Some aspects of atmospheric chemical reactions of atomic oxygen[1]

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ABSTRACT

Some features of atmospheric atomic oxygen chemistry that have received little attention, that need to be re-evaluated in the light of recent data, that have been studied in the author's laboratory, or that encompass some combination of these three are discussed.

Newly-calculated values for the concentrations of excited atomic oxygen below 100 km are so low that it is unlikely that its reactions contribute appreciably to the concentration of any atmospheric component in that region with the possible exception of excited molecular oxygen. Reactions of ground state atomic oxygen may constitute a sink for methane and a source of sulfate in this atmospheric region. Many chemionization reactions probably occur in the atmosphere, and three possible types are considered in detail.

Introduction

Atomic oxygen is one of the most chemically reactive species in the atmosphere and is present throughout most of the atmosphere, especially above the tropopause. Thus it plays a major role in atmospheric chemistry. The purpose of this paper is to discuss some features of atmospheric atomic oxygen chemistry that have received little attention, that need to be re-evaluated in the light of recent data, that have recently been studied in the author's laboratory, or that encompass some combination of these three.

Excited atomic oxygen

Equilibrium concentrations of ground state (^{3}P) atomic oxygen have been calculated for a large altitude range by many investigators, and concentration measurements have been made in a limited region. Electronically excited atomic oxygen is also present, namely O(^{1}S), which is responsible for the 5577 A (green) line in the airglow and O(^{1}D) which is responsible for the 6300 A (red) line. The concentrations of the latter are sufficiently high in the ionosphere that the intensity of the 6300 A line in the day airglow has been measured.

Very recent studies of the 6300 A line in the day airglow suggest that O(^{1}D) is produced in the ionosphere by the action of electrons possessing high kinetic energy (DALGARNO & WALKER, 1964). Impaction of ground state atomic oxygen, O(^{3}P), with such electrons may excite them to the ^{1}D state. O(^{1}D) is produced from ozone below 100 km by the strong absorption of solar radiation in the 2200–3140 A region leading to photodissociation with a quantum yield of about unity (LEIGHTON, 1961; VOLMAN, 1963). It is probably also produced, but with a lower quantum yield, by absorption in the 3140–3500 A region. The O(^{1}D) in the ozone region of the atmosphere is destroyed primarily by the following processes:

$$O(^1D) + O_2 + M \rightarrow O_3 + M \quad (1)$$

$$O(^1D) + M \rightarrow O(^3P) + M \quad (2)$$

$$O(^1D) \rightarrow O(^3P) + h\nu \quad (3)$$

It is readily demonstrated that 1 and 3 are insignificant compared with 2. There is considerable uncertainty concerning the relative effectiveness of molecular nitrogen and oxygen for collisional deactivation of O(^{1}D), especially

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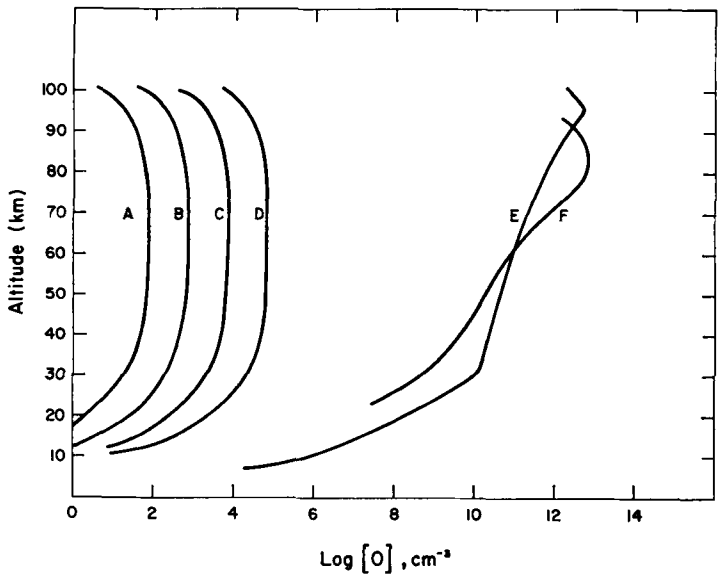

FIG. 1. Calculated atomic oxygen concentrations. *A*, *B*, *C*, and *D* represent O(¹D), assuming collisional deactivation coefficients of 10^{-9}, 10^{-10}, 10^{-11}, and 10^{-12} cm³ sec^{-1} respectively. *E* and *F* represent total daylight O, using data from the Handbook of Geophysics (MILLER, 1960) and recent calculations by LONDON (1965) for 0° latitude, respectively.

in the lower atmosphere. (DEMORE & RAPER, 1964). However, we can define an effective deactivation coefficient, k_2, for the ozone region based on molecular oxygen concentrations. Then the concentrations of O(¹D) can be calculated from the equation

$$[O(^1D)] = f[O_3]k_2^{-1}[O_2]^{-1}$$

where f is the rate of light absorption by ozone in photons/molecule sec. Values of f and of [O(¹D)] for various altitudes below 100 km were previously reported by CADLE (1964). The value of k_2, 10^{-12} cm³ sec^{-1}, was taken from the work of SEATON (1958) who considered it to be a minimum effective value for the aurora and airglow.

DALGARNO & WALKER (1964) have concluded that k_2 cannot be much less than 10^{-10} cm³ sec^{-1}. If so, the concentration of O(¹D) in the ozone region must be almost two orders of magnitude smaller than the previous calculations indicated. Figure 1 shows the calculated values for [O(¹D)] for the sun at the zenith for a number of values of k_2. The peak concentration of O(¹D) occurs at about 50 km rather than at the ozone peak because of both the rapid increase in f and decrease in O_2 with increasing altitude. Curves *B* and *D* correspond to Dalgarno's and Seaton's maximum values for k_2, respectively.

These considerations permit a logical choice between two sources which have been proposed for atmospheric nitrous oxide. Ground state atomic oxygen (³P) reacts very slowly if at all with molecular nitrogen, presumably because the reaction violates spin conservation rules and has an activation energy of about 13,000 cal mole^{-1}. However, O(¹D) does react fairly rapidly with nitrogen, and this reaction has been proposed by HARTECK & REEVES (1961) as a major source of atmospheric nitrous oxide. Another possible source that has often been suggested is bacterial action in the soil.

Using data of GROTH & SCHIERHOLZ (1957) for the reaction of O(¹D) with molecular nitrogen, estimates by GOODY & WALSHAW (1953) of the total rate of photochemical destruction of nitrous oxide, and concentrations of O(¹D) calculated on the basis of $k_2 = 10^{-12}$ cm³ sec^{-1}, CADLE (1964) showed that the reaction

$$N_2 + O(^1D) \rightarrow N_2O + h\nu \qquad (4)$$

might account for much of the nitrous oxide in the atmosphere. However, if k_2 is as large

as now seems likely, reaction 4 cannot be an important source of atmospheric nitrous oxide. BATES & WITHERSPOON (1952) discussed several other reactions that might produce nitrous oxide, and in addition to those discussed above, suggested the reactions

$$O_2 + N_2 \rightarrow N_2O + O_2 \quad (5)$$

and

$$O_3^* + N_2 \rightarrow N_2O + O_2 \quad (6)$$

However, both of these reactions violate spin conservation rules and must be very slow unless O_3^* is a triplet. The concentration of O_3^* must be very low since the photochemical yield of atomic oxygen by the photolysis of ozone, which may produce O_3^* as an intermediate product, is about unity. Thus O_3^* must decompose before it can undergo collisional deactivation. These considerations leave us with bacterial action in the soil as the most probable source of atmospheric nitrous oxide.

Similarly, it now seems highly unlikely that any reaction of $O(^1D)$ affects the concentration of any component of the atmosphere, at least below 100 km, to an appreciable extent with the possible exception of excited molecular oxygen ($^1\sum_g^+$) (SCHIFF & MEGILL, 1964).

Reaction of ground-state atomic oxygen with methane

An investigation has recently been undertaken in the senior author's laboratory of the reaction of $O(^3P)$ with methane (CADLE & ALLEN, 1965). This reaction is of interest since methane is a minor constituent of the natural atmosphere, the average concentration being about 1.4 parts per million by volume in the troposphere. Little is known concerning its distribution with height. It is introduced into the atmosphere by bacterial action at the earth's surface and by the liberation of natural gas. It is destroyed by reaction with atomic oxygen, OH, and H; by photolysis in the ionosphere; and possibly by other means such as electrical discharges.

Atmospheric methane has recently received considerable attention since the specific tritium content of atmospheric methane has been found to be several orders of magnitude greater than that of rainfall and somewhat less than that of atmospheric hydrogen and stratospheric water vapor. JUNGE (1963) states that a natural source of tritiated methane is excluded, and that it is unlikely that tritiated methane is produced in thermonuclear tests. Possibly it is produced industrially. Junge has used values for the tritium reservoir in the northern and southern hemispheres to estimate the exchange time between the hemispheres (3.5 years).

The reaction of atomic oxygen with methane was investigated using a high velocity flow system. Atomic oxygen was produced in many experiments by subjecting molecular nitrogen to a microwave discharge and titrating the atomic nitrogen produced with nitric oxide:

$$N + NO \rightarrow N_2 + O \quad (7)$$

The endpoint of the gas titration was indicated by the disappearance of the N_2^* and NO^* afterglows. The well-known "air afterglow" which results from the slow reaction

$$NO + O(+M) \rightarrow NO_2^*(+M) \quad (8)$$

was produced by adding a slight excess of nitric oxide. The intensity of this glow is proportional to the atomic oxygen concentration and was measured along the reaction tube to determine the rate of atomic oxygen disappearance as a result of reaction with the methane. The reaction of atomic oxygen with methane could also be catalytically quenched at various distances along the reaction tube and the amount of methane remaining after reaction determined by mass spectroscopy or gas chromatography. Means were provided for by-passing the discharge with molecular oxygen so that the effect of ground-state molecular oxygen on the reaction could be investigated.

Atomic oxygen was produced in other experiments by subjecting molecular oxygen to a microwave discharge and absolute determinations of the atomic oxygen produced were made by titration with nitrogen dioxide.

Atomic oxygen reacted much more rapidly in the presence of a large amount of molecular oxygen than when little or none was present. Rate constants based on the initial rates of atomic oxygen reaction in oxygen and nitrogen as the carrier gas were

$$k = 3.8(\pm 1.8) \times 10^{-11} \exp[-6600(\pm 1500)/RT] \text{ cm}^3 \text{ sec}^{-1}$$

and

$$k = 1.2(\pm 0.6) \times 10^{-11} \exp[-7300(\pm 1500)/RT] \text{ cm}^3 \text{ sec}^{-1}$$

respectively, where R is the gas constant (2.0 cal deg^{-1} mole^{-1}) and T the absolute temperature. Much more atomic oxygen was removed in the overall reaction than was required for the complete conversion of methane to carbon dioxide and water.

Rate constants calculated from the amounts of methane reacted were much less accurate than those based on oxygen atom disappearance because of the very small percentage of methane which reacted. However, from the standpoint of atmospheric behavior it is important to know whether the methane in the atmosphere reacts more rapidly with atomic oxygen than it otherwise would because of the presence of molecular oxygen. Therefore, the experiments described above were repeated using n-butane in place of the methane since n-butane reacts much more rapidly with atomic oxygen than does methane and rate constants for the hydrocarbon disappearance could be determined more accurately (ALLEN & CADLE, 1965). The effect of molecular oxygen on the rate constants for the initial rate of disappearance of atomic oxygen (k_0'), the initial rate of disappearance of n-butane (k_h'), and on the overall disappearance of n-butane (k_h) is shown in Table 1. The constants k_0', k_h, and k_h' were nearly the same in the absence of molecular oxygen when there was an excess of the hydrocarbon. This suggests that under these circumstances the calculated rate constant was that for the primary reaction of O with butane, possibly to form OH and butyl radicals. When there was an excess of atomic oxygen, or when appreciable molecular oxygen was present, k_0' increased in value and could not have represented the primary reaction. The presence of molecular oxygen may have had a small effect on k_h and k_h', but much less than on k_0'. Therefore, if the reaction involving methane is similar to that involving n-butane, the second of the two rate constants given above for the methane reaction is probably more nearly representative than the first of methane behavior in the atmosphere. In fact, the value which should be applied is probably between the two, but closer to the second than the first.

TABLE 1. *Variation of calculated rate constants with initial concentrations of atomic oxygen, molecular oxygen and hydrocarbon, at* 300°K.

$[O]_i \times 10_a^{-14}$	$[C_4H_{10}]_i \times 10_a^{-14}$	$k_0' \times 10_b^{14}$	$k_h \times 10_b^{14}$	$k_h' \times 10_b^{14}$	% O_2
1.08	2.96	5.25	4.26	4.08	0.0
2.16	4.05	8.95			0.0
3.74	1.84	20.5			0.0
2.50	0.82	30.4			0.0
4.42	1.27	35.8			0.0
9.88	0.67	41.1			0.0
11.1	1.31	38.0			0.0
11.1	1.40	39.5			5.0
9.00	0.52	70.8			20.0
10.5	0.29	89.6			33.3
6.15	0.40	110	5.70	5.38	50.0

a, molecules or atoms per cm^3 *b*, cm^3 sec^{-1}.

In order to investigate the significance of these rate constants to atmospheric methane concentrations, calculations were made of the methane concentrations at various altitudes assuming a constant mole fraction for methane of 1.4×10^{-6} and using the U.S. Standard Atmosphere (1962). Rates of methane reaction were then calculated using these methane concentrations, the atomic oxygen concentrations taken from the Handbook of Geophysics (MILLER, 1960) shown in Figure 1, and the two rate equations. The results are shown in Figure 2. They indicate that if residence times of air in the stratosphere and mesosphere are a year or more ($> 10^7$ sec), the atmosphere must be considerably depleted of methane at least above 40 km, even if the rates of reaction are closer to those indicated by curve B than curve C. The results in Figure 2 can be converted to values for $\tau(CH_4)$, defined[1] as $[CH_4]/d[CH_4]/dt$, by dividing the values of curve A by those of B or C for any given altitude. Similar results would have been obtained if the values for atomic oxygen concentrations in the atmosphere used for making the calculations had been those of LONDON (1965) shown in Figure 1. However, in that case calculated rates of methane oxidation would be lower below 60 km and higher between 60 and 90 km than those shown in Figure 2.

It is important to note that although the reaction of atomic oxygen with methane depletes the atmosphere of the latter, it has little effect on the atomic oxygen concentration. This

[1] $\tau(CH_4)$ is thus the time required for all of the methane existing at any moment to react if the reaction is first order in methane and $d[CH_4]/dt$ does not change with time.

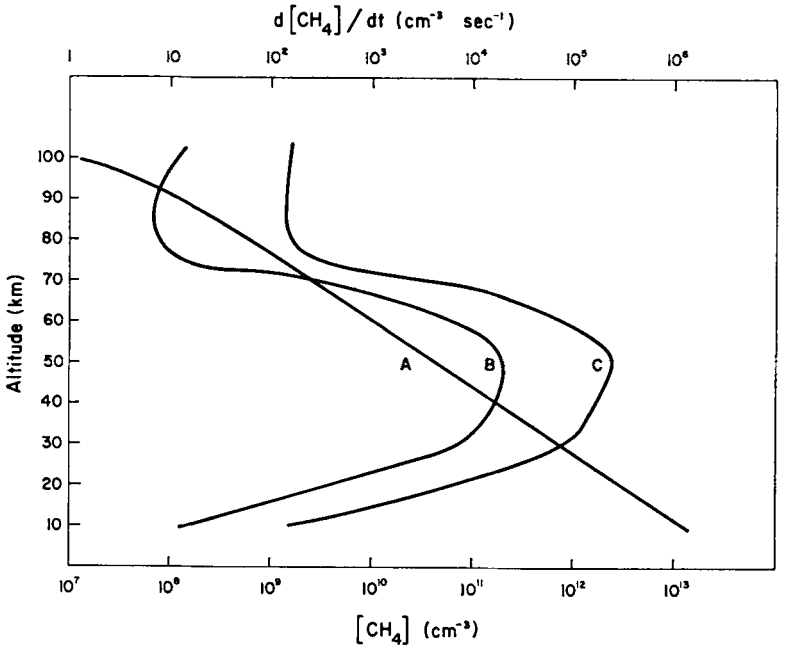

FIG. 2. Calculated atmospheric methane concentrations, assuming a constant mixing ratio, A, and corresponding rates of reaction with atomic oxygen, B and C. B is based on measurements of the rate constant in nitrogen and C on measurements of the rate constant in oxygen.

can be demonstrated using the calculated values of DÜTSCH (1961) for the number of quanta ($\lambda < 2420$ A) absorbed per oxygen molecule per second at various altitudes. This absorption leads to a production rate of atomic oxygen greatly in excess of the rate of atomic oxygen removal indicated by curve B or C of Figure 2.

Reaction of ground state atomic oxygen with sulfur dioxide

Ground state atomic oxygen also reacts with sulfur dioxide to form sulfur trioxide which in the atmosphere almost immediately hydrolyzes to form sulfuric acid droplets:

$$SO_2 + O(^3P) + M \rightarrow SO_3 + M \qquad (9)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (10)$$

Because reaction 9 can occur both in smog and in the natural atmosphere, and may be partially responsible for sulfates found in both, it has been investigated in our laboratory.

The method was much the same as that used for studying the atomic oxygen–methane reaction. Accurate rates were obtained from the decrease in concentrations of both atomic oxygen and sulfur dioxide. The reaction was found to be third order and to have a zero or nearly zero activation energy. Thus the rate constant is essentially independent of temperature, a common feature of third-order reactions. The rate constant calculated from the initial decrease in oxygen atom concentration for reaction 9 was essentially the same as that calculated from the overall drop in sulfur dioxide concentration. The arithmetic mean value from a number of runs was 1.3×10^{-32} cm^6 sec^{-1}. The rate constant was the same, within experimental error, whether the carrier gas was oxygen or nitrogen.

Not much is known concerning sulfur dioxide concentrations in the atmosphere except near the earth's surface. Judging from results quoted by JUNGE (1963), a typical concentration over continents, except close to sources of air pollutants, is 10 μg/m^3 and over oceans is 1 μg/m^3. However, the variations are large. The majority of the sulfur in the lower atmosphere is gaseous and most of this is sulfur dioxide.

Values of $\tau(SO_2)$ for reaction 9 calculated

TABLE 2. *Value of $\tau(SO_2)$ for the reaction of sulfur dioxide with ground-state atomic oxygen.*

Altitude (km)	$\tau(SO_2)$ (seconds)
10	8.7×10^6
15	1.2×10^6
20	2.1×10^5
30	2.0×10^4
50	9.0×10^4

from curve E of Figure 1, values of [M] for various heights taken from the U.S. Standard Atmosphere (1962), and the rate constant, are given in Table 2. The results demonstrate that although the concentrations of atomic oxygen in the lower stratosphere are not at all well known, it is likely that any sulfur dioxide reaching the stratosphere will be rapidly oxidized to sulfuric acid by reactions 9 and 10. Thus these reactions may contribute to the particulate sulfate that is found in the stratosphere (JUNGE, 1963). The maximum concentration of such particles at about 25 km may result from the combined effects of increasing concentration of atomic oxygen and decreasing concentration of sulfur dioxide with increasing altitude, but of course other explanations are possible.

The concentration of sulfur dioxide of 1 $\mu g/m^3$ at STP corresponds to a mole fraction of about 10^{-9}. Note that even if the mole fraction of sulfur dioxide entering the air is this high, reaction 9 will not greatly affect the concentration of atomic oxygen since this reaction is considerably slower than the primary rate of atomic oxygen production from molecular oxygen.

Chemionization

Chemionization can be defined as the production of primary ions as an integral part of a chemical reaction. The ionization energy is usually partially supplied by the making or breaking of chemical bonds. Since ionization potentials generally exceed the energy released by chemical reactions involving stable species, chemionization generally results from reactions involving excited and often metastable species such as electronically-excited atoms and molecules, and vibrationally-excited molecules.

The atmosphere, particularly the upper atmosphere, contains a vast assortment of such excited species, and chemionization has often been suggested as an important process in the atmosphere (FRANKLIN, 1963; POPPOFF & WHITTEN, 1963).

Laboratory studies of chemionization have been made during the last few years using a number of techniques such as mass spectroscopy (FRANKLIN, 1963; KNEWSTUBB & SUGDEN, 1959; BASCOMBE *et al.*, 1961), shock tubes (WRAY *et al.*, 1962; HAND & KISTIAKOWSKY, 1962), flames (CALCOTE, 1960, 1962; MUKHERJEE *et al.*, 1962), pairs of electrodes inserted in flow systems (GATZ *et al.*, 1963; BIONDI, 1952) and microwave techniques (JONES, 1956; GARDNER, 1955).

Although this field of investigation is very young, sufficient experimental results have been obtained so that the possibility of chemionization contributing appreciably to the ion content of the atmosphere or that the reactions producing the ionization materially influence the composition of the atmosphere can be examined.

The laboratory results demonstrate that chemionization is a very common phenomenon whenever the thermodynamic requirements are satisfied. They also indicate that such reactions are apt to have unusually large rate constants. The activation energies are probably quite low or zero except for reactions which are slightly endothermic. Thus the pre-exponential factor in the usual expression for the rate law is often unusually high. In terms of collision theory this suggests that the effective atomic or molecular diameters are orders of magnitude larger than those usually assigned to such species, probably because the molecules taking part in the reactions are highly polarized and coulombic forces are effective at distances which are large relative to molecular diameters. Many of these reactions are essentially the reverse of dissociative recombination reactions, which are known to have very large rate constants. Thus from equilibrium considerations the rate constants for chemionization reactions have to be large for them to be readily observed experimentally.

A large number of chemionization reactions were analyzed to determine their possible influence on the atmosphere. Conventional rate laws for second and third order reactions were used, assuming that the rate constants are 10^{-9}–10^{-10} $cm^3\ sec^{-1}$ and 10^{-27}–10^{-30} $cm^6\ sec^{-1}$, respec-

tively, and that chemionization reactions have zero activation energies.

Only three reactions or types of reactions among all of those analyzed seem to have much likelihood of appreciably influencing the nature of the atmosphere. They are highly speculative, none of them having been studied to an appreciable extent in the laboratory.

The reaction $N(^2P) + O(^3P) \rightarrow NO^+ + e$

The reaction

$$N + O + 2.8 \text{ ev} \rightarrow NO^+ + e \qquad (11)$$

apparently is responsible for much of the ionization in shocked air (LIN & LEARE, 1963). This reaction may occur in the ionosphere in the form

$$N(^2P) + O(^3P) \rightarrow NO^+ + e \qquad (12)$$

It is exothermic by about 0.5 ev and obeys the Wigner spin-conservation rule.

$N(^2P)$ is probably produced by dissociative recombination of N_2^+ and electrons, perhaps as MITRA (1952) suggests by

$$N_2^+ + e \rightarrow N(^2P) + N(^2D) \qquad (13)$$

It may be produced in auroras and the upper atmosphere as suggested by BATES (1960) by

$$x + N_2 \rightarrow x + N(^2P) + N$$

where x is an energetic electron, hydrogen atom, or proton. A very crude estimate can be made of the concentrations of $N(^2P)$ assuming that it is produced entirely by 13. Consider the situation at 140 km. BARTH (1961) has shown that the production of N at this altitude largely results from dissociative recombination of N_2^+; the production rate is probably about 10^2 cm^{-3} sec^{-1}. A similar result is obtained by combining the results of JOHNSON *et al.* (1958), which suggest that as much as three per cent of the positive ions at 140 km may be N_2^+, with the recombination coefficient of KASNER *et al.* (1961) for reaction 13 (6×10^{-7} cm^3 sec^{-1}). If the reaction is 13, half of the N is at first in the ^2P state. The reactions which remove $N(^2P)$ in addition to 12 are

$$N(^2P) + N + M \rightarrow N_2 + M \qquad (14)$$

$$N(^2P) + O + M \rightarrow NO + M \qquad (15)$$

$$N(^2P) + NO \rightarrow N_2 + O \qquad (16)$$

$$N(^2P) + O_2 \rightarrow NO + O \qquad (17)$$

$$N(^2P) + M \rightarrow N(^4S) + M \qquad (18)$$

$$N(^2P) \rightarrow N(^2D) + h\nu \qquad (19)$$

Assuming steady-state conditions,

$$\begin{aligned} d[N(^2P)]/dt = 0 \\ = 10^2 - (&k_{14}[N(^2P)][N][M] \\ &+ k_{15}[N(^2P)][O][M] \\ &+ k_{16}[N(^2P)][NO] \\ &+ k_{17}[N(^2P)][O_2] \\ &+ k_{18}[N(^2P)][M] + A[N(^2P)] \\ &+ k_{12}[N(^2P)][O]) \end{aligned}$$

The brackets refer to concentrations, the k's are rate constants, A is the transition probability for 19, and M is the concentration of all species. Order-of-magnitude values of these quantities are used. The values for k_{14}–k_{17} are those used by BARTH (1961), k_{18} is assumed to be 10^{-12} cm^3 sec^{-1}, A is assumed to be 0.1 (actually it is 0.2), N and NO are the values estimated by Barth, and the remaining concentrations are taken from the Handbook of Geophysics (MILLER, 1960). The equation then reduces to

$$N(^2P) = \frac{10^2}{k_{12} \times 10^{10} + 0.1}$$

If k_{12} is 10^{-9}, $[N(^2P)] = 10$ cm^{-3}; if k_{12} is 10^{-10}, $[N(^2P)] = 10^2$ cm^{-3}. Unless k_{12} is much smaller than suggested, or k_{18} much larger, 12 dominates the removal of $N(^2P)$ and about half of the electrons removed by 13 are liberated, at a rate of 10^2 sec^{-1}, by 12. The value of k_{18} might be as large as 10^{-10} cm^3 sec^{-1}, in which case the second term in the denominator of the equation becomes 10 instead of 0.1. This would not affect the above conclusion if k_{12} is as large as 10^{-9}. Since the peak rate of production of electrons, q_0, in the E-region has been represented by the equation (RATCLIFF & WEEKES, 1960)

$$q_0 = 180\ (1 + aR) \text{ cm}^{-3} \text{ sec}^{-1}$$

where R is the sunspot number and a is 7–9.5 $\times$ 10^{-3}, 12 may be an important process in maintaining the daytime electron concentration in the E-region. NORTON *et al.* (1962) have proposed a value for q_0 about an order of magnitude greater than that indicated by the Ratcliff and Weekes equation. Even so, reaction 12 may affect as much as ten per cent of the electron concentration in the E-region.

At night the concentrations of N_2^+ and thus of $N(^2P)$ decrease rapidly, so 12 is not important in maintaining the electron concentration of the E-region at night.

Reaction 12 is less important in maintaining the electron concentration in the F-region than in the E-region, since the rate of chemionization must be almost constant to at least 200 km and the rate of electron production in the F-region is several times that in the E-region.

If we extrapolate Barth's estimates of the rate of N production by dissociative recombination to 85 km, we find that the rate of $N(^2P)$ production can be no more than about one cm^{-3} sec^{-1}. Then $[N(^2P)] = 0.01$ cm^{-3}, assuming k_{12} is 10^{-10} and $[O] = 10^{12}$ cm^{-3}. Thus at this level reaction 12 may deplete the atmosphere of $N(^2P)$, but does not contribute to the electron concentration to an appreciable extent. Also, as in the E and F regions, 12 cannot help maintain the electron concentration at night.

If, as suggested by Barth, Mitra, and others, reaction 13 is largely responsible for the production of atomic nitrogen in the E-region, reaction 12, by removing $N(^2P)$ as fast as it is formed, will halve the effective production rate of atomic nitrogen. Thus reaction 12, if indeed it occurs, must be taken into account in any calculation of atomic nitrogen concentrations based on reaction 13.

CHAMBERLAIN (1961) has suggested that the absolute intensity of NI_{32}, arising from $N(^2D) - N(^2P)$, is 100 kR for IBC III auroras. Assuming a transition probability of 0.04 and an auroral thickness of 3×10^6 cm, $[N(^2P)]$ is about 10^6 cm^{-3}. Then, if k_{12} is 10^{-10} cm^3 sec^{-1} and $[O(^3P)]$ is assumed to be that in the normal atmosphere, about 10^{11} cm^{-3}, $d[e]/dt$ from reaction 12 is about 10^7 cm^{-3} sec^{-1}. Chamberlain has estimated the ionization rate at 120 km in such an aurora to be about 2×10^6 ion-pairs cm^{-3} sec^{-1}. Both of these estimates are very crude, but they suggest that chemionization may contribute appreciably to the electron concentration in auroras.

The reaction $Na + O + O \rightarrow Na^+ + O_2 + e$

POPPOFF & WHITTEN (1963) have suggested that the reaction

$$Na + O + O \rightarrow Na^+ + O_2 + e \qquad (20)$$

may help maintain the electron concentration in the D-region at night. It is not at all certain, of course, that 20 occurs at all. The gas-phase reaction of sodium with atomic oxygen may be

$$Na + O + O \rightarrow NaO + O \qquad (21)$$

It is of interest to estimate the influence 20 might have on the night time electron concentration at 85 km by making the following assumptions:

(*a*) Electron-positive ion recombination is mainly responsible for the night time decrease in $[e]$.

(*b*) The production of Na^+ by 20 has little effect on the total positive ion concentration.

(*c*) The effective recombination coefficient is 10^{-7} cm^3 sec^{-1}.

(*d*) $[O^-]$ remains equal to $[e]$ throughout the night.

(*e*) [Na] remains constant at 10^4 cm^{-3} throughout the night.

(*f*) [O] remains constant at 10^{12} cm^{-3} throughout the night.

Then

$$\frac{d[e]}{0.5\,k_{20}[Na][O]^2 - 10^{-7}[e]^2} = -dt$$

This equation was solved for various values of t and k_{20} assuming, as suggested by Whitten and Poppoff, that $[e]$ at sunset is 1300 cm^{-3}. The results are shown in Table 3. They indicate that if 20 occurs, it will contribute to the night D-region if k_{20} is as large as seems likely for chemionization reactions. On the other hand, it cannot be as large as 10^{-27} cm^6 sec^{-1} since then 20 would either deplete the atmosphere of atomic sodium or prevent any decrease in $[e]$ at night, or both. It is of interest to note that if k_{20} had a value close to 10^{-27} cm^6 sec^{-1}, reaction 20 would produce electrons at a sufficient rate to account for the daylight D-region. However, the difficulty just mentioned, if nothing else, probably removes 20 from serious consideration as an important mechanism for daylight D-region formation.

Reactions between excited species and neutral molecules

Near the earth's surface, in addition to the local effects of lightning and point discharge, ionization is produced by cosmic radiation and

TABLE 3. *Electron concentrations at two times after sunset for various values of k_{20}.*

$[e]$ (cm^{-3}) for k_{20}	$=10^{-27}$	$=10^{-29}$	$=10^{-30}$	$=10^{-31}$	$=0$
Time after sunset (hrs)					
0	1300	1300	1300	1300	1300
1	7010	1010	900	890	880
4	7070	763	490	460	450

radioactive emanations. This radiation produces excited species as well as ions and at comparable concentrations (LAIDLER, 1955; LIND, 1961). The reaction

$$N_2^+ + N_2 \rightarrow N_4^* + e \qquad (22)$$

has been observed using mass spectroscopy by FRANKLIN (1963). Other such reactions involving excited species which may occur include

$$O^* + O_2 \rightarrow O_3^+ + e \qquad (23)$$

$$O^* + N_2 \rightarrow N_2O^+ + e \qquad (24)$$

$$N^* + O_2 \rightarrow NO^+ + O + e \qquad (25)$$

These reactions are possible in the lower atmosphere because the very high energy of cosmic radiation can excite various species to much higher energy levels than can most solar radiation.

Very highly excited species are also found elsewhere in the atmosphere, as in auroras. However, reactions such as 22–25 are probably only important near the earth's surface since such highly excited species can undergo allowed transitions and the chemionization reactions can only compete with such transitions at relatively high pressures. It is possible that such reactions produce ion concentrations near the earth's surface of the same order of magnitude as those produced directly by cosmic radiation.

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НЕКОТОРЫЕ СВОЙСТВА ХИМИЧЕСКИХ РЕАКЦИЙ АТОМАРНОГО КИСЛОРОДА В АТМОСФЕРЕ

Рассматриваются такие химические свойства атмосферного атомарного кислорода, на которые либо обращалось мало внимания, либо которые необходимо пересмотреть в свете новых данных, либо изучавшиеся в лаборатории автора, либо, наконец, вопросы, связанные с комбинацией перечисленных причин. Согласно новым расчетам, концентрация возбужденного кислорода на высоте ниже 100 км так низка, что мало вероятно, чтобы его реакции давали заметный вклад в изменение концентрации других компонентов атмосферы в этой области, за исключением, быть может, возбужденного молекулярного кислорода. Реакции атомарного кислорода в невозбужденном состоянии могут являться в этой области источником увеличения сульфатов и уменьшения метана. В атмосфере, вероятно, имеет место много реакций химической ионизации, но только три возможных типа рассматриваются здесь подробно.