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On the vertical distribution of carbon monoxide and methane

in the stratosphere

by M.NICOLET and W. PEETERMANS

FOREWORD

This paper has been presented at the "Symposium on sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment" August 14-17, 1972, St. Pete. Beach, Fla. and at the "Symposium on Atmospheric Ozone" August 21-26, 1972, Arosa (Switzerland). It will be published in PAGEOPH.

AVANT-PROPOS

Ce texte a été présenté au "Symposium on sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment" 14-17 août, 1972, St. Pete. Beach, Fla. et au "Symposium on Atmospheric Ozone" 21-26 août 1972 à Arosa (Suisse). Il sera publié dans PAGEOPH.

VOORWOORD

Deze tekst werd zowel voorgedragen tijdens het "Symposium on souces, sinks, and concentrations of carbon monoxide and methane in the earth's environment" 14-17 augustus, 1972, St. Pete. Beach, Fla. als het "Symposium on Atmospheric Ozone" 21-26 augustus, 1972 te Arosa (Switserland). Hij zal gepubliceerd worden in PAGEOPH.

VORWORT

Dieser Text wurde zum "Symposium on sources, sinks, and concentrations of carbon monoxide and methane in the earth's environment" 14-17 August, 1972, St. Pete. Beach, Fla. und zum "Symposium on Atmospheric Ozone" 21-26 August, 1972 Arosa (Schweiz) vorgestellt. Er wird in PAGEOPH herausgegeben werden.

ON THE VERTICAL DISTRIBUTION OF CARBON MONOXIDE AND METHANE IN

THE STRATOSPHERE

by

M. NICOLET and W. PEETERMANS

ABSTRACT

The vertical distribution of the methane concentration in the stratosphere is related to its dissociation by two simultaneous daytime reactions with excited oxygen atoms $O(^1D)$ and with OH radicals and depends on the stratospheric eddy diffusion coefficient.

Dissociation of CH_4 in the lower stratosphere leads to the production of CO molecules while in the upper stratosphere the photodissociation of CO_2 molecules is an additional process to the CO production.

In the upper stratosphere (40 ± 10 km) there is an equilibrium between the formation and destruction processes of carbon monoxide which leads to a minimum of its mixing ratio. There is an increase of the CO mixing ratio in the troposphere and mesosphere compared with that of the stratosphere.

The vertical distribution of the CO mixing ratio is closely related to the eddy diffusion coefficient in the whole stratosphere but the absolute values of the hydroxyl radical concentration also determine the values of the CO mixing ratio.

RESUME
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La distribution du méthane dans la stratosphère est liée à sa disso-
ciation par deux réactions diurnes : l'une avec les atomes d'oxygène excités
$O(^1D)$, l'autre avec le radical OH ; elle dépend aussi de la diffusion turbulente
stratosphérique.

Dans la stratosphère inférieure, la dissociation des molécules de CH_4
entraîne la production de CO alors que dans la stratosphère supérieure la photo-
dissociation des molécules de CO_2 introduit une production supplémentaire de
monoxyde de carbone.

Dans la stratosphère supérieure (40 ± 10 km) il y a un équilibre
entre les processus de formation et de destruction du monoxyde de carbone qui
conduit à un minimum de son rapport de mélange. Il y a un accroissement du
rapport de mélange de CO dans la troposphère et dans la mésosphère par rapport
à la stratosphère.

La distribution verticale du rapport de mélange de CO quoique inti-
mement liée à la diffusion turbulente est aussi déterminée par la concentration
de OH.

SAMENVATTING

De verdeling van het methaan in de stratosfeer is hoofdzakelijk het gevolg van zijn ontbinding in het zonnelicht die volgens twee reacties gebeurt : de eerste met aangeslagen zuurstofatomen $O(^1D)$; de tweede met de OH-stam. Zij hangt eveneens of van de turbulente diffusie in de stratosfeer.

In de onderste lagen van dit gebied gaat de ontbinding van de CH_4 molecule gepaard met de productie van CO, daar waar in de bovenste lagen de fotolyse van CO_2 moleculen een aanvullende bijdrage van CO vormt.

In de opperstratosfeer $(40 \pm 10$ km$)$ is er evenwicht tussen de vormings- en afbraakprocessen van het CO dat leidt tot een minimum in zijn mengverhouding. Ten opzichte van de stratosfeer is er een toename der mengverhouding vast te stellen in de troposfeer en in de mesosfeer.

Het vertical verloop van de mengverhouding van CO, alhoewel innig verbonden met de turbulente diffusie, is alzo bepaald door de OH concentratie.

ZUSAMMENFASSUNG

In der Stratosphäre ist die Verteilung des Methan gleichzeitig von der Dissoziation duch zwei tägliche Reaktionen mit angeragtem Sauerstoff $O(^1D)$ und mit OH, und von der stratosphärischen Eddy Diffusion abhängig.

In der niedrigen Stratosphäre führt die Dissoziation von CH_4 zu einer Produktion von CO, während in der höheren Stratosphäre, die Photodissoziation von CO_2 eine Zusatzproduktion von CO gibt.

In der höheren Stratosphäre besteht ein Equilibrium zwischen der Bilding und der Untergang von CO, das ein Minimum des Mischungsverhältnis gibt. In der Troposphäre und in der Mesosphäre ist das CO Mischungsverhältnis grösser als in der Stratosphäre.

Die senkrechte Verteilung des CO Mischungsverhältnis ist streng von Eddy Diffusionskoeffizienten in der Stratosphäre abhängig aber ist auch durch die OH Konzentration bestimmt.

INTRODUCTION

Twenty years ago Bates and Witherspoon (1952) showed that the oxidation of methane and carbon monoxide by collision processes is important in the terrestrial atmosphere. Methane is produced primarily by various bacterial decomposition processes leading to an average production (Robinson and Robbins, 1971) of 1.5×10^9 tons-year^{-1} or 3.4×10^{11} CH_4 molecules cm^{-2} sec^{-1}. Since the total number of CH_4 molecules is about 3.2×10^{19} cm^{-2} column, such a production corresponds to an estimated residence time of about 3 years (day and night).

If the various <u>daytime</u> destruction processes of CH_4 lead to the production of CO in the troposphere (McConnell, McElroy and Wofsy, 1971) they correspond, with an average fractional volume concentration of 0.1 ppmv (Robinson and Robbins, 1971), to an average residence time of 0.4 year for CO. The carbon monoxide molecules apparently cannot have a life time exceeding 0.1 year (Weinstock and Niki, 1972 ; Levy II, 1972). There are different ways to reduce the differences between the various results by increasing the methane production and by reducing the carbon monoxide destruction. However, it seems that a factor of two is still the possible error to be considered in the analysis of the atmospheric behavior of CH_4 and CO.

2. AERONOMIC REACTIONS OF METHANE

Methane, which is in mixing in the troposphere (Bainbridge and Heidt, 1966 ; Ehhalt, 1967), is photodissociated in the mesosphere and is dissociated by oxidation processes in the stratosphere (see Nicolet, 1971).

Atomic oxygen attacks methane through

$$(c_1) \quad ; \quad O(^3P) + CH_4 \rightarrow CH_3 + OH - 2 \text{ kcal}, \tag{1}$$
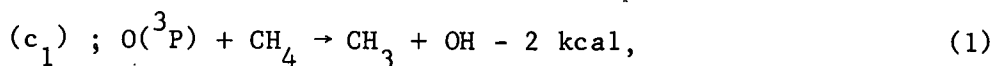
which is endothermic by about 2 kcal, and is a slow reaction. But the reaction of CH_4 with atomic oxygen in the electronically excited ^1D state is rapid :

$$(c_1^*) \; ; \; O(^1D) + CH_4 \rightarrow CH_3 + OH + 43.5 \; kcal \qquad (2)$$
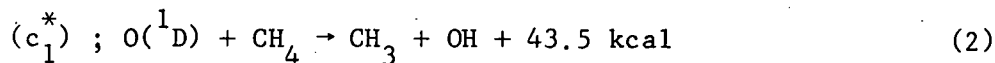
must have a rate coefficient $c_1^* = (3 \pm 1) \times 10^{-10} \; cm^3 \; sec^{-1}$ (Young et al, 1968 ; DeMore, 1969 ; Paraskevopoulos and Cvetanovic, 1969 ; Greenberg and Heicklen, 1972) ; more laboratory data are required in order to determine the exact value needed for aeronomic purposes.

The other important reaction in the stratosphere is

$$(c_2) \; ; \; OH + CH_4 \rightarrow CH_3 + H_2O + 15 \; kcal \qquad (3)$$
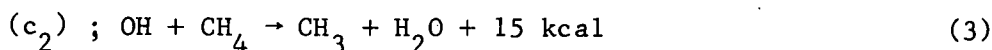
which has an activation energy less than 5 kcal (Wilson, 1970). Recent laboratory measurements by Greiner (1970) lead to

$$c_{2a} = 5.5 \times 10^{-12} \; e^{-1900/T} \; cm^3 \; sec^{-1} \qquad (4)$$

or

$$c_{2b} = 1.8 \times 10^{-13} \; T^{1/2} \; e^{-1740/T} \; cm^3 \; sec^{-1} \qquad (5)$$

while Wilson (1972) considers

$$c_{2c} = 4.8 \times 10^{-11} \; e^{-2500/T} \; cm^3 \; sec^{-1} \qquad (6)$$

All formulas lead to about $10^{-14} \; cm^3 \; sec^{-1}$ at $300°K$ but formula (6) gives the lowest values at stratospheric temperatures. The first formula will be tentatively adopted ; it corresponds approximatively to $5 \times 10^{-15} \; cm^3 \; sec^{-1}$ at the stratopause and reaches about $5 \times 10^{-16} \; cm^3 \; sec^{-1}$ as minimum value.

In the lower stratosphere CO_2 is photodissociated at a very low rate and the production of CO corresponds to the total oxidation process of CH_4 by reactions (3) and (2).

As it is well known (cf Pressman and Warneck, 1970) the oxidation of carbon monoxide is attributed to

$$(a_{36}) \; ; \; OH + CO \rightarrow CO_2 + H + 24 \text{ kcal} \tag{7}$$
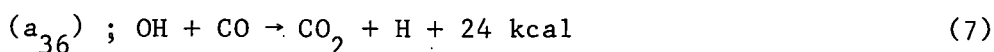
which has been observed between 300°K and 500°K (Greiner, 1969 ; Dryer, Naegeli and Glassman, 1971) with practically no activation energy. Thus, if we adopt

$$a_{36a} = (1.25 \pm 0.25) \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \tag{8}$$

we may consider that it corresponds to stratospheric conditions.

Evaluated rate data by Wilson (1972) and by Bauch et al (1968) lead to

$$a_{36b} = 5.1 \times 10^{-13} e^{-300/T} \text{ cm}^3 \text{ sec}^{-1} \tag{9}$$

and

$$a_{36c} = 9.3 \times 10^{-13} e^{-540/T} \text{ cm}^3 \text{ sec}^{-1}, \tag{10}$$

respectively. The last formula leads to smaller values than formules (8) and (9) at 200°K. In any case, precise values of the rate coefficient of reaction (7) are required between 200°K and 300°K for an exact aeronomic analysis of the stratosphere.

Methyl radicals, which are produced by oxidation processes of CH_4, react immediately with molecular oxygen to form methylperoxy radicals.

$$(c_{4a}) \quad CH_3 + O_2 + M \rightarrow CH_3O_2 + M + 26 \text{ kcal} \tag{11}$$
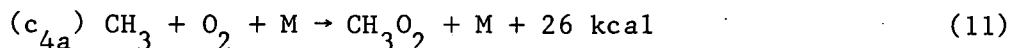
The rate coefficient, according to McMillan and Calvert (1965), would be of the order of $10^{-31} \text{ cm}^6 \text{ sec}^{-1}$ at room temperature. Recent measurements (Van den Bergh and Callear, 1971 and Basco et al, 1971) of the rate of the combination reaction of methyl radicals and molecular oxygen at 295°K lead at high pressure to the limiting values 2 x 10^{-12} and 5 x $10^{-13} \text{ cm}^3 \text{ sec}^{-1}$. Further laboratory work is needed since exact values of the concentration of methylperoxy radicals are required for a complete aeronomic analysis.

The reaction of CH_3 with atomic oxygen

$$(c_{4b}) \quad CH_3 + O \rightarrow H + H_2CO + 67 \text{ kcal} \tag{12}$$
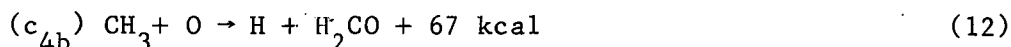
is negligible in the stratosphere compared with reaction (11).

Methylperoxy radicals react with oxides of nitrogen (Spicer et al, 1972) leading to

$$(c_{5a}) \quad CH_3O_2 + NO \rightarrow CH_3O_2NO \tag{13a}$$

or

$$(c_{5b}) \quad CH_3O_2 + NO \rightarrow H_2CO + HNO_2 \tag{13b}$$

as regards NO. The production of methylperoxynitrite would be about 1.5 times the simultaneous production of formaldehyde and nitrous acid. In the same way the reactions with NO_2 are

$$(c_{6a}) \quad CH_3O_2 + NO_2 \rightarrow CH_3O_2NO_2 \tag{14a}$$

$$(c_{6b}) \quad CH_3O_2 + NO_2 \rightarrow H_2CO + HNO_3 \tag{14b}$$
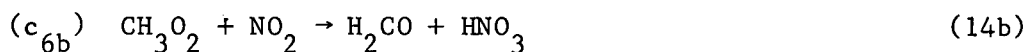
Here the production of formaldehyde and nitric acid would be about 3 times the production of methylperoxynitrate. According to Spicer et al (1972) there would be no evidence for the reaction between CH_3O_2 and NO producing $CH_3O + NO_2$ which is introduced by Levy (1972). Nevertheless, there is practically no difference when all aeronomic processes are considered.

The photochemistry of formaldehyde (McGuigg and Calvert, 1969) indicates that two distinct primary processes occur

$$(c_{7a}) \quad H_2CO + h\nu \rightarrow HCO + H \tag{15a}$$

$$(c_{7b}) \quad H_2CO + h\nu \rightarrow CO + H_2 \tag{15b}$$

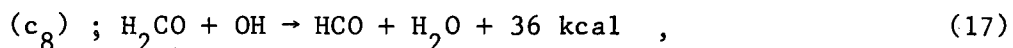which lead to the production of formyl and carbon monoxide with atomic and molecular hydrogen, respectively.

The photodissociation coefficients of H_2CO based on recently published cross sections (Calvert et al, 1972) are at zero optical depth

$$J_{H-HCO} = 9.4 \times 10^{-5} \ sec^{-1} \tag{16a}$$

and

$$J_{H_2-CO} = 1.3 \times 10^{-4} \ sec^{-1}. \tag{16b}$$

A rapid reaction such as

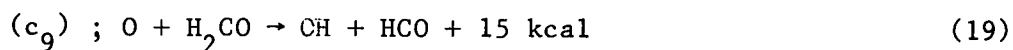$$(c_8) \quad ; \quad H_2CO + OH \rightarrow HCO + H_2O + 36 \ kcal \quad , \tag{17}$$

with a rate coefficient (Morris and Niki, 1971), at 300°K,

$$c_8 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}, \tag{18}$$

requires OH concentrations of the order of 10^7 cm^{-3} to compete with the direct photodissociation.
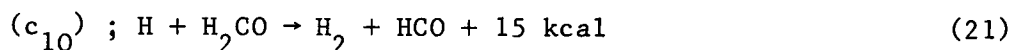
The reaction of atomic oxygen with formaldehyde leads also to HCO

$$(c_9) \; ; \; O + H_2CO \rightarrow OH + HCO + 15 \text{ kcal} \tag{19}$$

with a rate coefficient (Niki et al, 1968 ; Herron and Penzhorn, 1969), at 300°K,

$$c_9 = 1.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} . \tag{20}$$

The reaction of atomic hydrogen with formaldehyde is less rapid,

$$(c_{10}) \; ; \; H + H_2CO \rightarrow H_2 + HCO + 15 \text{ kcal} \tag{21}$$
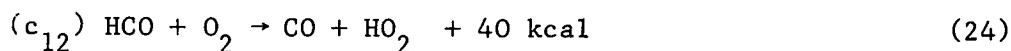
since its rate coefficient is only (Ridley et al, 1972) at 297°K

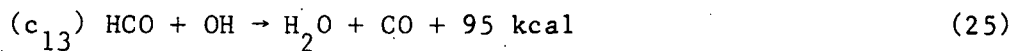$$c_{10} = (5.4 \pm 0.5) \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1} . \tag{22}$$

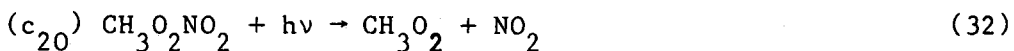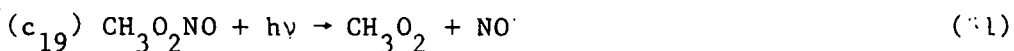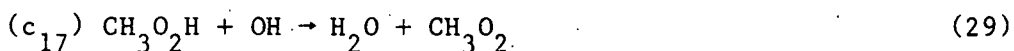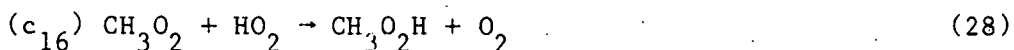The formyl radical is rapidly photodissociated (Johns et al, 1963)

$$(c_{11}) \; HCO + h\nu \rightarrow CO + H \tag{23}$$

or reacts with O_2 (McMillan and Calvert, 1965)

$$(c_{12}) \; HCO + O_2 \rightarrow CO + HO_2 + 40 \text{ kcal} \tag{24}$$

or reacts with OH (Morris and Niki, 1971)

$$(c_{13}) \quad HCO + OH \rightarrow H_2O + CO + 95 \text{ kcal} \qquad (25)$$

Even if the reaction between OH and HCO is rapid ($> 1.5 \times 10^{-11}$ $cm^3 \text{ sec}^{-1}$ according to Morris and Niki, 1971), reaction (24) should be very important in the atmosphere. Other reactions may be introduced (cf Levy, 1972) such as

$$(c_{14}) \quad CH_3O_2 + CH_3O_2 \rightarrow 2 \ CH_3O + O_2 \qquad (26)$$

$$(c_{15}) \quad CH_3O + O_2 \rightarrow HO_2 + H_2CO \qquad (27)$$

$$(c_{16}) \quad CH_3O_2 + HO_2 \rightarrow CH_3O_2H + O_2 \qquad (28)$$

$$(c_{17}) \quad CH_3O_2H + OH \rightarrow H_2O + CH_3O_2 \qquad (29)$$

$$(c_{18}) \quad CH_3O_2H + h\nu \rightarrow CH_3O + OH \qquad (30)$$

$$(c_{19}) \quad CH_3O_2NO + h\nu \rightarrow CH_3O_2 + NO \qquad (31)$$

$$(c_{20}) \quad CH_3O_2NO_2 + h\nu \rightarrow CH_3O_2 + NO_2 \qquad (32)$$
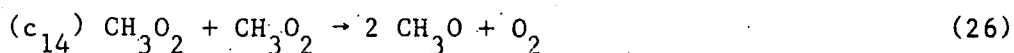
Thus, with equation (1) to (32), it is possible to write for equilibrium conditions that

$$n(H_2CO) \left[J_{H-HCO} + J_{H_2-CO} + c_8 \ n(OH) + c_9 \ n(O) + c_{10} \ n(H) \right]$$

$$= n(CH_4) \left[c_1 \ n(O) + c_1^* \ n(O*) + c_2 \ n(OH) \right]$$

$$= n(HCO) \left[J_{H-CO} + c_{12} \ n(O_2) + c_{13} \ n(OH) \right] + n(H_2CO) \ J_{H_2-CO} \qquad (33)$$

If we consider the various reactions involving the production and loss mechanisms of H, OH and HO_2, we may write

$$\frac{dn(H)}{dt} + \frac{dn(OH)}{dt} + \frac{dn(HO_2)}{dt} + \ldots$$

$$+ n(OH) \left[c_2 \, n(CH_4) + 2 \, c_{13} \, n(HCO) + 2 \, c_{17} \, n(CH_3 O_2 H) \right] = + \ldots +$$

$$n(CH_4) \left[c_1 \, n(O) + c_1^* \, n(O^*) \right] + 2 \, n(H_2CO) \left[J_{H-HCO} + c_9 \, n(O) \right]$$

$$+ n(CH_3O) \, c_{15} \, n(O_2). \tag{34}$$

The steady-state conditions with equations (33) lead to

$$\ldots + n(OH) \, c_2 \, n(CH_4) \left[1 - X \right] + 2 \, n(OH) \left[c_{13} \, n(HCO) + c_{17} \, n(CH_3O_2H) \right] = \ldots +$$

$$\ldots + n(CH_4) \left[c_1 \, n(O) + c_1^* \, n(O) \right] \left[1 + X \right] + n(CH_3O) \, c_{15} \, n(O_2)$$

with

$$X = \frac{2 \, J_{H-CO} + c_9 \, n(O)}{J_{H-HCO} + J_{H_2-CO} + c_8 \, n(OH) + c_9 \, n(O) + c_{10} \, n(H)} \tag{36}$$

The ratio $X \simeq 2 \, J_{H-HCO}/J_{H_2CO}$ varies from 0.8 at 50 km to 0.7 near 15 km and is about 0.55 at ground level.

3. RATIO OF HYDROXYL AND HYDROPEROXYL RADICALS CONCENTRATIONS

If equilibrium conditions are considered for H and HO_2, the following equation (see for example Nicolet, 1972) is obtained

$$n(HO_2) \left[a_7 \, n(O) + a_{17} \, n(OH) + 2 \, a_{27} \, n(HO_2) + a_{26} \, n(NO) + c_{16} \, n(CH_3O_2) \right]$$

$$\simeq n(OH) \left[a_5 \, n(O) + a_{19} \, n(H_2) + a_{30} \, n(H_2O_2) + a_{36} \, n(CO) + \right.$$

$$\left. c_8 \, n(H_2CO) + c_2 \, X \, n(CH_4) \right] \qquad (37)$$
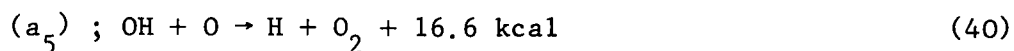
The ratio $n(HO_2)/n(OH)$ depends on reactions with atomic oxygen in the upper part of the stratosphere, i.e.

$$\frac{n(HO_2)}{n(OH)} = \frac{a_5}{a_7} \qquad (38)$$

and depends on reactions with NO and CO at the tropopause level, i.e.

$$\frac{n(HO_2)}{n(OH)} = \frac{a_{36} \, n(CO)}{a_{26} \, n(NO)} \qquad (39)$$

The process

$$(a_5) \; ; \; OH + O \rightarrow H + O_2 + 16.6 \text{ kcal} \qquad (40)$$
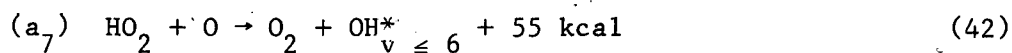
has a rate coefficient between 293°K and 300°K

$$a_5 = 3 \text{ to } 7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \qquad (41)$$

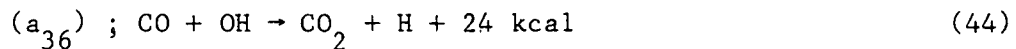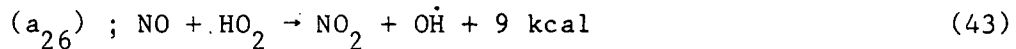according to laboratory measurement (Clyne and Thrush, 1963 ; Kaufman, 1964, 1969 ; Breen and Glass, 1970).

The other reaction

$$(a_7) \quad HO_2 + O \rightarrow O_2 + OH^*_{v \leq 6} + 55 \text{ kcal} \qquad (42)$$

has not been measured in the laboratory. Considering the work of Foner and Hudson (1962), Kaufman (1964) suggested that $a_7 \gtrsim 10^{-11}$ cm^3 sec^{-1}. The values of the rate coefficients a_5 and a_7, which are generally adopted leads to $a_5/a_7 = 5$. We consider here two ratios $a_5/a_7 = 9$ and 1 in order to indicate that the ratio is not known with sufficient precision.

In the lower stratosphere hydroxyl and hydroperoxyl radicals are involved in other important reactions with minor constituents which do not belong to the hydrogen-oxygen atmosphere ; CO and NO must be considered since they can react with OH and HO_2. Among all possible reactions (Nicolet, 1970, 1971, 1972 ; Levy 1970, 1972 ; McConnell et al, 1971) it seems that the following reactions are the most important processes at the tropopause,

$$(a_{26}) \; ; \; NO + HO_2 \rightarrow NO_2 + OH + 9 \text{ kcal} \tag{43}$$

$$(a_{36}) \; ; \; CO + OH \rightarrow CO_2 + H + 24 \text{ kcal} \tag{44}$$

The rate coefficient of reaction (44) is known with a certain approximation for stratospheric conditions (cf. equation 7 and 8)

$$a_{36} \simeq (1.25 \pm 0.25) \times 10^{-13} \text{ } cm^3 \text{ } sec^{-1} .$$

The rate coefficient of reaction (43) is not known with sufficient precision but according to unpublished data (Davis, 1972 ; see Levy, 1972),

$$a_{26} > 10^{-13} \text{ } cm^3 \text{ } sec^{-1} \tag{46}$$

at 300°K.

Precise experimental determination of the rate coefficients a_{26} and a_{36} are needed for an exact aeronomic analysis of the lower stratosphere. With fractional volume concentrations for CO and NO of the order of 4×10^{-8} and 4×10^{-9}, respectively, it is clear that

$n(HO_2)/n(OH) > 10$ if a_{26} has an activation energy. Neverthless, we adopt two ratios $n(HO_2)/n(OH) = 9$ and 1 keeping in mind that the ratio varies from the tropopause to the stratosphere and could be greater than 10 in the lower stratosphere. In any case, the ratio $n(HO_2)/n(OH)$ cannot be evaluated without an exact knowledge of the nitric oxide concentration in the lower stratosphere, since the reaction $CO + HO_2 \rightarrow CO_2 + OH$ is neglected. This reaction is very slow according to recent laboratory results (Simonaitis, Davis, private communications). See, however, Westenberg (1972).

4. CONCENTRATION OF HYDROXYL RADICALS

Since the reaction between CO and OH is a destruction process of carbon monoxide, it is important to determine the concentration of OH radicals.

For equilibrium conditions, neglecting the effects of H, OH, HCO and CH_3O_2 N)

$$n(OH) \left[a_{17}\, n(HO_2) + a_{30}\, n(H_2O_2) + c_2 \left\{ \frac{1-X}{2} \right\} n(CH_4) \right]$$

$$= \left[n(H_2O) + n(H_2) + n(CH_4) \left\{ \frac{1+X}{2} \right\} \right] a^*\, n(O^*) \qquad (47)$$

where X is given by (36).

An accurate evaluation (Hochanadel et al, 1972) of the rate coefficient of the reaction

$$OH + HO_2 \rightarrow H_2O + O_2 + 72 \text{ kcal} \qquad (48)$$

leads to

$$a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \qquad (49)$$

As far as the reaction with H_2O_2 is concerned

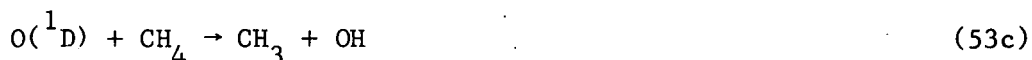$$OH + H_2O_2 \rightarrow H_2O + HO_2 + 30 \text{ kcal}, \tag{50}$$
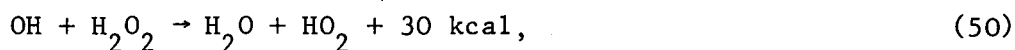
its rate coefficient (Greiner, 1968) is given by

$$a_{30} = 4 \times 10^{-13} T^{1/2} e^{-600/T} \tag{51}$$

Finally,

$$a^* = (3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \tag{52}$$

is an average coefficient of the reactions (Young et al. 1968 ;
Donovan et al, 1960 ; Paraskevopoulos and Cvetanovic, 1971 ; Heicklen
et al, 1971)

$$O(^1D) + H_2O \rightarrow 2 \text{ OH} \tag{53a}$$

$$O(^1D) + H_2 \rightarrow H + OH \tag{53b}$$

$$O(^1D) + CH_4 \rightarrow CH_3 + OH \tag{53c}$$

Calculation has been made here with the following approximation

$$n(OH) \, n(HO_2) = 5 \times 10^{-6} \, n(M) \, n[O(^1D)]. \tag{54}$$

where $n(M)$ is the total concentration. The atmospheric parameters
(temperature and concentration) are taken from Nicolet (1972). Numerical
results which are shown in Fig. 1 indicate that $n(OH) \geq 10^5 \text{ cm}^{-3}$;
an error of not less than a factor of two must be accepted, since far
too little is known about the exact values of the rate coefficients.
Average values corresponding to sec χ = 2 (solar zenith angle = 60°)
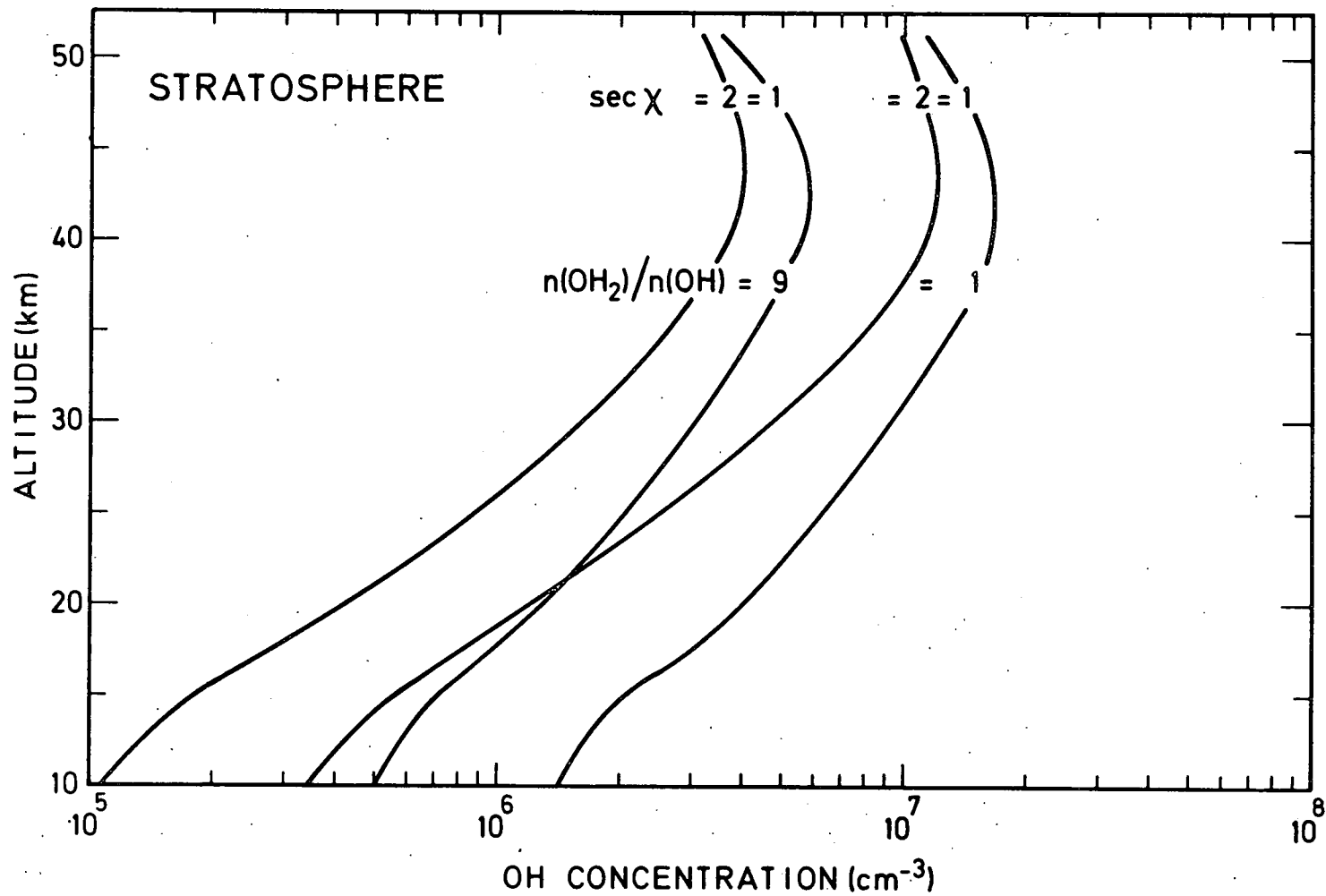will be used in the study of the stratospheric behavior of CH_4 and CO.

Fig. 1.- Concentrations of the hydroxyl radical in the stratosphere for solar conditions
corresponding to solar zenith angle 0° (sec χ = 1) and 60° (sec χ = 2), and
arbitrary ratios $n(HO_2)/n(OH)$ = 1 and 9.

5. DISCUSSIONS AND RESULTS

The basic equations used to calculate the variations in the concentrations of carbon monoxide and methane are

$$\frac{\partial n(CO)}{\partial t} + L(CO) + \frac{\partial \Phi(CO)}{\partial r} = P(CO) \qquad (55)$$

and

$$\frac{\partial n(CH_4)}{\partial t} + L(CH_4) + \frac{\partial \Phi(CH_4)}{\partial r} = 0 \qquad (56)$$

where P represents the production, L is the loss and Φ corresponds to the transport flux by eddy diffusion.

The eddy diffusion current is given by

$$\Phi_i = n_i w_i = n_i K \left[\frac{1}{H_i} - \frac{1}{H} \right] \qquad (57)$$

where n_i is the concentration of the i-th constituent, H_i its scale height. H denotes the atmospheric scale height and K is the eddy diffusion coefficient. H_i and H are given by

$$\frac{1}{H_i} = \frac{1}{n_i} \frac{\partial n_i}{\partial r} + \frac{1}{T} \frac{\partial T}{\partial r} \qquad (58)$$

and

$$\frac{1}{H} = \frac{1}{n} \frac{\partial n}{\partial r} + \frac{1}{T} \frac{\partial T}{\partial r} , \qquad (59)$$

respectively.

The reactions which affect CH_4 destruction are reactions (2) and (3) involving excited atoms $O(^1D)$ in the upper part of the stratosphere and OH radicals in the lower part of the stratosphere. The production reactions which are significant in the stratosphere for carbon monoxide are the oxidation processes of methane in the major part of the stratosphere and the photodissociation of carbon dioxide in the upper stratosphere. The destruction process by a three-body association of CO and O is not important compared with the reaction (44) between CO and OH.

Considering steady-state conditions, equation (55) and (56) can be written

$$n(CO_2) \; J_{CO-O} \; + \left[\; c_1^* \; n(O^*) + c_2 \; n(OH) \; \right] n(CH_4) =$$

$$\frac{\partial n(CO) \; w(CO)}{\partial r} + a_{36} \; n(CO) \; n(OH) \tag{60}$$

and

$$\frac{\partial n(CH_4) \; w(CH_4)}{\partial r} + \left[c_1^* \; n(O^*) + c_2 \; n(OH) \right] n(CH_4) = 0 \tag{61}$$

The lower boundary conditions are determined at the tropopause level by concentrations corresponding to certain mixing ratios of CH_4 and CO. A vanishing flux is adopted in the thermosphere for CH_4 and photoequilibrium conditions are used for CO at the stratopause level.

The coefficient of vertical diffusion is known to vary with latitude (Gudiksen et al, 1968), and in order to consider various possibilities, we have adopted not only constant eddy diffusion coefficient between 10^3 and 10^4 cm^2 sec^{-1}, but also two extreme conditions where the eddy diffusion coefficient varies with height (see fig. 2 for k_{min} and K_{max}). Furthermore, the stratospheric distribution of CH_4
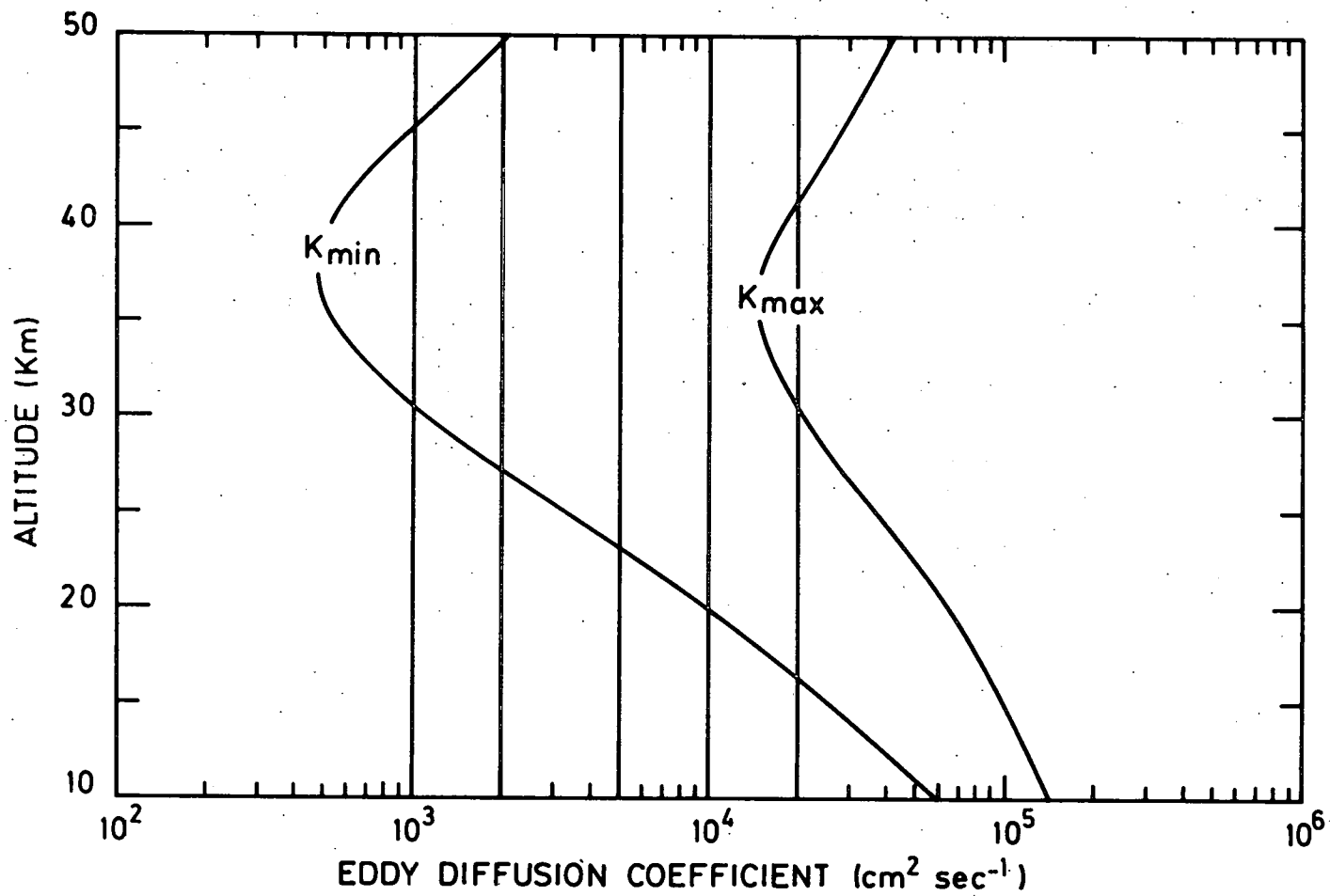
Fig. 2.- Assumed profiles for the eddy diffusion coefficients, K_{min}, K_{max}, 10^3, 2×10^3, 5×10^3, 1 et 2×10^4 cm^2 sec^{-1}.

is also sensitive to the average solar conditions which are adopted. This must be kept in mind since average conditions vary with latitude and seasons.

Considering the number of photons available at the top of the earth's atmosphere (cf. Ackerman, 1971) and the absorption cross sections measured by Shemansky (1972) the photodissociation coefficient of CO_2 can be determined. With a CO_2 mixing ratio of 320 ppmv the photodissociation rate corresponds to a CO production rate of 5×10^2 molecules cm^{-3} sec^{-1} at the stratopause. The result is given in Fig. 3 where the CO production by oxidation of CH_4 is also shown. In the lower part of the stratosphere the effect of hydroxyl radicals is important while the reaction of the excited oxygen atoms plays its role in the middle stratosphere. As far as the photodissociation of CO_2 is concerned, it must be introduced at the stratopause. Finally, photochemical equilibrium conditions can be accepted in the upper part of the stratosphere.

The average conditions for the production of CO molecules are presented in Fig. 4 where it can be seen that there is an important difference when the eddy diffusion coefficient varies from K_{min} to K_{max}. However, the effect of the photodissociation of CO_2 decrease the effect due to the difference in the oxidation of CH_4. The two corresponding vertical distributions of the mixing ratios of CH_4 are illustrated in Fig. 5 which shows the importance of the adopted values from the eddy diffusion coefficient. The recent observational results (Ehhalt et al, 1972 ; Ackerman et al, 1972) show (see Fig. 5 and 6) that relatively high eddy diffusion coefficients are required to explain the observations. They agree with the first observations of Bainbridge and Heidt (1966). However, since tropospheric variations are observed (Ehhalt, 1967) more stratospheric observations are needed before determining the exact profile of the eddy diffusion coefficient which is required to explain the vertical distribution of CH_4.
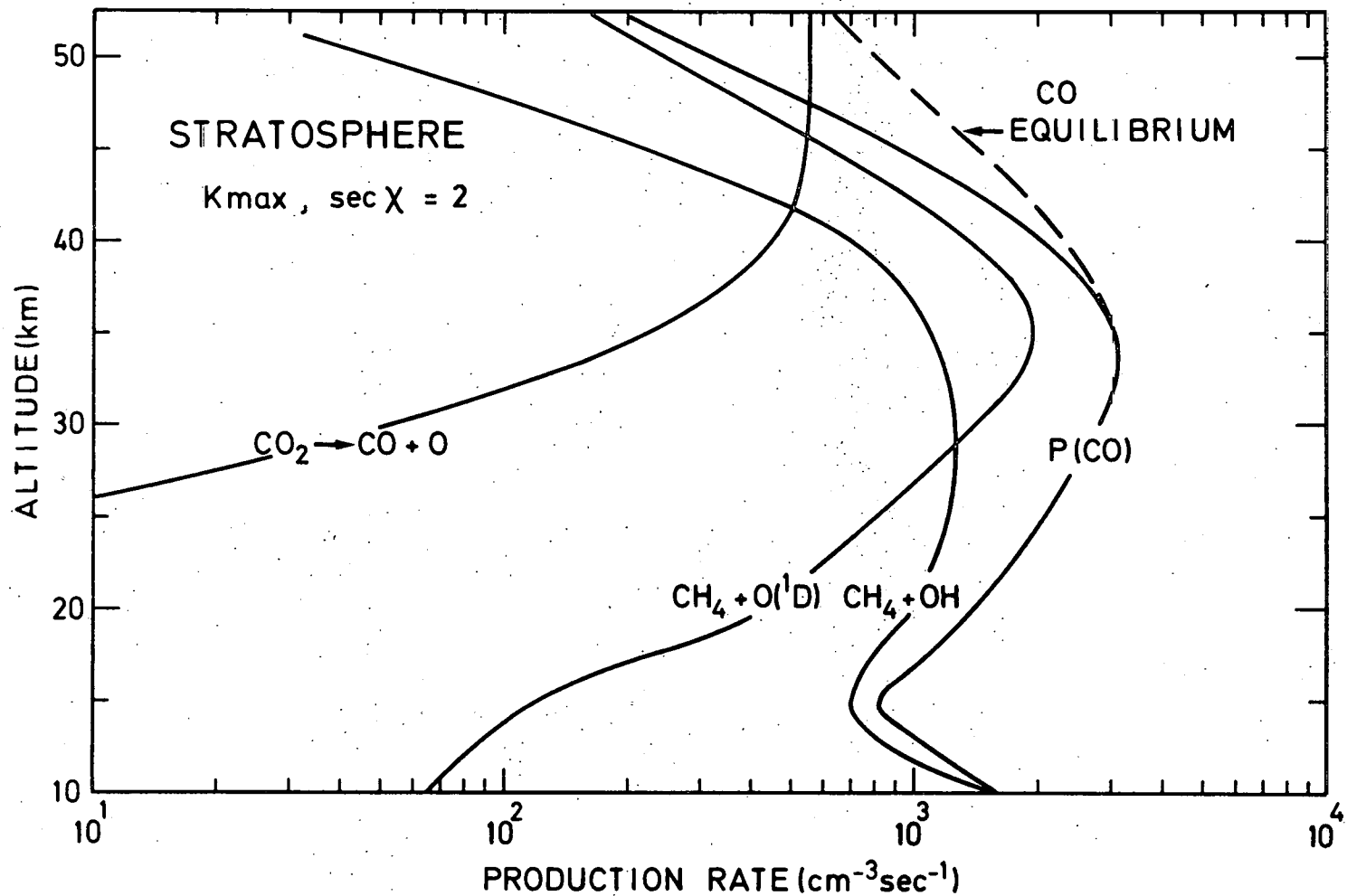
Fig. 3.- Production of CO (cm^{-3} sec^{-1}) by photodissociation of CO_2, reactions of $O(^1D)$ and OH with CH_4 for a maximum of the eddy diffusion coefficient, K_{max} and solar conditions, sec χ = 2.

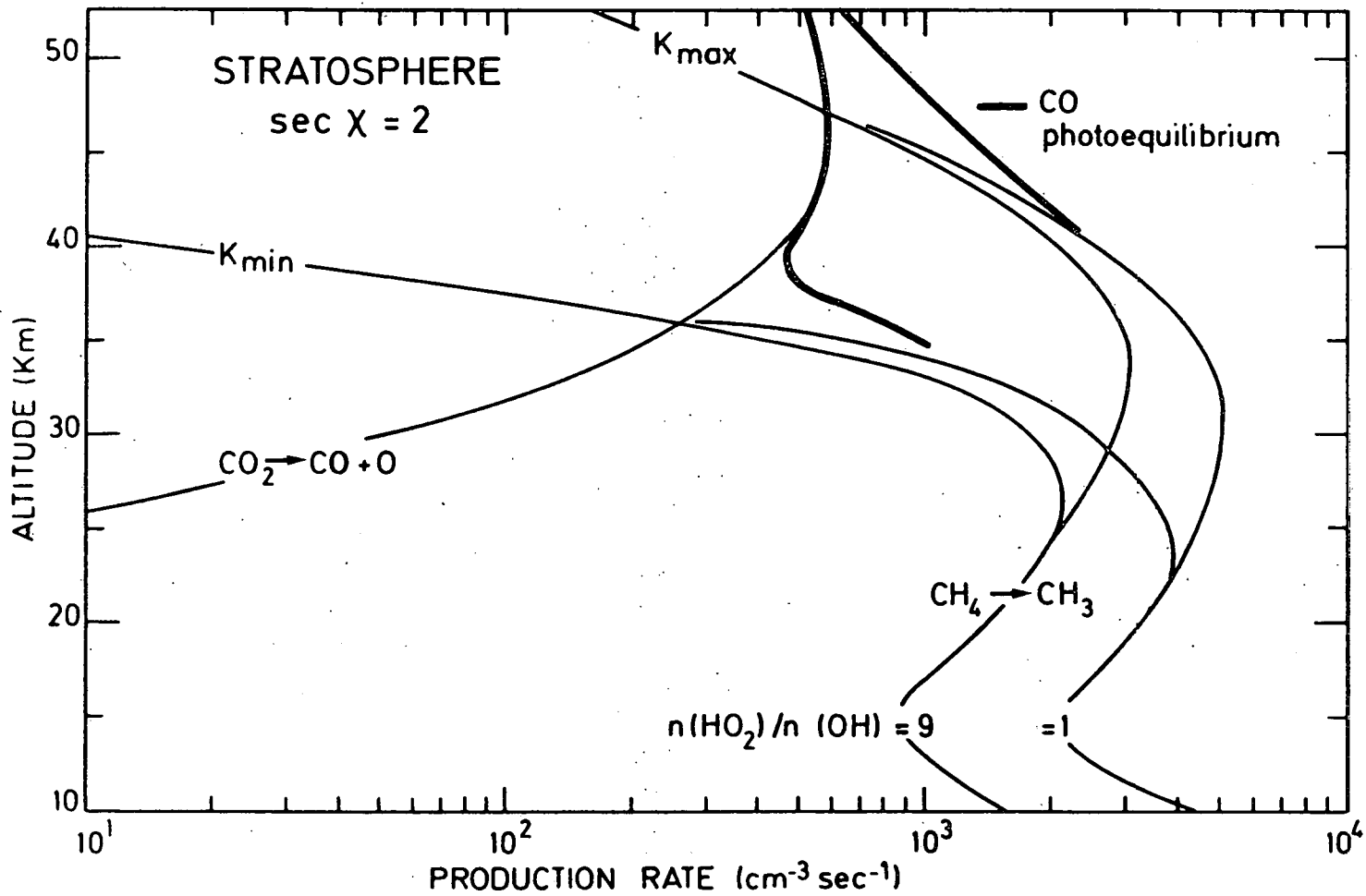Fig. 4.- Production rates of CO (cm^{-3} sec^{-1}) for different eddy diffusion coefficients, K_{min} and K_{max} and for ratios $n(HO_2/n(OH) = 9$ and 1.
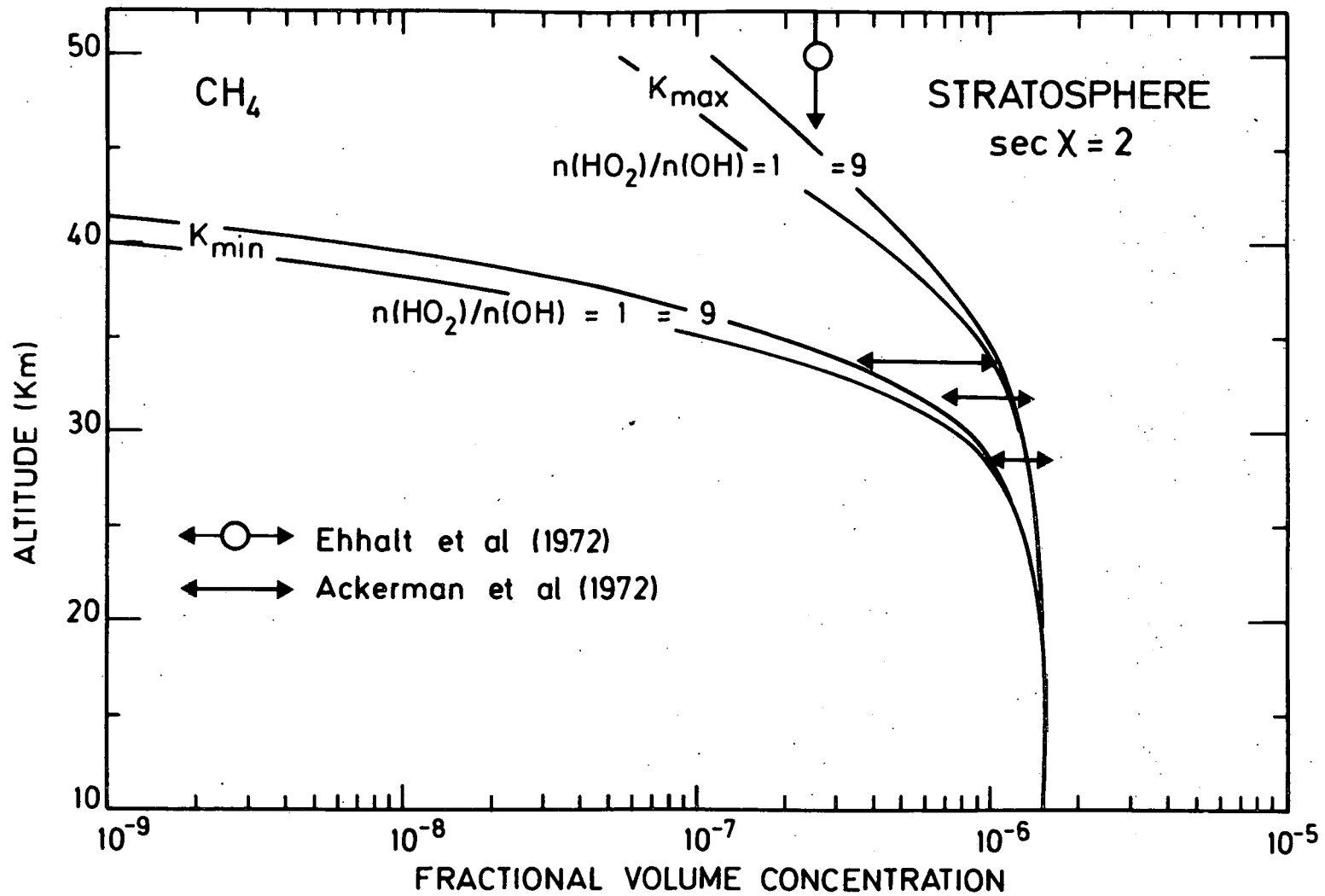
Fig. 5.- Fractional volume concentrations of methane for two extreme conditions of the eddy diffusion coefficient, K_{min} and K_{max}. Observational results are indicated.
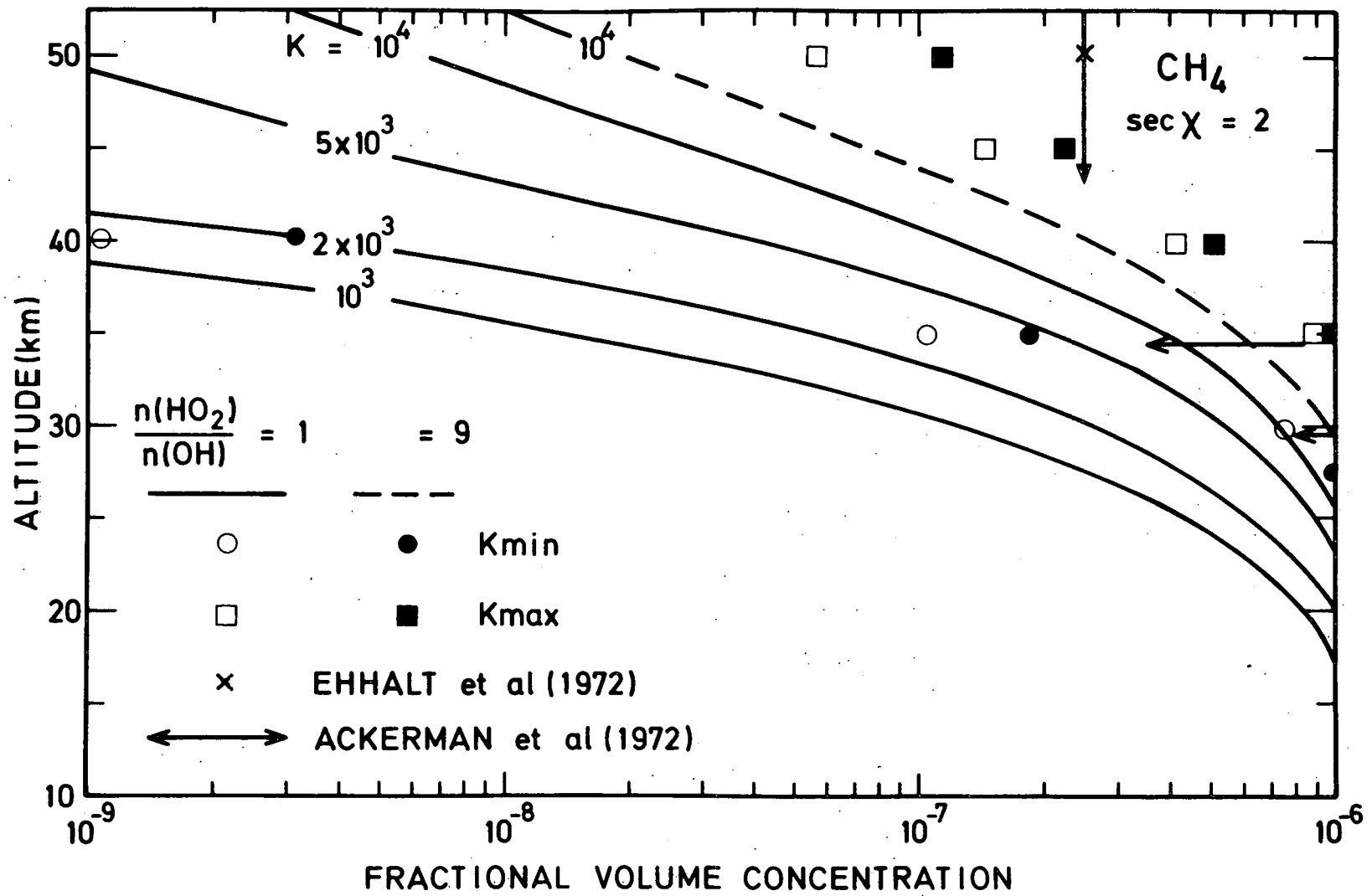
Fig. 6.- Fractional volume concentration of methane for various constant values of the eddy diffusion coefficient $K = 10^3$ to 10^4 compared with K_{min} and K_{max}.

In any case, it seems that the upward current of CH_4 molecules (fig. 7) could not be less than 5×10^9 molecules cm^{-2} sec^{-1} which corresponds to a stratospheric production of at least 5×10^9 CO molecules cm^{-2} sec^{-1} and not less than 10^{10} H_2O molecules cm^{-2} sec^{-1}.

As far as carbon monoxide is concerned the conditions in the neighborhood of the stratopause are determined by photochemical equilibrium conditions (Hays and Olivero, 1970). Examples of fractional volume concentrations of CO are given in Fig. 8 above 30 km. Below the strato-pause the mixing ratio decreases with the decrease of the eddy diffusion coefficient since the effect of the reaction OH + CH_4 becomes less and less important.

In the lower stratosphere there is a rapide decrease (Seiler and Junge, 1969) of the carbon monoxide concentration compared with the tropospheric concentration. It corresponds according to recent results of Seiler and Warneck to a difference in the mixing ratio from more than 10^{-7} below the tropopause to $5-6 \times 10^{-8}$ above the tropopause.

Various calculations have been made for different lower boundary conditions. Examples shown in Fig. 9 and 10 corresponds to the two extreme values of the eddy diffusion coefficients K_{min} and K_{max}. The fractional volume concentration of CO is between 10^{-8} and 10^{-7} when a high value of the eddy diffusion coefficient is adopted ; it decreases to less than 10^{-8} if a small value of the eddy diffusion coefficient is adopted in the upper stratosphere.

If it is assumed that there is no upward current of CO molecules at the tropopause (here 10 km) the lower boundary conditions are determined since they must correspond to mixing conditions. The vertical distribution of the mixing ratio (10^{-8} at 10 km) corresponding to such conditions may be compared (see Fig 9 and 10) with the vertical distribution of that
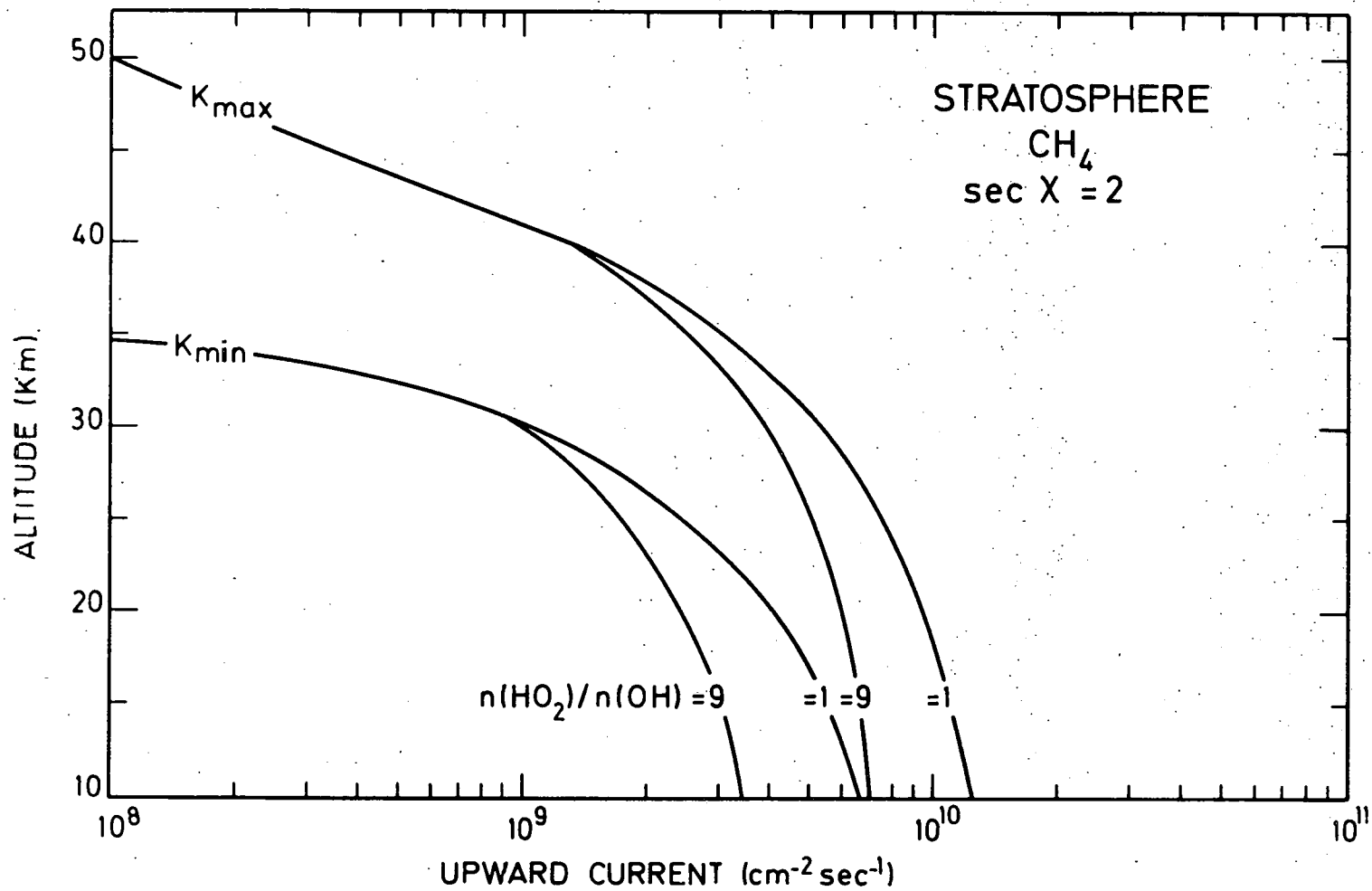
Fig. 7.- Upward current of CH_4 molecules in the stratosphere for extreme conditions of the eddy diffusion coefficient K_{min} and K_{max}. Solar conditions correspond to solar zenith angle of 60° (sec χ = 2).
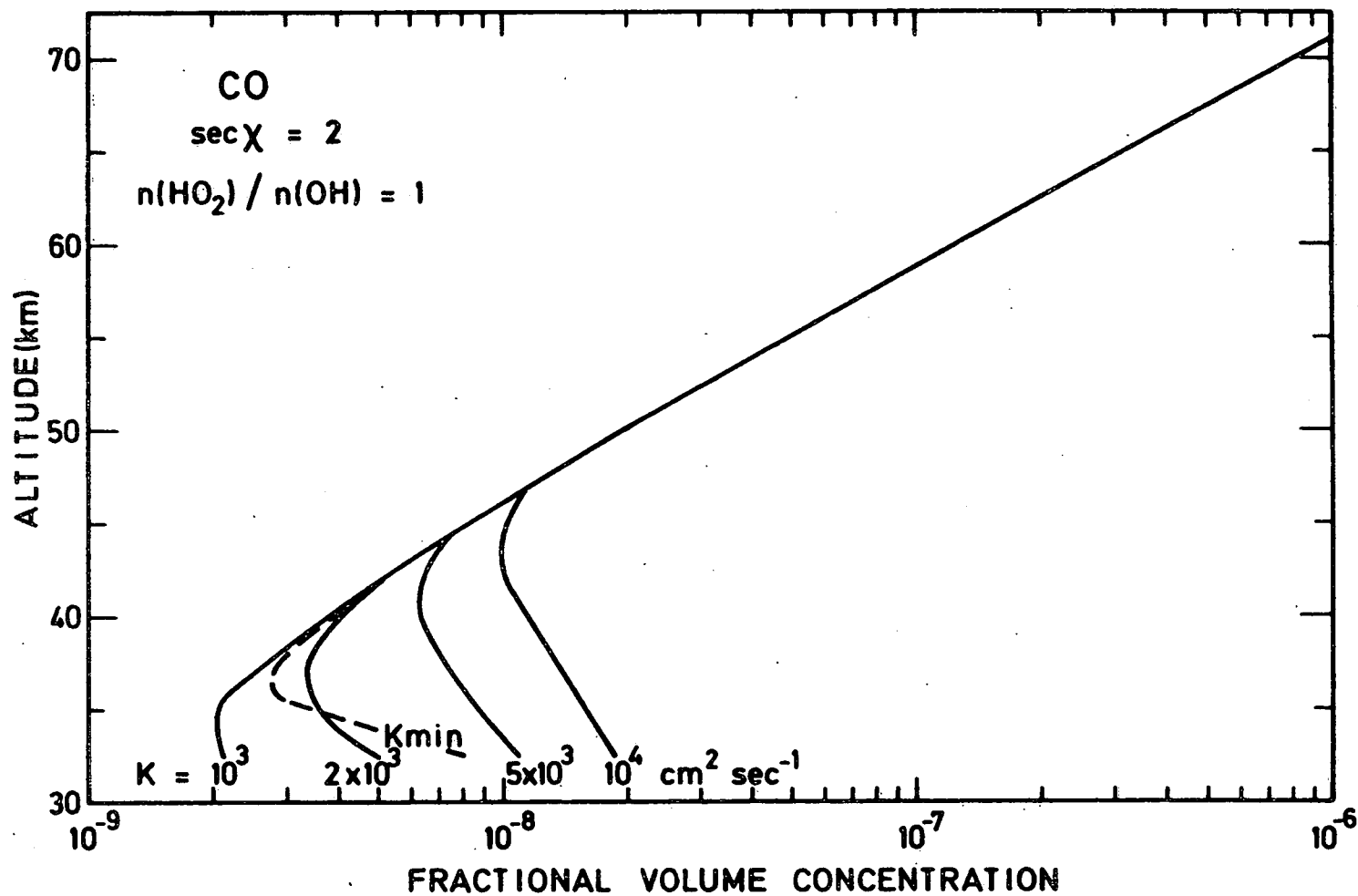
Fig. 8.- Fractional volume concentration of carbon monoxide above 30 km for various constant values of the eddy diffusion coefficient.

Fig. 9.- Fractional volume concentration of carbon monoxide in the stratosphere for high values of the eddy diffusion coefficient (K_{max}). The lower boundary conditions are 10^{-7}, 5×10^{-8} and mixing conditions (10^{-8}).
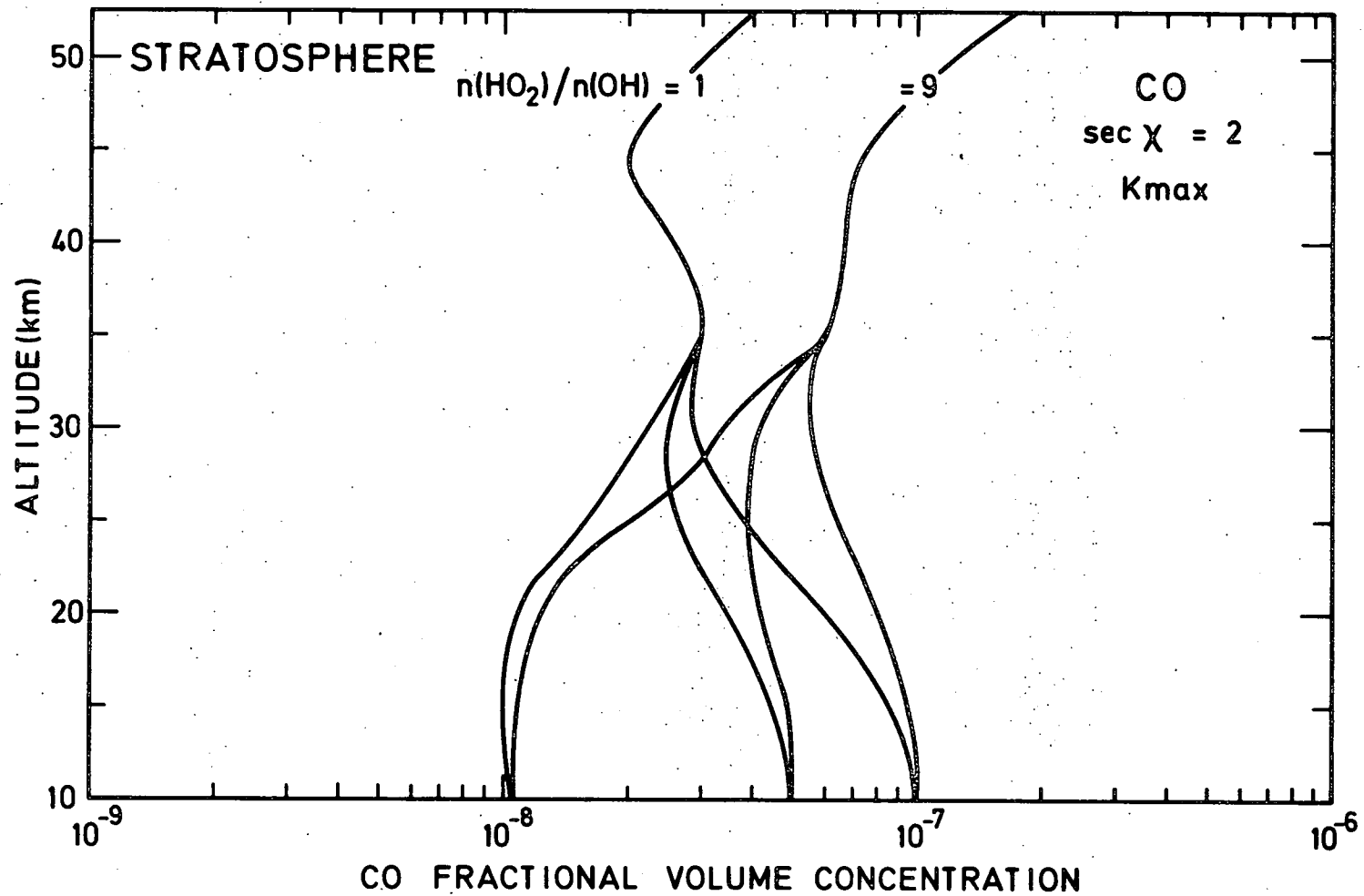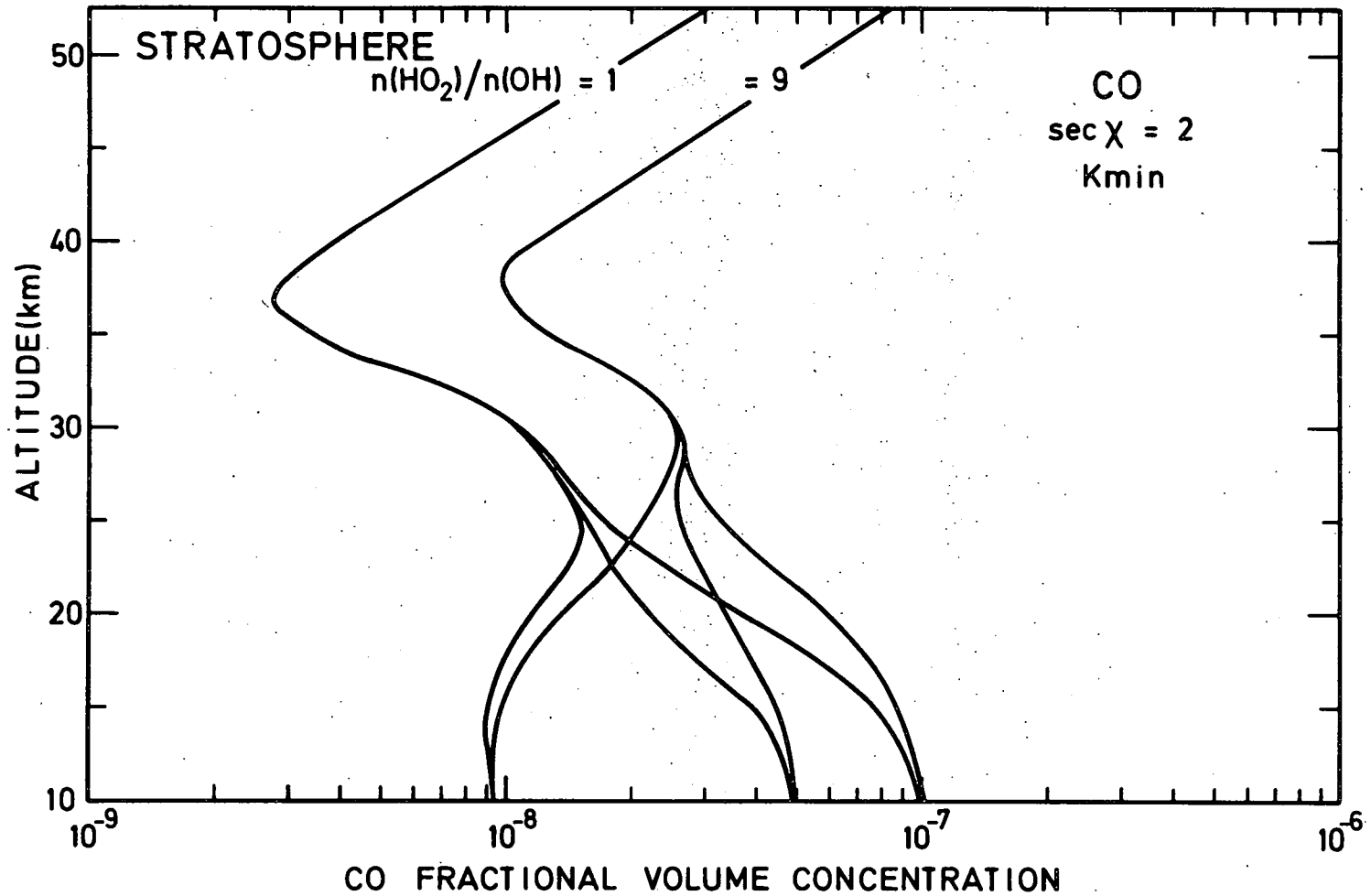
Fig. 10.- Fractional volume concentration of carbon monoxide in the stratosphere for low
values of the eddy diffusion coefficient, K_{min}. The lower boundary condition are
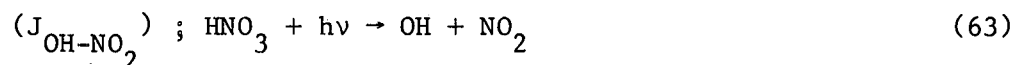10^{-7}, 5×10^{-8} and mixing conditions (10^{-8}).

corresponding to lower boundary values of 5×10^{-8} and 10^{-7}. Since the observations of Seiler and Warneck (1972) show that the mixing ratio of carbon monoxide above the tropopause is more than the equilibrium value ($\sim 10^{-8}$) and less than the tropospheric value ($\geq 10^{-7}$), there must be an upward current of CO molecules at the tropopause in addition to the production by the oxidation of CH_4 molecules. Depending on the ratio $n(HO_2)/n(OH)$ and on the exact value of the eddy diffusion coefficient, the average upward current of CO molecules would be between 5×10^9 cm^{-2} sec^{-1} and 2×10^{10} cm^{-2} sec^{-1}, i.e. not less than the injection of CH_4 molecules into the stratosphere. In any case, it seems that the vertical distribution of the carbon monoxide in the lower stratosphere is related to the upward current of CO and CH_4 molecules through the tropopause and, in the upper stratosphere, depends on photochemical equilibrium conditions in which OH radicals are involved.

Since our knowledge of tropospheric CO concentrations is still incomplete, with fractional volume concentration varying from an average of 0.14 ppmv in the Northern hemisphere to an average of 0.06 ppmv in the Southern hemisphere (Robinson and Robbins, 1971), the stratospheric behavior can only be understood for average conventional conditions. Detailed calculations require very precise atmospheric data since the average short life time of tropospheric carbon monoxide must lead to wide fluctuations of its concentration.

Finally, all processes must be introduced in order to determine the exact aeronomic behavior of the hydroxyl radicals . For example, the effect of nitric acid, which has been neglected here, could be introduced in a complete study. If the steady state conditions of HNO_3 in the stratosphere are given by the simple equation (Nicolet, 1972)

$$n(HNO_3) = \frac{b_{22} \, n(M) \, n(OH) \, n(NO_2)}{J_{OH-NO_2} + b_{27} \, n(OH)} \tag{62}$$

where the loss processes are the photodissociation

$$(J_{OH-NO_2}) \ ; \ HNO_3 + h\nu \rightarrow OH + NO_2 \tag{63}$$

and the reaction with OH

$$(b_{27}) \ ; \ HNO_3 + OH \rightarrow H_2O + NO_3 \tag{64}$$

and the principal process of formation

$$(b_{22}) \ ; \ OH + NO_2 + M \rightarrow HNO_3 + M \ , \tag{65}$$
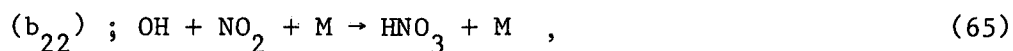
There is a final loss process of OH radicals due to the reactions of HNO_3 which is given by

$$\frac{1}{n(OH)} \ \frac{dn(OH)}{dt} = -2 \ b_{27} \ n(HNO_3) \tag{66}$$

Since the rate coefficient b_{27} should be about 1000 times less than a_{17} the rate coefficient of the reaction (48) between OH and HO_2, $n(HNO_3) \geqq 1000 \ n(HO_2)$ would play a role in the determination of OH in equation (47). Thus, a special study of the behavior of nitrogen oxides is of special interest in the hydrogen-oxygen stratosphere.

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