rho(E) \exp(-E/k_{\mathrm{B}}T)\, dE}{\int_{E_0}^{\infty} \rho(E) \exp(-E/k_{\mathrm{B}}T)\, dE} \tag{E5}$$

To calculate the unimolecular dissociation rate coefficients, variational transition state theory (VTST), as described by Gilbert and Smith,[32] was applied. The programs described in their book were used—both the RRKM program that produces a limiting high-pressure rate coefficient, and the master equation program that calculates the effect of pressure. Similar calculations for this reaction have been made by Forst and Caralp[33] and by Keiffer et al.[34] The observed rate coefficient for recombination depends on pressure, and the high-pressure limiting value at 300 K is given as 1.22×10^{-12} cm^3 molecule^{-1} s^{-1} in the data compilation of Baulch et al.[25] or $(1.8 \pm 0.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} in the compilation by DeMore et al.[24] A "tight" activated complex, with only the three external rotations and the vibrational frequencies of the CH_3O_2 molecule except for the C$-$O stretch (which becomes the reaction coordinate), gives a rate coefficient that is too small by an order of magnitude. The model finally used has the following properties:

1. Vibrational frequencies of the various isotopic molecules were taken from the normal coordinate calculations,[35] which are based on IR spectra.[36] However, the mode corresponding to a low-frequency torsion of the methyl group about the C$-$O bond has not been observed, and it has been used in these calculations as a variable parameter.

2. Bond lengths and bond angles for the molecule were taken from ab initio calculations of Cheung and Li.[37]

3. The activated complex was assumed to be essentially free methyl and dioxygen, with the appropriate vibrational frequencies for these species. To simplify calculations, the structure was assumed to have C_{3v} symmetry, with a planar methyl group and a linear C$-$O$-$O configuration. The bond lengths were taken to be those of the molecule, except for the C$-$O bond length which was varied. In addition to the overall external rotation of the complex, it was assumed that both the methyl and dioxygen had the moments of inertia of the free molecules.

In the application of VTST to association reactions of the type under consideration, the usual approach is to vary the distance ($R^{\ddagger}$) between the combining fragments until the calculated rate coefficient is minimized. In the present calculation, this is the C$-$O bond length and the only other parameters that change are the external rotations of the transition state and the centrifugal barrier. With the model just described, the minimum was found at C$-$O distances of 3.5$-$4.5 Å, and in the final calculations a value of 3.8 Å was used. As pointed out by Keiffer et al.,[34] the limiting high-pressure rate coefficient for this reaction is abnormally small for a radical recombination process. In order to fit the experimental value, a very low value of the methyl torsion frequency in methylperoxy (50 cm^{-1}) was assumed, giving a value for the calculated rate coefficient that is between the two experimental values.[24,25] Varying this frequency from 50 to 200 cm^{-1} changed the calculated rate coefficient by about a factor of 2. The calculated isotope effects (Table 3 and Figure 2) are somewhat sensitive to the value of $R^{\ddagger}$ because of its effect on moments of inertia; a change of 1 Å changes the ratio of rate coefficients ($^{18}k/^{16}k$) by a few parts per mil. The relatively large isotope effects for the $CH_3{}^{18}O^{16}O$ adduct, which is the form that leads to $C^{18}O$, result primarily from the ratio of equilibrium constants because the ratios of the dissociation rate coefficients are close to unity.

TABLE 3: Isotope Effects on Equilibrium Constants and Rate Coefficients[a]

	$CH_3{}^{16}O^{18}O$			$CH_3{}^{18}O^{16}O$			
T, K	K'_{18}/K_{16}	$^{18}k_d/^{16}k_d$	$^{18}k_r/^{16}k_r$	K_{18}/K_{16}	$^{18}k_d/^{16}k_d$	$^{18}k_r/^{16}k_r$	$\delta^{18}O$, ‰
200	0.9699	1.0239	0.9931	1.0560	0.9937	49.3	45.1
300	0.9772	1.0272	1.0038	1.0256	1.0008	26.4	22.3
400	0.9826	1.0206	1.0028	1.0133	0.9978	11.1	7.0

[a] $\delta^{18}O$ (per mil) $= 10^3\{(^{18}k_r/^{16}k_r)_{CH_3{}^{18}O^{16}O}[1 - (^{18}k_r/^{16}k_r)_{CH_3{}^{16}O^{18}O})([^{18}O]/[^{16}O])_{O_2}]\}$.

Master equation calculations with this model were used to obtain the pressure dependence of the rate coefficients for the $^{16}O_2$ reaction, and reasonable agreement with experimental values[24,25] was found. The calculated isotope effects were quite insensitive to pressure, but of course this model does not include any detailed consideration of possible vibrational effects on the rate of collisional energy transfer.

To convert the unimolecular dissociation rate coefficients discussed above to recombination rate coefficients, equilibrium constants for the dissociation are required. In the present case, a ratio of such equilibrium constants for two isotopic species is needed, i.e.

$$^{18}k_r/^{16}k_r = (^{18}k_d/^{16}k_d)(K_{18}/K_{16})$$

where

$$CH_3 + {}^{16}O_2 = CH_3{}^{16}O^{16}O, \quad K_{16} \tag{2}$$

$$CH_3 + {}^{18}O^{16}O = CH_3{}^{18}O^{16}O, \quad K_{18} \tag{2'}$$

$$CH_3 + {}^{16}O^{18}O = CH_3{}^{16}O^{18}O, \quad K'_{18} \tag{2''}$$

These can be combined to give

$$([CH_3{}^{18}O^{16}O]/[CH_3{}^{16}O^{16}O])/([^{18}O^{16}O]/[^{16}O^{16}O]) = K_{18}/K_{16}$$

$$([CH_3{}^{16}O^{18}O]/[CH_3{}^{16}O^{16}O])/([^{18}O^{16}O]/[^{16}O^{16}O]) = K'_{18}/K_{16} \tag{E6}$$

Thus

$$\delta^{18}O = 10^3[(K_{18}/K_{16}) - 1]$$

$$\delta'^{18}O = 10^3[(K'_{18}/K_{16}) - 1] \tag{E7}$$

As shown originally by Bigeleisen and Mayer,[30] the ratio of equilibrium constants can be written in terms of the appropriate f = s, the reduced partition functions:

$$K_{18}/K_{16} = f(CH_3OO)/f(O_2) \tag{E8}$$

The reduced partition functions can be calculated completely from vibrational frequencies of the reactants and products:

$$(s_2/s_1)f = (s_2Q_2/s_1Q_1)\prod_i (m_{1i}/m_{2i})^{3/2} = \prod_i (u_{2i}/u_{1i})\exp(\Delta u_i/2)[1 - \exp(-u_{1i})]/[1 - \exp(-u_{2i})], \quad i = 1, 3n - 6 \qquad \text{(E9)}$$

In this expression, s_1 and s_2 are symmetry numbers of the light and heavy isotopic species, respectively, n is the number of atoms, and

$$u_i = h\upsilon_i/k_bT \qquad \text{(E10)}$$

The vibrational frequencies of various isotopologues of methyldioxy have been determined,[35,36] except for the methyl group torsion which should be insensitive to isotopic substitution. The frequency for $^{18}O^{16}O$ can be calculated exactly from the measured frequency[38] of $^{16}O_2$, thus making the calculation of the above equilibrium constant ratios possible. The results for both ^{18}O substituted forms of methyldioxy are given in Table 3 and Figure 2 in the form of $\delta^{18}O$ as a function of temperature. It is evident that the $CH_3{}^{18}O^{16}O$ molecule, the important form for ultimate oxidation to carbon monoxide, is enriched in the heavy isotope relative to molecular oxygen.

5. Atmospheric Implications

Prather and Spivakovsky[39] found that detailed three-dimensional models of the removal of hydrochlorofluorocarbons by reaction with OH gave lifetimes that could be approximated on a global scale by using relative rate coefficients and a temperature of 277 K. At this temperature, the data of Figure 2 give a value of $\delta^{18}O = 24.8$. Manning et al.[4] estimate the lifetime of CO in the Southern Hemisphere to be about 2 months. This is similar to the estimate one could derive from the total atmospheric burden of CO and the sinks estimated by Logan[2] or Seiler and Conrad.[3] As the major sink is oxidation by OH, the lifetime is determined to a large extent by the rate coefficient of this reaction and the average global concentration of the hydroxyl radical, for which Prinn et al.[28] determined a value of $(9.7 \pm 0.6) \times 10^5$ radicals cm^{-3}. Combining this with a rate coefficient[25] of 2.4×10^{-13} cm^3 $molecule^{-1}$ s^{-1} at 277 K, we obtain a lifetime of slightly less than 2 months. The rate of production of CO by the oxidation of methane by OH is considerably slower, because the rate coefficient is smaller by 2 orders of magnitude. Nevertheless, the relative concentrations of CO and CH_4 are approximately what one would predict from a steady-state assumption, which is

$$[CO]_{ss}/[CH_4]_{ss} = k(CH_4 + OH)/k(CO + OH) \simeq 10^{-2}$$

If the steady-state assumption is applied to the isotopic composition of CO controlled by these two reactions, one finds

$$\delta^{18}O(CO) = \delta^{18}O(CH_3 + O_2) - \delta^{18}O\,(CO + OH)$$

Bergamaschi et al.[7] fit the pressure-dependent values of the reported[20,21] kinetic isotope effect for the sink reaction to obtain a value of $\delta^{18}O(CO + OH) = 9.2$ at ~300 K and 1 atm. The temperature dependence has not been determined, but if this value is assumed to be the same at 277 K, it can be combined with $\delta^{18}O(CH_3 + O_2)$ to give $\delta^{18}O(CO) = 15.6$ at 277 K. However, this is relative to atmospheric molecular oxygen, which has a $\delta^{18}O$ of 23.5 relative to VSMOW, so that we would predict the CO isotopic abundance from methane oxidation to be 23.5 + 15.6, or +39.1 relative to VSMOW.

As indicated above, the $[NO]/[HO_2]$ ratio determines the ultimate fate of the oxygen combining with the methyl radical, and this ratio is also important in determining the dependence of δ on the kinetic isotope effects. The temporal and spatial variations to be expected in this ratio have been modeled by Tie et al.[9] If this ratio is very large, essentially all molecular oxygen that reacts is converted to carbon monoxide, and after a very small extent of reaction δ is correctly given by expression E2. Even if the $[NO]/[HO_2]$ ratio is unity, δ quickly reaches the correct limiting value. However, if the ratio is very small, δ is initially several times as large as the limiting value, and only approaches the limit as the reaction nears completion. Thus the present work merely determines a theoretical estimate of the kinetic isotope effect, which would be necessary input data for atmospheric modeling that takes into account the temporal and spatial variations in the concentrations of both nitric oxide and the HO_2 radical.

What are the current estimates of the ^{18}O abundance in atmospheric CO derived from methane oxidation? Stevens and Wagner[11] estimate an overall value of $\delta^{18}O = +5‰$ for the Southern Hemisphere, based on +15‰ for CO derived from methane. Brenninkmeijer and Röckmann[6] consider the mean value of $\delta^{18}O$ for CO obtained at Baring Head, New Zealand, which is −4.5 l in March and −0.5l in October. The assumed contribution of methane oxidation to the total is 43% in March and 28% in October. With assumptions about the relative contributions of CO from other sources and the associated kinetic isotope effects, these authors obtain values of $\delta^{18}O$-(VMSOW) for the CO derived from methane oxidation ranging from −9.9‰ to −17.5‰ in March and from −6.2‰ to −20.8‰ in October. Taking into account the isotopic composition of atmospheric oxygen, and the known kinetic isotope effect for the CO + OH reaction, one would obtain values ranging from −20.5 to −35.1 for $\delta^{18}O$ for the $CH_3 + O_2$ reaction. More recent modeling[7] of the carbon and oxygen isotope abundances at this same location and at other observation points leads to positive values of $^{18}\delta$ ranging from 7.0 to 12.3 ‰, which would correspond to values of $\delta^{18}O$ for the $CH_3 + O_2$ reaction that are close to zero.

In conclusion, there remains considerable uncertainty about the modeling of kinetic isotope effects in the oxidation of methane to carbon monoxide, and this uncertainty would be greatly reduced if experimental methods were applied to this problem.

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References and Notes

(1) Hanst, P. L.; Spence, J. W.; Edney, E. O. *Atmos. Environ.* **1980**, *14*, 1077.

(2) Logan, J. A.; Prather, M. J.; Wofsy, F. C.; McElroy, M. B. *J. Geophys. Res.* **1981**, *86*, 7210.

(3) Seiler, W.; Conrad, R. Contribution of Tropical Systems to the Global Budget of Trace Gases, especially CH_4, H_2, and N_2O. In *The Geophysiology of Amazionia*; Dickenson, R. E., Ed.; Wiley: New York, 1987; pp 133−160.

(4) Manning, M. R.; Brenninkmeijer, C. A. M.; Allan, W. *J. Geophys. Res.* **1997**, *102*, 10, 673.

(5) Bergamaschi, P.; Hein, R.; Brenninkmeijer, C. A. M.; Crutzen, P. *J. Geophys. Res.* **2000**, *105*, 1909.

(6) Brenninkmeijer, C. A. M.; Röckmann, T. *J. Geophys. Res.* **1997**, *102*, 25, 477.

(7) Bergamaschi, P.; Hein, R.; Heiman, M.; Crutzen, P. *J. Geophys. Res.* **2000**, *105*, 1929.

(8) Kanakidou, M.; Crutzen, P. *Chemosphere: Global Change Sci.* **1999**, *1*, 91.

(9) Tie, X.; Kao, C.-Y. J.; Mroz, E. *Atmos. Environ. Part A* **1992**, *26*, 125.

(10) Stevens, C. M.; Krout, L.; Walling, D.; Venters, A.; Engelkemeier, A.; Ross, L. E. *Earth Planet. Sci. Lett.* **1972**, *16*, 147.

(11) Stevens, C. M.; Wagner, A. F. *Z. Naturforsch.* **1989**, *44a,* 376.

(12) Brenninkmeijer, C. A. M. *J. Geophys. Res.* **1993**, *98*, 10595.

(13) Mak, J. E.; Brenninkmeijer, C. A. M.; Tamaresis, J. *J. Geophys. Res.* **1994**, *99*, 22915.

(14) Brenninkmeijer, C. A. M., Lowe, D. C., Manning, M. R., Sparks, R. J., and van Velthoven, P. F. J. *J. Geophys. Res.* **1995**, *100*, 26, 163.

(15) Hodder, P. S.; Brenninkmeijer, C. A. M.; Thiemens, M. H. In *Mass Independent Fractionation in Tropospheric Carbon Monoxide*; Lansphere, M. A., Dalrymple, G. B., Turrin, B. D., Eds.; Abstracts of the 8th International Conference on Geochronology, Cosmochronology and Isotope Geology, Circular, C 1107, Berkeley, CA, June 5−11, 1994; p 138.

(16) Huff, A. K.; Thiemens, M. H. *Eos* **1996**, Fall Suppl., F124.

(17) Huff, A. K.; Thiemens, M. H. *Geophys. Res. Lett.* **1998**, *25,* 3509.

(18) For a review, cf. Weston, R. E., Jr. *Chem. Rev.* **1999**, *99*, 2115.

(19) Thiemens, M. *Science* **1999**, *283*, 341.

(20) Röckmann, T.; Brenninkmeijer, C. A. M.; Saueressig, G.; Bergamaschi, P.; Crowley, J. N.; Fischer, H.; Crutzen, P. *Science* **1998**, *281,* 544.

(21) Stevens, C. M.; Kaplan, L.; Gorse, R.; Durkee, S.; Compton, M..; Cohen, S.; Bielling, K. *Int. J. Chem. Kinet.* **1980**, *12,* 935.

(22) Ravishankara, A. R. *Annu. Rev. Phys. Chem.* **1988**, *39*, 367.

(23) Johnston, H. S.; Kinnison, D. *J. Geophys. Res.* **1998**, *103*, 21967.

(24) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. “Chemical kinetics and photochemical data for use in stratospheric modeling”, Evaluation No. 12; JPL Publication 97-4, Jet Propulsion Laboratory, California Institute of Technology, 1997.

(25) Baulch, D. L.; Cobos, C. J.; Cox, R. A.; Frank, P.; Hayman, G.; Just, Th.; Kerr, J. A.; Murrells, T.; Pilling, M. J.; Troe, J.; Walker, R. W.; Warnatz, J *J. Phys. Chem. Ref. Data* **1994**, *23*, 847.

(26) Jenkin, M. E. *Atmos. Environ.* **1997**, *31*, 81.

(27) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1992**, *21,* 1125.

(28) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang. J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E., Simmonds, P. G. *Science* **1995**, *269*, 187.

(29) Vaghjiani, G. L.; Ravishankara, A. R. *J. Phys. Chem.* **1989**, *93*, 1948.

(30) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15,* 261.

(31) Melander, L.; Saunders: W. A., Jr. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980.

(32) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell: Oxford, UK, 1990.

(33) Forst, W.; Caralp, F. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2307.

(34) Keiffer, M.; Pilling, M. J.; Smith, M. J. C. *J. Phys. Chem.* **1987**, *91*, 6028.

(35) Cyvin, B. N.; Cyvin, S. J.; and Snelson, A. *Z. Anorg. Allg. Chem.* **1986**, *542*, 193.

(36) Ase, P.; Bock, W.; Snelson, A. *J. Phys. Chem.* **1986**, *90,* 2099.

(37) Cheung, Y.-S.; Li, W.-K. *Chem. Phys. Lett.* **1994**, *223,* 383.

(38) Huber, H. P.; Herzberg, G. *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979; p 498.

(39) Prather, M.; Spivakovsky, C. M. *J. Geophys. Res.* **1990**, *95*, 18723.