The global balance of carbon monoxide

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ABSTRACT

Radioactive carbon-14 monoxide produced by cosmic ray neutrons provides a useful tracer to deduce the residence time of carbon monoxide in the troposphere. From the steady-state equations for stable carbon monoxide and radioactive carbon monoxide, the production rate of stable carbon monoxide can also be derived. This rate is an order of magnitude greater than that estimated for CO sources such as the oceans, combustion, and chlorophyll decay. The oxidation of tropospheric methane initiated by hydroxyl radicals has been postulated to account for this predominant source of CO in nature. Estimates of the steady-state hydroxyl radical concentration in the troposphere are of sufficient magnitude to support this possibility. Furthermore, the hydroxyl radical can also provide the major removal mechanism for carbon monoxide by oxidation to CO_2 to maintain the carbon monoxide balance in nature. A critical review of the above theories is given, and some possibilities for experimental verification are discussed. The earlier computations are modified to refer to the northern troposphere in view of differences recently found for CO concentrations in the northern and southern troposphere. Observations of the stable isotope composition of methane, $^{12}CH_4$ and $^{13}CH_4$, and of carbon monoxide, $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$ are also of significance to the proposed theory for the carbon monoxide balance. These data will be reviewed and discussed in terms of kinetic isotope effects in the reaction sequence, CH_4 to CO to CO_2. The results of this analysis of the stable CO isotope data will be shown to be consistent with the conclusions drawn from the analysis of the radiocarbon data.

Introduction

Previously, Weinstock (1969) proposed that a residence time for CO in the troposphere could be deduced from radiocarbon data because the "hot" ^{14}C nuclei produced by the ^{14}N (np) reaction of cosmic-ray neutrons are first fixed chiefly as ^{14}CO before being converted into $^{14}CO_2$. A residence time of 0.1 year for ^{14}CO in the troposphere was then derived from measurements of the concentration of ^{14}CO in the troposphere and an estimate of its rate of formation. In order to account for this residence time, which was much shorter than the 2.7 year value that had been previously believed, Weinstock (1969) suggested the oxidation of CO by OH as a possible mechanism for the major removal of CO from the troposphere. For this to be correct a mechanism to maintain OH in sufficient concentration would be required. Levy (1971) proposed a photochemical steady-state model that yielded an average daytime OH concentration of 1.2×10^6 molecule cm^{-3}, which is the required order of magnitude, and predicts a residence time for CO with respect to OH of 0.2 year. McConnell et al. (1971) from similar considerations derived a residence time for CO of 0.3 year and also suggested that oxidation of methane by OH in the troposphere would result in an order of magnitude greater source of CO than that from combustion (Robinson & Robbins, 1969), the oceans (Swinnerton et al., 1970; Seiler & Junge, 1970), and chlorophyll (Crespi et al., 1972).

From the steady-state equations for both radioactive and stable CO in the troposphere Weinstock & Niki (1972) have derived a residence time for CO of 0.1 year and a natural production rate of CO of 5×10^{15} gram $year^{-1}$, which is 25 times greater than that produced by combustion. They derived an average OH concentration of 2.3×10^6 molecule cm^{-3} to account for the 0.1 year residence time and show this to be consistent with the large value of CO

production by methane oxidation. The residence time of methane derived from this value of OH is 1.5 year and the production rate of methane 2.3×10^{15} gram year^{-1} compared with the estimated value of 1.5×10^{15} gram year^{-1} from other considerations (Robinson & Robbins, 1969; Ehhalt, 1972).

Recently, Stevens et al. (1972) have reported extensive measurements of the concentration of CO in the troposphere, particularly in the northern hemisphere, and of the stable carbon and oxygen isotope composition of these samples. Their data are consistent with the above considerations and provide an independent confirmation of the existence of a predominant natural source of carbon monoxide.

Recent measurements by Seiler (1974) and by Lamontagne et al., (1974) show that the CO mixing ratios in the southern hemisphere are significantly lower than those in the northern hemisphere. Since, at this time, ^{14}CO measurements are only available for the northern hemisphere, the steady-state calculations for radioactive and stable CO will be revised in this paper to include only the northern hemisphere instead of assuming that they are applicable to the entire troposphere. This restriction is appropriate in any case because the residence time deduced for CO is less than the exchange time between the two hemispheres.

The data of Stevens et al. will also be examined with respect to the steady-state model and will be used to derive kinetic isotope effects for the proposed CH_4–CO–CO_2 reaction sequence. Some critical experiments will be proposed to improve our quantitative understanding of the CO balance.

The steady-state model

Weinstock & Niki (1972) expressed the balance of CO in the troposphere by two steady-state equations,[1] one for stable CO and the other for radioactive ^{14}CO:

$$d(\mathrm{CO})/dt = P_1 + P_2 - k(\mathrm{CO}) \tag{1}$$

$$d(^{14}\mathrm{CO})/dt = NP_1 + P_3 - k(^{14}\mathrm{CO}) \tag{2}$$

In these equations, $d(\mathrm{CO})/dt$ and $d(^{14}\mathrm{CO})/dt$ were the rate of change with time of the total number of moles of stable CO and of radioactive ^{14}CO in the troposphere, respectively. The term P_1 was the sum of the production rates of CO from all processes that produce CO from "living" carbon, i.e. carbon in equilibrium with ^{14}C in nature. The term P_2 was the sum of the production rates of CO from all processes that produce CO from fossil carbon, i.e. carbon containing a negligible amount of ^{14}C. The term P_3 was the production rate of ^{14}CO in the troposphere by cosmic-ray neutrons. The term NP_1 was the production rate of ^{14}CO from "living" carbon, N being the mole fraction of ^{14}C in "living" carbon. The terms (CO) and (^{14}CO) were the total amount of stable CO and of radioactive ^{14}CO in the troposphere, respectively. The term k was a rate constant for the removal of CO, which was assumed to be the same for stable CO and for ^{14}CO in this approximation.

In the steady state, eqs. (1) and (2) are equal to zero and can be solved for the two unknown quantities, P_1 and k. The solutions are:

$$P_1 = \frac{P_3 - P_2(^{14}\mathrm{CO})/(\mathrm{CO})}{(^{14}\mathrm{CO})/(\mathrm{CO}) - N} \tag{3}$$

$$k = \frac{P_3 - P_2 N}{(^{14}\mathrm{CO})/(\mathrm{CO}) - N} \frac{1}{(\mathrm{CO})} \tag{4}$$

If the northern hemisphere is considered alone rather than the entire troposphere as assumed by Weinstock & Niki, then the values of P_3, (^{14}CO), and (CO) used by them will have to be divided by two. In addition, in view of the recent data of Seiler (1974) the value of (CO) will have to be changed to reflect an average mixing ratio of 0.14 ppm rather than that of 0.12 used previously. Further, a revised estimate of P_2 by Jaffe (1972) of 1.5×10^{13} mole year^{-1} should be used of which some 90% or 1.4×10^{13} can be assigned to the northern hemisphere. The revised values for the northern hemisphere are then:

$$P_3 = 145 \text{ mole year}^{-1}$$

$$P_2 = 1.4 \times 10^{13} \text{ mole year}^{-1}$$

$$(^{14}\mathrm{CO}) = 22.5 \text{ mole}$$

$$(\mathrm{CO}) = 1.0 \times 10^{13} \text{ mole}$$

$$N = 1.17 \times 10^{-12}$$

[1] In Ref. 8, there is a misprint; eq. (2) should read $d(^{14}\mathrm{CO})/dt = NP_1 + P_3 - k(^{14}\mathrm{CO}) = 0$.

Using these values, P_1 for the northern hemisphere is 1.0×10^{14} mole year^{-1} and k is 12 year^{-1}. These values are consistent with the previous values of Weinstock & Niki, and the uncertainty of about 50% assigned by them would still be applicable.

We would now like to discuss the uncertainty of these values in more detail and suggest an experimental plan that could improve their reliability. In the numerator of both eqs. (3) and (4), the term P_3 is much greater than the negative terms so that the uncertainty in P_2 is not important. The value of P_3 used was taken from Lal & Peters (1962) and was based on Lingenfelter's (1963) calculations of the rate of production of ^{14}C by cosmic-ray neutrons as a function of altitude, latitude, and time and on the average height of the tropopause as 11 km. Junge et al. (1971) have independently reported a calculation for P_3 in agreement with these authors. The assumption was made that all of the ^{14}C produced would first be fixed as ^{14}CO based on Pandow et al.'s work (1960). This may result in an overestimate for P_3 if not all of the ^{14}C is first fixed as ^{14}CO (Ache & Wolf, 1968). On the other hand, it was also assumed that none of ^{14}CO produced in the stratosphere would enter the troposphere as ^{14}CO. Junge et al. (1971) have analyzed this problem and conclude that there may be a net flux of ^{14}CO from the stratosphere into the troposphere. The uncertainties arising from these two assumptions would then be, in part, offsetting.

The value of (^{14}CO) was derived from three measurements of MacKay et al. (1963). Their three samples had an average deviation in specific activity of 23 percent and were contaminated with fossil-fuel-produced CO, the average CO concentration being 0.3 ppm. In using the value of (^{14}CO) derived from these measurements, the assumption is made that the concentration of ^{14}CO in the northern troposphere is uniform. This assumption implies that the vertical and lateral mixing of ^{14}CO in the northern troposphere is rapid compared with its residence time. The value of N used was 1.17×10^{-12} and assumed to be the same as that of "living carbon".

The 23% average deviation of the specific activity of MacKay et al. can in part be the result of counting statistics, sample weight uncertainty, and different degree of contamination by fossil-fuel-produced CO. The latter contamination is not of significance provided the concentration of CO is known, because one can then calculate the absolute ^{14}CO concentration from the average specific activity and the average CO concentration. This is the procedure that was followed.

It is clear that further measurements of the specific activity of CO in the troposphere are desirable. The actual samples of MacKay et al. had an average ^{14}CO mole fraction of 1.06×10^{-12}, which was lower than that of "living" carbon because of the contamination. However, upon correcting for the contamination their result suggests that the mole fraction of ^{14}CO in remote areas would be 2.25×10^{-12}, which is the value used for (^{14}CO)/(CO) in eqs. (3) and (4). It would appear that the most desirable additional experiments would be a collection of global samples in remote areas from which (^{14}CO)/(CO) can be obtained without correction for contamination. The absolute concentration of CO would not be required to obtain P_1, but would be needed to calculate k. Of particular interest would be a comparison of the ^{14}CO content of samples collected in the northern hemisphere with those from the southern hemisphere.

The hydroxyl radical cycle

In Weinstock's earlier report (1969) the oxidation of CO by OH was suggested as a possible mechanism for the major removal of CO from the troposphere. Subsequently, Levy (1971) and McConnell et al. (1971) proposed a CH_4–CO–CO_2 reaction mechanism that could provide the major mode of both production and removal of CO in the troposphere:

$$CH_4 + OH \xrightarrow{k_1} CH_3 + H_2O \qquad \text{(R 1)}$$

$$CH_3 + O_2 \xrightarrow{k_2} CH_3O_2 \qquad \text{(R 2)}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad \text{(R 3)}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \qquad \text{(R 4)}$$

$$CH_2O \begin{cases} + OH \rightarrow HCO + H_2O \\ + h\nu \rightarrow H_2 + CO \\ + h\nu \rightarrow HCO + H \end{cases} \qquad \text{(R 5)}$$

$$HCO + O_2 \rightarrow CO + HO_2 \qquad \text{(R 6)}$$

$$CO + OH \xrightarrow{k_7} CO_2 + H \qquad \text{(R 7)}$$

If eq. (R7) is the major removal process for CO, then the rate constant k in eqs. (1) and (2) is:

$$k = k_7(\mathrm{OH}) \tag{5}$$

If we take k to be 12 year^{-1} or 3.8×10^{-7} sec^{-1} and k_7 (Stuhl & Niki, 1972) to be 1.35×10^{-13} cm^3 molecule^{-1} sec^{-1}, the average OH concentration required to maintain CO in steady state in the northern troposphere is 2.8×10^6 molecule cm^{-3}. Levy (1971) and McConnell et al. (1971) obtained $1\text{–}3 \times 10^6$ molecule cm^{-3} for $(\mathrm{OH})_{\mathrm{av}}$ from their photochemical steady-state model, in reasonable agreement with the above value.

Two other mechanisms for the sink of CO from the troposphere have been investigated. One is transport into the stratosphere where CO would be rapidly converted to CO_2, and the other is consumption of CO by living organisms. Pressman & Warneck (1970) and Junge et al. (1971) have analyzed the stratospheric sink, and the latter authors estimate a residence time of 2.7 years for CO in the troposphere for that process. Inman et al. (1971) and more recently Ingersoll (1972) have reported studies of CO removal rates by biological action in a variety of soils. They estimate that soil could provide a significant sink for CO. However, their estimate is very uncertain because the CO removal rate is strongly concentration dependent and their studies were conducted at 100 ppm compared with the global average concentration of 0.1 ppm. To the extent that the stratosphere and soil provide sinks for CO in addition to the OH radical sink, the concentration of OH that was derived to account for P_1 would have to be reduced. Our present assessment is that the correction might be of the order of 10%. In addition, a flow of CO from the northern troposphere into the southern troposphere would be expected, which, in effect, would act as another minor sink for the northern troposphere.

McConnell et al. (1971) estimated the production rate of CO to be 9.9×10^{13} mole year^{-1} from the oxidation of CH_4 by OH, eq. (R1), and subsequent conversion of CH_3 to CO. Since they assumed the northern and southern tropospheres to be symmetrical, their estimate for the northern troposphere would be 5×10^{13} mole year^{-1}. Using the value of 2.5×10^6 molecule cm^{-3} for OH, a CH_4 mixing ratio of 1.4 ppm (Ehhalt, 1972), and the rate constant for eq. (R1) of 9.2×10^{-15} cm^3 molecule^{-1} sec^{-1} (Greiner, 1970), the production rate of CO by methane oxidation derived here would be 7.2×10^{13} mole year^{-1} for the northern hemisphere. These values are in reasonable agreement with P_1 equal to 1.0×10^{14} mole year^{-1} derived from the steady-state model.

Other natural sources for the production of CO are known. The most significant ones reported to date are the oceans (Swinnerton et al., 1970; Seiler & Junge, 1970) and degradation of chlorophyll (Crespi et al., 1972). Swinnerton and his co-workers (1970) estimate that the amount of CO produced in the oceans is 5% of that produced by combustion, whereas Junge et al. (1971) estimate it to be 29%. The production rate from degradation of chlorophyll appears to be an order of magnitude smaller than that of CH_4 oxidation (Stevens et al., 1972). (See also next section.) If these other sources of CO from "living" carbon are added to that estimated from methane oxidation, the agreement with P_1 would be improved, perhaps by 10%.

From the above considerations, it would appear that the balance of CO in the troposphere is largely controlled by hydroxyl radicals. Direct measurements of the OH concentration in the troposphere would provide a critical test of this hypothesis. Attempts to do this are presently under way (Baardsen & Terhune, 1972), and hopefully a definitive answer to this intriguing question will be forthcoming in the not too distant future.

Stable isotope composition of carbon monoxide

Stevens et al. (1972) have reported extensive measurements of the ^{13}C and ^{18}O concentration of atmospheric CO as a function of concentration and of season in nonurban areas. From an analysis of their data, they conclude that there may be five different isotopic varieties of CO, the relative amounts of which depend on the season and latitude. Two of these species are characterized by a low ^{18}O content, $\delta(^{18}O/^{16}O) = 5‰$, compared to engine CO, $\delta = 24.6‰$, and atmospheric oxygen, $\delta = 23.5‰$.[1] The two species had a small difference in ^{13}C content, but

[1] The δ values are the difference (‰) from the isotopic composition of a standard.

this was not judged as an indication of a different source. Taken together, they estimated by the isotope dilution method that the production rate of the light oxygen varieties was greater than 1×10^{14} mole/year. This result, which should apply to the northern hemisphere, is in remarkable agreement with the value of P_1 deduced from the radiocarbon data and the production rate of CO predicted from OH oxidation of methane. The work of Stevens et al. can thus be taken as direct experimental verification of the OH hypothesis. The three other species reported by Stevens et al. were of lesser estimated production rate and need not be considered in detail.

The $^{13}C/^{12}C$ kinetic isotope effect

In this section, measured atmospheric isotope data will be used to derive kinetic isotope effects for the CH_4–CO–CO_2 reaction sequence. Ehhalt (1972) noticed that the presumably largest sources of CH_4, paddy fields and marshes, emit CH_4 which has an average ^{13}C content of $\delta(^{13}C/^{12}C) = -65‰$ (Ehhalt, 1972). This is much lighter than the average for atmospheric CH_4, $\delta(^{13}C/^{12}C) = -41‰$ (Ehhalt, 1972). The average ^{13}C content of atmospheric CO is about $\delta(^{13}C/^{12}C) = -27‰$ (Stevens et al., 1972). Ehhalt speculated that these differences could be due to isotope fractionation effects, since the collision frequency and the kinetic effects would favor the reaction of the lighter molecules, $^{12}CH_4$ and ^{12}CO.

If the oxidation of atmospheric CH_4 by OH is the major source of CO and also the major sink of CH_4 in the northern troposphere, the above ^{13}C data may be used to estimate isotope fractionation effects for $^{13}C/^{12}C$. Noting that the removal of CH_4 is determined by eq. (R1), the balance of $^{12}CH_4$ and $^{13}CH_4$ in the northern troposphere can be expressed in terms of two steady-state equations:

$$d(^{12}CH_4)/dt = PN_{12} - {}^{12}k_p(^{12}CH_4) = 0 \qquad (6)$$

$$d(^{13}CH_4)/dt = PN_{13} - {}^{13}k_p(^{13}CH_4) = 0 \qquad (7)$$

where P is the production rate of CH_4 and N_{12} and N_{13} are the mole fractions of $^{12}CH_4$ and $^{13}CH_4$ in this CH_4; $(^{12}CH_4)$ and $(^{13}CH_4)$ are the total amounts of $^{12}CH_4$ and $^{13}CH_4$ in the northern troposphere; $^{12}k_p$ and $^{13}k_p$ are first-order rate constants for the removal of $^{12}CH_4$ and $^{13}CH_4$. Then,

$$^{12}k_p = {}^{12}k_1(OH) \quad \text{and} \quad {}^{13}k_p = {}^{13}k_1(OH) \qquad (8)$$

with $^{12}k_1$ and $^{13}k_1$ the rate constants for eq. (R1) written for $^{12}CH_4$ and $^{13}CH_4$ separately, and (OH) is the concentration of OH in the northern troposphere. If the ^{13}C content, $-65‰$, of paddy fields and marshes is representative of all CH_4 sources, then from eqs. (6) and (7), and the above data:

$$\frac{^{12}k_p}{^{13}k_p} = \frac{(^{13}CH_4)/(^{12}CH_4)}{N_{13}/N_{12}} = \frac{1-0.041}{1-0.065} = 1.026 = \frac{^{12}k_1}{^{13}k_1} \qquad (9)$$

In this discussion, we are assuming that, once the CH_3 radical is formed by eq. (R1), it will be quantitatively converted into CO by subsequent reactions. Therefor the value of 1.026 is the kinetic isotope effect for eq. (R1). The most stable intermediate in the reaction sequence is CH_2O, which appears to have a half-life of 75 minutes due to photodissociation, eq. (R5), in the sunlight-irradiated lower atmosphere (Calvert et al., 1972).

The steady-state equations for the balance of ^{12}CO and ^{13}CO in the northern troposphere may be approximated as:

$$d(^{12}CO)/dt = {}^{12}k_p(^{12}CH_4) - {}^{12}k_R(^{12}CO) = 0 \qquad (10)$$

$$d(^{13}CO)/dt = {}^{13}k_p(^{13}CH_4) - {}^{13}k_R(^{13}CO) = 0 \qquad (11)$$

Here (^{12}CO) and (^{13}CO) are the total amount of ^{12}CO and ^{13}CO in the northern troposphere. The $^{12}k_p$ and $^{13}k_p$ are given by eq. (8), and $^{12}k_R$ and $^{13}k_R$ are related to

$$^{12}k_R = {}^{12}k_7(OH); \quad {}^{13}k_R = {}^{13}k_7(OH) \qquad (12)$$

where $^{12}k_7$ and $^{13}k_7$ are the rate constants for eq. (R7), written for ^{12}CO and ^{13}CO separately. Eqs. (10) and (11), and the above data, give the relation:

$$\frac{^{12}k_p/^{13}k_p}{^{12}k_R/^{13}k_R} = \frac{(^{13}CH_4)/(^{12}CH_4)}{(^{13}CO)/(^{12}CO)} = \frac{1-0.041}{1-0.027} = 0.986 \qquad (13)$$

From eqs. (9) and (13)

$$^{12}k_R/^{13}k_R = 1.041 = {}^{12}k_7/^{13}k_7 \qquad (14)$$

For reactions of the type of eq. (R7) and eq.

(R 1), the maximum possible kinetic isotope effect has been estimated to be 1.25 (Biegeleisen & Wolfsberg, 1958). Thus, the kinetic carbon isotope effects deduced from the atmospheric isotopic data and the OH mechanism are qualitatively consistent and of reasonable magnitude. If these kinetic isotope effects could be obtained experimentally, they too could provide a critical test for the OH model.

The $^{18}O/^{16}O$ kinetic isotope effect

Stevens et al. (1972) suggested that the oxygen isotope fractionation effect for CO is not significant because the ratio of $^{18}O/^{16}O$ decreases as the mixing ratio of atmospheric CO decreases. This observed decrease in ^{18}O content with decreased CO mixing ratio is consistent with their observations of several varieties of CO being produced with different ^{18}O contents, but has no particular significance to the isotope fractionation question. Presumably, the light ^{18}O variety of CO is produced by methane oxidation more or less uniformly in the northern troposphere and is the predominant species globally. Near the surface, this may be mixed with CO with a greater ^{18}O content from all other sources. Thus, high ^{18}O contents correlate with high mixing ratios because of this contamination. As the mixing ratio falls, indicating less contamination, the ^{18}O content will fall and approach that of the light variety. The kinetic isotope effect is not influenced by this behavior but will instead result from the formation of the light species, $\delta(^{18}O/^{16}O) = 5‰$, from atmospheric oxygen with $\delta(^{18}O/^{16}O) = 23.5‰$ (Kroopnick & Craig, 1972).

To derive the $^{18}O/^{16}O$ kinetic isotope effect, we again assume that the CH_3 radical formed by eq. (R 1) is quantitatively converted to CO and also that the oxygen atom bonded to the carbon atom in CH_3O_2 by eq. (R 2) remains fixed in the subsequent reactions and appears in the product CO. Then, the $^{18}O/^{16}O$ fractionation effect is determined by:

$$CH_3 + {}^{18}O{}^{16}O \xrightarrow{{}^{18}k_2} H_3C{}^{18}O{}^{16}O \quad \text{or} \quad H_3C{}^{16}O{}^{18}O \qquad \text{(R 2 a)}$$

$$CH_3 + {}^{16}O{}^{16}O \xrightarrow{{}^{16}k_2} H_3C{}^{16}O{}^{16}O \qquad \text{(R 2 b)}$$

The steady-state equations for the balance of $C^{16}O$ and $C^{18}O$ in the northern troposphere are:

$$d(C^{16}O)/dt = {}^{16}k_p({}^{16}O{}^{16}O) - {}^{16}k_R(C^{16}O) = 0 \qquad (15)$$

$$d(C^{18}O)/dt = \tfrac{1}{2}{}^{18}k_p({}^{18}O{}^{16}O) - {}^{18}k_R(C^{18}O) = 0 \qquad (16)$$

where $({}^{16}O{}^{16}O)$, $({}^{18}O{}^{16}O)$, $(C^{16}O)$, and $(C^{18}O)$ are the total amount of $^{16}O^{16}O$, $^{18}O^{16}O$, $C^{16}O$, and $C^{18}O$ in the northern troposphere. The ${}^{16}k_p$ and ${}^{18}k_p$ are related to:

$${}^{16}k_p = {}^{16}k_2(CH_3); \quad {}^{18}k_p = {}^{18}k_2(CH_3) \qquad (17)$$

(CH_3) being the concentration of CH_3 in the northern troposphere. The ${}^{16}k_p$ and ${}^{18}k_R$ are related to

$${}^{16}k_R = {}^{16}k_7(OH); \quad {}^{18}k_R = {}^{18}k_7(OH) \qquad (18)$$

The ${}^{16}k_7$ and ${}^{18}k_7$ are the rate constants for eq. (R 7) involving $C^{16}O$ and $C^{18}O$. Since $({}^{16}O) = 2({}^{16}O{}^{16}O)$ and $({}^{18}O) = ({}^{18}O{}^{16}O)$, use of eqs. (15) and (16), and the values of $\delta(^{18}O/^{16}O)$ for atmospheric O_2 and the light CO species of Stevens et al. (1972) give

$$\frac{{}^{16}k_p/{}^{18}k_p}{{}^{16}k_R/{}^{18}k_R} = \frac{({}^{18}O)/({}^{16}O)}{(C^{18}O)/(C^{16}O)} = \frac{1+0.024}{1+0.005} = 1.019 \qquad (19)$$

Since ${}^{16}k_R/{}^{18}k_R \geqslant 1$ for a normal isotope effect, then

$${}^{16}k_p/{}^{18}k_p \geqslant 1.019 \qquad (20)$$

This result is not so definitive as that from consideration of the carbon isotope effects, because we do not have separate data from which to derive the production and removal fractionations. The maximum possible oxygen isotope effect has been estimated to be 1.19 (Biegeleisen & Wolfsberg, 1958), which is not inconsistent with these conclusions. Again, if the kinetic oxygen isotope effects for CO formation and CO removal can be determined experimentally, this would afford a direct verification of the proposed model.

Influence of kinetic isotope effect to the steady-state calculation

The isotopic fractionation effects can be incorporated in the steady-state calculation by modifying eq. (2),

$$d({}^{14}CO)/dt = \alpha_p \bar{N} P_1 + P_3 - \alpha_R k({}^{14}CO) \qquad (21)$$

where α_p and α_R are given by ${}^{14}k_p/{}^{12}k_p$ and ${}^{14}k_R/{}^{12}k_R$ (the definition of k_p and k_R have been given previously). Then eqs. (1) and (21) give

$$P_1 = \frac{P_3 - \alpha_R P_2({}^{14}\mathrm{CO})/(\mathrm{CO})}{\alpha_R({}^{14}\mathrm{CO})/(\mathrm{CO}) - \alpha_p N} \tag{22}$$

$$k = \frac{P_3 - \alpha_p P_2 N}{\alpha_R({}^{14}\mathrm{CO})/(\mathrm{CO}) - \alpha_p N} \frac{1}{(\mathrm{CO})} \tag{23}$$

The kinetic isotope effect for ${}^{12}C/{}^{14}C$ can be taken to be twice that for ${}^{12}C/{}^{13}C$ (Biegeleisen & Wolfsberg, 1958; Stern & Vogel, 1971), so that from eqs. (9) and (14),

$$\alpha_p = 0.951 \quad \text{and} \quad \alpha_R = 0.924$$

The modified values of P_1 and k are then 1.2×10^{14} mole year^{-1} and 13 year^{-1}, respectively. Thus, inclusion of the kinetic isotope effect increases the value of the natural production rate of CO, P_1, and the removal rate constant, k. The latter would decrease the residence time, but neither effect is significant within the uncertainty of the present results.

Summary

It appears likely that the residence time of CO in the northern troposphere is largely controlled by hydroxyl radicals, first in producing CO by methane oxidation and then in removing CO by conversion to CO_2. This possibility was first brought forth from ${}^{14}CO$ considerations (Weinstock, 1969), which predicted a short CO residence time and were later revised to include ${}^{14}CO$ production from ${}^{14}CH_4$ (Weinstock & Niki, 1972). Independently, photochemical models of the troposphere (Levy, 1971; McConnell et al., 1971) predicted OH concentrations of sufficient magnitude to maintain the CO balance and first suggested that the oxidation of methane provided the major source of CO (McConnell et al., 1971). Another independent verification of this picture has been provided from stable isotope measurements of atmospheric CO (Stevens et al., 1972), which study has provided the first experimental verification of this model. Consideration of kinetic isotope effects also appears to be consistent with this model.

A number of experiments could provide a better quantitative understanding of the CO balance based on this model. The most critical would be direct measurements of the OH concentration in the troposphere. In addition, further ${}^{14}CO$ measurements, particularly in remote areas, would be useful as well as a direct determination of the kinetic isotope effects.

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ГЛОБАЛЬНЫЙ БАЛАНС ОКИСИ УГЛЕРОДА

Радиоактивная окись углерода-14, производимая нейтронами космических лучей является полезным трассером для получения времени пребывания окиси углерода в тропосфере. Из уравнений равновесия для устойчивой окиси углерода и радиоактивной окиси углерода можно вывести скорость образования устойчивой окиси углерода. Эта скорость на порядок больше, чем это оценивалось из таких источников CO, как океаны, горение, распад хлорофилла. Для учета этого доминирующего источника CO в природе было постулировано окисление тропосферного метана, инициируемое гидроксильными радикалами. Оценки равновесной концентрации радикалов гидроксила в тропосфере оказываются достаточными по величине, чтобы обеспечить эти процессы. Более того, радикалы гидроксила могут также обеспечить основной механизм вывода окиси углерода из атмосферы путем окисления ее до CO_2, чтобы поддержать баланс окиси углерода в природе. Дается критический обзор этих теорий и обсуждаются некоторые экспериментальные возможности для их проверки. Более ранние расчеты модифицируются, чтобы учесть особенности тропосферы северного полушария в свете недавно найденных различий в концентрациях CO в тропосфере северного и южного полушарий. Наблюдения устойчивых изотопных составляющих метана: $^{12}CH_4$ и $^{13}CH_4$ и окиси углерода: $^{12}C^{16}O$, $^{13}C^{16}O$ и $^{12}C^{18}O$ также имеют значение для предлагаемой теории баланса окиси углерода. Эти данные обсуждаются в терминах кинетических изотопных эффектов в последовательности реакций от CH_4 до CO и CO_2. Результаты этого анализа данных по концентрации окиси устойчивых изотопов углерода согласуются с выводами, полученными из анализа радиоуглеродных данных.