Carbon Kinetic Isotope Effect in the Oxidation of Methane by the Hydroxyl Radical

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The reaction of the hydroxyl radical (HO) with the stable carbon isotopes of methane has been studied as a function of temperature from 273 to 353 K. The measured ratio of the rate coefficients for reaction with $^{12}$CH$_4$ relative to $^{13}$CH$_4$ ($k_{12}/k_{13}$) was 1.0054 ($\pm$0.0009 at the 95% confidence interval), independent of temperature within the precision of the measurement, over the range studied. The precision of the present value is much improved over that of previous studies, and this result provides important constraints on the current understanding of the cycling of methane through the atmosphere through the use of carbon isotope measurements.

INTRODUCTION

Methane (CH$_4$) is an important trace gas in the atmosphere [Wofsy, 1976]. It is a key sink for the tropospheric hydroxyl radical. Methane contributes to greenhouse warming [Donner and Ramanathan, 1980]; its potential warming effects follow only CO$_2$ and H$_2$O. Methane is a primary sink for chlorine atoms in the stratosphere and a major source of water vapor in the upper stratosphere. The concentration of CH$_4$ in the troposphere has been increasing at a rate of approximately 1% per year, at least over the past decade [Rasmussen and Khalil, 1984]. Ice core measurements indicate a rapid increase began a few hundred years ago [Craig and Chou, 1982; Rasmussen and Khalil, 1984]. The reasons for this increase have not been established, but it has been suggested that it could be due to an increase in source emissions, a decrease in the atmospheric loss rate, or both.

Several approaches have been applied in order to understand the sources and sinks of atmospheric methane (see review by Ravishankara [1988]), but data indicating the effect of isotope substitution in methane are scarce. Fractionation occurs in the atmosphere because the rate coefficient for reaction (R1) is slightly larger for the $^{12}$CH$_4$ relative to $^{13}$CH$_4$. This secondary (i.e., involving isotopic substitution at a position other than the direct reaction center and involving an atom not split off in the reaction) kinetic isotope effect is expected to be small, and indeed previous studies near room temperature have found an effect of 1% or less [Rust and Stevens, 1980; Davidson et al., 1987].

We attempted to improve the precision of the value for the carbon kinetic isotope effect in reaction (R1) (i.e., the ratio of the rate coefficients for the reaction of $^{13}$CH$_4$ with hydroxyl as compared to the reaction of $^{12}$CH$_4$) near room temperature. Additionally, we investigated the temperature dependence of this rate coefficient ratio.

EXPERIMENTAL PROCEDURES

The kinetic isotope effect in reaction (R1) has been studied in this laboratory previously [Davidson et al., 1987]. Many of the experimental details reported in that study apply here. Differences from our earlier study will be pointed out. The experiment involved the reaction of a mixture of methane containing both stable carbon isotopes, nominally at relative atmospheric abundances, with the hydroxyl radical. We measured the methane concentration and isotopic composition before and after a reaction period. The relation between the amount of methane converted, the change in the ratio of stable carbon composition and the ratio of rate coefficients for reaction (R1) for the two species is given by (see derivation in Davidson et al. [1987]):

\[
\eta = \frac{k_{12}}{k_{13}} = \frac{\ln(A)}{\ln(A) + \ln((\delta_{12} + 1000)/(\delta_{13} + 1000))}
\]

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where $k_3$ is the rate coefficient for reaction (R1) for methane containing carbon-12 and $k_{33}$ is for carbon-13 methane; $A$ is the fraction of methane remaining at time $t$; and $\delta$ is a measure of the ratio of carbon-13 to carbon-12 (in per mil, or parts per thousand difference), at the start of an experiment ($\delta_0$) and the end ($\delta_t$), defined as follows:

$$\delta_t = \left( \frac{R_{13}}{R_{12}} - \frac{R_{33}}{R_{32}} - 1 \right) \times 1000 \tag{2}$$

where $R_{13}$ and $R_{33}$ stand for the ratio of carbon-13 to carbon-12 in a sample, $x$, and in a standard, respectively. In this case, the standard is PeeDee Belemnite, which is the commonly accepted reference for stable carbon isotope work. The choice of standard has no effect on the final kinetic isotope effect derived. In the literature, the reciprocal of $\eta$ is often used, designated $\alpha$:

$$\alpha = \frac{k_{13}}{k_{12}} - 1 + \frac{\ln((\delta_t+1000)/1000)}{\ln(A)} \tag{3}$$

The accuracy of the measured kinetic isotope effect is sensitive to errors in determining the extent of conversion ($A$) and the isotope ratios ($\delta$). This sensitivity is minimized at relatively large fractional conversions, because of the increased amount of isotopic fractionation which occurs. Hydroxyl radicals were produced in sufficient amount to remove 50-90% of the methane in 24 hours. This design is relatively insensitive to contaminants found in the commercially prepared methane (such as light alkanes) because only the unreacted methane is analyzed (a problem with ethane is possible because it may be cryogenically trapped with methane in the isotope analysis, discussed below).

We used the same hydroxyl radical source as our previous study [Davidson et al., 1987]. Ozone was photolyzed in the Hartley band to produce excited oxygen atoms which react with water vapor:

(R2) \[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(D) \]

(R3) \[ \text{O}(D) + \text{H}_2\text{O} \rightarrow 2 \text{HO} \]

Ozone was added continuously during a run by passing helium through a trap of silica gel, which had previously been loaded with ozone produced through corona discharge of oxygen. The silica gel trap was maintained at 195 K with a dry ice/ethanol mixture. A typical flow of 5.0 standard cm$^3$ min$^{-1}$ caused a pressure increase in the cell of approximately 150 torr during a 24-hour experiment. The ozone was added in this fashion to maintain a low steady state concentration (< 10$^{13}$ cm$^{-3}$) which resulted in efficient use of the hydroxyl radicals produced; more OH radicals reacted with methane rather than with ozone. We calculated a steady state hydroxyl radical concentration of 2 to 6 x 10$^7$ cm$^{-3}$ from the rate of conversion of methane.

The cell was illuminated through a quartz window with radiation from a 300--W Xenon arc (ILC Corporation) filtered through a Corning glass filter 7-54. The filter was cooled by circulating tap water through the filter mount. This arrangement minimized possible effects of heating the reaction mixture by the photolysis lamp. The filter inhibited photolysis of ozone in the Chappius bands which produces ground state oxygen atoms. Ground state oxygen does not react with water vapor to produce hydroxyl radical.

The reaction mixture was continuously stirred throughout the course of a run with a stainless steel bellows pump. The volume of the pump and connecting tubing was minimized; less than 0.05% of the reaction mixture was outside of the cell at any given time. The entire cell mixture was circulated every 5 to 10 min. The cell was typically circulated for 10 min before the first sample was extracted, and for 10 min after the photolysis lamp was turned off before the final sample was taken.

The following procedure was used to prepare a reaction mixture. A volume of liquid water (0.2 to 0.8 cm$^3$) was added through a septum to an evacuated, temperature regulated stainless steel cell (approximately 48 L volume), which has been described previously [Shetter et al., 1987]. When the pressure within the cell reached the expected level (3 to 6 x 10$^7$ molecules cm$^{-3}$), a known pressure of methane (Linde Research Grade, greater than 99.999% purity), measured with a capacitance manometer (MKS Instruments), was added to a calibrated volume and swept into the cell with helium (Linde UHP, greater than 99.999% purity). Helium was used as the bath gas because it is ineffective in quenching the excited oxygen atoms produced in reaction (R2). The ratio of water to methane in the cell was kept as high as possible ([H$_2$O]/[CH$_4$] = 600 to 1700) in order to minimize loss of methane due to reaction with excited oxygen atoms (O$(D)$):

(R4) \[ \text{CH}_4 + \text{O}(D) \rightarrow \rightarrow \text{products} \]

The rate coefficient for reaction (R3) is about 1.4 times that for reaction reaction (R4). The reaction rate for O$(D)$ with H$_2$O is about 800 to 2400 times that for reaction with CH$_4$. Reaction (R4) almost certainly has a kinetic isotope effect which is less than that in reaction (R1) [Davidson et al., 1987]; thus any contribution to the methane loss from reaction (R4) would bias the measured fractionation in these experiments. In order to monitor the possible extent of reaction (R4), nitrous oxide (USP US Medical, greater than 99.0% purity) was added with a reactivity toward O$(D)$ approximately equal to that of the initial amount of methane in the cell ((1.0 to 2.5) x 10$^{14}$ molecules cm$^{-3}$). Nitrous oxide reacts with O$(D)$, but not with the hydroxyl radical. The concentration of N$_2$O throughout a given experimental run was monitored through the use of Fourier transform infrared spectroscopy (discussed below). The loss of nitrous oxide, if any, could then be used to apply a first order correction to the methane loss due to reaction with O$(D)$.

Oxygen (Linde UHP, greater than 99.999% purity) was added to the cell in order to insure that methyl radicals (CH$_3$), once formed, would be converted to stable products (CO or CO$_2$) rather than be converted back to methane, or be associated to form ethane. Back reaction to methane and ethane could provide alternate pathways for isotope fractionation.

(R5) \[ \text{CH}_4 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M} \]

Typically an oxygen concentration of 3 x 10$^{17}$ molecule cm$^{-3}$ was used. Reaction (R5) along with the reaction of methyl radicals with ozone, assures that no back reactions occur.

(R6) \[ \text{CH}_3 + \text{O}_3 \rightarrow \text{CH}_2\text{O} + \text{O}_2 \]
Nitrogen dioxide ((3 to 5) x 10^13 molecules cm^-3) was added in order to maintain a steady state of nitric oxide (NO), which speeds the conversion of methane to CO and CO₂ through reaction (R7):

\[ \text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{NO}_2 \]

The methoxy radicals formed react with oxygen to form formaldehyde, which subsequently photolyzes or reacts with hydroxyl.

The extent of conversion of methane and nitrous oxide was monitored by infrared spectroscopy. A BOMEM model DA3.01 Fourier transform spectrometer system was interfaced to the cell. An infrared beam from a heated SiC rod was collimated and passed through a CaF₂ beamsplitter. The beam was then transferred to the cell via matching optics through BaF₂ windows. The White-type internal multiple pass optics were arranged to yield 24 passes or a total optical path of 48.6 m. The beam exited the cell and was detected by a liquid N₂-cooled InSb detector. This beamsplitter and detector combination limited energies to those greater than 1800 cm^-1; however, this region allows quantification of methane, nitrous oxide, as well as carbon dioxide and carbon monoxide, if desired. The spectral resolution, 0.125 cm^-1, was sufficient to resolve and analyze individual rotational lines, and also operate in a region of linear relationship between measured absorbance and species concentration. The initial spectrum (100 interferometer scans) was taken before samples were withdrawn for GC and MS analysis.

The Beer-Lambert linearity for methane was verified for 10 individual lines which were free of spectral overlap with water or formaldehyde. These lines were due to the ^13CH₄ species only, but most of the methane in the cell contains carbon-12 (about 99%), and only a small fractionation takes place during the course of a run (less than 1%). Therefore it is expected that the ratio [^13CH₄]/[^13CH₄]₀ would be close to, but systematically low by less than 1% compared to [[^13CH₄] +[^13CH₄]]/[[^13CH₄] +[^13CH₄]], which is the factor, A, in equation (1). This error is small compared to the scatter of the CH₄ determination by this technique. Since only the fractional methane remaining is required for this study, the line integrations were not converted to absolute methane concentrations, but instead the areas from the spectrum at the end of the experiment and those from the beginning were ratioed, and an average of all 10 lines was used for the factor A, discussed above. This factor must be corrected for the amount of sample removed for the initial GC and MS measurements (determined though pressure measurements).

Samples of the reaction mixture were withdrawn before and after photolysis for gas chromatographic (GC) methane analysis and mass spectrometric (MS) isotopic composition. The 7.6 L electropolished stainless steel sample bulbs with stainless steel bellows valves were evacuated prior to sample collection. The methane mixing ratio was determined by gas chromatography and flame ionization detection [Zimmerman et al., 1988]. The methane mixing ratio in the samples was compared to two standard mixtures, 3.88 ppmv (NBS SRM1660a) and 71.83 ppmv (Specialty Gas Products). Absolute concentration is not required for this study, only the ratio of methane before and after photolysis. Typically 10 individual chromatograph runs were performed and averaged. The upper limit of the uncertainty in the measurement has been estimated at 0.4 ppbv [Zimmerman et al., 1988]. The final methane mixing ratio was corrected for dilution due to the addition of helium monitored by pressure measurements at the beginning and end of the photolysis period.

The relative standard deviation of the IR measurements (3–5%) was larger than that for the gas chromatographic determinations. The methane remaining as determined from spectroscopic measurements (FTIR) as compared to GC measurements is shown in Figure 1. The least squares fit of the data yields a slope of 0.98 (± 0.06), which is not significantly different from unity.

The isotope ratio determinations were performed in a fashion similar to that discussed by Tyler [1986; Tyler et al., 1988] and Davidson et al. [1987], using a new high-volume, fast-flow rate combustion train to convert CH₄ to CO₂. A major improvement over the earlier system is in the use of an oven catalyst of platinized alumina (1% loading) at 800°C. Carbon dioxide and water are removed prior to the entry of the sample gas stream into the oven using a series of four multiple loop traps at liquid nitrogen temperature (77 K). Since Pt-alumina is porous and potentially subject to high blanks, it is conditioned periodically by flushing with dry zero air. Our carbon blank is less than 1 µl of CO₂ for 300 L of clean zero air processed. The recovery of carbon dioxide produced from the conversion of methane is greater than 99%, even with relatively small samples such as those for this experiment (20 to 50 µL). The mass spectrometer used in this study was a Finnigan-Mat Delta-E model, which resulted in overall precision of better than 0.1% by the use of a specially designed cold finger inlet system. The working standard for this study was Oztech-002 (Oztech Gas Co.) which is ~30.011% relative to PDB carbonate. The δ¹³C values are reported with respect to PDB carbonate, with usual corrections for background, leakage, capillary fractionation, and δ¹⁸O. The separation and combustion procedure would not distinguish carbon originating in ethane from that in methane, therefore a run was chosen for analysis of light alkanes. All alkanes including ethane were below detection limits, and could constitute no more than 0.1% of the methane concentration, and thus present no interference in the isotope ratio analysis.

RESULTS AND DISCUSSION

Temperature and Conversion Dependence of k₂/k₁₁

The results of this study are analyzed in several ways. First a rate coefficient ratio (k₂/k₁₁) was calculated for each experiment from equation (1). These data are presented in Figure 2 and Table 1. The average and 95% confidence intervals for the room temperature recommendations for k₂/k₁₁ of Davidson et al. [1987] and Rust and Stevens [1980] are also shown (lower confidence interval for Davidson et al. and upper confidence interval for Rust and Stevens). The horizontal lines are averages of all the data from the present work. The results of this study are between the two previous studies. The kinetic isotope effect shows no temperature dependence, from 273 to 353 K. A linear regression of k₂/k₁₁ versus temperature yields slopes of -0.000004 per degree and 0.000001 per degree using the GC and FTIR conversion determinations, respectively. The standard deviations of these slopes are factors of 10 and 6 larger than the slopes, respectively; they are not statistically significant.

The kinetic isotope effect in this reaction is independent of temperature over the range studied, and so the results at all temperatures were averaged. The GC and FTIR conversions were analyzed separately, yielding values for the kinetic isotope
effect of 1.0056 (± 0.00091) and 1.0058 (± 0.0011), respectively (the error limits are the 95% confidence intervals).

The data from this study were treated in another fashion (although not independent) in order to demonstrate to lack of dependence of $k_3/k_4$ on extent of conversion. If equation (1) is rearranged to collect the $\ln(A_t)$ terms together, the following expression is derived:

$$\ln(A_t) = \frac{\eta}{1-\eta} \cdot \ln \left( \frac{8 + 1000}{8_{34} + 1000} \right)$$

where $\eta$ is the ratio of rate coefficients, $k_3/k_4$. Thus a fit of $\ln(A_t)$ versus the logarithm of the term in large brackets yields a slope which is related to $\eta$ [\(\eta = \text{slope} / (1 + \text{slope})\)]. The data are presented as $\ln(A_t)$ versus the logarithmic term on the right of equation (4) in Figure 3. The result of a fit (constrained to have an intercept, $A_0$ equal to unity) yields a value for $\eta$ of 1.0054 (± 0.0009, at the 95% confidence interval), which is essentially identical to the results of the other treatments. This treatment demonstrated the derived kinetic isotope effect is independent of the extent of conversion.

The extent of reaction (R4) was monitored with nitrous oxide as described above. There was no loss of N$_2$O within the uncertainty of the measurements (2% ± 5%, 95% confidence level). A 2% loss of N$_2$O would imply a loss of about 2.7% of methane due to reaction (R4), because the rate coefficient for O($^3$D) reaction with CH$_4$ is 1.34 times that for reaction with N$_2$O. If one accepts the N$_2$O loss as real, and assumes that the kinetic isotope effect for reaction (R4) is 1.000, then the values of $\eta$ would increase to about 1.0055 (from 1.0054). This small correction was not applied due to the uncertainty in the amount of N$_2$O depletion.

**Comparison with Previous Measurements**

Our new result is about one-half the calculated fractionation of methane carbon isotopes as determined by Davidson et al. [1987]. The present result has an uncertainty which is nearly an order of magnitude smaller than Davidson et al. [1987]. Possible reasons for this difference will be discussed below.

The present result is in agreement with the results of Davidson et al. [1987] and Rust and Stevens [1980] within the large uncertainties associated with those studies ($\eta = 1.010 ± 0.007$ and 1.003 ± 0.007 at the 95% confidence level; note the confidence interval for Rust and Stevens is calculated from the data, not as reported by them).

It has been pointed out that the individual $\eta$ values from the Davidson et al. study fall into two groups [Craig et al., 1988; Stevens and Engelkemeir, 1988]. At least two factors may have contributed to the large spread of values from the study of Davidson et al. [1987] as compared to the present one. The precision of the extent of methane conversion was greatly improved in the present study (less than 1%) as compared to the previous study (about 9%). Also, in this study isotope ratio measurements were performed on the methane at the beginning of every run. In the previous experiment, seven determinations
| T, °C | Time, hours | Initial Methane, ppmv | Final Methane, ppmv | Cell Pressures, mm Hg | δ (Relative to PDB) | Methane Left, % | (δ\textsubscript{δ+1000})/ (δ\textsubscript{δ+1000}) | KIE | From GC | From FTIR |
|------|-------------|-----------------------|---------------------|----------------------|---------------------|----------------|----------------|------|--------|---------|
| 0.0  | 19.12       | 5.35                  | 5.65                | 100.00               | 1.18                | 21.54          | 810.0          | 697.6 | 837.3  | -36.57  | 25.05   | 25.00   | 1.008138 | 1.00589 | 1.00588 |
| 0.0  | 15.53       | 16.56                 | 16.73               | 100.00               | 6.17                | 37.97          | 814.4          | 703.6 | 830.3  | -36.93  | 35.92   | 34.95   | 1.004896 | 1.00591 | 1.00596 |
| 0.4  | 16.32       | 15.06                 | 15.52               | 100.00               | 4.28                | 21.81          | 825.3          | 711.5 | 829.6  | -36.01  | 32.15   | 25.30   | 1.006753 | 1.00597 | 1.00492 |
| 0.5  | 15.75       | 14.53                 | 14.76               | 100.00               | 5.15                | 29.92          | 824.5          | 706.7 | 829.6  | -35.88  | 40.80   | 34.91   | 1.005290 | 1.00592 | 1.00504 |
| 19.5 | 16.58       | 63.82                 | 65.46               | 100.00               | 14.30               | 28.30          | 830.2          | 721.1 | 835.3  | -35.78  | 25.31   | 32.58   | 1.007280 | 1.00531 | 1.00651 |
| 20.0 | 19.67       | 41.26                 | 42.20               | 100.00               | 10.61               | 30.84          | 832.0          | 755.5 | 915.0  | -35.69  | 30.53   | 34.01   | 1.007000 | 1.00591 | 1.00651 |
| 20.0 | 25.44       | 42.74                 | 43.90               | 100.00               | 9.64                | 24.86          | 791.8          | 736.9 | 815.4  | -35.82  | 26.35   | 26.62   | 1.007945 | 1.00515 | 1.00602 |
| 20.1 | 6.50        | 45.16                 | 45.78               | 100.00               | 34.36               | 67.92          | 767.8          | 633.9 | 692.5  | -35.67  | 82.00   | 82.27   | 1.001172 | 1.00594 | 1.00604 |
| 20.1 | 22.33       | (d)                   | 34.36               | 100.00               | 10.54               | 30.57          | 692.5          | 557.6 | 662.5  | -34.54  | 37.79   | 39.12   | 1.005935 | 1.00612 | 1.00635 |
| 20.1 | 22.62       | 30.53                 | 31.11               | 100.00               | 35.30               | 18.02          | 831.8          | 620.7 | 791.5  | -35.87  | 21.72   | 24.15   | 1.007821 | 1.00513 | 1.00551 |
| 20.2 | 22.27       | 20.07                 | 20.12               | 100.00               | 3.31                | 22.78          | 832.6          | 717.4 | 935.1  | -35.80  | 19.84   | 24.46   | 1.007716 | 1.00477 | 1.00549 |
| 79.8 | 19.42       | 38.72                 | 38.87               | 100.00               | 2.12                | 4.34           | 785.9          | 641.9 | 822.8  | -38.40  | 6.99    | 5.31    | 1.015527 | 1.00582 | 1.00528 |
| 80.0 | 5.55        | 39.88                 | 40.44               | 100.00               | 15.87               | 38.87          | 772.2          | 629.9 | 681.6  | -36.16  | 42.46   | 47.65   | 1.004482 | 1.00525 | 1.00607 |

Mean 1.00562 1.00581
Standard Deviation 0.00042 0.00051

\(\text{\textsuperscript{a)}}\) Spectroscopic data for methane are relative percentages, not ppmv.
\(\text{\textsuperscript{b)}}\) Pressure after initial sample for GC and MS analysis.
\(\text{\textsuperscript{c)}}\) Pressure after photolysis period.
\(\text{\textsuperscript{d)}}\) This run is continuation of run from line above, the initial methane is the final methane from that run.
were performed and averaged. While one would expect the isotope ratio of the unreacted methane to be easily characterized and constant, some variability was found in the present study (average initial per value equals $-35.9 \pm 0.5\%$). The amount of methane measured in the initial samples was always slightly higher (0 to 3%) than the amount added to the cell, possibly entering the cell with the addition of water. This contaminant methane was probably atmospheric methane with a $\delta^{13}C$ value of about $-47$ as compared to the cylinder methane, presumably of thermogenic origin, with a $\delta^{13}C$ value of about $-36$. It is also possible that fractionation of methane could occur in the low pressure vacuum line used for addition of gases to the reaction cell. In the present study, use of the average initial per mil value results in the same average kinetic isotope effect with a slightly larger standard deviation.

If the Davidson et al. study had a problem with variability in the isotopic content of the unreacted methane and the per mil values were systematically less negative than the average of the measured values, then a systematically high value for the kinetic isotope effect would be measured. We do not know if this was the case.

**Modeling the Carbon Kinetic Isotope Effect**

Although Ehhalt et al. [1989] found that primary kinetic isotope effects in simple systems ($H_2$ and HD with HO) can be calculated quite successfully using the BEBOVIB-IV computer program [Burton et al., 1977], the use of this program for the carbon kinetic isotope effect in the methane-hydroxyl reaction gave a range of values (1.00 to 1.04). These values depend upon the shape assumed for the potential energy surface of the activated complex. A more sophisticated method apparently is required to perform accurate simulations on a secondary kinetic isotope effect such as occurs in this reaction.

**Implications for the Atmospheric Methane Budget**

What does the value for the ratio of the two rate constants tell us about the $^{13}CH_4/^{12}CH_4$ ratio in the sources of atmospheric methane? We performed a simplified calculation following Craig et al. [1988], with an extension to include possible soil sink fractionation as discussed by King et al. [1989].

We take

$$\delta_{\text{sample}} = \delta_{\text{in}} +$$

$$\left( \frac{F_{\text{in}}(1-\eta_{\text{in}})}{\eta_{\text{in}}} + \frac{F_{\text{out}}(1-\eta_{\text{out}})}{\eta_{\text{out}}} \right) \cdot \left( 1 + \frac{\delta_{\text{in}}}{1000} \right) \cdot (1000) \quad (5)$$

where $F_{\text{in}}$ is the fraction of methane that is removed chemically by tropospheric OH and $F_{\text{out}}$ is the fraction removed by soils. Equation (5) is only an approximation. A more complete analysis must recognize several factors, among those: that the spatial and temporal distributions of methane sources and sinks are not identical, and that the sources, sinks and atmospheric amounts are not necessarily in steady state.

With our value for $\eta_{\text{in}}$ (1.0054), and $\delta_{\text{in}} = -47.7\%$ [Craig et al., 1988] this equation yields $\delta_{\text{sample}} = -52.2\%$, assuming $F_{\text{out}}$ is negligible. With a value of $\delta_{\text{in}}$ per mil after Lowe et al. [1989], we obtain $\delta_{\text{sample}} = -1.4\%$. To account approximately for the fact that atmospheric methane is increasing in concentration, i.e., that sources exceed sinks, and for the
possibility that $\delta_{\text{nat}}$ is also changing (decreasing at a rate of about 0.05% yr$^{-1}$), Craig et al. would add about 0.4% to the two distinct values of $\delta_{\text{nat}}$ above, yielding $-51.8$ and $-51.0\%$. In either case, because most biogenic methane is considerably more depleted in $^{13}$C than $-52\%$, it is apparent that there must be very significant sources of heavier methane from, for example, natural gas processes, coal mining, biomass burning and possibly methane hydrate deposits. The earlier value for $\eta$ from Davidson et al. [1987] would have implied that $\delta_{\text{nat}}$ was $-55$ or $-56\%$. To the extent that this value of $\delta_{\text{nat}}$ has been used as a constraint in deducing budgets of atmospheric methane (see Wahlen et al. [1989] and Cicerone and Oremland [1988]) these budgets must be adjusted to allow for relatively more sources that are enriched in $^{13}$C. The inclusion of $\eta_{\text{nat}}$ of King et al. (1.016 to 1.026) and reasonable estimates of the size of $F_{\text{nat}}$ [Cicerone and Oremland, 1988], suggests that $\delta_{\text{nat}}$ could be more negative by about 1% (i.e., $\delta_{\text{nat}}$ is $-52$ to $-53\%$).

CONCLUSIONS

We performed a study of the temperature dependence of the stable carbon kinetic isotope effect in the oxidation of methane by hydroxyl. The average effect measured in our study is $k_f/k_3 = 1.0054 \pm 0.0009$ (95% confidence interval). This value is larger than that of Rust and Stevens [1980] and lower than that of Davidson et al. [1987], but with much better precision. The ratio is independent of temperature from 273 to 353 K, within the precision of the results. This new value may be used to constrain the atmospheric methane budget using isotope ratio studies, and suggests more measurements of methane sources and sinks are necessary in order to fully understand atmospheric methane.

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