



Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted

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aerosols in the range between 0.032 and 0.18, with the majority of the values lying around 0.10. These numbers also agree with recent observations of Herman *et al.* (22). We therefore adopt here a value of $\tau_{\text{VIS}} = 0.1$.

In regard to the rate of secular increase in the global background opacity of the aerosols, several recent studies suggest that the global dust content of the atmosphere has been increasing during the last few decades, perhaps by as much as a factor of 2 in the last 60 years (23, 24).

Even if we assume that the rate of scavenging and of other removal processes for atmospheric dust particles remains constant, it is still difficult to predict the rate at which global background opacity of the atmosphere will increase with increasing particulate injection by human activities. However, it is projected that man's potential to pollute will increase six- to eightfold in the next 50 years (24). If this increased rate of injection of particulate matter in the atmosphere should raise the present global background opacity by a factor of 4, our calculations suggest a decrease in global temperature by as much as 3.5°K. Such a large decrease in the average surface temperature of Earth, sustained over a period of few years, is believed to be sufficient (25) to trigger an ice age. However, by that time, nuclear power may have largely replaced fossil fuels as a means of energy production.

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increase in the surface temperature alone would result in a superadiabatic lapse rate, which is convectively unstable.

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12. Our computed surface temperature increase for an increase in the amount of CO₂ by a factor of 2 is less than one-third that of Manabe and Wetherald (11). There are three reasons for this difference: (i) The absorption coefficients for CO₂ used by Manabe and Wetherald [from G. Yamamoto and T. Sasamori, *Sci. Rep. Tohoku Univ. Ser.* **510** (No. 2), 37 (1958)] are higher than ours [from (4)]. (ii) In our calculations the temperature throughout the troposphere varies at the fixed critical lapse rate, whereas in Manabe and Wetherald's calculations the increase in temperature is confined to the lower troposphere, and the upper troposphere and stratosphere show an actual decreasing temperature. (iii) Our method of calculation for the overlap of H₂O and CO₂ absorption bands and our evaluation of the radiative flux integrals are not identical with theirs. However, since we are interested in studying the very long-term effects of increasing CO₂, up to a factor of 10 or more, the shape of the curves shown in Fig. 1, which indicates a leveling off of the temperature increase, is the major point of emphasis, rather than the absolute value of temperature change for a doubling of CO₂ in the atmosphere.
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26. We again thank Dr. J. E. Hansen for his many contributions. The work was done while S.H.S. held a NAS-NRS resident research associateship at the Institute for Space Studies, Goddard Space Flight Center, NASA.

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Normal Atmosphere: Large Radical and Formaldehyde Concentrations Predicted

Abstract. *A steady-state model of the normal (unpolluted) surface atmosphere predicts a daytime concentration of hydroxyl, hydroperoxyl, and methylperoxyl radicals approaching 5×10^8 molecules per cubic centimeter and a formaldehyde concentration of 5×10^{10} molecules per cubic centimeter or 2 parts per billion. A radical chain reaction is proposed for the rapid removal of carbon monoxide, leading to a carbon monoxide lifetime as low as 0.2 year in the surface atmosphere.*

Although numerous workers (1) have studied the photochemistry of minor constituents in the upper atmosphere, less attention has been paid to the photochemistry of the atmosphere near the ground where significant concentrations of water vapor, methane, carbon monoxide, ozone, and oxides of nitrogen are naturally present (2).

The dissociation of ozone at the ground level by sunlight in the wavelength range from 2900 to 3400 Å produces metastable atomic oxygen, O(¹D). The metastable species is rapidly quenched by collisions with air

molecules, but a small fraction, 1×10^{-2} , reacts with water to produce hydroxyl radicals at a rate exceeding 10^5 molecule $\text{cm}^{-3} \text{sec}^{-1}$. The hydroxyl radicals then react with carbon monoxide, ozone, and methane to produce hydroperoxyl radicals, which, in turn, oxidize nitric oxide to nitrogen dioxide and reform hydroxyl radicals. These chain reactions, which rapidly interconvert hydroxyl and hydroperoxyl radicals, may provide the dominant mechanism for removing atmospheric carbon monoxide and methane and for producing formaldehyde in the normal

Table 1. Calculated concentrations and ratios for hydroxyl and hydroperoxyl radicals and photodissociation rates for ozone.

Time (hour)	J_1^* (sec ⁻¹)	$\frac{[\text{HO}_2 + \text{OH}]^*}{[\text{HO}_2]}$ (cm ⁻³)	$\frac{[\text{OH}]}{[\text{HO}_2]}$
Noon	2.4 ⁻⁵	4.8 ⁺⁸	130
Noon ± 1/2	2.3 ⁻⁵	4.8 ⁺⁸	130
Noon ± 1	2.2 ⁻⁵	4.7 ⁺⁸	130
Noon ± 3/2	2.0 ⁻⁵	4.5 ⁺⁸	130
Noon ± 2	1.8 ⁻⁵	4.2 ⁺⁸	140
Noon ± 3	1.3 ⁻⁵	3.6 ⁺⁸	150
Noon ± 4	6.9 ⁻⁴	2.6 ⁺⁸	170
Noon ± 5	2.3 ⁻⁴	1.5 ⁺⁸	200

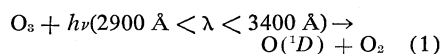
* The exponents indicate the power of ten by which each entry must be multiplied.

atmosphere. The reaction of carbon monoxide with a hydroxyl radical was considered by Bates and Witherspoon (3) to be the dominant loss mechanism for stratospheric carbon monoxide and has recently been suggested by Weinstock (4) as a loss mechanism in the troposphere.

The concentration of hydroxyl, hydroperoxyl, and methylperoxyl radicals, which approaches 5×10^8 molecule cm⁻³ in the unpolluted atmosphere, may be a basic ingredient for the production of photochemical smog (5). The predicted concentration of formaldehyde, 5×10^{10} molecule cm⁻³, is in harmony with an earlier estimate based on an analysis of rainwater (6, pp. 98-99).

For the ground-level unpolluted atmosphere, I adopted the following concentrations: air = $M = 2.5 \times 10^{19}$ molecule cm⁻³ (7); $[\text{O}_2] = 0.2 \times M$ (7); $[\text{H}_2\text{O}] = 0.02 \times M$ (8); $[\text{CH}_4] = 1.5 \times 10^{-6} \times M$ (9); $[\text{O}_3] = 5 \times 10^{-8} \times M$ (10); $[\text{CO}] = 0.12 \times 10^{-6} \times M$ (11); and $[\text{NO} + \text{NO}_2] = 3 \times 10^{-9} \times M$ (12). The concentration of O_3 at the ground fluctuates considerably with the time of day and the season of the year. I used a value appropriate to a summer latitude of 34°. The NO and NO₂ concentrations also vary with the time of day. To determine their concentrations, I assumed that ozone and the oxides of nitrogen are in equilibrium and used nitrogen dioxide photodissociation rates calculated by Leighton (13).

The driving photochemical reaction for this system is

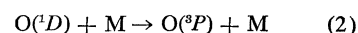


The dissociation rate, J_1 , is given in Table 1. It was calculated by use of ozone absorption cross sections (14), quantum yields for metastable atomic oxygen (15), and solar fluxes (14) corrected for absorption by ozone with a column density of 5.4×10^{18} molecule cm⁻² (16) and Rayleigh scattering (17) by the atmosphere. The rate coefficients for the various reactions are given in Table 2.

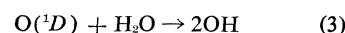
Table 2. Rate coefficients.

Reaction	Rate coefficient	Reference
<i>Two-body rates (cm³ molecule⁻¹ sec⁻¹)</i>		
2	$K_2 = 5 \times 10^{-11}$	(22)
3	$K_3 = 3 \times 10^{-11}$	(23)
4	$K_4 = 5 \times 10^{-13}$	(24)
5	$K_5 = 1.5 \times 10^{-13}$	(24)
7	$K_7 = 5 \times 10^{-13}$	(18)
8	$K_8 = 8.8 \times 10^{-15}$	(25)
10	$K_{10} = 5 \times 10^{-13}$	(26)
11	$K_{11} = 1.7 \times 10^{-17}$	(27)
12	$K_{12} = 1.5 \times 10^{-12}$	(24)
13	$K_{13} = 1 \times 10^{-11}$	(24)
14	$K_{14} = 1.5 \times 10^{-12}$	(24)
15	$K_{15} = 7 \times 10^{-12}$	(28)
<i>Three-body rates (cm⁶ molecule⁻² sec⁻¹)</i>		
6	$K_6 = 3 \times 10^{-32}$	(24)
9	$K_9 = 8 \times 10^{-32}$	(27)

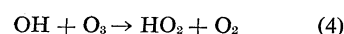
The principal reactions of metastable atomic oxygen are quenching



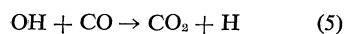
and the formation of hydroxyl radicals



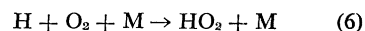
A short chain reaction is then initiated by hydroxyl radical attack of ozone



and of carbon monoxide



followed immediately by



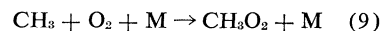
The chain reaction is completed by the oxidation of nitric oxide, which reforms the hydroxyl radical



A longer chain starts with hydroxyl radical attack of methane



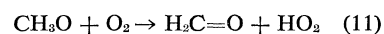
followed immediately by



The methylperoxyl radical oxidizes nitric oxide to give a methoxy radical



which reacts with molecular oxygen to form formaldehyde and a hydroperoxyl radical



The chain is then completed by reaction 7. The important loss reactions for the radicals are



and

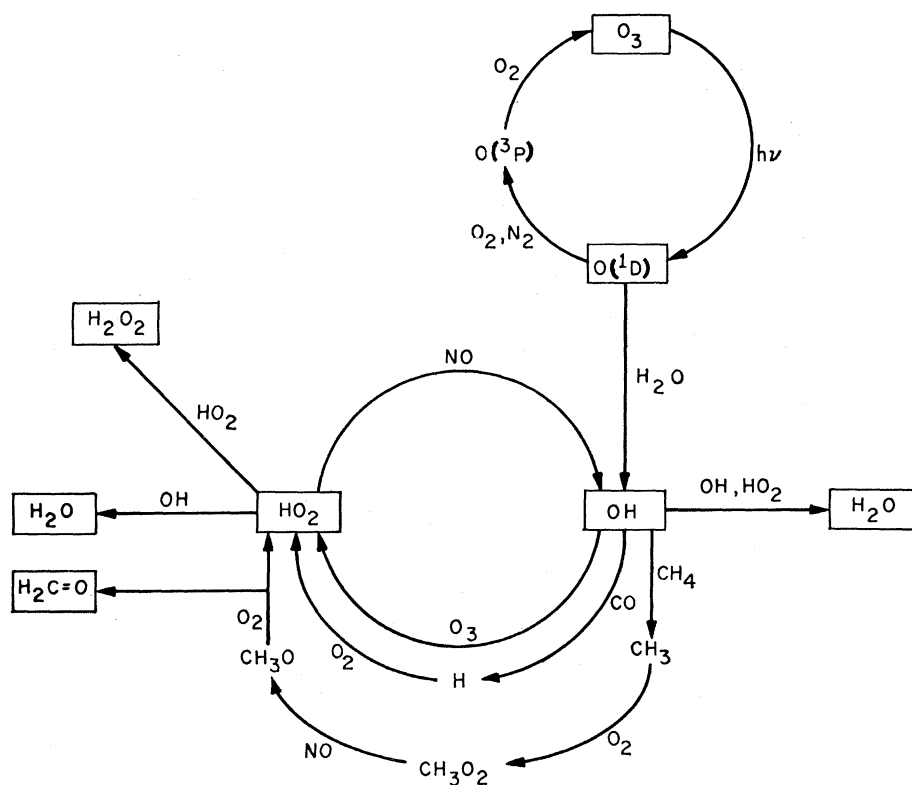


Fig. 1. Simplified photochemical reaction model for the normal atmosphere.

The photochemical reaction model is represented in Fig. 1. The radical concentration is fed by the photolysis of ozone and removed mainly by radical-radical collisions that form water or hydrogen peroxide. The cycle shown in the center of Fig. 1 serves as a sink for carbon monoxide, and the outermost cycle both removes methane from the atmosphere and produces formaldehyde. The principal loss mechanism for formaldehyde is



The steady-state concentration of hydroxyl and hydroperoxyl radicals is given by

$$[\text{HO}_2 + \text{OH}] = \left\{ \frac{(2[\text{O}^1\text{D}][\text{H}_2\text{O}]K_3)}{K_{12}} \right\}^{1/2}$$

and the ratio of hydroperoxyl to hydroxyl radical is given by

$$[\text{HO}_2]/[\text{OH}] = \frac{([\text{CO}]K_5 + [\text{O}_3]K_4 + [\text{CH}_4]K_8)/([\text{NO}]K_7)}{I}$$

where I have assumed $K_{13} = 2K_{12}$ to simplify the analysis. Values of K_{12} and K_{13} are listed in Table 1 as a function of the time of day for a summer latitude of 34° . The ratio depends inversely on the value of K_7 , which is not accurately known. For the calculations in Table 1, I chose an intermediate value from the literature estimates that range from 5×10^{-11} to 2×10^{-15} $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ (18).

The daytime concentration of the methylperoxyl radical is proportional to the concentration of the hydroxyl radical and is well approximated by

$$[\text{CH}_3\text{O}_2] = 33 [\text{OH}]$$

The concentration of the methoxy radical is quite small, owing to its fast removal by molecular oxygen (reaction 11).

On the basis of the hydroxyl radical concentrations given in Table 1, a carbon monoxide lifetime in the surface atmosphere can be calculated as follows:

$$\tau = 1/([\text{OH}]_{\text{av}} \times K_5) \cong 5.4 \times 10^6 \text{ sec} \cong 0.2 \text{ year}$$

where $[\text{OH}]_{\text{av}}$ is the average concentration of the hydroxyl radical during the day. This value of τ is in harmony with a recent experimental value (19).

With Junge's (6, pp. 113-124) model of particulate size distribution in the surface atmosphere, the collision frequency between atmospheric molecules and particulates is not more than 0.09

sec^{-1} over the continent and much less than this value over the ocean. Combining this upper limit for the collision frequency with experimental values for the fraction of surface collisions that result in the destruction of the gaseous species, which range from 3×10^{-3} (20) to 8×10^{-5} (21) for hydroxyl radicals, we find that the loss rate for hydroxyl radicals due to collisions with particulates may approach $3 \times 10^{-4} \text{ sec}^{-1}$. Loss rates for other radicals should be similar if not slower. Since this loss rate is significantly less than the gas phase radical-radical loss rate (reactions 12 through 14), atmospheric particulates are not important in this photochemical model.

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Light Production in the Luminous Fishes Photoblepharon and Anomalops from the Banda Islands

Abstract. *The unresolved mechanism of light production in Photoblepharon and Anomalops has been reinvestigated in fresh and preserved material. Based on biochemical evidence obtained with emulsions and cell-free extracts of the organs, especially the stimulation of light with reduced flavin mononucleotide, and on electron microscopy of organ sections showing the presence of numerous bacteria, we conclude that the light is produced by symbiotic luminous bacteria. Because of the continuing failure to cultivate the luminous bacteria and because of their morphology, we suggest that the bacteria are of a primitive type called bacteroids.*

Although bioluminescence is a very common characteristic of deepwater fishes, some shallow-water fishes are also luminous. Among the most famous are *Photoblepharon palpebratus* and *Anomalops katoptron*, which are indigenous to the Banda Sea at the eastern end of the Indonesian Archipelago. The flashes of light produced by these fishes at night are so spectacular that they have attracted the attention of students of bioluminescence for some 50 years. However, due to the remoteness of the

area, few studies have been carried out.

Studies by Vorderman (1), Steche (2), Harvey (3), Haneda (4), and Bassot (5) have shown that the light is emitted from a pair of large elliptical organs, each lying in a suborbital depression. Each organ is attached at the dorso-anterior edge by a small piece of cartilaginous tissue. The face of the organ, which emits light continuously, is cream-colored, whereas the opposite face is nearly black owing to a pigmented cell layer. In *Anomalops*, the light is