

The Evolution of Atmospheric Ozone

J. F. KASTING

National Center for Atmospheric Research, Boulder, Colorado 80307

T. M. DONAHUE

Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, Michigan 48109

A one-dimensional coupled chemistry and flow model of the earth's atmosphere is used to study the relationship between ozone content and oxygen level. The effects of the biogenic trace gases methane and nitrous oxide are considered, as well as the production of odd nitrogen in lightning discharges. The ozone column depth is found to increase monotonically with increasing oxygen content, in contrast with previous predictions that the column depth should peak at $\sim 10^{-1}$ PAL (present atmospheric level) of O_2 . The critical O_2 level at which an effective ultraviolet shield is produced is in the neighborhood of 10^{-1} PAL. Implications of this result for the emergence of terrestrial land life are considered.

INTRODUCTION

Atmospheric ozone plays an important role in shaping our modern terrestrial environment by shielding out solar ultraviolet light in the 2000 to 3000-Å range. This, together with the realization that the amount of oxygen in the earth's atmosphere must have been much lower in the past than it is today [Walker, 1977], has led several authors to investigate the evolution of ozone as a function of atmospheric oxygen content. A question of particular interest is whether or not the development of the ozone layer was responsible for the emergence of life on land during the Late Silurian period, about 420 m.y. (million years) ago.

The first serious attempt to solve this problem can in a series of papers by Berkner and Marshall [1964, 1965, 1966, 1967]. They predicted that a biologically effective ultraviolet shield would have been provided by a total ozone column of 0.2 atm cm, which should have reduced the ultraviolet flux at the earth's surface to less than $1 \text{ erg cm}^{-2} \text{ s}^{-1}$ (50 Å^{-1}). Using a semiempirical method to relate ozone densities to atmospheric oxygen levels, they found that this O_3 column depth should have been achieved at an O_2 level of approximately 10^{-1} PAL (present atmospheric level). Since their scenario for the rise of atmospheric oxygen called for an O_2 level of 10^{-2} PAL at the dawn of the Cambrian period (~ 600 m.y.), they suggested that the subsequent increase in oxygen to 10^{-1} PAL and the accompanying development of the ozone screen was directly responsible for the spread of life onto land during the Silurian.

The estimation of ozone column depth versus oxygen content was repeated in a more realistic fashion by Ratner and Walker [1972], who calculated ozone densities by assuming photochemical equilibrium in an oxygen-nitrogen atmosphere. Their model predicted that the ozone column depth should increase as the oxygen content decreased from 1 to 10^{-1} PAL, as a result of the speeding up of the three-body ozone formation reaction as the O_3 peak moved downward in the atmosphere. Below 10^{-1} PAL of O_2 the ozone column depth began to decline, but much more slowly than had been predicted by Berkner and Marshall. Thus in spite of their use of a stricter biological tolerance limit on ultraviolet flux, requiring a minimum O_3 column depth of $7 \times 10^{18} \text{ cm}^{-2}$ (0.26

atm cm), they found that the critical level should have been achieved at an oxygen content of only 10^{-3} PAL.

Previous to this calculation, Rhoads and Morse [1971] had proposed that the atmospheric oxygen level during the Cambrian must have been at least as high as 10^{-1} PAL. Their argument was based on evidence that calciferous fauna in contemporary marine environments require a dissolved oxygen concentration of at least 1 ml/l, compared to the 4–9 ml/l which would be in equilibrium with the current atmosphere. Comparing this result with that of Ratner and Walker, Margulis *et al.* [1976] concluded that the ozone screen was already fully established by the late Precambrian and consequently had little to do with the sequence of events during the Silurian, some 200 m.y. later.

Ratner and Walker's calculation, however, neglected several factors which influence the amount of ozone in the present-day atmosphere. Hesstvedt *et al.* [1974] constructed a more complete model which included vertical transport of ozone as well as the oxides of hydrogen, which are known to catalyze ozone destruction in the present-day stratosphere. Ozone was included as part of an odd oxygen family ($O_x \equiv O + O_3$), similar to its treatment in modern stratospheric models [Liu *et al.*, 1976]. Assuming equatorial geometry, Hesstvedt *et al.* found that the full ozone shield would not have developed until the oxygen level exceeded 2×10^{-2} PAL. While their finding cannot be compared directly with that of Ratner and Walker because of different ultraviolet tolerance limits, the factor of 20 increase in critical oxygen level indicates the need to proceed carefully in this study.

The study by Hesstvedt *et al.* was followed by two more photochemical equilibrium models for ozone. Blake and Carver [1977] included methane and carbon dioxide in their model, along with odd hydrogen and odd nitrogen species. Katsumori [1979] performed a combined photochemical-radiative transfer calculation, which confirmed previous predictions by Morss and Kuhn [1978] concerning the decline in stratospheric temperatures with decreasing ozone content. In both of these models the ozone column depth maximized at about 10^{-1} PAL of O_2 , establishing this peak as a consistent feature among photochemical equilibrium models of ozone evolution.

The most recent evaluation of the ozone problem has been

TABLE 1. Reactions and Rate Constants

Reaction Number	Reaction	Rate Constant, cm ³ s ⁻¹ or cm ⁶ s ⁻¹	References
(R 1)	H ₂ O + O(¹ D) → 2OH	2.1 × 10 ⁻¹⁰	Streit <i>et al.</i> [1976]
(R 2)	H ₂ + O(¹ D) → OH + H	1.0 × 10 ⁻¹⁰	Davidson <i>et al.</i> [1977]
(R 3)	H ₂ + O → OH + H	3 × 10 ⁻¹⁴ T exp (-4480/T)	Baulch <i>et al.</i> [1972]
(R 4)	H ₂ + OH → H ₂ O + H	1.8 × 10 ⁻¹¹ exp (-2330/T)	Smith and Zellner [1974]
(R 5)	H + O ₃ → OH + O ₂	2.6 × 10 ⁻¹¹	Hampson [1973a]
(R 6)	H + O ₂ + M → HO ₂ + M	2.1 × 10 ³² exp (290/T)	Hampson and Garvin [1975]
(R 7)	H + HO ₂ → H ₂ + O ₂	4.2 × 10 ⁻¹¹ exp (-350/T)	Baulch <i>et al.</i> [1972]
(R 8)	H + HO ₂ → H ₂ O + O	8.3 × 10 ⁻¹¹ exp (-500/T)	Lloyd [1974]
(R 9)	H + HO ₂ → OH + OH	4.2 × 10 ⁻¹⁰ exp (-950/T)	Lloyd [1974]
(R 10)	OH + O → H + O ₂	4.2 × 10 ⁻¹¹	Wilson [1972]
(R 11)	OH + HO ₂ → H ₂ O + O ₂	3 × 10 ⁻¹¹	Hudson [1977]
(R 12)	OH + O ₃ → HO ₂ + O ₂	1.5 × 10 ⁻¹² exp (-1000/T)	Hudson [1977]
(R 13)	HO ₂ + O → OH + O ₂	3.5 × 10 ⁻¹¹	Burrows <i>et al.</i> [1977]
(R 14)	HO ₂ + O ₃ → OH + 2O ₂	1.4 × 10 ⁻¹⁴ exp (-580/T)	M. S. Zahniser and C. J. Howard (personal communication, 1979)
(R 15)	HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	3 × 10 ⁻¹¹ exp (-500/T)	Hampson [1973a]
(R 16)	H ₂ O ₂ + OH → HO ₂ + H ₂ O	1.0 × 10 ⁻¹¹ exp (-750/T)	Hudson [1977]
(R 17)	O + O + M → O ₂ + M	2.76 × 10 ⁻³⁴ exp (710/T)	Campbell and Thrush [1967]
(R 18)	O + O ₂ + M → O ₃ + M	1.058 × 10 ⁻³⁴ exp (510/T)	Hampson and Garvin [1975]
(R 19)	O + O ₃ → 2O ₂	1.9 × 10 ⁻¹¹ exp (-2300/T)	Hampson and Garvin [1975]
(R 20)	H + H + M → H ₂ + M	8.3 × 10 ⁻³³	McEwan and Phillips [1975]
(R 21)	H + OH + M → H ₂ O + M	6.1 × 10 ⁻²⁶ / T ²	McEwan and Phillips [1975]
(R 22)	OH + OH → H ₂ O + O	1.4 × 10 ⁻¹²	Clyne and Down [1974]
(R 23)	CO + O + M → CO ₂ + M	2 × 10 ⁻³⁷	Simonaitis and Heicklen [1972]
(R 24)	CO + OH → CO ₂ + H	6 × 10 ⁻¹³ [(0.25 + A[M]) / (1 + A[M])] (A = 1.82 × 10 ⁻²⁰)	Perry <i>et al.</i> [1977]
(R 25)	N + O ₂ → NO + O	1.1 × 10 ⁻¹⁴ T exp (-3150/T)	Baulch <i>et al.</i> [1973]
(R 26)	N + O ₃ → NO + O ₂	5.7 × 10 ⁻¹³	Baulch <i>et al.</i> [1973]
(R 27)	N + OH → NO + H	5.3 × 10 ⁻¹¹	Baulch <i>et al.</i> [1973]
(R 28)	N + NO → N ₂ + O	2.7 × 10 ⁻¹¹	Baulch <i>et al.</i> [1973]
(R 29)	NO + O ₃ → NO ₂ + O ₂	9 × 10 ⁻¹³ exp (-1200/T)	Hampson and Garvin [1975]
(R 30)	NO + O + M → NO ₂ + M	4 × 10 ⁻³³ exp (940/T)	Baulch <i>et al.</i> [1973]
(R 31)	NO + HO ₂ → NO ₂ + OH	8 × 10 ⁻¹²	Howard and Evenson [1977]
(R 32)	NO ₂ + O → NO + O ₂	9.1 × 10 ⁻¹²	Hampson [1973a]
(R 33) ^a	NO ₂ + OH (+M) → HNO ₃ (+M)	8 × 10 ⁻¹²	Hampson and Garvin [1975]
(R 34) ^b	HNO ₃ + OH → H ₂ O + NO ₂ + O	1.3 × 10 ⁻¹³	Hampson and Garvin [1975]
(R 35)	O(¹ D) + N ₂ → O(³ P) + N ₂	3 × 10 ⁻¹¹	Streit <i>et al.</i> [1976]
(R 36)	O(¹ D) + O ₂ → O(³ P) + O ₂	4.1 × 10 ⁻¹¹	Streit <i>et al.</i> [1976]
(R 37)	N ₂ O + O(¹ D) → NO + NO	1.1 × 10 ⁻¹⁰	Garvin and Hampson [1974]
(R 38)	N ₂ O + O(¹ D) → N ₂ + O ₂	1.1 × 10 ⁻¹⁰	Garvin and Hampson [1974]
(R 39)	CH ₄ + OH → CH ₃ + H ₂ O	2.35 × 10 ⁻¹² exp (-1710/T)	Hudson [1977]
(R 40)	CH ₄ + O(¹ D) → CH ₃ + OH	1.3 × 10 ⁻¹⁰	Davidson <i>et al.</i> [1977]
(R 41)	¹ CH ₂ + H ₂ → CH ₃ + H	7 × 10 ⁻¹²	Braun <i>et al.</i> [1970]
(R 42)	¹ CH ₂ + CH ₄ → CH ₃ + CH ₃	1.9 × 10 ⁻¹²	Braun <i>et al.</i> [1970]
(R 43)	¹ CH ₂ + O ₂ → CH ₂ O + O	3 × 10 ⁻¹¹	Lauffer and Bass [1974]
(R 44)	¹ CH ₂ + N ₂ → ³ CH ₂ + N ₂	5 × 10 ⁻¹³	Bell [1971]
(R 45)	³ CH ₂ + H ₂ → CH ₃ + H	5 × 10 ⁻¹⁴	Braun <i>et al.</i> [1970]
(R 46)	³ CH ₂ + CH ₄ → CH ₃ + CH ₃	5 × 10 ⁻¹⁴	Braun <i>et al.</i> [1970]
(R 47)	³ CH ₂ + O ₂ → H ₂ CO + O	1.5 × 10 ⁻¹²	Lauffer and Bass [1974]
(R 48)	CH ₃ + H + M → CH ₄ + M	(3.3 × 10 ⁻¹⁰) / (1 + 1/2.0 × 10 ⁻¹⁹ [M])	Cheng and Yeh [1977]
(R 49)	H ₃ CO + O → H ₂ CO + H	1.3 × 10 ⁻¹⁰	Hampson and Garvin [1975]
(R 50)	CH ₃ + OH → H ₂ CO + H ₂	1 × 10 ⁻¹¹	recommendation of D. J. Bogan to D. Strobel (personal communication, 1978)
(R 51)	CH ₃ + O ₂ + M → CH ₃ O ₂ + M	3 × 10 ⁻³²	Heicklen [1968]
(R 52)	CH ₃ O ₂ + H → H ₃ CO + OH	3 × 10 ⁻¹¹ exp (-500/T)	assumed
(R 53)	H ₃ CO + OH → HCO + H ₂ O	3 × 10 ⁻¹¹ exp (-250/T)	Hudson [1977]
(R 54)	HCO + O ₂ → CO + HO ₂	5 × 10 ^{-12c}	Washida <i>et al.</i> [1974], Shibuya <i>et al.</i> [1977], Clark <i>et al.</i> [1978]
(R 55)	CH ₃ O ₂ + HO ₂ → CH ₃ OOH + O ₂	3 × 10 ⁻¹¹ exp (-500/T)	assumed ^d
(R 56)	CH ₃ O ₂ + CH ₃ O ₂ → 2H ₃ CO + O ₂	2.6 × 10 ⁻¹³	Heicklen [1968]
(R 57)	CH ₃ OOH + OH → CH ₃ O ₂ + H ₂ O	1.0 × 10 ⁻¹¹ exp (-750/T)	assumed ^e
(R 58)	CH ₃ O ₂ + NO → H ₃ CO + NO ₂	3 × 10 ⁻¹² exp (-500/T)	Hampson and Garvin [1975]
(R 59)	H ₃ CO + O ₂ → H ₂ CO + HO ₂	1.6 × 10 ⁻¹³ exp (-3300/T)	Hudson [1977]
(R 60)	H ₃ CO + O → H ₂ CO + OH	1 × 10 ⁻¹⁴	assumed
(R 61)	H ₃ CO + OH → H ₂ CO + H ₂ O	1.5 × 10 ⁻¹⁰ exp (-250/T)	assumed ^f
(R 62)	CH ₃ O ₂ + OH → CO + 2H ₂ O	1.5 × 10 ⁻¹⁰ exp (-500/T)	assumed ^g

^aTreated as a two-body reaction.^bAssuming NO₃ \rightleftharpoons NO₂ + O.^cAverage of different measurements.^dAssumed equal to rate for HO₂ + HO₂ → H₂O₂ + O₂.^eAssumed equal to rate for H₂O₂ + OH → HO₂ + H₂O.^fAssumed equal to 5 times the rate for H₂CO + OH → HCO + H₂O.^gAssumed equal to 5 times the rate for CH₃O₂ + HO₂ → CH₃OOH + O₂.

TABLE 2. Diurnally Averaged Photodissociation Rates at 180 km

Reaction Number	Reaction	Rate, s ⁻¹	References
(R 1)	O ₂ + <i>hν</i> → O(³ P)	3.5 × 10 ⁻⁷	Hudson <i>et al.</i> [1969], Ditchburn and Young [1962], Metzger and Cook [1964]
(R 2)	O ₂ + <i>hν</i> → O(³ P) + O(¹ D)	6.5 × 10 ⁻⁷	Hudson <i>et al.</i> [1969] Ditchburn and Young [1962], Metzger and Cook [1964]
(R 3)	H ₂ O + <i>hν</i> → H + OH	4.3 × 10 ⁻⁶	Thompson <i>et al.</i> [1963]
(R 4)	CO ₂ + <i>hν</i> → CO + O(³ P)	1.8 × 10 ⁻⁹	Shemansky [1972]
(R 5)	CO ₂ + <i>hν</i> → CO + O(¹ D)	3.7 × 10 ⁻⁸	Shemansky [1972]
(R 6)	O ₃ + <i>hν</i> → O ₂ + O(³ P)	3.0 × 10 ⁻⁴	Ackerman [1970]
(R 7)	O ₃ + <i>hν</i> → O ₂ + O(¹ D)	5.8 × 10 ⁻³	Ackerman [1970], DeMore and Raper [1966]
(R 8)	H ₂ O ₂ + <i>hν</i> → OH + OH	5.6 × 10 ⁻⁵	Schumb <i>et al.</i> [1955]
(R 9)	NO + <i>hν</i> → N + O	4.6 × 10 ⁻⁶	Cieslik and Nicolet [1973]
(R 10)	NO ₂ + <i>hν</i> → NO + O	5 × 10 ⁻³	Hampson [1973b]
(R 11)	HNO ₃ + <i>hν</i> → NO ₂ + OH	6.5 × 10 ⁻⁵	Johnston and Graham [1973]
(R 12)	N ₂ O + <i>hν</i> → N ₂ + O	5.5 × 10 ⁻⁷	Johnston and Selwyn [1975]
(R 13)	CH ₄ + <i>hν</i> → ¹ CH ₂ + H ₂	2.0 × 10 ⁻⁶	Sun and Weissler [1955], Watanabe <i>et al.</i> [1953], Hudson [1971]
(R 14)	CH ₃ OOH + <i>hν</i> → H ₃ CO + OH	5.6 × 10 ⁻⁵	assumed ^a
(R 15)	H ₂ CO + <i>hν</i> → H ₂ + CO	8.3 × 10 ⁻⁵	Calvert <i>et al.</i> [1972]
(R 16)	H ₂ CO + <i>hν</i> → HCO + H	5.7 × 10 ⁻⁵	Calvert <i>et al.</i> [1972]
(R 17)	HCO + <i>hν</i> → CO + H	1.4 × 10 ⁻⁴	assumed ^b

^aAssumed equal to photolysis rate for H₂O₂.^bAssumed equal to photolysis rate for H₂CO.

carried out by Levine *et al.* [1979], using a model which included odd hydrogen and odd nitrogen chemistry as well as the effects of vertical transport by eddy diffusion. Among other results they found that (1) the ozone column depth peaked at 10⁻¹ PAL of O₂, with the column depth at that level exceeding that in the present atmosphere by about 40%, and (2) the amount of ozone at ground level also maximized at 10⁻¹ PAL of O₂, at a value about 10 times greater than the current ground level ozone density.

Our model challenges both of these conclusions. We predict that ozone column depth should be a monotonically increasing function of atmospheric oxygen content and that ground level ozone densities should never have been much greater than those at present. The differences between our results and those of Levine *et al.* apparently stem from several factors, including (1) improved calculation of the effects of vertical transport resulting from our inclusion of ozone as part of an odd oxygen family (Levine *et al.* treat ozone as a species by itself), (2) self-consistent calculation of stratospheric water vapor profiles at different oxygen levels, (3) constant flux lower boundary conditions on N₂O and CH₄, and (4) a more realistic troposphere, which includes lightning production of odd nitrogen, rain-out of soluble trace gases, and carbon chemistry resulting from methane oxidation. Our conclusion will be that the development of an effective ozone screen awaited oxygen levels in the neighborhood of 10⁻¹ PAL, higher than any prediction since the original one by Berkner and Marshall. The relatively late appearance of the ozone screen leaves open the possibility that the development of the ultraviolet shield was a controlling factor in the emergence of terrestrial land life.

THE MODEL

The computer model used in the calculation is adapted from the technique used by Liu *et al.* [1976] to study ozone in the modern stratosphere. Continuity and flux equations are solved self-consistently for 12 long-lived families: O_x ≡ O + O₃, (the manner of calculating catalytic destruction of ozone

by odd nitrogen species is equivalent to redefining odd oxygen as O_x ≡ O + O₃ + NO₂ [see Kasting, 1979]), HO_x ≡ H + OH + HO₂, O₂, NO_x ≡ NO + NO₂ + HNO₃, H₂, H₂O, CO₂, CO, CH₄, CH₃OOH, N₂O, and H₂O₂. Within each family the density ratios of the individual species are found by assuming photochemical equilibrium at each height step. This method of calculation is justifiable as long as only one species within each family is chemically long-lived at any given altitude. Other short-lived species which are assumed to be in photochemical equilibrium include O(¹D), N, ¹CH₂, ³CH₂, CH₃, CH₃O₂, H₃CO, H₂CO, and HCO. A complete description of the numerical technique is given by Kasting [1979].

The model extends from the ground up to 180 km with a step size of 0.5 km below 10 km, 1 km from 10 to 40 km, 2 km from 40 to 100 km, and 5 km from 100 km to the top. Reactions and rate constants are given in Table 1. Photolysis rates are calculated at each height increment, assuming a solar zenith angle of 45° and then multiplying by a factor of 0.5 to account for diurnal variation (Table 2). Some experiments were also carried out with a solar zenith angle of 57.3°. Wavelengths longward of 1300 Å, plus the Lyman α line at 1216 Å, have been considered. For wavelengths longward of 1750 Å the solar flux data are taken from Ackerman [1970], while below 1750 Å we have used data obtained from the Atmospheric Explorer satellites [Heroux and Hinteregger, 1978].

Two different temperature profiles are employed in the model. At 1 PAL of O₂ we have used spring-fall values from the current U.S. Standard Atmosphere. At lower oxygen levels the height of the ozone peak decreases, so that stratospheric heating by O₃ should have been less important [Morss and Kuhn, 1978]. Thus at 10⁻¹ PAL of O₂ and below we let the temperature vary linearly between the tropopause and the mesopause.

The eddy diffusion profile used is taken from Hunten [1975] and is appropriate to the present-day atmosphere. In the past the eddy diffusion coefficient in the stratosphere may actually have been somewhat higher because of the absence of the

temperature inversion caused by ozone heating. Several experiments were performed to investigate the effects of such a change on ozone column depth.

Present-day amounts of nitrogen were assumed in the calculation, following the suggestion of Walker [1977] that P_{N_2} should not have been greatly affected by the changing oxygen content of the atmosphere. The mixing ratio of carbon dioxide was held constant at 257 ppm, corresponding to the present value less a 20% correction for the recent effects of fossil fuel and slash burning.

The odd nitrogen in our model atmosphere derives from two sources: (1) the reaction of N_2O with $O(^1D)$ and (2) the production of NO in lightning. The magnitude of the lightning source has been adjusted so as to produce reasonable agreement between calculated and measured ozone mixing ratios in the present-day troposphere, as discussed below. At lower oxygen levels the NO production rate has been scaled downward on the basis of thermodynamic equilibrium considerations, as suggested by Yung and McElroy [1979]. Using the freeze-out temperature of 2300°K predicted by Chameides *et al.* [1977], we calculated the following scaling factors relative to today's value:

PAL of O_2	NO Scaling Factor
10^{-1}	0.316
10^{-2}	0.1
10^{-3} and below	0.04

The NO production rate varies as $P_{O_2}^{1/2}$ when the O_2 content is high, then levels out at a constant value as H_2O and CO_2 become important sources of oxygen atoms. Recent calculations by Chameides and Walker [1979] and Chameides *et al.* [1979] suggest that NO freezes out at a higher temperature (~3500°K) than that supposed here. This change should not affect the scaling at 10^{-1} or 10^{-2} PAL of O_2 but would result in approximately 40% more NO at lower oxygen levels [Kasting, 1979].

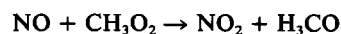
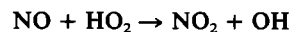
The methane oxidation scheme adopted here has been taken from the tropospheric model of Fishman and Crutzen [1977]. Reactions which are not part of their scheme, as well as CH_4 photolysis, have been included in an attempt to model methane oxidation at low oxygen levels. The values of the estimated rate constants have been chosen so as not to interfere with the reaction sequence in the present-day troposphere. Direct photolysis of methane is much less important than oxidation by OH radicals for oxygen levels of $\geq 10^{-5}$ PAL.

Rain-out of various water-soluble species, including H_2O_2 , HNO_3 , CH_3OOH , and H_2CO , was also treated in the manner described by Fishman and Crutzen [1977]. The assumed rain-out rate is $2.4 \times 10^{-6} s^{-1}$ below 6 km, decreasing exponentially to $4.6 \times 10^{-7} s^{-1}$ at 10 km. Above 10 km the rain-out rate is zero.

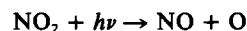
The first step in the calculation was to 'tune' the model by making it duplicate, as closely as possible, conditions in the present-day atmosphere. For the most part this was done by imposing appropriate lower boundary conditions. Following Fishman and Crutzen [1977], we specify deposition velocities for the more reactive constituents: O_x ($0.2 cm s^{-1}$), NO_x ($0.2 cm s^{-1}$), H_2O_2 ($0.1 cm s^{-1}$), and CH_3OOH ($0.1 cm s^{-1}$). HO_x is short lived in the lower atmosphere, so that its density was calculated by assuming photochemical equilibrium below 80 km. A similar procedure was employed for O_x , H_2O_2 , and CH_3OOH at lower oxygen levels, as their chemical life-

times decreased. O_x continues to flow in the lower atmosphere, however, down to 10^{-3} PAL of O_2 . Zero flux at the ground was assumed for H_2 and CO. The H_2O density was held constant at 10 km; the 3.8 ppm of H_2O at that height corresponds to the saturation vapor pressure. Below 10 km the relative humidity decreases, falling to 50% at the ground ($P_{H_2O} = 0.01 atm$). The rest of the species were assigned constant mixing ratios: O_2 (21%), CO_2 (257 ppm), CH_4 (1.4 ppm), and N_2O (0.33 ppm). The methane mixing ratio was taken from Ehhalt [1974], while our N_2O mixing ratio is slightly higher than the value of 0.25–0.29 ppm given by Schütz *et al.* [1970]. The constant mixing ratios for CH_4 and N_2O apply only for the present-day atmosphere. At lower oxygen levels we specify constant upward fluxes for these two constituents.

A parameter that remains to be determined is the rate of NO production in lightning. Theoretical considerations indicate that this rate should be of the order of 10^{10} NO molecules $cm^{-2} s^{-1}$, or 30–40 metric tons (N) yr^{-1} [Chameides *et al.*, 1977]. Since this figure is inherently uncertain, we calculated the NO production rate independently by looking at its effect on tropospheric ozone. Nitric oxide produces odd oxygen atoms via the reactions



followed by



To the extent that tropospheric ozone is controlled by photochemistry, as opposed to downward transport from the stratosphere, its density will vary in proportion to the NO concentration. Thus the NO production rate can be inferred by discovering how much NO must be present in order to produce observed tropospheric ozone densities.

The tuning was performed so as to produce roughly 55 ppb of ozone at an altitude of 5 km, corresponding to typical mid-latitude observations by Chatfield and Harrison [1977]. The NO production rate which was consistent with this ozone mixing ratio was 7.54×10^9 NO molecules $cm^{-2} s^{-1}$, which is in good agreement with the theoretically predicted value. This production rate produces a maximum NO_2 mixing ratio of 0.079 ppb, well below the upper limit of 0.1 ppb implied by the observations of Noxon [1975].

With the CH_4 and N_2O mixing ratios held constant at ground level the model itself calculates the upward fluxes required to support these observed densities. The calculated methane flux is $1.07 \times 10^{11} cm^{-2} s^{-1}$. Various independent estimates of the globally averaged methane flux based on direct measurements all give values of the order of $10^{11} cm^{-2} s^{-1}$, or 420 metric tons (CH_4) yr^{-1} [Koyama, 1963; Baker-Blocker *et al.*, 1977; Ehhalt and Schmidt, 1978]. The upward flux of N_2O is found to be equal to $1.89 \times 10^9 cm^{-2} s^{-1}$. This may be compared with the estimate by Liu *et al.* [1977] of $2\text{--}6 \times 10^9 cm^{-2} s^{-1}$ for the biological N_2O production rate. Their figure is based on a denitrification rate of 270 metric tons (N) yr^{-1} , with an N_2O to N_2 yield ranging from 1:16 to 1:4.4. Thus the calculated ground level fluxes of both CH_4 and N_2O show good agreement with current estimates for their globally averaged values.

The influence of these two trace gases on ozone in our present-day model atmosphere was determined by reducing their

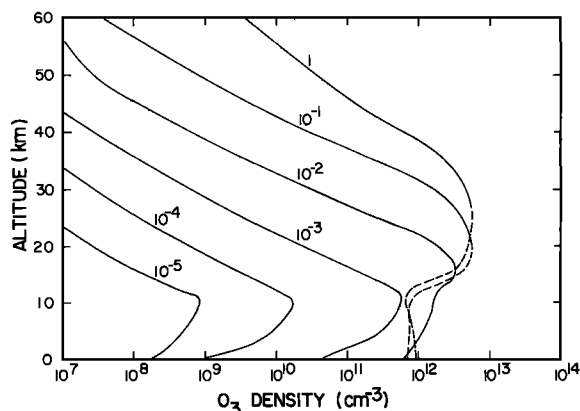


Fig. 1. Ozone profiles at various oxygen levels. The assumed solar zenith angle is 45° .

upward fluxes by a factor of 10. Reducing the N_2O flux produced a 7% increase in ozone column depth due to decreased NO_x concentrations in the stratosphere. Reducing the methane flux, on the other hand, produced an 8% decrease in ozone column depth, due almost entirely to a factor of 3 reduction in tropospheric ozone. This decrease occurs because the by-products of methane oxidation interact with odd nitrogen radicals to provide a photochemical source for ozone. In view of the strong dependence of tropospheric ozone on the methane flux we find it hard to believe the prediction of higher tropospheric ozone densities at lower oxygen levels made by Levine *et al.* [1979], whose model did not include any methane and did not take into account possible variations in tropospheric NO_x densities.

The question of how the methane and nitrous oxide production rates have varied as a function of oxygen level is, of course, not easy to answer. Although the generation of both gases is favored by anaerobic conditions, it is not clear that existing biological organisms would have been able to take advantage of that fact. Our assumption that the production rates have remained constant is no doubt increasingly invalid as the atmospheric oxygen content decreases. This error should not, however, have a serious impact on calculated ozone profiles, since the influence of both CH_4 and N_2O on ozone becomes less pronounced at the lower O_2 levels, as will be seen in the following section.

RESULTS

Ozone profiles for atmospheres containing from 10^{-5} to 1 PAL of O_2 are shown in Figure 1. Table 3 lists the important characteristics of these profiles. The column depth at 1 PAL of O_2 is equivalent to 0.417 atm cm, which is about 30% higher

TABLE 3. Characteristics of Ozone Profiles at Different Oxygen Levels

Present Atmospheric Level of O_2	Column Depth, cm^{-2}	Peak Height, km	Peak Density, cm^{-3}
1	1.12 (19)	24	5.37 (12)
10^{-1}	8.51 (18)	20	5.48 (12)
10^{-2}	4.15 (18)	16	3.22 (12)
10^{-3}	5.62 (17)	10	5.53 (11)
10^{-4}	1.50 (16)	10	1.86 (10)
10^{-5}	7.77 (14)	10	8.76 (8)

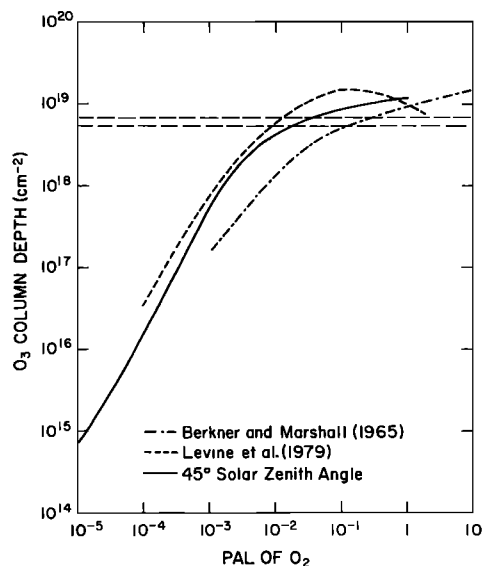


Fig. 2. Ozone column depth versus oxygen content. The horizontal dashed lines represent estimates for the amount of ozone required to produce an effective ultraviolet shield according to Berkner and Marshall (lower line) and Ratner and Walker (upper line).

than the observed mean column density of 0.32 atm cm [McClatchey *et al.*, 1971]. Part of this discrepancy may be due to the omission of the oxides of chlorine, which catalyze ozone destruction in the present-day stratosphere. However, most of the difference probably results from the choice of 45° for the solar zenith angle, which is appropriate for equatorial geometry. Experiments with larger solar zenith angles yielded smaller ozone column depths. These profiles therefore represent an upper limit on the amount of ozone present at a given oxygen level.

At O_2 levels below 1 PAL the peak ozone density decreases in magnitude and moves downward in the atmosphere as a result of the increased depth of penetration of solar ultraviolet radiation. At 10^{-3} PAL of O_2 and below, the O_3 peak is found at 10 km, corresponding to the height of the tropopause in our model. The peak is prevented from moving still lower by the presence of abundant hydrogen oxides resulting from rapid photolysis of water vapor in the troposphere. The maximum ground level ozone density, as well as ozone column depth, occurs at 1 PAL of O_2 .

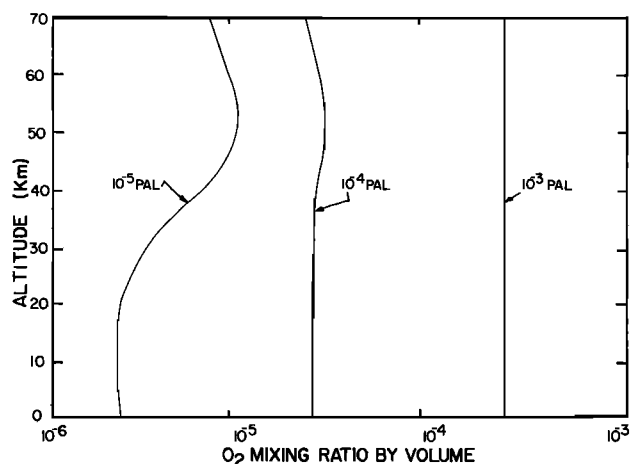


Fig. 3. O_2 mixing ratio versus altitude for different ground level oxygen concentrations.

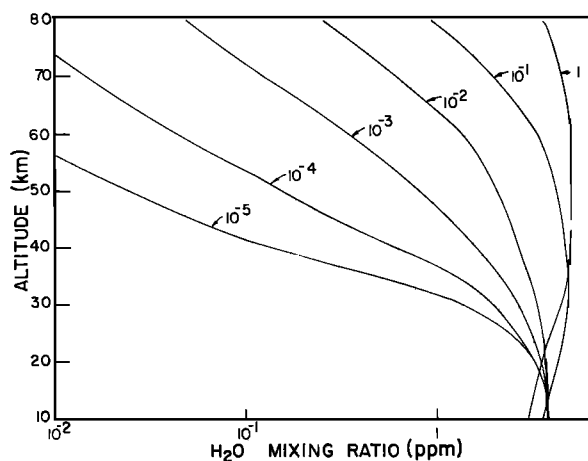


Fig. 4. Water vapor profiles for various oxygen levels. The H_2O density is fixed below 10 km.

The ozone column depth curve corresponding to these profiles is shown in Figure 2. The column depth increases monotonically with oxygen content, crossing Ratner and Walker's critical level at about 0.05 PAL of O_2 . Interpreting this result straightforwardly, one might predict that an effective ultraviolet shield was established in equatorial regions at about this oxygen level. A more general way of proceeding, however, is to look at relative ozone column depths predicted at different oxygen levels. The observed mean column depth today is roughly 25% greater than Ratner and Walker's required minimum value. The calculated column depth at 10^{-1} PAL of O_2 is about 25% less than the calculated value at 1 PAL. Together these figures imply that a globally effective ozone screen was established when the oxygen level reached approximately 10^{-1} PAL.

Consider now the behavior of some of the other atmospheric constituents at different oxygen levels. O_2 itself is well mixed only at the higher oxygen levels (Figure 3). At 10^{-5} PAL of O_2 (ground level) the O_2 mixing ratio profile exhibits a distinct peak near 50 km. The peak results from photolysis of CO_2 followed by three-body recombination of atomic oxygen and is a persistent feature even in the anoxygenic, prebiological atmosphere [Kasting *et al.*, 1979]. Thus the assumption of a uniform O_2 mixing ratio which has been made in some previous studies is not valid below 10^{-4} PAL of oxygen.

Previous studies have also assumed a constant stratospheric mixing ratio for water vapor. Figure 4 shows that this is not the case. At 1 and 10^{-1} PAL of O_2 the H_2O mixing ratio increases with height in the lower stratosphere owing to oxidation of methane. H_2O is eventually destroyed by photolysis in the upper stratosphere and mesosphere, and H_2 becomes the dominant hydrogen-bearing constituent. At lower oxygen levels both CH_4 oxidation and H_2O photolysis proceed at lower altitudes, so that the water vapor mixing ratio declines throughout the stratosphere.

Nitrous oxide profiles for the various oxygen levels are shown in Figure 5. As predicted by Levine *et al.* [1979], the impact of N_2O on ozone becomes less pronounced at lower oxygen levels owing to its increased rate of photolysis. This effect, however, is seen much more dramatically in our model because of our use of a constant flux lower boundary condition on N_2O . The lack of shielding by O_2 causes the ground level N_2O density to decrease by a factor of 3 at 10^{-1} PAL of O_2 and about 400 at 10^{-5} PAL. The constant mixing ratio

lower boundary condition employed by Levine *et al.* [1979] actually implies a biological denitrification rate on the early earth which was some 400 times greater than the present rate.

Biologically produced methane exhibits a similar kind of behavior for a different reason. The most important loss process for CH_4 at all O_2 levels under consideration is its reaction with hydroxyl radicals: $\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$. The lifetime of methane against oxidation is ~ 5 years in the modern troposphere, where typical OH densities are of the order of 10^6 cm^{-3} . The lifetime against vertical mixing is comparatively short (about 1 month), so that methane is well mixed throughout the troposphere. However, upward diffusion into the stratosphere is so slow that only 10% of the methane in our model makes it above the troposphere before being oxidized. Thus the methane mixing ratio is essentially inversely proportional to the tropospheric OH concentration. Below 10^{-2} PAL of O_2 , direct photolysis of tropospheric water vapor produces OH densities of the order of 10^8 cm^{-3} , 100 times higher than present values. The methane concentration decreases by this same factor, as is seen in Figure 6. The result is that at low O_2 levels, methane influences atmospheric composition only in the lowest few kilometers of the troposphere.

The point of the two preceding arguments is that changes in the biological production rates of methane and nitrous oxide should not invalidate the results of our model. Several other factors, however, may have had a more pronounced effect. The first of these is a possible decrease in the static stability of the stratosphere resulting from the removal of the temperature bulge due to ozone heating. To test the effects of such a change, we raised the minimum eddy diffusion coefficient in the lower stratosphere by factors of 3 and 10. At 10^{-1} PAL of O_2 , raising K_{eddy} produced a large enhancement in tropospheric ozone as a result of increased downward flow from the stratosphere. The resultant increases in ozone column depth were 8.5% and 21% for increases in K_{eddy} of 3 and 10 respectively. At 10^{-2} PAL of O_2 the increases in column depth were much less pronounced, amounting to 1.2% and 3.4% for the same two trial values of K_{eddy} . Downward transport of odd oxygen plays a smaller role at lower oxygen levels because of the shorter chemical lifetime of O_x and the fact that O_2 photolysis occurs at lower altitudes.

Another factor which may have affected these results is our use of a constant solar zenith angle in the calculations. More accurate ozone calculations in the present-day stratosphere have been carried out by using either diurnally varying time

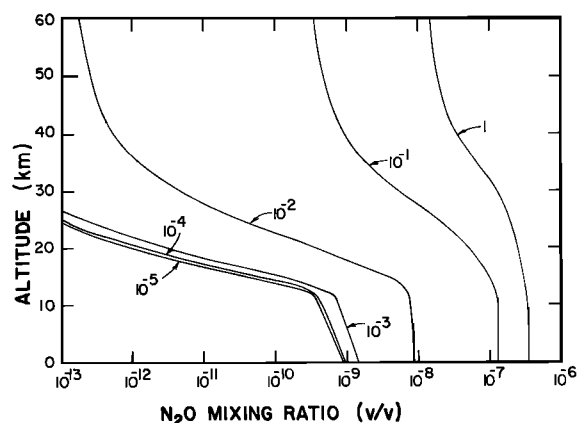


Fig. 5. N_2O profiles for various oxygen levels. A constant upward flux at ground level is assumed.

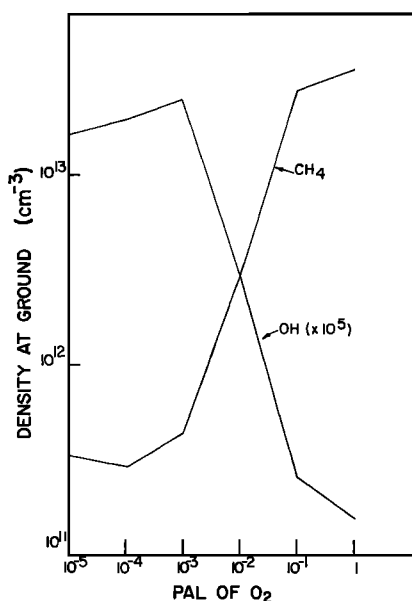


Fig. 6. Ground level CH_4 and OH densities at various oxygen levels.

dependent models or fixed zenith angle models which attempt to parameterize the diurnal variation [Rundel, 1977; Turco and Whitten, 1978]. We have not included such embellishments in this model. We have, however, carried out a sensitivity test on this factor by repeating our calculations using a solar zenith angle of 57.3° , which is the average daytime solar zenith angle used by Ratner and Walker [1972] and Levine *et al.* [1979]. The resulting ozone column depth at 1 PAL of O_2 was $8.97 \times 10^{18} \text{ cm}^{-2}$ ($\approx 0.334 \text{ atm cm}$), close to the observed mean value of 0.32 atm cm . The column depth at 10^{-1} PAL of O_2 was $7.00 \times 10^{18} \text{ cm}^{-2}$, which is just equal to Ratner and Walker's proposed critical level. Thus this test reinforces our conclusion that the ozone screen should have been established at approximately this oxygen level.

DISCUSSION

The major difference between these results and those of most previous studies is the fact that our ozone column depth curve does not maximize at 10^{-1} PAL of O_2 . The primary reason for the discrepancy would appear to be our treatment of vertical transport of ozone. Downward flow of odd oxygen from the altitude of maximum O_2 photolysis broadens the stratospheric ozone peak, increasing the column depth above that which would be predicted by a photochemical equilibrium model. The broadening is most pronounced at the highest oxygen levels when the chemical lifetime of odd oxygen is the longest. At lowered oxygen levels, increased photolysis rates of O_3 and H_2O shorten the chemical lifetime of odd oxygen, thereby inhibiting its downward flow.

The differences from the results of Levine *et al.* [1979] are not simply explained, since their model also included vertical transport of ozone. In their model, however, ozone was treated as a separate species rather than being included as part of an odd oxygen family. Since photolysis of ozone proceeds roughly 100 times faster in the middle stratosphere than do loss processes for odd oxygen as a whole, it may be that more sophisticated numerical techniques are required to calculate accurately the vertical flow of ozone by itself. We are cur-

rently investigating the influence of these two different assumptions on the calculated ozone profiles.

An additional contribution to the ozone peak at 10^{-1} PAL in the Levine *et al.* model comes from the high tropospheric ozone densities calculated at that oxygen level. Part of the reason for this finding may be their use of a zero flux lower boundary condition on ozone. The adoption of a constant deposition velocity, which we feel is a more reasonable assumption, would reduce their tropospheric ozone densities to some extent. Another possible cause for their result may be the lack of rain-out of HNO_3 and the assumption of a constant ground level NO_x mixing ratio of 3×10^{-9} at all oxygen levels. As we have demonstrated, the amount of tropospheric NO_x should decrease at lower oxygen levels, provided that the dominant low-altitude source is indeed the production of NO in lightning discharges. Even without including methane photochemistry the large amounts of NO_x in their model could interact with the HO_x produced from water vapor to provide an unrealistically large source for tropospheric ozone.

CONCLUSION

A biologically effective ozone screen was developed at a much higher oxygen level than was predicted by previous studies. The critical O_2 level of 10^{-1} PAL calculated here is the same as the lower limit on atmospheric oxygen content during the Cambrian era predicted by Rhoads and Morse [1971]. If the O_2 content of the Cambrian atmosphere was appreciably higher than this lower limit, as was suggested by Walker [1977, 1978], then the ozone screen was probably already established by that time and consequently was not primarily responsible for the emergence of land life during the Late Silurian. The uncertainty inherent in both calculations, however, leaves open the possibility that the ultraviolet shield developed after the Cambrian and was directly linked with the spread of life onto land.

Acknowledgments. The computer resources used for our calculations were provided by the National Center for Atmospheric Research in Boulder, Colorado, which is sponsored by the National Science Foundation. This research was supported in part by the Aeronomy Program, Division of Atmospheric Sciences, National Science Foundation.

REFERENCES

- Ackerman, M., Ultraviolet solar radiation related to mesospheric processes, *Inst. Aeronaut. Spatiale Belge Brussels, A-77*, 149-159, 1970.
- Baker-Blocker, A., T. M. Donahue, and K. H. Mancy, Methane flux from wetlands areas, *Tellus*, 29, 245-250, 1977.
- Baulch, D. L., D. D. Drysdale, D. G. Horne, and A. C. Lloyd, *Evaluated Kinetic Data for High Temperature Reactions, Homogeneous Gas Phase Reactions for the $\text{H}_2\text{-O}_2$ System*, vol. 1, Butterworths, London, 1972.
- Baulch, D. L., D. D. Drysdale, D. G. Horne, *Evaluated Kinetic Data for High Temperature Reactions, Homogeneous Gas Phase Reactions of the $\text{H}_2\text{-N}_2\text{-O}_2$ System*, vol. 2, Butterworths, London, 1973.
- Bell, J. A., Methylene reaction rates, quantum yields in the diazomethane-propane photolysis system: Effects of photolysis time, reactant ratios, and added gases, *J. Phys. Chem.*, 75, 1537-1549, 1971.
- Berkner, L. C., and L. L. Marshall, The history of oxygenic concentration in the earth's atmosphere, *Discuss. Faraday Soc.*, 37, 122-141, 1964.
- Berkner, L. C., and L. L. Marshall, On the origin and rise of oxygen concentration in the earth's atmosphere, *J. Atmos. Sci.*, 22, 225-261, 1965.
- Berkner, L. C., and L. L. Marshall, Limitation on oxygen concentra-

- tion in a primitive planetary atmosphere, *J. Atmos. Sci.*, **23**, 133–143, 1966.
- Berkner, L. C., and L. L. Marshall, The rise of oxygen in the earth's atmosphere with notes on the Martian atmosphere, *Advan. Geophys.*, **12**, 309–331, 1967.
- Blake, A. J., and J. H. Carver, The evolutionary role of atmospheric ozone, *J. Atmos. Sci.*, **34**, 720–728, 1977.
- Braun, W., A. M. Bass, and M. Pilling, Flash photolysis of ketene and diazomethane: The production and reaction kinetics of triplet and singlet methylene, *J. Chem. Phys.*, **52**, 5131–5143, 1970.
- Burrows, J. P., G. W. Harris, and B. A. Thrush, Rates of reaction of HO_2 with HO and O studied by laser magnetic resonance, *Nature*, **267**, 233–234, 1977.
- Calvert, J. G., J. A. Kerr, K. L. Demergian, and R. D. McQuigg, Photolysis of formaldehyde as a hydrogen atom source in the lower atmosphere, *Science*, **175**, 751–752, 1972.
- Campbell, I. M., and B. A. Thrush, The association of oxygen atoms and their combination with nitrogen atoms, *Proc. Roy. Soc. London, Ser. A*, **296**, 222–232, 1967.
- Chameides, W. L., and J. C. G. Walker, Rates of fixation by lightning of carbon and nitrogen in the primitive atmosphere, submitted to *Nature*, 1979.
- Chameides, W. L., D. H. Stedman, R. R. Dickerson, D. W. Rusch, and R. J. Cicerone, NO_x production in lightning, *J. Atmos. Sci.*, **34**, 143–149, 1977.
- Chameides, W. L., J. C. G. Walker, and A. F. Nagy, Planetary lightning: The possible chemical impact in the atmospheres of Venus and Mars, *Nature*, **280**, 820–822, 1979.
- Chatfield, R., and H. Harrison, Tropospheric ozone, 2, Variations along a meridional band, *J. Geophys. Res.*, **82**, 5969–5976, 1977.
- Cheng, J. T., and C. Yeh, Pressure dependence of the rate constant of the reaction $\text{H} + \text{CH}_3 \rightarrow \text{CH}_4$, *J. Phys. Chem.*, **81**, 1982–1984, 1977.
- Cieslik, S., and M. Nicolet, The aeronomical dissociation of nitric oxide, *Planet. Space Sci.*, **21**, 925–938, 1973.
- Clark, J. H., C. B. Moore, and J. B. Reilly, Oxomethyl (HCO) radical kinetics: Conjunction of laser photolysis and intracavity dye laser spectroscopy, *Int. J. Chem. Kinet.*, **10**, 427–431, 1978.
- Clyne, M. A. A., and S. Down, Kinetic behavior of $\text{OH}(X^2\Pi)$ and $(A^2\Sigma^+)$ using molecular resonance fluorescence spectrometry, *J. Chem. Soc. Faraday Trans. 2*, **70**, 253–266, 1974.
- Davidson, J. A., H. Schiff, G. E. Streit, J. R. McAfee, A. L. Schmeltekopf, and C. J. Howard, Temperature dependence of $\text{O}(^1D)$ rate constants for reactions with N_2O , H_2 , CH_4 , HCl , and NH_3 , *J. Chem. Phys.*, **67**, 5021–5025, 1977.
- DeMore, W. B., and O. F. Raper, Primary processes in ozone photolysis, *J. Chem. Phys.*, **44**, 1780–1783, 1966.
- Ditchburn, R. W., and P. A. Young, The absorption of molecular oxygen between 1850 and 2500 Å, *J. Atmos. Terr. Phys.*, **24**, 127–139, 1962.
- Ehhalt, D. H., The atmospheric cycle of methane, *Tellus*, **26**, 58–70, 1974.
- Ehhalt, D. H., and U. Schmidt, Sources and sinks of atmospheric methane, *Pure Appl. Geophys.*, **116**, 452–464, 1978.
- Fishman, J., and P. Crutzen, A numerical study of tropospheric photochemistry using a one-dimensional model, *J. Geophys. Res.*, **82**, 5897–5906, 1977.
- Garvin, D., and R. F. Hampson (Eds.), Chemical kinetics data survey, Tables of rate and photochemical data for modelling of the stratosphere, *Rep. NBSIR 74-430*, 101 pp., Nat. Bur. of Stand., Washington, D. C., 1974.
- Hampson, R. F. (Ed.), Survey of photochemical and rate data for twenty-eight reactions of interest in atmospheric chemistry, *J. Phys. Chem. Ref. Data*, **2**, 267–312, 1973a.
- Hampson, R. F. (Ed.), Chemical kinetics survey 6: Photochemical and rate data for twelve gas phase reactions of interest for atmospheric chemistry, *Rep. NBSIR 73-207*, 120 pp., Nat. Bur. of Stand., Washington, D. C., 1973b.
- Hampson, R. F., and D. Garvin, Chemical kinetic and photochemical data for modelling atmospheric chemistry, *Tech Note 866*, 113 pp., Nat. Bur. of Stand., Washington, D. C., 1975.
- Heicklen, J., Gas-phase reactions of alkyl peroxy and alkoxy radicals, *Advan. Chem. Ser.*, **76**, 23–39, 1968.
- Heroux, L., and H. E. Hinteregger, Aeronomical reference spectrum for solar UV below 2000 Å, *J. Geophys. Res.*, **83**, 5305–5308, 1978.
- Hesstvedt, E., S. Henrikson, and H. Hjartarson, On the development of an aerobic atmosphere, a model experiment, *Geophys. Norv.*, **31**, 1–8, 1974.
- Howard, C. J., and K. M. Evenson, Kinetics of the reaction of HO_2 with NO, *Geophys. Res. Lett.*, **4**, 437–440, 1977.
- Hudson, R. D., Critical review of ultraviolet photoabsorption cross sections for molecules of astrophysical and aeronomic interest, *Rev. Geophys. Space Phys.*, **9**, 305–406, 1971.
- Hudson, R. D. (Ed.), Chlorofluoromethanes and the stratosphere, *NASA Res. Pap.*, **RP-1010**, 1977.
- Hudson, R. D., V. L. Carter, and E. L. Breig, Predissociation in the Schumann-Runge band system of O_2 : Laboratory measurements and atmospheric effects, *J. Geophys. Res.*, **74**, 4079–4086, 1969.
- Hunten, D. M., Vertical transport in atmospheres, *Atmospheres of Earth and Planets*, edited by B. M. McCormac, pp. 59–72, D. Reidel, Hingham, Mass., 1975.
- Johnston, H. S., and R. Graham, Gas phase ultraviolet absorption spectrum of nitric acid vapor, *J. Phys. Chem.*, **77**, 62–63, 1973.
- Johnston, H. S., and G. Selwyn, New cross sections for the absorption of near ultraviolet radiation by nitrous oxide (N_2O), *Geophys. Res. Lett.*, **2**, 549, 1975.
- Kasting, J. F., Evolution and oxygen and ozone in the earth's atmosphere, Ph.D. Dissertation, Univ. of Mich., Ann Arbor, 1979.
- Kasting, J. F., S. C. Liu, and T. M. Donahue, Oxygen levels in the prebiological atmosphere, *J. Geophys. Res.*, **84**, 3097–3107, 1979.
- Katsumori, M., Photochemical-radiative equilibrium of the earth's paleo-atmospheres with various amounts of oxygen, *J. Meteorol. Soc. Jap.*, **57**, 243–253, 1979.
- Koyama, T., Gaseous metabolism in lake sediments and paddy soils and the production of atmospheric methane and hydrogen, *J. Geophys. Res.*, **68**, 3971–3973, 1963.
- Laufer, A. H., and A. M. Bass, Rate constants for reactions of methylene with carbon monoxide, oxygen, nitric oxide, and acetylene, *J. Phys. Chem.*, **78**, 1344–1348, 1974.
- Levine, J. S., P. B. Hays, and J. C. G. Walker, The evolution and variability of atmospheric ozone over geological time, *Icarus*, **39**, 295–309, 1979.
- Liu, S. C., T. M. Donahue, R. J. Cicerone, and W. L. Chameides, Effect of water vapor on the destruction of ozone in the stratosphere perturbed by Cl_x or NO_x pollutant, *J. Geophys. Res.*, **81**, 3111–3118, 1976.
- Liu, S. C., R. J. Cicerone, and T. M. Donahue, Sources and sinks of atmospheric N_2O and the possible ozone reduction due to industrial fixed nitrogen fertilizers, *Tellus*, **29**, 251–263, 1977.
- Lloyd, A. C., Evaluated and estimated kinetic data for gas phase reactions of the hydroperoxyl radical, *Int. J. Chem. Kinet.*, **6**, 169–228, 1974.
- Margulis, L., J. C. G. Walker, and M. Rambler, Reassessment of roles of oxygen and ultraviolet light in Precambrian evolution, *Nature*, **264**, 620–624, 1976.
- McClatchey, R. A., R. W. Fenn, J. E. A. Selby, F. E. Volz, and J. S. Garing, Optical properties of the atmosphere, *Tech. Rep. AFCRL-71-0279*, Air Force Cambridge Res. Lab., Bedford, Mass., 1971.
- McEwan, M. J., and L. F. Phillips, *Chemistry of the Atmosphere*, John Wiley, New York, 1975.
- Metzger, P. H., and G. R. Cook, A reinvestigation of the absorption cross section of molecular oxygen in the 1050–1800 Å region, *J. Quant. Spectrosc. Radiat. Transfer*, **4**, 107–116, 1964.
- Morss, D. A., and W. R. Kuhn, Paleoatmospheric temperature structure, *Icarus*, **33**, 40–49, 1978.
- Noxon, J. F., Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science*, **189**, 547–549, 1975.
- Perry, R. A., R. Atkinson, and J. N. Pitts, Jr., Kinetics of the reactions of OH radicals with C_2H_2 and CO, *J. Chem. Phys.*, **67**, 5577–5584, 1977.
- Ratner, M. I., and J. C. G. Walker, Atmospheric ozone and the history of life, *J. Atmos. Sci.*, **29**, 803–808, 1972.
- Rhoads, D. C., and J. W. Morse, Evolutionary and ecologic significant of oxygen-deficient marine basins, *Lethaia*, **4**, 413–428, 1971.
- Rundel, R. D., Determination of diurnal average photodissociation rates, *J. Atmos. Sci.*, **34**, 639–641, 1977.
- Schumb, W. C., C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, pp. 266–291, Reinhold, New York, 1955.
- Schütz, K., C. Junge, R. Beck, and B. Albrecht, Studies of atmospheric N_2O , *J. Geophys. Res.*, **75**, 2230–2246, 1970.

- Shemansky, D. E., CO₂ extinction coefficient 1700–3000 Å, *J. Chem. Phys.*, **56**, 1582–1587, 1972.
- Shibuya, K., T. Ebata, K. Obi, and I. Tanaka, Rate constant measurements for the reactions of HCO with NO and O₂ in the gas phase, *J. Phys. Chem.*, **81**, 2292–2294, 1977.
- Simonaitis, R., and J. Heicklen, Kinetics and mechanisms of the reaction of O(³P) with carbon monoxides, *J. Chem. Phys.*, **56**, 2004–2011, 1972.
- Smith, I. W. M., and R. Zellner, Rate measurements of reactions of OH by resonance absorption, 3, Reaction of OH with H₂, D₂, hydrogen and deuterium halides, *J. Chem. Soc. Faraday Trans. 2*, **70**, 1045–1056, 1974.
- Streit, G. E., C. J. Howard, A. L. Schmeltekopf, J. A. Davidson, and H. I. Schiff, Temperature dependence of O(¹D) rate constants for reactions with O₂, N₂, CO₂, O₃, and H₂O, *J. Chem. Phys.*, **65**, 4761–4764, 1976.
- Sun, H., and G. L. Weissler, Absorption cross sections of methane and ammonia in the vacuum ultraviolet, *J. Chem. Phys.*, **23**, 1160–1164, 1955.
- Thompson, B. A., P. Hartek, and R. R. Reeves, Jr., Ultraviolet absorption coefficients of CO₂, CO, O₂, H₂O, N₂O, NH₃, NO, SO₂, and CH₄ between 1850 and 4000 Å, *J. Geophys. Res.*, **68**, 6431–6436, 1963.
- Turco, R. P., and R. C. Whitten, A note on the diurnal averaging of aeronomical models, *J. Atmos. Terr. Phys.*, **40**, 13–20, 1978.
- Walker, J. C. G., *Evolution of the Atmosphere*, Macmillan, New York, 1977.
- Walker, J. C. G., The early history of oxygen and ozone in the atmosphere, *Pure Appl. Geophys.*, **117**, 498–512, 1978.
- Washida, N., R. I. Martinez, and K. D. Bayes, The oxidation of formyl radicals, *Z. Naturforsch. A*, **29**, 251–255, 1974.
- Watanabe, K., M. Zelikoff, and E. C. Y. Liu, Absorption coefficients of several atmospheric gases, *Tech. Rep. 53-23*, 79 pp., Air Force Cambridge Res. Lab., Bedford, Mass., 1953.
- Wilson, W. E., Jr., A critical review of the gas phase reaction kinetics of the hydroxyl radical, *J. Chem. Phys. Ref. Data*, **1**, 535–573, 1972.
- Yung, Y. L., and M. B. McElroy, Fixation of nitrogen in the prebiotic atmosphere, *Science*, **203**, 1002–1004, 1979.

(Received November 13, 1979;
revised February 6, 1980;
accepted February 11, 1980.)