Tropospheric Chemistry: A Global Perspective
JENNIFER A. LOGAN, MICHAEL J. PRATHER, STEVEN C. WOFSY, AND MICHAEL B. MCELROY

A model for the photochemistry of the global troposphere constrained by observed concentrations of H2O, O3, CO, CH4, NO, NO2, and HNO3 is presented. Data for NO and NO2 are insufficient to define the global distribution of these gases but are nonetheless useful in limiting several of the more uncertain parameters of the model. Concentrations of OH, HO2, H2O2, NO, NO2, NO3, N2O5, HNO2, HO2NO2, CH3O, CH3OOH, CH3O, and CH3CCI3 are calculated as functions of altitude, latitude, and season. Results imply that the source for nitrogen oxides in the remote troposphere is geographically dispersed and surprisingly small, less than 107 tons N yr-1. Global sources for CO and CH4 are 1.5 x 109 tons C yr-1 and 4.5 x 107 tons C yr-1, respectively. Carbon monoxide is derived from combustion of fossil fuel (15%) and oxidation of atmospheric CH4 (25%), with the balance from burning of vegetation and oxidation of biogenic hydrocarbons. Production of CO in the northern hemisphere exceeds that in the southern hemisphere by about a factor of 2. Industrial and agricultural activities provide approximately half the global source of CO. Oxidation of CO and CH4 provides sources of tropospheric O3 similar in magnitude to loss by in situ photochemistry. Observations of CH3CCI3 could offer an important check of the tropospheric model and results shown here suggest that computed concentrations of OH should be reliable within a factor of 2. A more definitive test requires better definition of release rates for CH3CCI3 and improved measurements for its distribution in the atmosphere.

1. INTRODUCTION

The hydroxyl radical plays an important role in the photochemistry of the troposphere. Reaction with OH provides the dominant path for removal of a variety of atmospheric species including CO, CH4, C2H6, H2, H2O, CH2Cl, CH2CCl3, CH2Br, H2S, and SO2.

The chemistry of tropospheric OH is complex. Hydroxyl is produced by reaction of O(1D) with H2O [Levy, 1971, 1972], with O(1D) produced by photolysis of O3 near 300 nm. In addition to the direct source, OH may be regenerated by a suite of reactions involving HO2 and H2O. Rates for these reactions vary appreciably in both time and space reflecting fluctuations in concentrations of species such as NO, CO, O3, and H2O. A comprehensive test of photochemical models for OH would require simultaneous measurement of these and a number of other species and has yet to be performed. The concentration of OH has been measured in selected environments by a number of investigators by using a variety of techniques [Wang et al., 1975; Davis et al., 1976; Perner et al., 1976; Pilien et al., 1978; Campbell et al., 1979]. The measurements are difficult, however, and concentrations reported so far are subject to considerable uncertainty [Selzer and Wang, 1979; Orgies et al., 1980; Davis et al., 1981a; b; Wang et al., 1981].

Analysis of data for atmospheric CH3CCI3 (1,1,1-trichloroethane, commonly called methylchlorofluor) may provide the best current check on photochemical models. Methylchlorofluor is used extensively, and in increasing quantities, as a solvent. It is released to the atmosphere at a known rate [Neely and Plonka, 1978], and chemical industry provides the only established source. The concentration of the gas in the atmosphere has increased by more than a factor of 3 since it was first measured by Lovelock in 1972 [Lovelock, 1974]. Methylchlorofluor is removed from the atmosphere primarily by reaction with tropospheric OH. To the extent that the source is determined, measurements of atmospheric CH3CCI3 may be used to check calculations for the global distribution of OH. Preliminary studies [Singh, 1977; Lovelock, 1977] suggested that the concentration of OH was overestimated in early models [e.g., Levy, 1972; Wofsy et al., 1972; Crutzen, 1974] by a factor between 2 and 5. We shall argue here that the discrepancies suggested by such comparisons may be attributed to a combination of factors: lack of a global model for the troposphere, inadequate information on the distribution of gases such as NO and NO2, uncertainties in rates for key reactions, uncertainty in release rates for CH3CCI3, and inadequacy of the data for atmospheric CH3CCI3. A more comprehensive analysis is given below.

An acceptable model for OH must be consistent with knowledge of budgets for other gases, in particular CO. Reaction with OH is the primary removal mechanism for atmospheric CO. Thus, information on the distributions of OH and CO may be used to calculate the magnitude of the source required to maintain present concentrations of CO. Carbon monoxide is released to the atmosphere as a byproduct of combustion. It is formed also as an intermediate in the oxidation of CH4 [McConnell et al., 1971] and other hydrocarbons [Wofsy et al., 1972; Levy, 1974], notably isoprene [Zimmerman et al., 1978; Logan et al., 1978]. As we shall see, rates for production of CO by automobiles and industry may be specified to within about a factor of 2. It is more difficult to quantify rates for production of CO associated with various agricultural practices. Fire is used extensively for land clearance in tropical agriculture and for maintenance of grassland in many regions of the world [Spencer, 1966; Webster and Wilson, 1967; Watters, 1971]. Rates for production of CO associated with oxidation of CH4 and other hydrocarbons are uncertain, due in part to gaps in our understanding of atmospheric chemistry, in part to deficiency in our knowledge of strengths and distributions of relevant sources. It is important to obtain quantitative data on such sources, and studies of OH can play an important role.

Development of a comprehensive model for tropospheric OH is hampered particularly by lack of data for NO and NO2. In the absence of such information we must rely on data for HNO3 and predictions of the model for apportionment of species of odd nitrogen (NO, NO2, NO3, N2O5, HNO2, HNO3, ClONO2, and NO3). The analysis is constrained to reproduce the few measurements available for NO and NO2 in...
clean air (~0.01–0.10 ppb), and leads to an estimate of 10 days for the average lifetime of HNO₃.

Tropospheric O₃ may be produced by in situ chemistry [Chameides and Walker, 1973; Crutzen, 1973; Fishman et al., 1979] or by transfer from the stratosphere. The stratosphere provides a source of about 5 × 10¹⁰ molecules cm⁻² s⁻¹ averaged over the globe [Danielson and Mohnen, 1977; Fabian and Pruchniewicz, 1977; Mahlman et al., 1980; Gidel and Shapiro, 1980]. In situ production arises from oxidation of CO and CH₄, and depends on the concentration of NO. Ozone is also consumed in the troposphere. Its loss by gas phase chemistry is independent of NO [Fishman et al., 1979]. Our model finds that in situ sources and sinks for O₃ averaged over the globe are in approximate balance.

We begin with a discussion of tropospheric chemistry emphasizing areas of particular uncertainty. We follow with a review of observational data of special relevance to OH, notably the distributions of CO, CH₄, O₃, H₂O, HNO₃, NO, and NO₂. The atmospheric model is developed in section 4, with special attention to OH, O₃, and odd nitrogen. Implications for global budgets of CH₃CCl₃, CO, and CH₄ are discussed in section 5. Conclusions are given in section 6.

2. CHEMISTRY

We shall be concerned here mainly with processes that affect the concentration of tropospheric OH. The chemistry of OH is linked directly to the chemistry of H, HO₂, and H₂O₂, as illustrated in Figure 1.

It is convenient to consider OH, H, HO₂, and H₂O₂ as a family, odd hydrogen. Major input to this family occurs through

$$ hν + O_3 \rightarrow O(¹D) + O_2 $$

followed by

$$ O(¹D) + H_2O \rightarrow OH + OH $$

The radical OH may react either with CO,

$$ OH + CO \rightarrow H + CO_2 $$

or with CH₄,

$$ OH + CH₄ \rightarrow H_2O + CH_3 $$

with (3) dominant, particularly in the northern hemisphere. Reaction (3) offers no net sink for odd hydrogen. The product H reacts with O₂ to form HO₂,

$$ H + O_2 + M \rightarrow HO_2 + M $$

and HO₂ is removed either by

$$ HO_2 + O_3 \rightarrow OH + 2O_2 $$

$$ HO_2 + NO \rightarrow OH + NO_2 $$

or by

$$ HO_2 + HO_2 \rightarrow H_2O_2 + O_2 $$

Hydrogen peroxide can be photolyzed,

$$ hν + H_2O_2 \rightarrow OH + OH $$

It can react with OH,

$$ OH + H_2O_2 \rightarrow H_2O + HO_2 $$

or it may be removed heterogeneously,

$$ H_2O_2 \rightarrow \text{products} $$

Odd hydrogen is conserved in reactions (3) and in (5)–(9).

Two molecules of odd hydrogen are lost in each of reactions (10) and (11). Reactions (10) and (11), together with

$$ OH + NO_2 + M \rightarrow HNO_3 + M $$

and

$$ HNO_3 \rightarrow \text{products} $$

constitute the dominant sinks for tropospheric odd H.

Table 1 summarizes kinetic data for reactions important in the chemistry of the troposphere. Absorption cross sections for ozone are well determined [Griggs, 1968] but quantum yields for production of O(¹D) are uncertain. There is good agreement among several groups on the quantum yield between 300 and 325 nm, measured relative to the value at 300 nm [Lin and DeMore, 1973; Moortgat and Kudszus, 1978; Brock and Watson, 1980]. Absolute values for the quantum yield are available only for wavelengths shorter than 280 nm. Analyses of reaction products indicate a quantum yield of unity from 230 to 280 nm [Arimoto et al., 1978; Karlmow and Cvetanovic, 1979] while molecular beam studies [Sparks et al., 1980; Fairchild et al., 1978] give evidence for production of O(3P). The molecular beam data imply a quantum yield of about 0.9 for O(¹D) at 266 and 274 nm. We adopted in the present model an absolute quantum yield of unity at 300 nm consistent with data presented in Brock and Watson [1980]. A quantum yield of 0.9 at 300 nm was recommended by the NASA panel for data evaluation [NASA, 1981]. The NASA result would provide a small (5–10%) reduction in calculated concentrations of HO₂.

Excited oxygen atoms react with H₂O (reaction (2)) or they may be quenched by O₃ and N₂,

$$ O(¹D) + N_2 \rightarrow O(P) + N_2 $$

$$ O(¹D) + O_2 \rightarrow O(P) + O_2 $$

The fraction of O(¹D) atoms that react that H₂O is given by

$$ k_a[H_2O]/(k_a[H_2O] + k_{1a}[N_2] + k_{1d}[O_2]). $$

Experimental determinations of $k_a$, $k_{1a}$, and $k_{13}$ by Streit et al. [1976] and Arimoto et al. [1979] give values for this ratio that agree within about 7%. Similar agreement is reported for $k_{1d}/k_{13}$ by Streit et al. [1976] and Lee and Slanger [1979] although results of Arimoto et al. are lower by 30%. It appears on the basis of these
comparisons that the results of Heidner et al. [1973] may be in error. We adopted values given by Streit et al. [1976] for $k_2$, $k_{14}$, and $k_{15}$.

The concentration of OH depends critically on rates for reactions (3) and (4). The rate constant for reaction with CO (reaction (3)) at 1 bar of air is about a factor of 2 larger than the value in the limit of low pressure [Biermann et al., 1978]. The pressure effect was unexpected, and there may be other reactions of importance in tropospheric chemistry whose rate constants could have as yet unknown, although significant, variations with pressure and temperature. For example, the kinetics of reaction (8), the source for H$_2$O$_2$, are presently not well de-

### TABLE 1. Kinetic Data

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>Rate expression</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O($^3P$) + N$_2$ → O($^3P$) + N$_2$</td>
<td>2.0-11 exp(+ 107/T)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>O($^3P$) + O$_2$ → O($^3P$) + O$_2$</td>
<td>2.9-11 exp(+ 67/T)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>O($^3P$) + H$_2$O → OH + OH</td>
<td>2.3-10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>O($^3P$) + CH$_4$ → OH + CH$_3$</td>
<td>1.3-10</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>O($^3P$) + CH$_3$ → H$_2$ + H$_2$CO</td>
<td>1.4-11</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>O($^3P$) + N$_2$O → NO + NO</td>
<td>6.2-11</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>O($^3P$) + N$_2$O → N$_2$ + O$_2$</td>
<td>4.8-11</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>O($^3P$) + H$_2$ → OH + H</td>
<td>1.0-10</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>OH + CO → CO$_2$ + H</td>
<td>1.35-13 [1 + P (atm)]</td>
<td></td>
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<tr>
<td>9</td>
<td>OH + CH$_4$ → H$_2$ + H$_2$O</td>
<td>2.4-12 exp(-1710/T)</td>
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<td>10</td>
<td>OH + O$_3$ → HO$_2$ + O$_2$</td>
<td>1.6-12 exp(-940/T)</td>
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<tr>
<td>11</td>
<td>HO$_2$ + O$_3$ → OH + 2O$_2$</td>
<td>1.1-14 exp(-580/T)</td>
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<tr>
<td>12</td>
<td>HO$_2$ + NO → OH + NO$_2$</td>
<td>4.3-12 exp(+200/T)</td>
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<tr>
<td>13</td>
<td>HO$_2$ + NO$_2$ → HNO$_3$ + O$_2$</td>
<td>3.0-10</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>HO$_2$ + HO$_2$ → H$_2$O$_2$ + O$_2$</td>
<td>3.8-14 exp(1250/T) × (1 + 2.5-18 [H$_2$O])</td>
<td>Howard [1977]</td>
</tr>
<tr>
<td>15</td>
<td>OH + HO$_2$ → H$_2$O + O</td>
<td>4.0-11</td>
<td></td>
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<tr>
<td>16</td>
<td>O$_3$ + NO → NO$_2$ + O$_3$</td>
<td>2.3-12 exp(-1450/T)</td>
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<tr>
<td>17</td>
<td>O$_3$ + NO$_2$ → O$_2$ + NO$_3$</td>
<td>1.2-13 exp(-2450/T)</td>
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<tr>
<td>18</td>
<td>NO + NO$_2$ → NO$_2$ + NO$_2$</td>
<td>2.0-11</td>
<td></td>
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<tr>
<td>19</td>
<td>OH + H$_2$ → H$_2$O + H</td>
<td>1.2-11 exp(-2200/T)</td>
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<tr>
<td>20</td>
<td>OH + H$_2$O$_2$ → H$_2$O$_2$ + O$_2$</td>
<td>2.9-12 exp(-164/T)</td>
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<td>21</td>
<td>OH + H$_2$O → H$_2$O + HCO</td>
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<td>22</td>
<td>OH + HNO$_3$ → H$_2$O + NO$_3$</td>
<td>8.5-14</td>
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<td>23</td>
<td>OH + HNO$_2$ → H$_2$O + NO$_3$</td>
<td>6.6-12</td>
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<tr>
<td>24</td>
<td>OH + NO$_2$ + H$_2$O → H$_2$O + O$_2$ + NO$_2$</td>
<td>5.0-13 (estimated)</td>
<td>Cox et al. [1976]</td>
</tr>
<tr>
<td>25</td>
<td>OH + CH$_3$CCL → Products</td>
<td>5.4-12 exp(-1820/T)</td>
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</tr>
<tr>
<td>26</td>
<td>CH$_3$OO + NO → CH$_3$O + NO$_2$</td>
<td>7.0-12</td>
<td></td>
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<tr>
<td>27</td>
<td>CH$_3$OO + HCO → CH$_3$OH + H$_2$O</td>
<td>6.0-12</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CH$_3$OO + CH$_3$OO → 2CH$_3$O + O$_2$</td>
<td>4.6-13</td>
<td>Baulch et al. [1980]</td>
</tr>
<tr>
<td>29</td>
<td>CH$_3$OO + O$_3$ → CH$_3$O + HO$_2$</td>
<td>5.0-13 exp(-2000/T)</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>CH$_3$OOH + OH → CH$_3$OH + H$_2$O</td>
<td>2.5-12 exp(-126/T) (estimated)</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>HNO$_3$ + NO → HO$_2$ + NO$_2$ + M</td>
<td>$k_1 = 1.7 + 28$ exp(-11977/T) × $k_2$</td>
<td>Uselman [1978]</td>
</tr>
<tr>
<td>32</td>
<td>N$_2$O$_5$ + NO$_2$ + NO$_2$ + M $k_1 = 8.4 + 26$ exp(-11178/T) × $k_2$</td>
<td>Graham and Johnson [1978]</td>
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### Termolecular Processes

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<th>Number</th>
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<th>$n$</th>
<th>$k_0^{300}$</th>
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<tbody>
<tr>
<td>33</td>
<td>O + O$_2$ + M → O$_3$ + M</td>
<td>6.3-34</td>
<td>2.0</td>
<td></td>
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<tr>
<td>34</td>
<td>H + O$_2$ + M → HO$_2$ + M</td>
<td>5.5-32</td>
<td>1.4</td>
<td></td>
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<tr>
<td>35</td>
<td>OH + NO + M → HNO$_2$ + M</td>
<td>6.7-31</td>
<td>3.3</td>
<td>3.0-11</td>
</tr>
<tr>
<td>36</td>
<td>OH + NO$_2$ + M → HNO$_3$ + M</td>
<td>2.6-30</td>
<td>2.9</td>
<td>2.4-11</td>
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<tr>
<td>37</td>
<td>HO$_2$ + NO$_2$ + M → HO$_2$NO$_2$ + M</td>
<td>2.1-31</td>
<td>3.0$^a$</td>
<td>6.5-12</td>
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<tr>
<td>38</td>
<td>NO$_2$ + NO$_2$ + M → N$_2$O$_5$ + M</td>
<td>1.4-30</td>
<td>2.8</td>
<td>9.0-13</td>
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### Photolytic Processes

<table>
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<th>Number</th>
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<th>$n$</th>
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<tr>
<td>40</td>
<td>O$_3$ + hv → O$_2$ + O</td>
<td></td>
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<tr>
<td>41</td>
<td>NO$_2$ + hv → NO + O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>NO$_2$ + hv → NO + O$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>N$_2$O$_5$ + hv → N$_2$O$_3$ + NO$_2$</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>44</td>
<td>HNO$_2$ + hv → OH + NO</td>
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</tr>
<tr>
<td>45</td>
<td>HNO$_2$ + hv → OH + NO$_2$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>HNO$_3$ + hv → OH + NO$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>H$_2$O + hv → OH + OH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>H$_2$O + hv → H + HCO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>CH$_3$OOH + hv → CH$_3$O + OH</td>
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TABLE 1. (continued)

<table>
<thead>
<tr>
<th>Number</th>
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<th>Rate Expression</th>
<th>Altitude</th>
</tr>
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<tbody>
<tr>
<td>50</td>
<td>Precipitation scavenging ((\text{H}_2\text{O}_2, \text{HNO}_2, \text{HNO}_3, \text{HO}_2\text{NO}_2, \text{H}_2\text{CO}, \text{CH}_3\text{OOH}))</td>
<td>2.31x10^{-6} (\text{exp}(1.6-0.4z)) (units: s^{-1})</td>
<td>0-4 km</td>
</tr>
<tr>
<td>51</td>
<td>(\text{H}_2\text{O}_2 + \text{aerosol} \rightarrow \text{loss}^e)</td>
<td>sticking probability (\phi = 0.0)</td>
<td>4-12 km</td>
</tr>
</tbody>
</table>

- Units: s^{-1} for unimolecular processes; cm^3 s^{-1} for bimolecular processes; cm^6 s^{-1} for termolecular processes. The notation 1.0-11 is intended to be read as 1.0 \(\times\) 10^{-11}. Rate constants and cross sections are taken from NASA [1979] unless otherwise indicated.
- \(k = \frac{k_0[M]}{(1 + k_0[M/K_\text{T}])}\); \(k_0 = k_0(300/T)^{-\alpha}; k_\text{m} = k_\text{m}(300/T)^{-\gamma}\).
- Estimated.
- The rate for reaction (39) is somewhat slower than that for reaction (26), and methyl peroxyxynitrate is thought to be the product [Niki et al., 1978a; Cox and Tyndall, 1980; Sander and Watson, 1980]. Analogous adducts (HOO\text{NO}_2, PAN) undergo thermal decomposition in the lower troposphere, but may be thermally stable in the upper troposphere [Graham et al., 1977; Uselman et al., 1978; Cox and Raffey, 1977]. Kinetic data are currently unavailable for the reverse of (39), and CH\text{3}O\text{ONO}_2 was not included in the present model for CH\text{4} oxidation.

The reaction is independent of pressure from 25 to 760 torr and appears to have a large negative activation energy. The rate appears to be directly proportional to pressure at low pressures, and the temperature dependence may be much weaker than at high pressure [Cox and Burrows, 1979; Thrush and Wilkinson, 1979]. The rate may be enhanced by the presence of water vapor at high pressures [Hamilton and Lii, 1977]. It is clear that (8) proceeds by a complex mechanism, and rate measurements are needed for conditions of pressure and humidity typical of the atmosphere.

Reaction of OH with H\text{2}O\text{2} (reaction (10)) is an important sink for odd hydrogen in the troposphere. Recent studies find that the rate for this reaction is almost independent of temperature [Keyser, 1980; Sridharan et al., 1980], in contrast to earlier work, which suggested a significant activation energy (~1.5 kcal mole^{-1}, see Hampson and Garvin [1978]). The new measurements imply that \(k_{10}\) at 230 K is about 4 times larger than recommended recently by NASA [1979].

Reaction (4) initiates a complex sequence of transformations in which carbon is oxidized, ultimately to CO and CO\text{2}, as shown schematically in Figure 2. Kinetic parameters for reactions shown in Figure 2 are given in Table 1. Reaction (4) is followed by

\[
\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_2\text{O}_2 + \text{M}
\]  

(16)

with CH\text{2}O\text{2} removed by

\[
\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \quad (17)
\]
\[
\text{CH}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{O}_2 \quad (18a)
\]
\[
\rightarrow \text{CH}_2\text{O} + \text{OH} + \text{O}_2 \quad (18b)
\]

and

\[
\text{CH}_2\text{O}_2 + \text{CH}_2\text{O}_2 \rightarrow \text{products} \quad (19)
\]

The rate constant for (17) is similar to that for the analogous reaction (7) (see Table 1). Work by Cox and Tyndall [1980] suggests that \(k_{18}\) may be comparable to \(k_{17}\) and that the reaction could have a negative activation energy similar to that exhibited by (8). The rate for (18) is independent of water vapor concentration, although the CH\text{3}O\text{2} radical appears to form a complex with H\text{2}O [Kan and Calvert, 1979]. The rate constant for (19) is considerably smaller than values reported for (17) and (18) [Parkes, 1977]. It would appear that reactions (17) and (18) should represent major paths for removal of CH\text{3}O\text{2} in the troposphere (see Figure 16).

The yield of CO from oxidation of methane could be less than unity if significant quantities of stable intermediates (e.g., CH\text{3}OH or CH\text{2}O were removed heterogeneously. Hydroperoxides undergo acid-catalyzed and sometimes base-catalyzed decomposition [Hiatt, 1971]. Consequently, CH\text{3}O\text{OH} might be destroyed by reactions on aerosols or in droplets. Likely decomposition products include formaldyde and perhaps methanol [Niki et al., 1978a]. These products could be removed by rain, but they could be vaporized also from the aerosol surface and oxidized in the atmosphere to CO (see also Appendix 1).

Photolysis of CH\text{2}O is more rapid than that of CH\text{3}OOH [Bass et al., 1980; Molina and Arguello, 1979]. Heterogeneous reactions are consequently less important for CH\text{2}O\text{2} than for CH\text{3}OOH. The low concentrations of CH\text{2}O measured in aerosols and rainwater [Klippel and Warneck, 1978, 1980; Zaffirou et al., 1980; Thompson, 1980] at remote locations are consistent with the view that loss of formaldehyde by heterogeneous processes is negligible relative to loss by photochemical reactions.
TABLE 2. Major Pathways for CH₄ Oxidation

<table>
<thead>
<tr>
<th>Path</th>
<th>Reaction</th>
<th>Effect on Odd-O&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Effect on OH</th>
<th>Effect on HO₂&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Effect on Odd-H</th>
</tr>
</thead>
</table>
| Ia   | CH₄ + OH → CH₃ + H₂O  
CH₃ + O₂ + M → CH₃O₂ + M  
CH₃O₂ + NO → CH₃O + NO₂  
CH₃O + O₂ → HO₂ + CH₂O  
net: CH₄ + OH + NO + O₂ → CH₂O + NO₂ + HO₂ + H₂O | +1 | -1 | +1 | 0 |
| Ib   | CH₄ + OH → CH₃ + H₂O  
CH₃ + O₂ + M → CH₃O₂ + M  
CH₃O₂ + HO₂ → CH₃OOH + O₂  
CH₃OOH + OH → CH₃OO + H₂O  
CH₃OOH + M → CH₃O + OH + M  
net: CH₄ + OH + HO₂ → CH₃O + 2H₂O | 0 | -1 | -1 | -2 |
| Ib'  | CH₃O₂ + HO₂ → CH₃OOH + O₂  
CH₃OOH + OH → CH₃OO + H₂O  
net: OH + HO₂ → H₂O + O₂ | 0 | -1 | -1 | -2 |
| Ic   | CH₄ + OH → CH₃ + H₂O  
CH₃ + O₂ + M → CH₃O₂ + M  
CH₃O₂ + HO₂ → CH₃OOH + O₂  
CH₃OOH + hr → CH₃O + OH  
CH₃O + O₂ → CH₃O₂ + HO₂  
net: CH₄ + O₂ + hr → CH₃O + H₂O | 0 | 0 | 0 | 0 |
| Id   | CH₄ + OH → CH₃ + H₂O  
CH₃ + O₂ + M → CH₃O₂ + M  
CH₃O₂ + HO₂ → CH₃OOH + O₂  
CH₃OOH → heterogeneous loss  
net: CH₄ + OH + HO₂ → H₂O + products | 0 | -1 | -1 | -2 |
| IIa  | CH₂O + hr → H + CHO  
H + O₂ + M → HO₂ + M  
CHO + O₂ → HO₂ + CO  
net: CH₂O + 2O₂ + hr → 2HO₂ + CO | 0 | 0 | 0 | 0 |
| IIb  | CH₂O + hr → H + CHO  
H + O₂ + M → HO₂ + M  
CHO + O₂ → HO₂ + CO  
net: CH₂O + OH + O₂ → HO₂ + H₂O + CO | 0 | -1 | +1 | 0 |
| IIc  | CH₂O + OH → H₂O + CHO  
CHO + O₂ → HO₂ + CO  
net: CH₂O + OH + O₂ → HO₂ + H₂O + CO | 0 | -1 | +1 | 0 |
| III  | CO + OH → CO₂ + H  
H + O₂ + M → HO₂ + M  
net: CO + O₂ + OH → CO₂ + HO₂ | 0 | -1 | +1 | 0 |

Average branching ratios IIa : IIb : IIc = 1.5 : 1 : 1.5.

<sup>a</sup> Production of odd oxygen may result also from reaction of HO₂ with NO.

Rainout of CH₃OOH and CH₂O was parameterized in the present model according to the loss profile given in Table 1. Mean rates for heterogeneous removal were chosen to be consistent with observations of species such as ²¹⁰Po and ²²⁸Rn formed from decay of ²²²Rn [Junge, 1963; Moore et al., 1973]. The yield of CO from methane oxidation calculated in this manner is 78%. The yield is lowered to 50% if we assume efficient loss of CH₃OOH on aerosols (see Appendix 1). The maximum rate for heterogeneous loss of CH₃OOH is controlled by (17) and (18). At most, 56% of the global methane flux could be removed heterogeneously with concentrations of NO adopted below.

Table 2 summarizes net reactions for the methane oxidation scheme and specifies the effect of each pathway on odd hydrogen. Oxidation of CH₄ could provide either a source or a sink for odd H, depending on relative rates for (17) and (18). It is likely to represent a source for odd H if NO were abundant. It could introduce a sink of comparable magnitude if NO were low. The source of odd H is dominated however by (2) over most of the troposphere with methane reactions accounting for approximately 20% of the net sink. Photolysis of CH₂O is the major source of odd H in the upper troposphere (~10 km).

The chemistry of odd H may be simplified if we neglect the influence of methane oxidation and assume that the concentration of NO is less than 200 ppt. Loss of odd hydrogen under these conditions proceeds mainly by reaction of OH with H₂O₂ and by heterogeneous removal of HO₂. The concentration of HO₂ is given by

\[
[\text{HO}_2] = \left( \frac{J_0 + k_o[\text{OH}] + k_{11}}{k_d(k_{10}[\text{OH}] + k_{11})} \right)^{1/2}
\]

where [X] denotes the number density of X and k, J, represent...
It is useful in this context to define a family of species undergoing rapid reactions leading to formation or removal of O₃. We identify this family, odd oxygen, with O('D), O(3P), NO₂, and O₃. Ozone is formed by

$$O(3P) + O_2 + M \rightarrow O_3 + M \quad (22)$$

and is removed mainly by photolysis

$$h \nu + O_3 \rightarrow O('D) + O_2 \quad (1a)$$

$$h \nu + O_3 \rightarrow O(3P) + O_2 \quad (1b)$$

The metastable O('D) is quenched by O₂ and N₂ (reactions (14) and (15)) though, as seen earlier, it can react with H₂O (reaction (2)). Nitric oxide reacts with O₃ to form NO₂:

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (23)$$

Nitrogen dioxide is removed mainly by photolysis

$$h \nu + NO_2 \rightarrow O(3P) + NO \quad (24)$$

Ozone lost in (23) is reconstituted by (24) and (22), and the cyclic nature of the chemistry is illustrated in Figure 4. Individual members of the odd oxygen family, O('D), O(3P), and NO₂ are transformed to O₃ in the troposphere on time scales of 2 × 10⁻³ s, 2 × 10⁻⁵ s, and 2 × 10⁻⁷ s, respectively.

Odd oxygen is conserved in reactions (1), (14), (15), and (22)–(24). It is formed in the troposphere by reactions of NO with H₂O and CH₃O₂ (reactions (7) and (17)). It is removed by reaction of O('D) with H₂O, by reaction of O₃ with H₂O and NO with OH, by formation of nitrates from NO₂ and by heterogeneous reactions of O₃ and NO₂ at the earth’s surface.

The chemistry shown in Figures 1, 2, and 4 leads to net consumption of odd oxygen at low concentrations of NO. Reaction (2) is the dominant sink for tropospheric odd O in the tropics while rates for removal of odd O by (2) and (6) are comparable at mid-latitudes. The time for removal of the total column of tropospheric O₃ by (2) and (6) ranges from 21 days in the tropics to about 75 days at a latitude of 45°. Loss of odd oxygen by (2) and (6) is balanced by production in (7) and (17) for concentrations of NO near 30 ppt [cf. Fishman et al., 1979]. Homogeneous reactions provide a net source for tropospheric O₃ if NO exceeds 30 ppt.

Production of O₃ in the troposphere is limited on a global scale by supply of CO, CH₄, and other hydrocarbons. One molecule of O₃ may be formed for each molecule of CO consumed by (3). The yield of O₃ from oxidation of CH₄ could be as large as 3.5 per molecule of CH₄ as may be seen from Table 2 and Figure 2. The yield from oxidation of other hydrocarbons depends on details of the oxidation path and could be much higher than that for CH₄. According to present knowledge, CH₄ is formed by anaerobic metabolism and released to the atmosphere at an average rate of about 1.5 × 10¹¹ molecules cm⁻² s⁻¹ [Wofsy et al., 1972; Ehshalt and Schmidt, 1978]. As we shall see, production of CO by sources other than oxidation of CH₄ provide about 2.5 × 10¹¹ molecules CO cm⁻² s⁻¹. The potential yield of O₃ from oxidation of CO and CH₄ could be as large as 8 × 10¹¹ molecules cm⁻² s⁻¹ if an adequate supply of NO were available. This source would suffice to double the concentration of tropospheric O₃ in about 2 weeks.

3. Observations

As is discussed above, the distribution of tropospheric OH depends on H₂O, O₃, CH₄, CO, NO, and NO₂. All of these species, with the exception of CH₄, show significant variation with latitude, altitude, and time. Variations of H₂O are deter-
Fig. 4. Major chemical reactions affecting odd oxygen (O₃, O(³P), O(¹D), NO₂) in the troposphere. Air molecules acting as third bodies are denoted by 'M' (N₂, O₂, Ar, H₂O).

mined mainly by physical processes. Ozone is affected by both chemistry and transport. Carbon monoxide, NO and NO₂ are influenced by physical and chemical processes in the atmosphere and by biogenic and anthropogenic sources at the ground. We begin with a review of observational data for H₂O.

The concentration of OH is proportional to the concentration of H₂O raised to a power, which varies between 0.5 and 1.0. The concentration of H₂O is quite variable, with largest fluctuations above 3 km, where concentrations may change over short distances and times by factors as large as 10⁵ [Mastenbrook, 1966, 1968, also private communication, 1980]. Figure 5 shows a number of profiles measured over Washington, D.C., and over Trinidad. It includes results from a statistical analysis of summer and winter data acquired over a period of about 10 years. Note that values for the mean concentration of OH could lead to errors as large as 15% in values calculated for the mean concentration of OH.

Most of the early measurements, between 1963 and 1966, were made with Regener chemiluminescent sondes, and it appears that concentrations obtained for the troposphere in this manner may be too small by about 30%. Sources of experimental error are discussed by Chatfield and Harrison [1977b] and by Wilcox [1978], who conclude that the Brewer-Mast electrochemical sonde favored in the later measurements should be more reliable than the chemiluminescent method used before 1966. The more recent observations are limited to six stations, in contrast to the 13 stations included earlier. Only one mid-latitude station, Bedford, Massachusetts (42.5°N), was operated during both observational periods. Six years of data for tropospheric ozone, obtained with the more reliable electrochemical technique, are available for two mid-latitude stations in Europe [Dütsch and Ling, 1973; Attmanspacher and Hartmannsrugger, 1976].

Ozone profiles selected for the northern hemisphere were derived from measurements made with the electrochemical technique and are given in Figure 7. The mid-latitude profiles were obtained by averaging measurements from four stations: Wallops Island, Virginia (37.5°N); Bedford, Massachusetts (42.5°N) [Chatfield and Harrison, 1977a]; Fayerne, Switzerland (47°N) [Dütsch and Ling, 1973]; and Hohenpeissenberg, Federal Republic of Germany (48°N) [Attmanspacher and Hartmannsrugger, 1976]. Measurements from Panama (9°N) [Chatfield and Harrison, 1977a] are assumed typical for conditions in the tropics.

Measurements are sparse for ozone in the southern hemisphere. A long record is available for one mid-latitude station, Aspendale, Australia (38°S). Profiles for O₃ were measured at this site with the electrochemical technique at weekly intervals for 8 years [Pittock, 1977]. The data show little seasonal variation below 3 km, in contrast to data from mid-latitudes in the northern hemisphere. Ozone is about 40% lower in summer at 2 km at Aspendale than at Wallops Island (37.5°N), as shown in Figure 8 (A. B. Pittock, private communication, 1980). Comparison of Figures 7 and 8 indicated that mid-latitude ozone is similar for the two hemispheres in autumn and winter.
Very few profiles have been reported for O$_3$ in the southern tropics. Fishman et al. [1979] analyzed 31 profiles from Canton Island (2°S) and 10 from La Paz (16°S). These were obtained by using the less reliable chemiluminescent technique. A comparison of measurements made with the chemiluminescent method indicates that ozone is about 35% lower at 2 km at southern tropical stations than at Panama (see Figure 8). Interhemispheric asymmetry is indicated also by data acquired over the Pacific Ocean [Routhier et al., 1980]. Figure 8 illustrates differences between results obtained by the two measurement techniques at Panama. It is obvious that north/south comparisons must be based on data acquired with a single observational method.

The ozone data are sparse, and it is difficult to separate true hemispheric differences from variations with longitude, or with oceanic, coastal or inland environments. It should be noted in particular that the sea-level stations between 35°-45°N are all located in North America, while the single mid-latitude station for the southern hemisphere is on the south coast of Australia, a less polluted environment than that of the northern stations. Urban pollution may lead to elevated concentrations of ozone in the lower troposphere of the eastern United States and Europe, particularly in the summer.

The data base allows us little choice but to assume that measurements at Aspendale are representative of ozone at southern mid-latitudes. The mean profile for ozone in the southern tropics is based on the chemiluminescent technique and must be corrected to account as far as possible for errors resulting from use of this method. The corrected profile, shown in Figure 8, was obtained by scaling the Canton Island and La Paz results by the ratio of concentrations measured, using the electrochemical technique at Panama to results derived with the chemiluminescent method at the same location (approximately 0.8). This ratio is available only above 2 km, and ozone at ground level in the southern tropics was taken equal to the mean value for Samoa, 14°S [Oltmans, 1981]. Resulting profiles are consistent with measurements by Routhier et al. [1980].

The concentration of O$_3$ is variable near the surface and may be very low at times, at least over the tropical ocean. Figure 7 shows mixing ratios for O$_3$ in the range 12–18 ppb near the surface at Panama, similar to concentrations observed at Samoa (14°S) [Oltmans, 1981]. Mixing ratios as low as 1–5 ppb have been reported for the tropical South Pacific [Routhier et al., 1980], though values as high as 30 ppb were observed by Rasmussen et al. [1976]. The data for tropospheric O$_3$ are obviously sparse, and information is particularly lacking for the marine environment. We believe that uncertainties
in the distribution of O₃ are comparable to those for H₂O and are likely to have similar impact on calculations for the distribution of OH.

The rate for production of odd hydrogen is sensitive to the overhead column of ozone. The seasonal and latitudinal distribution of the total ozone column was taken from Dütsch [1974], whose results agree with Gebhart et al. [1970] within 10%. Both studies used data from the global Dobson network. Comparison of ground-based measurements of total ozone with satellite observations shows similar agreement except at high latitudes (>50°) [Prior and Oza, 1978]. Angell and Korshover [1978] concluded that global ozone may vary temporally by as much as 10%. Their analysis suggests that errors in the absolute calibration of the Dobson network are of similar magnitude. A 10% error in the ozone column would be reflected by a 10% error in the global mean concentration of OH.

A summary of observations for tropospheric CO is given in Figure 9 and in Table 3. These data were selected from observations in the clean troposphere. Most of the measurements were taken over the ocean, either from ships or aircraft. The data shown in Figure 9 for northern mid-latitudes were derived exclusively from measurements over the North Atlantic and may be affected by transport from strong sources on the North American continent. The influence of sources is apparent in vertical soundings over Europe that show considerable variability, as evident in Figure 10. It appears that the northern hemisphere contains approximately 1.5-2 times as much CO as the southern hemisphere. The concentration of CO in surface air is significantly higher than at altitude, at least for the northern hemisphere.

Measurements at Mauna Loa Observatory in Hawaii (19.5°N) [Seiler et al., 1976] and at Cape Meares, Oregon (R. A. Rasmussen et al., private communication, 1980) indicate that CO may vary seasonally by about a factor of 2, with concentrations highest in winter, lowest in summer. The behavior at these sites might reflect relatively localized meteorological conditions. At Mauna Loa, for example, prevailing winds are...
from the northeast and are comparatively steady in summer. Conditions are more variable in winter with frequent storms, which would enhance exchange of air with higher latitudes, thus raising ambient concentrations of CO. On the other hand, variations in CO could reflect a seasonal dependence either of the source or of the loss, (reaction (2)). Stevens et al. [1972] reported an annual cycle for CO in rural Illinois (43°N). Concentrations of CO were generally lowest in summer, although there were large fluctuations associated with local sources of pollution. The seasonal variation of 14CO has been measured in Europe, and there, also a minimum was observed in summer [Volz et al., 1981]. Further data will be required to identify and quantify seasonal or other temporal variability in CO. It appears that the global budgets for CH4 and CH2CCl3 are insensitive to possible seasonal variations in CO (see Table 7).

The distribution shown in Figure 11 for CO was constructed on the basis of information in Figures 9 and 10. There is appreciable uncertainty, perhaps 20–30%, in the distribution of CO. The uncertainty may be attributed in part to the inhomogeneity of northern hemispheric CO, in part to inadequate definition of temporal variability, and in part to possible errors in the determination of absolute concentrations. We estimate that uncertainties in the distribution of CO could lead to uncertainty of about 15% in calculated values for OH. Inference regarding the magnitude of the net sink for CO is relatively insensitive to uncertainties in concentrations assumed for CO. Calculated concentrations of OH and CO tend to be inversely related since reaction with CO represents the major sink for tropospheric OH.

The latitudinal distribution of CH4 was derived from measurements of Seiler et al. [1978], Fabian et al. [1979], Ehhalt...
ratios for CH$_4$ were taken as 1.7 and 1.6 ppmv for the northern and southern hemispheres, respectively. The mixing ratio files are an average of data obtained at four mid-latitude stations as described in the text.

The largest uncertainty in our model of tropospheric chemistry may be attributed to lack of data for NO and NO$_2$. Information on the distribution of NO is available for the clean troposphere at only a few locations and times. The sparseness of the data reflects the difficulty in measuring concentrations of NO lower than about 0.5 ppbv, and it is clear that ambient concentrations of NO are often much smaller than this. Measurements for surface continental air are available for Colorado and Wyoming. Mixing ratios are sometimes lower than 20 ppbv, though often higher than 1 ppbv [Drummond, 1977; Bush et al., 1979; Kelly et al., 1980]. High values are associated with advected urban pollutants. The concentration of NO in air over cities is often as large as 10 ppbv [Spicer, 1977]. The data from Colorado and Wyoming suggest that concentrations of NO near the ground at clean continental sites should lie in the range 20-100 ppbv.

We expect sources of NO in the marine environment to be much smaller than those over land. The anthropogenic influence is minimal, and rates for emission of fixed nitrogen are small [Zasoff and True, 1979; Tsubogai, 1971; Georgii and Gravenhors, 1977]. McFarland et al. [1979] found concentrations of NO of about 4 ppbv in air above the midtropical Pacific. Schiff et al. [1979] reported mixing ratios for NO of 30-40 pptv both in and above the boundary layer over the Pacific Ocean, with slightly higher values (40-60 pptv) in clean air over North America. They emphasized, however, that their values represent upper limits. (An NO signal, presumably spurious, corresponding to about one half the daytime value was observed after sunset.) Kley et al. [1980] reported concentrations of (NO + NO$_2$) in the range 40-200 pptv at 7 km above Wyoming in December. Roy et al. [1980] observed 100-150 pptv NO in summer at 8 km over Australia (34°S) with 130-230 pptv at 10 km.

Optical measurements by Noxon [1978] near sunrise and sunset show that the integrated column of tropospheric NO$_2$ is typically less than 5 x 10$^{14}$ molecules cm$^{-2}$. If NO$_2$ were distributed uniformly throughout the troposphere, this result would correspond to concentrations of NO$_2$ less than about 25 pptv and would imply daytime average mixing ratios of NO smaller than 10 pptv. Somewhat higher values of NO could be accommodated by Noxon’s observations if NO and NO$_2$ were located primarily in the upper troposphere. The colder temperatures at these levels would allow a larger ratio NO/NO$_2$.

Measurements of HNO$_3$ provide a useful guide to distributions of NO and NO$_2$. Huebert and Lazrus [1978, 1980] found concentrations of HNO$_3$ nearly uniform with latitude in the middle troposphere with a median value of about 100 pptv and a range of <30-280 pptv. About 30% of observations over the ocean fell below their detection limit (<30 pptv). Concentrations of HNO$_3$ were somewhat lower in the marine boundary layer, about 60 pptv at ~1 km [Huebert and Lazrus, 1980], 15-70 pptv near the ocean surface [Huebert, 1980]. The surface measurements were made aboard ship at the same time that McFarland et al. [1979] observed NO concentrations of 4 ppt. Kelly et al. [1980] observed low concentrations of HNO$_3$ (<100 pptv) in unpolluted surface air in Colorado. The observations of HNO$_3$ are consistent with the view that the gas is removed rapidly from the boundary layer [Huebert and Lazrus, 1980; Kelly et al., 1980].

(It is possible that pernitric acid (HO$_2$NO$_2$) may contribute to the acidic nitrate observed by Huebert and Lazrus [1978, 1980]. The chemistry of HO$_2$NO$_2$ is not accurately known for atmospheric conditions. If we adopt the kinetic parameters recommended in NASA [1979, 1981] and the results of Molina and Molina [1980] for the absorption cross sections of HO$_2$NO$_2$, we would calculate that 30-50% of the observed acidic nitrate could be in the form of HO$_2$NO$_2$ in the upper atmosphere.)

![Fig. 7. Altitude profiles for ozone in the northern hemisphere.](image-url)
troposphere (see Figure 14). It is possible also that HO2NO may affect the response of the chemiluminescent instrument used to observe NO.

Conversion of NO and NO2 to HNO3 proceeds through (7), (17), and (23) followed by (12), with a time constant of about a day. In contrast, 2-4 weeks are required to convert HNO3 back to (NO + NO2). Nitric acid is a soluble gas, and it may be removed by heterogeneous processes such as rainout, washout, or loss to aerosols within a few days [Junge, 1963; Levine and Schwartz, 1981]. The concentration of HNO3 would be determined in this case by balance between (12) and (13). If heterogeneous processes are unimportant, NO, NO2, and HNO3 would tend to a photostationary state, and the data for HNO3 would imply concentrations of NO in summer.

**TABLE 3. Observational Data for Carbon Monoxide**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Date</th>
<th>Latitude</th>
<th>Location</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seiler and Schmidt [1974]</td>
<td>April-May 1969</td>
<td>60°N-10°S</td>
<td>Atlantic</td>
<td>open triangle</td>
</tr>
<tr>
<td>Heidi et al. [1980]</td>
<td>May 1978</td>
<td>30°N-60°S</td>
<td>Pacific</td>
<td>left-leaning hatching</td>
</tr>
<tr>
<td>Junge et al. [1971]</td>
<td>Jan.-April 1968</td>
<td>80°N-40°N</td>
<td>Pacific</td>
<td>cross</td>
</tr>
<tr>
<td>Junge et al. [1971]</td>
<td>Nov. 1968</td>
<td>85°N-26°S</td>
<td>Atlantic</td>
<td>open circle</td>
</tr>
<tr>
<td>Seiler and Schmidt [1974]</td>
<td>Nov. 1971</td>
<td>50°N-20°S</td>
<td>Atlantic</td>
<td>solid line</td>
</tr>
<tr>
<td>Heidi et al. [1980]</td>
<td>May 1978</td>
<td>30°N-60°S</td>
<td>Pacific</td>
<td>left-leaning cross hatching</td>
</tr>
</tbody>
</table>
Fig. 10. Tropospheric profiles for CO. The individual symbols indicate data from separate flights over Europe and are from Seiler et al. [1978] and Fabian et al. [1979]. Also shown are results from one flight over the eastern United States at 45°N in January (open triangle, Reichle and Condon [1979]). The solid line indicates the profile used in the model at northern mid-latitudes.

much smaller than was measured by Schiff et al. [1979] and Roy et al. [1980]. A role for heterogeneous loss is indicated further by observations of a relatively large fraction of nitrate in particulate form in the remote troposphere [Huebert and Lazrus, 1978, 1980].

We adopted an empirical model designed to fit the available observations for NO, NO₂, and HNO₃. Calculated values for OH were used to estimate the rate for (12) and heterogeneous loss was parameterized as shown in Table 1. One-dimensional diffusion calculations, constrained to give observed concentrations of HNO₃, were carried out for various latitudes and seasons (see Appendix 2). The model assumed that loss of HNO₃ was balanced in part by input from the stratosphere (~5%) and in part by production of NO and NO₂ in the troposphere (~95%). The loss frequency for HNO₃ was taken independent of latitude and season. The sources of (NO + NO₂) must be similarly uniform. With these assumptions, concentrations of (NO + NO₂) vary inversely with OH (see Figure 12). Model profiles for HNO₃, NO, and NO₂ are shown in Figure 12.

The model indicates 5–20 ppt NO in the lower troposphere at noon and implies a column abundance for NO₂ near twilight of about 3–7 × 10¹⁴ cm⁻². Concentrations calculated for NO and NO₂ are directly proportional to the rate adopted for

Fig. 12a. Calculated altitude profiles for nitric acid. Results are shown for the following conditions. (1) The stratospheric input of odd N is 1.4 × 10¹⁰ molecules cm⁻² s⁻¹. (2) The column production rate of (NO + NO₂) is 3 × 10⁹ molecules cm⁻² s⁻¹ and is distributed with altitude as shown in the right-hand panel. (3) Rainout of nitric acid is included, with an effective tropospheric lifetime of about 10 days (see Table 1). The corresponding loss rate for HNO₃ at 15°N is shown in the right-hand panel; results for 45°N are similar. (4) The deposition velocity for HNO₃ is 0.5 cm s⁻¹. (5) In model A, the surface flux of (NO + NO₂) is set equal to zero; in model B, the mixing ratio of (NO + NO₂) at the surface is prescribed at 100 pptv. All results shown are for equinox and global mean cloud cover. Results for cloud-free conditions and for other seasons are almost identical. Other model parameters are given in Table 4. The symbols show median concentrations of acidic nitrate: solid triangle Huebert and Lazrus [1980]; solid circle, Huebert [1980].
heterogeneous removal of HNO₃ and are sensitive to the vertical distribution assumed for the source of (NO + NO₂). The relatively large concentrations of HNO₃ observed in the middle troposphere suggest a globally distributed source for odd nitrogen. The model implies that the source should be about 10⁷ tons N yr⁻¹, which may be compared with the flux of odd N from the stratosphere, calculated to be about 5 × 10⁵ tons N yr⁻¹.
Levy et al. [1980] suggested that nitrogen oxides from the stratosphere could provide a dominant source for odd nitrogen in the upper troposphere. Heterogeneous removal should be slow at these altitudes, as indicated by studies of nuclear gen in the upper troposphere. Heterogeneous removal should tracers in the upper troposphere [Mahlman and Moxim, 1978].

The role of stratospheric odd N in the middle and lower troposphere is less clear. Levy et al. [1980] argue that stratospheric input could contribute significantly to the abundance of tropospheric odd N in marine locations far from continental sources, even below 8 km. It is difficult to reconcile this view with the high concentrations of NO reported in the mid-troposphere [Schiff et al., 1979; Roy et al., 1980] as discussed above, but the fragmentary data base precludes a definitive discussion.

Kley et al. [1981] and Liu et al. [1980] give global distributions for (NO + NO₂) derived from a one-dimensional ‘eddy-diffusion’ model used in conjunction with the tracer distributions of Levy et al. [1980]. The assumption underlying their calculations (stratospheric source only) is quite different from that adopted here. Our approach invokes a distributed tropospheric source. The resulting profiles for (NO + NO₂) in the two models are nonetheless quite similar. In particular, both models indicate concentrations of (NO + NO₂) sufficiently low as to imply that OH should be insensitive to NO (see Figures 3 and 246).

Suggestions for in situ sources of nitrogen oxides in the remote troposphere include lightning [Noxon, 1976], decomposition of PAN [Crateau, 1979], and oxidation of NH₃ [McConnell, 1973]. Estimates for production by lightning range from 4 to 90 x 10⁶ tons N per year [Tuck, 1976; Noxon, 1978; Chameides, 1979; Dawson, 1980; Hill et al., 1980], more than enough to supply the required source. The source must be relatively constant with latitude, however, to account for the observed distribution of HNO₃, and the lightning mechanism may fail to satisfy this constraint [Orville and Spencer, 1979].

It seems unlikely that peroxyacetyl nitrate or similar compounds should be the precursors for nitrogen oxides observed over the South Pacific, since these species are relatively short lived [Cox and Roffey, 1977; Hendry and Kenley, 1979; Winer et al., 1977] and are thought to originate on land.

Oxidation of ammonia could contribute in remote areas and might satisfy the need for a distributed source. Oxidation is initiated by reaction with OH [McConnell, 1973; Stuhl, 1973].

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- (\text{25})
\]

Reaction (28) would lead to production of NO and NO₂, while odd nitrogen is removed by (26) and (27). The kinetic data [Kurasawa and Lesclaux, 1980] imply that oxidation of ammonia should represent a source for oxides of nitrogen when the concentration of (NO + NO₂) is less than about 60 ppt. Oxidation of NH₃ could provide a sink for nitrogen oxides at concentrations of (NO + NO₂) above 60 ppt.

There are few observations of NH₃ in the remote troposphere. Tsunagai [1971] observed concentrations between 0.1 and 1 ppb in surface air over the Pacific Ocean, and Georgii and Gravenhorst [1977] reported similar values for the central Atlantic. J. D. Tjepkema and coworkers (private communication, 1981) found low values in Massachusetts (0.1 ppb). Concentrations at high southern latitudes are also about 0.1 ppb [Ayers and Gras, 1980]. Values between 0.1 and 1 ppb would imply a source of nitrogen oxides from (25) in the range 1-10 x 10⁶ tons N yr⁻¹, and would suggest that production from NH₃ could be comparable to or larger than input from the stratosphere.

The higher concentrations of (NO + NO₂) observed in the continental boundary layer may be derived from a variety of sources at the ground. Combustion of fossil fuel accounts for emissions of 2 x 10⁶ tons N yr⁻¹ of (NO + NO₂) [Soderlund and Svensson, 1976] and biomass burning might provide additional sources as large as 5 x 10⁶ tons N yr⁻¹ [Crateau et al., 1979]. Galbally and Roy [1978] observed fluxes of NO from soils in Australia, which they attributed to chemical reactions of NO₃⁻ in the soil. They speculated that this mechanism could provide 10⁷ tons N yr⁻¹, widely dispersed over land areas. We may note in this context that soil microorganisms (ammonium oxidizers) appear to generate similar quantities of NO and N₂O [Goreau et al., 1980; L. Lipschultz and others, private communication, 1981]. Our data indicate that soil microorganisms may account for the emissions observed by Galbally and Roy [1978]. The associated source of NO would be similar to the source for N₂O (10⁷ tons N yr⁻¹). Model B (see Appendix 2) attempts to simulate the influence of terrestrial sources with a relatively high mixing ratio for (NO + NO₂), 0.1 ppb, at the ground in continental areas. Such sources have only slight influence above 2 km owing to rapid removal of NO and HNO₃ in the boundary layer.

The major uncertainty in our model for tropospheric odd nitrogen derives from inadequate definition of mechanisms and rates for heterogeneous processes that remove soluble and reactive gases from the atmosphere. These processes may affect the distribution of H₂O₂, a key species in the odd hydrogen family. There is evident need for research to quantify rates for heterogeneous reactions.

4. Model

Most of the results presented here were obtained by solving time-dependent continuity equations as described in Appendix 2. The chemical model is discussed in section 2; kinetic data and model parameters are summarized in Tables 1 and 4, respectively. Rates for photolytic processes were allowed to vary diurnally with insolation. Calculations were carried out for cloud-free conditions, for full cloud cover, and for insolation intended to simulate the climatological mean distribution of clouds as discussed in Appendix 3. Results showing the diurnal variation of H₂O₂ and odd nitrogen in the absence of clouds are given in Figures 13 and 14 for two altitudes, 0 and 6 km, for latitudes of 15°N and 45°N, for equinoctial conditions. Computations used the standard model summarized in Table 4.

As might be expected, concentrations of OH and H₂O₂ respond rapidly to insolation, reaching maximum values at
noon. The concentration of OH drops rapidly near sunset as rates for (2), (7), and (9) become negligible. At night, HO and OH are cycled by (3), (5), and (6) and by the methane oxidation chain. Concentrations of OH and HO2 decline slowly during the night owing to formation of H2O2 (reaction (8)) and CH3OOH (reaction (18a)).

Figure 13 includes values calculated for the diurnally averaged concentration of OH. The mean value for the concentration of OH over the sunlit portion of the day is equal to approximately 0.5 times the value at noon. The diurnal mean value for OH may be estimated, therefore, with adequate accuracy from knowledge of the noontime result if one were to account for the number of hours of sunlight.

The relative abundances of NO and NO2 are determined primarily by (7), (17), (23), and (24). Nitric oxide is converted to NO2 by reaction with OH, HO2, and CH3O2. Abundances of NO and NO2, as shown in Figures 13 and 14, are comparable during the day, with NO2 dominant at night. The rate for oxidation of NO by reaction with HO2 and CH3O2 is similar to the rate for oxidation by O3. One might expect additional oxidation near the ground owing to reaction with RO2,

\[ \text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO} \]  

where R denotes an organic radical (R = CH3H, CH3CO, etc.) formed by oxidation of higher hydrocarbons.

The increase in NO2 immediately after sunrise results from rapid photolysis of NO2. Measured concentrations of NO2 in continental air at night are significantly lower than values predicted by photochemical models [Platt et al., 1980; Noxon et al., 1980]. Observations of NO2 near sunrise might provide clues to help solve this puzzle.

Rates for production and loss of OH are shown as functions of altitude and latitude in Figure 15. Results apply to noon at equinox under cloud-free conditions. As is discussed earlier, cycling of HO2 to OH is more important at high latitudes and altitudes, and at high concentrations of NO, while direct production of OH from (2) dominates in the tropics (cf. Figures 6, 7, and 12).

Rates for loss of HO2 and CH3O2, averaged over a 24-hour day, are shown in Figure 16. Reaction with HO2 is an important sink for CH3O2, especially in the tropics, and significant concentrations of CH3OOH are produced. Oxidation of meth-

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O</td>
<td>Figure 6</td>
</tr>
<tr>
<td>O3</td>
<td>Figures 7, 8b, 8c</td>
</tr>
<tr>
<td>CO</td>
<td>Figure 11</td>
</tr>
<tr>
<td>HNO3</td>
<td>Figure 12a, model A</td>
</tr>
<tr>
<td>NO + NO2</td>
<td>Figure 12b, model A</td>
</tr>
<tr>
<td>CH4</td>
<td>1.7 ppmv (NH); 1.6 ppmv (SH)</td>
</tr>
<tr>
<td>H2</td>
<td>0.55 ppmv</td>
</tr>
<tr>
<td>O3 column</td>
<td>Dütsch [1974]</td>
</tr>
</tbody>
</table>

### Model Parameter Notes

- **Model atmosphere** (T, M): U.S. Standard Atmosphere Supplements [1966]
- **Kinetic data**: Table 1 (without HO2NO2 chemistry)
- Aerosol loss of H2O2: None
- Ground albedo: 0.1
- Aerosol absorption: 0.1 at 3100 Å
- Vertical diffusion coefficient: \(1 \times 10^5 \text{ cm}^{-2} \text{s}^{-1}\)

Rates for production and loss of odd hydrogen and odd oxygen, averaged over a 24-hour day, are shown in Figure 17. Loss of odd oxygen is most important in the boundary layer below 2 km, while production of odd oxygen is distributed throughout the troposphere. As discussed earlier, the balance between photochemical sources and sinks for O3 is regulated by NO. In situ chemistry (i.e., the net balance of local sources and sinks) provides net global production for O3 of magnitude \(8 \times 10^{16} \text{ molecules cm}^{-2} \text{s}^{-1}\). Rates for production and loss of odd oxygen are nearly equal in the northern hemisphere, both at mid-latitudes and in the tropics, as shown in Table 5. Photochemical production exceeds loss by about 40% in the southern hemisphere, a result of the lower concentrations assumed for ozone in the south (see Figures 7 and 8). Photochemical sources and sinks of odd oxygen would balance if NO concentrations in Figure 12 were reduced by about 30% for the southern hemisphere or if southern hemispheric ozone were assumed to be similar to that in the north. Net production of ozone is much larger in model B than in model A, a reflection of the higher concentrations of NO in the boundary layer of model B. If relatively high values for NO + NO2 (>100 ppt) were in fact typical of the continental boundary layer, in situ photochemistry could dominate the tropospheric ozone budget at latitudes with large land areas, such as northern mid-latitudes [cf. Fishman and Seiler, 1980]. The net chemical source of ozone in the troposphere \((8 \times 10^{16} \text{ molecules cm}^{-2} \text{s}^{-1})\) is comparable to the flux of ozone from the stratosphere [Danielson and Mohnen, 1977; Fabian and Pruckniewicz, 1977; Mahlman et al., 1980; Gidel and Shapiro, 1980]. If NO concentrations were 10 times lower than values assumed in the standard model, ozone would be consumed by photochemistry in the troposphere at a rate in excess of \(4 \times 10^4\) times supply from the stratosphere.

The lifetime for odd hydrogen is about 2 days near the ground, increasing to ~8 days in the upper troposphere. Heterogeneous loss of H2O2 (reaction (11)) and reaction of OH with H2O2 (reaction (10)) provide the major sinks for odd H. Reaction (10) dominates loss of odd H in the upper troposphere and also in the lower tropical troposphere, while (11) dominates in the lower troposphere at mid-latitudes. The rate for gas phase removal of odd H exceeds the rate for heterogeneous removal over most of the troposphere. The OH distribution is consequently insensitive to the rate assumed for heterogeneous loss (see also Figure 24c).

Meridional cross sections for OH, HO2, H2O2, CH3O2, CH3OOH, and CH3O are given for summer and winter in Figures 18–23. These contours are appropriate for cloud-free conditions at noon. Calculated concentrations of CH3O are in good agreement with recent measurements of formaldehyde in clean air [Platt et al., 1979; Platt and Perner, 1980; Zafiriou et al., 1980; Lowe et al., 1980; Neitzert and Seiler, 1981]. It is probable that concentrations of CH3OOH, H2O2, and CH3O may be quite variable in the planetary boundary layer where heterogeneous reactions provide important paths for removal. Earlier studies suggested that OH should be lower on average in the northern hemisphere than in the southern hemisphere due to the higher levels of CO in the north [Wofsy, 1976; Sze, 1977]. In the present model, however, ozone concentrations are taken to be larger in the northern hemisphere than in the south. This asymmetry leads to enhanced production of HO2 in the north offsetting effects of elevated CO. Thus OH is (some-
Fig. 13a

Fig. 13. Diurnal variations of HOx and nitrogen oxides in the tropics and at mid-latitudes. Results are given for cloud-free equinoctial conditions at the surface and at 6 km. The solid lines are derived from the standard model described in Table 4, which does not include the chemistry of peroxy nitric acid. The diurnally averaged concentration of OH is indicated by the arrow.

what fortuitously) nearly symmetric about the equator [Fishman and Crutzen, 1978] while concentrations of HO2 and H2O2 are larger in the north than in the south. Sensitivity of OH to various parameters of the model is shown in Figure 24. The concentration of OH could vary significantly in response to H2O. Curve A of Figure 24a was obtained with a profile for H2O measured at Trinidad, (3/25/65 in Figure 5). A distribution of OH with altitude similar to that

Fig. 13b
exhibited by curve A has been reported by Davis et al. [1978].
Curve B (the standard model) exhibits a slight maximum at
about 2 km reflecting the local maximum in ozone (see Figure
7).
The dependence of OH on NO is illustrated in Figure 24b.
Curve A was obtained with the standard model for (NO +
NO₂), respectively. The range of results shown in Figure 24b
emphasizes the need for better measurements of global distri-
butions for NO and NO₂.
Figure 24c shows profiles for OH obtained with a variety of
models for heterogeneous loss of H₂O₂. Model A neglects het-
erogeneous processes in their entirety, while model B allows
for rainout (wet removal) of H₂O₂. Model C shows the effect
Fig. 14. Diurnal variations of nitrogen oxides at 6 km in the tropics and at mid-latitudes. Results are given for cloud-free, equinoctial conditions. The calculations use the standard model of Table 4 and, in addition, include the chemistry of HO$_2$NO$_2$. The concentration of HO$_2$NO$_2$ at the ground is shown by the dashed line in Figure 13. Concentrations of other species at the ground are changed by less than 10% by the inclusion of HO$_2$NO$_2$ chemistry in the model.

Fig. 15. Noontime rates for production and loss of OH (bottom and top panels, respectively). Results are given for cloud-free, equinoctial conditions and calculated for the standard model described in Table 4.
of efficient removal of \( \text{H}_2\text{O}_2 \) by aerosols. Model C1 assumes a probability of \( 8 \times 10^{-4} \) for \( \text{H}_2\text{O}_2 \) to stick on the surface of an aerosol, a value observed by Baldwin and Golden [1979] for attachment of \( \text{H}_2\text{O}_2 \) to a surface of sulfuric acid. Model C2 adopts a much larger probability for attachment, \( 3 \times 10^{-3} \), based on the sticking probability observed for attachment of water vapor to a water droplet [Chodes et al., 1974]. Models C1 and C2 assumed rapid destruction of \( \text{H}_2\text{O}_2 \) after incorporation in the aerosol, which implies lifetimes for \( \text{H}_2\text{O}_2 \) in the particulate phase of less than 10 and 0.3 s, respectively. Evidently, the OH profiles of models A and C1 differ insignificantly from those of model B in which aerosol processes were excluded. The assumptions of model C2 result in reduction of calculated concentrations for OH by 20% near the ground, by 40% in the upper troposphere. As discussed in Appendix 1, it is unlikely that aerosol processes could destroy \( \text{H}_2\text{O}_2 \) in the clean troposphere as rapidly as assumed in model C2. This conclusion is based on consideration of the physical and chemical properties of atmospheric aerosols and aqueous \( \text{H}_2\text{O}_2 \).

The concentration of OH should respond to changes in the intensity of ultraviolet radiation, influenced by the presence of clouds and aerosols, as shown in Figure 24d. Effects of clouds and aerosols on the radiation field are discussed in detail in Appendix 3. On average, absorption of radiation by aerosols leads to significant reduction in OH, while aerosol scattering has relatively little effect. The concentration of OH would decrease by about 20% at the ground if we assumed absorption by aerosols corresponding to a mean optical depth of 0.1 (see Appendix 3). Incorporation of clouds in the model further reduces OH by about 20% at the ground while producing a small increase above the clouds.

5. BUDGETS

We turn our attention now to consideration of sources and sinks for \( \text{CH}_3\text{CCl}_3 \) and CO. According to present understanding, the source of atmospheric \( \text{CH}_3\text{CCl}_3 \) may be attributed primarily to industrial activity, specifically the widespread and growing use of \( \text{CH}_3\text{CCl}_3 \) as a solvent. The magnitude of the release rate has been estimated by Neely and Plonka [1978], and we expect that about 95% of the release occurs in the northern hemisphere. The gas is removed by reaction with OH,

\[
\text{OH} + \text{CH}_3\text{CCl}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_2\text{CCl}_3
\]

Recent laboratory studies by Kurylo et al. [1979] and Jeong and Kaufman [1979] appear to resolve earlier discrepancies in our knowledge of the rate constant for (30). Therefore, measurement of the concentration of \( \text{CH}_3\text{CCl}_3 \) may be used to check the accuracy of models for OH.

We shall argue that the concentration of OH may be estimated within a factor of 2 for mean conditions in the tropical troposphere. The discussion that follows explores implications of this analysis for attempts to quantify the budget of CO. As we shall see, estimates for the rate at which CO is removed from the atmosphere by reaction with OH may be used to place valuable constraints on the magnitude of several possible sources for CO.
Fig. 17a. Diurnally averaged rates for production and loss of odd oxygen (top and bottom panels, respectively).

Fig. 17b. Diurnally averaged rates for production and loss of odd hydrogen. Results are given for cloud-free, equinoctial conditions and are calculated for the standard model described in Table 4. The net effect of each methane oxidation pathway on odd-H is given in Table 2.
TABLE 5. Photochemical Production and Loss of Odd-Oxygen

<table>
<thead>
<tr>
<th>Model A</th>
<th>45°N</th>
<th>15°N</th>
<th>15°S</th>
<th>45°S</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production (odd-O)</td>
<td>2.1</td>
<td>3.5</td>
<td>3.4</td>
<td>2.1</td>
<td>2.8</td>
</tr>
<tr>
<td>Loss (odd-O)</td>
<td>1.9</td>
<td>3.4</td>
<td>2.4</td>
<td>1.3</td>
<td>2.2</td>
</tr>
<tr>
<td>(Production-Loss)</td>
<td>0.19</td>
<td>0.11</td>
<td>1.0</td>
<td>0.86</td>
<td>0.54</td>
</tr>
</tbody>
</table>

| Model B | 2.6  | 4.8  | 4.7  | 2.7  | 3.7  |
| Production (odd-O) | 1.9  | 3.4  | 2.5  | 1.3  | 2.3  |
| Loss (odd-O) | 0.70 | 1.3  | 2.2  | 1.4  | 1.4  |
| (Production-Loss) | 0.70 | 1.3  | 2.2  | 1.4  | 1.4  |

| Global Model | 2.3  | 3.9  | 3.7  | 2.2  | 3.0  |
| Production (odd-O) | 1.9  | 3.4  | 2.4  | 1.3  | 2.2  |
| Loss (odd-O) | 0.45 | 0.46 | 1.3  | 0.94 | 0.78 |
| (Production-Loss) | 0.45 | 0.46 | 1.3  | 0.94 | 0.78 |

Odd oxygen is defined as \((\text{O}_3 + \text{O}^3\text{P} + \text{O}(\text{LD}) + \text{NO}_2)\). Rates are given in units of \(10^{11}\) molecules \(\text{cm}^{-2} \text{s}^{-1}\). The profiles for \((\text{NO} + \text{NO}_2)\) for models A and B are given in Figure 12b. The calculations assumed global mean cloud cover, and the results have been seasonally averaged.

- The major sources for odd-O are reactions (7) and (17).
- The major sinks for odd odd-O are reactions (2), (6), and \(\text{OH} + \text{O}_3\).
- The global model represents an average of models A and B weighted by the areas of the oceans and continents, respectively.

Concentrations of \(\text{CH}_3\text{CCl}_3\) were obtained as functions of time and latitude by using a simple parameterized model for transport. The troposphere was divided into four latitude zones of equal area with boundaries at 30°N, 0°, and 30°S. Mixing ratios of \(\text{CH}_3\text{CCl}_3\) were assumed uniform in each zone. Rates for exchange between zones were obtained by application of the model to data for \(\text{CF}_2\text{Cl}_2\) and \(\text{CFC}_1\). Parameters of the exchange model are given in Table 6. Results for \(\text{CF}_2\text{Cl}_2\), \(\text{CFC}_1\), and \(\text{CH}_3\text{CCl}_3\) are shown in Figures 25 and 26.

Concentrations of \(\text{OH}\) were calculated as functions of altitude and time as described earlier (see Table 4 and Appendix 2). Each latitude zone was subdivided into land and ocean compartments, and it was assumed that concentrations of \((\text{NO} + \text{NO}_2)\) over oceans and continents were given by curves A and B of Figure 12b, respectively. Concentrations of \(\text{OH}\) were obtained for each latitude zone by suitably averaging land and ocean areas. Calculations were performed for climatological mean cloud cover as discussed in Appendix 3. Results in Figure 27b reflect an average over diurnal, seasonal, and cloud-related changes in insolation.

The model predicts concentrations for \(\text{CH}_3\text{CCl}_3\) in reasonable accord with observation, as shown in Figure 26. There

![Fig. 18. Concentration of OH at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.](image)

![Fig. 19. Concentration of HO2 at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.](image)
Fig. 20. Concentration of H$_2$O at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.

Fig. 21. Concentration of CH$_3$O$_2$ at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.

Fig. 22. Concentration of CH$_3$OOH at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.

Fig. 23. Concentration of CH$_3$O at noon as a function of latitude, altitude, and season. Results are given for cloud-free conditions and are calculated for the standard model of Table 4.
Fig. 24a. Altitude profiles for diurnally averaged OH. Results are given for cloud-free, equinoctial conditions. Model parameters are those for the standard model described in Table 4, unless otherwise specified. Curve A: The water vapor profile is taken from Figure 5 (Trinidad, March 25, 1965). Curve B: Standard water vapor profile for spring, 15°N.

are systematic discrepancies, however. We show, for comparison, concentrations of CH$_3$CCl$_3$ that would apply in the limit of an infinite tropospheric lifetime and also results that would obtain if concentrations of OH were increased or decreased by a factor of 2. Evidently, concentrations of OH lower than values of the standard model would provide a better fit to the recent observational data.

Results shown in Figure 26 must be interpreted with caution. The accuracy of the observational data is uncertain owing to difficulties in calibration and sampling. The magnitude of the calibration problem may be gauged from a comparison of measurements by Lovelock [1977] and Rasmussen et al. [1981] or from results of the laboratory intercalibration exercise conducted by Rasmussen [Rasmussen, 1978; NASA, 1979]. Concentrations measured by Rasmussen are higher than values measured by Lovelock by about 20%. Discrepancies of similar magnitude were observed during an intercalibration exercise involving several laboratories. Further, samples from the North American continent or Europe could be influenced by proximity to sources. It is possible, therefore, that hemispheric mean values for CH$_3$CCl$_3$ may be somewhat lower than implied by the data in Figure 26.

The model results rely on release rates for CH$_3$CCl$_3$ provided by Neely and Plonka [1978], and it is difficult to ascertain the accuracy of these data. The quality of the data base differs from that for CF$_2$Cl$_2$ and CFC$_3$. The study of chlorofluorocarbons was based on a survey of manufacturers and included estimates for sources in Eastern Bloc countries.

Fig. 24b. Same as Figure 24a except curve A: The (NO + NO$_2$) profile is taken from model A, Figure 12. Curve B: The (NO + NO$_2$) concentrations of model A are multiplied by a factor of 3. Curve C: The (NO + NO$_2$) concentrations of model A are decreased by a factor of 3.

Fig. 24c. Same as Figure 24a except curve A: Heterogeneous loss of H$_2$O$_2$ is omitted. Curve B: Rainout of H$_2$O$_2$ is included (see Table 1). The rainout rate corresponds to an effective tropospheric lifetime of about 10 days. Curve C1: Aerosol loss of H$_2$O$_2$ is included, using the parameterization given in Table 1. A sticking probability of 8 x 10$^{-4}$ for H$_2$O$_2$ on the surface of an aerosol is adopted. Curve C2: Same as Curve C1, with a sticking probability of 3 x 10$^{-2}$.

Fig. 24d. Altitude profiles for diurnally averaged OH. Results are shown for cloud-free conditions with molecular scattering only (M), for cloud-free conditions with aerosol absorption (A) and molecular scattering, and for global mean cloud cover with aerosol absorption and molecular scattering (AC). The aerosol absorption (0.1) and altitude distribution are given in Tables 1 and 4 and the cloud model is described in Table A2. Results are shown for equinoctial conditions. Calculations used the standard model of Table 4 with the exception of the parameters given above.
Difficulties associated with the use of atmospheric measurements to verify or adjust models are illustrated also by Figure 25. The data for CFC11 indicate a relatively abrupt rise in the concentration of this gas in the southern hemisphere over a period of about a year in 1976. The magnitude of the rise would imply a hemispheric source of magnitude $4 \times 10^7$ tons yr$^{-1}$, which may be compared with estimates for global production of $3.2 \times 10^7$ tons yr$^{-1}$ [Bauer, 1979]. It is possible that the discrepancies in Figure 25 could be explained if one were to invoke a relatively abrupt increase in the rate for interhemispheric exchange, with exchange assumed to be quite slow before 1976. It seems more likely, however, that problems in Figure 25, and some of the difficulties in Figure 26, reflect sampling errors and the absence of continuous and consistent calibration.

Exchange rates in Table 6 were obtained from a comparison of the model with observations for CF$_2$Cl$_2$ and CFC$_3$ made subsequent to 1976. The model provides a good fit to interhemispheric gradients derived from upper tropospheric measurements by Goldan et al. [1980] and surface measurements by Singh et al. [1979] and by Rowland et al. [1980] as shown in Figure 28. The north/south gradient for CH$_3$CCl$_3$ depends on concentrations of OH as well as on parameters describing exchange. There is sufficient scatter in the observations to preclude accurate experimental definition of the gradient. The data in Figure 28 (lower panel) are of limited use therefore as a test of the model for OH.

The model indicates that methylchloroform is removed from the atmosphere mainly in the tropical troposphere, a point illustrated in Figure 29. Thus, model results in Figure 26 are particularly sensitive to values of OH in the tropics, a region that accounts for approximately 70% of the global sink. Approximately 50% of the global sink occurs over the tropical ocean, and it is important to emphasize the lack of observational data in this regime for trace gases such as H$_2$O, O$_3$, and NO.

Table 7 gives estimates for the effect of uncertainties in concentrations of CO, O$_3$, H$_2$O, and NO on globally averaged rates for removal of CH$_3$CCl$_3$. Concentrations of NO in the standard model are sufficiently low that reaction (7), which cycles odd hydrogen, is of minor importance in the tropics (see Figure 15.). The rate for removal of CH$_3$CCl$_3$ is insensitive consequently to a decrease in NO. A uniform increase in NO would lead to significant increase in OH (cf. Figures 3 and 24b) with obvious effects for CH$_3$CCl$_3$. However, an increase in NO in the continental boundary layer (model B) has only a modest effect on the average rate for removal of CH$_3$CCl$_3$.

Assumption of an efficient aerosol loss process for H$_2$O$_2$ could reduce the removal rate for CH$_3$CCl$_3$ by as much as 20% and would improve agreement between model and observational data from different groups of investigators:

- a: (30$^\circ$-90$^\circ$); b: (0-30$^\circ$),
- c: Lovelock [1971, 1972, 1974], Lovelock et al. [1973], Pack et al. [1977], NASA [1979];
- b: (30$^\circ$-90$^\circ$); e: (0-30$^\circ$) Wilkness et al. [1973, 1975a, b, 1978];
- f: Zafonte et al. [1975], Hester et al. [1975]; g: Heidt et al. [1975];
- h: Singh et al. [1977a, b, 1979]; i: Grimard and Rasmussen [1975], Robinson et al. [1976], Cronn et al. [1977], Pierotti et al. [1978], Rasmussen et al. [1981]; j: Fraser and Pearman [1978]; k: Tyson et al. [1978]; l: Krey et al. [1977]; m: Goldan et al. [1980]. The solid lines show results of the model calculations, which used the mass exchange parameters given in Table 6 and the CFC$_3$ and CF$_2$Cl$_2$ release rates given by Bauer [1979]. We assumed that 90% of the release takes place in the northern hemisphere. Model results are mean hemispheric values. The arrows (a) show the range of concentrations from the model for mid-latitudes and the tropics.

![Fig. 25a](image)

![Fig. 25b](image)
Fig. 26. Measurements of CH₃CCl₃ in the northern and southern hemispheres as a function of time. Each symbol represents data from a different group of investigators: a: Lovelock [1974, 1977]; b: Rasmussen et al. [1981]; c: Grimrud and Rasmussen [1975], Cronn et al. [1977], Pierotti et al. [1978]; d: (hemispheric mean); e: (range, 0–30°); f: (range, 30°–60°), Singh et al. [1977a, b]; h: (1978, mid-latitude mean; 1979, hemispheric mean) Rowland et al. [1980]. Model calculations used the mass exchange parameters given in Table 6 and the release rate for CH₃CCl₃ given by Neely and Plonka [1978]. We assumed that 95% of the release takes place in the northern hemisphere. Model results are mean hemispheric values. The arrows (i) show the range of concentrations from the model for mid-latitudes and the tropics. The solid lines give the results of the standard model (OH profiles from Figure 27b). In each latitude zone a mean OH profile is derived from marine and continental profiles, weighted by the appropriate area in each zone. The dashed curves show results in which OH concentrations from the standard model are multiplied by 0.5 while the dotted curves are for OH concentrations multiplied by 2. The dot-dash curves show results for an infinite tropospheric lifetime for CH₃CCl₃ (OH concentration = 0).

Fig. 27a. Altitude profiles for diurnally averaged OH as a function of latitude and season. Results are given for global mean cloud cover (see Table 6) and for the standard model of Table 4. These calculations adopt the NOₓ concentrations of model A, Figure 12 (assumed to be representative of marine air).

Fig. 27b. Altitude profiles for OH averaged over an annual cycle. Annual averages of the seasonal profiles of Figure 27a are shown by the solid lines. Annual averages of seasonal OH profiles based on model B of Figure 12 are shown by the dashed lines. (Model B includes higher concentrations for (NO + NO₂) near the surface than does Model A and is assumed to be representative of continental air.)

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i.  

The standard model omitted possible removal of OH by hydrocarbons other than CH₄. Omission of reactions with saturated hydrocarbons such as C₂H₆ is probably justified owing to the low concentration of these gases in the atmosphere. The mixing ratio for C₂H₆ is about 1 ppb [Robinson, 1978; Singh et al., 1979; Cronn and Robinson, 1979]. Although the rate constant for OH + C₂H₆ is larger than that for OH + CH₄ by about a factor of 30 [Atkinson et al., 1979], the difference in rate constants is not sufficiently large to offset the difference in concentrations. Similar arguments may be used to exclude the possibility of significant OH loss by reaction with other alkanes and with acetylene [Robinson, 1978; Cronn and Robinson, 1979; Atkinson et al., 1979; Chameides and Cicerone, 1978]. Removal of OH by C₂H₆ in the boundary layer could be comparable to removal by CH₄ if the mixing ratio for C₂H₆ were about 1 ppb [Atkinson et al., 1979]. Preliminary observational data for C₂H₆ in clean air suggest that concentrations are generally lower than 0.5 ppb [Rudolph et al., 1979; Rasmussen and Khalil, 1980].

Limited data are available for isoprene and terpenes. Isoprene is a major component of the volatile emissions of many species of land plants, and concentrations as high as 2 ppb have been observed in forests [Sanadze, 1963; Rasmussen, 1970; Robinson, 1978]. Concentrations of terpenes appear to lie in the range 10 ppt to 1 ppb [Holden et al., 1979]. This suggests that reaction with unsaturated hydrocarbons could be important for OH, at least under some conditions. Isoprene could be removed also by reaction with O₃, although laboratory data are lacking. Studies of analogous reactions involving butenes, pentenes [Japp et al., 1974] and terpenes [Ripper et al., 1972; Grimrud et al., 1975] indicate that the relevant rate constant could be as large as 5 x 10⁻¹⁶ cm³ s⁻¹. Rates for removal of isoprene by O₃ and OH would be comparable if
the isoprene +O₃ rate constant were of order 10⁻¹⁶ cm³ s⁻¹. The standard model does not account for possible removal of OH by either isoprene or terpenes. Present uncertainties are such as to preclude quantitative analysis. Observational studies are needed to define better the distribution of reactive hydrocarbons, and there is an additional need for laboratory work to characterize mechanisms for decomposition in the atmosphere. Zimmerman et al. [1978] estimate a global source for isoprene of about 3.5 x 10⁶ tons C yr⁻¹, subject to an uncertainty of about a factor of 3. If we were to assume that each molecule of isoprene could remove one molecule of OH, isoprene could account for an increase in the lifetime for CH₃CCl₃ of about 5%. Reaction of OH with degradation products of isoprene could have a larger effect on OH. The isoprene +O₃ rate constant was of order 10⁻¹⁶ cm³ s⁻¹. The standard model does not account for possible removal of OH by either isoprene or terpenes. 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Table 8. Global CO Budget (10^12 gm CO yr^-1)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Total</th>
<th>Northern Hemisphere</th>
<th>Southern Hemisphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel use</td>
<td>450</td>
<td>425</td>
<td>25</td>
</tr>
<tr>
<td>(400-1000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of anthropogenic hydrocarbons</td>
<td>90</td>
<td>85</td>
<td>5</td>
</tr>
<tr>
<td>(0-180)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of natural hydrocarbons</td>
<td>560</td>
<td>380</td>
<td>180</td>
</tr>
<tr>
<td>(280-1200)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emissions by plants</td>
<td>130</td>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>(50-200)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood used as fuel</td>
<td>51</td>
<td>33</td>
<td>17</td>
</tr>
<tr>
<td>(25-150)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forest wild fires</td>
<td>25</td>
<td>22</td>
<td>3</td>
</tr>
<tr>
<td>(10-50)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forest clearing</td>
<td>380</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td>(200-800)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Savanna burning</td>
<td>200</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(100-400)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ocean</td>
<td>40</td>
<td>13</td>
<td>27</td>
</tr>
<tr>
<td>(20-80)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₄ oxidation</td>
<td>810</td>
<td>405</td>
<td>405</td>
</tr>
<tr>
<td>(400-1000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2740</td>
<td>1820</td>
<td>920</td>
</tr>
<tr>
<td>(1500-4000)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sinks</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil uptake</td>
<td>250</td>
<td>210</td>
<td>40</td>
</tr>
<tr>
<td>Photochemistry</td>
<td>3170</td>
<td>1890</td>
<td>1280</td>
</tr>
<tr>
<td>Total</td>
<td>3420</td>
<td>2100</td>
<td>1320</td>
</tr>
<tr>
<td>(1600-4000)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The source of CO associated with oxidation of CH₄ may be taken as relatively well known. Both CO and CH₄ are removed by reaction with OH. Thus the fractional contribution of CH₄ to the total source of CO may be calculated with some confidence. The estimate is insensitive to details of the chemical model for OH, depending primarily on the yield for CO from oxidation of CH₄. The oxidation scheme discussed earlier implies a yield of about 80%, and suggests that CH₄ oxidation accounts for 25% of global production of CO. As indicated in Table 8, our analysis implicates a source for CO owing to oxidation of CH₄ of magnitude 8.0 x 10^8 tons yr^-1, distributed evenly between hemispheres.

The source of CO due to combustion of fossil fuel could be comparable to that from oxidation of CH₄. Combustion gave rise to a source of CO₂ of magnitude 4.6 x 10^9 tons C in 1976 [United Nations, 1978a]. The source was divided more or less equally between North America, Europe, and the rest of the world. Liquid fuel accounted for 44% of the net source of CO₂; solid fuel and natural gas represented 41% and 15%, respectively, as summarized in Table 9.

Use patterns for various forms of fossil fuel are displayed

Table 9. Fuel Consumption Patterns, 1976 (10^6 tons carbon)

<table>
<thead>
<tr>
<th>Region</th>
<th>Solid fuel</th>
<th>Liquid fuel</th>
<th>Gas</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>North America</td>
<td>399</td>
<td>670</td>
<td>328</td>
<td>1397</td>
</tr>
<tr>
<td>Europe</td>
<td>804</td>
<td>740</td>
<td>251</td>
<td>1795</td>
</tr>
<tr>
<td>Western Europe</td>
<td>276</td>
<td>467</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td>Rest of the World</td>
<td>684</td>
<td>600</td>
<td>91</td>
<td>1375</td>
</tr>
<tr>
<td>Totals</td>
<td>1887</td>
<td>2010</td>
<td>670</td>
<td>4567</td>
</tr>
</tbody>
</table>

These values were compiled from statistics for energy use published by the United Nations [1978a]. The U.N. gives energy consumption in units of metric tons of coal equivalent (MTCE), which is defined as 7000 calories per gram (1 MTCE = 1 metric ton coal = 0.64 metric tons liquid fuel = 7.51 x 10^2 m³ natural gas). The U.N. has taken into account the percentages of carbon in different grades of coal and lignite, and solid fuel is taken to be 70% carbon. The carbon content of liquid fuel is 84% and that of natural gas 0.536 gm l^-1 [Keeling, 1973].

a North America includes the United States and Canada.

b The values for Europe include 80% of fuel use in the U.S.S.R. [Lydolph, 1970].
The source of CO from fossil fuel, with approximately equal factors appropriate for Germany. The source of CO from residential use of coal in North America would be small, however, even if we were to adopt emission factors given for the two continents in Table 10. Emission factors for the United States are much lower [U.S. Environmental Protection Agency, 1977]. The data for other industrial economies are obviously needed. Production of steel could represent a major source if substantial quantities of CO produced during manufacture were allowed to vent to the atmosphere. One might note that the United States accounts for only 17% of total steel production. The remainder is widely distributed, with the U.S.S.R., Japan, F.R.G., and China contributing 21%, 16%, 6%, and 4%, respectively [United Nations, 1976b].

Table 8 shows an estimate of $9.0 \times 10^7$ tons CO due to atmospheric oxidation of industrial hydrocarbons. These hydrocarbons for the United States and Europe in Table 10. Emission factors, defined as the amount of CO produced per unit of fuel consumed, are given in Table 11, while Table 12 summarizes amounts of CO released during manufacture of various industrial commodities. Automobiles account for about 50% of the source of CO from fossil fuel, with approximately equal contributions from North America, Europe, and the rest of the world, as indicated in Table 13. North America consumes 2.5 times as much gasoline as Europe. The similarity of CO source strengths given for the two continents in Table 13 reflects a view that emission control measures are more effective in North America. The data on which this conclusion is based are summarized in Table 14. Our estimate for the total of CO emissions from burning of fossil fuel is similar to earlier estimates by Jaffe [1973] and Seiler [1974].

The source of CO due to use of coal in residential heating is Angelis and Reznik [1979]. The low values for utility and industrial practices in the United States [U.S. Environmental Protection Agency, 1977]. Data for other industrial economies are obviously needed. Production of steel could represent a major source if substantial quantities of CO produced during manufacture were allowed to vent to the atmosphere. One might note that the United States accounts for only 17% of total steel production. The remainder is widely distributed, with the U.S.S.R., Japan, F.R.G., and China contributing 21%, 16%, 6%, and 4%, respectively [United Nations, 1976b].

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Table 8 shows an estimate of $9.0 \times 10^7$ tons CO due to atmospheric oxidation of industrial hydrocarbons. These hydrocarbons...
TABLE 12. Industrial Sources of CO

<table>
<thead>
<tr>
<th>Process</th>
<th>Emission Factora (kg/ton of Product)</th>
<th>Total Productionb (tons)</th>
<th>CO Production (10^6 tons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pig iron production</td>
<td>80</td>
<td>5.1 x 10^8</td>
<td>42</td>
</tr>
<tr>
<td>Steel production</td>
<td>69.5</td>
<td>6.7 x 10^8</td>
<td>47</td>
</tr>
<tr>
<td>Catalytic cracking of crude oilc</td>
<td>39.2 kg 10^3 1-1</td>
<td>3.47 x 10^11</td>
<td>13.6</td>
</tr>
<tr>
<td>Carbon black production</td>
<td>2000</td>
<td>3.9 x 10^6</td>
<td>7.8</td>
</tr>
<tr>
<td>Ammonia production</td>
<td>100</td>
<td>4.4 x 10^7</td>
<td>4.4</td>
</tr>
<tr>
<td>Pig iron, foundry</td>
<td>72.5</td>
<td>2.5 x 10^7</td>
<td>1.8</td>
</tr>
<tr>
<td>Miscellaneous industrial processesd</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>130</td>
</tr>
</tbody>
</table>

a Emission factors were taken from U.S. Environmental Protection Agency [1977] and Kemp and Dykema [1978] and are typical of current industrial practices in the United States.
b Production rates were taken from the Yearbook of Industrial Statistics, 1976 [United Nations, 1978].
c About 12% of crude oil is catalytically cracked [International Petroleum Encyclopedia, 1979]. The production rate is given in liters.
d Estimated to be about a factor of 3 larger than the U.S. source [U.S. Environmental Protection Agency, 1976, 1978].

The sources discussed so far are relatively well defined. They contribute, according to our estimates, 9.1 x 10^8 tons CO yr^-1 in the northern hemisphere and 4.4 x 10^8 tons CO yr^-1 in the southern hemisphere, less than half of the estimated net source in each hemisphere. It remains to account for additional production of about 1.4 x 10^8 and 7.6 x 10^8 tons CO yr^-1 in the northern and southern hemispheres, respectively. Possible sources include the oceans, combustion of wood for fuel, wild forest fires, burning of vegetation in land clearance for agriculture, emission by plants, and oxidation of natural hydrocarbons. Observations by Linnenbom et al. [1973] and Seiler [1974] suggest that the marine biosphere should represent at most a small source for CO as shown in Table 8. According to United Nations statistics [Food and Agricultural Organization, 1979], 8.5 x 10^6 tons of wood are used annually as fuel. Wood is the major source of energy for about 1.5 billion people [Eckholm, 1979] with use averaging between 0.1 and 2 tons per capita per year [Openshaw, 1974; Revelle and Munk, 1978]. In different countries, between 6 and 40% of wood fuel is converted to charcoal prior to combustion [Openshaw, 1974; Arnold and Jongma, 1978]. The emission factor for wood (60 kg CO per ton of wood) is appropriate for combustion in an open fire [U.S. Environmental Protection Agency, 1977]. Insufficient data exist for emission associated with the manufacture and combustion of charcoal. Accordingly, we used an emission factor similar to that for wood fuel. The source for CO given in Table 8 could be uncertain to at least a factor of 3. Our estimate of the uncertainty assumes that the United Nations survey is reliable within about a factor of 2 and that emission factors could be different from values adopted here by about 50%.

The estimate for production of CO in wild forest fires reflects a product of three factors: the area of forests burned per year, the quantity of fuel consumed per unit area, and the product of CO per unit of fuel. Relatively accurate data are available for forests in the United States, Canada, and Austra-

TABLE 13. CO Emissions (10^6 tons yr^-1)

<table>
<thead>
<tr>
<th></th>
<th>Europe</th>
<th>North America</th>
<th>Rest of the World</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal</td>
<td>24</td>
<td>1</td>
<td>23</td>
<td>48</td>
</tr>
<tr>
<td>Lignite</td>
<td>3</td>
<td>—</td>
<td>—</td>
<td>3</td>
</tr>
<tr>
<td>Gas</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Oil</td>
<td>4.6</td>
<td>2.2</td>
<td>3.7</td>
<td>11</td>
</tr>
<tr>
<td>Total Combustion</td>
<td>32</td>
<td>3.4</td>
<td>27</td>
<td>62</td>
</tr>
<tr>
<td>Transportation^</td>
<td>71</td>
<td>94</td>
<td>66</td>
<td>233</td>
</tr>
<tr>
<td>Sub total</td>
<td>103</td>
<td>97</td>
<td>93</td>
<td>295</td>
</tr>
<tr>
<td>Industrial Processes</td>
<td>46</td>
<td>36</td>
<td>48</td>
<td>130</td>
</tr>
<tr>
<td>Waste Disposal^</td>
<td>6</td>
<td>3</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>Total</td>
<td>155</td>
<td>137</td>
<td>152</td>
<td>445</td>
</tr>
</tbody>
</table>

These estimates are derived from the statistics for fossil fuel consumption, fuel use patterns, and emission factors, given in Tables 9, 10, 11, 12, and 14. Emission factors for the United States were used except for two categories. Residential use of coal is discussed in the text. For the transportation source of CO, we used the emission factors derived in Table 14 for gasoline and the German emission factor for diesel vehicles. The uncertainty in the transportation source is considered to be about 30% and in all other sources about a factor of 2.

^ The total includes a source of CO from aviation of 1.6 x 10^6 tons. (A. Broderick, private communication, 1980).

^ Estimate, based on limited data for the United States [U.S. Environmental Protection Agency, 1977] and world population figures.
lia, regions containing approximately 25% of the world's forests [Persson, 1974]. About 0.4% of the forested area of these countries is affected annually by fire [U.S. Environmental Protection Agency, 1977; Yamate, 1975]. Approximately 30 tons of fuel are consumed for each hectare burnt in North America, with a somewhat smaller value associated with tropical fires according to Yamate [1975]. The estimate in Table 8 assumes that 100 kg of CO are produced per ton of fuel, a compromise between values of 70 and 130 kg CO ton⁻¹ quoted by the U.S. Environmental Protection Agency [1977] and by Crutzen et al. [1979], respectively. The values for North America are taken from fuel economy figures for all vehicles for 1976 and 1977 [U.S. Department of Transportation, 1977] in the United States. For elsewhere, fuel economy was derived from statistics for Europe given in United Nations 1973, 1976b for 1971-1975. The emission rates for rural and urban traffic were averaged in deriving the final emission factors. These factors may be compared with limited estimates for countries other than the United States. In Germany, where exhaust emissions are checked annually, a mean value of 244 kg 10⁻³ CO kg⁻¹ fuel is reported for domestic vehicles. Becker et al. [1976] give an emission factor of 300 kg 10⁻³ for gasoline-powered vehicles only.

Table 8 also includes estimates for the source of CO due to burning of forest and grassland for purposes of agriculture. Fire plays a central role in the shifting cultivation characteristic of agriculture over large areas of the tropics, especially in Africa [Nye and Greenland, 1960; Gourou, 1966; Webster and Wilson, 1967; Watters, 1971; Ruthenberg, 1976]. If we were to use a median value of 0.15 ha person⁻¹ year⁻¹ for the burning of savanna to maintain a grassland suitable for grazing, estimates for the source of CO due to burning of forest and grassland for purposes of agriculture would be as large as 0.4% of the total forest area [Yamate, 1975]. It appears that the fraction of the total agricultural population involved in shifting cultivation in Africa, Latin America, and Asia is 1.5 × 10⁸, 2 × 10⁷, and 5 × 10⁷, respectively. Our analysis suggests that the total area of cropland cleared annually in tropical forests could be as large as 2.4 × 10¹¹ m², with perhaps an additional 1.6 × 10¹¹ m² obtained from clearing of woodland and savanna in Africa (see Table 16).

It appears that the fraction of the total agricultural population involved in shifting cultivation is largest for Africa. We assume for present purposes that the number of people involved in shifting cultivation in Africa, Latin America, and Asia is 1.5 × 10⁸, 2 × 10⁷, and 5 × 10⁷, respectively. Our analysis suggests that the total area of cropland cleared annually in tropical forests could be as large as 2.4 × 10¹¹ m², with perhaps an additional 1.6 × 10¹¹ m² obtained from clearing of woodland and savanna in Africa (see Table 16).
TABLE 15. Agricultural Populations in the Tropics, 1976

<table>
<thead>
<tr>
<th>Region</th>
<th>10^6 Persons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td></td>
</tr>
<tr>
<td>All countries</td>
<td>225</td>
</tr>
<tr>
<td>Population in the region of shifting cultivation</td>
<td>150</td>
</tr>
<tr>
<td>Population in the tropical forest region</td>
<td>45</td>
</tr>
<tr>
<td>Central and South America</td>
<td></td>
</tr>
<tr>
<td>All countries</td>
<td>116</td>
</tr>
<tr>
<td>Population in the tropical forest region</td>
<td>22</td>
</tr>
<tr>
<td>Southeast Asia</td>
<td></td>
</tr>
<tr>
<td>All countries</td>
<td>685</td>
</tr>
<tr>
<td>Population living by shifting cultivation in the tropical forest region</td>
<td>49</td>
</tr>
</tbody>
</table>

Agricultural populations for individual countries were taken from Food and Agricultural Organization [1977].

- All countries between 22°N and 22°S.
- This is based on maps showing the extent of shifting cultivation in Africa [Grigg, 1974] and discussions of agricultural practices in Africa [Stamp and Morgan, 1972] and is the total agricultural population in these regions.
- Total agricultural population of countries where the major form of vegetation is tropical forest [Persson, 1974; World Atlas of Agriculture, 1969; Phillips, 1959; Stamp and Morgan, 1972].
- Includes all of Mexico.
- It is assumed that shifting cultivation is practiced primarily by inhabitants of the tropical forest regions. In Brazil, less than 10% of the agricultural population live in the tropical forest [World Atlas of Agriculture, 1969; Camargo, 1958], while in Peru the fraction is 13% [Watters, 1971].
- The fractions of the agricultural populations in regions where shifting cultivation is dominant in Mexico and Venezuela are 20 and 50%, respectively. Estimates for other countries are based on maps showing the extent of shifting cultivation [Whitley, 1939] and descriptions of vegetation zones [World Atlas of Agriculture, 1969; Persson, 1974].
- Taken from Spencer [1966]. Shifting cultivation is not significant outside the tropical forest region.

TABLE 16. CO Emissions From Biomass Burning

<table>
<thead>
<tr>
<th>Area, 10^10 m^2 yr^-1</th>
<th>Fuel Loading, kg m^-2</th>
<th>Total Fuel, 10^14 gm yr^-1</th>
<th>CO Emitted, 10^6 tons yr^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Forest wildfires*</td>
<td>11</td>
<td>0.6-3.3</td>
<td>2.5</td>
</tr>
<tr>
<td>(5-22)</td>
<td></td>
<td></td>
<td>(8-75)</td>
</tr>
<tr>
<td>Clearing of forests</td>
<td>24</td>
<td>13</td>
<td>32</td>
</tr>
<tr>
<td>for crops</td>
<td>(8-36)</td>
<td>(9-26)</td>
<td>(70-940)</td>
</tr>
<tr>
<td>Clearing of woodland</td>
<td>16</td>
<td>4</td>
<td>6.4</td>
</tr>
<tr>
<td>for crops</td>
<td>(5-32)</td>
<td>(2-8)</td>
<td>(10-250)</td>
</tr>
<tr>
<td>Burning of pasture land</td>
<td>500</td>
<td>0.4</td>
<td>20</td>
</tr>
<tr>
<td>(250-750)</td>
<td>(0.2-0.8)</td>
<td></td>
<td>(50-600)</td>
</tr>
<tr>
<td>Wood used as fuel</td>
<td></td>
<td>8.5</td>
<td>51</td>
</tr>
<tr>
<td>Total b</td>
<td></td>
<td>70</td>
<td>660</td>
</tr>
</tbody>
</table>

Fuel loading is the amount of dry matter per unit area that is consumed by fire. Dry matter is taken to be 45% carbon. All categories except wood fuel assumed a CO emission factor of 100 kg CO per ton of fuel. For wood fuel a value of 60 kg CO per ton of wood was used.

- Persson [1974] gives the total area of the world's forests as 2.8 x 10^13 m^2. We assumed that 0.4% of this area is affected by forest wildfires annually, and we used Yamada's [1974] estimates of the amount of fuel burned per unit area, which range from 0.6 kg m^-2 for tropical forests to 3.3 kg m^-2 for temperate forests.

- This total does not include an estimate of CO emissions from the burning of agricultural waste. CO emissions from this source in the United States, prior to regulation, amounted to 1.5 x 10^6 tons yr^-1 [U.S. Environmental Protection Agency, 1978c]. Since the total area of land harvested in the United States is about 10% of the total in the world [Food and Agricultural Organization, 1978], this suggests that burning of these wastes should not provide a large source of CO.
TABLE 17. Land Use in the Tropics (10^6 m^2)

<table>
<thead>
<tr>
<th>Region</th>
<th>Land Area (1)</th>
<th>Closed Forest (2)</th>
<th>Forest and Woodland (3)</th>
<th>Permanent Pasture (4)</th>
<th>Arable Land (5)</th>
<th>Total area Harvested (6)</th>
<th>Shifting Cultivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>2291</td>
<td>190</td>
<td>627</td>
<td>660</td>
<td>174</td>
<td>75</td>
<td>45</td>
</tr>
<tr>
<td>Central and South America</td>
<td>1654</td>
<td>570</td>
<td>924</td>
<td>340</td>
<td>102</td>
<td>50</td>
<td>7</td>
</tr>
<tr>
<td>Far East</td>
<td>777</td>
<td>290</td>
<td>360</td>
<td>28</td>
<td>247</td>
<td>186</td>
<td>18</td>
</tr>
<tr>
<td>Total</td>
<td>4722</td>
<td>1050</td>
<td>1911</td>
<td>1028</td>
<td>523</td>
<td>311</td>
<td>70</td>
</tr>
</tbody>
</table>

Areas given are for countries located between 22°N and 22°S. Information in columns 1 and 3-6 is taken from Food and Agricultural Organization [1978] and column 2 is from Persson [1974]. The areas in columns 7 and 8 for the Far East are taken from Spencer [1966]. The areas for Africa and Central and South America are estimated from the populations given in Table 12, and the assumptions that 0.15 ha of land is cleared annually per shifting cultivator and that the land is harvested for 2 years.

one, and to perhaps as many as three, molecules of CO [Zimmerman et al., 1978]. A recent laboratory study of oxidation initiated by reaction with OH [Cox et al., 1979] found evidence for production of formaldehyde, methyl vinyl ketone (CH3COCH = CH2) and methyl acrolein (CH2 = C(CH3)CHO) in the presence of NO. Production of such compounds is consistent with the oxidation mechanism postulated by Niki et al. [1978b] for reaction of OH with unsaturated hydrocarbons. One would expect that product carbonyl compounds should be photooxidized readily in the atmosphere with consequent production of CO. Oxidation of isoprene initiated by reaction with ozone should also lead to production of CO. Studies investigating the mechanism for reaction of O3 with simpler alkenes [Herron and Huie, 1977, 1978] show significant production of formaldehyde and other carbonyl compounds, and there is reason to believe that these species should be formed during photodecomposition of isoprene. It is probable that at least two molecules of CO should be produced during oxidation of isoprene even at very low ambient concentrations of NO, with uncertainty imposed largely by lack of knowledge of the possible role of heterogeneous chemistry for reactive intermediates.

Formation of particulate material may play an important role in the photodecomposition of terpenes such as α-pinene, β-pinene, 3-carene, and limonene [Went, 1960; Schuetzle and Rasmussen, 1978; Graedel, 1979]. These compounds are observed in forest environments with concentrations as high as 1 ppb [Holdren et al., 1979]. It is difficult to make a reliable estimate for production of CO due to oxidation of isoprene and other terpenes. The difficulty may be attributed to uncertainties in the atmospheric photochemistry of these species and lack of global data for the magnitude of the relevant biospheric source. We assumed for purposes of Table 8 a source for isoprene of magnitude 4 x 10^8 tons yr^-1, with a similar source for other reactive hydrocarbons, and we adopted a yield of two molecules of CO per hydrocarbon precursor. The source strength for CO obtained in this manner could be uncertain to at least a factor of 5. The upper limit for the corresponding source in Table 8 was obtained by imposing a constraint that production from all processes should not exceed

TABLE 18. Global Budgets for Trace Gases

<table>
<thead>
<tr>
<th>Species</th>
<th>Mixing Ratio a</th>
<th>k(OH + X) a</th>
<th>Molecules cm^-2 s^-1</th>
<th>Tons year^-1</th>
<th>Lifetime b (Years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>5.5-7</td>
<td>1.2-11</td>
<td>3.9 x 10^10</td>
<td>2.1 x 10^7</td>
<td>9.4</td>
</tr>
<tr>
<td>CH4</td>
<td>1.65-6</td>
<td>2.4-12</td>
<td>1.4 x 10^11</td>
<td>5.8 x 10^8</td>
<td>7.9</td>
</tr>
<tr>
<td>CH3Cl</td>
<td>6.0-10</td>
<td>2.20-12</td>
<td>3.8 x 10^8</td>
<td>5.2 x 10^6</td>
<td>1.0</td>
</tr>
<tr>
<td>CH3Br</td>
<td>2.0-11</td>
<td>7.90-13</td>
<td>1.2 x 10^3</td>
<td>3.0 x 10^3</td>
<td>1.1</td>
</tr>
<tr>
<td>C2H6</td>
<td>1.0-9</td>
<td>1.86-11</td>
<td>3.9 x 10^9</td>
<td>3.1 x 10^7</td>
<td>0.17</td>
</tr>
<tr>
<td>C2H2</td>
<td>2.0-11</td>
<td>1.91-12</td>
<td>...</td>
<td>...</td>
<td>0.06</td>
</tr>
<tr>
<td>C2H4</td>
<td>...</td>
<td>2.18-12</td>
<td>...</td>
<td>2 days</td>
<td></td>
</tr>
<tr>
<td>C2H8</td>
<td>1.0-9</td>
<td>7.40-11</td>
<td>...</td>
<td>0.2 days</td>
<td></td>
</tr>
</tbody>
</table>

a Mixing ratios for H2, CH4, CH3Cl and CH3Br were assumed to be uniform throughout the troposphere. Mixing ratios for C2H6, C2H2, and C2H4 were assumed to be uniform below 1 km. The notation 1.0-11 should be read as 1.0 x 10^-11.

b Photochemical loss rates were calculated from the OH profiles of Figure 27. Loss rates are given in tons of H2, CH4, etc.

c Average tropospheric lifetimes towards reaction with OH are given. For C2H6, C2H2, and C2H4 lifetimes are given for the boundary layer.

d The photochemical source of H2 from photolysis of CH2O is approximately equal to the photochemical sink by reaction with OH.

* Rate constant from NASA [1979].

† Rate constant from Atkinson et al. [1979].

‡ Rate constant from Cox et al. [1979].
the magnitude of the global removal rate for CO given earlier. The upper limit for CO production due to burning of biocatalytic material is similarly constrained.

It would appear that greatest uncertainty is attached to the combined roles of biocatalytic burning and hydrocarbon oxidation. One might attempt to use overall budget constraints to refine estimates for these terms. It is clear, for example, that the quantity of CO removed photochemically from the atmosphere in the northern hemisphere exceeds that removed by this mechanism in the southern hemisphere by about 6 x 10^8 tons CO yr^-1. Net transport of CO-rich air from north to south removes an additional 1.2 x 10^9 tons CO yr^-1 from the northern hemisphere. Uptake of CO by soils in the northern hemisphere exceeds that in the southern hemisphere by 1.7 x 10^6 tons CO yr^-1. This suggests that the source of CO in the northern hemisphere should exceed that in the southern hemisphere by about 1.0 x 10^7 tons CO yr^-1. A portion of this differential (4.8 x 10^8 tons CO yr^-1) is provided by combustion of fossil fuels and oxidation of anthropogenic hydrocarbons. The remainder, 5.4 x 10^8 tons CO yr^-1, must be produced largely by burning of biomass for purposes of agriculture and by oxidation of volatile biocatalytic hydrocarbons. Consideration of the geographical distribution of lands involved in shifting agriculture suggests that the agricultural source can account for at most a small part of the interhemispheric bias, about 1.4 x 10^8 tons CO yr^-1. It appears that most of the deficit should be attributed to a differentially larger source of CO in the northern hemisphere due to oxidation of isoprene and other hydrocarbons. Literal interpretation of the data in Table 8 suggests that the hemispheric and global budgets of CO would be balanced if we were to assume sources of CO from fossil fuels and oxidation of anthropogenic hydrocarbons equal to 7.9 x 10^8 and 4.6 x 10^8 tons CO yr^-1 in the northern and southern hemispheres, respectively. A bias in favor of the northern hemisphere would not be unreasonable in that 67% of the total land area of the earth is located in the northern hemisphere, with similar concentration of the land-based biosphere. The accuracy of various data in Table 8, in particular the interhemispheric distribution of the photochemical sink and the source from fossil fuel, however, is probably insufficient to justify such fine tuning of estimates for other components of the budget. It is clear that atmospheric considerations may be used to place valuable constraints on the magnitude of otherwise uncertain contributions to CO and that they may be employed to refine our understanding of the role of the biosphere.

A number of other gases are removed primarily by reaction with OH. A summary of computed rates for removal of CH_{4}, H_{2}, C_{2}H_{6}, CH_{2}Cl, and CH_{3}Br is given in Table 18, which includes data and assumptions made regarding abundances and distributions of these species.

6. DISCUSSION

Concentrations of OH obtained here are similar to those derived almost a decade ago by Levy [1971] and McConnell et al. [1971]. However, models for the troposphere have evolved considerably in the interim. Recent progress may be attributed to refinement in our understanding of rates for certain key reactions and to advances in instrumentation allowing measurement of a number of important tropospheric gases, notably NO. It is clear that the rate at which CO is oxidized by OH is sensitive to pressure [Bierman, 1978]. It appears that reaction of OH with H_{2}O_{2} is the major mechanism for removal of odd hydrogen. Previously, this rate was thought to be slow throughout the troposphere. The rate constant for reaction of NO with HO_{2} is 40 times larger than values used in models prior to 1976 [Howard, 1979]. The faster rate for (7) ensures more efficient cycling of OH from HO_{2}, maintaining a higher concentration of OH for any given concentration of NO. The impact of the change in rate for (7) on models for OH is offset in part by the observations of NO and NO_{2} [McFarland et al., 1979; Noxon, 1978] that imply concentrations for NO much lower than values reported earlier by Robinson and Robbins [1969].

Early analyses of observational data for CH_{3}CCl_{3} [Lovelock, 1977; Singh, 1977a, b; Derwent and Eggleton, 1978; McConnell and Schiff, 1978; Neely and Plonka, 1978; Chang and Penner, 1978] suggested lifetimes for CH_{3}CCl_{3} in the range 3 -11 years implying mean values for OH between 2.5 x10^6 cm^-3 and 10^6 cm^-3. Concentrations of OH obtained in this manner must be revised upward by a factor of about 1.3 to account for more recent measurements of the rate constant for reaction of OH with CH_{3}CCl_{3} [Kurylo et al., 1978; Jeong and Kaufman, 1979]. It is difficult, however, to relate the single number derived for OH in these studies to the complex distribution which must apply for the real atmosphere. Analysis of CH_{3}CCl_{3} in the present study involves comparison of observed and computed concentrations for the gas. The model indicates that about 70% of CH_{3}CCl_{3} is removed in the tropics. The global lifetime, obtained by integrating loss over latitude and altitude, is 5 years, and it should be emphasized that one-dimensional models are inappropriate in this case for calculation of the lifetime. In what follows we emphasize comparison of present results with two-dimensional studies. The model for OH given by Wofsy [1976] predates recent measurements for (3) and (7) and used concentrations for NO from Robinson and Robbins [1969]. Assumptions and choice of data made by Crutzen and Fishman [1977] and by Fishman et al. [1979] are more directly comparable to those employed in the present work.

Crutzen and Fishman [1977] reported a mean value of 2.5 x 10^6 cm^-3 for the concentration of OH in the northern hemisphere. Their model included an average over latitude, altitude, and season in the troposphere. Our model, on a similar basis, gives a mean value for the northern hemisphere of 1 x 10^6 cm^-3. The models are similar in their choice of quantum yields for O(D) and in the selection of data for other key parameters such as the rate constant for reaction of CO with OH and concentrations for O_{3}, CO and CH_{4}. Crutzen and Fishman [1977] used higher values for the concentrations of NO in the boundary layer, a choice that should result in larger, rather than smaller, values for OH as shown in Figure 3. Part of the discrepancy may be attributed to differences in the choice of rate constants for the reactions of O(D) with H_{2}O, N_{2}, and O_{2}. Crutzen and Fishman took rate constants from NASA [1977]. Use of more recent data for these reactions leads to an upward revision in the source of odd hydrogen by a factor of 1.8 but is not in itself sufficient to account for the discrepancy. Differences in the choice for H_{2}O_{2} lifetime in the two models also fail to account for the discrepancy (see Figure 24c and Table 7). Results could be reconciled if we were to assume that Crutzen and Fishman [1977] used concentrations for H_{2}O lower than values adopted here by a factor of about 3. The discrepancy might also reflect differences in the treatment of solar radiation (cf. Appendix 3).

Values for OH quoted by Fishman et al. [1979] are larger than those of Crutzen and Fishman [1977]. Fishman et al.
[1979] studied the functional dependence of OH on (NO + NO$_3$) and considered a range of models characterized by constant values for the mixing ratio for (NO + NO$_3$). Their model gave $3.8 \times 10^5$ cm$^{-2}$ for the mean concentration of OH in the northern hemisphere in the limit where NO was set equal to zero. Our results agree to within a factor of 2 with this more recent study. Detailed comparison is impossible, however, since Fishman et al., [1979] give only a partial summary of values used for rate constants and concentrations of background gases.

We argued that photochemistry should account for consumption of $3 \times 10^7$ tons CO yr$^{-1}$, with approximately 60% of the loss in the northern hemisphere. Loss of CO due to uptake by soil could provide additional removal of about $2.5 \times 10^4$ tons CO yr$^{-1}$, of which 80% might be expected in the northern hemisphere. We concluded that production of CO in the northern hemisphere should exceed production in the southern hemisphere by $1.0 \times 10^9$ tons CO yr$^{-1}$. Burning of fossil fuel accounts for part of the excess. There must be additional sources biased in favor of the northern hemisphere. These sources are attributed tentatively to oxidation of isoprene and other volatile biospheric hydrocarbons. Our budget for CO implies that approximately 60% of the global source is natural (biospheric hydrocarbons, wild fires, methane), while the remainder (fossil and wood fuels, agricultural burning) is directly or indirectly under the influence of man. If OH were a factor of 2 smaller than obtained here, as suggested by analysis of the budget for CH$_3$CCl$_3$, the estimates in Table 8 for CO sources from natural hydrocarbons and from biomass burning would be correspondingly reduced. In this case, 60% of the global source for CO would be attributed to human activities.

The distribution of odd nitrogen in clean air is an important component of current models for tropospheric photochemistry. We used calculated values for OH and observed distributions for HNO$_3$ to derive profiles for (NO + NO$_3$) consistent with the few available observations of these species in clean air. Concentrations derived for (NO + NO$_3$) are directly proportional to an uncertain parameter, the rate for heterogeneous loss of HNO$_3$. Loss rates adopted here correspond to a mean lifetime of 10 days for HNO$_3$, somewhat shorter than the lifetime implied by a recent study using a general circulation model [Mahlman and Maxim, 1978; Levy et al., 1980]. If removal rates for HNO$_3$ were reduced to agree with Levy et al. [1980], we would predict (NO + NO$_3$) concentrations equal to about 1/4 of those shown in Figure 12.

Our model implies a source strength for (NO + NO$_3$) in the remote troposphere of about $10^7$ tons N yr$^{-1}$. The source would be smaller if the lifetime for heterogeneous removal of HNO$_3$ were longer than we assumed. It appears that the magnitude of the source of odd N from lightning must be significantly smaller than some recent estimates, which range from 0.4-9 x $10^7$ tons N yr$^{-1}$. A source in excess of $10^7$ tons N yr$^{-1}$ could be accommodated only if the mean residence time for HNO$_3$ were very short (less than 10 days) or if odd N produced by lightning were removed efficiently in the rain cloud.

The model indicates consumption of O$_3$ by gas phase tropospheric chemistry at an average rate of $2 \times 10^{11}$ molecules cm$^{-2}$ s$^{-1}$. About two thirds of the loss occurs in the tropics. Heterogeneous chemistry provides an additional, more distributed sink, about $7 \times 10^{10}$ molecules cm$^{-2}$ s$^{-1}$ [Fabian and Junge, 1970; Galbally and Roy, 1980]. The total removal rate is significantly higher than the source from the stratosphere, 5-8 x $10^{10}$ molecules cm$^{-2}$ s$^{-1}$ [Danielson and Mohnen, 1977; Mahlman et al., 1980; Gidel and Shapiro, 1980]. It is balanced in the present model by photochemical production associated with oxidation of CO and CH$_4$. The magnitude of the photochemical source is proportional to NO but less sensitive to CO. The balance obtained for O$_3$ provides indirect support for the distribution calculated for NO.

A well-calibrated and reliable model for OH places important constraints on global budgets for a variety of gases including CH$_4$, H$_2$, and CH$_3$Cl in addition to CO. Accurate measurements of species such as CH$_3$CCl$_3$ can provide valuable checks on global models that must integrate over a variety of atmospheric conditions (cloudiness, moisture, etc.). However, emission rates for the relevant gases must be adequately quantified. Kinetic features of models are best tested by selected local measurements of OH, with simultaneous definition of radiation, H$_2$O, O$_3$, CO, CH$_4$, and NO. Local measurements, however, cannot substitute for more inclusive tests attended by measurement of globally dispersed gases such as CH$_3$CCl$_3$. Such tests are hampered at present by discrepancies in concentrations measured by different observers and by uncertainties in estimates of global emission rates. We believe that present results for the global distribution of OH are accurate to about a factor of 2. Similar accuracy may be attached to the global source strengths quoted for a number of gases in Table 18. These gases reflect the complex metabolism of the biosphere. Studies of tropospheric chemistry can provide important, indeed invaluable, information on the overall function of the global ecosystem. Further observational and theoretical work is required to realize this potential.

**APPENDIX 1. ROLE OF AEROSOLS IN CHEMISTRY OF PEROXIDES**

Hydrogen peroxide and organic peroxides (CH$_3$OOH, ROOR') may be removed from the atmosphere by heterogeneous reactions involving aerosols. Observations of aerosols in the marine boundary layer imply a volume of particles per unit volume of air ('specific volume') in the range 5-20 x $10^{-12}$ cm$^3$ cm$^{-3}$. The surface area of the particles lies typically between $1 \times 10^{-7}$ and $8 \times 10^{-7}$ cm$^2$ cm$^{-3}$ [Jaenicke et al., 1971; Junge, 1963, 1972; Mesaroz and Vissy, 1974; Jaenicke, 1978; Parungo et al., 1979]. Somewhat larger concentrations of aerosols are observed in clean continental areas (specific volumes of $5-30 \times 10^{-12}$ cm$^3$ cm$^{-3}$ and specific areas of about $2 \times 10^{-4}$ cm$^2$ cm$^{-3}$ [Junge, 1963; Jaenicke et al., 1978; Whitby, 1978]) while aerosol concentrations in the upper troposphere are at least a factor of 10 lower than those in the marine boundary layer [Toba, 1965; Blifford and Ringer, 1969; Blifford, 1970; Etterman, 1969; Bigg, 1977; Gras and Michael, 1979]. Values adopted for the aerosol size distribution are given in Table 1.

It seems reasonable to assume that the physical properties of aerosols should be similar to those of liquid water droplets or of solid particles coated with liquid water [cf. Ho et al., 1974]. In this case, partitioning of ambient H$_2$O between gas and aerosol phases may be estimated from solubility data for H$_2$O in water [Scatchard et al., 1952]. We find at equilibrium that the fraction of peroxide molecules contained in or on aerosols should be quite small, about $5-30 \times 10^{-6}$ for the marine boundary layer or upper troposphere. Furthermore, the time required to achieve equilibrium should be less than 10 s. This estimate is based on the observed aerosol size distribution and on a sticking probability of $10^{-2}$ for H$_2$O colliding with an aerosol [Baldwin and Golden, 1979].
Since only a small fraction of ambient H₂O₂ resides in the aerosol phase, destruction in aerosols would be negligible compared to homogeneous loss (5 × 10⁻⁶ s⁻¹) unless the loss frequency for absorbed molecules was quite large (>0.2 s⁻¹). Aqueous peroxide can be photolyzed, or it can react with oxidizable species, but loss frequencies associated with these reactions are likely to be much slower than 0.2 s⁻¹. Photolysis rates for dissolved H₂O₂ are less than 10⁻⁴ s⁻¹ [Molina et al., 1977; Lin et al., 1978]. Reactions of aqueous H₂O₂, with I⁻, SO₃⁻, or Fe⁺⁺ are slow even at 25°C, with rate constants of 1.2 × 10⁻⁹, 0.2, and 63 1 mole⁻¹ s⁻¹, respectively, and these reactions have large activation energies [Edwards, 1962; Behrman and Edwards, 1967; Bamford and Tipper, 1972]. Thus the concentration of ferrous iron (Fe⁺⁺) in natural aerosols would have to exceed 2 mmol 1⁻¹ in order to oxidize of this species to represent a significant sink for atmospheric H₂O₂. The concentration of sulfite (SO₃⁻) would have to exceed 1000 mmol 1⁻¹. Marine and background aerosols appear to contain much smaller concentrations of such species [Junge, 1963]. However, air parcels influenced by urban pollution have considerably higher concentrations of aerosols [Whitby, 1978] and might contain sufficient quantities of reduced material to provide an efficient sink for atmospheric H₂O₂. Note that if rapid chemical destruction of H₂O₂ were to occur in natural aerosols, the loss rate would be limited by supply of H₂O₂ to particle surfaces. For a sticking probability of 10⁻³, this limit corresponds to an effective removal frequency of about 5 × 10⁻⁴ s⁻¹ in the boundary layer.

In summary, the limited data available for aerosol distributions and for solution chemistry of H₂O₂ suggest that aerosol processes do not represent a significant sink for H₂O₂ in clean air. Similar arguments may be advanced for CH₃OH, OH, and HO₂. Aerosol losses could be marginally important for HO₂ if the sticking probability were anomalously high (≥0.1) and if destruction of adsorbed HO₂ were instantaneous [Warneck, 1974]. In this case, OH concentrations would be reduced slightly (1-5%). It is possible, however, that aerosols could play an important role in removal of peroxides (including HO₂) from the polluted atmosphere, and in clouds these species would be significantly depleted by solution in liquid droplets.

APPENDIX 2. MODEL DESCRIPTION

The photochemical model discussed here is similar to the stratospheric model described by Wofsy [1978] and Logan et al. [1978]. Numerical methods are the same as those of the earlier work. Distributions for the long-lived gases (H₂O, O₃, CO, CH₄, and H₂) are prescribed as functions of latitude and season using observational data (see Table 4). The vertical resolution of the model is 2 km except near the ground where computations are carried out at 0, 0.5, 1, and 2 km. The latitudinal resolution is 15° from 0° to 60° latitude. Atmospheric structure (T, P) [U.S. Standard Atmosphere Supplements, 1966] and stratospheric ozone profiles [Herling and Borden, 1975] are specified.

Distributions for NOx could not be specified from available data and were derived therefore from a series of one-dimensional eddy diffusion calculations. Nitric acid and NOx (= NO + NO₂ + NO₃ + N₂O₅ + ClNO₂ + HNO₃ + HO₂ NO₃) were allowed to diffuse separately. Partitioning among NOx species and rates of chemical interchange between HNO₃ and NOx were calculated by using the photochemical model discussed in the text. The vertical transport coefficient was taken as constant (10⁷ cm² s⁻¹) from the ground to 2 km below the tropopause. A somewhat smaller value (3 × 10⁶ cm² s⁻¹) was adopted in the upper 2 km of the troposphere. (Concentrations of NOx are insensitive to the vertical transport coefficient except near the boundaries.) The transport parameterization did not attempt to simulate in detail the boundary layer near the surface. The lowest 100 m may be shown to have little influence on the global budgets of interest here.

The NOx model was run for four seasons in each hemisphere at latitudes of 15° and 45°. The following boundary conditions were adopted:

1. A downward flux of (HNO₃ + NO₃) was assumed across the tropopause, with magnitude 1.4 × 10⁶ cm⁻² s⁻¹. This value was calculated in two-dimensional and three-dimensional model studies [Wofsy, 1978; Logan et al., 1978; Levy et al., 1980] as the net flux resulting from photolysis of stratospheric N₂O (2 × 10⁸ cm⁻² s⁻¹), less recombination of NO with N (6 × 10⁷ cm⁻² s⁻¹). The relative abundances of HNO₃ and NO₃ at the upper boundary were fixed at a global mean value (7:1) derived from model calculations.

2. A relatively large deposition velocity (0.5 cm s⁻¹) was adopted for HNO₃ at the surface, reflecting the high reactivity and solubility of the gas.

3. Rainout and washout of HNO₃ were parameterized as given in Table 1, consistent with the recent discussion of Levine and Schwartz [1981]. The lifetime for tropospheric HNO₃ in the model had a mean value of 10 days.

4. The surface flux of NOx was set equal to zero over the oceans (model A). The concentration of odd nitrogen was prescribed over the continents (model B) to have a value of 100 ppt at the ground.

5. Oxidation of NH₃, lightning, and other processes were assumed to produce an in situ source of NO distributed through the troposphere as shown in Figure 12. The height-integrated magnitude of this source was set equal to 3 × 10⁶ cm⁻² s⁻¹.

The budget studies of CH₃CCl₃, CFCl₃, CF₂Cl₂, and CO employed the box model for tropospheric transport described in section 5. Profiles for OH were calculated in each box at an appropriate mean latitude (45°N, 15°N, 15°S, and 45°S) for four seasons. Separate calculations were performed for marine and continental distributions of NOx (models A and B, respectively) weighted by appropriate ocean/land coverage in each box. More detailed latitude resolution produced insignificant changes (<5%) in global budgets. Production and loss rates for various species (CO, CH₄, CH₃CCl₃, etc.) were calculated by suitably weighting these 32 calculations.

Since completion of the calculations presented here, revised rate constant data have been reported for reactions involving HNO₃ and HO₂NO₂ [NASA, 1981]. Incorporation of these data in the model leads to slight reduction (<5%) in calculated concentrations of OH. The model indicates significant concentrations of H₂O₂NO₃ in the colder regions of the middle and upper troposphere, ([H₂O₂NO₃] ≈ [HNO₃]). The new rates reduce photochemical production of O₃ by as much as 20% at midlatitudes, by ~5% in the tropics, but have only minor influence on budgets for CH₄, CO, CH₃CCl₃, etc.

APPENDIX 3. INFLUENCE OF AEROSOLS AND CLOUDS ON THE MEAN INSOLATION

Estimates of rates for photolysis of O₃ and NOx require accurate computation of the ultraviolet radiation field. The intensity of light in the troposphere is determined by the extra-
TABLE A1. Ultraviolet Fluxes and Cross Sections

<table>
<thead>
<tr>
<th>$\lambda$(Å)</th>
<th>$F_\lambda$(photon cm$^{-2}$ s$^{-1}$) in 50 Å Interval</th>
<th>$\sigma_{o\lambda}$(cm$^2$)</th>
<th>O($^1D$) Quantum Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2825</td>
<td>2.00 x 10$^{14}$</td>
<td>27 x 10$^{-19}$</td>
<td>1.00</td>
</tr>
<tr>
<td>2875</td>
<td>2.70</td>
<td>16</td>
<td>1.00</td>
</tr>
<tr>
<td>2925</td>
<td>3.63</td>
<td>10</td>
<td>1.00</td>
</tr>
<tr>
<td>2975</td>
<td>3.88</td>
<td>4.7</td>
<td>1.00</td>
</tr>
<tr>
<td>3025</td>
<td>3.97</td>
<td>2.6</td>
<td>0.98</td>
</tr>
<tr>
<td>3075</td>
<td>4.64</td>
<td>1.4</td>
<td>0.63</td>
</tr>
<tr>
<td>3125</td>
<td>5.43</td>
<td>0.68</td>
<td>0.09</td>
</tr>
<tr>
<td>3175</td>
<td>6.18</td>
<td>0.36</td>
<td>0.00</td>
</tr>
<tr>
<td>3225</td>
<td>6.99</td>
<td>0.18</td>
<td>0.00</td>
</tr>
<tr>
<td>3275</td>
<td>7.79</td>
<td>0.077</td>
<td>0.00</td>
</tr>
<tr>
<td>3325</td>
<td>8.09</td>
<td>0.041</td>
<td>0.00</td>
</tr>
<tr>
<td>3375</td>
<td>8.33</td>
<td>0.020</td>
<td>0.00</td>
</tr>
<tr>
<td>3425</td>
<td>8.59</td>
<td>0.007</td>
<td>0.00</td>
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<tr>
<td>3475</td>
<td>8.85</td>
<td>0.004</td>
<td>0.00</td>
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<tr>
<td>3525</td>
<td>9.13</td>
<td>0.002</td>
<td>0.00</td>
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<tr>
<td>3575</td>
<td>9.56</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3625</td>
<td>10.05</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3675</td>
<td>10.25</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3725</td>
<td>10.15</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3775</td>
<td>10.05</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3825</td>
<td>10.3</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>3875</td>
<td>11.4</td>
<td></td>
<td>0.00</td>
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<tr>
<td>3925</td>
<td>13.6</td>
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<td>0.00</td>
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<tr>
<td>3975</td>
<td>16.3</td>
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</tr>
<tr>
<td>4025</td>
<td>17.1</td>
<td></td>
<td>0.00</td>
</tr>
</tbody>
</table>

The influence of aerosols and clouds must be included in a realistic calculation of the tropospheric radiation field. Data collected by the World Meteorological Organization (WMO) [1972–1976] show that the contribution of aerosols to the optical depth at 3100 Å is about 0.4, on average, for tropical sites, and also for mid-latitude locations during summer. Extinction by aerosols is less important in winter at middle and high latitudes. Observations of turbidity by McCartney and Unsworth [1978] and Elterman et al. [1969] indicate aerosol extinction similar to that derived from the WMO network. More than half of the aerosol extinction occurs in the lowest 2 km of the atmosphere, although as much as 20% may be distributed through the middle and upper troposphere [Elterman et al., 1969].

Optical depths associated with extinction by aerosols are comparable to the optical depth due to Rayleigh scattering, about 1.2 at 3100 Å [Edlen, 1953; Penndorf, 1957]. Extinction by natural aerosols results from both scattering and absorption. Fischer [1973], Hanel [1976], Levin and Lindberg [1979], and Gerber [1979] report absorption amounting to 11–37% of scattering for a variety of marine and continental aerosols collected at unpolluted sites. We adopt a single scattering albedo of 0.75 for tropospheric aerosols, consistent with these observations [Livshits, 1977; Hanel, 1976; Gerber, 1979].

Figure 30 compares calculated extinction with data obtained by Stair et al. [1952, 1954, 1958] at several clean mountain locations. Daily minimum values for the optical depth at terrestrial solar flux, transmission through the stratosphere, absorption and scattering by tropospheric gases and aerosols, and reflection from clouds and the earth's surface. The flux of solar radiation was taken from recent observations [Vernazza et al., 1976], averaged over 50 Å intervals, as given in Table A1. Absorption cross sections were averaged over the same intervals. The influence of attenuation, molecular scattering, and reflection was modeled in each wavelength interval by the equation of radiative transfer for an inhomogeneous, plane-parallel atmosphere [Chandrasekhar, 1960]. A second-order finite difference scheme [Prather, 1974] was used to solve for the intensity of radiation at three quadrature angles. The angular distribution of light scattered by air molecules was approximated by Rayleigh's phase function.

The influence of wavelength resolution was examined by carrying out calculations for wavelength intervals of 10 Å. Rates for important photolytic processes, for example production of O($^1D$), changed by less than 2%. We conclude that negligible error is introduced by averaging solar flux and absorption cross sections over the wavelength intervals adopted here.

The influence of aerosols and clouds must be included in a realistic calculation of the tropospheric radiation field. Data collected by the World Meteorological Organization (WMO) [1972–1976] show that the contribution of aerosols to the optical depth at 3100 Å is about 0.4, on average, for tropical sites, and also for mid-latitude locations during summer. Extinction by aerosols is less important in winter at middle and high latitudes. Observations of turbidity by McCartney and Unsworth [1978] and Elterman et al. [1969] indicate aerosol extinction similar to that derived from the WMO network. More than half of the aerosol extinction occurs in the lowest 2 km of the atmosphere, although as much as 20% may be distributed through the middle and upper troposphere [Elterman et al., 1969].

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performed with a variety of models for scattering and absorp-
tion of \( \text{O}(1\text{D}) \) (see dashed curve in Figure 32). It ap-
tunities at low sun angles, with corresponding en-
significant reduction in the intensity of UV light, with a corre-
and aerosols leads to sig-
rate of \( \text{O}(1\text{D}) \) are shown in Figure 31. The calculations were
for summer at Boulder, Colorado, are compared in Figure 32
and 0.055 to 0.156 at the tropics and 0.087 to 0.095 at mid-
light of \( \text{O}(1\text{D}) \) production
ears that the observed variability of \( \text{O}(1\text{D}) \) production
pears as a function of the slant path column of ozone. The corrected \( \text{J}(\text{O}(1\text{D})) \)
values of Dickerson et al. [1979, 1980] are shown as a function of the
overhead ozone column and the solar zenith angle (\( \theta \)). The theoretical
calculations are described in Appendix 3 and used the 45°N July at-
sphere with a lower boundary of 300°K at 1.8 km. The shape of the
zome profile was taken from Kruge and Minzer [1976] with a
albedo of 0.35 to 0.4 at 4500 Å. These haze models span the range of size distribu-
tions reported by London [1952]. The model repro-
cures reported by London [1952]. The model repro-
ues of Dickerson et al. [1979, 1980] are shown as a function of the
These haze models span the range of size distribu-
tions observed for natural aerosols [Junge, 1972; Meszaros and
1978; Jaenicke, 1978]. The radiative transfer equation was solved in a manner similar to
that described above but with 20 quadrature angles. The fig-
ure shows that scattering by aerosols is unimportant for opti-
cal depths typical of clean conditions. This result follows from
the forward-peaked scattering that characterizes natural haze.

Model calculations for production of \( \text{O}(1\text{D}) \) at Boulder, Colorado, are compared in Figure 32 with observations by Dickerson [1980]. Model and observations agree fairly well at small solar zenith angles. Observations are significantly higher (~70%) than calculations, however, when the sun is low in the sky. Specular reflection of sunlight might increase the e-
sive ground albedo at low sun angles, with corresponding en-
hancement of \( \text{J}(\text{O}(1\text{D})) \) (see dashed curve in Figure 32). It ap-
ears that the observed variability of \( \text{O}(1\text{D}) \) production
Dickerson et al., 1979; Dickerson, 1980] may be mediated largely by fluctuations in atmospheric aerosols.

Cloudiness plays a major role in determining the intensity of solar radiation in the troposphere, and the mean concentra-
tion of \( \text{OH} \) is sensitive to the global distribution of clouds. We
measured the net effects of clear, cloudy, and partly cloudy condi-
tions by averaging radiation fields for cloudy and cloudy-
free atmospheres. Cloud layers were represented by totally re-

ducing the mean insolation observed at ground stations [Burt and

The distribution of cloud cover given by London [1952] has been
calculated the net effects of clear, cloudy, and partly cloudy condi-
tions by averaging radiation fields for cloudy and cloud-
free atmospheres. Cloud layers were represented by totally re-
flecting Lambertian surfaces with cloud coverage adjusted to

tropics and 0.35 at mid-latitudes [Raschke et al., 1973; Jacob-
bowitz et al., 1979]. Cloud heights were chosen to reflect the
distribution reported by London [1952]. The model repro-
uses reported by London [1952]. The model repro-
ues of Dickerson et al. [1979, 1980] are shown as a function of the

FIG. 31. Mean intensity of radiation at 3500 Å in the troposphere. The calculations were made with a 45°N summer atmosphere and a solar zenith angle of 30°. The right panel shows results for a clear, molecular atmosphere with Lambertian ground albedos of 0.10 and 0.35. This panel also shows the effects of the mean mid-latitude cloud model that has a planetary albedo of 0.35 and a ground albedo of 0.10 (curve C, see also Table 6). The left panel shows the effect of including aerosol scattering (S) and absorption (A) in the model, which has a ground albedo of 0.1. Curve M includes only molecular scattering. Curve S includes an aerosol extinction of 0.4, with a single scattering albedo of \( \omega = 1.00 \). Curve S+A includes the same aerosol extinction with \( \omega = 0.75 \). Curve A includes only the aerosol absorption component of S+A (i.e., total extinction of 0.1 with \( \omega = 0.00 \)). In these calculations, aerosols are assumed to have a 2-km scale height and a scattering phase function described by Deirmendjian [1969] (haze L at 4500 Å).

3100 Å due to aerosols is observed to be in excess of 0.08 on
75% of clear days at Mauna Loa [WMO, 1972–1976, statistics
for May], and the figure suggests that similar values may appli-
cate at other mountain sites. Thus, aerosols may contribute to
extinction of sunlight even under very clear conditions.

The omnidirectional intensity at 3500 Å and the production
rate of \( \text{O}(1\text{D}) \) are shown in Figure 31. The calculations were
performed with a variety of models for scattering and absorp-
tion by aerosols, with conditions appropriate for summer at
mid-latitudes. The angular dependence of scattering by aero-
sols was represented by Deirmendjian's [1969] haze L, H, or M
(4500Å). These haze models span the range of size distribu-
tions observed for natural aerosols [Junge, 1972; Meszaros and
Visny, 1974; Hanel and Bullrich, 1978; Jaenicke, 1978]. The radiative
transfer equation was solved in a manner similar to
that described above but with 20 quadrature angles. The fig-
ure shows that scattering by aerosols is important for optical
depths typical of clean conditions. This result follows from
the forward-peaked scattering that characterizes natural haze.
On the other hand, absorption by aerosols leads to signif-
ificant reduction in the intensity of UV light, with a corre-
sponding decrease in production of \( \text{O}(1\text{D}) \). The marked differ-
ence between these results and Fiocco et al. [1979] reflects
their choice of single-scattering albedo (0.99) and their selec-
tion of a size distribution for aerosols dominated by very small
(Rayleigh) particles.

Model calculations for production of \( \text{O}(1\text{D}) \) at Boulder,
Colorado, are compared in Figure 32 with observations by Dickerson [1980]. Model and observations agree fairly well at small solar zenith angles. Observations are significantly higher (~70%) than calculations, however, when the sun is low in the sky. Specular reflection of sunlight might increase the effective ground albedo at low sun angles, with corresponding enhancement of \( \text{J}(\text{O}(1\text{D})) \) (see dashed curve in Figure 32). It appears that the observed variability of \( \text{O}(1\text{D}) \) production
Dickerson et al., 1979; Dickerson, 1980] may be mediated largely by fluctuations in atmospheric aerosols.

Cloudiness plays a major role in determining the intensity of solar radiation in the troposphere, and the mean concentration of \( \text{OH} \) is sensitive to the global distribution of clouds. We calculated the net effects of clear, cloudy, and partly cloudy conditions by averaging radiation fields for cloudy and cloud-free atmospheres. Cloud layers were represented by totally reflecting Lambertian surfaces with cloud coverage adjusted to give the observed mean albedo of the earth, about 0.25 in the tropics and 0.35 at mid-latitudes [Raschke et al., 1973; Jacob-
bowitz et al., 1979]. Cloud heights were chosen to reflect the distribution reported by London [1952]. The model reproduces the mean insolation observed at ground stations [Burt and Quinn, 1967].

### TABLE A2. Global Mean Cloud Distribution

<table>
<thead>
<tr>
<th>Cloud Type</th>
<th>Albedo ( \rho )</th>
<th>Altitude, km</th>
<th>Tropics</th>
<th>Mid-latitudes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cirrus</td>
<td>0.20</td>
<td>9</td>
<td>0.081</td>
<td>0.107</td>
</tr>
<tr>
<td>Cumulonimbus</td>
<td>0.90</td>
<td>5</td>
<td>0.069</td>
<td>0.125</td>
</tr>
<tr>
<td>Nimbostratus</td>
<td>0.70</td>
<td>3</td>
<td>0.087</td>
<td>0.095</td>
</tr>
<tr>
<td>Cumulus</td>
<td>0.50</td>
<td>1.5</td>
<td>0.055</td>
<td>0.156</td>
</tr>
<tr>
<td>Stratus</td>
<td>0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average surface</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Land</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( \* \) Conover [1965].

\( ^\text{a} \) The distribution of cloud cover given by London [1952] has been
calculated to give an albedo of 0.25 in the tropics and 0.35 at mid-latitudes [Raschke et al., 1973].
Table A2 gives a summary of parameters used to calculate the radiation field for global-average conditions. The standard model incorporates absorption and scattering by molecules and absorption due to aerosols (curve A in Figure 31). Scattering by aerosols is neglected.

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