

## An Overview of Aeronomic Processes in the Stratosphere and Mesosphere

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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 also react 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.

La différence que l'on note entre les concentrations théoriques et expérimentales du  $O_3$  dans la mésosphère et la stratosphère peut être expliquée par une influence des composés d'hydrogène et des oxydes d'azote. La radiation solaire dissocie 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 le méthane et l'oxyde nitreux mène à la destruction de ces deux molécules dans la stratosphère, ce qui correspond à la production respective du monoxyde de carbone avec de la vapeur d'eau et de l'oxyde nitrique. L'hydrogène et les molécules de vapeur d'eau réagissent aussi avec l'atome d'oxygène  $O(^1D)$ , excité électroniquement, produisant des radicaux hydroxyles. Des sources de  $H_2$  existent *in situ* dans la stratosphère et la mésosphère; la réaction du OH avec du  $CH_4$ , la photodissociation du formaldéhyde et aussi la réaction entre les radicaux hydroperoxydes et les atomes d'hydrogène. La distribution verticale de la vapeur d'eau n'est pas modifiée par sa dissociation dans la stratosphère et la mésosphère puisque sa reformation est rapide.

Le rapport des concentrations des radicaux hydroxyle et hydroperoxyde ne peut être

établi avec une précision convenable; il complique le calcul de la destruction de l'ozone qui se produit durant les réactions du OH et du H<sub>2</sub>O, non seulement avec l'oxygène atomique à la stratopause, mais aussi directement dans la stratosphère moyenne et avec du CO et du NO dans la stratosphère inférieure.

En plus des diverses réactions concernant l'oxyde nitrique et le bioxyde d'azote, les réactions qui conduisent à la production et à la destruction de l'acide nitrique et de l'acide nitreux devraient être envisagées. Les molécules d'acide nitrique sont impliquées dans un transport de diffusion turbulent de la stratosphère inférieure à la troposphère, et sont, par conséquent, la cause de l'élimination de l'oxyde nitrique produit dans la stratosphère. Les conditions atmosphériques doivent être connues à la tropopause.

[Traduit par le journal]

### 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 (1, 2) have led to a knowledge of the photochemistry of atmospheric oxygen in a pure oxygen atmosphere. Bates and Nicolet (3) in their general survey of the photochemistry of water vapor have investigated the extent to which atomic hydrogen and certain radicals catalyze 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 (4, 5) and in particular of methane (6, 7) and of water vapor (3). 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 (8-11) 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 ref. 12) and  $0.5 \times 10^{-6}$  (see refs. 12, 13). Unlike water vapor, however, their fractional concentrations are practically not affected through the troposphere. Consequently, above the tropopause, the combined H-atom content in CH<sub>4</sub> is more than 50% of the content in H<sub>2</sub>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 thermo-

sphere, the reaction of H<sub>2</sub>O with the electronically excited atomic oxygen in the <sup>1</sup>D state (14, 15) leads to the possibility of its dissociation in the stratosphere and troposphere. The concentrations of O(<sup>1</sup>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.

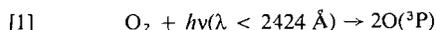
While the desirability of similar studies of the effect of nitrogen compounds has long been realized, comparatively few have been made because of lack of basic data. The importance of nitrogen oxides in controlling the ozone concentration was pointed out only in 1970 (16). Information on N<sub>2</sub>O was given before by the calculation of its photodissociation rate (7, 17) and on NO, NO<sub>2</sub>, and HNO<sub>3</sub> by the analysis of the principal reactions (18). Recently, new experimental and observational results have been obtained on nitrogen oxides, particularly by direct observation of the vertical distribution in the stratosphere of HNO<sub>3</sub> (19, 20), NO<sub>2</sub> (21), and NO (22, 23).

The importance of methane has been generally realized since McConnell *et al.* (24) 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 (25) to provide the destruction of carbon monoxide required by Weinstock (26). 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 is of the order of 10 km; a folded tropopause at mean latitudes may change the lower boundary conditions of the stratosphere. In other words, the nature of

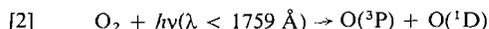
the tropopause is an important factor which must be introduced in the study of the lower stratosphere.

**Oxygen Photodissociation and Ozone Formation**

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

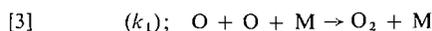


which occurs in the stratosphere. In the strong Schumann–Runge continuum

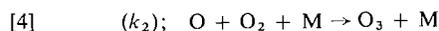


the dissociation occurs in the thermosphere. In the spectral range of the Schumann–Runge bands, where predissociation is observed, the absorption is extremely variable and the dissociation occurs in the mesosphere and upper stratosphere.

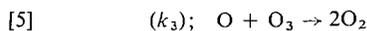
In the presence of a third body ( $N_2, O_2$ ) the atoms liberated by photodissociation recombine



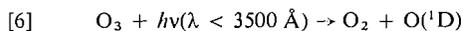
or they unite with oxygen molecules



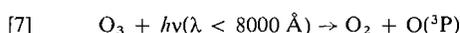
forming ozone. This molecule is destroyed by a two-body collision process



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 number of  $O(^1D)$  atoms produced which react with  $H_2O, H_2, CH_4,$  and  $N_2O$  before they can be 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

[8] 
$$\frac{dn(O)}{dt} + 2k_1n(M)n^2(O) + k_2n(M)n(O_2)n(O) + k_3n(O_3)n(O) = 2n(O_2)J_2 + n(O_3)J_3$$

[9] 
$$\frac{dn(O_3)}{dt} + n(O_3)J_3 - k_2n(M)n(O_2)n(O) + k_3n(O)n(O_3) = 0$$

which lead to the general form

[10] 
$$\frac{dn(O)}{dt} + \frac{dn(O_3)}{dt} + 2k_1n(M)n^2(O) + 2k_3n(O_3)n(O) = 2n(O_2)J_2$$

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 a major constituent. In the major part of the mesosphere,  $n(O) > n(O_3)$  and there is a daytime photo-equilibrium for ozone with a photodissociation coefficient  $10^{-3} \leq J_3 \leq 10^{-2} \text{ s}^{-1}$ . Thus, from [9]

[11] 
$$\frac{n(O_3)}{n(O)} = \frac{k_2n(M)n(O)}{J_3 + k_3n(O)} \approx \frac{k_2n(M)n(O_2)}{J_3}$$

since  $J_3 > k_3n(O)$ , and from [10],

[12] 
$$\frac{dn(O)}{dt} + 2k_1n(M) \times \left\{ 1 + \frac{k_3k_2n(O_2)}{k_1J_3} \right\} n^2(O) = 2n(O_2)J_2$$

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

[13] 
$$\tau_0(50\%) = 0.275 \times \left\{ \left[ k_1n(M) + \frac{k_3k_2n(M)n(O_2)}{J_3} \right] n(O_2)J_2 \right\}^{-1/2}$$

or

[14] 
$$\tau_0(50\%) = 0.275n_c(O)/n(O_2)J_2$$

if  $n_c(O)$  is the photochemical equilibrium concentration. Application of [14] leads to the following times:

Altitude (km)	90	85	80	75	70
Time (h)	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 exceeds 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 (27). 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 first introduced by Bates and Nicolet (3), and various other studies (28-31) have shown how the ozone behavior in the mesosphere may be affected by hydrogen compounds.

Near the stratopause and in the whole stratosphere  $n(O_3) > n(O)$  and another regime is established. The equation normally used in studies of the main part of the ozone layer in a pure oxygen atmosphere is

$$[15] \quad \frac{dn(O_3)}{dt} + \frac{2k_3 J_3}{k_2 n(M) n(O_2)} n^2(O_3) = 2n(O_2) J_2$$

with  $n(O)$  in photochemical equilibrium. The differential eq. 15 indicates that the time  $\tau_{O_3}$  required to attain equilibrium (in fact, to pass from zero concentration to 50% of the equilibrium value or from 50% to 80%) is

$$[16] \quad \tau_{O_3} = 0.275 n_c(O_3) / n(O_2) J_2$$

where  $n_c(O_3)$  is the photochemical equilibrium value

$$[17] \quad n_c^2(O_3) = \frac{k_2 n(M) n^2(O_2) J_2}{k_3 J_3}$$

Figures 1a and 1b show the numerical results of eq. 16 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 1 day at the stratopause and more than 10 years at 20 km. It is 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 photo-equilibrium conditions in an oxygen atmosphere are shown in Fig. 2. It is seen that it is difficult to obtain agreement between the calculated values and an average value (32) representing the observations. In the upper stratosphere, the limits of the observational and theoretical uncertainties are such that the effect of hydrogen and nitrogen compounds must be taken into account.

### Reactions in a Hydrogen-Oxygen Atmosphere

Inspection of the rates of the reactions introduced by Bates and Nicolet (3) indicates

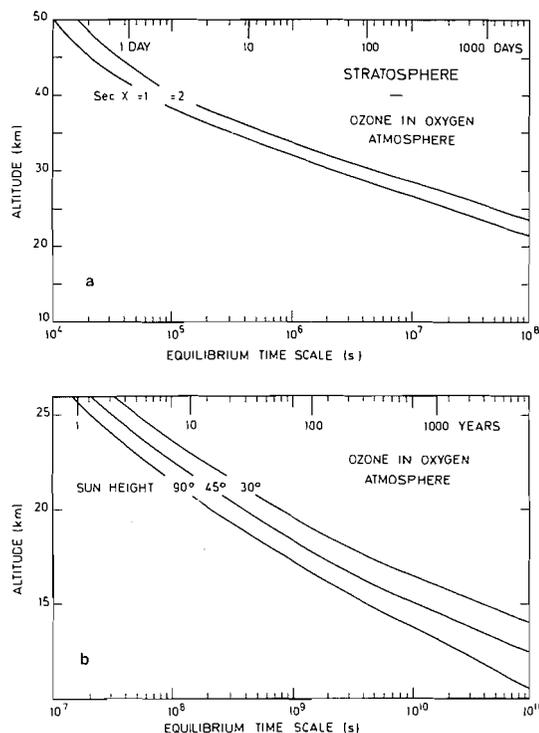


FIG. 1. (a) Equilibrium time scales for ozone in a pure oxygen atmosphere. Less than 1 day above 45 km, more than 1 year below 25 km (daytime). Overhead sun,  $\sec \chi = 1$ , and  $70^\circ$ ,  $\sec \chi = 2$ . (b) Equilibrium time scales for ozone of a pure oxygen atmosphere in the lower stratosphere for various solar heights  $90^\circ$ ,  $45^\circ$ , and  $30^\circ$ . With times greater than 1 year, there is always departure from photo-equilibrium conditions.

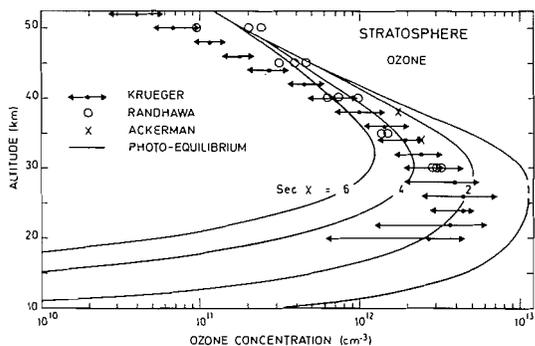


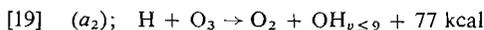
FIG. 2. Observed and calculated ozone profiles. Calculations for various solar zenith angles,  $\text{sec } \chi = 1, 2, 4,$  and  $6$ , photo-equilibrium conditions. Range in ozone concentrations observed by Krueger (32) of 24 rocket flights between  $60^\circ \text{ S}$  and  $64^\circ \text{ N}$ . Three observations by Randhawa (33) over White Sands and two observations by Ackerman (private communication, 1973) over Aire-sur-l'Adour, France.

that, in the mesosphere and stratosphere, a large number of them can be ignored.

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

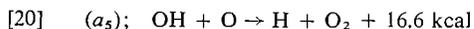


In the upper stratosphere and mesosphere the reaction of H with  $\text{O}_3$  is also important



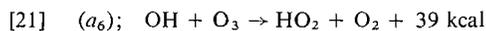
It may be concluded that hydrogen atoms are immediately transformed into hydroperoxyl radicals in the major part of the stratosphere since reaction 18 is rapid. However, in the neighborhood of the stratopause and in the mesosphere, reaction 19 which leads to OH has an important role.

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

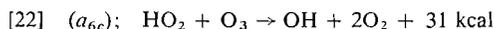


It is clear that if the effects of [20] are impor-

tant in the mesosphere, they are relatively unimportant in the lower stratosphere where other processes involving ozone are more important. The chain reaction introduced by McGrath and Norrish (34)

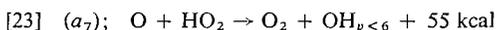


and



must be finally considered after having been rejected (35). Very recent measurements have been reported (36–38) with  $a_6 = 1.3 \times 10^{-12} e^{-950/T} \text{ cm}^3 \text{ s}^{-1}$  which leads to  $(5.5 \pm 1.5) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  at room temperature and to 1 to  $2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  at temperatures of the lower stratosphere. Such values are less than those which were used in previous aeronomic studies. An upper limit  $a_6 \leq 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at room temperature (39) was adopted as the actual value in many studies of the stratosphere (28–31, 40, 41). According to Simonaitis and Heicklen (42) the reaction rate of [22] is  $a_{6c} = 3.3 \times 10^{-14} e^{-1000/T} \text{ cm}^3 \text{ s}^{-1}$  which gives a value of  $1.25 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  at room temperature and low values of between 3 and  $6 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$  in the lower stratosphere.

Instead of reaction 22 in the upper stratosphere and mesosphere the reaction leading to OH involves atomic oxygen (39)



Kaufman (39) has suggested that  $a_7 \geq 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Reactions 20 and 23 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. Experimental data are needed in order to determine the ratio  $a_3/a_7$  which must be known accurately 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 (43)

$$[24] \quad \frac{dn(\text{O})}{dt} + 2n^2(\text{O}) \left[ k_1 n(\text{M}) + \frac{k_3 k_2 n(\text{M}) n(\text{O}_2)}{J_{3a}} \right] + n(\text{O}) \left[ a_2 n(\text{H}) \frac{k_2 n(\text{M}) n(\text{O}_2)}{J_{3a}} + a_5 n(\text{OH}) + a_7 n(\text{HO}_2) \right] = 2n(\text{O}_2) J_2$$

with

$$[25] \quad \frac{n(\text{O}_3)}{n(\text{O})} = \frac{k_2 n(\text{M})n(\text{O}_2)}{J_3 + k_3 n(\text{O}) + a_2 n(\text{H}) + a_6 n(\text{OH}) + a_{6c} n(\text{HO}_2)} \approx \frac{k_2 n(\text{M})n(\text{O}_2)}{J_{3a}}$$

and

$$[26] \quad J_{3a} \approx J_3 + a_2 n(\text{H})$$

Such an equation 25 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.

The minimum which is observed near 75 km in the ozone concentration by Hays and Roble (27) is due to the action of atomic hydrogen; the net effect of the action of hydroxyl and hydroperoxyl radicals on atomic oxygen is to cause an important decrease of the ozone concentration.

In the region where atomic oxygen is in photochemical equilibrium, the conventional stratospheric equation 15 indicates that photochemical equilibrium values can be reached in the lower mesosphere and upper stratosphere. However, [15] must be replaced in a hydrogen-oxygen atmosphere (43, 44) by

$$[27] \quad \frac{dn(\text{O}_3)}{dt} + 2n^2(\text{O}_3) \frac{J_3 k_3}{k_2 n(\text{M})n(\text{O}_2)} + n(\text{O}_3) a_2 n(\text{H}) + n(\text{O}_3) \left[ a_6 + \frac{a_5 J_3}{k_2 n(\text{M})n(\text{O}_2)} \right] n(\text{OH}) \\ + n(\text{O}_3) \left[ a_{6c} + \frac{a_7 J_3}{k_2 n(\text{M})n(\text{O}_2)} \right] n(\text{HO}_2) = 2n(\text{O}_2) J_2$$

If [27] is compared with [15], it is clear that the effect of hydrogen compounds is equivalent to an increase in the photodissociation coefficient  $J_3$ . In other words, the ozone dissociation is increased by additional processes involving H, OH, and  $\text{HO}_2$  so that the equivalent  $\text{O}_3$  photodissociation coefficient is written (43)

$$[28] \quad J_{3A} = J_3 [1 + A]$$

where  $A$  is given by

$$[29] \quad 2J_3 k_3 n(\text{O}_3) \cdot A = a_2 n(\text{H}) k_2 n(\text{M}) n(\text{O}_2) + a_5 n(\text{OH}) \left[ 1 + \frac{a_6 k_2 n(\text{M}) n(\text{O}_2)}{J_3} \right] \\ + a_7 n(\text{HO}_2) \left[ 1 + \frac{a_{6c} k_2 n(\text{M}) n(\text{O}_2)}{J_3} \right]$$

By assuming reasonable numerical values, it is easy to see that  $a_6 k_2 n(\text{M}) n(\text{O}_2) / a_5 J_3 < 1$  and  $a_{6c} k_2 n(\text{M}) n(\text{O}_2) / a_7 J_3 < 1$  in the upper stratosphere and mesosphere and  $> 1$  in the lower stratosphere. Thus, at the stratopause, the conventional equation for equilibrium conditions is

$$[30] \quad n(\text{O}_3) = \left[ \frac{k_2}{k_3} n(\text{M}) n^2(\text{O}_2) \frac{J_2}{J_3 (1 + A)} \right]^{1/2}$$

with the correction term  $n(\text{H})$  being negligible,

$$[31] \quad [1 + A]^{1/2} = \left[ 1 + \frac{a_5 n(\text{OH}) + a_7 n(\text{HO}_2)}{2k_3 n(\text{O}_3)} \right]^{1/2}$$

By assuming that the values of  $n(\text{OH})$  and

$n(\text{HO}_2)$  are known, it can be shown that the correction term can be applied in the mesosphere and at the stratopause where  $2k_3 n(\text{O}_3) \approx a_5 n(\text{OH}) + a_7 n(\text{HO}_2)$ . Below the stratopause it is difficult to see how a correction term could be introduced except if the OH and  $\text{HO}_2$  concentrations were increased by a factor of 5, at least. By assuming that the values of  $n(\text{OH})$  and  $n(\text{HO}_2)$  are known, it is possible to see (Fig. 3) 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  $10^{-8} \text{ s}^{-1}$  for  $\text{sec } \chi = 1$  and  $10^{-9} \text{ s}^{-1}$  for  $\text{sec } \chi = 2$  the times which are required to reach chemical equilibrium are longer

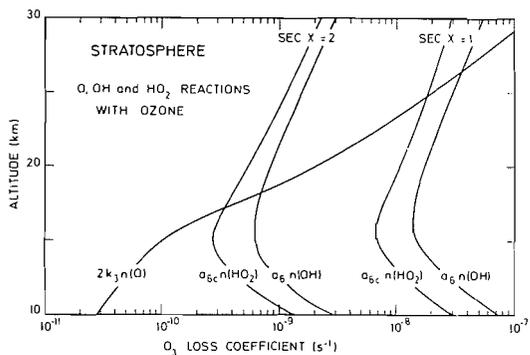


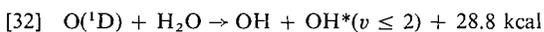
FIG. 3. Comparison between the various reactions (with O, OH, and HO<sub>2</sub>) leading to the destruction of ozone molecules. Effect of OH and HO<sub>2</sub> is particularly important in the lower stratosphere for overhead sun conditions.

than 1 year. An increase of  $n(OH)$  or  $n(HO_2)$  would be necessary in order to reduce the time to less than 1 year.

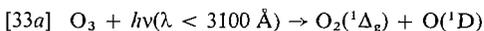
### Production of Hydroxyl and Hydroperoxyl Radicals

Water vapor can be dissociated by sunlight and its photodissociation coefficient for zero optical depth is  $10^{-5} \text{ s}^{-1}$ . 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 (43).

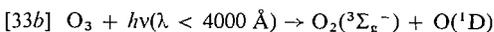
In the stratosphere, the photodissociation process is less important than the oxidation process. An effect caused by oxygen atoms, in their normal state <sup>3</sup>P, on H<sub>2</sub>O has not been detected since the reaction is endothermic, but atoms in their first excited state <sup>1</sup>D lead to (45)



The production of O(<sup>1</sup>D) atoms by photolysis of stratospheric ozone is important. A precise determination depends on the exact efficiency of O(<sup>1</sup>D) production in the processes



and



According to DeMore and Raper (46), 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 of

production of O(<sup>1</sup>D) atoms (47). At 3130 Å and 25 °C the efficiency for O(<sup>1</sup>D) production was found to be 0.5 (48). However, at stratospheric temperatures it becomes very small (49). We may consider (50) the following working value for the quenching rate coefficient

$$[34] \quad k_Q(^1D) = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

due to N<sub>2</sub> and O<sub>2</sub>. With this average value of  $k_Q$ , the production rate of O(<sup>1</sup>D) atoms leads to the photo-equilibrium concentration for various solar zenith angles illustrated in Fig. 4 for a conventional vertical distribution of O<sub>3</sub> (43). In the lower stratosphere, the concentration  $n(O(^1D))$  is 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 Å.

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>. 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 (51-55) leads to a rate coefficient

$$[35] \quad a^* = (3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

The production of HO radicals is illustrated in Fig. 5 where the minimum occurs at the tropopause, chosen here at 15 km.

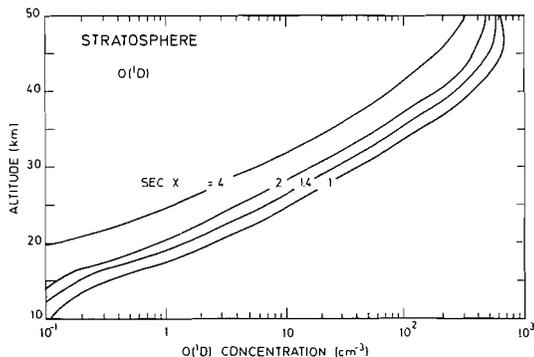


FIG. 4. Concentration of oxygen atoms in the excited state <sup>1</sup>D produced by ozone photodissociation. Variation with solar zenith angle for a constant ozone concentration.

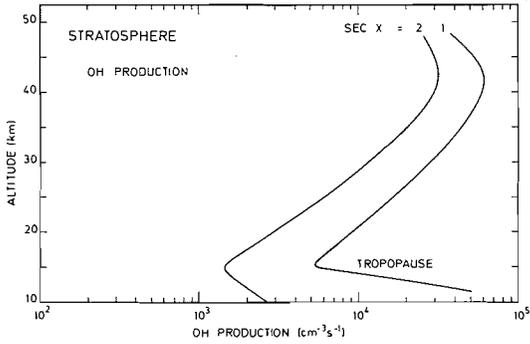


FIG. 5. Production of OH radicals in the stratosphere by reaction of  $O(^1D)$  atoms with  $H_2O$  (4 p.p.m.v.),  $CH_4$  (1.5 p.p.m.v.), and  $H_2$  (0.5 p.p.m.v.) for two solar zenith angles,  $\sec \chi = 1$  and 2.

### Reactions in a Nitrogen-Oxygen Atmosphere

The theory of nitric oxide in the upper atmosphere is based on the ionospheric properties of

the F and E regions (56–60). Ionic reactions lead to excited atoms  $N(^2D)$  which react with  $O_2$  to form nitric oxide molecules. In the stratosphere, the reaction of the electronically excited oxygen atom  $O(^1D)$  with nitrous oxide (43, 62–65) is a natural source of nitric oxide. Cosmic rays (64, 66) must also be 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 (67, 68) 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 (18, 62, 69–71), we write the differential equation for total odd nitrogen ( $N + NO + NO_2 + NO_3 + 2N_2O_5 + HNO_2 + HNO_3$ ):

$$[36] \quad \frac{dn(N)}{dt} + \frac{dn(NO)}{dt} + \frac{dn(NO_2)}{dt} + \frac{dn(NO_3)}{dt} + 2 \frac{dn(N_2O_5)}{dt} + \frac{dn(HNO_2)}{dt} + \frac{dn(HNO_3)}{dt} = P(N) + P(NO) - 2b_6n(N)n(NO)$$

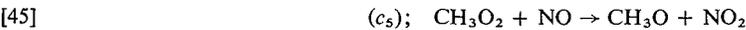
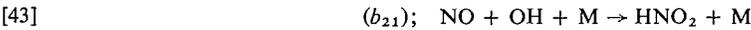
$P(N)$  is the direct production of nitrogen atoms and  $P(NO)$  is the direct production of nitric oxide molecules and



Considering photo-equilibrium conditions, for each constituent we obtain

$$[38] \quad n(NO_2)[J_{NO_2} + b_3n(O)] + n(NO_3)J_{NO-O_2} + n(HNO_2)J_{OH-NO} = n(NO)[b_2n(M)n(O) + b_4n(O_3) + b_{11}n(NO_3) + b_{21}n(M)n(OH) + b_{29}n(HO_2) + c_5c_n(CH_3O_2)]$$

where



Making the usual approximations appropriate for the stratosphere (43) and assuming that

$$[49] \quad n(NO_2)J_{NO_2} < n(O_3)J_3$$

$$[50] \quad a_2n(H) < a_6n(OH)$$

the general equation for  $O_3$  may be simplified to yield

$$[51] \quad \frac{dn(O_3)}{dt} + n(O_3)\{[a_6n(OH) + a_{6c}n(HO_2) + b_9n(NO_2)] + \frac{J_3}{k_2n(M)n(O_2)}[2k_3n(O_3) + a_5n(OH) + a_7n(HO_2) + a_{31}n(H_2O_2) + 2b_3n(NO_2)]\} = 2n(O_2)J_2 + n(NO)[2J_{NO} + b_{11}n(NO_3) + b_{21}n(M)n(OH) + b_{29}n(HO_2) + c_{5c}n(CH_3O_2)] - n(HNO_2)J_{OH-NO} - n(NO_3)[J_{NO-O_2} - J_{NO_2-O}]$$

where

$$[52] \quad (b_9); \quad O_3 + NO_2 \rightarrow NO_3 + O_2$$

$$[53] \quad (J_{NO}); \quad NO + hv \rightarrow N + O$$

$$[54] \quad (J_{NO_2-O}); \quad NO_3 + hv \rightarrow NO_2 + O$$

If we compare [51] with [27] without the introduction of nitrogen oxide effects, it is clear that we must compare the effect of  $b_9n(NO_2)$  (nighttime and daytime reaction) with  $a_6n(OH) + a_{6c}n(HO_2)$  (daytime reactions) and also  $2b_3n(NO_2)$  with  $2k_3n(O_3) + a_5n(OH) + a_7n(HO_2)$ .

The reaction of  $NO_2$  with  $O_3$  has been studied in the laboratory (72, 73). Its rate coefficient is  $b_9 = 1.23 \times 10^{-13} e^{-2470/T} \text{ cm}^3 \text{ s}^{-1}$  which leads to a rate of the order of  $10^{-18} \text{ cm}^3 \text{ s}^{-1}$  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  $a_6n(OH)$  (see Fig. 3) for  $n(NO_2)/n(M) = 3 \times 10^{-9}$ . Since reaction of  $NO_2$  with  $O_3$  plays its principal role for nighttime conditions, it seems that such a reaction cannot be neglected.

The rate coefficient of reaction 40 has been determined very accurately (74-76) to be  $b_3 = 9.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . In order to compare the effects of reactions 40 and 52,  $b_9$  has been compared with  $b_3J_3/k_2n(M)n(O_2) = b_3^e$ , in Fig. 6. The reaction between atomic oxygen and nitrogen dioxide is generally more important than the reaction between ozone and nitrogen dioxide except near the tropopause even though the absolute value of the rate coefficient  $b_9$  is only of the order of  $10^{-18} \text{ cm}^3 \text{ s}^{-1}$ . 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  $n(NO_2)$  by Ackerman and Muller (21) it is possible to make the comparison which is shown in Fig. 7. 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. Concentrations of  $NO_2$  greater than  $10^8 \text{ cm}^{-3}$  have a more important role in the  $NO_2$  reaction with atomic oxygen than with ozone.

If we consider the production term in the general equation 51, there is in addition to the normal production by molecular oxygen  $2n(O_2)J_2$  a general term depending on nitrogen oxides

$$[55] \quad n(NO)[2J_{NO} + b_{11}n(NO_3) + b_{21}n(M)n(OH) + b_{29}n(HO_2) + c_{5c}n(CH_3O_2)] - n(HNO_2)J_{OH-NO} - n(NO_3)[J_{NO-O_2} - J_{NO_2-O}]$$

Neglecting the effect of  $NO_3$  and using photo-equilibrium conditions for  $HNO_2$ , [55] is written

$$[56] \quad n(NO)[2J_{NO} + c_{5c}n(CH_3O_2) + n(HO_2)[b_{29}n(NO) - b_{33}n(NO_2)]]$$

where

$$[57] \quad (b_{33}); \quad HO_2 + NO_2 \rightarrow HNO_2 + O_2$$

The importance of [56] in the lower stratosphere depends on the values of  $c_{5c}n(CH_3O_2)$  which is about  $5 \times 10^{-7} \text{ s}^{-1}$  according to calculated values (71) at 15 km. Since  $n(NO) < 10^9 \text{ cm}^3$  in the

lower stratosphere the effect of  $CH_3O_2$  is negligible. However, it depends also on the difference  $b_{29}n(NO) - b_{33}n(NO_2)$  which seems to be positive in a sunlit atmosphere. According to Simonaitis (private communication, 1973) the ratio  $b_{29}/b_{33} = 7 \pm 2$  and, therefore, for  $n(NO_2) < 7n(NO)$  a positive term must be added to the production term  $2n(O_2)J_2$ . 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  $\text{cm}^{-3} \text{ s}^{-1}$  at 15 and 20 km, respectively, the cor-

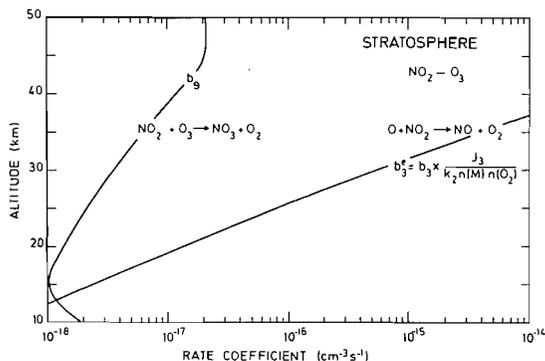


FIG. 6. Rate coefficients of nitrogen oxide with ozone and atomic oxygen. The equivalent rate coefficient  $b_3'$  increases with height and is far greater than  $b_9$  in the middle and upper stratosphere.

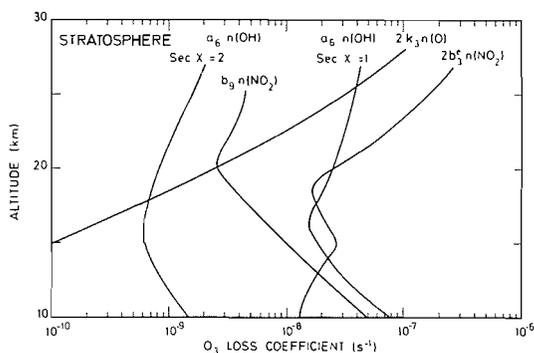


FIG. 7. Comparison of the various loss coefficients of ozone in the lower stratosphere when hydrogen and nitrogen compounds are involved; the  $\text{NO}_2$  concentration is given by Ackerman and Muller (21).

responding values for a solar zenith angle of  $60^\circ$  are only 50 and  $5 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$ . With NO concentrations of the order of  $5 \times 10^8 \text{ cm}^{-3}$  and a rate coefficient which is perhaps not less than  $2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , the addition of  $10^4$  ozone molecules  $\text{cm}^{-3} \text{ s}^{-1}$  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 [56] compared with  $2n(\text{O}_2)J_2$  when there is an artificial injection of nitrogen oxides in the stratosphere.

### Production of Nitric Oxide

The reaction of the electronically excited atom  $\text{O}(^1\text{D})$  with nitrous oxide (43) 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  $\text{N}_2\text{O}$ , 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  $\text{N}_2\text{O}$  which depends strongly on the values of the eddy diffusion coefficient which are adopted (61, 64).

A second process which can produce nitric oxide is the reaction of nitrogen atoms with molecular oxygen. This leads, in less than 10 s in the lower stratosphere, to nitric oxide molecules. The production of nitrogen atoms is related to the normal ionization by cosmic rays (64, 66). One nitrogen atom, and consequently one nitric oxide molecule, is produced per ion pair due to the cosmic rays (77). The production of N atoms is shown in Fig. 8 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. 8 for two solar zenith angles  $\text{sec } \chi = 1$  and 2.

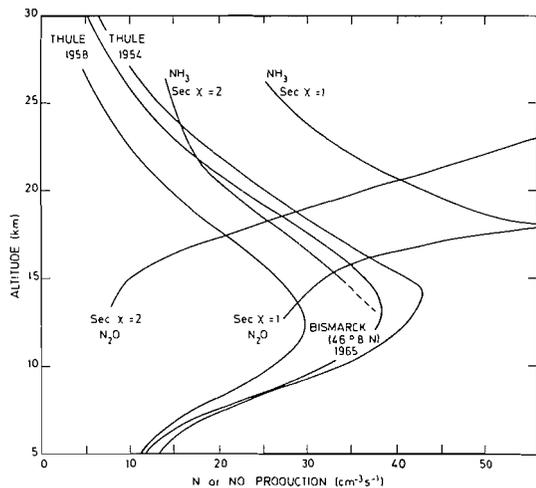


FIG. 8. Production of nitrogen atoms and nitric oxide molecules. The production of nitrogen atoms is given at Thule (Polar Cap) for maximum conditions (1954) and minimum conditions (1958) and at Bismark in 1965 (maximum conditions). The production of nitric oxide molecules from  $\text{N}_2\text{O}$  and  $\text{NH}_3$  is given for  $\text{sec } \chi = 1$  and 2, overhead sun conditions and height sun =  $30^\circ$ , respectively. Cosmic ray data from Neher (78, 79).

A third process for the production of nitric oxide in the stratosphere which can be considered is the oxidation of ammonia (67, 68, 80). The oxidation is initiated by the reaction

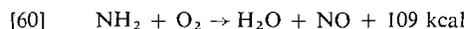


with a rate coefficient of  $(1.5 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at room temperature (68). According to Dove and Nip (81) its activation energy (measured between 1500 and 2000 °K) would be 1.1 kcal and the rate coefficient

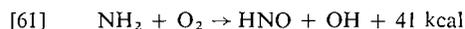
[59] 
$$k_{\text{OH-NH}_3} = 1.3 \times 10^{-14} T^{0.68} e^{-550/T} \text{ cm}^3 \text{ s}^{-1}$$

Such a formula leads to  $1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  at 300 °K in good agreement with the value deduced by Stuhl.

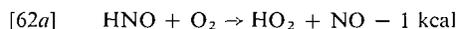
The production of nitrogen oxide molecules may come directly from the following reaction



or



with



The 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 have been presented by Junge (82) 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 (83) lead to mixing ratios as low as  $5 \times 10^{-10}$  to  $1 \times 10^{-9}$  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  $\text{NH}_3$  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. 8 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.

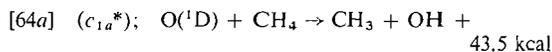
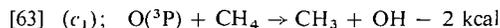
### Oxidation of Methane and Production of Carbon Monoxide

Methane is produced primarily by various bacterial decomposition processes leading to an average production (84) of  $3.4 \times 10^{11} \text{ CH}_4$  molecules  $\text{cm}^{-2} \text{ s}^{-1}$ . 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).

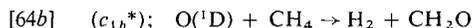
The daytime destruction process of  $\text{CH}_4$  leads to the production of CO (24, 85) with an average residence time of 0.4 year for CO if its volume fractional concentration is of the order of 0.1 p.p.m.v. The carbon monoxide molecules apparently could have a lifetime of the order of 0.1 year (71, 86-88). The sink of methane is a source for formaldehyde (25, 88) 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 (89) of the distribution of CO mixing ratios with latitude in the northern and southern hemisphere which were measured by Seiler (90).

Methane, which is mixed in the troposphere (12) is photodissociated in the mesosphere and is dissociated by oxidation processes in the stratosphere.

Atomic oxygen attacks methane through (64)

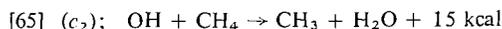


and



which occurs to the extent of 9% (91).

The other important reaction in the stratosphere is

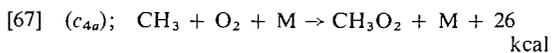


In the lower stratosphere  $\text{CO}_2$  is photodissociated at a very low rate and the production of CO

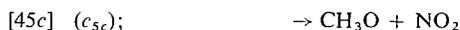
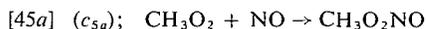
corresponds to the total oxidation process of  $\text{CH}_4$  by reactions 64 and 65. The oxidation of carbon monoxide is attributed to



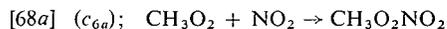
Methyl radicals, which are produced by oxidation processes of  $\text{CH}_4$ , react immediately with molecular oxygen to form methylperoxy radicals



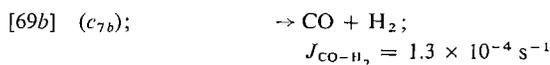
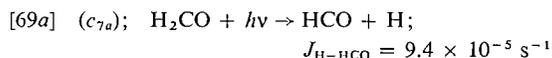
Methylperoxy radicals react with NO (92) leading to



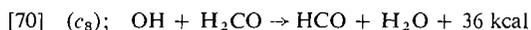
According to Spicer *et al.* (92), there was no evidence for  $\text{CH}_3\text{O}$  radical production in their studies and they concluded that reaction 45c did not occur, contrary to expectation from atmospheric evidence. Levy (71) has considered that 45c is the reaction occurring with  $c_{5c} \geq 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . In the same way the reactions with  $\text{NO}_2$  are



The photochemistry of formaldehyde (93, 94) indicates that two distinct primary processes occur



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

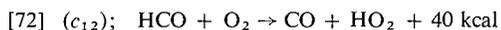


must also be introduced.

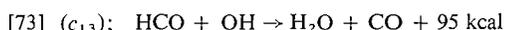
The formyl radical is photodissociated (95)



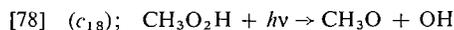
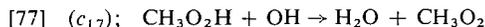
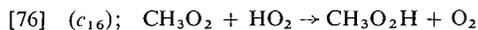
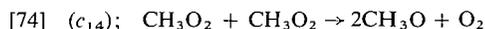
or reacts with  $\text{O}_2$  (96)



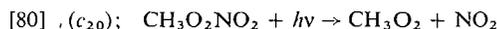
or reacts with OH



Other reactions have been introduced (24, 71, 80, 85, 88):



The two following reactions are also considered



Thus, with eqs. 63 to 80, it is possible to write for equilibrium conditions that

$$[81] \quad n(\text{H}_2\text{CO})[J_{\text{H-HCO}} + J_{\text{H}_2-\text{CO}} + c_8 n(\text{OH})] = n(\text{CH}_4)[c_1 n(\text{O}) + c_1^* n(\text{O}^*) + c_2 n(\text{OH})]$$

$$= n(\text{HCO})[J_{\text{H-CO}} + c_{12} n(\text{O}_2) + c_{13} n(\text{OH})] + n(\text{H}_2\text{CO})J_{\text{CO-H}_2}$$

If we consider the various reactions involving the production and loss mechanisms of H, OH, and  $\text{HO}_2$  and use [81] we obtain

$$[82] \quad \frac{dn(\text{H})}{dt} + \frac{dn(\text{OH})}{dt} + \frac{dn(\text{HO}_2)}{dt} + n(\text{OH})c_2 n(\text{CH}_4)[1 - X] + 2n(\text{OH})[c_{13} n(\text{HCO})$$

$$+ c_{17} n(\text{CH}_3\text{O}_2\text{H})] = n(\text{CH}_4)[c_1 n(\text{O}) + c_1^* n(\text{O}^*)][1 + X] + n(\text{CH}_3\text{O})c_{15} n(\text{O}_2)$$

with

$$[83] \quad X = \frac{2J_{\text{H-HCO}} + c_9 n(\text{O})}{J_{\text{H-HCO}} + J_{\text{CO-H}_2} + c_8 n(\text{OH}) + c_9 n(\text{O}) + c_{10} n(\text{H})}$$

The ratio  $X \approx 2J_{\text{H-HCO}}/J_{\text{CO-H}_2}$  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 eq. 82 lead to

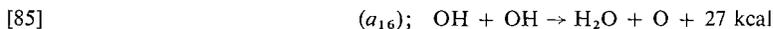
$$[84] \quad +n(\text{OH})c_2 n(\text{CH}_4)[1 - X] = n(\text{CH}_4)[c_1 n(\text{O}) + c_1^* n(\text{O}^*)][1 + X] + \dots$$

which are the principal terms which must be introduced when methane is present. In the stratosphere, oxidation leads to a decrease in the mixing ratio of CH<sub>4</sub>. However, the transport from the troposphere is such that its vertical profile has a weak gradient, as is shown from balloon samples and a rocket sample (12, 97).

### Removal of Hydroxyl Radicals

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

In addition to the previous reactions discussed it is necessary to consider the following reactions leading to the re-formation of H<sub>2</sub>O

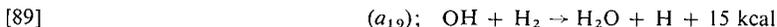
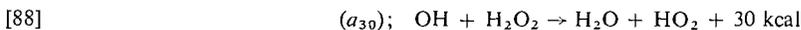
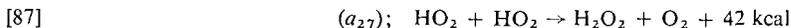


and



Reaction 86 is extremely important since recent measurements by Hochanadel *et al.* (98) indicate a rate coefficient  $a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ .

In the discussion concerning the more important reactions of hydroxyl and hydroperoxyl radicals, the reactions involving HO<sub>2</sub> must be considered (43)



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

$$[90] \quad n(\text{OH}) \left[ a_{16}n(\text{OH}) + a_{17}n(\text{HO}_2) + a_{30}n(\text{H}_2\text{O}_2) + c_2 \left( \frac{1-X}{2} \right) n(\text{CH}_4) + b_{27}n(\text{HNO}_3) \right] \\ = n(\text{H}_2\text{O}) [J_{\text{H-OH}} + a^*n(\text{O}^*)] + n(\text{H}_2)a_{24}^*n(\text{O}^*) + n(\text{CH}_4) \left[ \frac{1+X}{2} \{c_1^*n(\text{O}^*) + c_1^*n(\text{O}^*)\} \right]$$

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

$$[91] \quad n(\text{HO}_2) [a_{6c}n(\text{O}_3) + a_7n(\text{O}) + a_{17}n(\text{OH}) + 2a_{27}n(\text{HO}_2) + b_{29}n(\text{NO}) + b_{33}n(\text{NO}_2)] \\ = n(\text{OH}) [a_5n(\text{O}) + a_6n(\text{O}_3) + a_{19}n(\text{H}_2) + a_{30}n(\text{H}_2\text{O}_2) + a_{36}n(\text{CO}) \\ + c_8n(\text{H}_2\text{CO}) + c_2Xn(\text{CH}_4)]$$

Equations 90 and 91 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 Fig. 9, 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 to H + HO<sub>2</sub> is the reaction with CO. In the lower stratosphere when  $n(\text{CO})/n(\text{M}) \leq 5 \times 10^{-8}$  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 to 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. 9 is deduced for a mixing ratio of 10<sup>-7</sup> in the troposphere and 5 × 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. 10 that, in the lower stratosphere, the reactions with nitric oxide cannot be neglected.

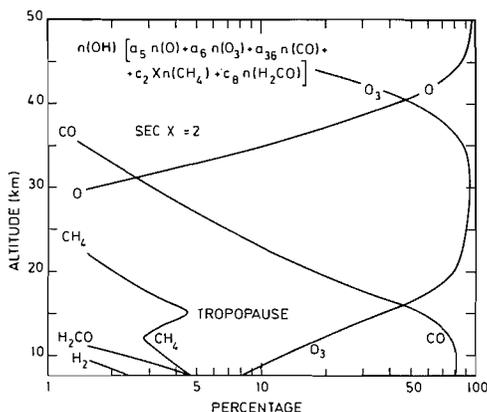


FIG. 9. Profiles (%) of the various terms affecting OH in the determination of the ratio  $n(\text{HO}_2)/n(\text{OH})$ . CO effect due to its mixing ratio  $5 \times 10^{-8}$  in the stratosphere.

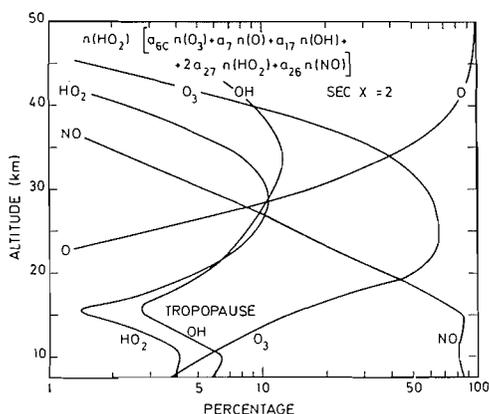


FIG. 10. Profiles (%) of the various terms affecting  $\text{HO}_2$  in the determination of the ratio  $n(\text{HO}_2)/n(\text{OH})$ . NO effect due to a mixing ratio  $3 \times 10^{-9}$  for  $\text{NO}_x$ .

Its exact role depends on the value of the rate coefficient and on the vertical distribution of its concentration which here is  $n(\text{NO}_x)/n(\text{M}) = 3 \times 10^{-9}$ . As for OH, the effects of the reaction of  $\text{HO}_2$  with  $\text{O}_3$  and  $\text{O}$  occur in the middle and upper stratosphere, respectively. However, it must be pointed out that the simultaneous effects of the reactions with OH,  $\text{HO}_2$ , and  $\text{O}$  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  $b_{29}$  (here  $3 \times 10^{-13}$ ) (99) and on the vertical distribution of the nitric oxide concentration in the lower stratosphere. A value of the order of  $10^{-12} \text{ cm}^3 \text{ s}^{-1}$  or more for the reaction between NO and  $\text{HO}_2$  would increase its effect and the OH concentration.

Thus, the main features of Figs. 9 and 10 correspond to the effect on OH and  $\text{HO}_2$  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.

The essential features of the calculations appear very sensitive in the lower stratosphere to the adopted values for the concentration of CO and NO. In Fig. 11 the ratio  $n(\text{HO}_2)/n(\text{OH})$  is represented for the condition illustrated in Figs. 9 and 10. Another curve (NO = 0) shows that for a relative concentration of  $\text{NO}_x$  of  $5 \times 10^{-10}$ , the ratio  $n(\text{HO}_2)/n(\text{OH})$  increases 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 less than 10 at 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. 11, 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. 12). If the value of  $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  reported by Hochanadel *et al.* (98) is reduced by a factor of 4, the impor-

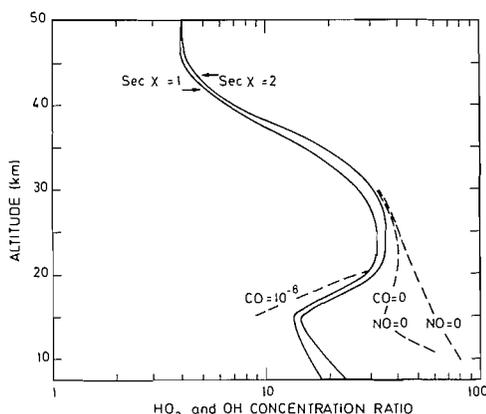


FIG. 11. Ratio  $n(\text{HO}_2)/n(\text{OH})$  in the stratosphere. Curve (NO— $\text{HO}_2$ ) using values given in Figs. 9 and 10. Curve NO = 0 when the mixing ratio of  $\text{NO}_x$  is reduced to  $5 \times 10^{-10}$ . Curve CO = 0, when CO is neglected. Curve CO = 0, NO = 0, neglecting the effect of CO and NO.

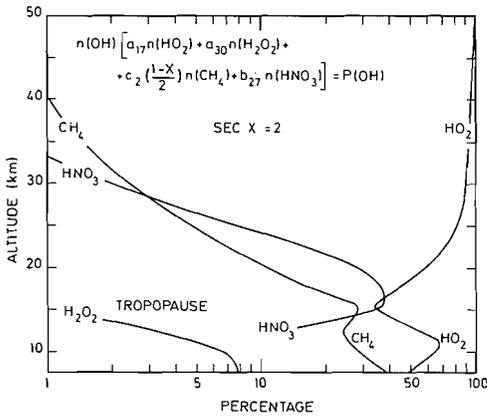


FIG. 12. Profiles (%) of the various terms determining the concentration of the hydroxyl radical, using values corresponding to profiles of Figs. 9 and 10. The HNO<sub>3</sub> concentrations correspond to an average value of observational results by Murcay *et al.* (20).

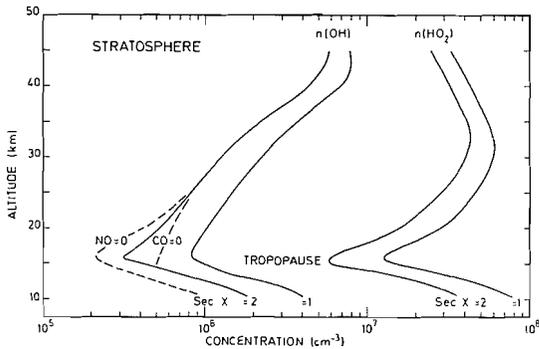


FIG. 13. OH and HO<sub>2</sub> concentrations in the stratosphere for conditions defined in Figs. 9 and 10. Changes when CO (curve CO = 0) is neglected, and when NO was a reduced mixing ratio to  $5 \times 10^{-10}$  (curve NO = 0).

tance of CH<sub>4</sub> and HNO<sub>3</sub> increases in the lower stratosphere. The effect of HNO<sub>3</sub> reaches more than 50% between 15 and 20 km. Calculated profiles for OH and HO<sub>2</sub> are presented in Fig. 13. 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 now known in the stratosphere within a factor of 4. The OH and HO<sub>2</sub> profiles have to be provided to determine the wide range of reactions in which CO, CH<sub>4</sub>, O<sub>3</sub>, O, NO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub>, HNO<sub>2</sub>, and H<sub>2</sub>O are involved in the stratosphere.

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