

AERONOMIC CHEMISTRY OF THE STRATOSPHERE*

MARCEL NICOLET

Institut d'Aéronomie Spatiale, 3 Avenue Circulaire, 1180 Brussels, Belgium

(Received 30 March 1972)

Abstract—In the stratosphere, dissociation of H_2O , CH_4 and H_2 is brought about, mainly by reaction processes with excited oxygen atoms produced by the photodissociation of ozone. A discrepancy noted between theoretical and observational concentrations of O_3 in the upper stratosphere suggests two possible explanations: solar radiation fluxes for O_2 photodissociation which are too large along with too large rate coefficients and absorption cross sections or ozone reduction brought about by the effect of hydrogen compounds or of nitrogen oxides.

The reaction of the excited oxygen atom 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. The vertical distribution of water vapor is not affected by its dissociation in the stratosphere since its reformation is rapid.

The fact that the ratio of the hydroxyl and hydroperoxyl radical concentrations cannot be determined with adequate precision complicates the calculation of the destruction of ozone which occurs through reactions of OH and HO_2 not only with atomic oxygen in the upper stratosphere but also with CO and NO in the lower stratosphere, respectively. The same difficulty arises in connection with the dissociation of nitric acid molecules formed by the reaction of OH and NO_2 ; destruction processes by photodissociation or by reaction with OH are not yet known with precision. Another difficulty, of a different kind, is that the nitric oxide concentration is not well known at the stratopause level.

I. INTRODUCTION

Theories of the ozone distribution in the terrestrial atmosphere have been given by Chapman (1930, 1943). He first considered the balance between the formation and destruction of ozone in relation to its regular daily and annual variations. The atmosphere was considered as static without horizontal or vertical transfer of ozone. Any reactions with nitrogen or other atmospheric constituents were ignored.

The introduction of hydrogen compounds in the photochemical treatment of the ozone problem by Bates and Nicolet (1950) led to the first indication of a possible action of hydroxyl and hydroperoxyl radicals on the ozone distribution, especially in the mesosphere where the photodissociation of water vapor and methane occur. Furthermore, in the stratosphere, the reaction of H_2O with the electronically excited atomic oxygen in the 1D state (Cadle, 1964; Hampson, 1964) leads to the possibility of its dissociation in the stratosphere. The concentrations of $O(^1D)$ produced by ozone photolysis in the stratosphere and troposphere are sufficiently large to lead to OH radicals (and H atoms) not only from water vapor but also from methane and molecular hydrogen. Finally, the action of nitrogen oxides on ozone (Crutzen, 1970; Johnston, 1971), may be considered in the atmospheric ozone equilibrium. However, the formation of nitric acid (Nicolet, 1965, 1970b; Johnston, 1971) seems to be the mechanism responsible for the removal of nitrogen oxides.

II. THE OZONE FORMATION

The equations governing the rates of change of the concentration of ozone and atomic oxygen, $n(O_3)$ and $n(O)$, are

$$\frac{dn(O)}{dt} + 2k_1n(M)n^2(O) + k_2n(M)n(O_2)n(O) + k_3n(O_3)n(O) = 2n(O_2)J_2 + n(O_3)J_3 \quad (1)$$

* Invited paper at the Survey Conference on Climatic Impact Assessment Program of the United States Department of Transportation, Cambridge, Massachusetts, February 15 and 16, 1972.

and

$$\frac{dn(\text{O}_3)}{dt} + n(\text{O}_3)J_3 + k_3n(\text{O})n(\text{O}_3) = k_2n(\text{M})n(\text{O}_2)n(\text{O}) \quad (2)$$

which lead to the general form

$$\frac{dn(\text{O})}{dt} + \frac{dn(\text{O}_3)}{dt} + 2k_1n(\text{M})n^2(\text{O}) + 2k_3n(\text{O}_3)n(\text{O}) = 2n(\text{O}_2)J_2. \quad (3)$$

In these equations, J_2 and J_3 are the photodissociation coefficients of O_2 and O_3 , respectively,



The rate coefficients are



In the stratosphere, Reaction (6) takes place very slowly and can be omitted in all photochemical discussions of stratospheric ozone (Bates and Nicolet, 1950). Furthermore, atomic oxygen is always in photochemical equilibrium with ozone. Therefore, the rate of change of $n(\text{O}_3)$ in the stratosphere becomes

$$\frac{dn(\text{O}_3)}{dt} + \frac{2k_3J_3}{k_2n(\text{M})n(\text{O}_2)} n^2(\text{O}_3) = 2n(\text{O}_2)J_2. \quad (9)$$

Introducing the time $\tau_q(\text{O}_3)$, necessary to attain 50 per cent of the photochemical value $n_*(\text{O}_3)$, the following equation is obtained

$$\tau_{eq}(\text{O}_3) = 0.275n_*(\text{O}_3)/n(\text{O}_2)J_2. \quad (10)$$

With numerical values (Table 1), it can be shown (see Fig. 5a) that photochemical equilibrium can be adopted for $n(\text{O}_3)$ at the stratopause. From (9), the following equation

$$n_*^2(\text{O}_3) = \frac{k_2}{k_3} n(\text{M})n^2(\text{O}_2) \frac{J_2}{J_3} \quad (11)$$

represents photochemical equilibrium conditions in the stratosphere for a pure oxygen atmosphere. The numerical values of the ozone concentration $n(\text{O}_3)$ depend on the ratios k_2/k_3 and J_2/J_3 .

TABLE 1. ATMOSPHERIC PARAMETERS IN THE STRATOSPHERE

Altitude (km)	Temperature (°K)	Total concentration (cm ⁻³)	Ozone (example) (cm ⁻³)
15	211	3.9 × 10 ¹⁸	1.0 × 10 ¹³
20	219	1.7 × 10 ¹⁸	2.9 × 10 ¹²
25	227	7.7 × 10 ¹⁷	3.2 × 10 ¹²
30	235	3.6 × 10 ¹⁷	2.9 × 10 ¹²
35	252	1.7 × 10 ¹⁷	2.0 × 10 ¹²
40	268	8.1 × 10 ¹⁶	1.0 × 10 ¹²
45	274	4.3 × 10 ¹⁶	3.2 × 10 ¹¹
50	274	2.3 × 10 ¹⁶	1.0 × 10 ¹¹

The ratio k_2/k_3 is not yet known with sufficient accuracy for aeronomic purposes. According to Clyne *et al.* (1965) the following expression for k_2 represents their experimental data over the temperature range 188–373°K, (if $M = \text{N}_2, \text{O}_2$),

$$k_2 = 3.7 \times 10^{-35} e^{900/T} \text{ cm}^6 \text{ sec}^{-1}. \quad (12a)$$

From Kaufman and Kelso (1967) the result is

$$k_2(\text{N}_2, \text{O}_2) = (5.8 \pm 1.0) \times 10^{-34} \text{ cm}^6 \text{ sec}^{-1} \quad (12b)$$

for $T = 300^\circ\text{K}$. Other measurements (Hochanadel *et al.*, 1968; Mulcahy and Williams, 1968; Donovan *et al.*, 1970) lead to various values of the same order of magnitude, indicating differences of about a factor of two over the temperature range 200–300°K. The value recommended by Johnston (1968) is (see Fig. 1a)

$$k_2(\text{N}_2, \text{O}_2) = 1.85 \times 10^{-35} e^{1050/T} \text{ cm}^6 \text{ sec}^{-1}, \quad (12c)$$

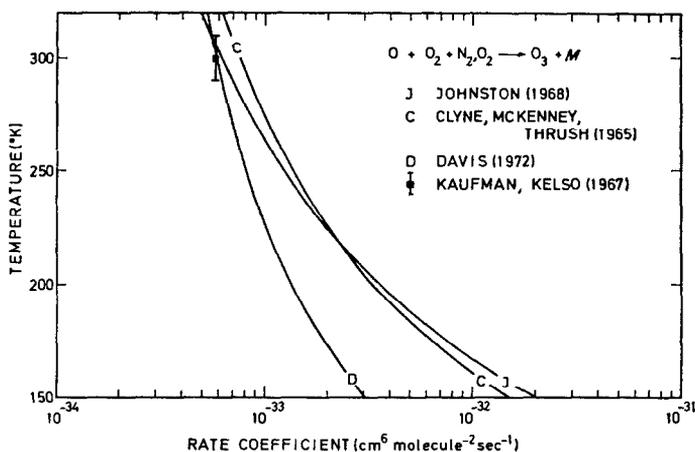


FIG. 1(a). EXPERIMENTAL VALUES OF THE RATE COEFFICIENT k_2 ($\text{cm}^6 \text{ sec}^{-1}$) OF THE THREE BODY REACTION $\text{O}_2 + \text{O} + \text{M} \rightarrow \text{O}_3 + \text{M}$ WHEN THE THIRD BODY IS N_2 (4/5) AND O_2 (1/5).

while a recent measurement by Davis (1972) between 200°K and 346°K leads to (see Fig. 1a)

$$k_2(\text{N}_2) = (1.1 \pm 0.7) \times 10^{-34} e^{(500 \pm 50)/T} \text{ cm}^6 \text{ sec}^{-1}. \quad (12d)$$

A comparison made between (12a–d) is illustrated in Fig. 1a over the temperature range 150–300°K. It shows that there is a difference of about a factor of 2 at 225°K, reaching a factor of 4 near 160°K. At 300°K there is good agreement between the various measurements (cf. Kaufman's and Kelso's data).

As far as the rate coefficient k_3 is concerned the value recommended by Johnston (1968) is

$$k_3 = 2 \times 10^{-11} e^{-2395/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (13a)$$

Recent measurements over the temperature range 200–300°K by Krezenski, Simonaitis and Heicklen (1971) leads to

$$k_3 = (1.1 \pm 0.2) \times 10^{-11} e^{-(2150 \pm 100)/T} \text{ cm}^3 \text{ sec}^{-1} \quad (13b)$$

and over the temperature range 269–409°K by McCrumb and Kaufman (1972) leads to

$$k_3 = (1.05 \pm 0.88) \times 10^{-11} e^{-(2150 \pm 50)/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (13c)$$

Expressions (13b) and (13c) lead to the same numerical values below 200°K where the difference with (13a) is about a factor of 2 (see Fig. 1b).

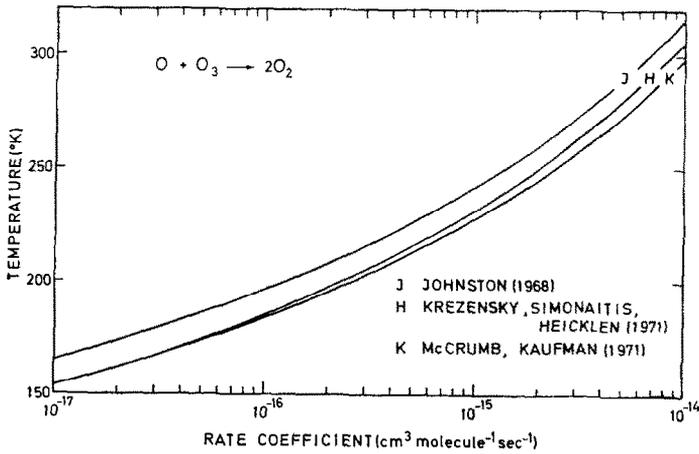


FIG. 1(b). EXPERIMENTAL VALUES OF THE RATE COEFFICIENT k_3 ($\text{cm}^3 \text{sec}^{-1}$) OF THE REACTIONS $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$.

Therefore, using (12d) with (13b) and (12c) with (13a), the ratio k_2/k_3 which plays an important role in Equation (11) can be written,

$$\frac{k_2(\text{Davis})}{k_3(\text{Heicklen})} = (1.0 \pm 0.2) \times 10^{-23} e^{(2650 \pm 250)/T} \text{ cm}^3 \tag{14a}$$

and

$$\frac{k_2(\text{Johnston})}{k_3(\text{Johnston})} = 9.26 \times 10^{-25} e^{3445/T} \text{ cm}^3, \tag{14b}$$

respectively. Differences of a factor of about 5 and of about 2 occur at 200 and 270°K, respectively, as it is shown in Fig. 1c. A special and careful analysis of the ratio k_2/k_3 over

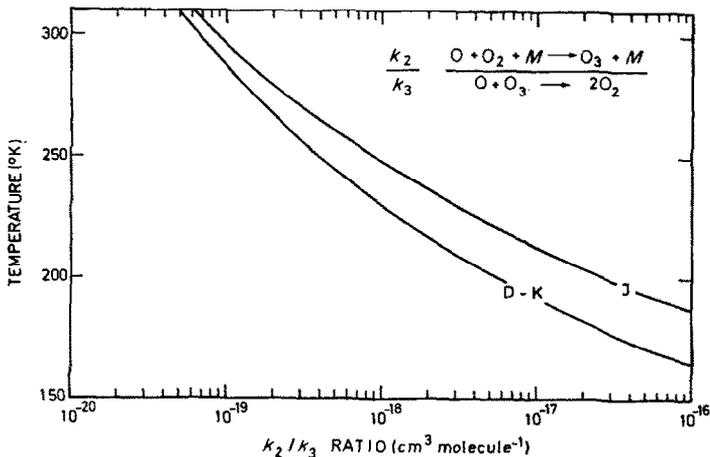


FIG. 1(c). EXPERIMENTAL VALUES OF THE RATIOS OF THE RATE COEFFICIENT k_2 AND k_3 GIVEN IN Fig. 1a AND Fig. 1b.

the temperature range 150–300°K is required for the analysis of aeronomic processes in the stratosphere and mesosphere.

As far as the photodissociation coefficients are concerned, it seems that new observations of the solar radiation are needed in the 2300–2000 Å spectral range where O_2 is photodissociated. The photodissociation coefficients J_2 , which are given in Fig. 2, depend on the

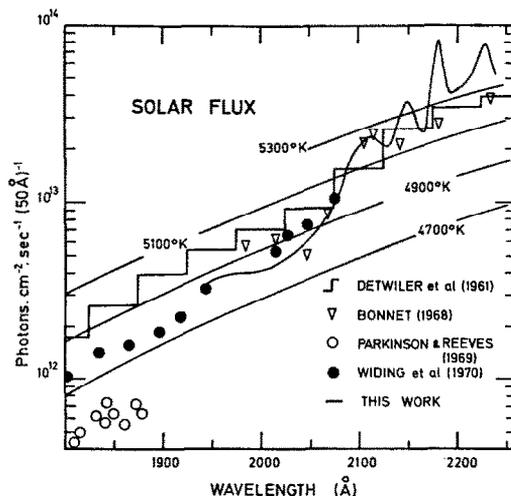


FIG. 2. OBSERVATIONAL DATA OF SOLAR RADIATION IN THE 1800–2250 Å SPECTRAL RANGE ACCORDING TO ACKERMAN, FRIMOUT AND PASTIELS (1971).

u.v. solar flux data (Fig. 3) deduced by Ackerman *et al.* (1971). Using the data tabulated by Ackerman (1971) and a ratio k_2/k_3 equivalent to formula (14b) (Nicolet, 1970), the results obtained are shown in Fig. 4 indicating that the theoretical values of the ozone concentrations are greater than the observational values (Krueger, 1969; Hilsenrath, 1969 and 1971; Randhava, 1971) above 30 km.

It is clear that it is possible to decrease the theoretical value $n_*(O_3)$ if the recent ratio k_2/k_3 obtained from (14a) is used instead of the ratio (14b). Furthermore, two other additional factors must be considered: either a decrease in J_2 or an increase in the effective value of J_3 . A decrease in J_2 may be due to a simultaneous reduction in the photodissociation cross sections and in the solar flux over the 2300–2000 Å spectral range. A careful analysis of the spectral absorption in the Herzberg continuum is required since the absorption cross sections are very small (Ditchburn and Young, 1962; Shardanand, 1969; Ogawa, 1971; Hasson and Nicholls, 1971). A reduced solar flux has been suggested (Wilson, 1966). A reduction in the effective value of J_3 may be due to an effect of HO_x (Hampson, 1964; Roney, 1965) or of NO_x (Crutzen, 1970; Johnston, 1971). Instead of (11) an equivalent equation may be written as follows (Nicolet, 1970, 1971).

$$n_*^2(O_3) = \frac{k_2}{k_3} n(M)n^2(O_2) \frac{J_2}{J_3(1+A)} \quad (15)$$

where A is a correction term of the form

$$A = \frac{an(HO_x) + bn(NO_x)}{k_3n(O_3)} \quad (16)$$

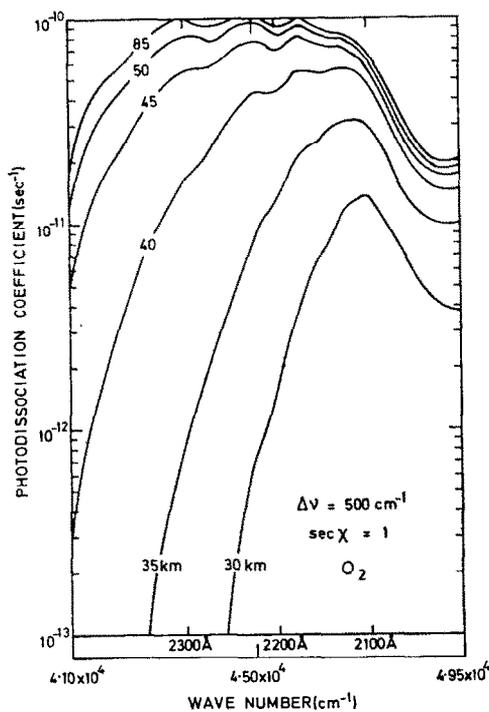


FIG. 3. PHOTODISSOCIATION COEFFICIENTS OF MOLECULAR OXYGEN IN THE STRATOSPHERE FOR SPECTRAL RANGES CORRESPONDING TO $\Delta\nu = 500 \text{ cm}^{-1}$ BETWEEN 2400 AND 2000 Å.

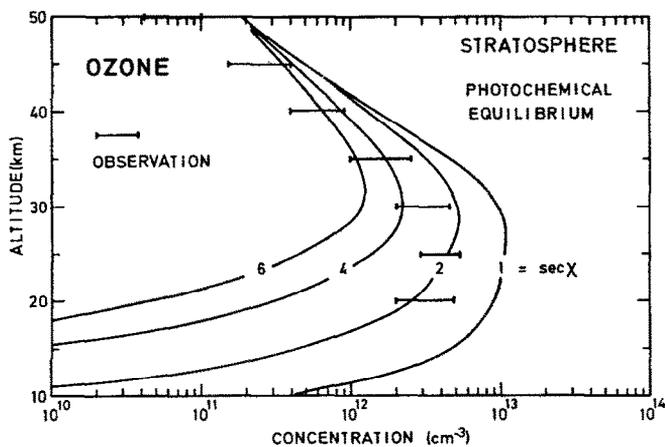


FIG. 4. OZONE CONCENTRATIONS FOR PHOTOCHEMICAL EQUILIBRIUM CONDITIONS COMPARED WITH OBSERVATIONAL DATA. χ IS THE SOLAR ZENITH ANGLE.

and a and b are the rate coefficients of the reactions of HO_x and NO_x , respectively, with atomic oxygen.

The reduction of the photochemical values $n_*(\text{O}_3)$ to the observed values was considered by Crutzen (1970) and Johnston (1971) by including an NO_x effect leading to an increasing mixing ratio of nitrogen oxide with altitude in the stratosphere. Near the stratopause the correction term must also include the effect of the hydrogen compounds. Above the

tropopause the catalytic chain involving OH and HO₂ with O₃ (McGrath and Norrish, 1958) which was introduced in order to remove ozone (see, for example, Hunt, 1966; Hesstvedt, 1968; Leovy, 1969) seems unlikely since the rate coefficients which were adopted are too large.

It appears, therefore, that the difficulty has not yet been resolved. In the upper part of the stratosphere (see Fig. 5a) the equilibrium times are short and the ozone concentration is

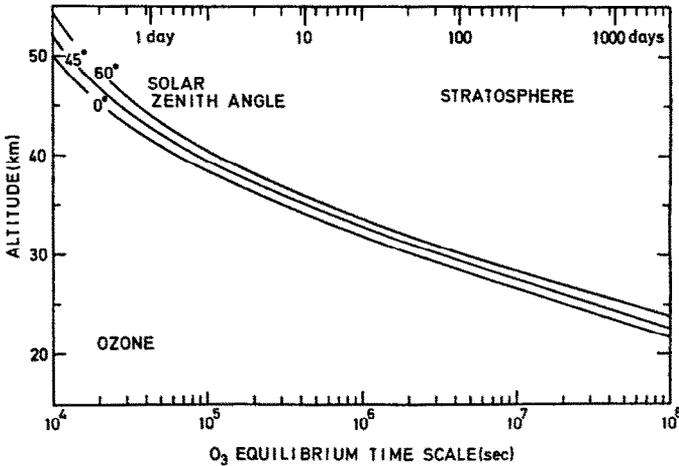


FIG. 5(a). THE TIME TO REACH EQUILIBRIUM INCREASES FROM LESS THAN A DAY AT THE STRATOPAUSE TO MORE THAN A YEAR AT 25 km.

insensitive to atmospheric transport. In the lower stratosphere (Fig. 5b) the equilibrium ozone concentration depends strongly on zenith angle and the O₃ concentration is controlled by downward transport. There is a complete departure from photochemical equilibrium conditions since equilibrium times are greater than 1 yr and dynamic considerations must be

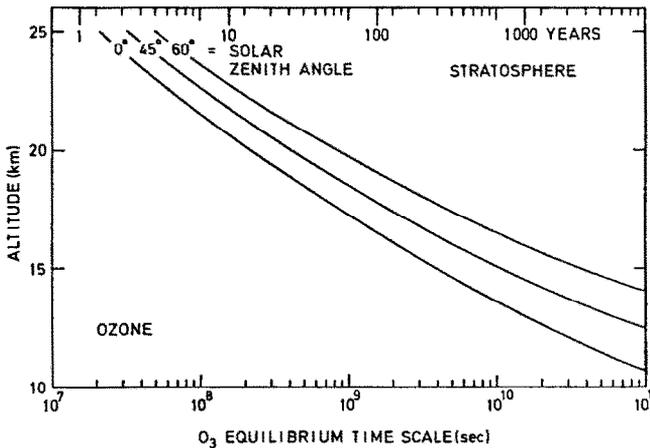


FIG. 5(b). THERE IS A DEPARTURE FROM PHOTOCHEMICAL EQUILIBRIUM CONDITIONS IN THE LOWER STRATOSPHERE SINCE THE O₃ EQUILIBRIUM TIMES INCREASES FROM 1 yr AT 25 km TO MORE THAN 100 yr AT 15 km.

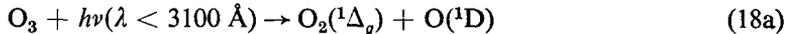
introduced. Thus, instead of (9), the general equation becomes, (16)

$$\frac{\partial n(\text{O}_3)}{\partial t} + \text{div} [n(\text{O}_3)w_{\text{O}_3}] + \frac{2k_3J_3}{k_2n(M)n(\text{O}_2)} \{n^2(\text{O}_3) + an(\text{HO}_x) + bn(\text{NO}_x)\} = 2n(\text{O}_2)J_2 \quad (17)$$

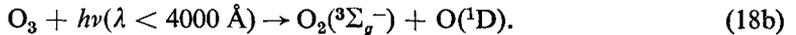
where w_{O_3} is the transport velocity of O_3 .

III. THE HYDROGEN-OXYGEN ATMOSPHERE

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



and



According to DeMore and Raper (1966), all oxygen atoms are $\text{O}(^1\text{D})$ at $\lambda \leq 3100 \text{ \AA}$; for $\lambda > 3100 \text{ \AA}$ there is a drop in the efficiency leading to $\text{O}(^3\text{P})$ atoms at 3340 \AA . (Jones and Wayne, 1969).

Two extreme values of the $\text{O}(^1\text{D})$ production have been adopted, and considering the following working value for the quenching rate coefficient

$$k_Q(^1\text{D}) = 5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (19)$$

due to N_2 and O_2 (Young *et al.*, 1968; Paraskevopoulos and Cvetanovic, 1969; DeMore, 1970; Noxon, 1970), the photoequilibrium values of $\text{O}(^1\text{D})$ concentrations for various solar zenith angles are illustrated in Fig. 6. At the stratopause the variation is small but, in the lower stratosphere, the values depend significantly on zenith angle and are sensitive to the spectral efficiency of $\text{O}(^1\text{D})$ production which is chosen from the experimental data.

The study of the reaction of $\text{O}(^1\text{D})$ with H_2O , CH_4 and H_2 is an important step in the

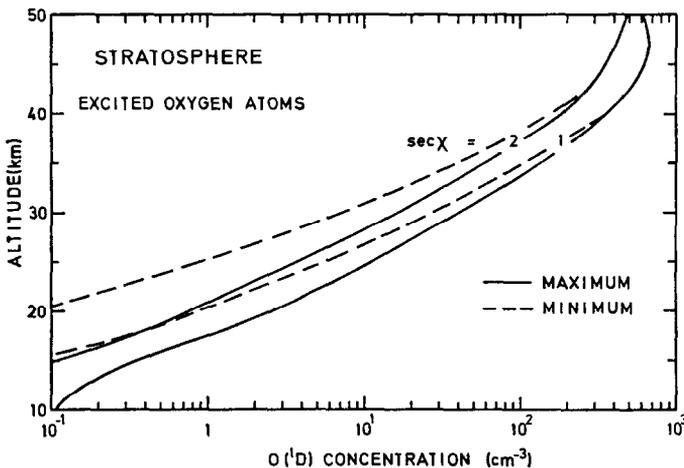
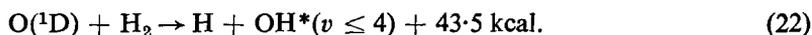
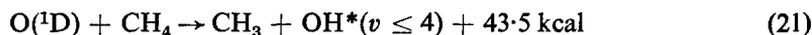


FIG. 6. CONCENTRATION OF EXCITED OXYGEN ATOMS FOR TWO SOLAR ZENITH ANGLES AND TWO DIFFERENT (MINIMUM AND MAXIMUM) PRODUCTIONS.

analysis of the aeronomic behavior in the stratosphere. The following reactions occur



Thus the presence of $\text{O}(^1\text{D})$ atoms leads to the possibility of the production of H atoms and OH radicals by H_2O , H_2 and CH_4 in the stratosphere. With the fractional volume concentrations that can be adopted (see Nicolet, 1971 for references and explanation) as conventional values at the tropopause for $\text{H}_2(0.5 \times 10^{-6})$, for $\text{CH}_4(1.5 \times 10^{-6})$ and for $\text{H}_2\text{O}(3 \times 10^{-6})$, the total production $P(\text{HO}_x)$ of HO_x radicals at the bottom of the stratosphere is

$$P(\text{HO}_x) = 13 \times 10^{-6} n(M) \cdot n^*(\text{O}) a^* \quad (23)$$

where a^* is the rate coefficient for (20–22). Such a coefficient has a value greater than $10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ (Nicolet, 1970, 1971). Recent experimental analysis (Young *et al.*, 1968; Donovan *et al.*, 1970; Paraskevopoulos and Cvetanovic, 1971; Heicklen *et al.*, 1971) leads to

$$a^* = (3 \pm 1) \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}. \quad (24)$$

Thus the production of HO_x in the stratosphere near the tropopause may attain

$$P(\text{HO}_x) \simeq 10^{-4} n(\text{O}_3) J_3^* \quad (25)$$

where J_3^* is the photodissociation rate coefficient leading to $\text{O}(^1\text{D})$ atoms. Numerical results lead to a production of OH radicals from the H_2O dissociation of not less than $10^4 \text{ cm}^{-3} \text{ sec}^{-1}$ above 20 km for an overhead sun and reaching $7 \times 10^4 \text{ cm}^{-3} \text{ sec}^{-1}$ in the upper stratosphere.

Inspection of the reactions introduced by Bates and Nicolet (1950) indicates that, in the 'stratosphere' (Nicolet, 1971) a large number of them can be ignored when the rate coefficients are sufficiently well known.

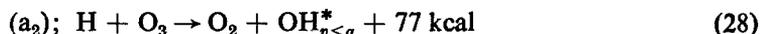
At the stratopause level, a three-body reaction involving atomic hydrogen and molecular oxygen leads to a hydroperoxyl radical



The rate coefficient based on measurements made at low temperature by Clyne and Thrush (1963b) and Larkin and Thrush (1964) has a negative temperature coefficient

$$a_1 n(M) = 3.3 \times 10^{-33} e^{800/T} n(\text{N}_2, \text{O}_2) \text{ cm}^3 \text{ sec}^{-1}. \quad (27)$$

At the stratopause, and in the upper part of the stratosphere, the reaction of H with O_3 cannot be neglected;



has practically no activation energy (Kaufman, 1964) and

$$a_2 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (29)$$

corresponding to the experimental value of $(2.6 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K (Philips and Schiff, 1962). The dependence on temperature indicated by a plus one-half power in (29), and other reactions, shows that the activation energy must be small and that a

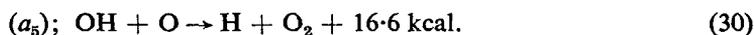
measurement over the 150–300°K temperature range is required. Such a form also shows that there is a certain steric hindrance factor, as it can be seen when (29) is compared with a conventional value, relevant to the present reactions, of $1.5 \times 10^{-11} T^{1/2}$ as given by the elementary kinetic theory of elastic spheres.

Thus, it may be concluded that hydrogen atoms are immediately transformed into hydroperoxyl radicals in the stratosphere since Relation (27) is rapid (see Table 2). However, at and in the neighbourhood of the stratopause, Reaction (28), which leads to OH, cannot be forgotten.

TABLE 2. AERONOMIC RATE COEFFICIENTS IN THE STRATOSPHERE

Altitude (km)	$a_1 n(M)n(O_2)$ (sec ⁻¹)	$a_2 n(O_3)$ (sec ⁻¹)	$a_5 n(O)$ (sec ⁻¹)
15	4.7×10^5	2.4×10^1	2.4×10^{-6}
20	7.7×10^4	6.4×10^1	4.2×10^{-5}
25	1.4×10^4	7.3×10^1	3.0×10^{-4}
30	2.6×10^3	6.7×10^1	1.8×10^{-3}
35	4.6×10^2	4.8×10^1	1.1×10^{-2}
40	1.2×10^2	2.5×10^1	6.0×10^{-2}
45	2.3×10^1	7.9	1.8×10^{-1}
50	6.8	2.5	3.3×10^{-1}

An important reaction which forms a chain leading to the reformation of oxygen molecules with the production of hydrogen atoms, in conjunction with Reaction (28), is the bimolecular process

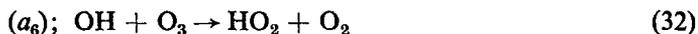


Laboratory data (Clyne and Thrush, 1963; Kaufman, 1964, 1969; Breen and Glass, 1970) lead to values of a_5 from $(5 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ between 265°K and 293°K to $(4.3 \pm 1.3) \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ at 300°K. A working value

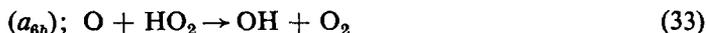
$$a_5 = 3 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (31)$$

is adopted with a possible error of 50 per cent. With the conventional value of the ozone concentration which is adopted here (Table 1) the loss coefficient of OH is given in Table 2.

It is clear that Reaction (30), if it is rapid in the major part of the stratosphere, is relatively slow in the lower stratosphere where other processes may be more important. The chain reaction introduced by McGrath and Norrish (1958)



and



as the potent ozone-destroying mechanism can be neglected. No direct measurement has been reported. An upper limit $a_6 \geq 5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at room temperature (Kaufman, 1964, 1969) was adopted (Hampson, 1966; Hunt, 1966; Dütsch, 1968; Hesstvedt, 1968; Leovy, 1969; Shimazaki and Laird, 1970) as the actual value in the stratosphere and mesosphere. A recent analysis by Langley and McGrath (1971) shows that a_6 should be less than $10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ at room temperature. With a steric hindrance factor of the order of 10^{-2} and an activation energy of about 6 kcal, a_6 should be not more than

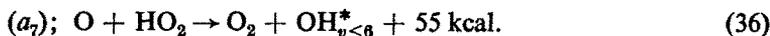
$$a_6 = 1.5 \times 10^{-13} T^{1/2} e^{-3000/T} \quad (34)$$

leading to $a_6 n(\text{O}_3) < a_5 n(\text{O})$ in the entire stratosphere. Furthermore, Reaction (33) which was introduced with a rate coefficient

$$a_{6b} = 5 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}, \quad (35)$$

must be rejected (DeMore, 1967; Nicolet, 1970). Measurements of Reactions (32) and (33) are required at 200°K which corresponds to the temperature of the lower stratosphere.

Instead of Reaction (33) the reaction leading to OH involves atomic oxygen (Kaufman, 1964)



No measurement of reaction (36) has been made. Considering the work of Foner and Hudson (1962), Kaufman (1964) suggests that $a_7 \geq 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. Reactions (36) and (30) must be compared since they represent, in the major part of the stratosphere and 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 values of the rate coefficients a_5 and a_7 which are generally adopted (Hampson, 1966; Hunt, 1966; Hesstvedt, 1968; Dütsch, 1968; Crutzen, 1969; Leovy, 1969) give

$$a_5/a_7 = 5 \times 10^{-11}/10^{-11} = 5. \quad (37)$$

Since no direct measurement of Reaction (36) has been reported, the ratio $a_5/a_7 = 5$ cannot be invoked to explain the aeronomic behavior of OH and HO_2 . The following value is adopted here for a_7 (see remark for a_2),

$$a_7 = 1.5 \times 10^{-12} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (38)$$

with the possibility that the ratio a_5/a_7 is not known with sufficient precision and may be between 10 and 1. According to a recent analysis of the HO_2 reactions by Hochenadel *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 . There is, therefore, a possibility that $a_5/a_7 \approx 1$. In any case, 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 stratosphere and mesosphere.

Expressions for the equilibrium ratios of $n(\text{OH})/n(\text{H})$ and $n(\text{HO}_2)/n(\text{H})$ can be easily obtained if it is assumed, as a first approximation, that only reactions (26–36) are involved. Thus

$$\frac{n(\text{OH})}{n(\text{H})} = \frac{a_1 n(\text{M})n(\text{O}_2) + a_2 n(\text{O}_3)}{a_5 n(\text{O})} \quad (39)$$

$$\frac{n(\text{HO}_2)}{n(\text{H})} = \frac{a_1 n(\text{M})n(\text{O}_2)}{a_7 n(\text{O})} \quad (40)$$

and

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_1 n(\text{M})n(\text{O}_2) + a_2 n(\text{O}_3)}{a_1 n(\text{M})n(\text{O}_2)} \cdot \frac{a_7}{a_5} \quad (41a)$$

The ratio given by (41a) must be used at the stratopause (see Table 2), but below 40 km it becomes

$$\frac{n(\text{OH})}{n(\text{HO}_2)} \approx \frac{a_7}{a_5} \quad (41b)$$

In the lower stratosphere, hydroxyl and hydroperoxyl radicals are involved in other important reactions with minor constituents which do not belong to the hydrogen-oxygen atmosphere. CO and NO must be considered since they can react with OH and HO₂, respectively. Among all possible reactions (Nicolet, 1971; Levy, 1971; McConnell *et al.*, 1971) it seems that these two reactions are the most important processes at and above the tropopause.

A simplified reaction scheme is illustrated in Fig. 7 for the hydroxyl radical. The

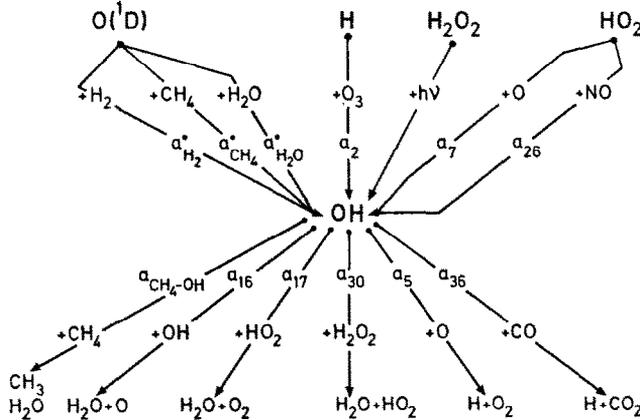


FIG. 7. REACTION SCHEME OF THE HYDROXYL RADICAL IN A HYDROGEN-OXYGEN ATMOSPHERE.

radical OH is produced by reactions (20-22) of O(¹D) atoms with H₂O, CH₄ and H₂ molecules. Reactions of ozone (28) and of atomic oxygen (36) with H atoms and HO₂ radicals, respectively, lead also to OH radicals. The photodissociation of hydrogen peroxide cannot be excluded; the process is



with a photodissociation rate coefficient (Fig. 8) which is not less than 10⁻⁶ sec⁻¹ in the

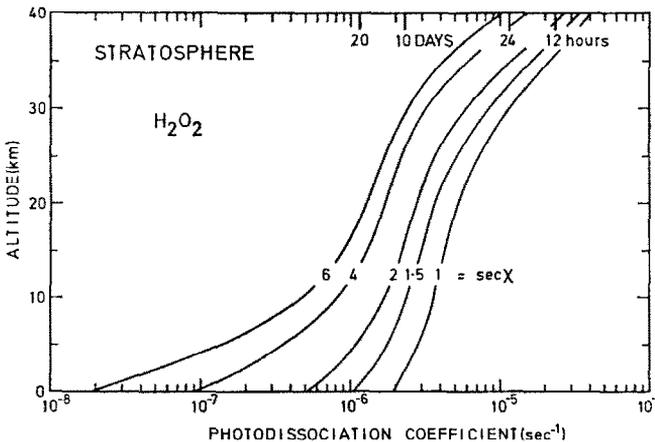
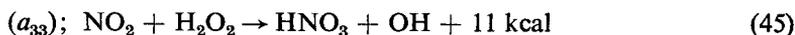
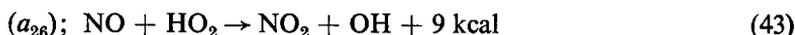


FIG. 8. PHOTODISSOCIATION COEFFICIENT OF HYDROGEN PEROXIDE IN THE STRATOSPHERE FOR VARIOUS SOLAR ZENITH ANGLES χ .

stratosphere. The following reactions (Nicolet, 1965, 1970), in which nitrogen oxides are involved,



also lead to OH radicals. However, (44) and (45) are very slow reactions ($< 5 \times 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$) which cannot play a role in the stratosphere according to recent measurements made by Gray, Lissi and Heicklen (1972). The rate coefficient a_{26} is not well known; nevertheless, it seems that working values of the order of $5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ are needed (Levy, 1971) at ground level and it is certain that such a reaction must play a role in the lower stratosphere where $a_7 n(\text{O})$ is less than 10^{-5} sec^{-1} . A precise experimental determination of the rate coefficient is needed for the analysis of the exact action of nitric oxide on the ratio $n(\text{HO}_2)/n(\text{OH})$ in the lower stratosphere.

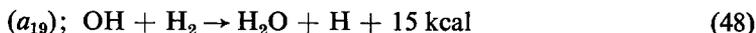
On the other hand, the radical OH, if it reacts rapidly with atomic oxygen (reaction 30) in the stratosphere, also has a role when H_2O_2 , H_2 , CO and CH_4 are present. The processes (46), (48), (50) and (52), shown below, have been observed:



with the rate coefficient (Greiner, 1968)

$$a_{30} = 4.1 \times 10^{-13} T^{1/2} e^{-600/T} \quad (47)$$

which leads to a rate coefficient of about $3 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at 200°K .



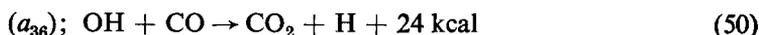
with the rate coefficient (Greiner, 1969)

$$a_{19} = 7 \times 10^{-12} e^{-2000/T} \quad (49a)$$

or

$$a_{19} = 2 \times 10^{-13} T^{1/2} e^{-1800/T} \quad (49b)$$

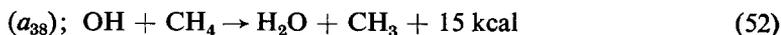
which leads to about $5 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ at 200°K .



with the rate coefficient (Greiner, 1969)

$$a_{36} = (1.25 \pm 0.25) \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (51)$$

for temperatures of the lower stratosphere.



with the rate coefficient (Greiner, 1970)

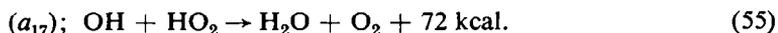
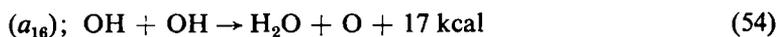
$$a_{38} = 5 \times 10^{-12} e^{-1900/T} \text{ cm}^3 \text{ sec}^{-1} \quad (53a)$$

or

$$a_{38} = 2 \times 10^{-13} T^{1/2} e^{-1750/T} \text{ cm}^3 \text{ sec}^{-1} \quad (53b)$$

which leads to about $5 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$ at 200°K . It must be pointed out that reactions (46), (48) and (52) lead to the formation of water vapor. Very precise rate coefficients are required for these reactions involving OH since they play a role in the lower stratosphere

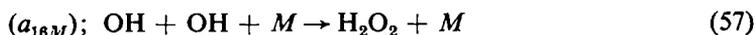
where the temperature is not far from 200°K. In addition, the following loss processes of OH lead to the re-formation of H₂O



Several measurements of reaction (54) have been made (Kaufman, 1964, 1969; Westenberg and DeHaas, 1965; Dixon-Lewis *et al.*, 1966, Wilson and O'Donovan, 1967; Mulcahi and Smith, 1971). Experimental values are well represented by a value of about 2×10^{-12} at 300°K. With a working value of 1 kcal for the activation energy, a_{16} can be written

$$a_{16} = 7.5 \times 10^{-13} T^{1/2} e^{-500/T} \quad (56)$$

leading to about $9 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}$ at 200°K. However, at sufficiently high pressures (lower stratosphere, for example) reaction (54) is replaced by



with a rate coefficient (Caldwell and Back, 1965)

$$a_{16M} = 4 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \quad (58)$$

leading to $8 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ at 20 km.

The Reaction (55) is extremely important in the stratosphere and mesosphere since it must be used to determine $n(\text{OH})n(\text{HO}_2)$ before determining the OH and HO₂ concentrations. In 1964, Kaufman suggested that $a_{17} \geq 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$. Almost all aeronomic studies treated this as an exact value but such an assumption was not appropriate for the analysis of the ozone problem in the stratosphere. Recent measurement by Hochanadel *et al.* (1972) indicate that the rate coefficient

$$a_{17} = 2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad (59a)$$

i.e. an extremely rapid reaction.

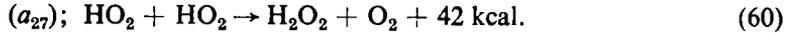
With such a high value of the rate coefficient, it is possible to consider that reaction (55) is the principal process leading to the re-formation of water vapor in the mesosphere. In the upper stratosphere a constant mixing ratio of H₂O corresponding to 3 ppmv leads to $n(\text{OH})n(\text{HO}_2) > 10^{14} \text{ cm}^{-6}$. The values of the hydroxyl and hydroperoxyl concentrations depend on the various reactions which are involved between OH and HO₂. With two arbitrary constant ratios $n(\text{HO}_2)/n(\text{OH}) = 9$ and 1, the OH concentrations are given in Table 3a, if only H₂O is involved in the production of OH radicals and if Reaction (55)

TABLE 3a. EXAMPLES OF HYDROXYL RADICAL CONCENTRATIONS [$n(\text{H}_2\text{O}) = 3 \text{ ppm}$;
 $n(\text{HO}_2)/n(\text{OH}) = 9$ OR 1; SOLAR CONDITIONS: BETWEEN $\text{sec } \chi = 1$ AND 2]

Altitude (km)	$n(\text{HO}_2)/n(\text{OH}) = 9$	$n(\text{HO}_2)/n(\text{OH}) = 1$
15	$(1.1 \pm 0.3) \times 10^6$	$(3 \pm 1) \times 10^6$
20	$(2.0 \pm 0.5) \times 10^6$	$(6 \pm 2) \times 10^6$
25	$(2.8 \pm 0.6) \times 10^6$	$(8 \pm 2) \times 10^6$
30	$(3.5 \pm 0.7) \times 10^6$	$(1 \pm 0.2) \times 10^7$
35	$(4.5 \pm 0.9) \times 10^6$	$(1.4 \pm 0.2) \times 10^7$
40	$(5.4 \pm 0.8) \times 10^6$	$(1.6 \pm 0.3) \times 10^7$
45	$(5.2 \pm 0.8) \times 10^6$	$(1.6 \pm 0.2) \times 10^7$
50	$(4.1 \pm 0.3) \times 10^6$	$(1.2 \pm 0.1) \times 10^7$

between OH and HO₂ is the re-formation process of H₂O. Such examples are introduced here to show that important errors may occur in the aeronomic analysis and that experimental data are urgently needed in order to determine the exact ratio $n(\text{HO}_2)/n(\text{OH})$.

Before ending this discussion concerning the hydroxyl and hydroperoxyl radicals, the following two-body process must be considered,



If it is assumed that the rate coefficient a_{27} cannot be too different from a_{18} as it was indicated by indirect laboratory measurements (Foner and Hudson, 1962; Dixon-Lewis and Williams, 1962; Kaufman, 1964) the following value should be noted

$$a_{27} = 7.5 \times 10^{-13} T^{1/2} e^{-500/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (61a)$$

However, recent measurements by Hochanadel *et al.* (1972) lead to almost 4 times the value given by (61a) since the laboratory results at 298°K give

$$a_{27} = (9.5 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}. \quad (62b)$$

This value is higher than another recent estimate by Paukert (1969).

An idea of the behavior of hydrogen peroxide can be obtained with the simplified equation, based only on (42) and (60),

$$\frac{dn(\text{H}_2\text{O})}{dt} + n(\text{H}_2\text{O}_2)J_{\text{H}_2\text{O}_2} = a_{27}n^2(\text{HO}_2). \quad (62)$$

The relation $n(\text{HO}_2) \leq n(\text{H}_2\text{O}_2)$ is valid at the stratopause if $n(\text{HO}_2) \geq 10^7 \text{ cm}^{-3}$, and in the lower stratosphere ($\sim 20 \text{ km}$), if $n(\text{HO}_2) \geq 10^6 \text{ cm}^{-3}$, when photoequilibrium conditions are used for (62).

Finally, considering equilibrium conditions for HO₂ and OH, the following equations are obtained (cf. Fig. 9)

$$n(\text{HO}_2)[a_7n(\text{O}) + a_{28}n(\text{NO}) + a_{17}n(\text{OH}) + 2a_{27}n(\text{HO}_2)] = n(\text{OH})[a_5n(\text{O}) + a_{38}n(\text{CO}) + a_{30}n(\text{H}_2\text{O}_2)] \quad (63)$$

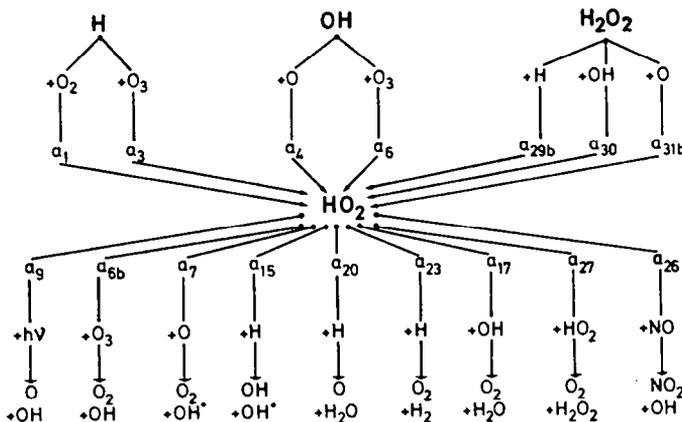


FIG. 9. REACTION SCHEME OF THE HYDROPEROXYL RADICAL IN A HYDROGEN-OXYGEN ATMOSPHERE.

and, (Fig. 7),

$$a^*n^*(O)[n(\text{H}_2\text{O}) + n(\text{CH}_4) + n(\text{H}_2)] = n(\text{OH})[\frac{1}{2}a_{38}n(\text{CH}_4) + a_{17}n(\text{HO}_2) + a_{18}n(\text{OH})]. \quad (64a)$$

In the upper stratosphere (63) and (64) are written as follows

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_7}{a_5} \quad (41b)$$

and

$$[n(\text{CH}_4) + n(\text{H}_2) + n(\text{H}_2\text{O})]a^*n^*(O) = a_{17}n(\text{HO}_2)n(\text{OH}). \quad (65)$$

Numerical results based on Equation (65) are given in Table 3b. However, in the lower stratosphere for daytime conditions

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_7n(O) + a_{26}n(\text{NO})}{a_5n(O) + a_{36}n(\text{CO})} \quad (66a)$$

and at the tropopause for daytime conditions

$$\frac{n(\text{OH})}{n(\text{HO}_2)} = \frac{a_{26}n(\text{NO})}{a_{36}n(\text{CO})}. \quad (66b)$$

As far as (64) is concerned, it may be assumed, in the lower stratosphere and particularly near the tropopause level, that

$$[n(\text{CH}_4) + n(\text{H}_2) + n(\text{H}_2\text{O})]a^*n^*(O) \geq a_{38}n(\text{OH})n(\text{CH}_4)/2 \quad (64b)$$

which leads to a determination of the concentration of hydroxyl radicals

$$n(\text{OH}) \leq \frac{a^*n^*(O)[n(\text{CH}_4) + n(\text{H}_2) + n(\text{H}_2\text{O})]}{n(\text{CH}_4)a_{38}/2}. \quad (67a)$$

With numerical values (see Table 3b) corresponding to mixing ratios, 0.5 ppmv for H_2 , 1.5 ppmv for CH_4 and 3 ppmv for H_2O , $n(\text{OH}) = (6 \pm 3) \times 10^5 \text{ cm}^{-3}$ at 15 km for solar conditions varying from an overhead sun to a zenith angle of 60° , $n(\text{OH}) = (3 \pm 2) \times 10^6$ at 20 km and $n(\text{OH}) = (10 \pm 3) \times 10^6 \text{ cm}^{-3}$ at 25 km. Thus, the OH concentrations in the lower stratosphere decrease when methane is present and values given in Table 3a below 25 km are too high.

After sunset, instead of (67a), we must write

$$\frac{1}{n(\text{OH})} \frac{dn(\text{OH})}{dt} = -a_{38}n(\text{CH}_4) \quad (67b)$$

TABLE 3b. EXAMPLES OF HYDROXYL RADICAL CONCENTRATIONS
 $[n(\text{H}_2\text{O}) = 3 \text{ ppm}; n(\text{CH}_4) = 1.5 \text{ ppm}; n(\text{H}_2) = 0.5 \text{ ppm}; \text{CH}_4 \text{ EFFECT}]$

Altitude (km)	sec $\chi = 1$ (overhead Sun)	= 1.4 $\chi = 45^\circ$	= 2 $\chi = 60^\circ$
15	1.1×10^6	6.3×10^5	3.1×10^5
20	6.0×10^6	3.5×10^6	2.0×10^6
25	1.6×10^7	9.8×10^6	5.8×10^6

which shows that OH is rapidly transformed into H₂O since the life time of OH radicals is relatively short in the lower stratosphere. With a loss coefficient of the order of $3 \times 10^{-3} \text{ sec}^{-1}$ at 20 km, the initial concentration of hydroxyl radicals is reduced to 10^{-5} in a very short time of the order of 3 hr. Furthermore, Equation (66a) cannot be applied since atomic oxygen is present only in the daytime atmosphere. Finally, NO is transformed into NO₂ in the night-time stratosphere and equation (66b) cannot be used.

If the mixing ratios of NO and CO in the lower stratosphere are taken as 4 ppbv and 40 ppbv, respectively, Equations (66a) and (66b) indicate that the ratio $n(\text{HO}_2)/n(\text{OH})$ depends on the carbon monoxide and nitric oxide concentrations. With $a_{26} \simeq 10a_{36}$, $n(\text{HO}_2)/n(\text{OH}) \simeq 1$. Near 30 km the role of oxygen atoms is important.

Thus, the importance of reactions with hydrogen compounds in the photochemistry of ozone and atomic oxygen in the lower stratosphere depends strongly on the actions of carbon monoxide and of nitric oxide. The action of methane must be introduced in the process of H₂O re-formation above the tropopause level.

Finally, instead of (9), the rate of change of O₃ in the stratosphere must be written (Nicolet, 1966, 1970)

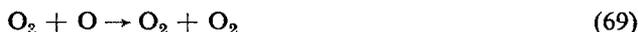
$$\frac{dn(\text{O}_3)}{dt} + \frac{J_3}{k_2 n(M)n(\text{O}_2)} n(\text{O}_3)[2kn(\text{O}_3) + a_5 n(\text{OH}) + a_7 n(\text{HO}_2)] = 2n(\text{O}_2)J_2. \quad (68a)$$

In the upper stratosphere (68a) becomes, using (41b),

$$n(\text{O}_3) = \frac{k_2}{k_3} n(M)n(\text{O}_2) \frac{n(\text{O}_2)J_2}{n(\text{O}_3)J_3 + a_5 n(\text{OH})}. \quad (68b)$$

IV. NITROGEN-OXYGEN ATMOSPHERE

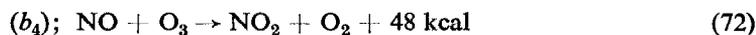
In a pure oxygen atmosphere the photochemical destruction of ozone is given by Reaction (8)



and in a hydrogen-oxygen atmosphere by a catalytic cycle of an HO-HO₂ system involving Reactions (30) and (36) in the stratosphere



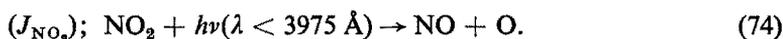
In a nitrogen-oxygen atmosphere the catalytic cycle involves NO and NO₂ (Crutzen, 1970; Johnston, 1971; Nicolet, 1971). Nitric oxide reacts with ozone as follows



with a rate coefficient which is sufficiently well known (Johnston and Crossby, 1954; Clyne, Thrush and Wayne, 1964)

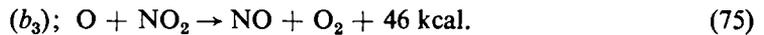
$$b_4 = 1 \times 10^{-12} e^{-1250/T}. \quad (73)$$

NO₂ is subject to photodissociation



The photodissociation rate coefficient is about $4 \times 10^{-3} \text{ sec}^{-1}$ at 50 km and it is not less than $3 \times 10^{-3} \text{ sec}^{-1}$ at 15 km. An average value of $(3.4 \pm 0.5) \times 10^{-3} \text{ sec}^{-1}$ may be adopted in the stratosphere.

However, the following reaction plays a role in the upper stratosphere



It is relatively a rapid reaction (Schiff, 1964; Klein and Herron, 1964; Westenberg and deHaas, 1969). At 200°K, the extrapolation of such experimental data leads to 2 and to $7 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1}$ which may be given either by

$$b_{3a} = 5 \times 10^{-13} T^{1/2} \text{ cm}^3 \text{ sec}^{-1} \quad (76a)$$

or by

$$b_{3b} = 1 \times 10^{-12} T^{1/2} e^{-350/T} \text{ cm}^3 \text{ sec}^{-1}. \quad (76b)$$

An unpublished result (Davis, 1972) gives

$$b_{3c} = 9.2 \times 10^{-12} \text{ cm}^3 \text{ sec}^{-1} \quad (76c)$$

over the 235–350°K temperature range.

Thus, this is again a clear illustration that the experimental values of many rate coefficients must be known with greater accuracy for the study of aeronomic processes in the stratosphere.

Considering that (72), (74) and (75) are the principal reactions in the stratosphere, (Nicolet, 1965),

$$\frac{dn(\text{NO}_2)}{dt} + n(\text{NO}_2)[J_{\text{NO}_2} + b_3n(\text{O})] = b_4n(\text{NO})n(\text{O}_3) \quad (77a)$$

and, for daytime conditions since $1/J_{\text{NO}_2} \leq 3 \times 10^2 \text{ sec}$,

$$\frac{n(\text{NO}_2)}{n(\text{NO})} = \frac{b_4n(\text{O}_3)}{J_{\text{NO}_2} + b_3n(\text{O})}. \quad (77b)$$

With the numerical values adopted here (73) and (76c), the $n(\text{NO}_2)/n(\text{NO})$ ratio is given in Table 4 at various altitudes and for two values of the zenith angle. The ratio increases from about 1 at 15 km to nearly 4 at 30 km and decreases above 35 km to the order of 2×10^{-2} at 50 km. Thus, the daytime ratio $n(\text{NO}_2)/n(\text{NO})$ should be of the order of 1 in the lower stratosphere, but is related to the ozone variation.

Thus, if we introduce the effect of nitrogen oxides (NO and NO_2) in the ozone equation (9), we must write from (72), (74) and (75),

$$\frac{dn(\text{O}_3)}{dt} + \frac{J_3n(\text{O}_3)}{k_2n(\text{M})n(\text{O}_2)} [2k_3n(\text{O}_3) + b_4n(\text{NO}) + b_3n(\text{NO}_2)] = 2n(\text{O}_2)J_2 + n(\text{NO}_2)J_{\text{NO}_2} \quad (78a)$$

TABLE 3c. EXAMPLES OF HYDROXYL RADICAL CONCENTRATIONS (cm^{-3}) IN THE LOWER STRATOSPHERE.

Altitude (km)	Table 3a (HO_2)	Table 3b (CH_4)	Effect of HNO_3
15	(1 ± 0.3) to $(3 \pm 1) \times 10^6$	$(6 \pm 3) \times 10^5$	$(4 \pm 2) \times 10^4$
20	(2 ± 0.5) to $(6 \pm 2) \times 10^6$	$(3 \pm 2) \times 10^6$	$(1 \pm 0.5) \times 10^5$
25	(3 ± 0.6) to $(8 \pm 2) \times 10^6$	$(10 \pm 3) \times 10^6$	$(1 \pm 0.6) \times 10^6$

TABLE 4. RATIO $n(\text{NO}_2)/n(\text{NO})$ IN THE STRATOSPHERE

Altitude (km)	Solar zenith angle	
	sec $\chi = 1$	sec $\chi = 2$
15	0.9*	0.95*
20	2.7	2.9
25	3.6	3.8
30	3.6†	3.7†
35	2.7	2.7
40	0.6	0.9
45	8.9×10^{-2}	1.4×10^{-1}
50	1.6×10^{-2}	2.1×10^{-2}

* only effect of J_{NO_2} alone† also effect of $b_2 n(\text{O})$

which becomes, with (77),

$$\frac{dn(\text{O}_3)}{dt} + \frac{2J_3 n(\text{O}_3)}{k_2 n(\text{M}) n(\text{O}_2)} [k_3 n(\text{O}_3) + b_3 n(\text{NO}_2)] = 2n(\text{O}_2) J_2 \quad (78b)$$

Comparing (78) with (68), which involves the effect of hydroxyl and hydroperoxyl radicals, the ozone concentration in the upper stratosphere is given by

$$n(\text{O}_3) = \frac{k_2}{k_3} n(\text{M}) n(\text{O}_2) \frac{n(\text{O}_2) J_2}{n(\text{O}_3) J_3 + a_5 n(\text{OH}) + b_3 n(\text{NO}_2)} \quad (78c)$$

which shows that the correction term to J_3 (see 15 and 16) can be written

$$A = \frac{a_5 n(\text{OH}) + b_3 n(\text{NO}_2)}{k_3 n(\text{O}_3)} \quad (79)$$

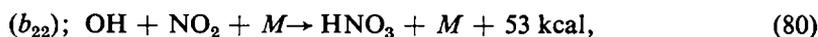
Table 5 shows that the same effect is obtained for a ratio $n(\text{OH})/n(\text{NO}_2)$ of the order of 10^{-1} .

TABLE 5. NUMERICAL VALUES OF $\frac{a_5}{k_3} \frac{n(\text{OH})}{n(\text{O}_3)} + \frac{b_{3b}}{k_3} \frac{n(\text{NO}_2)}{n(\text{O}_3)}$

Altitude (km)	a_5/k_3	b_{3b}/k_3
15	9.6×10^4	6.1×10^3
20	6.8	4.6
25	4.9	3.5
30	3.6	2.7
35	2.0	1.7
40	1.2	1.1
45	1.0	1.0
50	1.0	1.0

For example, if between 35 km and 40 km the ozone concentration is of the order of 10^{12} cm^{-3} , then from 5×10^7 to about 10^8 OH molecules have the same effect as from 5×10^8 to about 10^9 NO_2 molecules.

In the ozonosphere, various reactions with nitrogen oxides may be considered (see Nicolet, 1965, 1971; Johnston, 1971). Among the possible reactions, a three-body association leading to nitrous and nitric acids,



is an important process for which the rate coefficient, b_{22} , for $T = 300^\circ\text{K}$ is (Simonaitis and Hecklen, 1971)

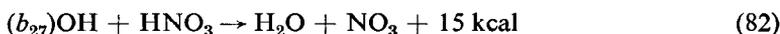
$$b_{22} = 1.3 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1} \quad (81a)$$

for $M = \text{He}$, or

$$b_{22} = 1.1 \times 10^{-29} \text{ cm}^3 \text{ sec}^{-1} \quad (81b)$$

if $M = \text{H}_2\text{O}$.

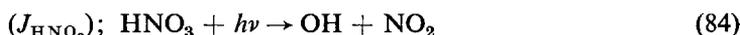
With $b_{22} = 5 \times 10^{-30} \text{ cm}^6 \text{ sec}^{-1}$ for O_2 and N_2 , it can be seen that the life-time of OH is very short in the lower stratosphere if there is no re-formation process of OH. In fact,



with a coefficient which, according to Hussain and Norrish (1963), should be of the order of

$$b_{26} = 1.5 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1} \quad (83)$$

The possibility of finding a reformation process for OH from HNO_3 is a photodissociation (see Leighton, 1961)



Another reaction



is slow, and according to Morris and Niki (1971), its rate coefficient is less than $2 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}$. It seems, therefore, that the relevant differential equation for the HNO_3 concentration is

$$\frac{dn(\text{HNO}_3)}{dt} + n(\text{HNO}_3)[J_{\text{HNO}_3} + b_{27}n(\text{OH}) + b_{28}n(\text{O})] = b_{22}n(\text{OH})n(\text{NO}_2)n(M). \quad (86)$$

Night-time equilibrium conditions would lead to

$$\frac{n(\text{HNO}_3)}{n(\text{NO}_2)} < \frac{b_{22}n(M)}{b_{27}} \simeq 10^2 \quad (87a)$$

at 15–20 km. However, according to computations based on equation (67b), the hydroxyl radicals disappear in the lower thermosphere after sunset and, consequently, a night-time equilibrium cannot be attained for the ratio $n(\text{HNO}_3)/n(\text{NO}_2)$. Thus, the photodissociation process (84) cannot be eliminated as an effective loss process of HNO_3 in the lower stratosphere since J_{HNO_3} could be greater than 10^{-7} sec^{-1} . Photoequilibrium conditions, which, perhaps, do not exist in the lower stratosphere, lead to

$$\frac{n(\text{HNO}_3)}{n(\text{NO}_2)} = \frac{n(\text{OH})b_{22}n(M)}{J_{\text{HNO}_3} + b_{27}n(\text{OH})}. \quad (87b)$$

Once again, exact values of the parameters are needed for a determination of the theoretical ratio $n(\text{HNO}_3)/n(\text{NO}_2)$. Observational results indicate that the HNO_3 mixing ratio in the lower stratosphere is not less than 10^{-9} (Murcray *et al.*, 1969; Rhine *et al.*, 1969) and that the NO_2 mixing ratio is less than 3×10^{-8} (Ackerman and Frimout, 1969).

Thus, it seems that the OH radicals are not only subject to reactions with hydrogen compounds (Fig. 7) but also depend on nitrogen compounds. The equilibrium value in the

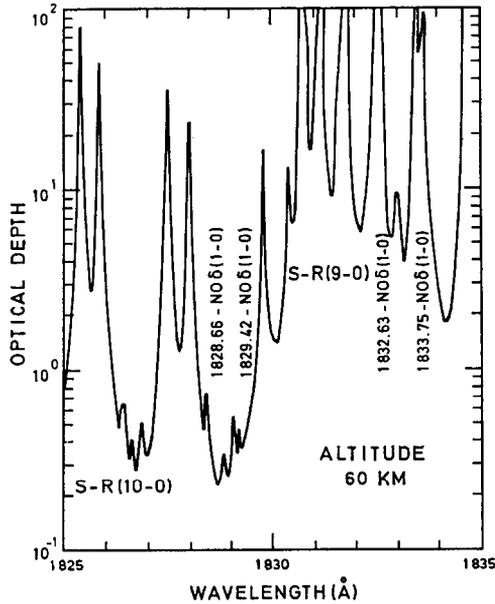


FIG. 11. THE δ BANDS OF NITRIC OXIDE ARE ABSORBED IN THE MESOSPHERE BY THE SCHUMANN-RUNGE BANDS OF MOLECULAR OXYGEN AND DETERMINE THE PHOTODISSOCIATION COEFFICIENT.

becomes

$$\frac{\partial n(\text{NO})}{\partial t} + \frac{\partial}{\partial z} [n(\text{NO})w_{\text{NO}}] = 0 \quad (90)$$

at the stratopause since J_{NO} is very small at that level. Observational values of the NO concentration (Pontano and Hale, 1970) of the order of 10^9 cm^{-3} at the stratopause are larger than the theoretical values deduced by Strobel (1972) [$10^6 < n(\text{NO}) < 10^7 \text{ cm}^{-3}$] and also more than a mixing distribution [$n(\text{NO}) \sim 10^8 \text{ cm}^{-3}$] if $[n(\text{NO}_2) + n(\text{NO})]/n(M) = 3 \times 10^{-9}$ at the tropopause (Nicolet, 1965).

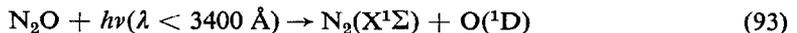
Nitric oxide is produced in the stratosphere by a reaction between nitrous oxide and the excited oxygen atom in the $\text{O}(^1\text{D})$ state (Nicolet, 1970)



with a global rate coefficient of the order of $2 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1}$ (Young *et al.*, 1968) and a ratio $b_{38}/b_{39} \simeq 1$ according to Greenberg and Hecklen (1970). Thus the production of NO molecules is given by

$$\frac{dn(\text{NO})}{dt} = 2 \times 10^{-10} n(\text{N}_2\text{O})n[\text{O}(^1\text{D})] \text{ cm}^{-3} \text{ sec}^{-1}. \quad (92)$$

Since N_2O is photodissociated by $\lambda < 3400 \text{ \AA}$ (Bates and Hayes, 1967) leading only to (Nicolet, 1970; Nicolet and Vergison, 1971)



in the stratosphere, the vertical distribution of nitrous oxide, which does not produce NO by

photodissociation, decreases rapidly with height according to the differential equation

$$\frac{\partial n(\text{N}_2\text{O})}{\partial t} + \text{div} [n(\text{N}_2\text{O})w_{\text{N}_2\text{O}}] + n(\text{N}_2\text{O})J_{\text{N}_2\text{O}} = 0. \quad (94)$$

Examples of the vertical distribution of nitrous oxide with a mixing ratio of 2.5×10^{-7} at the tropopause are illustrated in Fig. 12. It is clear that the distribution depends on the eddy

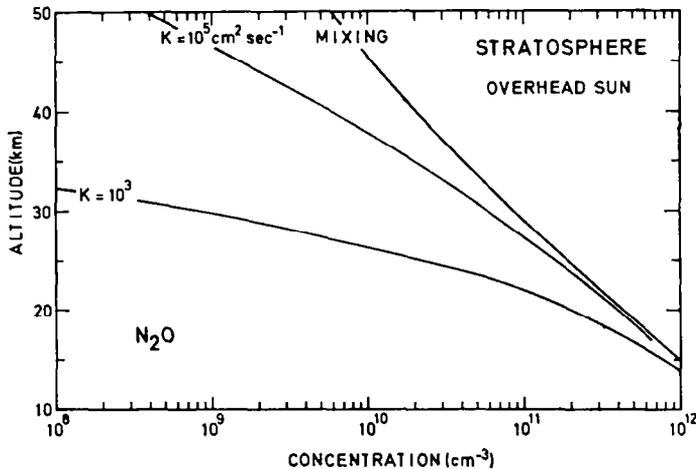


FIG. 12. VERTICAL DISTRIBUTIONS OF THE NITROUS OXIDE CONCENTRATION IN THE STRATOSPHERE RELATED TO VARIOUS EDDY DIFFUSION COEFFICIENTS $K = 10^3 \text{ cm}^2 \text{ sec}^{-1}$, $K = 10^5 \text{ cm}^2 \text{ sec}^{-1}$ AND MIXING.

diffusion coefficients which are adopted (Nicolet and Vergison, 1971; McElroy and McDonnell, 1971). The measurements in the stratosphere by Schutz *et al.* (1970) and Goldman *et al.* (1970) indicate that more observations are needed in order to determine the stratospheric distribution of N_2O with latitude and altitude.

Nevertheless, it is possible to consider (Nicolet and Vergison, 1970) that the stratospheric production of nitric oxide P_n is of the order of

$$P_n(\text{NO}) = (1.5 \pm 1) \times 10^8 \text{ cm}^2 \text{ sec}^{-1} \quad (95)$$

which is of the same order of magnitude as the artificial injection by 500 supersonic transport aircraft.

Finally, the differential equation pertaining to the variation of nitric oxide in the stratosphere is

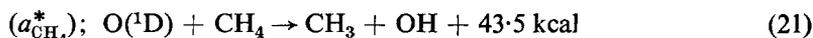
$$\frac{\partial n(\text{NO})}{\partial t} + \text{div} [n(\text{NO})w_{\text{NO}}] + \text{div} [n(\text{HNO}_3)w_{\text{HNO}_3}] = P(\text{NO}) \quad (96)$$

where $P(\text{NO})$ is given by (92). The downward transport of nitric acid from the stratosphere into the troposphere may be considered as a destruction process of stratospheric nitrogen oxides. Thus, special attention should be given to atmospheric conditions relating to the tropopause and its multiple structure. The exchange between troposphere and stratosphere must be studied at various latitudes.

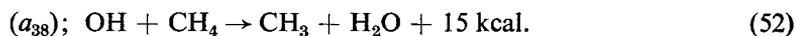
V. THE CO AND CH₄ PROBLEM IN THE STRATOSPHERE

Methane, which has been found as a permanent constituent of the troposphere, has continuous sources at ground level. It is dissociated by ultraviolet radiation in the mesosphere and by oxidation processes in the stratosphere (Nicolet, 1971)

The dissociative reactions in the stratosphere are



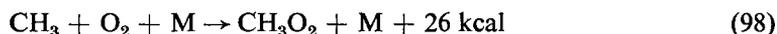
and



In the lower stratosphere CO₂ is photodissociated at a very low rate. In the upper stratosphere the production is not less than 10³ CO molecules cm⁻³ sec⁻¹. In the lower stratosphere the photodissociation process is less important than the oxidation process (21) which can be considered as follows



as far as the CO production is concerned. Methyl radicals which are produced by Reactions (21) and (52) react with molecular oxygen

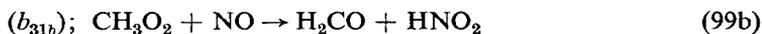


with a rate coefficient of the order of 10⁻³¹ cm⁶ sec⁻¹ at room temperature (Heicklen, 1968; Spicer *et al.*, 1972).

Methylperoxy radicals react with oxides of nitrogen via



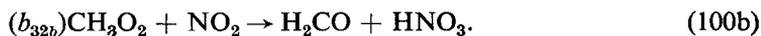
or



as regards NO. The production of methyl peroxy nitrite is about 1.5 times the simultaneous production of formaldehyde and nitrous acid. In the same way the reactions with NO₂ are



or



Here the production of formaldehyde and nitric acid is about 3 times the production of methylperoxynitrate. There is no evidence for the reaction between CH₃O₂ and NO producing CH₃O + NO₂ (Spicer *et al.*, 1972).

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



and



which lead to CO and HCO. It should be noted that the photodissociation of formaldehyde leads to the production of molecular hydrogen in the stratosphere.

The photodissociation coefficients of H₂CO based on recently published cross sections (Calvert *et al.*, 1972) can be determined. For the production of hydrogen atoms and formyl

radicals, the photodissociation coefficient $J_{\text{H-HCO}}$ is

$$J_{\text{H-HCO}} = 9.4 \times 10^{-5} \text{ sec}^{-1} \quad (101b)$$

at zero optical depth; the simultaneous production of molecular hydrogen and carbon monoxide leads to the photodissociation coefficient $J_{\text{H}_2\text{-CO}}$

$$J_{\text{H}_2\text{-CO}} = 1.3 \times 10^{-4} \text{ sec}^{-1}. \quad (102b)$$

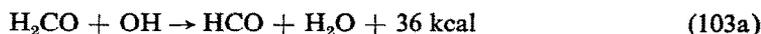
The photodissociation coefficients are given in Table 6 at three altitudes in the lower

TABLE 6. PHOTODISSOCIATION COEFFICIENTS OF FORMALDEHYDE (sec^{-1})

Altitude (km)	H-HCO and H ₂ -CO	H-HCO	H ₂ -CO
15	$(1.2 \pm 0.1) \times 10^{-4}$	$(3.3 \pm 0.6) \times 10^{-5}$	$(8.5 \pm 0.7) \times 10^{-5}$
20	$(1.3 \pm 0.1) \times 10^{-4}$	$(3.8 \pm 0.5) \times 10^{-5}$	$(9.5 \pm 0.6) \times 10^{-4}$
25	$(1.4 \pm 0.1) \times 10^{-4}$	$(4.3 \pm 0.5) \times 10^{-5}$	$(1.0 \pm 0.5) \times 10^{-5}$

stratosphere and for solar zenith angles between 0 and 60°. Thus, the total photodissociation coefficient of H₂CO is $(1.3 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$ in the lower stratosphere.

A rapid reaction such as



with a rate coefficient (Morris and Niki, 1971)

$$a_{\text{OH-CH}_2\text{O}} = 1.5 \times 10^{-11} \text{ cm}^3 \text{ sec}^{-1} \quad (103b)$$

seems to be a less important process in the lower stratosphere than the direct photodissociation process; it requires OH concentrations greater than 10^7 cm^{-3} to compete with the photodissociation having a coefficient $J_{\text{H}_2\text{CO}}$ which is of the order of $1.3 \times 10^{-4} \text{ sec}^{-1}$ in the lower stratosphere.

Thus, with Equations (98–101), it is possible to consider that the oxidation of methane leads to the production of carbon monoxide (97) and to the simultaneous production of formaldehyde and nitric acid. The production of formaldehyde $P(\text{CH}_2\text{O})$ is given by

$$P(\text{CH}_2\text{O}) = \frac{0.4b_{31}n(\text{NO}) + 0.75b_{32}n(\text{NO}_2)}{b_{31}n(\text{NO}) + b_{32}n(\text{NO}_2)} [a_{\text{CH}_4}^*n^*(\text{O}) + a_{38}n(\text{OH})]n(\text{CH}_4) \quad (103c)$$

$$\simeq \frac{1}{2}[a_{\text{CH}_4}^*n^*(\text{O}) + a_{38}n(\text{OH})]n(\text{CH}_4). \quad (103d)$$

From (101–103), we may write

$$n(\text{CH}_2\text{O}) \simeq \frac{[a^*n^*(\text{O}) + a_{38}n(\text{OH})]n(\text{CH}_4)}{2[J_{\text{H-HCO}} + J_{\text{H}_2\text{-CO}} + 1.5 \times 10^{-11} n(\text{OH})]} \quad (104a)$$

and in the lower stratosphere an oversimplified equation

$$n(\text{CH}_2\text{O}) \leq \frac{a^*n^*(\text{O})n(\text{CH}_4)}{2J_{\text{H}_2\text{CO}}} \quad (104b)$$

since $a_{38}n(\text{OH})$ may be of the same order of magnitude as $a^*n^*(\text{O})$.

With a mixing ratio of CH₄ of the order of 1.5 ppmv between 15 and 25 km, the CH₂O

concentrations could reach the following photochemical equilibrium values: $(2 \pm 1) \times 10^6 \text{ cm}^{-3}$ at 15 km, $(9 \pm 5) \times 10^6 \text{ cm}^{-3}$ at 20 km and $(1 \pm 0.5) \times 10^7$ at 25 km. Such concentrations should lead to productions of H_2 molecules of the order of $10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ near 20 km. Reaction (101a) would lead also to the production of hydrogen atoms of about $10^3 \text{ cm}^{-3} \text{ sec}^{-1}$ near 20 km which corresponds to an indirect production of HO_2 radicals. In the same way the formyl radical also leads directly by reaction with O_2 or indirectly by photodissociation to hydroperoxyl radicals in the stratosphere. An additional source of nitric acid which, not previously considered, is given by

$$P(\text{HNO}_3) = \frac{0.75b_{32}n(\text{NO}_2)}{b_{31}n(\text{NO}) + b_{32}n(\text{NO}_2)} [a_{\text{CH}_4}^* n^*(\text{O}) + a_{38}n(\text{OH})]n(\text{CH}_4). \quad (105)$$

Such a source increases when the NO_2 and O_3 concentrations increase. The reaction scheme of Fig. 10 shows the relative importance of process (105).

In order to determine the importance of Reaction (97) in leading to the production of CO it is necessary to know the vertical distribution of CH_4 in the entire stratosphere. Measurements made in the stratosphere by Bainbridge and Heidt (1966) indicate that the transport of methane $F_K(\text{CH}_4)$ across the tropopause is given by

$$F_K(\text{CH}_4) = n(\text{CH}_4)K \left[\frac{1}{H_{\text{CH}_4}} - \frac{1}{H_M} \right] \quad (106)$$

where K is the eddy diffusion coefficient, H_{CH_4} and H_M are the scale height of CH_4 and of the atmosphere respectively and corresponds to an eddy diffusion flux of about 5×10^9 molecules $\text{CH}_4 \text{ cm}^{-2} \text{ sec}^{-1}$. Such a transport is equivalent to a stratospheric production of 5×10^9 carbon monoxide molecules $\text{cm}^{-2} \text{ sec}^{-1}$ and also results in an addition of 10^{10} water vapor molecules $\text{cm}^{-2} \text{ sec}^{-1}$ in the stratosphere. Such an addition does not differ greatly from an artificial injection by 500 SST aircraft.

However, a vertical flow of about $5 \times 10^9 \text{ CH}_4$ molecules $\text{cm}^{-2} \text{ sec}^{-1}$ corresponds to an average eddy diffusion coefficient of $2 \times 10^3 \text{ cm}^2 \text{ sec}^{-1}$ which would lead to a decrease of about a factor of 1000 in the mixing ratio of methane from the tropopause to the stratopause.

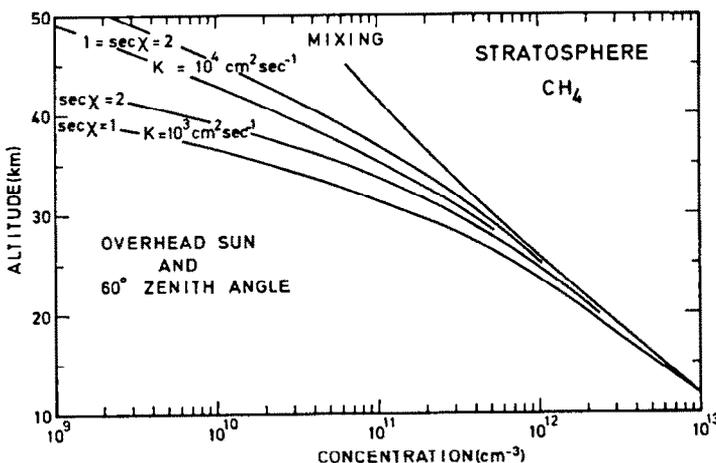


FIG. 13. VERTICAL DISTRIBUTION OF THE METHANE CONCENTRATION IN THE STRATOSPHERE FOR 2 SOLAR ZENITH DISTANCES (0° AND 60°) AND 2 EDDY DIFFUSION COEFFICIENTS $K = 10^3 \text{ cm}^2 \text{ sec}^{-1}$ AND $10^4 \text{ cm}^2 \text{ sec}^{-1}$ COMPARED WITH MIXING.

The examples (Fig. 13) of the vertical distribution of methane in the stratosphere show the important differences for two typical values of the average eddy diffusion coefficient $K = 10^3$ and $10^4 \text{ cm}^2 \text{ sec}^{-1}$. The first observational result (Scholz *et al.*, 1970) leading to $\leq 5 \times 10^{-8}$ for the CH_4 mixing ratio at the tropopause corresponds to $K < 10^4 \text{ cm}^2 \text{ sec}^{-1}$ but a second analysis (Ehhalt *et al.*, 1972) leading to a CH_4 mixing ratio of 2.5×10^{-7} requires an eddy diffusion coefficient of about $2 \times 10^4 \text{ cm}^2 \text{ sec}^{-1}$.

If we accept this last result, we must assume that the scale height h of the CH_4 mixing ratio is not less than 20 km. In other words (see Equation 106), if

$$\frac{1}{h} = \frac{1}{H_{\text{CH}_4}} - \frac{1}{H_M} = \frac{1}{2.2 \times 10^6} \quad (107)$$

as given by Bainbridge and Heidt (1966) for their second profile between 15 to 24 km, is extended up to 50 km, the CH_4 mixing ratio decreases from 15 km to 50 km to 20 per cent of its tropopause value as given by Ehhalt *et al.* (1972). But, such a relatively high mixing ratio at the stratopause requires an average eddy diffusion coefficient for the total stratosphere greater than $10^4 \text{ cm}^2 \text{ sec}^{-1}$. Such a high value indicates that new observational results are needed.

As far as carbon monoxide is concerned the general equation for its vertical distribution in the stratosphere must be written as follows:

$$\begin{aligned} \frac{\partial n(\text{CO})}{\partial t} + \text{div} [n(\text{CO})w_{\text{CO}}] + a_{36}n(\text{OH})n(\text{CO}) \\ = n(\text{CO}_2)J_{\text{CO}_2} + n(\text{CH}_4)[a^*n^*(\text{O}) + a_{38}n(\text{OH})]. \end{aligned} \quad (108a)$$

At the stratopause, there is a photochemical equilibrium (Hays and Olivero, 1970); the principal process for the production of carbon monoxide is the photodissociation of carbon dioxide and the principal loss process is the reaction of CO with OH radicals since the transport is too slow. Instead of (108a), the photochemical conditions may be considered as follows

$$n(\text{CO}_2)J_{\text{CO}_2} = a_{36}n(\text{OH})n(\text{CO}). \quad (108b)$$

In the major part of the stratosphere the CO production is due to the oxidation process of methane by excited oxygen atoms $\text{O}(^1\text{D})$ and by the reaction of OH with methane. However, in the lower stratosphere the dissociative reaction of CH_4 with $\text{O}(^1\text{D})$ is a very slow process and below 25 km the reaction between OH and CH_4 is the principal process even for small concentrations of the hydroxyl radical.

In the lower stratosphere there is a decrease of carbon monoxide (Seiler and Junge, 1969). It corresponds to a very rapid decrease of the mixing ratio above the tropopause (Seiler and Warneck, 1972) from the tropospheric ratio $(1.4 \pm 0.2) \times 10^{-7}$ to another mixing ratio of the order of 4×10^{-8} . Such results (Junge *et al.*, 1970; Seiler and Warneck, 1972) show that the mixing ratio decreases to $1/e$ of its tropopause in about 1 km. Thus

$$\frac{n(\text{CO})}{n(M)} = \frac{n_{tr}(\text{CO})}{n_{tr}(M)} \cdot e^{-z/h} \equiv \frac{n_{tr}(\text{CO}) \cdot e^{-z/H_{\text{CO}}}}{n_{tr}(\text{CO}) \cdot e^{-z/H_M}} \quad (109)$$

with

$$\frac{1}{h} = \frac{1}{H_{\text{OC}}} - \frac{1}{H_M} = \frac{1}{10^5}. \quad (110)$$

In this transition region the transport leads to

$$F_{CO} = n_{tr}(CO)w(CO) = n(CO)K\left(\frac{1}{H_{CO}} - \frac{1}{H_M}\right) \tag{111a}$$

and with (110)

$$F_{CO} = n_{tr}(CO)K/10^5 \text{ cm}^{-2} \text{ sec}^{-1}. \tag{111b}$$

With $n_{tr}(CO) = 1.5 \times 10^{12} \text{ cm}^{-3}$ at the tropopause ($\leq 9 \text{ km}$), the vertical flux of CO molecules above the tropopause is

$$F_{CO} = 1.5 \times 10^7 \text{ K cm}^{-2} \text{ sec}^{-1} \tag{111c}$$

which is very important;

$$F_{CO} \geq 5 \times 10^{10} \text{ cm}^{-2} \text{ sec}^{-1} \tag{111d}$$

if the eddy diffusion coefficient is not less than $3 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}$.

If the CO molecules which are injected by (111d) are removed by the oxidation of CO by OH (Pressman and Warneck, 1970; Hesstvedt, 1970), an equivalent recycling of hydroxyl radicals corresponding to more than $10^5 \text{ OH radicals cm}^{-3} \text{ sec}^{-1}$ is required.

Furthermore, if the diffusive upward current of CO molecules by eddy diffusion given by (111a) corresponds to the oxidation of CO by OH, we may write

$$n(CO)K\left(\frac{1}{H_{CO}} - \frac{1}{H_M}\right) = n(CO)a_{36}n(OH)H_1 \tag{112}$$

Equation (112) with $K = 3 \times 10^8$ and $H_{CO} \simeq 1 \text{ km}$, leads to $n(OH) > 10^6 \text{ cm}^{-3}$ (Seiler and Warneck, 1972). Such a value is very high when the reaction between OH and CH_4 is considered. With a concentration of about 10^{-2} O(1D) atoms at 10 km as given by McConnell *et al.* (1971) it is difficult to produce more than $5 \times 10^2 \text{ OH molecules cm}^{-3} \text{ sec}^{-1}$ and to reach a concentration of $10^6 \text{ OH molecules cm}^{-3}$ at 10 km. The loss process by the reaction between OH and CH_4 reaches about $1.5 \times 10^{-2} \text{ sec}^{-1}$.

In conclusion, the aeronomic conditions (Fig. 14) are different in the lower and upper

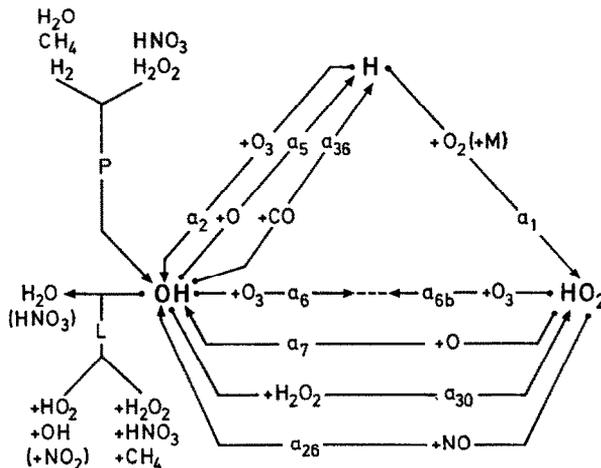


FIG. 14. REACTION SCHEME SHOWING THE WATER VAPOR CYCLE IN THE STRATOSPHERE.

stratosphere. The ratio of the hydroxyl and hydroperoxyl radical concentrations depends on reactions with oxygen atoms in the upper stratosphere but is related to the carbon monoxide and nitric oxide concentrations in the lower stratosphere. Furthermore, the dissociation and re-formation of water vapor are related to the presence of CH_4 and H_2 and their vertical distribution in the lower stratosphere. On the other hand, the nitrogen oxides concentrations depend not only for the vertical transport from or to the stratosphere of NO and NO_2 but also on the formation of nitric acid, on its dissociation process and finally on its downward transport to the troposphere.

REFERENCES

- ACKERMAN, M. (1971). Ultraviolet solar radiation related to mesospheric processes, in *Mesospheric Models and Related Experiments*, pp. 149–159. D. Reidel, Dordrecht.
- ACKERMAN, M. and FRIMOUT, D. (1969). Mesure de l'absorption stratosphérique du rayonnement solaire de 3,05 à 3,70 microns. *Bul. Acad. R. Belgique, Cl. Sc.* **55**, 948.
- ACKERMAN, M., FRIMOUT, D. and PASTIELS, R. (1971). New ultraviolet solar flux measurements at 2000 Å using a balloon borne instrument, in *New Techniques in Space Astronomy*, pp. 251–253. D. Reidel, Dordrecht.
- BAINBRIDGE, A. E. and HEIDT, L. E. (1966). Measurements of methane in the troposphere and lower stratosphere. *Tellus* **18**, 221.
- BATES, D. R. and HAYS, P. B. (1967). Atmospheric nitrous oxide. *Planet. Space Sci.* **15**, 189.
- BATES, D. R. and NICOLET, M. (1950). Photochemistry of water vapour. *J. geophys. Res.* **55**, 301.
- BREEN, J. E. and GLASS, G. P. (1970). Rates of some hydroxyl radical reactions. *J. chem. Phys.* **52**, 1082.
- CADLE, R. D. (1964). Daytime atmospheric $\text{O}(^1\text{D})$. *Disc. Faraday Soc.* **37**, 66.
- CALDWELL, J. and BACK, R. A. (1965). Combination reactions of hydroxyl radicals in the flash photolysis of water vapor. *Trans. Faraday Soc.* **61**, 1939.
- CALVERT, J. G., ALISTAIR KERR, J., DEMERJIAN, K. L. and MCQUIGG, R. D. (1972). Photolysis of formaldehyde as a hydrogen source in the lower atmosphere. *Science* **175**, 751.
- CHAPMAN, S. (1930). A theory of upper atmospheric ozone. *Memoirs R. met. Soc.* **3**, 103.
- CHAPMAN, S. (1943) Photochemistry of atmospheric oxygen. *Rep. Prog. Phys.* **9**, 92.
- CLYNE, M. A. A. and THRUSH, B. A. (1963a). Rates of elementary processes in the chain reaction between hydrogen and oxygen I. Reactions of oxygen atoms. *Proc. R. Soc. A275*, 544.
- CLYNE, M. A. A. and THRUSH, B. A. (1963b) Kinetics of the reaction of hydrogen atoms with molecular oxygen. *Proc. R. Soc. A275*, 559.
- CLYNE, M. A. A., MCKENNEY, D. J. and THRUSH, B. A. (1965). Rate of combination of oxygen atoms with oxygen molecules. *Trans. Faraday Soc.* **61**, 2701.
- CLYNE, M. A. A., THRUSH, B. A. and WAYNE, R. P. (1964). Kinetics of the chemiluminescent reaction between nitric oxide and ozone. *Trans. Faraday Soc.* **60**, 359.
- CRUTZEN, P. J. (1970). The influence of nitrogen oxides on the atmospheric ozone content. *Quart. J. R. met. Soc.* **96**, 320.
- DAVIS, D. D. (1972). Private communication.
- DIXON-LEWIS, G. and WILLIAMS, A. (1962). Role of hydroperoxyl in hydrogen oxygen flames. *Nature* **196**, 1309.
- DIXON-LEWIS, G., WILSON, W. E. and WESTENBERG, A. A. (1966). Studies of hydroxyl radical kinetics by quantitative ESR. *J. chem. Phys.* **44**, 2877.
- DEMORE, W. D. (1967). New mechanism for OH catalyzed chain decomposition of ozone. *J. chem. Phys.* **46**, 813.
- DEMORE, W. D. (1970). $\text{O}(^1\text{D})$ quenching efficiency of O_2 relative to other gases. *J. chem. Phys.* **52**, 4309.
- DEMORE, W. D. and RAPER, O. F. (1966). Primary processes in the ozone photolysis. *J. chem. Phys.* **44**, 1780.
- DITCHBURN, R. W. and YOUNG, P. A. (1962). The absorption of molecular oxygen between 1850 and 2500 Å. *J. atmos. terr. Phys.* **24**, 127.
- DONOVAN, R. J., HUSAIN, D. and KIRSCH, L. J. (1970). Reactions of oxygen atoms, Part. II. Relative rate data for the quenching of $\text{O}(^2\text{D}_2)$ using the OH radical as a spectroscopic marker. *Chem. Phys. Lett* **6**, 488.
- DONOVAN, R. J., HUSAIN, D. and KIRSCH, L. J. (1970). The rate of the reaction $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$ ($\text{M} = \text{He, Ar and Kr}$). *Trans. Faraday Soc.* **66**, 2551.
- DÜTSCH, H. U. (1968). The photochemistry of stratospheric ozone, *Quart. J. R. Met. Soc.* **94**, 483.
- EHHALT, D. H., HEIDT, L. E. and MARTELL, E. A. (1972). The concentration of atmospheric methane between 44 and 62 kilometers altitude. *J. geophys. Res.* **77**.
- FONER, S. N. and HUDSON, R. L. (1962). Mass spectrometry of the HO_2 free radical. *J. chem. Phys.* **36**, 2681.
- GRAY, D., LISSI, E. and HEICKLEN, J. (1972). The reaction of H_2O_2 with NO_2 and NO . (To be published).

- GREENBERG, R. I. and HEICKLEN, J. (1970). Reaction of O(¹D) with N₂O. *Int. J. Chem. Phys.* **2**, 185.
- GOLDMAN, A., MURCRAY, D. G., MURCRAY, F. H., WILLIAMS, W. J., KYLE, T. G. and BROOKS, J. N. (1970). Abundance of N₂O in the atmosphere between 4.5 and 13.5 km. *J. opt. Soc. Am.* **60**, 1466.
- GREINER, N. R. (1968). Hydroxyl radical kinetics by kinetic spectroscopy, III, Reactions with H₂O₂ in the range 300–450°K. *J. phys. Chem.* **72**, 406.
- GREINER, N. R. (1969). Hydroxyl radical kinetics by kinetic spectroscopy, V. Reactions with H₂ and CO in the range 300–500°K. *J. chem. Phys.* **51**, 5049.
- GREINER, N. R. (1970). Hydroxyl radical kinetics by kinetic spectroscopy, VI. Reactions with alkanes in the range 300–500°K. *J. chem. Phys.* **53**, 1070.
- HAMPSON, J. (1964). Photochemical behavior of the ozone layer. Technical Note 1627, Canadian Arm. Res. and Dev. Establishment.
- HASSON, V. and NICHOLLS, R. W. (1971). Absolute spectral measurements on molecular oxygen from 2640–1920 Å, II Continuum measurements 2430–1920 Å. *J. Phys.* **B4**, 1789.
- HAYS, P. B. and OLIVERO, J. J. (1970) Carbon dioxide and monoxide above the troposphere, *Planet. Space Sci.* **18**, 1729.
- HEICKLEN, J. (1968). Gas-phase reactions of Alkylperoxy and alkoxy radicals. *Advances in Chemistry Series*, n° 76, p. 23.
- HEICKLEN, J., SIMONAITIS, P., GREENBERG, R., KREZENSKI, D., GOLDMAN, R., and LISS E. (1971). Reaction of oxygen atoms O(¹D). to be published.
- HESSTVEDT, E. (1968). On the photochemistry of ozone in the ozone layer. *Geof. Publik*, n° 27.
- HESSTVEDT, E. (1970). Vertical distribution of CO near the stratopause. *Nature* **225**, 50.
- HILSENATH, E. (1969). An ozone measurement in the mesosphere and stratosphere by means of a rocket sonde. *J. geophys. Res.* **74**, 6873.
- HILSENATH, E. (1971). Ozone measurements in the mesosphere and stratosphere during two significant geophysical events. *J. Atmos. Sci.* **28**, 295.
- HOCHANADEL, C. J., GHORMLEY, J. A. and BOYLE, J. W. (1968). Vibrationally excited ozone in the pulse radiolysis and flash photolysis of oxygen. *J. chem. Phys.* **48**, 2416.
- HOCHANADEL, C. J., GHORMLEY, J. A. and OGREN, P. J. (1972). Absorption spectrum and reaction kinetics of the HO₂ radical in the gas phase. *J. chem. Phys.* **56**, 4426.
- HUNT, B. G. (1966). Photochemistry of ozone in a moist atmosphere. *J. geophys. Res.* **71**, 1385.
- HUSSAIN, D. and NORRISH, R. G. W. (1963). The production of NO₂ in the photolysis of nitrogen dioxide and of nitric acid vapour under isothermal conditions. *Proc. R. Soc.* **273A**, 165.
- JOHNSTON, H. (1968). Gas phase reaction kinetics of neutral oxygen species. *Nat. Standard Ref. Data Series*, NBS 20.
- JOHNSTON, H. (1971). Reduction of stratospheric ozone by nitrogen oxide catalysts from SST exhaust. *Science* **173**, 517.
- JOHNSTON, H. S. and CROSSBY, H. J. (1954). Kinetics of the fast gas phase reaction between ozone and nitric oxide. *J. chem. Phys.* **22**, 689.
- JONES, I. T. N. and WAYNE, R. P. (1969). Photolysis of ozone by 254-, 313- and 334-nm radiation. *J. chem. Phys.* **51**, 3617.
- JUNGE, C. E., SEILER, W. and WARNECK, P. (1971). The atmospheric ¹²CO and ¹⁴CO budget. *J. geophys. Res.* **76**, 2866.
- KAUFMAN, F. (1964). Aeronomic reactions involving hydrogen. A review of recent laboratory studies. *Annls. Géophys.* **20**, 106.
- KAUFMAN, F. (1969). Neutral reactions involving hydrogen and other minor constituents. *Canadian J. Chem.* **47**, 1917.
- KAUFMAN, F. and KELSO, J. R. (1967). M effect in the gas-phase recombination of O with O₂. *J. chem. Phys.* **46**, 4541.
- KLEIN, F. S. and HERRON, J. T. (1964). Mass-spectrometry study of the reactions of O atoms with NO and NO₂. *J. chem. Phys.* **41**, 1285.
- KREZENSKI, D. C., SIMONAITIS, R. and HEICKLEN, J. (1971). The reactions of O(³P) with ozone and carbonyl sulfide. *Int. J. Chem. Kinetics* **3**, 467.
- KRUEGER, A. J. (1969). Rocket measurements of ozone over Hawaii. *Annls. Géophys.* **25**, 307.
- LANGLEY, K. F. and MCGRATH, W. D. (1971). The ultraviolet photolysis of ozone in the presence of water vapor. *Planet Space Sci.* **19**, 413.
- LARKIN, F. S. and THRUSH, B. A. (1964). Recombination of hydrogen atoms in the presence of atmospheric gases. *Disc. Faraday Soc.* **37**, 112.
- LEIGHTON, P. A. (1961) *Photochemistry of air pollution*. Academic Press, New York.
- LEVY II, H. (1971). Normal atmosphere: Large radical and formaldehyde concentrations predicted. *Science* **173**, 141.
- LEOVY, C. B. (1969). Atmospheric ozone: An analytic model for photochemistry in the presence of water vapor. *J. geophys. Res.* **74**, 417.

- McCONNELL, J. C., McELROY, M. B. and WOFSEY, S. C. (1971). Natural sources of CO, *Nature* **233**, 187.
- McCRUMB, J. L. and KAUFMAN, F. (1971). Kinetics of the O + O₃ reaction. *J. Chem. Phys.* (In press).
- McELROY, M. B. and McCONNELL, J. C. (1971). Nitrous oxide: A natural source of stratospheric NO. *J. Atmos. Sci.* **28**, 1095.
- MCGRATH, W. D. and NORRISH, R. G. W. (1958). Influence of water on the photolytic decomposition of ozone. *Nature* **182**, 235.
- MCGUIGG, R. D. and CALVERT, J. G. (1969). The photodecomposition of CH₂O, CD₂O, CHDO and CH₂O-CD₂O mixtures at Xenon flash lamp intensities. *J. Am. Chem. Soc.* **91**, 1590.
- MORRIS, E. D. and NIKI, H. (1971). Mass spectrometric study of the reactions of nitric acid with O atoms and H atoms. *J. Phys. Chem.* **75**, 3193.
- MORRIS, E. D. and NIKI, H. (1971). Mass spectrometric study of the reaction of hydroxyl radical with formaldehyde. *J. Chem. Phys.* **55**, 1991.
- MORRIS, E. D. and NIKI, H. (1971). Reactivity of hydroxyl radicals with olefins. *J. Phys. Chem.* **75**, 3640.
- MULCAHY, M. F. R. and WILLIAMS, D. J. (1968). Kinetics of combination of oxygen atoms with oxygen molecules. *Trans. Faraday Soc.* **64**, 59.
- MULCAHY, M. F. R. and SMITH, R. H. (1971). Reactions of OH radicals in the H-NO₂ and H-NO₂-CO systems. *J. Chem. Phys.* **54**, 5215.
- MURCRAY, D. R., KYLE, T. G., MURCRAY, F. H. and WILLIAMS, W. J. (1969). Presence of HNO₂ in the upper atmosphere. *J. Opt. Soc. Am.* **59**, 1131.
- NICOLET, M. (1965). Nitrogen oxides in the chemosphere. *J. Geophys. Res.* **70**, 679.
- NICOLET, M. (1970a). Ozone and hydrogen reactions. *Annls Géophys.* **26**, 531.
- NICOLET, M. (1971). Aeronomic reactions of hydrogen and ozone. *Aeronomica Acta A-79*, 1970b; and in *Mesospheric Models and Related Experiments*, pp. 1-51. D. Reidel, Dordrecht.
- NICOLET, M. (1971). Photochimie de l'ozone dans la stratosphère sous l'action des oxydes d'azote et des composés de l'hydrogène. *Bull. Acad. R. Belgique, Cl. Sc.* **57**, 935.
- NICOLET, M. (1971). Un regard sur la stratosphère. *Aeronomica Acta A-91*.
- NICOLET, M. et VERGISON, E. (1971). L'oxyde azoteux dans la stratosphère. *Aeronomica Acta A-90*.
- NIKI, H. (1966). Reaction of O(³P) atoms with formaldehyde. *J. Chem. Phys.* **45**, 2330.
- NIKI, H., DABY, E. and WEINSTOCK, B. (1969). Reaction of atomic oxygen with methyl radicals. *J. Chem. Phys.* **48**, 5729.
- NOXON, J. F. (1970). Optical emission from O(¹D) and O₂(b¹Σ_g⁻) in ultraviolet photolysis of O₂ and CO₂. *J. Chem. Phys.* **52**, 1852.
- OGAWA, M. (1971). Absorption cross sections of O₂ and CO₂ continua and far uv regions. *J. Chem. Phys.* **54**, 2550.
- PARASKEVOPOULOS, G. and CVETANOVIC, R. J. (1969). Competitive reactions of the excited oxygen atoms, O(¹D). *J. Am. Chem. Soc.* **91**, 7572.
- PARASKEVOPOULOS, G. and CVETANOVIC, R. J. (1971). Relative rate of reaction of O(¹D₂) with H₂O. *Chem. Phys. Lett.* **9**, 603.
- PAUKERT, T. T. (1969). *Spectra and kinetics of the hydroperoxyl free radical in the gas phase*. University of California, Berkeley, UCRL-19109.
- PHILLIPS, L. F. and SCHIFF, H. I. (1962). Reactions of hydrogen atoms with nitrogen dioxide and with ozone. *J. Chem. Phys.* **37**, 1233.
- PONTANO, B. A. and HALE, L. C. (1970). Measurements of an ionizable constituent of the low ionosphere using a Lyman-α source and blunt probe. *Space Res.* **10**, 208.
- PRESSMAN, J. A. and WARNECK, P. (1970). The stratosphere as chemical sink for carbon monoxide. *J. Atmos. Sci.* **27**, 155.
- RANDHAVA, J. S. (1971). The vertical distribution of ozone near the equator. *J. Geophys. Res.* **76**, 8139.
- RHINE, P. E., TUBBS, L. D. and WILLIAMS, D. (1969). Nitric acid vapor above 19 km in the earth's atmosphere. *Appl. Optics* **8**, 1500.
- RONEY, P. L. (1965). On the influence of water vapour on the distribution of stratospheric ozone. *J. Atmos. Terr. Phys.* **27**, 1177.
- (SCEP) (1970). *Man's Impact on the Global Environment, Report on the Global Environment*, MIT Press, Cambridge, Mass.
- SCHIFF, H. I. (1964). Reactions involving nitrogen and oxygen. *Annls. Géophys.* **20**, 115.
- SCHOLZ, T. G., EHHALT, D. H., HEIDT, L. E., MARTELL, E. A. (1970). Water vapor, molecular hydrogen, methane and tritium concentrations near the stratopause. *J. Geophys. Res.* **75**, 3049.
- SCHÜTZ, K., JUNGE, C., BECK, B. and ALBRECHT, B. (1970). Studies of atmospheric N₂O. *J. Geophys. Res.* **75**, 2230.
- SEILER, W. and JUNGE, C. (1969). Decrease of carbon monoxide mixing ratio above the polar tropopause. *Tellus* **21**, 447.
- SEILER, W. and WARNECK, P. (1972). Decrease of CO—mixing ratio at the tropopause. *J. Geophys. Res.* **77**.
- SHARDANAND (1969). Absorption cross sections of O₂ and O₃ between 2000 and 2800 Å. *Phys. Rev.* **186**, 5.

- SHIMAZAKI, T. and LAIRD, A. R. (1970). A model calculation of the diurnal variation in minor neutral constituents in the mesosphere and lower thermosphere including transport effects. *J. geophys. Res.* **75**, 3221.
- SINGER, S. F. (1971). Stratospheric water vapour increase due to human activities. *Nature* **233**, 543.
- SIMONAITIS, R. and HEICKLEN, J. (1971). The kinetics of the reaction of OH with NO₂. *EOS*, **52**, 835.
- SMIC (1971). Inadvertent climate modification, *Report of the Study of Man's Impact on Climate*. MIT Press, Cambridge, Mass.
- SPICER, C. W., VILLA, A., WIEBE, H. A. and HEICKLEN, J. (1972). The reactions of methylperoxy radicals with NO and NO₂. To be published.
- STROBEL, D. F. (1971). Odd nitrogen in the mesosphere. *J. geophys. Res.* **76**, 8384; and (1972); Nitric oxide in the D region. To be published.
- WESTENBERG, A. A. and DEHAAS, N. (1969). Atom-molecule kinetics using ESR detection. Results for O + OCS, O + CS₂, O + NO₂ and H + C₂H₄. *J. chem. Phys.* **50**, 707.
- WILSON, A. W. (1966). Ozone production in the stratosphere. in, *Les problèmes météorologiques de la stratosphère et de la mésosphère*, pp. 383-392. Presses Universitaires Paris.
- WILSON, W. E. and O'DONOVAN, J. T. (1967). Mass-spectrometry study of the reaction rate of OH with itself and with CO. *J. chem. Phys.* **47**, 5455.
- YOUNG, R. A., BLACK, G. and SLANGER, T. G. (1968). Reaction and deactivation of O(¹D). *J. chem. Phys.* **49**, 4758.