The Role of Isotope Fractionation Effects in Atmospheric Chemistry

C. M. Stevens and A. F. Wagner

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

Z. Naturforsch. **44a,** 376–384 (1989); received February 3, 1989

Dedicated to Professor Jacob Bigeleisen on the occasion of his 70th birthday

Kinetic isotopic fractionation plays an important role in the quantitative analysis by isotopic studies of the cycles of the two atmospheric trace gases, CO and CH_4, which are important because of their impact on the environment. These gases are scavenged from the atmosphere mainly by homogeneous gas phase oxidation reactions with OH radicals. The isotopic composition of these gases provides constraints on the relative distribution of the fluxes from sources, natural or anthropogenic, of different isotopic compositions. The relationship between the composition of the gas in the atmosphere and the average value of the sources is determined by the fractionation effect of the scavenging processes, in particular the reaction with OH. Thus, knowledge of the fractionation effect is essential to determining the relative distribution of the fluxes from isotopically different sources. The reactions $CO + OH$ and $CH_4 + OH$ exhibit several types of KIE's including normal, inverse, and compound effects resulting from the bimodal character of the former. A brief discussion of the measured values of the KIE for these reactions and their application to interpretation of the atmospheric cycles of CO and CH_4 is presented.

Key words: Kinetic isotopic fractionation, $CO + OH$, $CH_4 + OH$, Atmospheric carbon monoxide, Atmospheric methane

Introduction

The isotopic composition of an atmospheric trace gas can be significantly different from the average composition of the source fluxes as a result of isotopic fractionation in the scavening mechanisms. This is described by the mass balance relations for two isotopic masses, a and b,

$$P_a = N_a \lambda_a , \qquad P_b = N_b \lambda_b ,$$

where P, N, and λ are the fluxes to the atmosphere, steady state content (proportional to concentration) in the atmosphere, and removal rates, respectively. The ratio of the isotopic species in the atmosphere, $R_A = N_a/N_b$, is then

$$R_A = R_S (\lambda_b/\lambda_a) ,$$

where $R_S = P_a/P_b$ is the isotopic ratio of the source fluxes. For gases scavenged only by reaction with OH radicals, the relative rates of removal are equal to the relative rate constants of the reaction, $k_b/k_a = \alpha$, the kinetic isotopic fractionation effect (KIE). The quantity $(\alpha - 1) \times 10^3$ expressed in per mil will be used frequently in this report as the KIE. The above equation becomes

$$\delta_S = \delta_A + (\alpha - 1)(1 + \delta_A \times 10^{-3})\, 10^3 , \qquad (1)$$

where δ_x is defined as $\delta_x = (R_x/R_0 - 1) \times 10^3$ and R_0 is the isotopic ratio of an arbitrary standard.

When a gas undergoes a series of reactions, the isotopic composition for an element at any intermediate state, compared to that of the initial source, is determined only by the KIE of the loss reaction involving that state; the KIE of the intermediate reactions leading to that state are cancelled out providing that there are no competing mechanisms. For example, in the case of atmospheric CH_4, which goes through several reactions leading to CO, the carbon isotopic composition of the CO product is

$$\delta_{CO} = \delta_S - (\alpha_{CO} - 1)\, 10^3$$

and

$$\delta_{CO} = \delta_{CH_4} + (\alpha_{CH_4} - 1)\, 10^3 - (\alpha_{CO} - 1)\, 10^3 ,$$

where α_{CH_4} and α_{CO} are the ratios of the reaction rates of ^{13}C and ^{12}C with OH for CH_4 and CO, respectively.

Reprint requests to Dr. C. M. Stevens, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, USA

0932-0784 / 89 / 0500-0376 $ 01.30/0. – Please order a reprint rather than making your own copy.

In the cases of atmospheric CO and CH_4 the source fluxes are a mixture of natural and anthropogenic emissions with different isotopic compositions. The average isotopic composition of the sources, determined from the isotopic composition measured for the gas in the atmosphere from the above relation, provides constraints on the relative distribution of the fluxes of the isotopically different sources, with the fractionation effect (KIE) of the removal mechanism being a key factor in the determination. In the case of atmospheric CO both the stable isotopes of carbon, ^{13}C and ^{12}C, and oxygen, ^{18}O and ^{16}O, are important in the analysis; and in the case of atmospheric CH_4, the carbon and hydrogen isotopes can be used. A brief review of the published values for the KIE values of the removal mechanisms for these atmospheric gases will be presented. Then the application of these values in the interpretation of the atmospheric cycles of both these trace gases will be discussed, namely, the estimation of the fluxes of important source elements.

Kinetic Isotopic Fractionation Effect for CO + OH

The KIE's for carbon and oxygen in the reaction of CO with OH exhibit a variety of different effects [1]. The reaction has two routes [2, 3]; in the presence of oxygen

$$\begin{array}{l} CO + OH \underset{-a}{\overset{+a}{\rightleftarrows}} COOH^{\dagger} \xrightarrow{b} CO_2 + H \\ \qquad\qquad\quad \downarrow \text{(M)} \\ \qquad\qquad\quad COOH + O_2 \rightarrow CO_2 + HO_2 \end{array}$$

with the partitioning dependent on the total pressure; at low pressures the KIE, k^{12}/k^{13}, is less than unity, extrapolating to ca. 0.994 at zero pressure, but increases with pressure, becoming greater than unity above 0.5 atm, at a limiting value of 1.009 (Figure 1). These features of the carbon KIE, with similar values, were reported by Smith et al. [4], using a different experimental technique. As described by Stevens et al. [1], the ratio of isotope effects for the reversion of the activated $HOCO^{\dagger}$ radical to reactants versus decomposition to products by route b is given by the expression

$$\frac{(k^{12}/k^{13})_{-a}}{(k_{12}/k_{13})_b} = \frac{r}{(\alpha - 1)(k^{12}/k^{13})_0 (k^{12}/k^{13})_\infty - 1}, \qquad (2)$$

where r is the ratio of the unimolecular rate constants $-a$ and b shown to be about unity. The ratio of the KIE calculates to be about 1.03, which is attributed to the rupture of the C–O bond in the reversion of the activated $HOCO^{\dagger}$ to reactants. From the calculated values of $(k^{12}/k^{13})_a = 1.009$ and $(k^{12}/k^{13})_{-a} = 1.03$ one can derive a value for the isotopic equilibrium con-

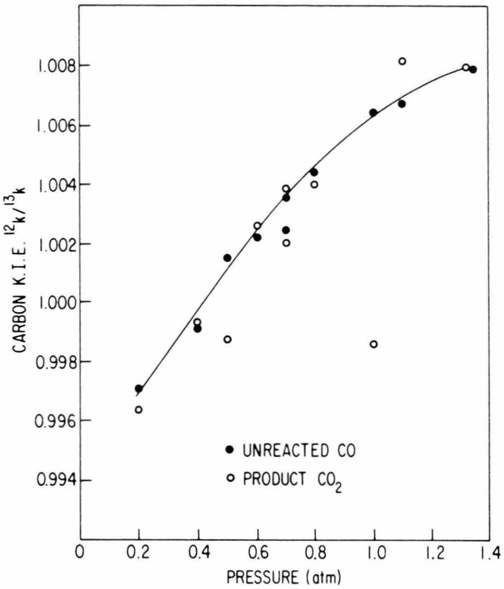

Fig. 1. KIE for carbon isotopes vs. pressure of air for the reaction CO + OH + M.

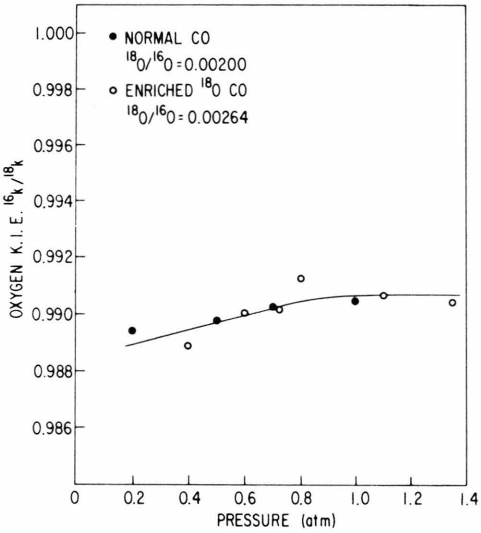

Fig. 2. KIE for oxygen isotopes vs. pressure of air for the reaction CO + OH + M.

stant:

$$\frac{(^{13}C/^{12}C)_{HOCO}}{(^{13}C/^{12}C)_{CO}} = 1.02\,. \tag{3}$$

This is substantially smaller than the ^{13}C enrichment, 1.086 [5] in CO_2 versus CO, in accord with the expected weaker bonding in the radical. The oxygen KIE k^{18}/k^{16} has a value close to 1.010 with little dependency on pressure (Figure 2). This implies an inverse isotope effect for the CO oxygen in the initial step, and essentially equal isotope effects for the two modes of dissociation ($-a$ and b) of the activated HOCO radical.

Kinetic Isotopic Fractionation for $CH_4 + OH$

Table 1. Measurements of the KIE for the reaction of the isotopic species of CH_4 with OH, expressed as the ratio, α, of the rate constant for that species relative to that for $^{12}CH_4$.

Isotopic Species	α	Reference
$^{13}CH_4$	0.997 ± 0.001	[6]
	0.990 ± 0.003	[7]
CH_3D	0.67	[8]
CH_2D_2	0.54	[8]
CHD_3	0.20	[8]
CD_4	0.09	[8]

The measured KIE values for carbon and hydrogen in the reaction $CH_4 + OH$ are listed in Table 1 [6–8]. In the case of carbon, the higher value of 0.990 measured by Davidson et al. [7], is probably the better value because of a superior experimental method, which produced higher OH concentrations by photolysis of ozone, with larger fractions of CH_4 reacted and consequently greater changes in the unreacted CH_4. Their method was very carefully designed with numerous tests for interfering effects. There is a puzzling bimodal distribution in their results of 20 measurements; nine of the values have a mean of $(\alpha - 1) = 7.0 \pm 0.4‰$ and seven have a mean of $10 \pm 0.3‰$. In the experimental method of Rust and Stevens [6], which utilized the photolysis of H_2O_2 by a Hg lamp, the OH concentration was limited to 10^8 molecules/cm^3 which yielded a very low reaction rate of about 5% per day. With such a small reaction rate for $CH_4 + OH$, the experiment was vulnerable to possible interfering reactions of CH_4 which could cause the disagreement with the results of Davidson et al.

Another argument favoring the larger value is that theoretical calculations show that a relatively large effect is expected. These calculations are based on a transition state theory (TST) analysis of a model of both the $CH_4 + OH$ asymptote and the CH_3-H-OH transition state that is constructed from theoretical and experimental information. The structures, which provide the moments of inertia used in the rotational partition functions of the TST analysis, are experimental for CH_4 and OH but theoretical for CH_3-H-OH, as derived from the ab initio electronic structure calculation of the C_2H_5-H-OH transition state done by Tully et al. [9]. The force fields, which provide the frequencies used in the vibrational partition function of the TST analysis, are theoretical for both CH_4 and CH_3-H-OH [10]. However, in the case of CH_3-H-OH, OH is treated as a point particle and the published force field for CH_3-H-H is used with the appropriate $H \rightarrow OH$ mass substitution for the attacking H atom made in solving for the frequencies. This is a severe approximation required by the absence of published calculations directly for CH_3-H-OH. Implicit in this approximation is the presumption that the O atom motion is decoupled from the C atom motion and consequently irrelevant for the calculation of the desired isotope effect.

The calculated isotope effect can be decomposed into contributions from the reduced collisional mass (translational partition function), the moments of inertia (external rotation partition function), and the vibrational frequencies (vibrational partition function). The contribution from the reduced collisional mass comes from the fact that the rate constant is inversely proportional to this mass raised to the 3/2 power via the translational partition function in the TST expression. In terms of α, this temperature-independent effect alone gives a value of 0.9549. However, the contribution from the moments of inertia tends to cancel this contribution. Through the rotational partition function in the TST expression, the product of the square root of each of three moments enters either the denominator (CH_4) or numerator (CH_3-H-OH) of the TST expression. However, since the rotation axis for each moment of inertia for CH_4 passes through the carbon atom, there is no $^{13}C/^{12}C$ contribution from the CH_4 reactant. For CH_3-H-OH, only one rotation axis, that associated with the linear $C-H-O$ axis, passes nearly through the C atom and consequently has almost no isotope effect. The other two rotation axes do not pass through the C atom and have an isotope effect approximating the ratio of the reduced collisional mass. Consequently, the contribution to the isotope effect from the moments of inertia (which favor the ^{13}C reaction) does not cancel the contribution from the reduced collisional mass (which favors the ^{12}C reaction). The product of these two contributions gives $\alpha = 0.9836$.

The final contribution from vibrational frequencies adds a small temperature-dependent effect that primarily involves about a 1.76 cm^{-1} change in the activation energy which favors ^{12}C reactions. At 300 K, the vibrational contribution alone gives an α of 0.9934. The final net isotope effect from all contributions at 300 K is 0.9771. This is much larger than either experimental value. The calculations are most uncertain in the vibrational contribution because of the approximations involved in the force field. But they would certainly tend to support the larger of the two measurements.

The only measurements for the reactions of the deuteromethane species with OH are those of Gordon and Mulac [8]. These KIE effects are very large, $\alpha = 0.67$, 0.54, 0.20, and 0.09 for CH_3D, CH_2D_2, CHD_3, and CD_4, respectively. These measurements were made at 427 K, so one might expect larger effects in the temperature range 260–300° of the atmosphere.

Application to Atmospheric Carbon Monoxide and Methane

Knowledge of these fractionation effects is essential for the general problem of deriving a budget of fluxes from isotopically different sources of an atmospheric gas to equal the isotopic composition in the atmosphere, i.e.

$$\sum S_i \delta_i = C \lambda [\delta + (\alpha - 1)\, 10^3] + d(C\delta)/dt \qquad (4)$$

The discussion on atmospheric CO presents an analysis of the isotopic data obtained in 1971 and published before the measurements of the KIE for the CO + OH sink were done. This is the first quantitative interpretation of some highlights of those 1971 results, but is not a complete analysis of all results in all seasons, which is planned for another paper. The discussion on atmospheric CH_4 is a review of work already published.

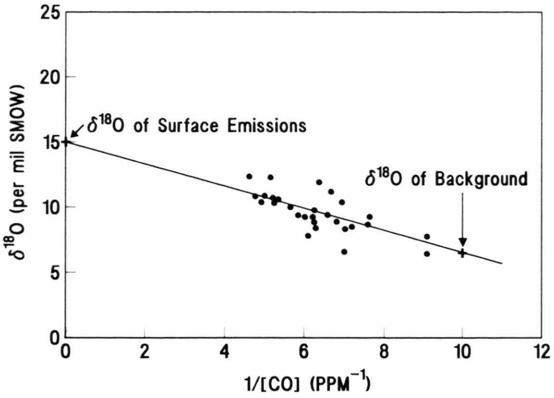

Fig. 3. The $\delta^{18}O$ vs. reciprocal concentration for surface air collected in rural northern Illinois, U.S., from June to October, 1971.

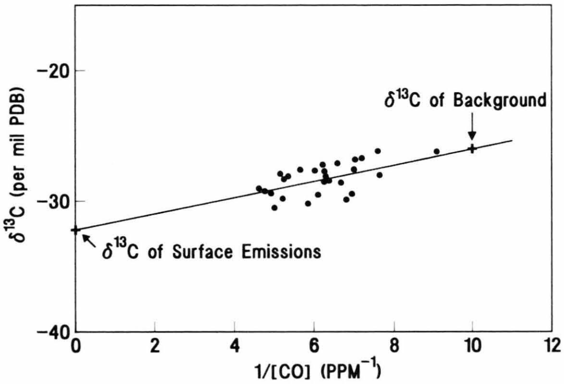

Fig. 4. The $\delta^{13}C$ of atmospheric CO vs. reciprocal concentration for surface air collected in rural northern Illinois, U.S., from June to October, 1971.

Atmospheric Carbon Monoxide

Atmospheric CO is especially interesting because the two elements, carbon and oxygen have opposite KIE and the major sources have much varied origins [11]. The carbon and oxygen isotopic composition of atmospheric CO was measured by Stevens et al. [12] in 1970–71 in surface air samples from rural northern Illinois for all seasons as well as several other locations in both hemispheres. The concentration and carbon and oxygen isotopic composition all showed regular seasonal changes with large amplitudes for both the concentration and oxygen isotopic composition. During the summer, the concentration was a minimum and $\delta^{18}O$ the smallest and different from the CO emitted from automobiles. Figures 3 and 4 show both the $\delta^{18}O$ and $\delta^{13}C$ measured values versus the measured reciprocal concentration between June 14 and October 15, 1971. The concentration distribution was bimodal with most of the samples falling in a low concentration group below 0.20 ppm which are shown in these figures. About a dozen results at concentrations >0.20 ppm were omitted in these plots because they showed the admixture of freshly emitted CO from automobiles under conditions of low winds and are not good examples of typical background surface CO. Even these results with the lowest concentrations are not representative of CO in the free troposphere. Numerous studies have shown that the concentration of CO is significantly higher in the boundary layer over continental regions [13–16]. From these studies the concentration in the northern hemisphere temperate zone at 45°N levels out to about 0.10 ppm in the free troposphere during the summer. The isotopic plots are similar to isotopic dilution plots of a fixed amount of one isotopic species mixing with a variable amount of another species. We interpret the distribution in these plots to be representative of summertime background CO in the northern hemisphere temperate zone at 0.10 ppm, mixing with 0.03 to 0.10 ppm of a freshly emitted or produced source of CO, coming from the surface. The extrapolated isotopic compositions of the variable diluting species are $\delta^{18}O = 14.9‰$ and $\delta^{13}C = -32.2‰$. The values for oxygen is radically different from the isotopic composition of CO from engine combustion, 24‰, and, in addition, it is 10‰ more enriched than the $\delta^{18}O$ of 5‰ measured in air samples from the southern hemisphere [12]. This difference of 10‰ is just the amount of the KIE for $^{18}O/^{16}O$ and, therefore, it is reasonable to assume that the CO in the southern hemisphere is at the steady state condition and consists of mainly CO from oxidation of natural hydrocarbons including atmospheric CH_4. The contribution from engine emissions in this hemisphere is small. The data for this study in rural Illinois suggest that the source which causes the increased surface concentrations is CO from the oxidation of nonmethane hydrocarbons and plant emissions; this CO is only a few days old, too young to be dispersed throughout the troposphere or altered isotopically by the KIE of the OH oxidation reaction. The hydrocarbons are presumed to be the isoprenes and terpenes emitted by trees and plants [17, 18] which have been suggested as a major source of CO. It is clear from the isotopic composition that this source dominates over engine emissions upwind of rural central U.S.

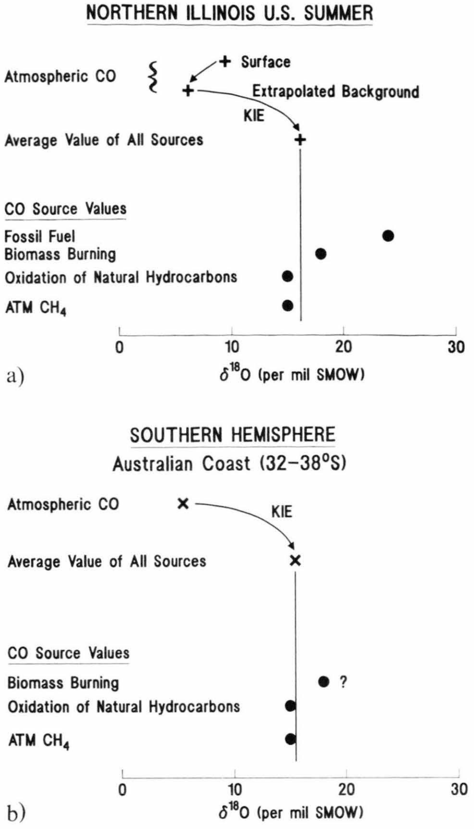

Fig. 5. The average $\delta^{18}O$ of the sources of atmospheric CO compared to the isotopic composition of the principal sources: (a) northern Illinois, U.S., summertime; (b) southern hemisphere, May 1971 and February 1974 (Australian coast, 32–38°S).

Figure 5a compares the values for the isotopic composition of the major sources with the average value of 16.2‰ for the oxygen isotopic composition of the major sources of CO in the temperature zone of the northern hemisphere during the summer, derived by extrapolation to the background concentration of the free troposphere as shown in Fig. 3 and corrected for the KIE = +10‰ for oxygen by (1). The value for global fossil fuel CO which is mainly emissions from automobiles was measured by Stevens et al. [12], as 24‰. The value for CO from biomass burning is based on the average of 18 ± 1‰ for five samples of emissions from a controlled burn of a pine forest, an open field grass fire, and three brush fires. The value for CO from the oxidation of natural hydrocarbons is based on the value deduced for the surface emissions from Figure 3. Since the final chemistry in the proposed

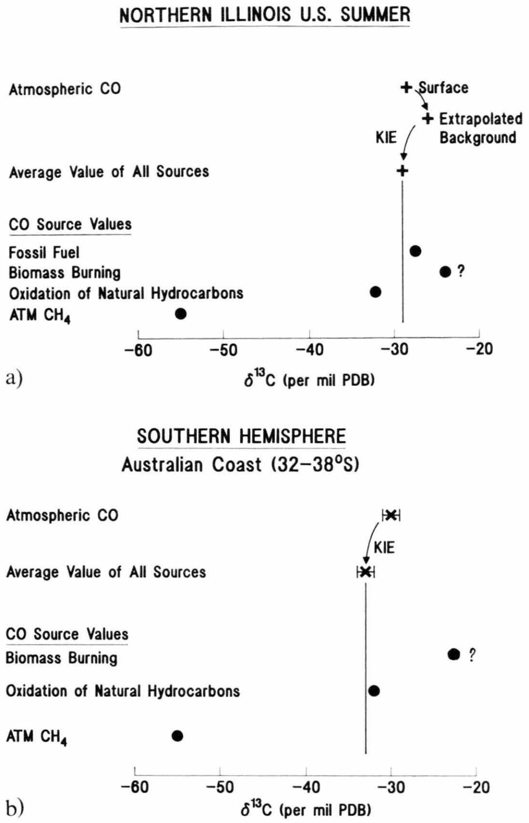

Fig. 6. The average $\delta^{13}C$ of the sources of atmospheric CO compared to the isotopic composition of the principal sources: (a) northern Illinois, U.S., summertime; (b) southern hemisphere, May 1971 and February 1974 (Australian coast, 32–38°S).

conversion of hydrocarbons to CO [18] is probably the same as that for oxidation of CH_4 to CO, we adopt the same value for the latter source as deduced for the former, viz. 15‰. The flux from natural hydrocarbons including CH_4 must be 3–5 times greater than the combined fluxes from fossil fuel and biomass burning based on this comparison. The flux of the hydrocarbon based source exists only during the 4–5 months of the summer season. The fossil fuel source is quite constant all year and concentrated in the northern temperate zone. However, the biomass burning source would be quite seasonal being mainly due to burning of agricultural wastes in the spring or autumn. Based on these seasonal factors, the flux from hydrocarbons was 240 Tg/mo ($Tg \equiv 10^{12}$ g) or 1000–1250 Tg/yr if fossil fuel fluxes were 40 Tg/mo in 1971 [11].

Figure 6a presents a similar comparison of the average carbon isotopic composition of all sources compared to the values of the individual sources. The value for fossil fuel is −27.5‰ [12]; for nonmethane natural hydrocarbons, −32‰, deduced from the analysis of Fig. 4; and for atmospheric CH_4, −55‰, based on the value of −47.8‰ for atmospheric CH_4 in 1978 [19] corrected for the KIE of the $CH_4 + OH$ sink. The value for biomass burning is uncertain. The $\delta^{13}C$ for the CO from the controlled burn of a pine forest was −24.5‰. Other measurements reported by Stevens and Engelkemeir [20] were ±2‰ for three fires and +13‰ for one brush fire compared to the CO_2 produced. These indicate that the carbon isotopic composition of the CO from this source is nearly the same or possibly more enriched than that of the biomass. Since the KIE for CO + OH is pressure dependent, its average value for the free troposphere should be less than the value at atmospheric pressure. The altitude averaged value is calculated at −3‰, leading to the averaged carbon isotopic composition of all sources equal to −29‰. Compared to the isotopic values for the principal sources from fossil fuel and oxidation of natural hydrocarbons, the fluxes of the former would have been twice as much as the latter, in disagreement with the analysis of the oxygen isotopic results. The cause of the disagreement is not understood. The results based on the oxygen data are regarded as more reliable because of the large isotopic differences, the independence of the KIE with altitude, and the reliability of the oxygen isotopic composition of the fossil fuel source. The largest uncertainty in the carbon isotopic data is the altitude dependence of the KIE. A plausible explanation for the disagreement is that the altitude-averaged KIE is greater than the calculated value of −3‰. A value of −5‰ would make for approximate agreement within the accuracy of the estimates of all the isotopic compositions entering into the calculation. A larger altitude-averaged KIE value, if true, implies that most of the scavenging of CO by CO + OH takes place at the very lowest altitudes, under several kilometers.

The average isotopic composition of CO in four samples of air collected in the southern hemisphere (32–38°S) in 1971 [12] and 1973 [unpublished] was $\delta^{13}C = -30.3 \pm 0.5$‰ and $\delta^{18}O = 5 \pm 1.0$‰, with the average concentration 70 ppb. Applying the KIE for the sink, then the average carbon and oxygen isotopic composition of the sources was −33.3‰ and 15‰, Figure 6b. We have deduced from the analysis of the surface source in the northern hemisphere that $\delta^{18}O = 15$‰ is the value for the CO source coming from the oxidation of natural hydrocarbons and CH_4. As shown in Fig. 6 b, the average ^{13}C of the sources is more depleted in ^{13}CO than the values for the hydrocarbon or biomass burning sources, and indicates a contribution from CH_4 oxidation. The magnitude of this contribution depends on the magnitude of the flux from biomass burning. From the oxygen isotopic data (Fig. 5 b) it is reasonable to put an upper limit of 25% for the contribution from biomass burning. This is based on a possible difference of one per mil between the average value of all sources and the value for the hydrocarbon sources. Then, from the carbon isotopic values, a lower limit for the average value for the combined sources of CH_4 and nonmethane hydrocarbons would be $-33.3 - [0.25 \times (-24 + 33.3)] = -35.6‰$. This corresponds to a ratio of NMHC : CH_4 fluxes of 5.5 and an upper limit of the partial concentration of CO from CH_4 of about 9 ppb. The lower limit is 4 ppb corresponding to zero flux from biomass burning. The upper limit of 9 ppb is significantly less than the value of ~20 ppb based on the ratio of the rate constants for OH oxidation of CH_4/CO (0.016) assuming that all atmospheric CH_4 (concentration in 1971 estimated at 1.4 ppm) is converted to CO. This means that a significant fraction of the CH_4 oxidation products are removed from the atmosphere by rainout.

The contribution of a fractionation effect for the uptake of atmospheric CO by soil bacteria has not been considered in the analysis of the isotopic data above. The global estimates of this loss rate are in the range of 120–450 Tg/yr (TG = 10^{12} g) [11, 21] compared to the total global flux estimates of 2800 Tg/yr [11, 22]. The fractionation effects for this process were measured with enclosed chambers in the laboratory and by field sampling during nocturnal inversions and gave values of −6‰ for carbon and −11‰ for oxygen [unpublished]. The combined fractionation effect for this sink and the OH oxidation sink is

$$\alpha_\Sigma = f_{sb}\,\alpha_{sb} + (1 - f_{sb})\,\alpha_{OH}\,,$$

where f_{sb} is the fraction of the total loss rate due to the former. Since the carbon fractionation effect of the soil sink is comparable to the KIE for OH loss, there would be little effect on the overall fractionation effect from the relatively small loss of the former. However, the oxygen fractionation effect for the soil sink is equal and opposite to the inverse KIE for OH loss; thus, even a 10% loss to the soil would make the average overall fractionation effect +8‰, 2‰ less than that for only the OH oxidation sink used in the treatment of the isotopic data presented above. Several features of the atmospheric isotopic data indicate that the soil sink is much smaller than 10%: first, Figs. 5 a and 5 b show that the $\delta^{18}O = 5‰$ for CO in the southern hemisphere is just 10‰ depleted compared to $\delta^{18}O = 15‰$ of the CO from the surface source in the northern hemisphere, the same amount as the KIE for oxygen by the OH sink. It is plausible that the CO in the southern hemisphere was produced from remote similar surface sources and was at steady state equilibrium isotopically, indicating a KIE with little contribution from the soil sink. Secondly, the difference between the $\delta^{18}O$ of the background CO in the northern hemisphere and the southern hemisphere is $1.5 \pm 1.0‰$. This difference is more likely attributed to the much greater emissions of isotopically heavy CO from fossil fuel sources, mainly automobiles, in the northern hemisphere, than to a difference in the average KIE which would be expected if the soil loss were the cause because of the much greater land area in the northern hemisphere. There is the possibility that the above treatment of the isotopic data is oversimplified and not correct because of the complex sources and sinks of atmospheric CO. Measurements of the carbon isotopic composition of the natural hydrocarbons emitted by trees, and if possible the oxygen isotopic composition of the CO product from atmospheric chemistry would be useful in interpreting the atmospheric CO isotopic data more reliably.

Application to Atmospheric Methane

Because the $CH_4 + OH$ reaction is the principal removal mechanism for atmospheric CH_4, the KIE is an important factor in establishing the relative magnitudes and the temporal trends of the fluxes of the isotopically different sources. The global average carbon isotopic composition of the sources in 1978 was calculated by Stevens and Engelkemeir [20] at −55.3‰ based on Davidson's et al. [7] value of the KIE of −10‰ and $\delta^{13}C = -47.7‰$ for atmospheric CH_4. This takes into account a 10% nonfractionating loss to the stratosphere [23] and a correction for both the increasing concentration and changing isotopic composition [20]. Figure 7 shows the comparison of the average source value with the measured values for the various natural and anthropogenic sources. The $\delta^{13}C$ of the natural sources was calculated to be −58.3‰ based on measurements of CH_4 (−49.6‰) in

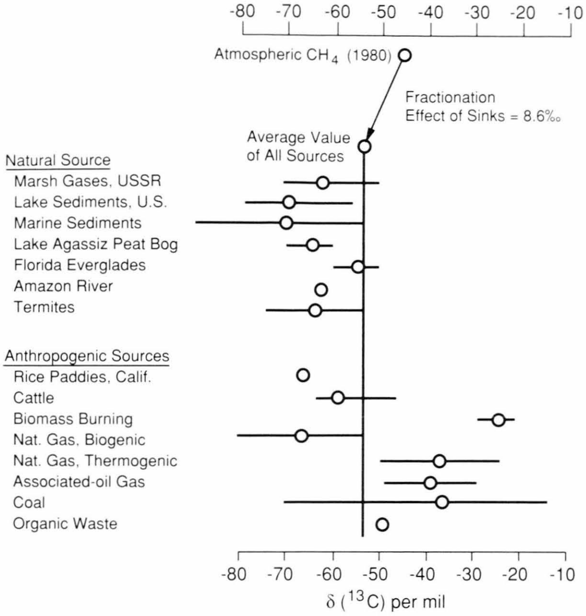

Fig. 7. The average $\delta^{13}C$ of the sources of atmospheric CH_4 compared to the measured values of the natural and anthropogenic sources [20]. The open circles are the mean values of the individual measurements over the indicated range.

old polar ice cores [24]. Since the concentration in 1978 was twice as much as that in the 200–300 yr old ice [25–27], due to the anthropogenic sources, the average $\delta^{13}C$ of the anthropogenic sources must be -52.3‰. The average $\delta^{13}C$ value for the natural sources is larger than most of the measured values for the natural sources, which indicates either that these values are not representative of the major wetland sources or that there is a heavier CH_4 source unknown at present. Among the anthropogenic sources, biomass burning is the most isotopically heavy (-25‰) and its flux the most uncertain; therefore its flux was calculated as 47 Tg/yr using the independent estimates for the other anthropogenic sources and the average value derived above [20, 24]. The importance of the magnitude of the KIE in these calculations is illustrated by comparing the above results with those which come from using the smaller KIE of -3‰ measured by Rust and Stevens [6]. In that case the $\delta^{13}C$ of the natural sources would be -52.3‰, which is very significantly larger than the measured values for natural wetlands and would require a much larger source of some unknown heavy CH_4. The average value of the anthropogenic sources would be about -48‰, and lead to a calculated flux from biomass burning of 125 Tg/yr.

Wahlen et al. [28] measured the δD of atmospheric CH_4 at -80‰ (SMOW) and several of the principal isotopically different sources. Applying the large KIE of -330‰ [8], they estimate the flux from biomass burning at 5–10% of the total, estimated at 400–550 Tg/yr [20, 29, 30].

Acknowledgements

The theoretical calculations were supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-31-109-Eng-38. The remainder was supported by NASA Grant W16188.

[1] C. Stevens, L. Kaplan, R. Gorse, S. Durkee, M. Compton, S. Cohen, and K. Bielling, Int. J. Chem. Kinetics **XII,** 935 (1980).
[2] I. W. Smith, Chem. Phys. Lett. **49,** 112 (1977).
[3] H. W. Biermann, C. Zetsch, and F. Stuhl, Ber. Bunsenges. Phys. Chem. **82,** 62 (1978).
[4] H. G. J. Smit, A. Volz, D. H. Ehhalt, and H. Knappe, in Stable Isotopes, Eds. H. L. Schmidt, H. Förstel, and K. Heinzinger, Analytical Chem. Symposia Series Vol. 11, Proceedings of the 4th Int. Conference, Julich, March, 1981, Elsevier Scientific Pub. Co., Amsterdam 1982.
[5] H. Urey, J. Chem. Soc. 1947, 562.
[6] F. E. Rust and C. M. Stevens, Int. J. of Chem. Kinetics **12,** 371 (1980).
[7] J. A. Davidson, C. A. Cantrell, S. C. Tyler, R. E. Shetter, R. J. Cicerone, and J. G. Calvert, J. Geophys. Res. **92,** 2195 (1987).
[8] S. Gordon and W. Mulac, Int. J. Chem. Kinetics, Proceedings of the Symposium on Chemical Kinetics Data for the Upper and Lower Atmosphere, 1975, p. 289.
[9] F. Tully, A. Droege, M. Koszykowski, and C. Melius, J. Phys. Chem. **90,** 691 (1986).
[10] G. Schatz, S. Walch, and A. Wagner, J. Phys. Chem. **73,** 4536 (1980).
[11] J. A. Logan, M. J. Prather, S. C. Wofsy, and M. B. McElroy, J. Geophys. Res. **86,** 7210 (1981).
[12] C. M. Stevens, L. Krout, D. Walling, A. Venters, A. Engelkemeir, and L. E. Ross, Earth Planet. Sci. Lett. **16,** 147 (1972).
[13] M. A. K. Khalil and R. Rasmussen, Science **224,** 54 (1984).
[14] M. A. K. Khalil and R. Rasmussen, Nature, London **332,** 242 (1988).
[15] W. Seiler and J. Fishman, J. Geophys. Res. **86,** 7255 (1981).
[16] P. Fabian, R. Borchers, G. Flantje, W. A. Matthews, W. Seiler, H. Giehl, K. Bunse, F. Muller, U. Schmidt, A. Volz, A. Khedim, and F. J. Johnen, J. Geophys. Res. **86,** 5179 (1981).
[17] H. Levy, Photochem. **9,** 369 (1974).

[18] P. R. Zimmerman, R. B. Chatfield, J. Fishman, P. J. Crutzen, and P. L. Hanst, Geophys. Res. Lett. **5,** 679 (1978).

[19] C. M. Stevens, A. Engelkemeir, and R. A. Rasmussen, WMO Technical Conference on Observations and Measurements of Atmospheric Contaminants, Spec. Environ. Rep. 16, WMO 647, World Meterol. Organ., Geneva, Switzerland 1985, p. 237.

[20] C. M. Stevens and A. Engelkemeir, J. Geophys. Res. **93,** 725 (1988).

[21] W. Seiler, Tellus **26,** 116 (1974).

[22] A. Volz, D. H. Ehhalt, and R. G. Derwent, J. Geophys. Res. **86,** 5163 (1981).

[23] D. Ehhalt and A. Schmidt, Pure Appl. Geophys. **116,** 452 (1978).

[24] H. Craig, C. C. Chou, J. A. Welhan, C. M. Stevens, and A. Engelkemeir, Science **242,** 1535 (1988).

[25] H. Craig and C. C. Chou, Geophys. Res. Lett. **99,** 1221 (1982).

[26] R. A. Rasmussen and M. A. K. Khalil, J. Geophys. Res. **89,** 11599 (1984).

[27] B. Stauffer, G. Fischer, A. Neftel, and H. Oeschger, Science **229,** 1386 (1985).

[28] M. Wahlen, N. Tanaka, R. Henry, T. Yoshimori, R. G. Fairbanks, A. Sheruesh, and W. S. Broecker, EOS **68,** 1220 (1987).

[29] E. W. Mayer, D. R. Blake, S. C. Tyler, Y. Makide, D. C. Montague, and F. W. Rowland, Proc. Natl. Acad. Sci. **79,** 1366 (1982).

[30] M. A. K. Khalil and R. A. Rasmussen, J. Geophys. Res. **88,** 5131 (1983).