

I N S T I T U T D ' A E R O N O M I E S P A T I A L E D E B E L G I Q U E

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An overview of aeronomic processes  
in the stratosphere and mesosphere

by

M. NICOLET

B E L G I S C H I N S T I T U U T V O O R R U I M T E - A E R O N O M I E

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## FOREWORD

"An overview of aeronomic processes in the stratosphere and mesosphere" is an invited paper given at the Symposium on aeronomic processes in the stratosphere and mesosphere during the Second General Scientific Assembly of Geomagnetism and Aeronomy (IAGA) held in Kyoto, September 9-21, 1973. It will be published in Canadian Journal of Chemistry.

## AVANT-PROPOS

"An overview of aeronomic processes in the stratosphere and mesosphere" a été présenté comme "invited paper" au "Symposium on aeronomic processes in the stratosphere and mesosphere" au cours de la Seconde Assemblée Générale de l'Association Internationale de Géomagnétisme et d'Aéronomie (IAGA) à Kyoto, 9-21 septembre, 1973. Il sera publié dans Canadian Journal of Chemistry.

## VOORWOORD

"An overview of aeronomic processes in the stratosphere and mesosphere" werd als "invited paper" voorgedragen tijdens het "Symposium on Aeronomic processes in the stratosphere and mesosphere" gehouden ter gelegenheid van de tweede algemene vergadering van "The International Association of Geomagnetism and Aeronomy" (IAGA) te Kyoto, 9-21 september, 1973. De tekst zal gepubliceerd worden in Canadian Journal of Chemistry.

## VORWORT

"An overview of aeronomic processes in the stratosphere and mesosphere" wurde als "invited paper" zum "Symposium on aeronomic processes in the stratosphere and mesosphere" während der zweiten Generalversammlung der Internationalen Vereinigung von Geomagnetismus und Aeronomie in Kyoto, 9.-21. September, 1973 vorgestellt. Diese Arbeit wird in Canadian Journal of Chemistry herausgegeben werden.

# AN OVERVIEW OF AERONOMIC PROCESSES IN THE STRATOSPHERE AND MESOSPHERE

by

M. NICOLET

## *Abstract*

The discrepancy noted between theoretical and observational concentrations of  $O_3$  in the mesosphere and stratosphere can be explained by an effect of hydrogen compounds and of nitrogen oxides. Solar radiation dissociates water vapor and methane in the thermosphere and upper mesosphere. In the stratosphere the reaction of the excited oxygen atom  $O(^1D)$  with methane and *nitrous oxide* leads to a destruction of these two molecules in the stratosphere which corresponds to a production of carbon monoxide with water vapor and of *nitric oxide*, respectively. Hydrogen and water vapor molecules react also with the electronically excited oxygen atom  $O(^1D)$  leading to hydroxyl radicals. In situ sources of  $H_2$  exist in the stratosphere and mesosphere : reaction of OH with  $CH_4$ , photodissociation of *formaldehyde* and also reaction between hydroperoxyl radicals and hydrogen atoms. The vertical distribution of water vapor is not affected by its dissociation in the stratosphere and mesosphere since its reformation is rapid.

The ratio of the hydroxyl and hydroperoxyl radical concentrations cannot be determined with adequate precision and complicates the calculation of the destruction of ozone which occurs through reactions of OH and  $HO_2$  not only with atomic oxygen at the stratopause but also directly in the middle stratosphere and with CO and NO in the lower stratosphere.

In addition to the various reactions involving *nitric oxide* and *nitrogen dioxide*, the reactions leading to the production and destruction of *nitric acid* and *nitrous acid* must be considered. *Nitric acid* molecules are involved in an eddy diffusion transport from the lower stratosphere into the troposphere and are, therefore, responsible for the removal of *nitric oxide* which is produced in the stratosphere. Atmospheric conditions must be known at the tropopause.

## Résumé

La différence que l'on note entre les valeurs théoriques calculées et les valeurs observées de la concentration de l'ozone dans la stratosphère et dans la mésosphère s'explique par un effet des composés de l'hydrogène et des oxydes d'azote.

La radiation solaire photodissocie la vapeur d'eau et le méthane dans la thermosphère et dans la mésosphère supérieure. Dans la stratosphère, la réaction de l'atome excité d'oxygène  $O(^1D)$  avec  $CH_4$  et  $N_2O$  conduit à la destruction de ces deux molécules dans la stratosphère et ainsi à une production d'une part, de  $CO$  et de  $H_2O$  et d'autre part de  $NO$ . Les molécules d'hydrogène et de vapeur d'eau réagissent aussi avec l'atome d'oxygène  $^1D$  avec formation du radical  $OH$ . D'autre part, des sources de  $H_2$  existent dans la stratosphère et dans la mésosphère : réaction de  $OH$  avec  $CH_4$ , photodissociation de  $H_2CO$  et aussi réaction de  $HO_2$  avec  $H$ . La distribution verticale de la vapeur d'eau n'est pas influencée par sa dissociation dans la stratosphère et dans la mésosphère car sa reformation est très rapide.

Le rapport des concentrations des radicaux  $OH$  et  $HO_2$  ne peut être déterminé avec une précision suffisante, ce qui complique le calcul de la destruction de l'ozone qui est due à des réactions de  $OH$  et  $HO_2$  avec  $O$  à la stratopause. Dans la basse stratosphère, la difficulté provient de réactions de  $OH$  et  $HO_2$  respectivement avec  $CO$  et  $NO$ .

Dans le cas des oxydes d'azote avec les diverses réactions de  $NO$  et de  $NO_2$ , il faut tenir compte des réactions conduisant à la production et à la destruction de l'acide nitrique et de l'acide nitreux.  $HNO_3$  est transporté de la basse stratosphère vers la troposphère et est donc responsable pour la disparition de  $NO$  produit dans la stratosphère. Les conditions atmosphériques doivent être bien connues à la tropopause.

### *Samenvatting*

Het verschil tussen theoretisch berekende en waargenomen concentraties van  $O_3$  in de mesosfeer en in de stratosfeer kan verklaard worden als een gevolg van waterstofverbindingen en van de stikstofoxydes. De zonnestraling dissocieert waterdamp en methaan in de thermosfeer en in de hogere mesosfeer. In de stratosfeer leidt de reactie van het aangeslagen zuurstofatoom  $O(^1D)$  met methaan en  $N_2O$  tot de vernietiging van deze twee molekulen in de stratosfeer, hetgeen gepaard gaat met de produktie van koolstofmonoxyde met waterdamp en van  $NO$ , respectievelijk. Waterstof en waterdamp reageert ook met geëxciteerde atomaire zuurstof  $O(^1D)$  en vormt aldus hydroxyl radicalen. In situ bronnen van  $H_2$  bestaan in de stratosfeer en mesosfeer : reactie van  $OH$  met  $CH_4$ , fotodissociatie van  $H_2CO$  en ook nog de reactie van hydroperoxyl radicalen met waterstofatomen. De verticale distributie van waterdamp wordt niet beïnvloed door de waterdampdissociatie in de stratosfeer en mesosfeer aangezien de recombinate zeer vlug geschiedt.

De verhouding van de concentratie der hydroxyl en hydroperoxyl radicalen kan niet met voldoende nauwkeurigheid bepaald worden en bemoeilijkt de berekening van de vernietiging van ozon. Deze vernietiging geschiedt door de reacties van  $OH$  en  $HO_2$  met atomaire zuurstof aan de stratopauze en in het centrale gedeelte der stratosfeer, en met  $CO$  en  $NO$  in de lagere stratosfeer.

Buiten de verscheidene reacties met  $NO$  en  $NO_2$ , moet men ook nog rekening houden met de reacties die leiden tot de produktie of het verlies van  $HNO_3$  en  $HNO_2$ . Eddy diffusie leidt  $HNO_3$  van de lagere stratosfeer naar de troposfeer, en bijgevolg zijn de  $HNO_3$  molekulen verantwoordelijk voor het verwijderen van  $NO$  dat geproduceerd wordt in de stratosfeer. Atmosferische voorwaarden moeten gekend zijn aan de tropopauze.

## *Zusammenfassung*

Der Unterschied zwischen den gerechneten und beobachteten Werten der Ozonkonzentration in der Stratosphäre und in der Mesosphäre kann durch die Wasserstoffkomponenten und durch die Stickstoffoxyden erklärt werden.

Die Sonnenstrahlung photodissoziiert Wasserdampf und Methan in der Thermosphäre und in der oberen Mesosphäre. Die Reaktion des angeregten Sauerstoffatom  $O(^1D)$  mit  $CH_4$  und  $N_2O$  zerstört diese Elementen in der Stratosphäre und bringt so zu einer Produktion von  $CO$  und  $H_2O$  einerseits und zu  $NO$  andererseits. Die Reaktionen von  $H_2O$  und  $H_2$  mit dem Sauerstoffatom  $^1D$  geben  $OH$  Radikalen. Andererseits existieren auch  $H_2$  Quellen in der Stratosphäre:  $OH$ -Reaktion mit  $CH_4$ ,  $H_2CO$  Photodissoziation und  $HO_2$ -Reaktion mit  $H$ . Die senkrechte Verbreitung des Wasserdampfes ist nicht durch die Dissoziation in der Stratosphäre und Mesosphäre beeinflusst, denn die Wiederbildung ist sehr schnell.

Das Verhältnis der  $OH$  und  $HO_2$  Konzentrationen kann nicht sehr genau berechnet werden und so ist die Berechnung der Ozonvernichtung durch  $OH$  und  $HO_2$  Reaktionen mit  $O$  in der Umgebung der Stratopause kompliziert. In der unteren Stratosphäre kommen die Schwierigkeiten durch die  $OH$  und  $HO_2$  Reaktionen mit  $CO$  und  $NO$ .

Im Falle der Stickstoffoxyden müssen die Reaktionen, die zur Aufbildung und Vernichtung von  $HNO_2$  und  $HNO_3$  führen, einbegriffen werden.  $HNO_3$  wird aus der unteren Stratosphäre zur Troposphäre transportiert und ist so verantwortlich für des Verschwinden von  $NO$  in der Stratosphäre. Die atmosphärische Bedingungen müssen sehr gut bekannt sein in der Umgebung der Tropopause.

## 1. INTRODUCTION

Even if much detailed work remains to be done, there is a general understanding of the various factors which are involved in the formation of the ozone layer and in the production of atomic oxygen. The researches of Chapman (1930, 1943) have led to a knowledge of the photochemistry of atmospheric oxygen in a pure oxygen atmosphere. Bates and Nicolet (1950c) in their general survey of the photochemistry of water vapor have investigated the extent to which atomic hydrogen and certain radicals catalyse the formation of molecular oxygen. Vibration-rotation bands of the hydroxyl radical OH, which appear in the airglow, aroused interest in the photochemistry of hydrogen-oxygen compounds [Bates and Nicolet, 1950a; Herzberg 1951] and in particular of methane [Bates and Nicolet 1950b; Bates and Witherspoon 1952] and of water vapor [Bates and Nicolet, 1950c]. Water vapor, which is quite abundant near ground level with a fractional volume concentration reaching  $10^{-2}$ , decreases in mixing ratio with altitude. The water vapor content is very small in the stratosphere;  $(4 \pm 1) \times 10^{-6}$  is not an unreasonable value to adopt for the order of magnitude of the fractional volume concentration of water vapor [Williamson and Houghton, 1965; Mastenbrook, 1968, 1971; Sissenwine *et al.*, 1968; 1972] in the stratosphere. Methane and molecular hydrogen, which have been found as permanent constituents of the troposphere have continuous sources at ground level. Their total amounts by volume are, respectively,  $1.5 \times 10^{-6}$  (see Ehhalt and Heidt, 1973) and  $0.5 \times 10^{-6}$  (see Schmidt 1973; Ehhalt and Heidt, 1973). Unlike water vapor, however, their fractional concentrations are practically not affected through the troposphere. Consequently, above the tropopause, the combined H-atom content in  $\text{CH}_4$  is more than 50% than the content in  $\text{H}_2\text{O}$ . Thus, the total amount of free hydrogen in the lower stratosphere cannot be far from  $10^{-5}$ .

If the photodissociation of water vapor and methane occurs in the mesosphere and thermosphere, the reaction of  $\text{H}_2\text{O}$  with the electronically excited atomic oxygen in the  $^1\text{D}$  state (Cadle, 1964; Hampson, 1964) leads to the possibility of its dissociation in the stratosphere and troposphere. The concentrations of  $\text{O}(^1\text{D})$  produced by ozone photolysis in the stratosphere and troposphere are sufficiently large to lead to OH radicals not only from water vapor but also from methane and molecular hydrogen.

While the desirability of similar studies of the effect of nitrogen compounds has long been realized, comparatively little has been made because of lack of basic data. The importance of nitrogen oxides in controlling the ozone concentration was pointed out only in 1970. [Crutzen, 1970]. Information on  $N_2O$  was given before by the calculation of its photodissociation rate [Bates and Witherspoon, 1952; Bates and Hays, 1967] and on  $NO$ ,  $NO_2$  and  $HNO_3$  by the analysis of the principal reactions [Nicolet, 1965]. Recently, new experimental and observational results have been obtained on the nitrogen oxides, particularly by direct observation on the vertical distribution in the stratosphere (Williams *et al.*, 1972, Murcray *et al.*, 1973) on nitric acid, Ackerman and Muller (1972) on nitrogen dioxide and Ackerman *et al.* (1973) on nitric oxide.

The importance of methane has been generally realized since McConnell *et al.* (1971) showed that it was a major source of carbon monoxide in the troposphere through a reaction with hydroxyl radicals. Furthermore, these hydroxyl radicals are produced in sufficient concentration (Levy, 1971) to provide the destruction of carbon monoxide required by Weinstock (1969). However, in moving through the latitudinal distribution of the tropopause, from high latitudes to the tropical zone, very different atmospheric conditions are detected; the difference in altitude of the polar and equatorial tropopauses which is of the order of 10 km; a folded tropopause at mean latitudes which may change the lower boundary conditions of the stratosphere. In other words, the nature of the tropopause is an important factor which must be introduced in the study of the lower stratosphere.

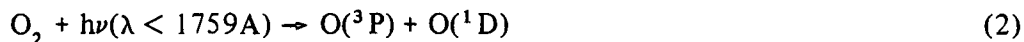
## 2. OXYGEN PHOTODISSOCIATION AND OZONE FORMATION

Photodissociation of molecular oxygen is produced by the absorption of solar radiation in the weak Herzberg continuum beginning at 2424A,



which occurs in the stratosphere. In the strong Schumann-Runge continuum





the dissociation occurs in the thermosphere. In the spectral range of the Schumann-Runge bands, where predissociation is observed, the absorption is extremely variable and the dissociation occurs in the mesosphere and upper stratosphere.

Since the photodissociation coefficient varies between  $4 \times 10^{-7} \text{ sec}^{-1}$  and  $4 \times 10^{-6} \text{ sec}^{-1}$  (zero optical depth) above 100 km, i.e. a relatively small value, it is certain that molecular oxygen cannot be in photochemical equilibrium in the lower thermosphere but is subject to atmospheric transport related to eddy and molecular diffusion.

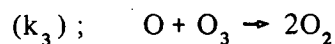
In the presence of a third body ( $\text{N}_2, \text{O}_2$ ) the atoms liberated by photodissociation recombine



or they unite with oxygen molecules



forming ozone. This molecule is destroyed by a two-body collision process



and is also subject to photodissociation in the strong Hartley continuum



and in the weak Chappuis bands in the visible



An important aspect of the photodissociation of  $O_3$  is the production of  $O(^1D)$  atoms which react with  $H_2O$ ,  $H_2$ ,  $CH_4$  and  $N_2O$  when they are not deactivated by atmospheric  $N_2$  and  $O_2$ .

Considering the theoretical problem of oxygen dissociation and ozone formation, the equations governing the rates of change of the concentrations  $n(O)$  and  $n(O_3)$  are

$$\frac{dn(O)}{dt} + 2k_1 n(M) n^2(O) + k_2 n(M) n(O_2) n(O) + k_3 n(O_3) n(O) = 2n(O_2) J_2 + n(O_3) J_3 \quad (7)$$

$$\frac{dn(O_3)}{dt} + n(O_3) J_3 - k_2 n(M) n(O_2) n(O) + k_3 n(O) n(O_3) = 0 \quad (8)$$

which lead to the general form

$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1 n(M) n(O) + 2k_3 n(O_3) n(O) = 2n(O_2) J_2 \quad (9)$$

where  $J_2$  and  $J_3$  are the photodissociation coefficients of  $O_2$  and  $O_3$ , respectively.

It seems appropriate to discuss the photochemical behavior within the various atmospheric layers where various regimes can be distinguished. In the lower thermosphere, atomic oxygen becomes an important constituent playing a role in the mean molecular mass. In the major part of the mesosphere,  $n(O) > n(O_3)$  and there is a daytime photoequilibrium for ozone with a photodissociation coefficient  $10^{-3} \leq J_3 \leq 10^{-2} \text{ sec}^{-1}$ . Thus, from (8),

$$\frac{n(O_3)}{n(O)} = \frac{k_2 n(M) n(O)}{J_3 + k_3 n(O)} \cong \frac{k_2 n(M) n(O_2)}{J_3} \quad (10)$$

since  $J_3 > k_3 n(O)$ , and from (9),

$$\frac{dn(O)}{dt} + 2k_1 n(M) \left\{ 1 + \frac{k_3 k_2 n(O_2)}{k_1 J_3} \right\} n^2(O) = 2n(O_2) J_2 \quad (11)$$

The time  $\tau_0$  which is required in a sunlit atmosphere to reach about 50% of the photochemical equilibrium value (or to reach 80% from 50%) is given by

$$\tau_0(50\%) = 0.275 \left\{ \left[ k_1 n(M) + \frac{k_3 k_2 n(M) n(O_2)}{J_3} \right] n(O_2) J_2 \right\}^{1/2} \quad (12)$$

or

$$\tau_0(50\%) = 0.275 n_e(O)/n(O_2) J_2 \quad (13)$$

if  $n_e(O)$  is the photochemical equilibrium concentration. Application of (13) leads to the following times

Altitude (km)	90	85	80	75	70
Time (hour)	200	90	32	12	4

Thus, at the mesopause and above in the lower thermosphere, the vertical distribution of atomic oxygen concentration depends on the relative importance of atmospheric transport conditions as compared with chemical conditions.

During the night  $J_2$  and  $J_3$  vanish;  $n(O)$  slowly decays and  $n(O_3)$  increases to attain the value  $k_2 n(M) n(O_2)/k_3$  but never exceeding the combined initial concentration  $n(O) + n(O_3)$  of the odd oxygen atoms. Comparison of the observed and calculated ozone concentration in the mesosphere reveals that the calculated ozone concentration values are greater than those observed, particularly in the upper mesosphere. In an oxygen atmosphere, the steady state concentration of ozone molecules in the mesosphere is between  $1 \times 10^{10} \text{ cm}^{-3}$  and  $8 \times 10^{10} \text{ cm}^{-3}$ , which is more than the observed values (see Fig. 1). The reason for the difference is that hydrogen acts as a catalyst for the destruction of odd oxygen atoms. The catalytic action of hydrogen was introduced by Bates and Nicolet (1950c) and various studies (Hampson, 1966; Hunt 1966; Hesstvedt, 1968; Dütsch, 1968) have shown how the

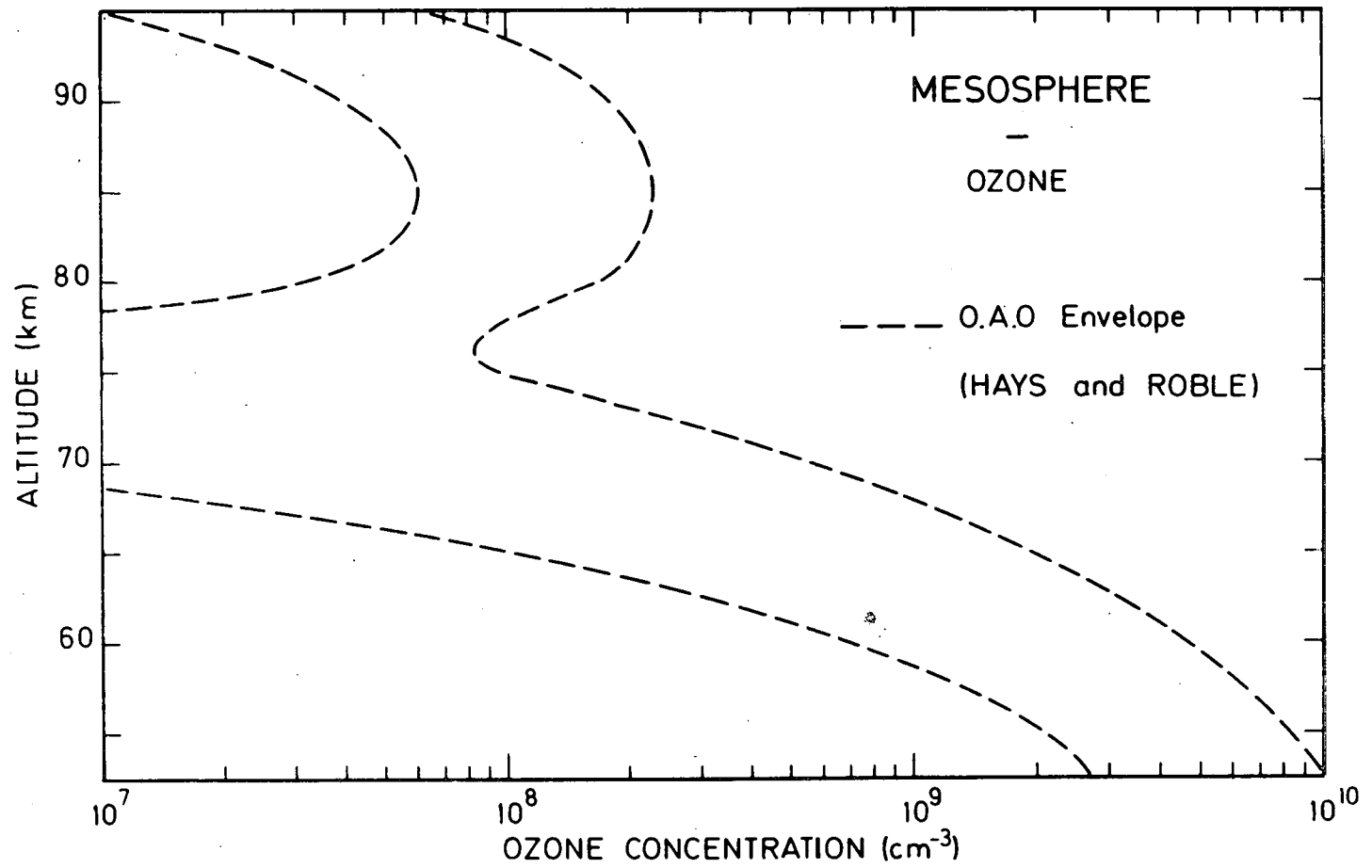


Fig. 1.- Envelope of altitudes profiles for mesospheric ozone obtained by Hays and Robbe (1973). The nighttime ozone concentration has a bulge in its vertical profile with a peak of the order of  $10^5 \text{ cm}^{-3}$  near the mesopause and a minimum in the mesosphere near 75 km.

ozone behavior in the mesosphere may be affected by hydrogen compounds.

Near the stratopause and in the whole stratosphere  $n(\text{O}_3) > n(\text{O})$  and another regime is established. The form normally used in studies of the main part of the ozone layer in a pure oxygen atmosphere is

$$\frac{dn(\text{O}_3)}{dt} + \frac{2k_3 J_3}{k_2 n(\text{M}) n(\text{O}_2)} n^2(\text{O}_3) = 2 n(\text{O}_2) J_2 \quad (14)$$

with  $n(\text{O})$  in photochemical equilibrium. The differential equation (14) indicates that the time  $\tau_{0_3}$  required to attain equilibrium (in fact, to pass from zero concentration to 50% of the equilibrium value or from 50% to 80%) is

$$\tau_{0_3} = 0.275 n_e(\text{O}_3)/n(\text{O}_2) J_2 \quad (15)$$

where  $n_e(\text{O}_3)$  is the photochemical equilibrium value

$$n_e^2(\text{O}_3) = \frac{k_2 n(\text{M}) n^2(\text{O}_2)}{k_3} \frac{J_2}{J_3} \quad (16)$$

Fig. 2a and 2b show the numerical results of equation (15) for various solar conditions: overhead sun,  $90^\circ$ ;  $45^\circ$  and  $30^\circ$ . It can be seen immediately that the time required to reach photochemical equilibrium conditions is less than one day at the stratopause and more than 10 years at 20 km. It is very well known that the ozone concentration in the lower stratosphere does not reach equilibrium conditions and that its vertical and horizontal distribution depends on its transport conditions. Thus, there are important differences between the upper and lower stratosphere; below the stratopause photochemical equilibrium conditions can be considered and above the tropopause a complete departure from steady state conditions must be observed. The results of the calculation of the ozone concentration under photoequilibrium conditions in an oxygen atmosphere are shown in Fig. 3; it is seen that it is difficult to obtain agreement between the calculated values and an average value (Krueger, 1973) representing the observations. In the upper stratosphere, the limits of the observational and theoretical uncertainties are such that the effect of hydrogen and nitrogen

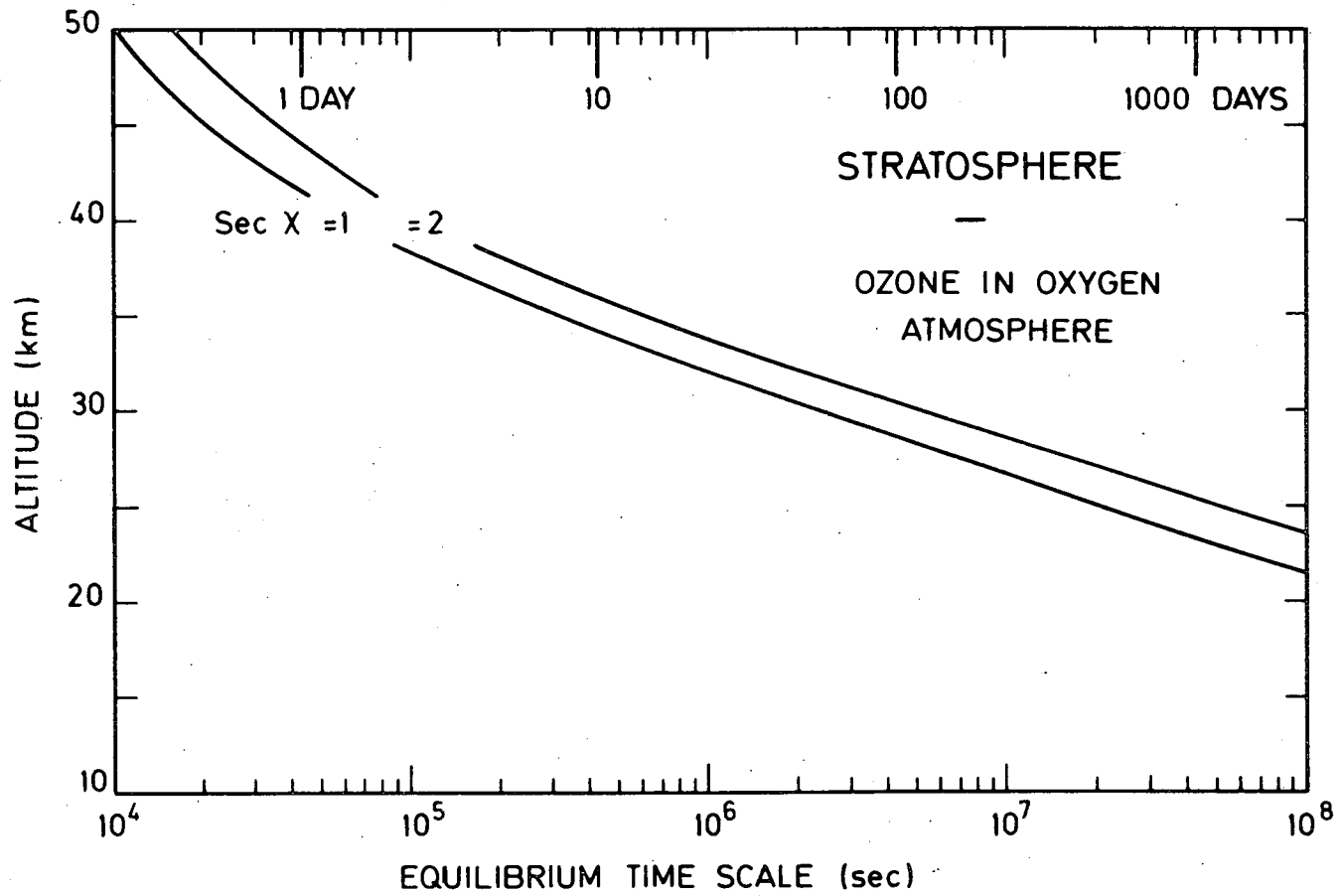


Fig. 2a.- Equilibrium time scales for ozone in a pure oxygen atmosphere. Less than one day above 45 km, more than one year below 25 km. (Daytime). Overhead sun, sec  $\chi = 1$ , and  $30^\circ$ , sec  $\chi = 2$ .

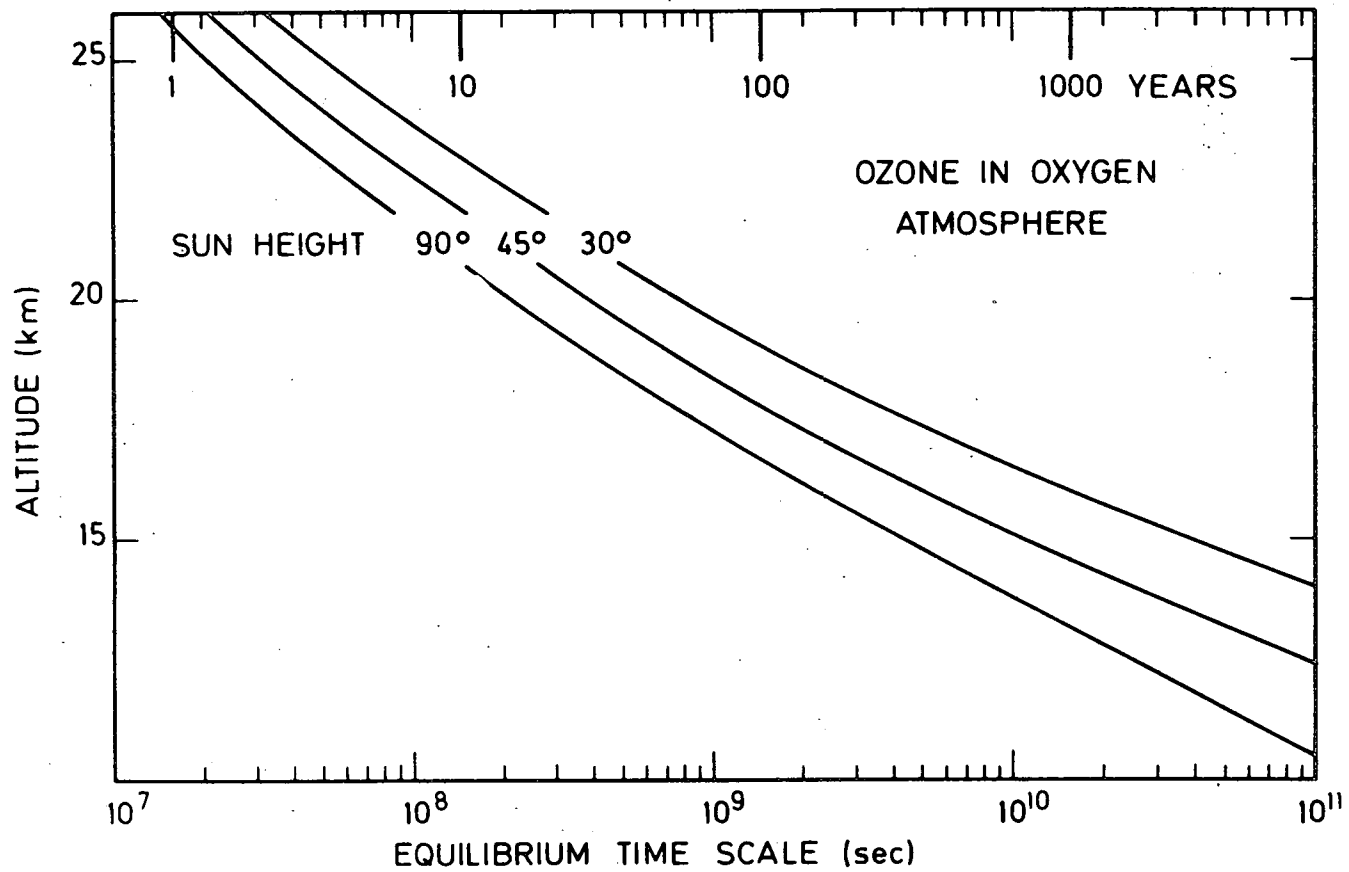


Fig. 2b.- Equilibrium time scales for ozone of a pure oxygen atmosphere in the lower stratosphere for various solar heights 90°, 45° and 30°. With times greater than one year, there is always departure from photoequilibrium conditions.

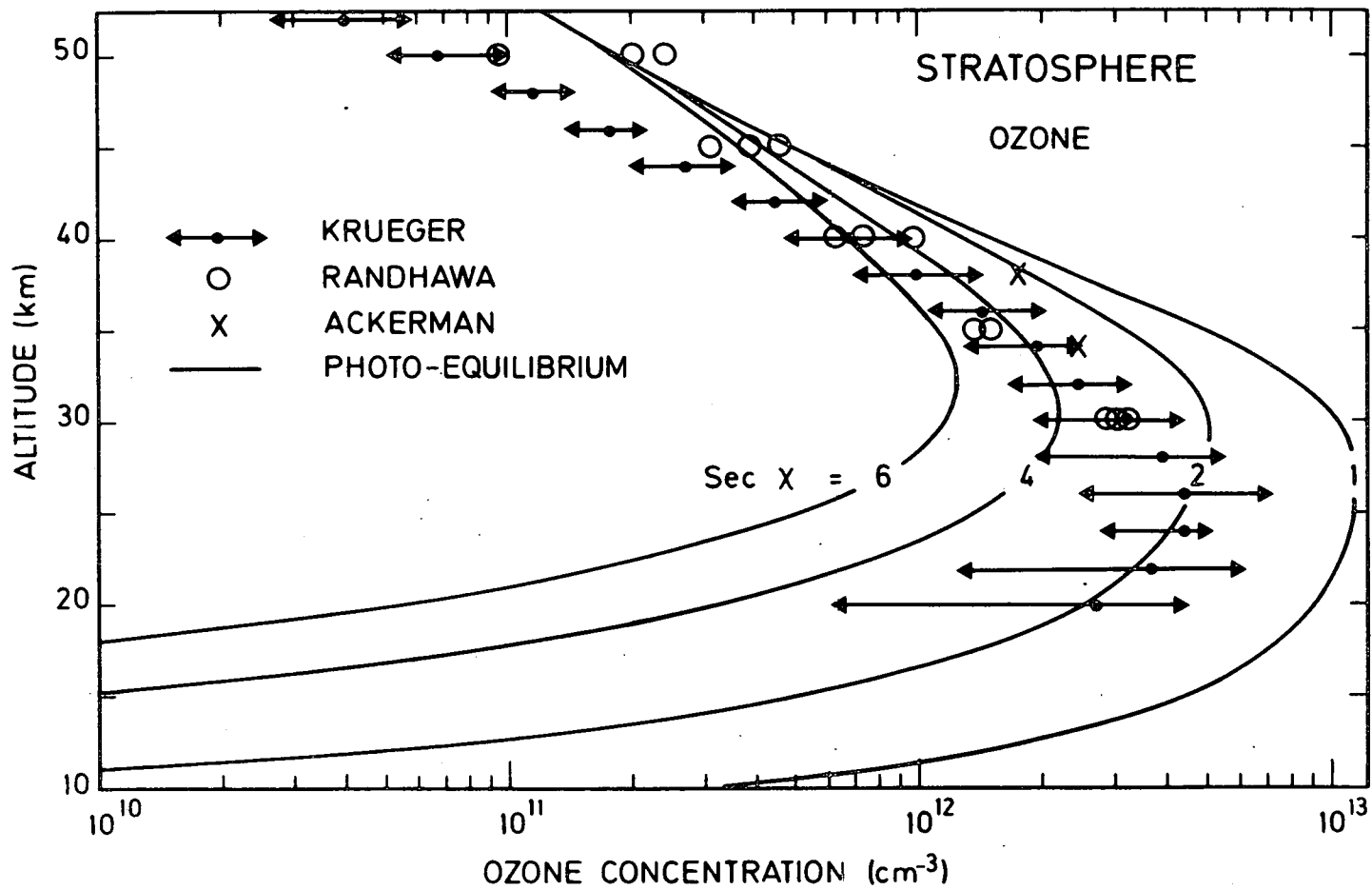


Fig. 3.- Observed and calculated ozone profiles. Calculations for various solar zenith angles,  $\text{sec } \chi = 1, 2, 4$  and  $6$ , photoequilibrium conditions. Range in ozone concentrations observed by Krueger (1973) of 24 rocket flights between  $58^{\circ}\text{S}$  and  $64^{\circ}\text{N}$ . Three observations by Randhawa (1973) over White Sands and two observations by Ackerman (1973) over Aire-sur-l'Adour, France.

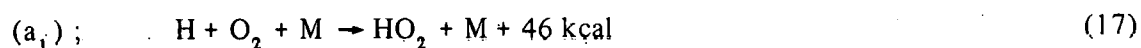


compounds must be taken into account.

### 3. REACTIONS IN A HYDROGEN-OXYGEN ATMOSPHERE

Inspection of the reactions introduced by Bates and Nicolet (1950c) indicates that, in the mesosphere and stratosphere, a large number of them can be ignored since their rate coefficients are sufficiently small.

In the stratosphere and mesosphere, a three-body reaction involving atomic hydrogen and molecular oxygen leads to hydroperoxyl radicals

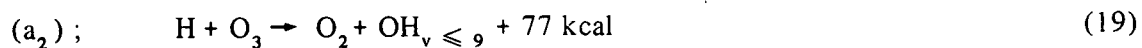


The rate coefficient based on recent measurements (Kurylo, 1973; Wong and Davis, 1973) is

$$a_1 = 2.1 \times 10^{-32} e^{290/T} \text{ cm}^6 \text{ sec}^{-1} \quad (18)$$

corresponding to  $5.5 \times 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$  at 300°K. The resulting life-time of a hydrogen atom is of the order of 0.1 sec at the stratopause.

In the upper stratosphere and mesosphere the reaction of H with O<sub>3</sub> is also important ;

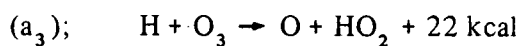


has practically no activation energy (Kaufman 1964, 1966). Only one experimental value has been obtained (Philips and Shiff, 1962); it is

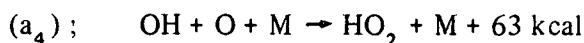
$$a_2 = (2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}. \quad (20)$$

It may be concluded that hydrogen atoms are immediately transformed into hydroperoxyl radicals in the major part of the stratosphere since reaction (17) is rapid. However, in the

neighbourhood of the stratopause and in the mesosphere, reaction (19) which leads to OH has an important role. The production of hydroperoxyl radicals which occurs by



with a rate coefficient  $a_3$ , which has not been measured, and by a three-body association



with a conventional value of the three-body rate coefficient,  $a_4$ , is neglected.

An important reaction in the mesosphere and at the stratopause level which forms a chain leading to the reformation of oxygen molecules with the production of hydrogen atoms, in conjunction with reaction (19) is the bimolecular process

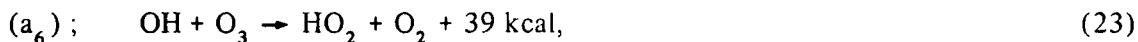


Laboratory data (Clyne and Thrush, 1963; Kaufman 1964, 1969; Breen and Glass, 1970; Westenberg *et al.*, 1970) indicate values between 5 and  $3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . A value such as

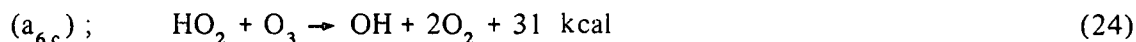
$$a_5 = (4 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (22)$$

may be considered as a working value with a possible error of  $\pm 50$  percent. At and above the stratopause the lifetime of the OH radical is less than 1 sec.

It is clear that reaction (21), if it is rapid in the mesosphere, is relatively slow in the lower stratosphere where other processes involving ozone are more important. The chain reaction introduced by McGrath and Norrish (1958),



and



must be finally considered after having been rejected (Nicolet, 1970a). Very recent measurements have been reported. (Anderson and Kaufman, 1973; DeMore, 1973; Simonaitis and Heicklen, 1973c).

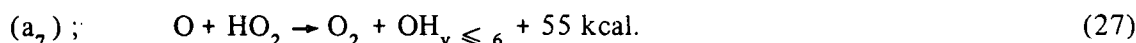
$$a_6 = 1.3 \times 10^{-12} e^{-950/T} \text{ cm}^3 \text{ sec}^{-1} \quad (25)$$

which leads to  $(5.5 \pm 1.5) \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$  at room temperature (Anderson and Kaufman 1973) and to 1 to  $2 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$  at temperatures of the lower stratosphere. Such values are less than the values which were used in previous aeronomic studies. An upper limit  $a_6 \leq 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at room temperature (Kaufman, 1964) was adopted as the actual value in the stratosphere (Hampson 1966; Hunt 1966; Dütsch 1968; Hesstvedt 1968; Leovy 1969; Shimazaki and Laird, 1970). Reaction (24) which was introduced in the analysis of the stratosphere with a rate coefficient  $a_{6c} = 5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$  leads, according to Simonaitis and Heicklen (1973d), to

$$a_{6c} = 3.3 \times 10^{-14} e^{-1000/T} \text{ cm}^3 \text{ sec}^{-1} \quad (26)$$

which gives a value of  $1.25 \times 10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  at room temperature and to low values of between 3 and  $6 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$  in the lower stratosphere.

Instead of reaction (24) in the upper stratosphere and mesosphere the reaction leading to OH involves atomic oxygen (Kaufman, 1964),



No measurement of reaction (27) has yet been made. Considering the work of Foner and Hudson (1962), Kaufman (1964) has suggested that  $a_7 \geq 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ . Reactions (21) and (27) must be compared since they represent, in the upper part of the stratosphere and in the mesosphere, the chain reaction which is involved in the ozone destroying mechanism through the direct attack of oxygen atoms and re-formation of oxygen molecules. The

following value adopted here for  $a_7$

$$a_7 = 1 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (28)$$

has no special support, since according to a recent analysis of the  $\text{HO}_2$  reactions by Hochanadel *et al.* (1972), their experimental results can be simulated if a value of the order of  $7 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  is used for  $a_7$ . Experimental data are needed in order to determine the ratio  $a_5/a_7$  which must be known exactly for the calculation of the ratio  $n(\text{HO}_2)/n(\text{OH})$  in the upper stratosphere and mesosphere

In the mesosphere, where  $n(\text{O}) > n(\text{O}_3)$ , the differential equation for atomic oxygen is written (Nicolet, 1970b),

$$\begin{aligned} \frac{dn(\text{O})}{dt} + 2n^2(\text{O}) \left[ k_1 n(\text{M}) + \frac{k_3 k_2 n(\text{M}) n(\text{O}_2)}{J_{3a}} \right] + \\ + n(\text{O}) \left[ a_2 n(\text{H}) \frac{k_2 n(\text{M}) n(\text{O}_2)}{J_{3a}} + a_5 n(\text{OH}) + a_7 n(\text{HO}_2) \right] = 2n(\text{O}_2) J_2 \end{aligned} \quad (29)$$

$$\text{with } \frac{n(\text{O}_3)}{n(\text{O})} = \frac{k_2 n(\text{M}) n(\text{O}_2)}{J_3 + k_3 n(\text{O}) + a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2)} \equiv \frac{k_2 n(\text{M}) n(\text{O}_2)}{J_{3a}} \quad (30)$$

$$\text{and } J_{3a} \cong J_3 + a_2 n(\text{H}) \quad (31)$$

Such an equation (30) corresponds to photochemical equilibrium conditions in the lower thermosphere and in the upper mesosphere. Numerical calculations near the mesopause level show that the rate coefficients are too small to lead to photochemical equilibrium conditions for atomic oxygen. Its vertical distribution in the lower thermosphere is subject to vertical transport conditions controlled by eddy diffusion. A possible approximation for equation (29) is

$$\frac{dn(O)}{dt} + \left[ a_2 n(H) \frac{k_2 n(M) n(O_2)}{J_{3a}} + a_5 n(OH) + a_7 n(HO_2) \right] n(O) = 2n(O_2) J_2 \quad (32)$$

or even

$$\frac{dn(O)}{dt} + \left[ a_2 n(H) \frac{k_2 n(M) n(O_2)}{J_3 + a_2 n(H)} \right] n(O) = 2n(O_2) J_2 \quad (33)$$

at the mesopause. The minimum which is observed near 75 km in the ozone concentration by Hays and Roble (1973) is due to the action of atomic hydrogen; the net effect of the action of hydroxyl and hydroperoxyl radicals on atomic oxygen is an important decrease of the ozone concentration.

In the region where atomic oxygen is in photochemical equilibrium, the conventional stratospheric equation (14) indicates that photochemical equilibrium values can be reached in the lower mesosphere and upper stratosphere. Below 35 km, the times required become too long and departures from equilibrium conditions must exist. However, (14) must be replaced in a hydrogen-oxygen atmosphere (Nicolet, 1966, 1971) by

$$\begin{aligned} \frac{dn(O_3)}{dt} + 2n^2(O_3) \frac{J_3 k_3}{k_2 n(M) n(O_2)} + n(O_3) a_2 n(H) + \\ n(O_3) \left[ a_6 + \frac{a_5 J_3}{k_2 n(M) n(O_2)} \right] n(OH) + n(O_3) \left[ a_{6c} + \frac{a_7 J_3}{k_2 n(M) n(O_2)} \right] n(HO_2) = \\ 2n(O_2) J_2 \end{aligned} \quad (34)$$

in which the effect of H, OH and HO<sub>2</sub> is represented by the symbol a from reactions (19), (21), (23), (24) and (27). If (34) is compared with (14), it is clear that the effect of hydrogen compounds is equivalent to an increase in the photodissociation coefficient J<sub>3</sub>. In other words, the ozone dissociation is increased by additional processes involving H, OH and HO<sub>2</sub> so that the equivalent O<sub>3</sub> photodissociation coefficient is written (Nicolet, 1971)

$$J_{3A} = J_3 [1 + A] \quad (35)$$

where A is given by

$$2 J_3 k_3 n(O_3) A = a_2 n(H) k_2 n(M) n(O_2) + a_5 n(OH) \left[ 1 + \frac{a_6}{a_5} \frac{k_2 n(M) n(O_2)}{J_3} \right] \\ + a_7 n(HO_2) \left[ 1 + \frac{a_{6c}}{a_5} \frac{k_2 n(M) n(O_2)}{J_3} \right] \quad (36)$$

By assuming reasonable numerical values, it is easy to see (Fig. 4) that  $a_6 k_2 n(M) n(O_2) / a_5 J_3 < 1$  and  $a_{6c} k_2 n(M) n(O_2) / a_7 J_3 < 1$  in the upper stratosphere and mesosphere and  $> 1$  in the lower stratosphere. Thus, at the stratopause, the conventional equation for equilibrium conditions is

$$n(O_3) = \left[ \frac{k_2}{k_3} n(M) n^2(O_2) \frac{J_2}{J_3 (1 + A)} \right]^{1/2} \quad (37)$$

with the correction term,  $n(H)$  being negligible,

$$[1 + A]^{1/2} = \left[ 1 + \frac{a_5 n(OH) + a_7 n(HO_2)}{2k_3 n(O_3)} \right]^{1/2} \quad (38)$$

By assuming that the values of  $n(OH)$  and  $n(HO_2)$  are known, it can be shown that the correction term can be applied in the mesosphere and at the stratopause where  $2k_3 n(O_3) \cong a_5 n(OH) + a_7 n(HO_2)$ . Below the stratopause it is difficult to see how a correction term could be introduced except if the  $OH$  and  $HO_2$  concentrations were increased by a factor of five, at least. In the lower stratosphere, equation (34) becomes

$$\frac{dn(O_3)}{dt} + n(O_3) \left[ 2k_3 n(O) + a_6 n(OH) + a_{6c} n(HO_2) \right] = 2n(O_2) J_2 \quad (39)$$

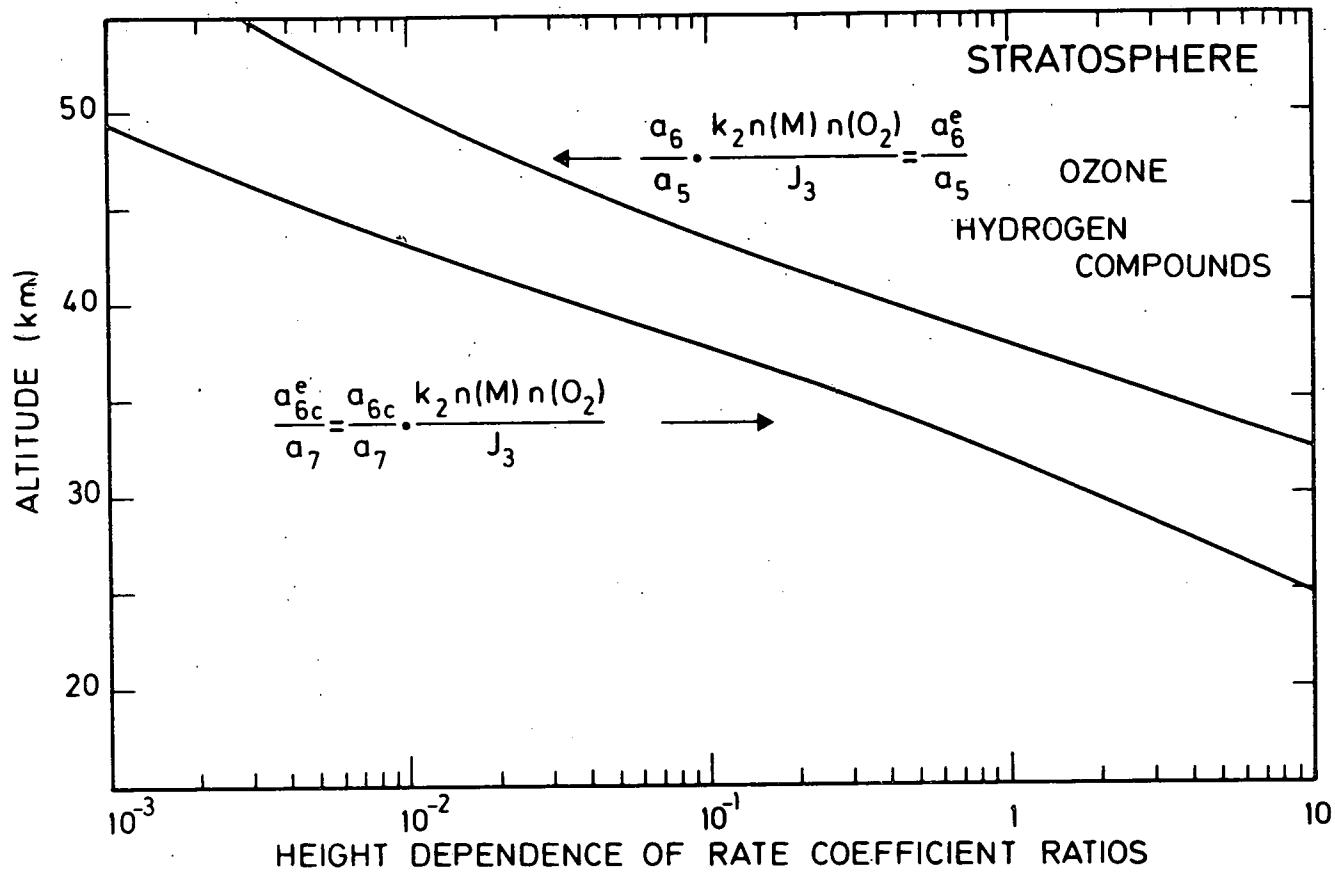


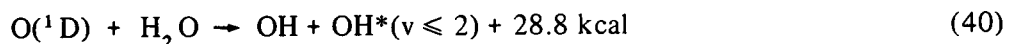
Fig. 4.- Action of the various rate coefficients in the stratosphere defined by the ratios of rate coefficients of reactions of OH and HO<sub>2</sub> with ozone and atomic oxygen. The height dependence indicates that in the lower stratosphere reactions of OH and HO<sub>2</sub> with ozone are more important than reactions with atomic oxygen which play a role only in the neighbourhood of the stratopause.

By assuming that the values of  $n(\text{OH})$  and  $n(\text{HO}_2)$  are known, it is possible to see (Fig. 5) that the effect of hydroxyl and hydroperoxyl radicals can be considered in the lower stratosphere as loss processes for ozone. However, since the maximum value of the loss coefficient is, between 15 and 25 km, of the order of  $10^{-8} \text{ sec}^{-1}$  for  $\text{sec } \chi = 1$  and  $10^{-9} \text{ sec}^{-1}$  for  $\text{sec } \chi = 2$  the times which are required to reach chemical equilibrium are longer than one year. An increase of  $n(\text{OH})$  or  $n(\text{HO}_2)$  would be necessary in order to reduce the time to less than one year.

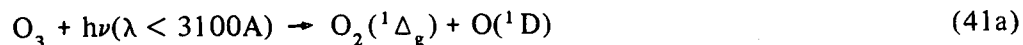
#### 4. PRODUCTION OF HYDROXYL AND HYDROPEROXYL RADICALS

Water vapor can be dissociated by sunlight and its photodissociation coefficient for zero optical depth is  $10^{-5} \text{ sec}^{-1}$ . The photodissociation occurs in the upper mesosphere due to the effect of Lyman- $\alpha$  and goes to the lower mesosphere by absorption in the spectral range of the Schumann-Runge bands. The photodissociation rate coefficient decreases in the mesosphere by a factor of the order of 1000, since it reaches about  $10^{-8} \text{ sec}^{-1}$  at the stratopause.

In the stratosphere, the photodissociation process is less important than the oxidation process. An effect caused by oxygen atoms, in their normal state  $^3\text{P}$ , on  $\text{H}_2\text{O}$  has not been detected since the reaction is endothermic, but atoms in their first excited state  $^1\text{D}$  lead to (Engleman, 1965)



The production of  $\text{O}(^1\text{D})$  atoms by photolysis of stratospheric ozone is important. A precise determination depends on the exact efficiency of  $\text{O}(^1\text{D})$  production in the processes



and



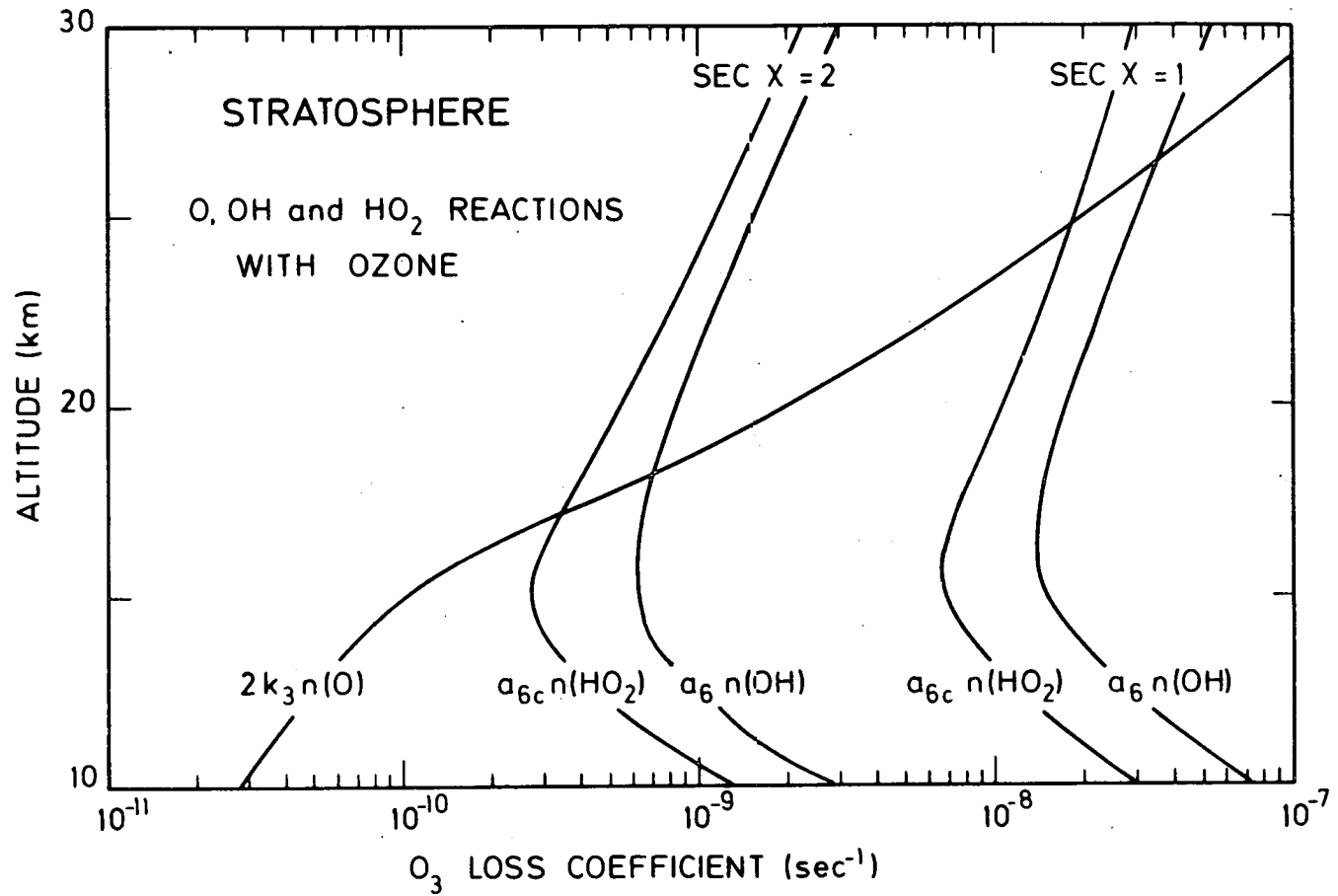
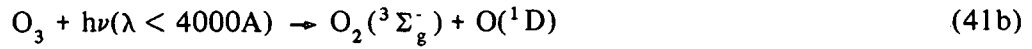


Fig. 5.- Comparison between the various reactions (with O, OH and HO<sub>2</sub>) leading to the destruction of ozone molecules. Effect of OH and HO<sub>2</sub> is particularly important in the lower stratosphere for overhead sun conditions.



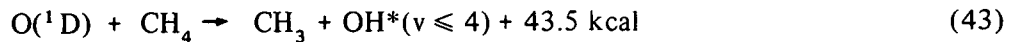
According to DeMore and Raper (1966), all oxygen atoms are O(<sup>1</sup>D) at  $\lambda \leq 3100\text{\AA}$ ; for  $\lambda > 3100\text{\AA}$  there is a drop in the efficiency leading to O(<sup>3</sup>P) atoms at 3340\text{\AA} (Jones and Wayne, 1969). At 3130\text{\AA} and 25°C the efficiency for O(<sup>1</sup>D) production was found to be 0.5 (Simonaitis *et al.*, 1973). However, at stratospheric temperatures it becomes very small (Lin and Demore, 1973). We may consider (Nicolet, 1972) the following working value for the quenching rate coefficient

$$k_Q(^1\text{D}) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (42)$$

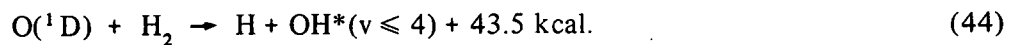
due to N<sub>2</sub> and O<sub>2</sub> which is an average value between the maximum value of  $8 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$  and the minimum value  $3 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ .

With the average value  $k_Q(^1\text{D}) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ , the production rate of O(<sup>1</sup>D) atoms leads to photoequilibrium concentrations for various solar zenith angles which are illustrated in Fig. 6 for a conventional vertical distribution of O<sub>3</sub> (Nicolet, 1971). In the lower stratosphere, the concentration n(O<sup>1</sup>D) is of the order of 1 and a peak concentration of more than 100 cm<sup>-3</sup> occurs near the stratopause. At the stratopause, the variation is small with solar zenith angle, but is very important in the lower stratosphere due to the sensitivity on the spectral efficiency of wavelengths near 3100\text{\AA}.

The reaction of O(<sup>1</sup>D) occurs not only with H<sub>2</sub>O, but also with CH<sub>4</sub> and H<sub>2</sub>



and



Thus, the presence of O(<sup>1</sup>D) atoms leads to the production of H atoms and OH radicals by H<sub>2</sub>O, H<sub>2</sub> and CH<sub>4</sub> in the troposphere and stratosphere without a direct photodissociation process. Recent experimental analysis (Young *et al.*, 1968; Donovan *et al.*, 1970;

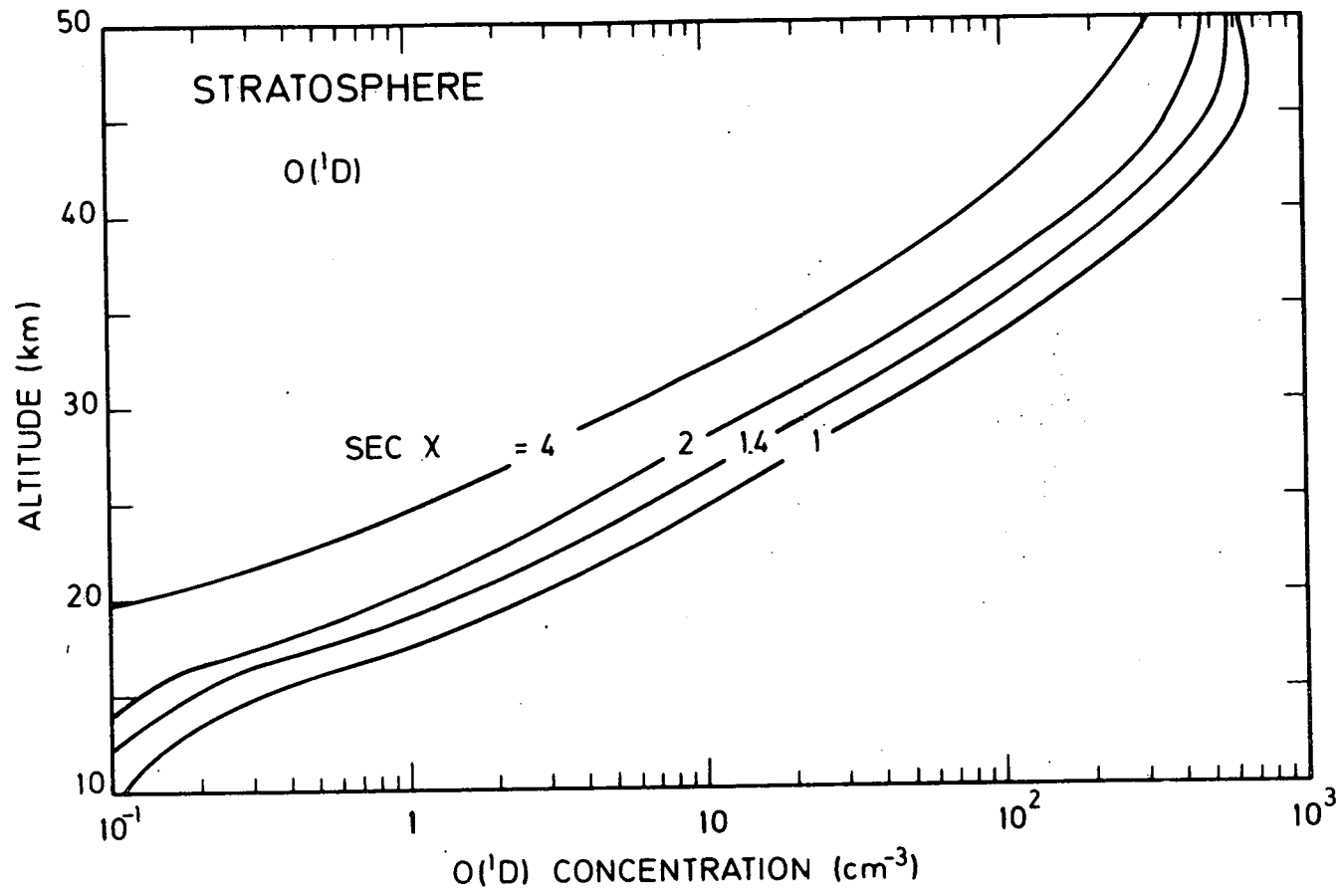


Fig. 6.- Concentration of oxygen atoms in the excited state <sup>1</sup>D produced by ozone photodissociation. Variation with solar zenith angle for a constant ozone concentration.

Paraskevopoulos and Cvetanovic, 1970; Simonaitis and Heicklen, 1973a, b; Greenberg and Heicklen, 1972; Heidner and Husain, 1973) leads to a rate coefficient a

$$a^* = (3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (45)$$

The production of HO radicals is illustrated in Fig 7 where the minimum occurs at the tropopause chosen here at 15 km.

### 5. REACTIONS IN A NITROGEN-OXYGEN ATMOSPHERE

The theory of nitric oxide in the upper atmosphere is based on the ionospheric properties in the F and E regions (Norton and Barth, 1970; Strobel *et al.*, 1970; Nicolet 1970c; Strobel, 1971a, 1971b). Ionic reactions lead to excited atoms  $N(^2D)$  which react with  $O_2$  in order to form nitric oxide molecules. In the stratosphere, the reaction of the electronically excited oxygen atom  $O(^1D)$  with nitrous oxide (Nicolet, 1970b; Nicolet and Vergison, 1971; Crutzen, 1971; McElroy and McConnell, 1971; Nicolet and Peetermans, 1972; Johnston, 1972), is a natural source of nitric oxide. As far as cosmic rays are concerned (Warneck 1972; Nicolet and Peetermans, 1972) they must be also considered as a source particularly at high latitude since the production of nitrogen atoms is of the order of 1 atom per ion pair. Another source of nitric oxide at low levels (McElroy and McConnell, 1973; Stuhl, 1973) is the reaction of OH radicals with  $NH_3$ ; depending on its concentration in the stratosphere, ammonia may be an additional source of nitric oxide in the lower stratosphere.

If we consider the various reactions which are involved in the mesosphere and stratosphere (Nicolet, 1965; Crutzen, 1971; Johnston, 1971a, b; Levy, 1973), we must write



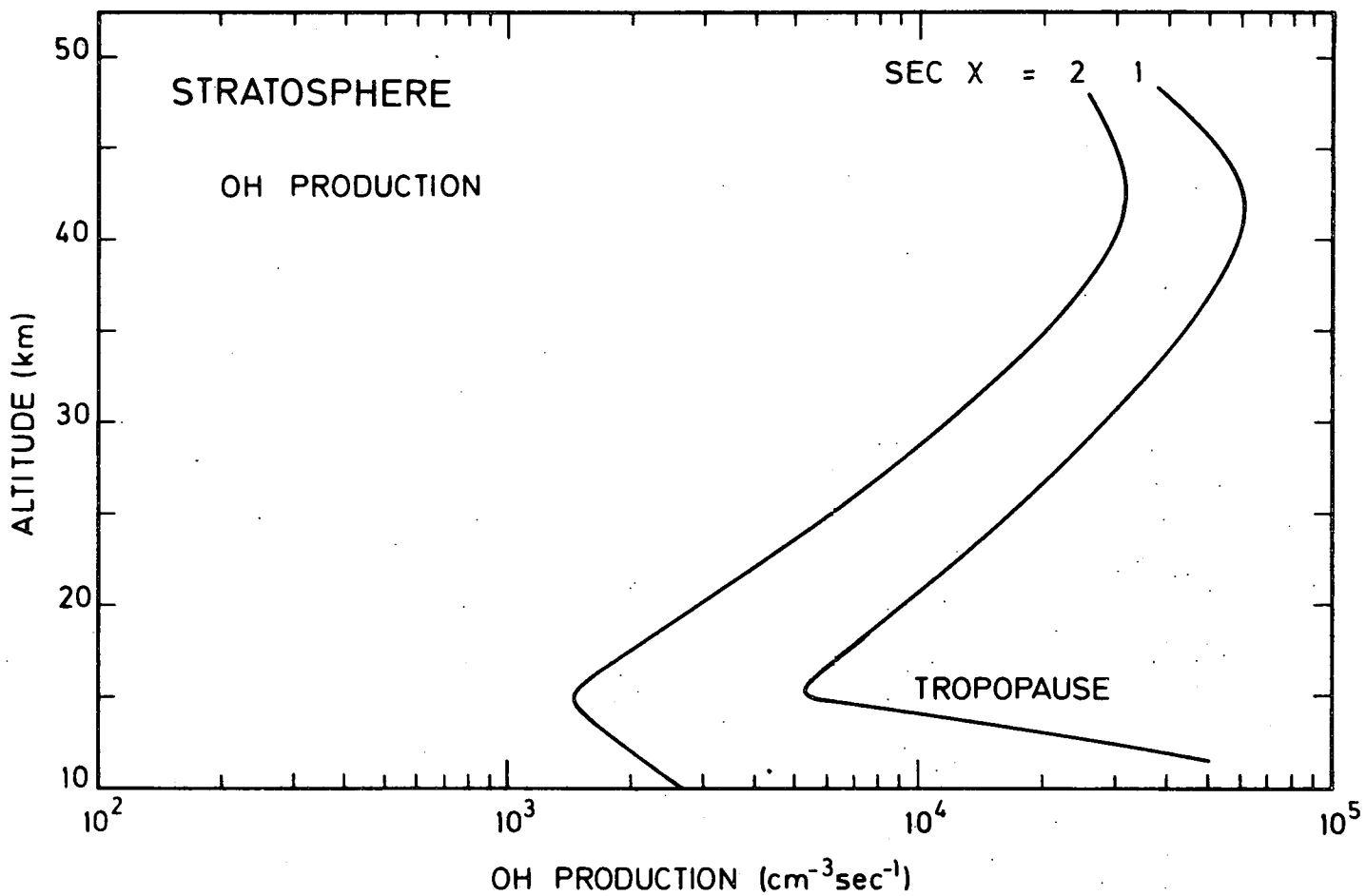
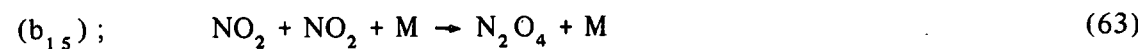
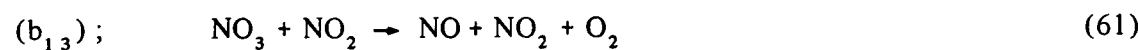
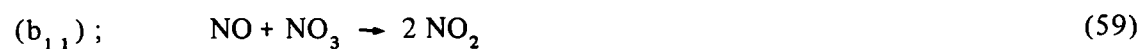
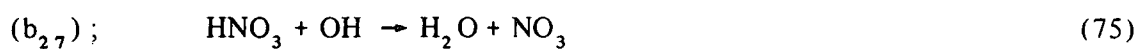
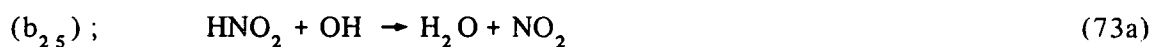
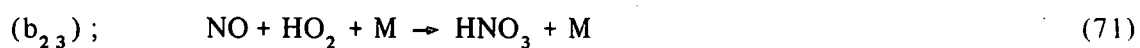
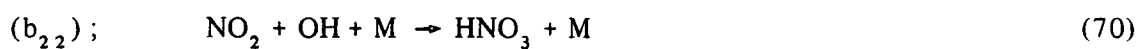
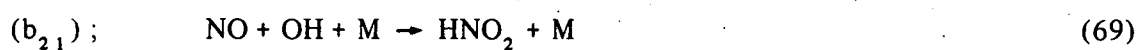
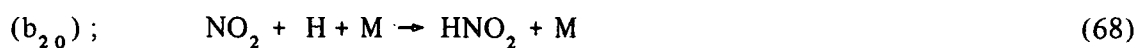
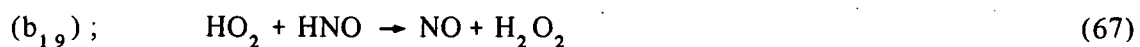
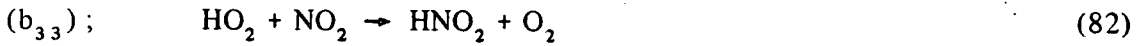
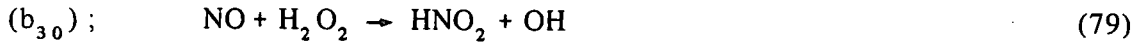


Fig. 7.- Production of OH radicals in the stratosphere by reaction of O(<sup>1</sup>D) atoms with H<sub>2</sub>O (4ppmv), CH<sub>4</sub> (1.5 ppmv) and H<sub>2</sub> (0.5 ppmv) for two solar zenith angles, sec χ = 1 and 2.







The various differential photochemical equations are written as follows: (neglecting reactions with atomic hydrogen and very slow reactions)

$$\frac{dn(\text{N}_2\text{O}_5)}{dt} + n(\text{N}_2\text{O}_5) \left[ b_{32} + b_{31} n(\text{H}_2\text{O}) \right] = b_{12} n(\text{M}) n(\text{NO}_2) n(\text{NO}_3) \quad (83)$$

$$\begin{aligned} \frac{dn(\text{NO}_3)}{dt} + n(\text{NO}_3) \left[ J_{\text{NO}_2-\text{O}} + J_{\text{NO}-\text{O}_2} + b_{11} n(\text{NO}) + b_{12} n(\text{M}) n(\text{NO}_2) \right] \\ = n(\text{NO}_2) \left[ b_9 n(\text{O}_3) + b_{10} n(\text{M}) n(\text{O}) \right] + b_{27} n(\text{OH}) n(\text{HNO}_3) + b_{32} n(\text{N}_2\text{O}_5) \end{aligned} \quad (84)$$

$$\begin{aligned} \frac{dn(\text{HNO}_3)}{dt} + n(\text{HNO}_3) \left[ J_{\text{OH}-\text{NO}_2} + b_{27} n(\text{OH}) \right] = b_{22} n(\text{M}) n(\text{OH}) n(\text{NO}_2) + \\ 2 b_{31} n(\text{H}_2\text{O}) n(\text{N}_2\text{O}_5) \end{aligned} \quad (85)$$

$$\begin{aligned} \frac{dn(\text{HNO}_2)}{dt} + n(\text{HNO}_2) \left[ J_{\text{OH}-\text{NO}} + J_{\text{H}-\text{NO}_2} + b_{25} n(\text{OH}) \right] = b_{21} n(\text{M}) n(\text{NO}) n(\text{OH}) \\ + b_{33} n(\text{NO}_2) n(\text{HO}_2) \end{aligned} \quad (86)$$



$$\begin{aligned}
& \frac{dn(\text{NO}_2)}{dt} + n(\text{NO}_2) \left[ J_{\text{NO}_2} + b_3 n(\text{O}) + b_{10} n(\text{M}) n(\text{O}) + b_{12} n(\text{M}) n(\text{NO}_3) + 2b_{15} \right. \\
& \left. n(\text{M}) n(\text{NO}_2) + b_{22} n(\text{M}) n(\text{OH}) + b_{33} n(\text{HO}_2) \right] = \\
& n(\text{HNO}_2) \left[ J_{\text{H-NO}_2} + b_{25} n(\text{OH}) \right] = n(\text{HNO}_3) J_{\text{OH-NO}_2} + n(\text{NO}_3) J_{\text{NO}_2-\text{O}} + b_{32} n(\text{N}_2\text{O}_5) + \\
& n(\text{NO}) \left[ b_2 n(\text{M}) n(\text{O}) + b_4 n(\text{O}_3) + 2b_{11} n(\text{NO}_3) + b_{29} n(\text{HO}_2) + c_{5c} n(\text{CH}_3\text{O}_2) \right] \quad (87)
\end{aligned}$$

$$\begin{aligned}
& \frac{dn(\text{NO})}{dt} + n(\text{NO}) \left[ J_{\text{NO}} + b_2 n(\text{M}) n(\text{O}) + b_6 n(\text{N}) + b_4 n(\text{O}_3) + b_{11} n(\text{NO}_3) + b_{21} n(\text{M}) \right. \\
& \left. n(\text{OH}) + b_{29} n(\text{HO}_2) + c_{5c} n(\text{CH}_3\text{O}_2) \right] = b_1 n(\text{M}) n(\text{O}) n(\text{N}) + 2b_5 n(\text{N}) n(\text{NO}_2) \\
& + b_7 n(\text{N}) n(\text{O}_2) + b_8 n(\text{N}) n(\text{O}_3) + n(\text{NO}_2) J_{\text{NO}_2} + b_3 n(\text{O}) n(\text{NO}_2) + \\
& n(\text{NO}_3) J_{\text{NO-O}_2} + n(\text{HNO}_2) J_{\text{OH-NO}} + P(\text{NO}) \quad (88)
\end{aligned}$$

$$\begin{aligned}
& \frac{dn(\text{N})}{dt} + n(\text{N}) \left[ b_1 n(\text{M}) n(\text{O}) + b_6 n(\text{NO}) + b_7 n(\text{O}_2) + b_8 n(\text{O}_3) \right] = \\
& n(\text{NO}) J_{\text{NO}} + P(\text{N}). \quad (89)
\end{aligned}$$

In these equations, reaction of NO with  $\text{CH}_3\text{O}_2$  producing  $\text{NO}_2$  is introduced;  $P(\text{N})$  is the direct production of nitrogen atoms and  $P(\text{NO})$  is the direct production of nitric oxide molecules.

By combining all equations, we write the differential equation for odd nitrogen

$$\begin{aligned}
& \frac{dn(\text{N})}{dt} + \frac{dn(\text{NO})}{dt} + \frac{dn(\text{NO}_2)}{dt} + \frac{dn(\text{NO}_3)}{dt} + 2 \frac{dn(\text{N}_2\text{O}_5)}{dt} + \frac{dn(\text{HNO}_2)}{dt} + \frac{dn(\text{HNO}_3)}{dt} \\
& = P(\text{N}) + P(\text{NO}) - 2 b_6 n(\text{N}) n(\text{NO}). \quad (90)
\end{aligned}$$

Considering photoequilibrium conditions, (87) becomes

$$\begin{aligned}
 & n(\text{NO}_2) \left[ J_{\text{NO}_2} + b_3 n(\text{O}) + 2 b_{15} n(\text{M}) n(\text{NO}_2) \right] + \\
 & n(\text{NO}_3) J_{\text{NO}_3} + n(\text{HNO}_2) J_{\text{OH}\cdot\text{NO}} \\
 & = n(\text{NO}) \left[ b_2 n(\text{M}) n(\text{O}) + b_4 n(\text{O}_3) + b_{11} n(\text{NO}_3) + b_{21} n(\text{M}) n(\text{OH}) + b_{29} n(\text{HO}_2) \right. \\
 & \left. + c_{5c} n(\text{CH}_3\text{O}_2) \right] \tag{91}
 \end{aligned}$$

If we consider reactions (46) to (57) with rate coefficient  $b_1$  to  $b_{10}$ , we can see that they play a role in the atomic oxygen ozone chemistry. Equations are as follows

$$\begin{aligned}
 \frac{dn(\text{O}_3)}{dt} + n(\text{O}_3) \left[ J_3 + k_3 n(\text{O}) + a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2) + \right. \\
 \left. b_4 n(\text{NO}) + b_8 n(\text{N}) + b_9 n(\text{NO}_2) \right] = k_2 n(\text{M}) n(\text{O}_2) \tag{92}
 \end{aligned}$$

$$\begin{aligned}
 \frac{dn(\text{O})}{dt} + n(\text{O}) \left[ k_2 n(\text{M}) n(\text{O}_2) + k_3 n(\text{O}_3) + a_5 n(\text{OH}) + a_7 n(\text{HO}_2) + a_{31} n(\text{H}_2\text{O}_2) \right. \\
 \left. + b_1 n(\text{M}) n(\text{N}) + b_2 n(\text{M}) n(\text{NO}) + b_3 n(\text{NO}_2) + b_{10} n(\text{M}) n(\text{NO}_2) \right] = \\
 2n(\text{O}_2) J_2 + n(\text{O}_3) J_3 + n(\text{NO}) J_{\text{N}\cdot\text{O}} + n(\text{NO}_2) J_{\text{NO}_2} + n(\text{NO}_3) J_{\text{NO}_3} \\
 + n(\text{N}) \left[ b_6 n(\text{NO}) + b_7 n(\text{NO}_2) \right] \tag{93}
 \end{aligned}$$

Since  $dn(\text{O})/dt = 0$  in the stratosphere, (92) and (93) can be written if (91) is introduced

$$\begin{aligned}
 \frac{dn(\text{O}_3)}{dt} + n(\text{O}_3) \left[ a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2) + b_9 n(\text{NO}_2) \right] \\
 + n(\text{O}) \left[ a_5 n(\text{OH}) + a_7 n(\text{HO}_2) + \left\{ 2b_3 + b_{10} n(\text{M}) \right\} n(\text{NO}_2) \right]
 \end{aligned}$$

$$\begin{aligned}
& + n(\text{NO}_2) 2b_{15} n(\text{M}) n(\text{O}_2) + n(\text{NO}_3) J_{\text{NO-O}_2} + n(\text{HNO}_2) J_{\text{OH-NO}} = \\
& 2n(\text{O}_2) J_2 + n(\text{NO}) \left[ J_{\text{NO-O}} + b_{11} n(\text{NO}_3) + b_{29} n(\text{HO}_2) + b_{21} n(\text{M}) n(\text{OH}) \right. \\
& \left. + c_{5c} n(\text{CH}_3\text{O}_2) \right] + n(\text{NO}_3) J_{\text{NO}_2-\text{O}} \quad (94)
\end{aligned}$$

Replacing  $n(\text{O})$  by its equilibrium value from (93), neglecting the term  $2b_{15} n(\text{M}) n(\text{O}_2) n(\text{NO}_2)$  and writing

$$\begin{aligned}
& k_2 n(\text{M}) n(\text{O}_2) + k_3 n(\text{O}_3) + a_5 n(\text{OH}) + a_7 n(\text{HO}_2) + b_1 n(\text{M}) n(\text{N}) + \\
& b_2 n(\text{M}) n(\text{NO}) + \left\{ b_3 + b_{10} n(\text{M}) \right\} n(\text{NO}_2) \cong k_2 n(\text{M}) n(\text{O}_2) \quad (95)
\end{aligned}$$

the general chemical equation for the ozone concentration in the stratosphere is

$$\begin{aligned}
& \frac{dn(\text{O}_3)}{dt} + \frac{2k_3 J_3}{k_2 n(\text{M}) n(\text{O}_2)} n^2(\text{O}_3) \left[ 1 + \frac{n(\text{NO}_2) J_{\text{NO}_2}}{n(\text{O}_3) J_3} \right] \\
& + n(\text{O}_3) \left\{ \left[ a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2) + b_9 n(\text{NO}_2) \right] + \right. \\
& \left. \frac{J_3}{k_2 n(\text{M}) n(\text{O}_2)} \left[ 1 + \frac{n(\text{NO}_2) J_{\text{NO}_2}}{n(\text{O}_3) J_3} \right] \left[ a_5 n(\text{OH}) + a_7 n(\text{HO}_2) + a_{31} n(\text{H}_2\text{O}_2) + 2b_3 n(\text{NO}_2) \right] \right\} \\
& = 2n(\text{O}_2) J_2 + n(\text{NO}) \left[ 2 J_{\text{NO}} + b_{11} n(\text{NO}_3) + b_{21} n(\text{M}) n(\text{OH}) + b_{29} n(\text{HO}_2) + \right. \\
& \left. c_{5c} n(\text{CH}_3\text{O}_2) \right] - n(\text{HNO}_2) J_{\text{OH-NO}} - n(\text{NO}_3) \left[ J_{\text{NO-O}_2} - J_{\text{NO}_2-\text{O}} \right] \quad (96)
\end{aligned}$$

In the stratosphere, it may be assumed that

$$n(\text{NO}_2) J_{\text{NO}_2} < n(\text{O}_3) J_3 \quad (97)$$

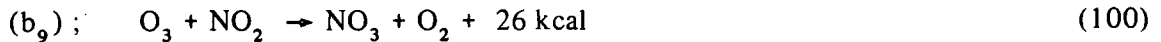
$$a_2 n(\text{H}) < a_6 n(\text{OH}) \quad (98)$$

and the general equation may be simplified :

$$\begin{aligned}
& \frac{dn(O_3)}{dt} + n(O_3) \left[ a_6 n(OH) + a_{6c} n(HO_2) + b_9 n(NO_2) \right] + \\
& \frac{J_3}{k_2 n(M) n(O_2)} \left[ 2k_3 n(O_3) + a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2) + 2b_3 n(NO_2) \right] \\
& = 2n(O_2) J_2 + n(NO) \left[ 2J_{NO} + b_{11} n(NO_3) + b_{21} n(M) n(OH) + b_{29} n(HO_2) + \right. \\
& \left. c_{5c} n(CH_3O_2) \right] - n(HNO_2) J_{OH \cdot NO} - n(NO_3) \left[ J_{NO-O_2} - J_{NO_2 \cdot O} \right] \quad (99)
\end{aligned}$$

If we compare (99) with (34) without the introduction of nitrogen oxide effects, it is clear that we must compare the effect of  $b_9 n(NO_2)$  (nighttime and daytime reaction) with  $a_6 n(OH) + a_{6c} n(HO_2)$  (daytime reactions) and also  $2b_3 n(NO_2)$  with  $2k_3 n(O_3) + a_5 n(OH) + a_7 n(HO_2) + a_{31} n(H_2O_2)$ .

Reaction (55)



has been studied in the laboratory (Johnston and Yost, 1949; Graham 1973). Its rate coefficient which is

$$1.23 \times 10^{-13} e^{-2470/T} \text{ cm}^3 \text{ sec}^{-1} \quad (101)$$

leads to a rate of the order of  $10^{-18} \text{ cm}^3 \text{ sec}^{-1}$  in the lower stratosphere. Nevertheless, such a low value leads to an effect in the lower stratosphere which is of the same order of magnitude as  $a_6 n(OH)$  (see figure 5) for  $n(NO_2)/n(M) = 3 \times 10^{-9}$ . Since reactions of  $NO_2$  with  $O_3$  plays its principal role for nighttime conditions, it seems, that such a reaction cannot be neglected.

As far as reaction (48)



is concerned, its rate coefficient has been determined with high precision by Davis *et al* (1973) and confirmed by Slinger *et al.*(1973) and by Bemand *et al.*(1973). Its value is

$$b_3 = 9.2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (103)$$

which must be used in the stratosphere. In order to compare the effects of reactions (100) and (102),  $b_4$  has been compared with  $b_3 J_3 / k_2 n(M) n(O_2) = b_3^e$ , in Fig. 8. The reaction between atomic oxygen and nitrogen dioxide is generally more important than the reaction between ozone and nitrogen dioxide except near the tropopause where the absolute value of the rate coefficient is only of the order of  $10^{-18} \text{ cm}^3 \text{ sec}^{-1}$ . However, this very small value leads to a more important effect than the action of the reaction between atomic oxygen and ozone. Using the observational values of  $n(\text{NO}_2)$  by Ackerman and Muller (1972) it is possible to make the comparison which is given in the following table.

(km)	$2k_3 n(\text{O}_3) \frac{J_2}{k_2 n(M) n(\text{O}_2)}$	$2b_3 n(\text{NO}_2) \frac{J_2}{k_2 n(M) n(\text{O}_2)}$	$b_9 n(\text{NO}_2)$
10	$3.3 \times 10^{-11}$	$1.3 \times 10^{-8}$	$4.9 \times 10^{-8}$
15	$1.1 \times 10^{-11}$	$2.6 \times 10^{-8}$	$1.2 \times 10^{-8}$
20	$2.2 \times 10^{-9}$	$2.3 \times 10^{-8}$	$2.7 \times 10^{-9}$
25	$3.2 \times 10^{-8}$	$1.6 \times 10^{-7}$	$4.4 \times 10^{-9}$
30	$2.0 \times 10^{-7}$	$4.8 \times 10^{-7}$	$3.4 \times 10^{-9}$

With such numerical values it can be seen (Fig. 9) that the effect of nitrogen oxides is clearly shown in the lower stratosphere. When the sun is overhead, it seems that the action of hydroxyl and hydroperoxyl is of the same order of magnitude as the action of nitrogen oxides. Concentration of  $\text{NO}_2$  greater than  $10^8 \text{ cm}^{-3}$  has a more important role in its reaction with atomic oxygen than with ozone.

If we consider the production term in the general equation (99), there is in addition to the normal production by molecular oxygen  $2n(\text{O}_2) J_2$  a general term depending on

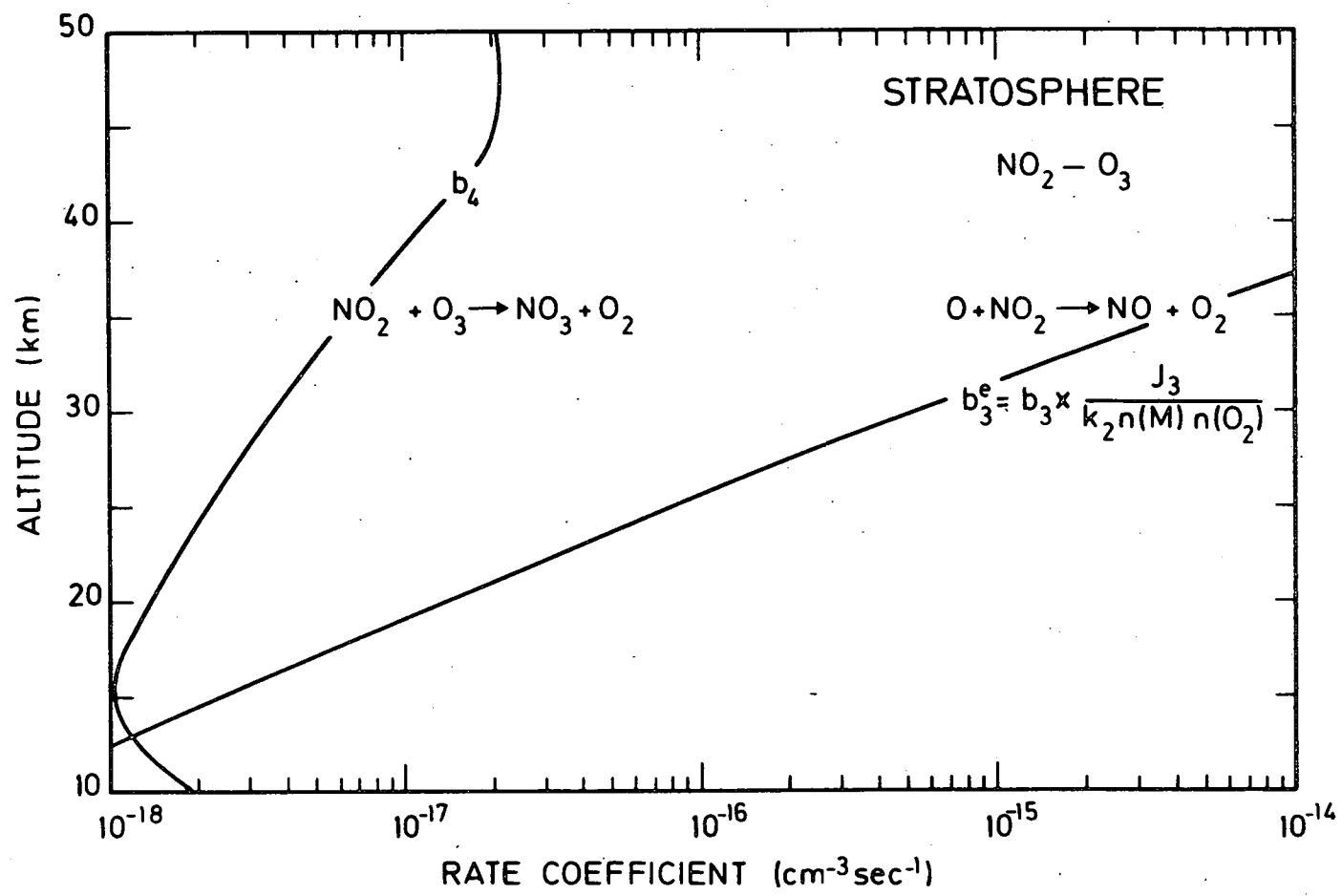


Fig. 8.- Rate coefficients of nitrogen oxide with ozone and atomic oxygen. The equivalent rate coefficient  $b_3^e$  increases with height and is far greater than  $b_4$  in the middle and upper stratosphere.

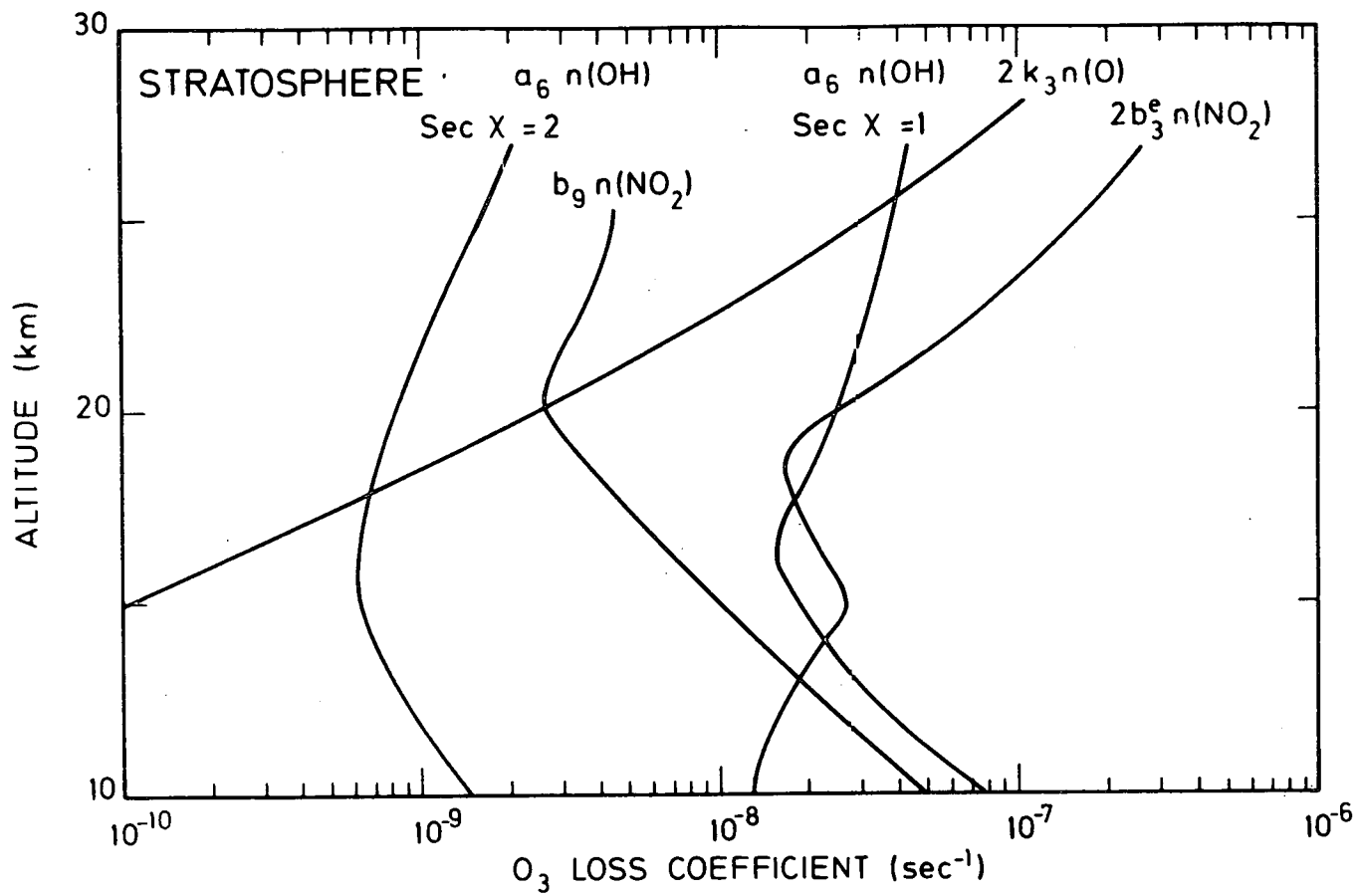


Fig. 9. Comparison of the various loss coefficients of ozone in the lower stratosphere when hydrogen and nitrogen compounds are involved ; The  $\text{NO}_2$  concentration is given by Ackerman *et al.* (1973).

nitrogen oxides

$$n(\text{NO}) \left[ 2J_{\text{NO}} + b_{11} n(\text{NO}_3) + b_{21} n(\text{M}) n(\text{OH}) + b_{29} n(\text{HO}_2) + c_{5c} n(\text{CH}_3\text{O}_2) \right] - n(\text{HNO}_2) J_{\text{OH}\cdot\text{NO}} - n(\text{NO}_3) \left[ J_{\text{NO}\cdot\text{O}_2} - J_{\text{NO}_2\cdot\text{O}} \right] \quad (104)$$

Neglecting the effect of  $\text{NO}_3$  and using photoequilibrium conditions in (86) for  $\text{HNO}_2$ , (104) is written

$$n(\text{NO}) \left[ 2J_{\text{NO}} + c_{5c} n(\text{CH}_3\text{O}_2) \right] + n(\text{HO}_2) \left[ b_{29} n(\text{NO}) - b_{33} n(\text{NO}_2) \right] \quad (105)$$

The importance of (105) in the lower stratosphere depends on the values of  $c_{5c} n(\text{CH}_3\text{O}_2)$  which is about  $5 \times 10^{-7} \text{ sec}^{-1}$  according to calculated values (Levy, 1973) at 15 km. Since  $n(\text{NO}) < 10^9 \text{ cm}^3 \text{ sec}^{-1}$  in the lower stratosphere the effect of  $\text{CH}_3\text{O}_2$  is negligible. However, it depends also on the difference  $b_{29} n(\text{NO}) - b_{33} n(\text{NO}_2)$  which seems to be positive in a sunlit atmosphere. According to Simonaitis (1973) the ratio  $b_{29}/b_{33} = 7 \pm 2$  and, therefore, for  $n(\text{NO}_2) < 7 n(\text{NO})$  a positive term must be added to the production term  $2 n(\text{O}_2) J_2$ . In the lower stratosphere there is a large variation of the photodissociation of molecular oxygen with the solar zenith angle ; if the production for overhead sun conditions is  $1 \times 10^5$  and  $1 \times 10^6$  oxygen atoms  $\text{cm}^{-3} \text{ sec}^{-1}$  at 15 and 20 km, respectively, the corresponding values for a solar zenith angle of  $60^\circ$  are only 50 and  $5 \times 10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ . With a NO concentration of the order of  $5 \times 10^8 \text{ cm}^{-3}$  and a rate coefficient which is perhaps not less than  $2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ , the addition of  $10^4$  ozone molecules  $\text{cm}^{-3} \text{ sec}^{-1}$  is possible. Thus, the aeronomic behavior must be discussed in detail and special attention is required to consider the effect of the nitric oxide term of (105) compared with  $2 n(\text{O}_2) J_2$  when there is an artificial injection of nitrogen oxides in the stratosphere..

## 6. PRODUCTION OF NITRIC OXIDE

The reaction of the electronically excited atom  $\text{O}(^1\text{D})$  with nitrous oxide (Nicolet, 1970) is a natural source of nitric oxide in the stratosphere. It depends on the vertical distribution of  $\text{N}_2\text{O}$  molecules which is related to the photodissociation rate and to the



variable flux of molecules from the troposphere. There is practically no stratospheric source of  $N_2O$ , and no transport of nitric oxide from the mesosphere is possible. A total production of the order  $(1 \pm 0.5) \times 10^8$  NO molecules is possible. It is clear that the exact value is related to the vertical distribution of  $N_2O$  which depends strongly on the values of the eddy diffusion coefficient which are adopted (Nicolet and Vergison, 1971; McElroy and McConnell, 1971; Nicolet and Peetermans, 1972).

A second process which can produce nitric oxide is the reaction of nitrogen atoms with molecular oxygen. This leads, in less than 10 seconds in the lower stratosphere, to nitric oxide molecules. The production of nitrogen atoms is related to the normal ionization by cosmic rays (Nicolet and Peetermans, 1972; Warneck, 1972). One nitrogen atom, and consequently one nitric oxide molecule, is produced per ion pair due to the cosmic rays (Brasseur and Nicolet, 1973). The production of N atoms is shown in Fig. 10 for Thule in 1954 (solar activity minimum) and in 1958 (solar activity maximum) with a station of mean latitude Bismark in 1965 (solar activity minimum). It is clear that the production of nitrogen atoms (day and night process) is always more important in the polar (or high latitude) lower stratosphere than the production of nitric oxide which is shown in Fig. 10 for two solar zenith angles  $\sec \chi = 1$  and 2.

A third process for the production of nitric oxide in the stratosphere which can be considered is the oxidation of ammonia (Crutzen, 1973; McElroy and McConnell, 1973; Stuhl, 1973). The oxidation is initiated by the reaction



with a rate coefficient of  $(1.5 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at room temperature (Stuhl, 1973). According to Dove and Nip (1973) its activation energy (measured between 1500° K and 2000° K) would be 1.1 kcal and the rate coefficient

$$k_{OH-NH_3} = 1.3 \times 10^{-14} T^{0.68} e^{-550/T} \text{ cm}^3 \text{ sec}^{-1} \quad (107)$$

Such a formula leads to  $1 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at 3000° K in good agreement with the value

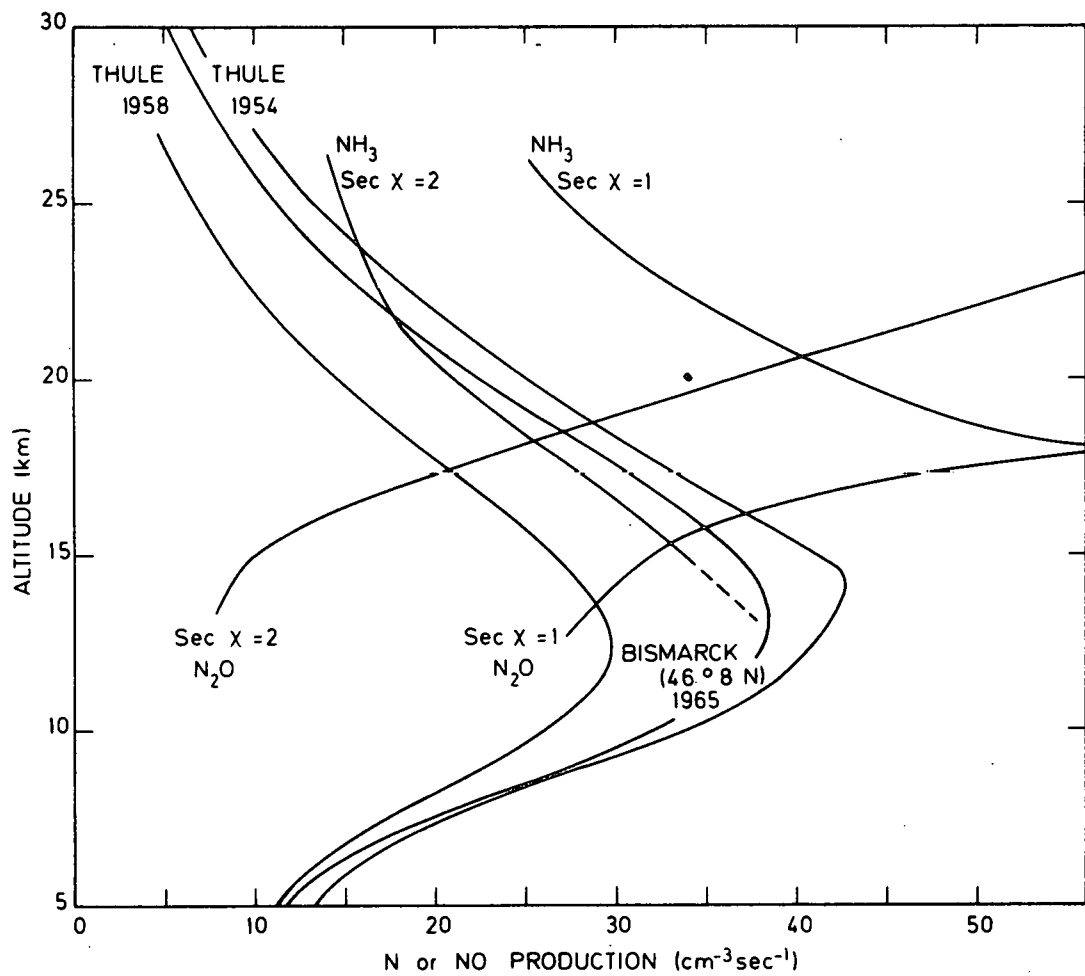
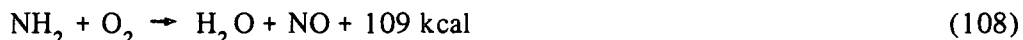


Fig. 10.- Production of nitrogen atoms and nitric oxide molecules. The production of nitrogen atoms is given at Thule (polar Cap) for maximum conditions (1954) and minimum conditions (1958) and at Bismark in 1965 (maximum conditions). The production of nitric oxide molecules from  $N_2O$  and  $NH_3$  is given for  $\sec \chi = 1$  and 2, overhead sun conditions and height sun =  $30^\circ$ , respectively. Cosmic ray data from Neher (1967, 1971).

deduced by Stuhl.

The production of nitrogen oxide molecules may come directly from the following reaction



or



with



These reactions should be studied in the laboratory in order to determine the exact oxidation paths of  $\text{NH}_2$  and also the effect of  $\text{O}_3$  and  $\text{NO}$ .

$\text{NH}_3$  concentrations at the ground surface have been presented by Junge (1963) and mixing ratios of  $1.2 \times 10^{-9}$  have been observed above the trade wind inversion on Mauna Kea (3200 m) in Hawaii. Recent measurements by Georgii and Muller (1973) leads to mixing ratios as low as  $5 \times 10^{-10}$  -  $1 \times 10^{-9}$  in the polar maritime air and to about  $5 \times 10^{-9}$  over the continent. Winter and summer values at 3 km are about  $2 \times 10^{-8}$  and  $6 \times 10^{-9}$ , respectively.

A knowledge of the flux of  $\text{NH}_3$  probably less than  $10^8 \text{ cm}^2 \text{ sec}^{-1}$  into the stratosphere is required in order to determine the exact production of nitric oxide molecules. If we adopt as a working value a mixing ratio of the order of  $10^{-9}$  in the lower stratosphere, we can determine the production of nitric oxide molecules if we know the concentration of OH radicals. Considering the OH concentration which will be determined later, we have represented in Fig. 10 the vertical distribution of the NO production in the lower stratosphere. With such conditions, it is clear that the production of nitric oxide due to the

oxidation of  $\text{NH}_3$  by OH occurs below 20 km.

Thus, it seems that the three sources which have been considered play a role in the production of nitric oxide in the stratosphere. However, there will be very important differences with latitude and season. A stratospheric observation of  $\text{NH}_3$  is required since its mixing ratio cannot be greater than  $10^{-9}$ .

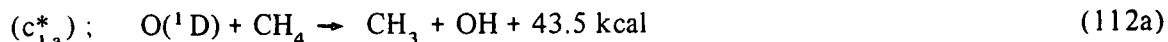
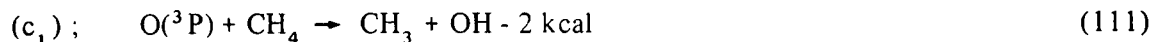
## 7. OXIDATION OF METHANE AND PRODUCTION OF CARBON MONOXIDE

Methane is produced primarily by various bacterial decomposition processes leading to an average production (Robinson and Robbins, 1971) of  $3.4 \times 10^{11}$   $\text{CH}_4$  molecules  $\text{cm}^{-2}$   $\text{sec}^{-1}$ . Since the total number of  $\text{CH}_4$  molecules is about  $3.2 \times 10^{19}$   $\text{cm}^{-2}$  column, such a production corresponds to an estimated residence time of about 3 years (day and night).

The daytime destruction process of  $\text{CH}_4$  leads to the production of CO (McConnell *et al.*, 1971; Wofsy *et al.*, 1972), with an average residence time of 0.4 year for CO if its volume fractional concentration is of the order of 0.1 ppmv. The carbon monoxide molecules apparently could have a lifetime of the order of 0.1 year (Weinstock and Niki, 1972; Weinstock and Chang, 1973; Levy II, 1972, 1973). The sink of methane is a source for formaldehyde (Levy, 1971, 1972) which leads to the production of  $\text{H}_2$  and CO. There are different ways to reduce the differences between the various results. However, there are still difficulties in the interpretation according to a recent analysis made by Warneck (1973) of the distribution of CO mixing ratios with latitude in the northern and southern hemispheres which were measured by Seiler (1973).

Methane, which is mixed in the troposphere (Ehhalt and Heidt, 1972) is photodissociated in the mesosphere and is dissociated by oxidation processes in the stratosphere.

Atomic oxygen attacks methane through (see for example, Nicolet and Peetermans, 1973)

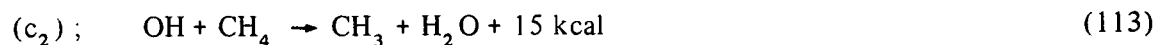


and



which occurs to the extent of 9% (Lin and DeMore, 1973).

The other important reaction in the stratosphere is



A recent measurement by Davis (1973) between 240 - 320° K leads to

$$c_2 = 2.5 \times 10^{-12} e^{-1660/T} \text{ cm}^3 \text{ sec}^{-1} \quad (114)$$

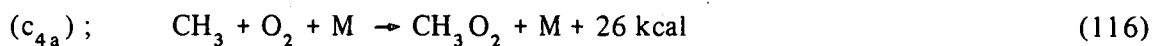
which corresponds to about  $10^{-15} \text{ cm}^3 \text{ sec}^{-1}$  in the lower stratosphere. In the lower stratosphere  $CO_2$  is photodissociated at very low rate and the production of CO corresponds to the total oxidation process of  $CH_4$  by reaction (113) and (112).

The oxidation of carbon monoxide is attributed to



which has been observed at 300° K (Greiner, 1969; Westenberg and de Haas, 1973) and below 300° K (Zellner and Smith, 1973; Davis 1973). The value of the rate coefficient is about  $1.4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at 300° K and is about  $1.25 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$  at temperature of the lower stratosphere.

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



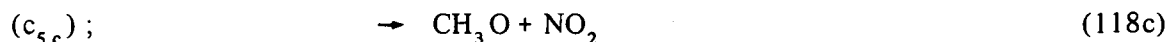
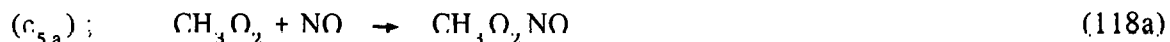
The rate coefficient is (Basco *et al.*, 1972)

$$c_{4a} = 2.6 \times 10^{-31} \text{ cm}^6 \text{ sec}^{-1} \quad (117a)$$

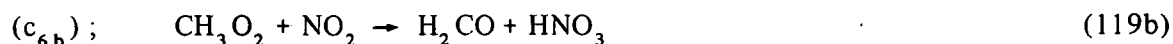
if the third body is nitrogen and the limiting value at high pressures is

$$c_{4a}^{\infty} = 4.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (117b)$$

Methylperoxy radicals react with oxide of nitrogen (Spicer *et al.*, 1973) leading to

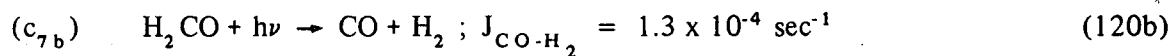


as regards NO. According to Spicer *et al.* (1973), there was no evidence for  $\text{CH}_3\text{O}$  radical production in their studies and they concluded that reaction (118c) did not occur contrary to every expectation from atmospheric evidence. Levy (1973) has considered that (118c) is the reaction occurring with  $c_{5c} \geq 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ . In the same way the reactions with  $\text{NO}_2$  are

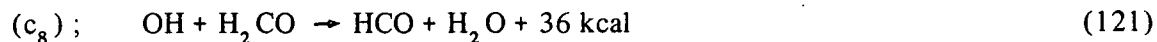


The photochemistry of formaldehyde (McGuigg and Calvert, 1969; Calvert *et al.*, 1972) indicates that two distinct primary processes occur





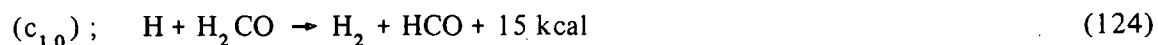
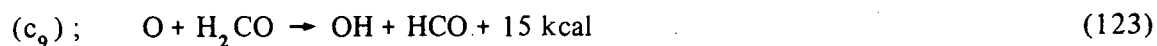
which lead to the production of formyl and carbon monoxide with atomic and molecular hydrogen, respectively. In addition, a rapid reaction such as



must also be introduced since (Morris and Niki, 1971)

$$c_8 = 1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (122)$$

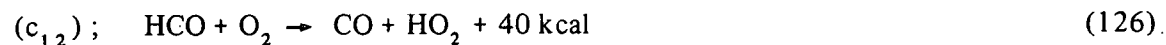
The reaction



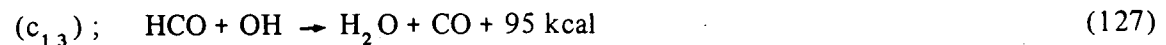
can be neglected compared to (120) and (121). The formyl radical is rapidly photodissociated (Johns *et al.*, 1963)



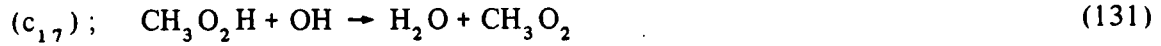
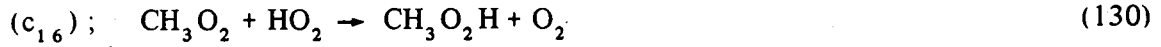
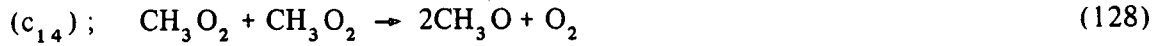
or reacts with  $\text{O}_2$  (McMillan and Calvert, 1965)



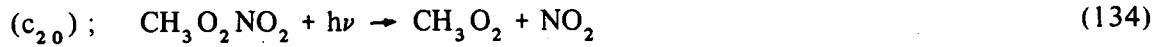
or reacts with OH



Other reactions have been introduced by Levy (1972, 1973)



The two following reactions are also considered



Thus, with equations (111) to (134), it is possible to write for equilibrium conditions that

$$\begin{aligned} n(\text{H}_2\text{CO}) & \left[ J_{\text{H-HCO}} + J_{\text{H}_2\text{-CO}} + c_8 n(\text{OH}) + c_9 n(\text{O}) + c_{10} n(\text{H}) \right] \\ & = n(\text{CH}_4) \left[ c_1 n(\text{O}) + c_1^* n(\text{O}^*) + c_2 n(\text{OH}) \right] \\ & = n(\text{HCO}) \left[ J_{\text{H-CO}} + c_{12} n(\text{O}) + c_{13} n(\text{OH}) \right] + n(\text{H}_2\text{CO}) J_{\text{H}_2\text{-CO}} \end{aligned} \quad (135)$$

If we consider the various reactions involving the production and loss mechanisms of H, OH and HO<sub>2</sub>, we may write

$$\begin{aligned} \frac{dn(\text{H})}{dt} + \frac{dn(\text{OH})}{dt} + \frac{dn(\text{HO}_2)}{dt} + n(\text{OH}) \left[ c_2 n(\text{CH}_4) + 2c_{13} n(\text{HCO}) + 2c_{17} n(\text{CH}_3\text{O}_2\text{H}) \right] \\ = n(\text{CH}_4) \left[ c_1 n(\text{O}) + c_1^* n(\text{O}^*) \right] + 2n(\text{H}_2\text{CO}) \left[ J_{\text{H-HCO}} + c_9 n(\text{O}) \right] + n(\text{CH}_3\text{O}_2) c_{15} n(\text{O}_2) \end{aligned} \quad (136)$$



With conditions (135), equation (136) may be written

$$\begin{aligned} \frac{dn(\text{H})}{dt} + \frac{dn(\text{OH})}{dt} + \frac{dn(\text{HO}_2)}{dt} + n(\text{OH}) c_2 n(\text{CH}_4) [1 - X] + 2n(\text{OH}) \left[ c_{13} n(\text{HCO}) \right. \\ \left. + c_{17} n(\text{CH}_3\text{O}_2\text{H}) \right] = n(\text{CH}_4) \left[ c_1 n(\text{O}) + c_1^* n(\text{O}^*) \right] [1 + X] + n(\text{CH}_3\text{O}) c_{15} n(\text{O}_2) \end{aligned} \quad (137)$$

with

$$X = \frac{2J_{\text{H-HCO}} + c_9 n(\text{O})}{J_{\text{H-HCO}} + J_{\text{H}_2\text{-CO}} + c_8 n(\text{OH}) + c_9 n(\text{O}) + c_{10} n(\text{H})} \quad (138)$$

The ratio  $X \cong 2J_{\text{H-HCO}}/J_{\text{H}_2\text{-CO}}$  varies from 0.8 at 50 km to 0.7 near 15 km and is about 0.5 at ground level. Keeping only the important terms, the steady state conditions of equation (137) lead to

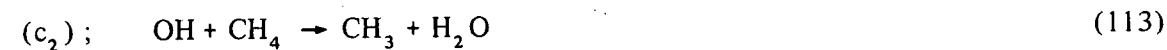
$$+ n(\text{OH}) c_2 n(\text{CH}_4) [1 - X] = n(\text{CH}_4) \left[ c_1 n(\text{O}) + c_1^* n(\text{O}^*) \right] [1 + X] + \dots \quad (139)$$

which are the principal terms which must be introduced when methane is present. In the stratosphere, the oxidation of  $\text{CH}_4$  leads to a decrease of the mixing ratio. However, the transport from the troposphere is such that its vertical profile has a weak gradient as it is shown from the balloon samples and a rocket sample (Ehhalt and Heidt, 1973; Ehhalt *et al.*, 1972; Ackerman and Muller, 1972; Cumming and Lowe, 1973).

## 8. REMOVAL OF HYDROXYL RADICALS

The complexity of the chemical model requires a precise determination of the profile of hydroxyl and hydroperoxyl radicals in the stratosphere and mesosphere.

In addition to



it is necessary to consider the following reactions leading to the re-formation of  $\text{H}_2\text{O}$



with a rate coefficient of the order of

$$a_{16} = (2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (141)$$

and

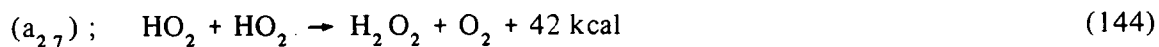


Reaction (142) is extremely important since recent measurements by Hochanadel *et al.* (1972) indicate a rate coefficient

$$a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (143)$$

which could be too high.

Before ending the discussion concerning the more important reactions of hydroxyl and hydroperoxyl radicals, the reactions involving  $\text{HO}_2$  must be considered.



with a coefficient

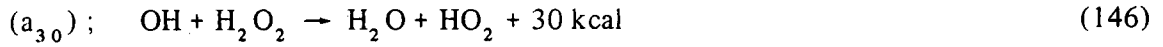
$$a_{27} = (9.5 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (145a)$$

according to Hochanadel *et al.* (1972), or

$$a_{27} = (3.6 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (145b)$$

according to Paukert and Johnston (1972).

Finally, the following processes cannot be neglected



with

$$a_{30} = 4.1 \times 10^{-13} T^{1/2} e^{-600/T} \text{ cm}^3 \text{ sec}^{-1} \quad (147)$$

according to Greiner (1968), and



with

$$a_{19} = 2.3 \times 10^{-11} e^{-2400/T} \text{ cm}^3 \text{ sec}^{-1} \quad (149)$$

according to Smith and Zellner (1973).

Since photoequilibrium conditions can be considered in the stratosphere where  $n(\text{H})$  is small, the equation for  $n(\text{OH})$  is written as follows :

$$\begin{aligned} n(\text{OH}) & \left[ a_{16} n(\text{OH}) + a_{17} n(\text{HO}_2) + a_{30} n(\text{H}_2\text{O}_2) + c_2 \left( \frac{1-X}{2} \right) n(\text{CH}_4) + b_{27} n(\text{HNO}_3) \right] \\ & = n(\text{H}_2\text{O}) \left[ J_{\text{H-OH}} + a^* n(\text{O}^*) \right] + n(\text{H}_2) a_{24}^* n(\text{O}^*) + n(\text{CH}_4) \left[ \frac{1+X}{2} \left\{ c_1^* n(\text{O}^*) + \right. \right. \\ & \left. \left. c_1 n(\text{O}) \right\} \right] \end{aligned} \quad (150)$$

The ratio  $n(\text{OH})/n(\text{HO}_2)$  is

$$\begin{aligned} n(\text{HO}_2) & \left[ a_{6c} n(\text{O}_3) + a_7 n(\text{O}) + a_{17} n(\text{OH}) + 2a_{27} n(\text{HO}_2) + b_{29} n(\text{NO}) + b_{33} n(\text{NO}_2) \right] = \\ & n(\text{OH}) \left[ a_5 n(\text{O}) + a_6 n(\text{O}_3) + a_{19} n(\text{H}_2) + a_{30} n(\text{H}_2\text{O}_2) + a_{36} n(\text{CO}) + \right. \\ & \left. c_8 n(\text{H}_2\text{CO}) + c_2 X n(\text{CH}_4) \right] . \end{aligned} \quad (151)$$

Equations (150) and (151) have been used to derive the ratio  $n(\text{OH})/n(\text{HO}_2)$  and  $n(\text{OH})$  using the values of the rate coefficients which were adopted here. With the aim of illustrating the day equilibrium in the stratosphere various figures have been prepared. In figure 11, the various percentages of the different coefficients affecting  $n(\text{OH})$  are given. In the upper troposphere and lower stratosphere, the dominant path transforming OH in H - HO<sub>2</sub> is the reaction with CO. In the lower stratosphere when  $n(\text{CO})/n(\text{M}) \leq 5 \cdot 10^{-8}$  and in the middle stratosphere, the reaction of OH with O<sub>3</sub> plays the leading role (almost 100%). At the stratopause and in the upper stratosphere, the reaction with atomic oxygen transforming OH in H-HO<sub>2</sub> becomes the principal reaction. The effect of H<sub>2</sub>, H<sub>2</sub>CO and CH<sub>4</sub> may be neglected in the first approximation although they can play a role in the lower troposphere. A remark must be made concerning the effect of CO in the lower stratosphere ; the curve of fig. 11 is deduced for a mixing ratio of 10<sup>-7</sup> in the troposphere and 5 x 10<sup>-8</sup> in the stratosphere. A decrease of these values leads to an increase of the effect of the reaction of OH with O<sub>3</sub>, particularly in the lower stratosphere.

As far as HO<sub>2</sub> is concerned, it can be seen in Fig. 12 that, in the lower stratosphere, the reaction with nitric oxide cannot be neglected. Its exact role depends on the value of the rate coefficient and on the vertical distribution of its concentration which is here  $n(\text{NO}_x)/n(\text{M}) = 3 \times 10^{-9}$ . As for OH, the effects of the reaction of HO<sub>2</sub> with O<sub>3</sub> and O occur in the middle and upper stratosphere, respectively. However, it must be pointed out that the simultaneous effects of the reactions with OH, HO<sub>2</sub> and O at 30 km lead to a total of about 30% of the effect of all reactions. Another remark must be made concerning the effect of NO which depends strongly on the assumed value of the rate coefficient (here 3 x 10<sup>-13</sup>, cf. Davis *et al.*, 1972) and on the vertical distribution of the nitric oxide concentration in the lower stratosphere. A value of the order of 10<sup>-12</sup> cm<sup>3</sup> sec<sup>-1</sup> or more for the reaction between NO and HO<sub>2</sub> would increase its effect and the OH concentration.

Thus, the main features of Fig. 11 and 12 correspond to the effect on OH and HO<sub>2</sub> of atomic oxygen at the stratopause and in the upper stratosphere, of ozone in the middle stratosphere and lower stratosphere and of carbon monoxide and nitric oxide in the lower stratosphere.

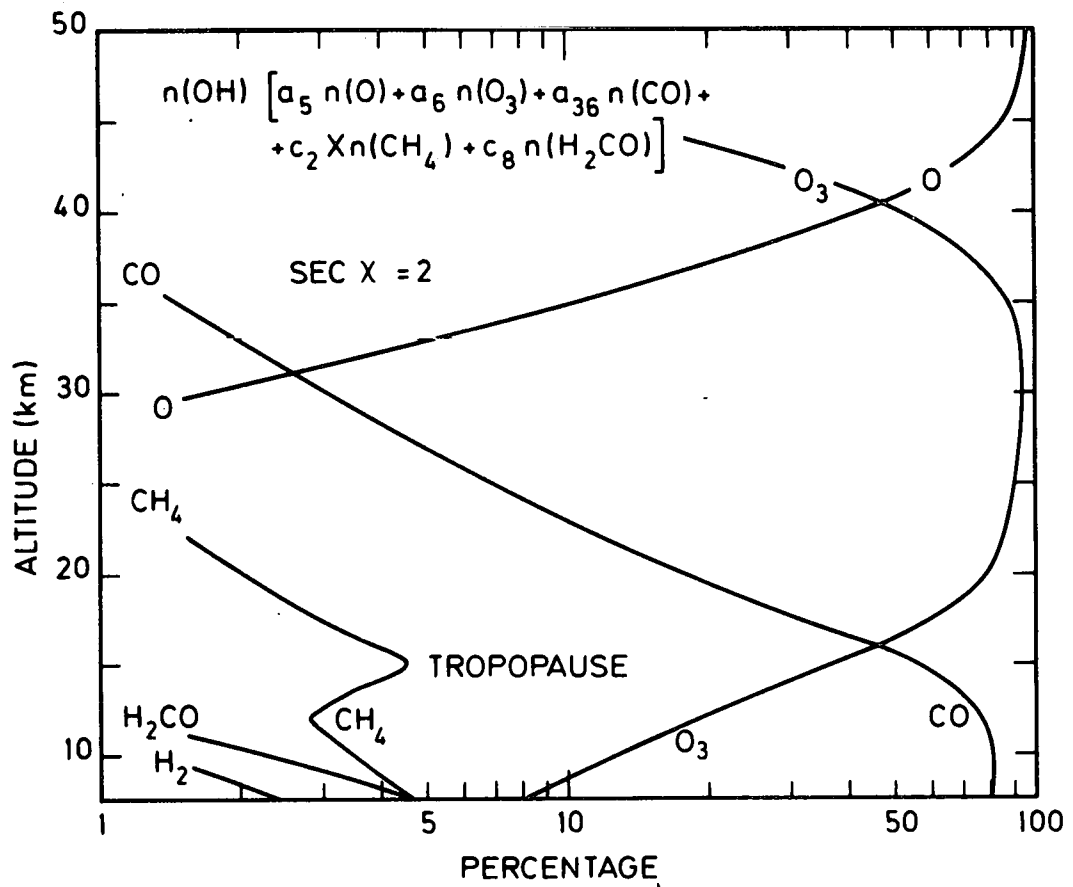


Fig. 11.- Profiles (%) of the various terms affecting OH in the determination of the ratio  $n(\text{HO}_2)/n(\text{OH})$ . CO effect due to its mixing ratio  $5 \times 10^{-8}$  in the stratosphere.

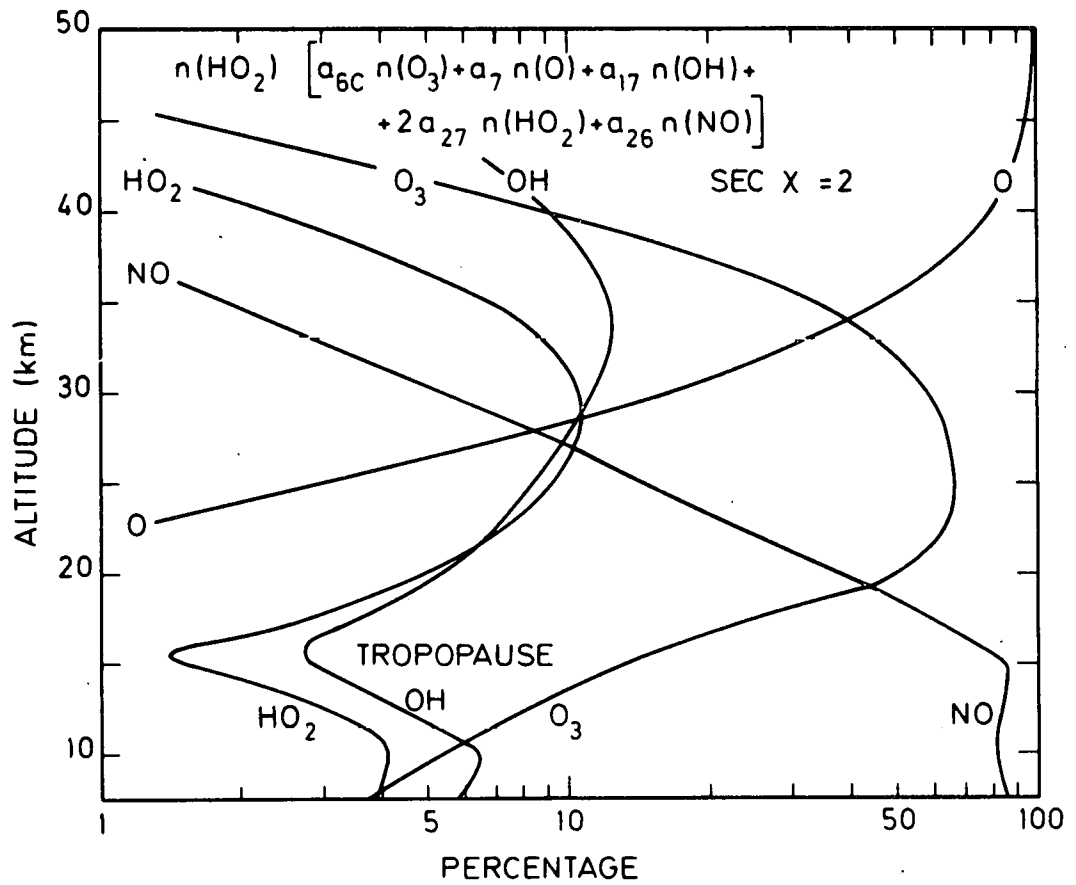


Fig. 12.- Profiles (%) of the various terms affecting HO<sub>2</sub> in the determination of the ratio n(HO<sub>2</sub>)/n(OH). NO effect due to a mixing ratio 3 × 10<sup>-9</sup> for NO<sub>x</sub>.

The essential features of the calculations appear very sensitive in the lower stratosphere to the adopted values for the concentrations of CO and NO. In fig. 13 the ratio  $n(\text{HO}_2)/n(\text{OH})$  is represented for the condition illustrated in Fig. 11 and 12. Another curve ( $\text{NO} = 0$ ) shows that for a relative concentration of  $3 \times 10^{-10}$ , the ratio  $n(\text{HO}_2)/n(\text{OH})$  increase from 15 to 60 at 15 km. When the reaction with CO is reduced (mixing ratio  $10^{-8}$ ), the ratio  $n(\text{HO}_2)/n(\text{OH})$  becomes smaller less than 10 to 15 km. Thus, the behavior of OH and  $\text{HO}_2$  in the lower stratosphere requires an exact knowledge of their rate coefficients with NO and  $\text{NO}_2$ .

With the ratio  $n(\text{HO}_2)/n(\text{OH})$  obtained from the numerical results illustrated in Fig. 13, it is easy to determine the vertical profile of OH. From the various effects occurring in the troposphere and mesosphere, we find that the reaction between OH and  $\text{HO}_2$  is the dominant path for removal of hydroxyl and hydroperoxyl radicals in the stratosphere. However, in the lower stratosphere  $\text{CH}_4$  and  $\text{HNO}_3$  are also of the same importance (Fig. 14). If the value of  $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$  reported by Hochanadel *et al.* (1972) is reduced by a factor of 4, the importance of  $\text{CH}_4$  and  $\text{HNO}_3$  increases in the lower stratosphere (see Fig. 15). The effect of  $\text{HNO}_3$  reaches more than 50% between 15 and 20 km. Calculated profiles for OH and  $\text{HO}_2$  are presented in Fig. 16. As need scarcely be emphasized, the calculated values of the concentrations depend on the coefficients which are not yet well known for aeronomic purposes. It is clear that the OH concentration is not known in the stratosphere within a factor of 4. The OH and  $\text{HO}_2$  profiles have to be provided to determine the wide range of reactions in which CO,  $\text{CH}_4$ ,  $\text{O}_3$ , O, NO,  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ ,  $\text{HNO}_2$  and  $\text{H}_2\text{O}$  are involved in the stratosphere.



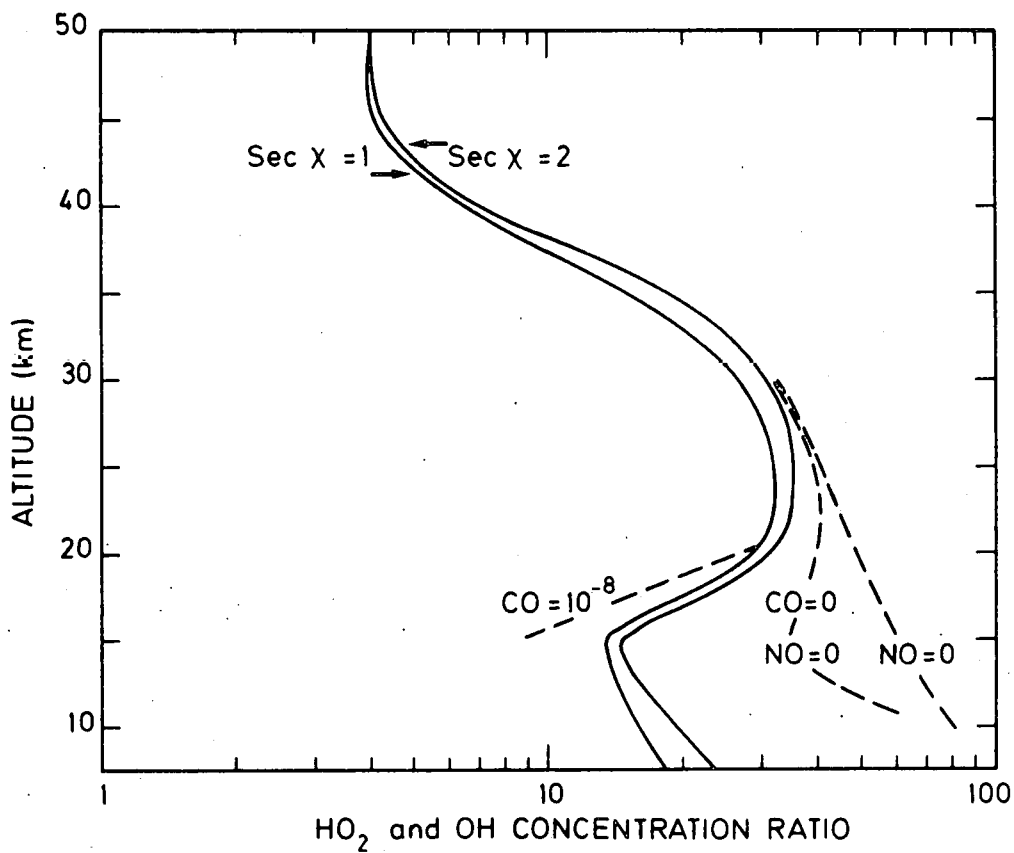


Fig. 13.- Ratio  $n(\text{HO}_2)/n(\text{OH})$  in the stratosphere. Curve (NO- $\text{HO}_2$ ) using values given in Fig. 11 and 12. Curve NO = 0 when the mixing ratio of  $\text{NO}_x$  is reduced to  $5 \times 10^{-10}$ . Curve CO = 0, when CO is neglected. Curve CO = 0, NO = 0, neglecting the effect of CO and NO.

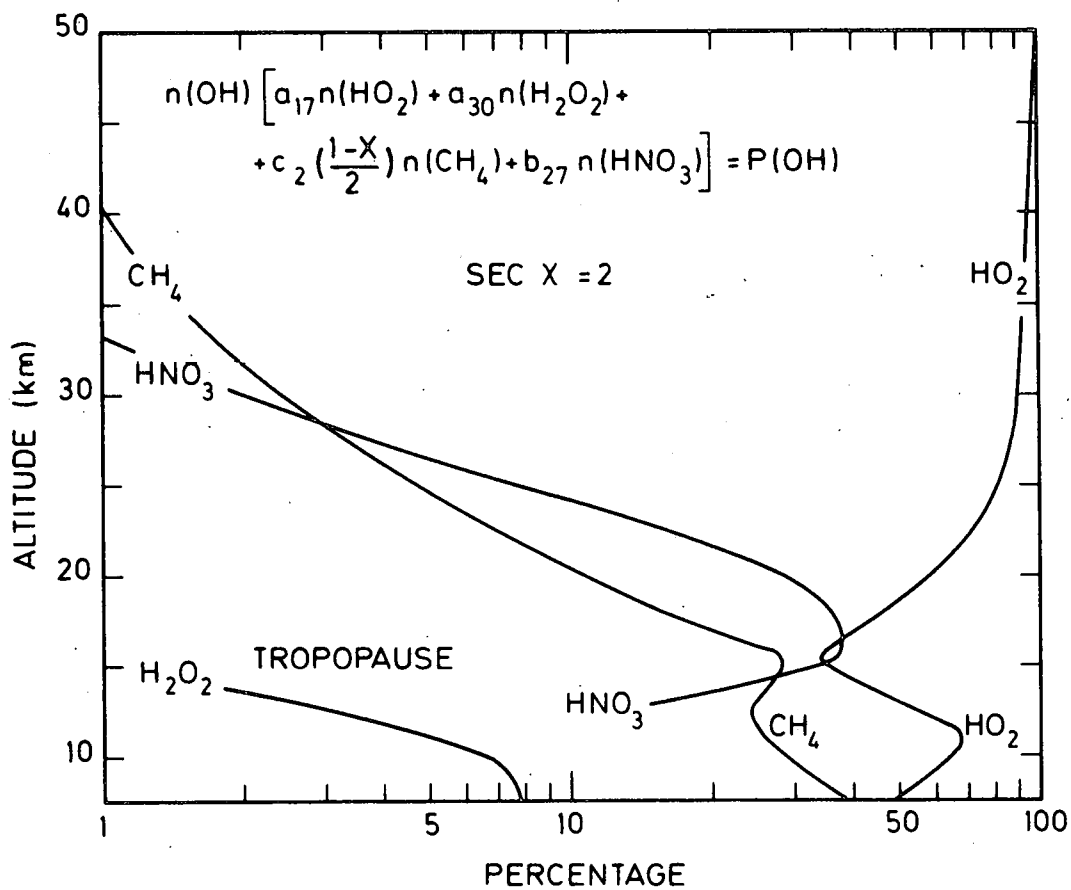


Fig. 14.- Profiles (%) of the various terms determining the concentration of the hydroxyl radical, using values corresponding to profiles of fig. 11 and 12. The  $\text{HNO}_3$  concentrations correspond to an average value of observational results by Murcray *et al.* (1973).

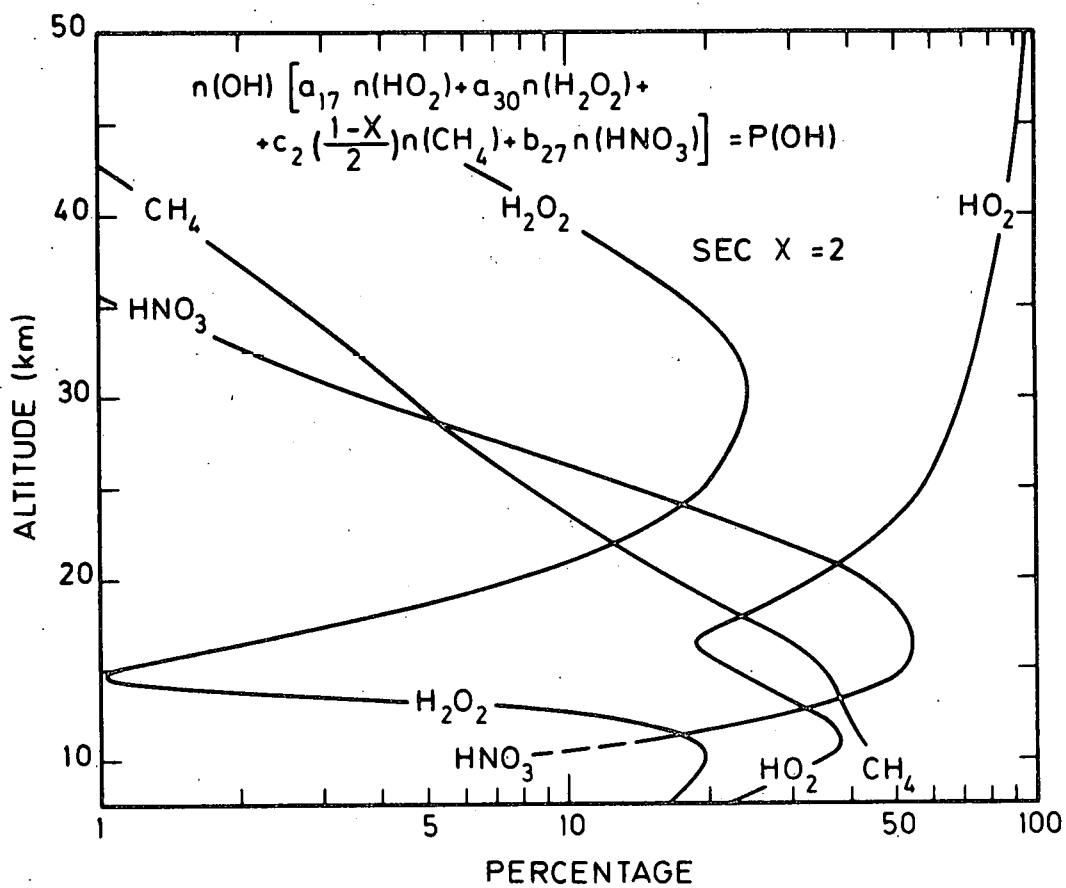


Fig. 15.- Profiles (%) of the various terms determining the concentration of the hydroxyl radical, using values corresponding to fig. 11 and 12, except for the reaction  $\text{OH} + \text{HO}_2$  with a rate coefficient reduced by a factor of 4.

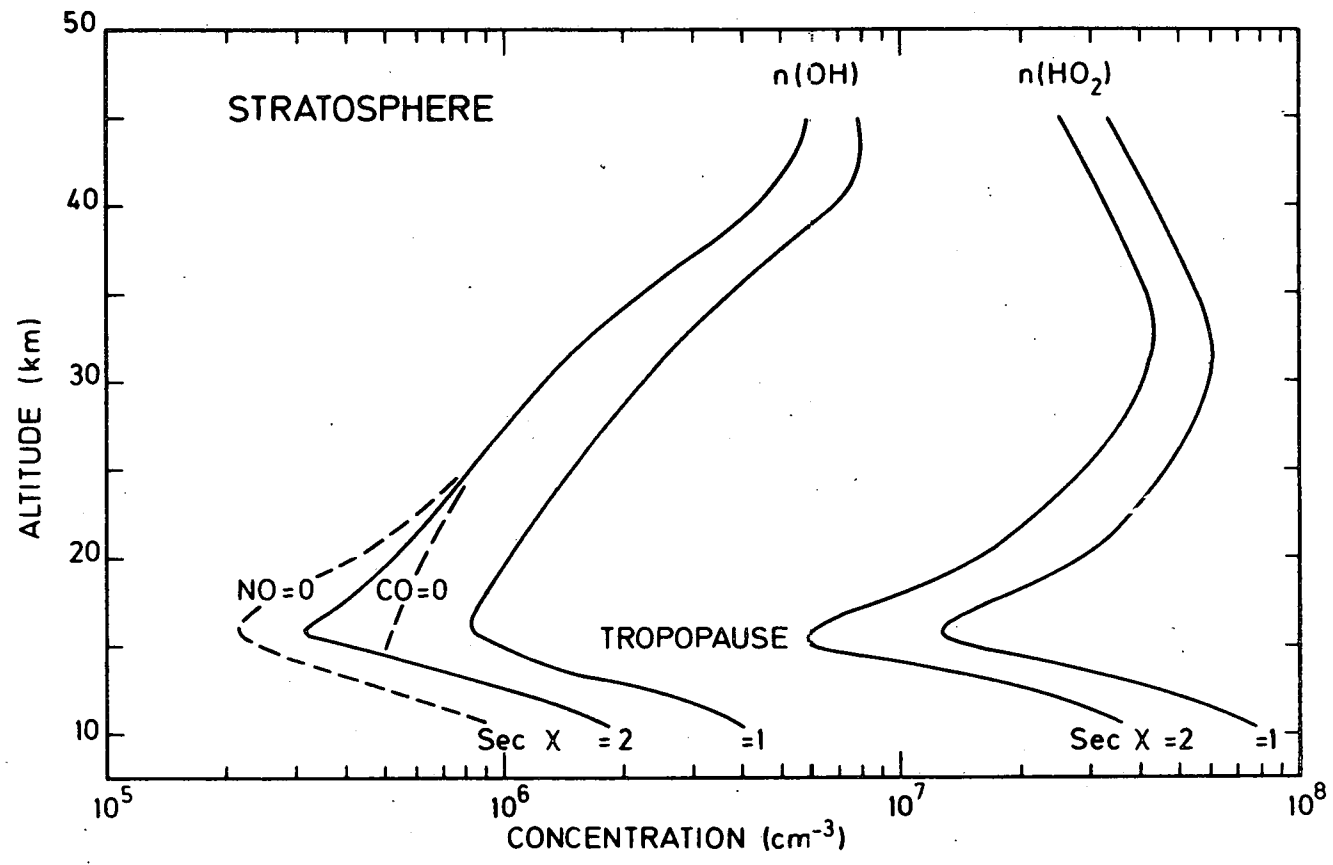


Fig. 16.- OH and HO<sub>2</sub> concentrations in the stratosphere for conditions defined in Fig. 11 and 12. Changes when CO (curve CO = 0) is neglected, and when NO was a reduced mixing ratio to  $5 \times 10^{-10}$ , (curve NO = 0).

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