Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air

By PAUL J. CRUTZEN,[1] *National Center for Atmospheric Research,*[2] *and University of Colorado, Boulder, Colorado 80302*

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ABSTRACT

This paper presents theoretical arguments in favour of OH-concentrations larger than 10^6 molecules cm^{-3} in the sunlit lower troposphere even if allowance is made for heterogeneous removal of OH, HO_2 and HNO_3 molecules. The OH-concentrations, presented in this paper, were calculated considering for the first time the photochemical effect of both scattered and direct radiation at ground levels and adopting recent accurate data for the quantum efficiency of $O(^1D)$ production in the ozone photolysis near 310 nm. The significant role played by OH in the atmospheric carbon, nitrogen and possibly sulphur cycles is discussed. Low background mixing ratios of NO_x molecules ($< 10^{-9}$) in the unpolluted atmosphere are calculated. The oxidation of NH_3, initiated by the reaction with OH, may provide a significant source of tropospheric NO_x-molecules, if its rate constant is about 10^{-13} cm^3 s^{-1} near the ground. The conversion of NO_2 into HNO_3, followed by heterogeneous removal of HNO_3, is the most important tropospheric sink for NO_x-molecules. The photodissociation of ozone in ultraviolet light between 300 and 330 nm, which leads to the formation of the excited $O(^1D)$ atom, "drives" several sequences of reactions treated in this study. Several chains of reactions, involving carbon and nitrogen compounds, lead to large rates of formation and destruction of ozone in the troposphere. These rates partly balance each other. Whether there is a net production or destruction of ozone in the troposphere cannot be determined at present. Ozone is a very active, catalytic component in the tropospheric chemical systems. Globally, the combustion source of CO for the year 1970 is more than 20 % of the natural source of CO as provided by the oxidation of biologically produced CH_4. For middle latitudes of the Northern Hemisphere the combustion source is about equal to the natural source. However, too little is known about homogeneous and heterogeneous reactions affecting the methane oxidation products.

1. Introduction

During unfavourable meteorological conditions ozone appears as an important, unhealthy ingredient in sunlit atmospheres which are polluted through intense car traffic. In such cases, ozone is a product of chemical reactions taking place between unburnt hydrocarbons, oxides of nitrogen and related species, under the influence of sunlight (Haagen-Smit, 1952; Leighton, 1961). Interest in the detailed mechanism of photochemical "smog" formation has been intense (e.g. Altshuller & Bufalini, 1971; Westberg & Cohen, 1969; Kerr et al., 1972). In the stratosphere and mesosphere ozone is produced by the photodissociation of molecular oxygen and recombination of the oxygen atom with the oxygen molecule. The photochemistry of ozone in the before mentioned regions of the atmosphere has been studied extensively. On the other hand, very few photochemical studies have been made of background ozone in the unpolluted troposphere. Most studies of tropospheric ozone were concerned with the exchange processes between the stratosphere and troposphere (see for example: Fabian et al., 1971). However, after Levy's important proposal (1971) that significant quantities of the very reactive OH-radical are produced in the sunlit natural atmosphere by the interaction between ozone, ultraviolet light and water vapour, it has now become clear that the presence of ozone in the

[1] Present address: Meteorological Institute, University of Stockholm, Sweden.

[2] The National Center for Atmospheric Research is sponsored by the National Science Foundation.

troposphere is of large importance for the chemistry of this region of the atmosphere. It was estimated that the oxidation of biologically produced methane, which is initiated by its reaction with OH, leads to a natural global production of carbon monoxide, at least a factor of ten larger than that presently provided in the car exhaust and by industrial processes (McConnell et al., 1971; Levy, 1972; Weinstock & Niki, 1972; Jaffe, 1973).

It has commonly been assumed that almost all of the ozone in the troposphere is of stratospheric origin, that no significant production or destruction of ozone can take place within the troposphere, and that ozone is destroyed mainly by contact with the material of the earth's surface. After measuring the decay with time of mechanically well-mixed ozone inside a box, which was placed over different types of surfaces, Aldaz (1971) estimated the mean global ozone destruction rate at the earth's surface to be between 1.1×10^{11} and 1.6×10^{11} molecules cm^{-2} s^{-1}. By taking into account the normal transfer of ozone in the atmospheric boundary layer, however, Fabian & Junge (1970) proposed a reduction of these estimates to 3.6×10^{10} and 6.0×10^{10} molecule cm^{-2} s^{-1}. A large uncertainty in these estimated values remained due to inadequate knowledge of ozone destruction rates at the sea surface. An extensive series of measurements of ozone profiles above sea surface under different wind conditions led Tiefenau & Fabian (1972) to conclude that the global mean destruction rate of ozone, by contact with the earth's surface, is less than 4.9×10^{10} molecules cm^{-2} s^{-1}.

Crutzen (1972*b*, 1973), in agreement with Ripperton & Vukovich (1971), came to the conclusion that ozone in the unpolluted troposphere is not an inert gas and pointed out several photochemical reaction chains among ozone, methane-oxidation products and oxides of nitrogen which could bring about significant rates of production or destruction of ozone in comparison with the estimated rate of destruction of ozone by contact with ground material. Some observational evidence of photochemical or chemical production and destruction of ozone in the unpolluted atmosphere does indeed exist (Kelley & McTaggart-Cowan, 1968; Ripperton & Vukovich, 1971). This paper reports a further study of the role of ozone in tropospheric chemistry. Quantitative estimates will be made of ozone production and destruction rates in an atmosphere containing H_2O and the trace gases HN_3, CH_4, CO, NO_x and related chemical species. The chemical processes affecting these and other trace gases and the role of heterogeneous reactions (Warneck, 1974) will be discussed.

2. Discussion of the reaction chain

The set of reactions, considered to be of importance for this study, is shown in Table 1 and is similar to that adopted by Levy (1972, 1973*a*); Wofsy et al. (1972) and Crutzen (1971, 1972*b*). Most of the rate coefficients, which were used in this study, were derived from the references in these studies or from a recent NBS report (Garvin, 1973). However, for a number of reactions recent laboratory work was taken into account: R1a (Demore, 1973*b*; Johnston et al., 1973*b*), R7 (Anderson & Kaufman, 1973), R10a (Davis et al., 1973), R10b (DeMore, 1973*a*; Simonaitis & Heicklen, 1973), R12 (Johnston & Graham, 1973*a*), R20 (Hochanadel et al., 1972), R24 (Johnston & Graham, 1973*b*), R26 (Harker & Johnston, 1973), R29 (Davis, 1973), R39 (Stuhl, 1973*a*). Johnston (1973) claims that reaction R25b does indeed occur and has recently measured the absorption cross sections of NO_3, which were adopted in this study. The rate coefficient for reaction R11b is theoretically estimated, applying Lindemann theory and making use of the parameters derived for reaction R11a (Simonaitis & Heicklen, 1972). The followed approach is uncertain and experimental data are strongly needed for reaction R11b. Reactions R29–R38 of the methane oxidation chain were discussed by Heicklen (1968) and Levy (1972). Little is known, however, about the coefficients for the reactions R31–R35 and R38. A few adopted values of reaction coefficients are only estimations as no measurements have been made. Such reactions and other critical reactions with insufficiently known rate constants are indicated in Table 1 with an asterisk.

Included in this study are also a number of heterogeneous processes, affecting HO_2, HNO_3 and H_2O_2, in order to indicate their possible importance (Warneck, 1974). This is done by comparing the results obtained when the heterogeneous reactions are neglected with those ob-

Table 1. *List of reactions used in this study*

The units adopted for the reaction coefficients are s^{-1}, cm^3 molecule^{-1} s^{-1}, and cm^6 molecule^{-2} s^{-2} for unimolecular, bimolecular and termolecular reactions respectively

Reactions				Reaction coefficient
R1a*	$O_3 + h\nu$	→	$O(^1D) + O_2$	$\lambda \leqslant 330$ nm $J_{1a} = 8.5 \times 10^{-6}$
R1b	$O_3 + h\nu$	→	$O + O_2$	$\lambda \leqslant 1.1\ \mu$ $J_{1b} = 3.0 \times 10^{-4}$
R2	$O + O_2 + M$	→	$O_3 + M$	$k_2 = 1.1 \times 10^{-34} \exp(500/T)$
R3	$O(^1D) + M$	→	$O + M$	$k_3 = 6.0 \times 10^{-11}$
R4	$O(^1D) + H_2O$	→	$2OH$	$k_4 = 3.5 \times 10^{-10}$
R5	$NO + NO_2 + H_2O$	→	$2HNO_2$	$k_5 = 1.0 \times 10^{-34}$
R6a	$OH + OH(+M)$	→	$H_2O_2(+M)$	$k_{6a} = 1.0 \times 10^{-30}$
R6b	$HO_2 + HO_2$	→	$H_2O_2 + O_2$	$k_{6b} = 2.5 \times 10^{-12}$
R6c	$H_2O_2 + h\nu$	→	$2OH$	$\lambda < 536$ nm $J_{6c} = 3.3 \times 10^{-6}$
R7	$O_3 + OH$	→	$HO_2 + O_2$	$k_7 = 1.3 \times 10^{-12} \exp(-950/T)$
R8	$CO + OH$	→	$H + CO_2$	$k_8 = 2.1 \times 10^{-13} \exp(-115/T)$
R9	$H + O_2 + M$	→	$HO_2 + M$	$k_9 = 3.0 \times 10^{-32}$
R10a*	$NO + HO_2$	→	$OH + NO_2$	$k_{10a} = 5.0 \times 10^{-13}$
R10b*	$O_3 + HO_2$	→	$OH + 2O_2$	$k_{10b} = 3 \times 10^{-15}$
R11a	$OH + NO_2(+M)$	→	$HNO_3(+M)$	$k_{11a} = 5.0 \times 10^{-12}$
R11b*	$HO_2 + NO + M$	→	$HNO_3 + M$	$k_{11b} = 5 \times 10^{-33}$ (estimate)
R12	$HNO_3 + h\nu$	→	$OH + NO_2$	$\lambda < 546$ nm $J_{12} = 3.4 \times 10^{-7}$
R13	$OH + NO(+M)$	→	$HNO_2(+M)$	$k_{13} = 1.5 \times 10^{-12}$
R14	$HNO_2 + h\nu$	→	$OH + NO$	$\lambda < 485$ nm $J_{14} = 5.0 \times 10^{-4}$
R15*	HNO_3 + aerosol	→	nitrates	see text, $k_{15} = 5 \times 10^{-6}$
R16*	H_2O_2 + aerosol	→	products	see text, $k_{16} = 0$
R17*	HO_2 + aerosol	→	products	see text, $k_{15} = 0$
R18*	$HNO_3 + OH$	→	$H_2O + NO_3$	$k_{18} = 2.0 \times 10^{-13}$
R19	$OH + OH$	→	$H_2O + O$	$k_{19} = 2.0 \times 10^{-12}$
R20*	$OH + HO_2$	→	$H_2O + O_2$	$k_{20} = 2.0 \times 10^{-10}$
R21	$OH + H_2O_2$	→	$H_2O + HO_2$	$k_{21} = 8.0 \times 10^{-13}$
R22	$NO + O_3$	→	$NO_2 + O_2$	$k_{22} = 1.7 \times 10^{-12} \exp(-1310/T)$
R23	$NO_2 + h\nu$	→	$NO + O$	$\lambda < 400$ nm $J_{23} = 8.0 \times 10^{-3}$
R24*	$NO_2 + O_3$	→	$NO_3 + O_2$	$k_{24} = 1.23 \times 10^{-13} \exp(-2470/T)$
R25a*	$NO_3 + h\nu$	→	$NO_2 + O$	$\lambda < 541$ nm $J_{25a} = 0$
R25b*	$NO_3 + h\nu$	→	$NO + O_2$	$\lambda \leqslant 10\ \mu$ $J_{25b} = 6.6 \times 10^{-2}$
R26	$NO_3 + NO$	→	$2NO_2$	$k_{26} = 8.7 \times 10^{-12}$
R27a	$NO_3 + NO_2(+M)$	→	$N_2O_5(+M)$	$k_{27a} = 3.0 \times 10^{-12}$
R27b	$N_2O_5(+M)$	→	$NO_2 + NO_3(+M)$	$k_{27b} = 2.5 \times 10^{13} \exp(-9650/T)$
R28a	$N_2O_5 + h\nu$	→	$NO + NO_2 + O_2$	$\lambda \leqslant 1.4\ \mu$ $J_{28a} = 0$
R28b	$N_2O_5 + h\nu$	→	$NO_2 + NO_3$	$\lambda \leqslant 1.4\ \mu$ $J_{28b} = 0$
R28c	$N_2O_5 + h\nu$	→	$2NO_2 + O$	$\lambda < 800$ nm $J_{28c} = 2 \times 10^{-5}$
R29	$CH_4 + OH$	→	$CH_3 + H_2O$	$k_{29} = 2.5 \times 10^{-12} \exp(-1160/T)$
R30	$CH_3 + O_2 + M$	→	$CH_3O_2 + M$	$k_{30} = 8.0 \times 10^{-32}$
R31*	$CH_3O_2 + NO$	→	$CH_3O + NO_2$	$k_{31} = 5.0 \times 10^{-13}$
R23*	$CH_3O_2 + HO_2$	→	$CH_3O_2H + O_2$	$k_{32} = 2.5 \times 10^{-12}$
R33*	$CH_3O_2H + h\nu$	→	$CH_3O + OH$	$k_{33} = 3.3 \times 10^{-6}$
R34*	$CH_3O_2H + OH$	→	$CH_3O_2 + H_2O$	$k_{34} = 8.0 \times 10^{-13}$
R35*	$CH_3O + O_2$	→	$CH_2O + HO_2$	$k_{35} = 1.0 \times 10^{-12} \exp(-3300/T)$
R36a*	$CH_2O + h\nu$	→	$H + CHO$	$\lambda \leqslant 350$ nm $J_{36a} = 4.0 \times 10^{-5}$
R36b*	$CH_2O + h\nu$	→	$CO + H_2$	$\lambda \leqslant 350$ nm $J_{36b} = 1.0 \times 10^{-4}$
R37	$CH_2O + OH$	→	$CHO + H_2O$	$k_{37} = 1.4 \times 10^{-11}$
R38*	$CHO + O_2$	→	$CO + HO_2$	$k_{38} = 1.0 \times 10^{-13}$
R39*	$OH + NH_3$	→	$NH_2 + H_2O$	$k_{39} = 1.5 \times 10^{-13}$

tained when they are included. Only, for the sake of discussion, an unrealistically short removal time of only 5 seconds by aerosol was adopted for HO_2 and HNO_3. As can be estimated by simple optical considerations, this corresponds roughly to conditions in a turbid atmosphere in which the visibility is only a few kilometers (over which distance the optical thickness is approximately equal to unity), assuming that each molecule of HO_2 or HNO_3 is collected

at every collision by an aerosol particle. Little is known about the efficiency with which these molecules are removed per collision. In the normal atmosphere the heterogeneous removal time of HO_2 and HNO_3 should be at least one order magnitude longer than 5 seconds. The rate of removal of HO_2 and HNO_3 on a global scale by clouds cannot be faster than the above indicated removal rates by aerosol particles as clouds only occupy a minor portion of the total tropospheric volume. Furthermore, this study is concerned mainly with the chemistry in the lowest two kilometers of the atmosphere, which are located mainly below the mean condensation level.

The "starter" reaction to the adopted photochemical chain is the photodissociation process

$$\text{R1a}\quad O_3 + h\nu \rightarrow O(^1D) + O_2 \quad \lambda < 340 \text{ nm}$$

which is followed either by reaction R3 or by R4. The latter reaction leads to the formation of the OH-radical (Levy, 1971). Reaction R3 is followed by R2, so that the sequence of reactions R1a + R3 + R2 does not lead to destruction of ozone. However, the pair of reactions R1a + R4, which will be called sequence A, combines into

$$\text{A: R1a} + \text{R4} = O_3 + H_2O + h\nu \rightarrow O_2 + 2OH$$

and leads to a significant loss rate of ozone (Crutzen, 1973; Levy, 1973*b*), according to the formula

$$\frac{\partial}{\partial t}(O_3)_A = -k_4(O^*)(H_2O) \qquad (1)$$

The quantum yield $\phi(\lambda)$ of $O(^1D)$ formation in the photolysis of ozone as a function of wavelength (λ) below 330 nm is a very critical factor. Jones & Wayne (1970) determined $\phi(\lambda < 300$ nm$) = 1.0$, $\phi(\lambda = 313$ nm$) = 0.1$ and $\phi(330$ nm$) = 0$. Several published sets of data were in conflict with those of Jones & Wayne (Castellano & Schumacher, 1969; Simonaitis et al., 1972). Recent accurate experiments by DeMore (1973*b*) and Johnston et al. (1973*b*) have shown Jones and Wayne's data to be more correct. Thus, for the first time, sufficiently accurate values of $\phi(\lambda)$ are available for aeronomic studies. The probability of $O(^1D)$ production per second and per ozone molecule is calculated from the relationship:

$$J_{1a} = 2.5 \int \alpha_{3\lambda} F(\lambda) \phi(\lambda) \exp(-T_\lambda) d\lambda \qquad (2)$$

where $\alpha_{3\lambda}$ = ozone absorption cross section at wavelength λ,

$F(\lambda)d\lambda$ = solar irradiance in wavelength interval λ, $\lambda + d\lambda$ at zero optical depth,

$\Delta\lambda$ = 10 Å,

$$T_\lambda = \frac{\alpha_{3\lambda} d_3 + \alpha_{R\lambda} d_M}{\cos\theta}$$

d_3 = 3 mm ozone STP (mean summer time value, Dütsch (1969)),

$\alpha_{R\lambda}$ = Rayleigh cross section for scattering by air molecules,

d_M = number of air molecules in vertical column with unit area base.

θ = solar zenith angle, chosen to be equal to 45° and kept constant. No diurnal variations were thus considered in this study.

The factor 2.5 in expression (2) is an approximate correction factor to take into account the effect of diffuse radiation. This factor was derived by interpolating from the data calculated by Dave & Furukawa (1966) and DeLuisi & Furukawa (1973). It applies for $\theta = 45°$ only.

A similar method was used to calculate the photodissociation rate J_{12} for HNO_3. The ozone absorption cross section and solar irradiance values were obtained from the compilation by Ackerman (1971).

As indicated in previous studies (Crutzen, 1972*b* and 1973) several chains of reactions, starting with reaction R29, besides leading to natural production of CO and H_2 (McConnell et al., 1971; Levy, 1972) and affecting the concentrations of OH (Crutzen, 1972*a*), may also lead to a significant rate of production of ozone in the troposphere, for example by the chains

R29	$CH_4 + OH$	$\rightarrow CH_3 + H_2O$
R30	$CH_3 + O_2 + M$	$\rightarrow CH_3O_2 + M$
R31	$CH_3O_2 + NO$	$\rightarrow CH_3O + NO_2$
R23	$NO_2 + h\nu_1$	$\rightarrow NO + O$
R2	$O + O_2 + M$	$\rightarrow O_3 + M$
R35	$CH_3O + O_2$	$\rightarrow CH_2O + HO_2$
R10a	$HO_2 + NO$	$\rightarrow OH + NO_2$
R23	$NO_2 + h\nu_1$	$\rightarrow NO + O$
R2	$O + O_2 + M$	$\rightarrow O_3 + M$
R36b	$CH_2O + h\nu_2$	$\rightarrow CO + H_2$
B1:	$CH_4 + 4O_2 + 2h\nu_1 + h\nu_2$	$\rightarrow H_2O + CO + H_2 + 2O_3$

and

R8	$CO + OH$	$\rightarrow$	$H + CO_2$
R9	$H + O_2 + M$	$\rightarrow$	$HO_2 + M$
R10a	$HO_2 + NO$	$\rightarrow$	$OH + NO_2$
R23	$NO_2 + h\nu$	$\rightarrow$	$O + NO$
R2	$O + O_2 + M$	$\rightarrow$	$O_3 + M$
B2:	$CO + 2O_2 + h\nu$	$\rightarrow$	$CO_2 + O_3$

A more elaborate discussion of such ozone producing "smog-type" chain reactions was given elsewhere (Crutzen, 1972*b* and 1973). Nitrogen oxides play an important role in these chains. The production rate of ozone due to chains like B1 and B2 is equal to

$$\frac{\partial}{\partial t}(O_3)_B = (NO)\{k_{10a}(HO_2) + k_{31}(CH_3O_2)\} \qquad (3)$$

On the other hand catalytic, photochemical destruction of ozone by oxides of nitrogen may also take place (Crutzen, 1972*b* and 1973) by the chain:

C1: R22 + R24 + R25b = $2O_3 + h\nu \rightarrow 3O_2$

Good knowledge of the photodissociation products in reaction R25 is required for a correct evaluation of the importance of chain C1. According to Johnston (1973) process R25b is the main path of NO_3 photodissociation. It is assumed in this study that the quantum yield for this reaction is unity. This should be checked experimentally.

The chain

C2: R22 + R24 + R27a + R28a = $2O_3 \rightarrow 3O_2$

is not important, due to the low calculated concentration of N_2O_5 (4×10^6 cm^{-3}). The rate of ozone destruction by chain C1 is, therefore, calculated according to the formula:

$$\frac{\partial}{\partial t}(O_3)_C = -2k_{24}(NO_2)(O_3)\frac{J_{25b}}{J_{25a} + J_{25b} + k_{26}(NO)} = -2J_{25b}NO_3) \qquad (4)$$

It is important to include the term $k_{26}(NO)$ in the denominator of expression (4), as the chain R22 + R24 + R26 + 2*R23 + 2*R2 does not lead to net destruction of ozone.

Recent work (Simonaitis & Heicklen, 1973; DeMore, 1973*a*) has indicated the possibility of a small but significant rate constant for reaction R10b. Consequently also the reactions

D: R7 and R10b

$$\frac{\partial}{\partial t}(O_3)_D = -(O_3)\{k_7(OH) + k_{10b}(HO_2)\} \qquad (5)$$

must be included as important sinks for atmospheric ozone.

3. Numerical procedure

Computations were performed for only one level in the troposphere which is thought to be located at an altitude of a few hundred meters. The adopted mean temperature was 290°K. According to observations (Pruchniewicz, 1973), the mean concentration of ozone at this level was assumed to be equal to 7.5×10^{11} molecules per cm^3. The volume mixing ratios of H_2O, CH_4 and CO were chosen to be equal to 10^{-2}, 1.4×10^{-6} and 10^{-7} respectively (Ehhalt, 1974; Seiler, 1974). The concentrations of these chemical compounds were kept constant in the model and steady state concentrations of each of the other minor constituents, as indicated in Table 1, were calculated, assuming photochemical steady state for the constituents $O(^1D)$, $O(^3P)$, OH, H, HO_2, CH_3O_2, CH_3O_2H, CH_3O, CH_2O, and CHO, and using a numerical integration technique with forward time stepping ($\Delta t = 50$ s) for the remaining species. Convergence was reached after an integration time of 3×10^6 seconds. Production and destruction rates of ozone, methane and carbon monoxide were likewise computed. A source of NO, equal to 3×10^5 molecules cm^{-3} s^{-1} was introduced at the level of computation in order to simulate the biological source of NO from the ground of 3×10^{10} molecules cm^{-2} s^{-1} (Robinson & Robbins, 1970), assuming this source to be uniformly distributed over the lowest kilometer of the atmosphere. Nitrogen oxides are thought to be removed again from the atmosphere via the reactions R11a, R11b and R15. If reaction R11a is the only reaction converting NO_2 to NHO_3 (as discussed in Chapter 2, there is uncertainty about the rate coefficient for reaction R11b), then the set R22 + R23 + R11a + R15, converting NO into nitrates, will also remove ozone from the

Table 2. *Calculated concentrations of OH, HO_2, H_2O_2, HNO_2, CH_3O_2, CH_3O_2H, CH_3O, and CH_2O and volume mixing ratios of NO, NO_2 and HNO_3 for the six alternatives a, b, c, d, e, and f, as defined in Chapter 3 (2.6(6) = 2.6 × 10⁶).*

Case	Concentrations (cm^{-3}) and volume mixing ratios (μ)										
	(OH)	(HO_2)	(H_2O_2)	(HNO_2)	(CH_3O_2)	(CH_3O_2H)	(CH_3O)	(CH_2O)	μ(NO)	$\mu(NO_2)$	$\mu(HNO_3)$
(*a*) standard	2.6(6)	3.4(8)	5.3(10)	2.7(7)	3.0(8)	4.7(10)	1.2(4)	5.1(9)	1.8(−10)	3.5(−10)	2.2(−9)
(*b*) $k_{11b} = 0$	3.3(6)	3.4(8)	4.8(10)	8.8(7)	1.9(8)	2.7(10)	1.5(4)	6.2(9)	4.0(−10)	7.8(−10)	2.2(−9)
(*c*) $k_{15} = 0.2$	2.5(6)	3.6(8)	5.7(10)	2.2(7)	3.4(8)	5.5(10)	1.1(4)	5.1(9)	1.5(−10)	2.9(−10)	0.5(−13)
(*d*) $k_{16} = 0.2$	2.2(6)	2.7(8)	9.2(5)	2.9(7)	2.2(8)	3.0(10)	9.8(3)	4.5(9)	2.2(−10)	4.3(−10)	2.2(−9)
(*e*) $k_{17} = 0.2$	7.8(5)	3.5(6)	9.2(7)	2.9(8)	1.3(7)	3.0(7)	3.5(3)	1.8(9)	1.8(−9)	3.5(−9)	2.2(−9)
(*f*) $k_{17} = 10^{-3}$	2.3(6)	2.6(8)	3.3(10)	3.1(7)	2.3(8)	2.9(10)	1.0(4)	4.7(9)	2.3(−10)	4.5(−10)	2.2(−9)

atmosphere at a rate equal to 3×10^{10} molecules cm^{-2} s^{-1}. A thorough analysis should take into account accurately the diffusion of NO (and other species) through the atmospheric boundary layer.

The calculated concentrations of OH, HO_2, H_2O_2, NO, NO_2, HNO_2, HNO_3, CH_3O_2H, CH_3O_2 and CH_2O are collected in Table 2, while production and destruction rates of CH_4, CO and O_3 (by each of the mechanisms A, B, C, D, see Chapter 2) are collected in Table 3 for the following cases:

(*a*) standard case, adopting rate coefficients from Table 1. Except for reaction R15 only gas phase reactions important.

(*b*) $k_{11b} = 0$, neglect reaction R11b, all other coefficients from Table 1.

(*c*) $k_{15} = 0.2$, fast removal of HNO_3 by aerosol particles. All other rate coefficients from Table 1.

(*d*) $k_{16} = 0.2$, fast removal of H_2O_2 by aerosol. All other rate coefficients from Table 1.

(*e*) $k_{17} = 0.2$, rapid removal of HO_2 by aerosol. All other rate constants from Table 1.

(*f*) $k_{17} = 10^{-3}$, removal of HO_2 by aerosol in about 15 minutes. A still fast removal of HO_2, but more realistic than case *e*. All other rate constants from Table 1.

4. Discussion

From a study of the results shown in Tables 2 and 3 the following main conclusions may be drawn:

(*a*) Calculated column ozone production and destruction rates for each of the detailed mechanisms A, B, C, and D are much larger than the estimated ozone destruction rates at the ground (Tiefenau & Fabian, 1972). This confirms the hypothesis from previous studies (Crutzen, 1972*b* and 1973), that ozone is not an inert, but a very reactive, gas in the troposphere.

Net column production of destruction rates of ozone of the order of $10^{10} - 1.5 \times 10^{11}$ molecules cm^{-2} s^{-1} are calculated for the lowest two kilometers of the atmosphere. Whether there is

Table 3. *Calculated production rates of CH_4, CO and O_3 by each of the detailed chains A, B, C, and D as defined in Chapter 2 for the six alternatives a, b, c, d, e, and f, as defined in Chapter 3. To obtain column produktion rates, multiply all values by a factor of 2×10^6.*

Case	Production rates (cm^{-3} s^{-1})						
	CH_4	CO	A	B	C	D	A+B+C+D
(*a*) standard	−9.0(5)	−2.0(5)	−3.5(5)	1.6(6)	−2.9(5)	−4.5(5)	+1.0(5)
(*b*) $k_{11b} = 0$	−1.2(6)	−2.5(5)	−3.5(5)	3.0(6)	−3.8(5)	−8.9(5)	+1.3(6)
(*c*) $k_{15} = 0.2$	−8.9(5)	−2.0(5)	−3.5(5)	1.4(6)	−2.3(5)	−8.8(5)	−1.4(4)
(*d*) $k_{16} = 0.2$	−7.7(5)	−1.7(5)	−3.5(5)	1.5(6)	−3.1(5)	−7.0(5)	+1.4(5)
(*e*) $k_{17} = 0.2$	−2.7(5)	−6.1(4)	−3.5(5)	3.5(5)	−5.4(5)	−3.8(4)	−5.8(5)
(*f*) $k_{17} = 10^{-3}$	−8.0(5)	−1.8(5)	−3.5(5)	1.5(6)	−3.1(5)	−6.7(5)	+1.7(5)

net production or destruction of ozone in the lower troposphere cannot be concluded at present due to insufficient knowledge of some essential chemical processes. The sets of reactions leading to loss of ozone are the sets A, C, and D (see Chapter 2). If there were no reactions which would partly compensate for this loss of ozone (reaction chains B), the tropospheric residence time of ozone would be only one month. The degree of compensation is mainly dependent on the concentrations of NO in the natural troposphere. Although the destruction rate of ozone by the reaction chains C also increases with growing concentrations of NO, the rate of production of ozone by the chains B increases even more. This is due to the fact that with larger NO concentrations the species NO_3 will be more removed by reaction R26 than by reaction R25b, making the chain R22 + R24 + R26 + 2 × R23 + 2 × R2 which does not deplete the ozone content of the atmosphere, relatively more important.

(*b*) Although the calculations show that heterogeneous reactions may affect the concentrations of HO_2, H_2O_2 and HNO_3 (respective cases *e*, *d*, *c*) considerably (Warneck, 1974), they also show that the concentration of OH is only slightly affected. This is not surprising as it takes the OH-radicals, which are produced in reaction R4, only about one second to react homogeneously with CH_4 or CO. It is clear from the discussion given in Chapter 2 that the OH-radical cannot be removed so quickly from the unpolluted atmosphere by heterogeneous reactions. As reactions with CO and CH_4 are the most important gas-phase reactions of OH in the atmosphere, it is possible to estimate the minimum concentration of OH in the lower troposphere from the relationship

$$(OH) = \frac{2k_4(O^*)\,(H_2O)}{k_8(CO) + k_{29}(CH_4)} = 7 \times 10^5 \text{ cm}^{-3}$$

thereby neglecting any recycling of OH, for example by the reactions R6c and R10a.

(*c*) As discussed by McConnell et al. (1971), Levy (1972, 1973*a*, 1973*b*) and Wofsy et al. (1972) the presence of OH in the troposphere has a pronounced influence on the carbon cycle of the atmosphere, the methane oxidation providing a dominant natural source for carbon monoxide. This study seems again to confirm this hypothesis, because the net calculated destruction rate of CO is small compared with the destruction rate of CH_4, indicating a rather close balance between production of CO by oxidation of CH_4 and destruction of CO by its reaction R8 with OH. The natural source for CO calculated by this simple model is on the average somewhat less than 2×10^{11} molecules cm^{-2}, s^{-1}, approximately five times the average global anthropogenic source of CO. In order to compare the anthropogenic and natural sources of CO at a given latitude, it is necessary to perform detailed calculations of CO production rates by integrating over 24 hours. It seems that, in middle latitudes of the Northern Hemisphere, the anthropogenic source may be of the same size as the natural source. It is also important to investigate whether heterogeneous reactions could be important reactions in the CH_4 oxidation cycle. Unfortunately, too little is known about reactions (R31–R35) affecting methane and its oxidation products. It cannot be excluded that heterogeneous reactions play a role in removing for example CH_3O_2H, in which case the importance of the production of CO via reactions R36a, R36b, R37 and R38 may be reduced in the troposphere.

(*d*) The presence of the OH-radical is of large importance for the atmospheric nitrogen cycle. In the first place, reaction R11a provides an efficient loss process for atmospheric NO_x (NO and NO_2) into HNO_3. The calculated mixing ratios of NO and NO_2 were less than 10^{-9}, except for the unlikely case *e* (see Table 2). These estimates are in accordance with recommended mean value of mixing ratios over the oceans, but are much less than that recommended for land areas (Robinson & Robbins, 1970). But as these authors point out, data on NO_2 and NO are few and widely scattered, so that representative background values are not available yet. Nitric acid appears to be a sink for tropospheric NO_x as it is probable that HNO_3 is efficiently converted to nitrates via reactions with aerosol particles and cloud droplets, which are removed from the atmosphere by washout and rainout processes or dry deposition (Warneck, 1974; Robinson & Robbins, 1970). Contrary to conditions in the stratosphere (Murcray et al., 1969) nitric acid may never build up to significant concentrations in the troposphere due to heterogeneous reactions. The injection rate of 3×10^{10} NO_x-molecules cm^{-2} s^{-1} (Robinson & Robbins, 1970) should, therefore, be balanced by a similar rate

of deposition of nitrates on the earth' surface in accordance with the results from rainfall analysis by Eriksson (1952).

Another reaction which may be of large importance for the atmospheric nitrogen cycle is the reaction

R39 $NH_3 + OH \rightarrow NH_2 + H_2O$, $k_{39} = 1.5 \times 10^{-13}$ (Stuhl, 1973*a*)

which is probably followed by reactions leading to the oxidation of NH_2 into NO_x (Crutzen, 1972*b*; Stuhl, 1973*a*). Adopting the background mixing ratios of 6×10^{-9} for NH_3 (Robinson & Robbins, 1970) and an OH-concentration of about 3×10^6 cm^{-3}, the rate of production of NO_x-molecules initiated by reaction R39 is approximately 10^{10} molecules cm^{-2} s^{-1}, which is significant in comparison with the estimated production rate in the soil of 3×10^{10} NO_x-molecules cm^{-2} s^{-1} (Robinson & Robbins, 1970).

(*e*) It can be concluded from a look at the results presented as case *e* in Table 2 that heterogeneous processes affecting HO_2 may influence the OH-concentrations (Warneck, 1974). However, even with a fast removal time of HO_2 of only 15 minutes (case *f*) OH-concentrations are still equal to 2.3×10^6 cm^{-3}. Case *f* is more representative for mean situations in the natural atmosphere than case *e*. Thus, probably, (OH) $> 2.3 \times 10^6$ cm^{-3}.

(*f*) Good knowledge of the rate constant k_{11b} is important for estimating prevailing background NO_x-concentrations and ozone production rates (case *b*). If reaction R11b is as fast as assumed in standard case *a*, then this reaction is the main one converting NO_x into HNO_3.

(*g*) It has been proposed that the OH-radical could play a significant role in the sulphur cycle via reactions with H_2S and $(CH_3)_2S$ (Stuhl, 1973*b*; Levy, 1973*b*). Furthermore, the following two reactions

R40 $SO_2 + OH\,(+M) \rightarrow HSO_3\,(+M)$

R41 $HSO_3 + OH\,(+M) \rightarrow H_2SO_4\,(+M)$

(Johnston et al., 1973*a*; Davis, 1973; Castleman, 1973) to which should be added the reactions

R42a $HSO_3 + hv \rightarrow OH + SO_2$(?)

R42b $HSO_3 + OH \rightarrow H_2O + SO_3$

R42c HSO_3 + aerosol $\rightarrow$ products

R43 $H_2O + SO_3 \rightarrow H_2SO_4$ (heterogeneous)

may be important for the conversion of SO_2 to H_2SO_4 and sulfate aerosol particles. According to Castleman (1973) reaction R40 is fast and Davis (1973) has obtained a preliminary rate constant $k_{40} = 4.0 \times 10^{-32}$. An even faster rate constant was measured by Wayne (1973). Adopting the preliminary results from Davis (1973), the above sequence of reactions would lead to a lifetime of SO_2 in the sunlit troposphere of about one week, assuming (OH) $\propto 3 \times 10^6$ cm^{-3}, which is short enough to be of interest (Junge, 1972; Kellogg et al., 1972). An influence from reactions R40–R43 could explain the observations by Atkins et al. (1972), who observed a strong enhancement in the rate of increase of H_2SO_4 during periods of photochemical "smog" formation when ozone concentrations also increased to high levels.

5. Conclusions

Arguments are presented in this paper in favour of prevailing OH-concentrations of more than 10^6 cm^{-3} in the sunlit lower troposphere at least during summer, as was calculated by Levy (1971). This seems still to be true even if the effect of aerosol particles in removing OH, HO_2 and HNO_3 is taken into account (Warneck, 1974). The presence of OH with concentrations larger than 10^6 cm^{-3} is of large importance for the carbon, nitrogen and probably sulphur cycles in the atmosphere. This study confirms the hypothesis that the oxidation of methane provides a large global natural source of carbon monoxide which is about five times larger than the combustion source (McConnell et al., 1971). In the industrialized middle latitude belts of the Northern Hemisphere the total yearly anthropogenic CO source may, however, well be equal to or larger than the natural CO source.

It has been shown that there exist several chains of reactions leading to significant rates of production and destruction of ozone in the lower troposphere. The calculated rates of production of ozone by "smog-type" reactions within the methane oxidation cycle are smaller than indicated in previous studies (Crutzen,

1972*b* and 1973), which is due to both the use of newly measured accurate rate coefficients and the fact that the present model predicts smaller concentrations of NO than those adopted before. This model indicates rather low background mixing ratios of less than 10^{-9} for NO and NO_2, being due to the efficient conversion of NO_2 into HNO_3 by reaction with OH and heterogeneous removal of HNO_3 from the troposphere. The oxidation of NH_3, initiated by reaction R39 with OH-radicals, may provide a significant source for tropospheric NO_x-molecules.

The following experimental work is of the utmost importance:

(*a*) Laboratory studies of all reactions indicated with an asterisk in Table 1.

(*b*) Laboratory studies of OH-reactions with sulphur compounds, especially, SO_2.

(*c*) Determinations of the background concentrations in the first place of OH, NH_3, and NO_x, and in the second place of H_2O_2, HNO_3 and CO in the unpolluted atmosphere.

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REFERENCES

Ackerman, M. 1971. *Ultraviolet solar radiation related to mesospheric processes, mesospheric models and related experiments* (ed. G. Fiocco), pp. 149–160. D. Reidel Publ. Co., Dordrecht, Holland.

Aldaz, L. 1971. Flux measurements of atmospheric ozone over land and water. *J. Geophys. Res. 74*, 6943–6946.

Altshuller, A. P. & Bufalini, J. J. 1971. Photochemical aspects of air pollution; a review. *Environmental Science and Technology 5(1)*, 39–64.

Anderson, J. G. & Kaufman, F. 1973. Kinetics of the reaction $OH(v=0)+O_3 \rightarrow HO_2+O_2$. *Chem. Phys. Letters 19*, 483–486.

Atkins, D. H. F., Cox, R. A. & Eggleton, A. E. J. 1972. Photochemical ozone and sulphuric acid aerosol formation in the atmosphere over Southern England. *Nature 235*, 372–376.

Castellano, E. & Schumacher, H. J. 1969. Photochemischer Ozonzerfall im Licht der Wellenlänge 313 mμ. *Zeitschrift für Physikalische Chemie*, Neue Folge, *65*, 62–85.

Castleman, A. W., Jr. 1973. Private communication of preliminary results of laboratory work.

Crutzen, P. J. 1971. Ozone production rates in an oxygen-hydrogen-nitrogen oxide atmosphere. *J. Geophys. Res. 76*, 7311–7327.

Crutzen, P. J. 1972*a*. The photochemistry of the stratosphere with special attention given to the effects of NO_x emitted by supersonic aircraft. *Proc. Survey Conference CIAP, U.S. Dept. of Transportation, Cambridge, Mass.*, pp. 80–89.

Crutzen, P. J. 1972*b*. Gas-phase nitrogen and methane chemistry in the atmosphere. Report AP-10, Institute of Meteorology, University of Stockholm, June 1972, to be published in *Physics and Chemistry of Planetary Atmospheres*. D. Reidel Publ. Co., Dordrecht, Holland, 1973.

Crutzen, P. J. 1973. A discussion of the chemistry of some minor constituents in the stratosphere and troposphere. *Pure and Applied Geophysics*, 106–108, 1385–1399.

Davis, D. D. 1973. Private communication of preliminary results of laboratory work.

Davis, D. D., Payne, W. A. & Stief, L. J. 1973. The hydroperoxyl radical in atmospheric chemical dynamics: Reaction with carbon monoxide. *Science 179*, 280–282.

Dave, N. & Furukawa, P. 1966. Scattered radiation in the ozone absorption bands at selected levels of a terrestrial, Rayleigh atmosphere. *Meteorological Monographs 7*, 334–350.

DeLuisi, J. & Furukawa, P. 1973. *CIAP Monograph II*, preprint.

DeMore, W. B. 1973*a*. Rate constants for the reaction of hydroxyl and hydroperoxyl radicals with ozone. *Science 180*, 735–737.

DeMore, W. B. 1973*b*. $O(^1D)$ production in ozone photolysis near 3 100 Å, preprint.

Dütsch, H. U. 1969. Atmospheric ozone and ultraviolet radiation, climate of the free atmosphere. *World survey of climatology* (ed. D. Rex), vol. 4. Elsevier, New York.

Ehhalt, D. H. 1974. To be published in *Tellus*.

Eriksson, E. 1952. Composition of atmospheric precipitation, I. Nitrogen compounds. *Tellus 4*, 215–232.

Fabian, P. & Junge, Chr. E. 1970. Global rate of ozone destruction at the earth's surface. *Arch. Met. Geoph. Biokl., A, 19*, 161–172.

Fabian, P., Pruchniewicz, P. G. & Zand, A. 1971. Transport und Austauschvorgänge in der Atmosphäre. *Naturwissenschaften 58*, 541–549.

Garvin, D. (ed.) 1973. *Chemical kinetics data survey, IV. Preliminary tables of chemical data for modelling of the stratosphere*, NBSIR-203, National Bureau of Standards, Washington, D.C., 20234.

Haagen-Smit, A. J. 1952. Chemistry and physiology of Los Angeles smog. *Ind. Eng. Chem. 44*, 1342–1346.

Harker, A. & Johnston, H. S. 1973. Photolysis of nitrogen dioxide to produce nitrogen pentoxide (in press).

Heicklen, J. 1968. Gas-phase reactions of alkylperoxy and alkoxy radicals. *Advances in Chemistry Series 76*, 23–39.

Hochanadel, C. J., Ghormley, J. A. & Ogren, P. J.

1972. Absorption spectrum and reaction kinetics of the HO_2 radical in the gas phase. *J. Chem. Phys. 56(9)*, 4426–4432.
Jaffe, L. S. 1973. Carbon monoxide in the biosphere: sources, distribution and concentrations. *J. Geophys. Res. 78*, 5293–5305.
Johnston, H. S. 1973. Private communication.
Johnston, H. S., Cvetanovic, R. J., Davis, D. D., Ferguson, E. E., Garvin, D., Hudson, R. D., Schiff, H. I. & Taylor, R. 1973*a*. Chemistry of the stratosphere. *CIAP monograph: The natural stratosphere* (in preparation).
Johnston, H., Martin, D. & Girman, J. 1973*b*. The quantum yield to form $O(^1D)$ in the photolysis of ozone (preprint).
Johnston, H. S. 1973*a*. Gas-phase ultraviolet absorption spectrum of nitric acid vapor. J. Phys. Chem. *77*, 62–63.
Johnston, H. & Graham, R. 1973*b*. Kinetics of the reaction between nitrogen dioxide and ozone (preprint).
Jones, I. T. N. & Wayne, R. P. 1970. The photolysis of ozone by ultraviolet radiation. IV. Effect of photolysis wavelength on primary step. *Proc. Roy. Soc. London A 319*, 277–280.
Junge, C. 1972. *Sulphur supplies of atmopheric origin. Annales Agronomiques*, pp. 235–247.
Kelley, J. J., Jr & McTaggart-Cowan, J. D. 1968. *Vertical gradient of new oxidant near the ground surface at Barrow, Alaska. J. Geophys. Res. 73(10)*, 3328–3330.
Kellogg, W. W., Cadle, R. D., Allen, E. E., Lazrus, A. L. & Martell, E. A. 1972. The sulphur cycle. *Science 175*, 587–596.
Kerr, J. A., Calvert, J. G. & Demerjian, K. L. 1972. The mechanism of photochemical smog formation. *Chemistry in Britain 8*, 252–257.
Leighton, P. A. 1961. Photochemistry of air pollution. Academic Press, New York.
Levy, H. 1971. *Normal atmosphere: large radical and formaldehyde concentrations predicted. Science 173*, 141–143.
Levy, H. 1972. *Photochemistry of the lower troposphere. Planet. Space Sci. 20*, 919–935.
Levy, H. 1973*a*. *Photochemistry of minor constituents in the troposphere. Planet. Space Sci. 21*, 575–591.
Levy, H. 1973*b*. Photochemistry of the troposphere. To appear in *Advances in Photochemistry*, vol. 9.
McConnell, J. C., McElroy, M. B. & Wofsy, S. C. 1971. Natural sources of atmospheric CO. *Nature 233*, 187–188.
Murcray, D. G., Kyle, T. G., Murcray, F. H. & Williams, W. J. 1969. Presence of HNO_3 in the upper atmosphere. *J. Opt. Soc. Am. 59(9)*, 1131–1134.
Pruchniewicz, P. G. 1973. The average tropospheric ozone content and its variation with season and latitude as a result of the global ozone circulation. *Pure and Applied Geophysics*, 106–108, 1058–1073.
Ripperton, L. A. & Vukovich, F. M. 1971. Gas phase destruction of tropospheric ozone. *J. Geophys. Res. 76(30)*, 7328–7333.
Robinson, E. & Robbins, R. C. 1970. Gaseous Nitrogen compound pollutants from urban and natural sources. *APCA Journal 20(5)*, 303–306.
Seiler, W. 1974. To be published in *Tellus*.
Simonaitis, R. & Heicklen, J. 1972. Reaction of OH with nitrogen dioxide and the activation energy of oxygen (^1D) by carbon monoxide. *Int. J. Chem. Kin. 4*, 529–540.
Simonaitis, R., Braslavsky, S., Heicklen, J. & Nicolet, M. 1972. Photolysis of O_3 at 3130A. Scientific Report 411, The Pennsylvania State University, 8 pp.
Simonaitis, R. & Heicklen, J. 1973. The reaction of HO_2 with O_3. *J. Phys. Chem. 77*, 1932–1935.
Stuhl, F. 1973*a*. Absolute rate constant for the reaction $OH + NH_3 \rightarrow NH_2 + H_2O$. Publication Preprint, Scientific Research Staff, Ford Motor Company.
Stuhl, E. 1973*b*. Experimental studies (private communication).
Tiefenau, H. & Fabian, P. 1972. The specific ozone destruction at the ocean surface and its dependence on horizontal wind velocity from profile measurements. *Arch. Met. Geop. Biokl., Ser. A, 21*, 399–412.
Warneck, P. 1974. To be published in *Tellus*.
Wayne, R. P., 1973. Private communication.
Weinstock B. & Niki, H. 1972. Carbon monoxide balance in nature. *Science 176*, 290–292.
Westberg, K. & Cohen, N. 1969. The chemical kinetics of photochemical smog as analyzed by computer. The Aerospace Corporation, Report No. ATR-70 (8107)-1.
Wofsy, S. C., McConnell, J. C. & McElroy, M. B. 1972. Atmospheric CH_4, CO and CO_2. *J. Geophys. Res. 77(24)*, 4477–4493.

ФОТОХИМИЧЕСКИЕ РЕАКЦИИ, ИНИЦИИРУЕМЫЕ ОЗОНОМ И ВЛИЯЮЩИЕ НА НЕГО В НЕЗАГРЯЗНЕННОМ ВОЗДУХЕ ТРОПОСФЕРЫ

В статье представлены теоретические аргументы в пользу существования концентраций OH, больших 10^6 молекул на $см^3$ в освещенной солнцем нижней тропосфере даже при учете гетерогенного удаления молекул OH, HO_2 и HNO_3. Концентрации OH, представленные в статье, были вычислены в условиях, когда впервые учитывался фотохимический эффект как для прямой, так и для рассеянной радиации вблизи поверхности земли, а также при учете недавних аккуратных данных о квантовой эффективности выхода $O(^1D)$ при фотолизе озона в области спектра вблизи 310 *мм*. Обсуждается существенная роль, которую играет OH в атмосферных циклах для углерода, азота и, возможно, серы. Вычислены низкие фоновые соотношения смеси для молекул NO_x($< 10^{-9}$) в незагрязненной атмосфере. Окисление NH_3, инициируемое реакцией с OH, может оказаться значительным источником молекул NO_x в тропосфере, если ста реакция имеет

константу скорости на поверхности порядка 10^{-13}. Превращение NO^2 в HNO_3, сопровождаемое гетерогенным удалением HNO_3, является важнейшим стоком в тропосфере для молекул NO_x. Фотодиссоциация озона в ультрафиолетовом свете в спектральном интервале 300–330 нм, которая ведет к образованию возбужденного атома $O(^1D)$, возбуждает несколько последовательностей реакций, рассматриваемых в настоящем исследовании. Несколько цепей реакций, включающих углеродные и азотные составляющие, ведет к большим скоростям образования и разрушения озона в тропосфере. Эти скорости частично балансируют друг друга. Будет ли в сумме образование или разрушение озона в тропосфере, в настоящее время нельзя определить. Озон является очень активным катализатором в химических системах в тропосфере. Глобально производство CO путем горения в 1970 г. более чем на 20 % превысило естественное производство CO путем окисления CH_4 биологического происхождения. В средних широтах Северного полушария горение поставляет примерно такое же количество CO, что и естественные источники.