UC Irvine
UC Irvine Previously Published Works

Title
Effects of nonmethane hydrocarbons in the atmosphere

Permalink
https://escholarship.org/uc/item/62f2g7fb

Journal
Journal of Geophysical Research, 83(C2)

ISSN
0148-0227

Authors
Chameides, WL
Cicerone, RJ

Publication Date
1978-02-20

DOI
10.1029/jc083ic02p00947

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, availalbe at https://creativecommons.org/licenses/by/4.0/

Peer reviewed

eScholarship.org Powered by the California Digital Library
University of California

Effects of Nonmethane Hydrocarbons in the Atmosphere

W. L. CHAMEIDES

Department of Physics and Astronomy, University of Florida, Gainesville, Florida 32611

R. J. CICERONE

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

The photochemistry of several unreactive and moderately reactive nonmethane hydrocarbons (NMHC) in the background troposphere and stratosphere was investigated. A one-dimensional steady state model was employed to determine the vertical distributions of C_2H_6, C_2H_2, C_3H_8, C_4H_{10}, and C_5H_{12}. The impact of these species upon the tropospheric and stratospheric odd-hydrogen, odd-oxygen, chlorine, and carbon systems was studied for various possible free radical profiles and eddy diffusion coefficients. Our results indicate that NMHC probably have only a small effect upon the background atmospheric photochemistry, although they might constitute a nonnegligible source of atmospheric CO. Also, Cl atoms, in predicted present-day concentrations, comprise the major sink for stratospheric NMHC. Finally, if the chlorovinyl molecule (CHCl = CH) were stable in the lower stratosphere, it would then be conceivable that C_2H_2 could be partially effective as a chain terminator to impede catalytic removal of stratospheric O_3 by Cl and ClO.

INTRODUCTION

While the photochemistry of methane in the background troposphere and stratosphere has been studied in detail [cf. *Levy*, 1972; *Wofsy et al.*, 1972; *Crutzen*, 1974; *Wofsy*, 1976; *Chameides et al.*, 1977], the photochemistry of nonmethane hydrocarbons (NMHC) in the ambient atmosphere has been largely ignored. Many of the more reactive anthropogenically produced NMHC, such as propylene, are believed to play a key role in photochemical smog formation in urban areas. However, because of their relatively short photochemical lifetimes (the photochemical lifetime of propylene in the background troposphere is about 0.5 day) the ambient concentrations of these reactive NMHC are probably small, the effects of reactive NMHC being limited to the local source regions. Similarly, while terpenes, which are produced naturally by vegetation, may play a role in the production of ozone and blue haze near heavily forested areas [cf. *Went*, 1960], their short photochemical lifetimes probably preclude effects in regions removed from intense terpene production. However, the less reactive NMHC, such as ethane and acetylene, are longer lived, and depending on their production rates they could have significant abundances throughout the troposphere and lower stratosphere. For instance, we estimate lower tropospheric photochemical lifetimes of 25 and 50 days for C_2H_6 and C_2H_2, respectively. By comparison, the photochemical lifetime of CO, whose global distribution indicates considerable vertical and horizontal transport [*Seiler*, 1974], is about 40 days in the lower troposphere. *Singh* [1977] has suggested that long-lived NMHC may be sufficiently abundant in the stratosphere to act as chain terminators for stratospheric chlorine. To determine if NMHC are abundant enough to have a significant impact upon the ambient photochemistry, we have calculated the vertical distribution of C_2H_6 and C_2H_2 as well as some moderately reactive (lower tropospheric lifetimes of about 5 days) NMHC: C_3H_8, C_4H_{10}, and C_5H_{12}. (All hydrocarbons were taken to be the normal isomer; i.e., C_5H_{12} is $n-C_5H_{12}$.)

MODEL CALCULATIONS

Using a one-dimensional steady state model with coupled photochemistry and vertical transport, we calculated the vertical profiles of C_2H_6, C_2H_2, C_3H_8, C_4H_{10}, and C_5H_{12} between 0 and 40 km. Transport was parameterized by using an eddy diffusion coefficient K. The input parameters used in our calculations were appropriate for 30°N at equinox. Table 1 lists the parameters used for the standard model; however, as will be discussed below, calculations were also carried out for different free radical profiles and eddy diffusion coefficients. Owing to uncertainties in key reaction rates the abundance of tropospheric OH is uncertain by an order of magnitude. The tropospheric OH profile we have adopted from *Chameides and Stedman* [1977] implies a lifetime for CH_3CCl_3 of about 5 years, as compared with *Singh*'s [1977] inferred result of (7.2 ± 1.2) years. The Cl profile was obtained by assuming a total inorganic chlorine (ClX) stratospheric mixing ratio profile that increases monotonically from about 0.1 ppb at 15 km to 1.4 ppb at 40 km. This abundance of Cl should roughly approximate present-day stratospheric concentrations.

The photochemical reactions included in our model are listed in Table 2. Calculations indicate that in the troposphere the major sink for NMHC is reaction with OH. In the stratosphere, for Cl densities greater than about 10^3 cm^{-3}, reaction with Cl is the major loss process for the alkanes, while for C_2H_2 the reaction with OH remains the major sink for the entire altitude region. Note that many of the rate constants are uncertain, e.g., the reaction of Cl with C_2H_2. *Lee and Rowland* [1977] suggest that the reaction produces the excited $C_2H_2Cl^*$ radical which either stabilizes to CHCl=CH or decomposes to form C_2H_2 and Cl again. They estimate the effective rate constant for conversion of Cl to CHCl=CH to be 10^{-12} cm^3 molecule^{-1} s^{-1}, which we have used in our calculations for the reaction of Cl with C_2H_2:

$$\text{(R11)} \qquad Cl + C_2H_2 \xrightarrow{M} CHCl = CH$$

The only source of hydrocarbons in our model was a flux from the ground, which could be a result of natural and/or anthropogenic activities. We did assume a photochemical source of CO via the methane oxidation chain [*McConnell et al.*, 1971], so that for every CH_4 oxidized a CO was produced. We did not include the production of CO from the oxidation of NMHC. However, our results indicate that the oxidation of NMHC may produce significant quantities of CO depending

Copyright © 1978 by the American Geophysical Union.

Paper number 7C0859.
0148-0227/78/027C-0859$03.00

TABLE 1. Input Parameters

Z, km	Number Density,* cm^{-3}	T,* °K	K,† $cm^2 s^{-1}$	n(OH),‡ cm^{-3}	n(Cl),§ cm^{-3}	n(O(^1D)),‡ cm^{-3}	n(O),‡ cm^{-3}
0	2.63 (19)	288	1.00 (5)	1.45 (6)		4.70 (−3)	
2	2.17 (19)	275	1.00 (5)	1.08 (6)		6.41 (−3)	
4	1.90 (19)	262	1.00 (5)	8.61 (5)		9.16 (−3)	
6	1.42 (19)	249	1.00 (5)	6.75 (5)		1.35 (−2)	
8	1.13 (19)	236	1.00 (5)	5.22 (5)		1.90 (−2)	
10	8.89 (18)	223	1.00 (5)	2.53 (5)	3.37 (1)	2.10 (−2)	1.13 (4)
12	6.71 (18)	217	2.16 (4)	3.30 (5)	1.63 (2)	2.36 (−2)	3.06 (4)
14	4.90 (18)	217	4.62 (5)	4.21 (5)	8.32 (2)	7.25 (−2)	1.23 (5)
16	3.58 (18)	217	5.16 (3)	4.83 (5)	2.30 (3)	1.90 (−1)	4.00 (5)
18	2.61 (18)	217	6.46 (3)	5.42 (5)	4.09 (3)	3.95 (−1)	9.77 (5)
20	1.91 (18)	217	8.12 (3)	6.33 (5)	6.22 (3)	7.84 (−1)	2.16 (6)
22	1.39 (18)	219	1.02 (4)	7.70 (5)	8.62 (3)	1.55	4.58 (6)
24	1.01 (18)	221	1.28 (4)	9.69 (5)	1.15 (4)	3.06	9.29 (6)
26	7.37 (17)	223	1.68 (4)	1.28 (6)	1.57 (4)	5.98	1.78 (7)
28	5.39 (17)	225	2.30 (4)	1.79 (6)	2.29 (4)	11.4	3.21 (7)
30	3.96 (17)	227	3.12 (4)	2.67 (6)	3.59 (4)	21.4	5.56 (7)
32	2.92 (17)	229	4.28 (4)	4.25 (6)	6.08 (4)	38.5	9.34 (7)
34	2.13 (17)	234	5.84 (4)	7.04 (6)	1.06 (5)	64.2	1.53 (8)
36	1.56 (17)	239	7.98 (4)	1.14 (7)	1.80 (5)	95.4	2.43 (8)
38	1.15 (17)	245	1.09 (5)	1.73 (7)	2.90 (5)	1.32 (2)	3.81 (8)
40	8.59 (16)	250	1.49 (5)	2.31 (7)	4.36 (5)	1.69 (2)	6.02 (8)

Read 2.63(19) as 2.63×10^{19}.
*Data are taken from U.S. Standard Atmosphere Supplements.
†Eddy diffusion coefficient is 2 times the value deduced by *Hunten* [1975].
‡Profiles are taken from models of *Chameides and Stedman* [1977] and *Liu et al.* [1976].
§Cl profile is calculated from model of *Liu et al.* [1976] by assuming a stratospheric ClX mixing ratio of 1.4 ppb.

upon the reaction path of oxidation and the background abundances.

Measurements of ground level NMHC in remote areas are unfortunately scarce. *Cavanaugh et al.* [1969] observed an average of ≤0.05 ppb C_2H_6, ~0.06 ppb C_4H_{10}, and ~0.15 ppb C_5H_{12} as well as 0.09 ppm CO and 1.6 ppm CH_4 at Point Barrow, Alaska. Significantly higher minimum concentrations of about 4 ppb C_2H_6, 1 ppb C_2H_2, 1 ppb C_3H_8, 2 ppb C_4H_{10}, and 0.7 ppb C_5H_{12} as well as 0.3 ppm CO and 1.5 ppm CH_4 were observed in rural Kane, Pennsylvania [*Research Triangle Institute*, 1974], possibly indicating the presence of pollutants. Similarly, *Grenda and Goldstein* [1977] observed averages of about 4 ppb C_2H_6, 1 ppb C_3H_8, 6 ppb C_4H_{10}, 4 ppb C_5H_{12}, 0.2 ppm CO, and 1.7 ppm CH_4 in a nonurban area of Ohio. R. A. Rasmussen's (private communication, 1977) observations indicate background levels of about 2 ppb C_2H_6 and 0.5 ppb C_2H_2. Clearly, more detailed measurements are needed before we can be certain of the background abundance of NMHC.

In these calculations we have normalized our results to ground level mixing ratios of 1 ppb for C_2H_6 and C_2H_2 and 0.1 ppb for C_3H_8, C_4H_{10}, and C_5H_{12}, the moderately reactive NMHC. As future measurements materialize, our results can be multiplied by the appropriate factor to yield the proper densities, fluxes, or reaction rates. For instance, if 0.1 ppb is more realistic for C_2H_6 than 1 ppb, our results for C_2H_6 should be multiplied by a factor of 0.1. Finally, we adopted ground level mixing ratios of 1.4 ppm for CH_4 and 0.11 ppm for CO [*Ehhalt and Heidt*, 1973; *Seiler*, 1974].

RESULTS

The calculated profiles for the standard model are presented in Figure 1. Our results indicate that detectable quantities of C_2H_6 and C_2H_2 may be present in the stratosphere. Although we know of no published data on stratospheric NMHC concentrations, upper limits (without detection) of 1 ppb C_2H_6 and C_2H_2 were obtained from an interferometer-spectrometer in the lower stratosphere (R. Toth, private communication, 1977). These results are consistent with our Figure 1. The calculated ground level fluxes or production rates necessary to support these profiles were (in units of molecules $cm^{-2} s^{-1}$) 2.6×10^9 for C_2H_6, 1.8×10^9 for C_2H_2, 9.3×10^8 for C_3H_8, 1.5×10^9 for C_4H_{10}, and 2.1×10^9 for C_5H_{12}, compared with 1.0×10^{11} for CH_4 and 1.3×10^{11} for CO. Thus assuming 1 ppb C_2H_6 and C_2H_2 and 0.1 ppb C_3H_8, C_4H_{10}, and C_5H_{12} at the ground, we infer a total NMHC production rate due to natural and/or anthropogenic activities of about 3×10^{10} atoms of C $cm^{-2} s^{-1}$ (or 94 Mton (10^6 metric tons) C yr^{-1}). This result is comparable to *Went*'s [1960] estimated volatization rate from living and dead vegetation of 180 Mton C yr^{-1}, primarily in the form of terpenes. Proportionately larger or smaller NMHC densities were obtained for larger or smaller ground level mixing ratios. Furthermore, relatively larger NMHC abundances result from decreasing the Cl or OH densities, thereby slowing the NMHC loss rate, or increasing K, thereby enhancing the upward transport of NMHC.

PHOTOCHEMICAL EFFECTS

Stratospheric CH_4, via

$$\text{(R2)} \qquad CH_4 + Cl \rightarrow CH_3 + HCl$$

plays a major role in impeding the Cl-catalyzed destruction of O_3 [*Stolarski and Cicerone*, 1974]:

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (1)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (2)$$

It is conceivable that NMHC, if sufficiently abundant, could play a similar role. (Note that (R7), (R15), (R19), and (R23)

TABLE 2. Reactions and Rate Coefficients

Reaction	Rate Coefficient, cm^3 $molecule^{-1}$ s^{-1}	Reference
(R1) $CH_4 + OH \rightarrow CH_3 + H_2O$	$k_1 = 2.36 \times 10^{-12} \exp(-1710/T)$	*Davis et al.* [1974]
(R2) $CH_4 + Cl \rightarrow CH_3 + HCl$	$k_2 = 2.95 \times 10^{-12} \exp(-1170/T)$	*Davis et al.* [1975]
(R3) $CH_4 + O(^1D) \rightarrow CH_3 + OH$	$k_3 = 3.6 \times 10^{-10}$	*Hampson and Garvin* [1975]
(R4) $CH_4 + O(^1D) \rightarrow CH_2O + H_2$	$k_4 = 4 \times 10^{-11}$	*Hampson and Garvin* [1975]
(R5) $CH_4 + O(^3P) \rightarrow$ products	$k_5 = 3.5 \times 10^{-11} \exp(-4550/T)$	*Herron and Huie* [1973]
(R6) $C_2H_6 + Cl \rightarrow C_2H_5 + HCl$	$k_6 = 1.86 \times 10^{-11} \exp(-1230/T)$	*Greiner* [1970]
(R7) $C_2H_6 + Cl \rightarrow C_2H_5 + HCl$	$k_7 = 7.3 \times 10^{-11} \exp(-60/T)$	B. Watson (personal communication, 1977)
(R8) $C_2H_6 + O(^1D) \rightarrow C_2H_5 + OH$ $C_2H_6 + O(^1D) \rightarrow CH_3 + CH_3O$	$k_8 = 6.2 \times 10^{-10}$	*Hampson and Garvin* [1975]
(R9) $C_2H_6 + O(^3P) \rightarrow$ products	$k_9 = 4.1 \times 10^{-11} \exp(-3200/T)$	*Herron and Huie* [1973]
(R10) $C_2H_2 + OH \rightarrow HC_2O + H_2$	$k_{10} = 5.3 \times 10^{-12} \exp(-1000/T)$	*Breen and Glass* [1970], *Fenimore and Jones* [1964[
(R11) $C_2H_2 + Cl \xrightarrow{M} CHCl{=}CH$	$k_{11} = 1 \times 10^{-12}$	*Lee and Rowland* [1977]
(R12) $C_2H_2 + O(^1D) \rightarrow$ products	$k_{12} = 3 \times 10^{-10}$	assumed
(R13) $C_2H_2 + O(^3P) \rightarrow$ products	$k_{13} = 0.5k_9$	assumed
(R14) $C_3H_8 + OH \rightarrow C_3H_7 + H_2O$	$k_{14} = 1.2 \times 10^{-11} \exp(-675/T)$	*Greiner* [1970]
(R15) $C_3H_8 + Cl \rightarrow C_3H_7 + HCl$	$k_{15} = 3.2 \times 10^{-10} \exp(-340/T)$	*Trotman-Dickenson and Milne* [1967]
(R16) $C_3H_8 + O(^1D) \rightarrow$ products	$k_{16} = 7 \times 10^{-10}$	assumed
(R17) $C_3H_8 + O(^3P) \rightarrow$ products	$k_{17} = 5 \times 10^{-11} \exp(-2900/T)$ $+ 4.4 \times 10^{-11} \exp(-2250/T)$	*Herron and Huie* [1973]
(R18) $C_4H_{10} + OH \rightarrow C_4H_9 + H_2O$	$k_{18} = 1.41 \times 10^{-11} \exp(-521/T)$	*Greiner* [1970]
(R19) $C_4H_{10} + Cl \rightarrow C_4H_9 + HCl$	$k_{19} = 1.4 \times 10^{-10} \exp(-388/T)$ $+ 1.48 \times 10^{-10} \exp(-126/T)$	*Trotman-Dickenson and Milne* [1967]
(R20) $C_4H_{10} + O(^1D) \rightarrow$ products	$k_{20} = 7 \times 10^{-10}$	assumed
(R21) $C_4H_{10} + O(^3P) \rightarrow$ products	$k_{21} = 1.5 \times 10^{-11} \exp(-2920/T)$ $+ 7.7 \times 10^{-11} \exp(-2410/T)$	*Herron and Huie* [1973]
(R22) $C_5H_{12} + OH \rightarrow C_5H_{11} + H_2O$	$k_{22} = 6 \times 10^{-12} \exp(-820/T)$ $+ 1.4 \times 10^{-11} \exp(-430/T)$	*Greiner* [1970]
(R23) $C_5H_{12} + Cl \rightarrow C_5H_{11} + HCl$	$k_{23} = 2.04 \times 10^{-10} \exp(-352/T)$	*Trotman-Dickenson and Milne* [1967] (based on rate for i-C_5H_{12})
(R24) $C_5H_{12} + O(^1D) \rightarrow$ products	$k_{24} = 7 \times 10^{-10}$	assumed
(R25) $C_5H_{12} + O(^3P) \rightarrow$ products	$k_{25} = 4.8 \times 10^{-11} \exp(-2920/T)$ $+ 1.3 \times 10^{-10} \exp(-2320/T)$	*Herron and Huie* [1973]
(R26) $CO + OH \rightarrow CO_2 + H$	$k_{26} = 2.15 \times 10^{-13} \exp(-80/T)$	*Davis et al.* [1974]

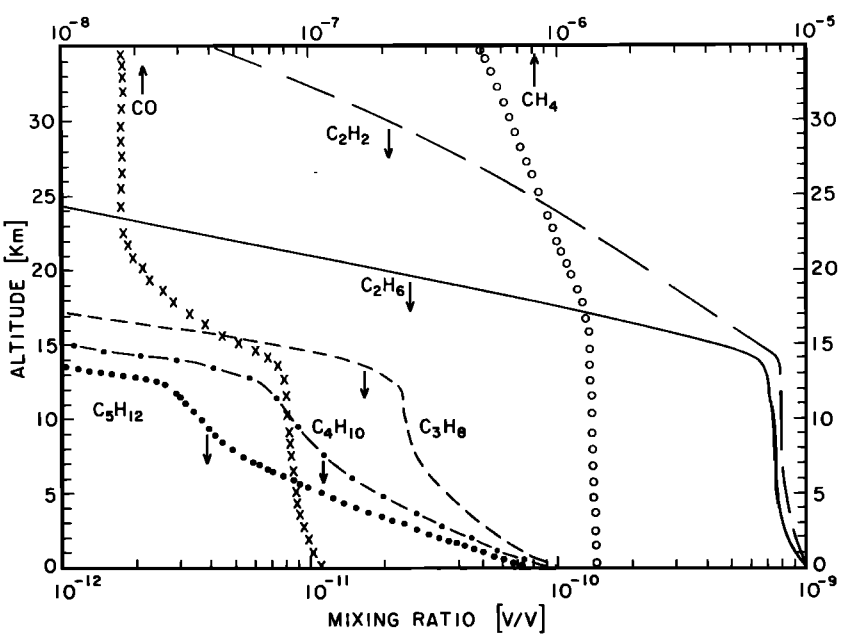

Fig. 1. Calculated mixing ratio profiles using the standard model. The profile of C_2H_6 is represented by the solid line and bottom abscissa, C_2H_2 by the long-dash line and bottom abscissa, C_3H_8 by the short-dash line and bottom abscissa, C_4H_{10} by the dot-dash line and bottom abscissa, C_5H_{12} by the dotted line and bottom abscissa, CH_4 by the open circles and top abscissa, and CO by the crosses and top abscissa.

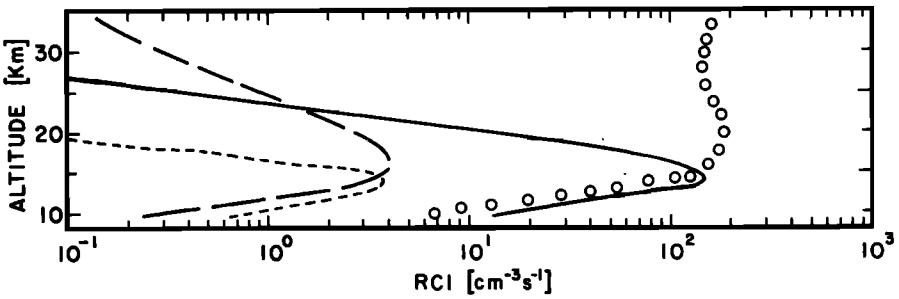

Fig. 2. The rate of reaction with Cl. The solid line is the reaction rate of Cl with C_2H_6, the long-dash line with C_2H_2, the short-dash line with C_3H_8 + C_4H_{10} + C_5H_{12}, and the open circles with CH_4.

convert Cl to HCl, but (R11) represents a loss process for total inorganic chlorine, ClX.) Figure 2 illustrates the rate at which Cl reacts with the hydrocarbons for the standard model. The ratio of the total rate at which Cl reacts with NMHC to the rate at which Cl reacts with CH_4 for a variety of assumed OH, Cl, and K profiles is depicted in Figure 3. Note that while C_2H_6 attacks Cl at a large rate compared with CH_4 in the lower stratosphere, in the 25- to 40-km region, where Cl-catalyzed destruction of O_3 is effective, the loss of Cl due to NMHC is relatively small. For instance, in the standard model, for the Cl loss rate due to NMHC to be 10% of the loss rate due to CH_4 at 25 and 30 km, we would have had to assume 10 times and 50 times larger ground level NMHC mixing ratios, respectively. Background concentrations of 10–50 ppb C_2H_6 and C_2H_2 are much larger than observations indicate. The relative rate of attack of NMHC upon Cl can be enhanced by decreasing OH and Cl densities and/or increasing K, as illustrated in Figure 3. For instance, assuming a Cl profile of 1/10, the standard model yielded a rate of NMHC attack upon Cl which was 15% that of CH_4 at 25 km. Decreasing Cl by a factor of 100 yields an even greater relative role for NMHC. However, for this low an abundance of Cl the loss of O_3 due to Cl-catalyzed reactions is small in comparison with other loss processes. Thus our calculations indicate that for low levels of stratospheric ClX (0.1 ppb or less near 40 km), NMHC may have a small but significant effect upon the chlorine chemistry near 30 km. However, for abundances of ClX sufficient to affect the stratospheric ozone budget the destruction of NMHC by reactions with Cl below 25 km is large enough to prevent NMHC from having a significant impact upon ClX above 25 km; this applies for ground level NMHC densities of a few ppb or less.

Since Cl comprises such a small fraction of the total ClX reservoir [cf. *Liu et al.*, 1976], below 25 km an increase in the rate of conversion of Cl to HCl by (R7) will not significantly alter the HCl or ClX density. On the other hand, the production of CHCl=CH by (R11) represents a net loss of ClX. Our standard model calculations yielded a column-integrated ClX loss rate via (R11) of 4×10^6 cm^{-2} s^{-1}, while a ClX loss rate of 6×10^6 cm^{-2} s^{-1} was obtained when we reduced the tropospheric OH density by one half. These loss rates are comparable to the ClX source of about 1.3×10^7 cm^{-2} s^{-1} needed to maintain the assumed stratospheric ClX profile [*Rowland and Molina*, 1975; *Cicerone et al.*, 1975]. Thus if the chlorovinyl molecule (CHCl=CH) were stable enough to be transported downward into the troposphere in significant quantities before chemical decomposition could release the Cl atom, one would expect the projected loss of O_3 due to Cl-ClO catalytic

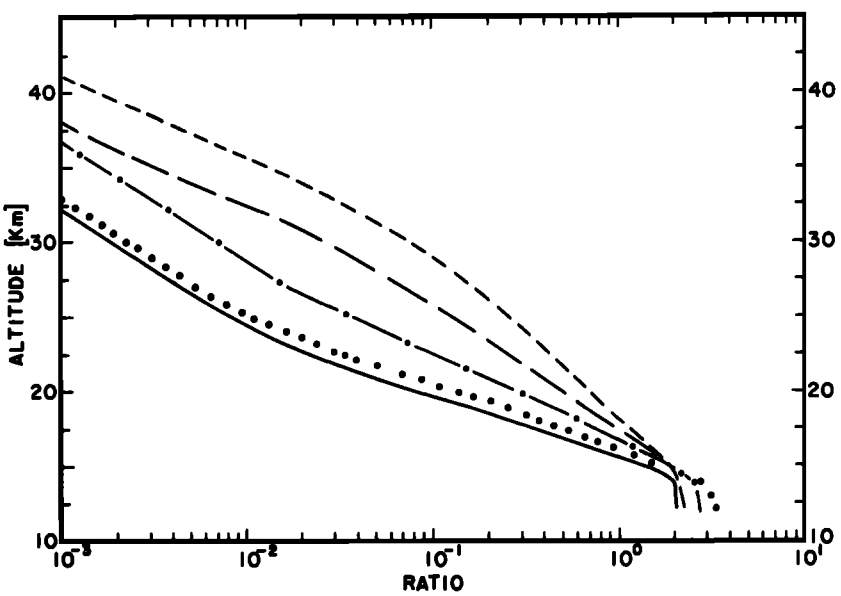

Fig. 3. The ratio of total rate of reactions of Cl with NMHC ((R7) + (R11) + (R15) + (R19) + (R23)) to the rate of reaction of Cl with CH_4 (R2) as a function of altitude. The solid line is for the standard model, the dotted line is for $K = 2 \times 10^6$ cm^2 s^{-1} between 0 and 10 km, the dot-dash line is for OH and Cl decreased by a factor of 2, the long-dash line is for Cl decreased by a factor of 10, and the short-dash line is for Cl decreased by a factor of 100.

chains to be smaller. As was noted by *Lee and Rowland* [1977], it is likely that O_2 will attach to the radical to form a peroxy radical; the product so formed is not very likely to be stable against further photochemical attack, but this should be investigated.

Note that the possible existence of the asymmetric chlorine dioxide molecule ClOO could alter our results. Using a lower limit for ΔH_f(ClOO), 84 kJ/mol [*Watson*, 1974], we calculate that ClOO may be 50–100 times more concentrated than Cl in the lower stratosphere. While the calculated Cl atom densities (Table 1) used in our model are strongly independent of the ClOO abundance, if ClOO abstracts H atoms from NMHC (in slightly endothermic reactions), it could represent another lower stratospheric sink for NMHC.

Our calculations indicate that the impact of NMHC upon tropospheric photochemistry is also small. We have estimated the effects of NMHC upon tropospheric hydrogen oxides and ozone using the model of *Chameides and Stedman* [1977] and incorporating the photochemistry of the NMHC [cf. *Demerjian et al.*, 1974] in an approximate manner. These calculations indicate that for the ground level mixing ratios that we have assumed, NMHC cause only an approximate 10% decrease in the OH/HO_2 ratio in the lower troposphere, a 6% increase in the column-integrated photochemical loss rate of tropospheric ozone, and a 20% increase in the column-integrated photochemical production rate. In view of several larger uncertainties remaining in our understanding of tropospheric photochemistry, these effects are small.

Perhaps the most significant role of NMHC is the production of atmospheric CO. *Seiler*'s [1974] observations and recent model calculations [*Wofsy*, 1976; *Chameides et al.*, 1977; *Sze*, 1977] indicate that anthropogenic production of CO is approximately equal in magnitude to natural production via the oxidation of CH_4 [*Levy*, 1971; *McConnell et al.*, 1971; *Weinstock*, 1969]. It is possible that the oxidation of NMHC ultimately results in the production of CO via oxidation chains similar to the CH_4 oxidation chain [cf. *Demerjian et al.*, 1974; *Breen and Glass*, 1970; *Williamson and Bayes*, 1967]. If we assume 1 ppb C_2H_6 and C_2H_2 at the ground and 0.1 ppb C_3H_8, C_4H_{10}, and C_5H_{12} at the ground and if we assume that every carbon atom eventually becomes CO, then we obtain a CO production rate due to these NMHC of about 3×10^{10} CO molecules cm^{-2} s^{-1} (or 220 Mton CO yr^{-1}). This compares with a calculated production rate from CH_4 of 1×10^{11} cm^{-2} s^{-1} (or 730 Mton CO yr^{-1}), a photochemical sink via (R26) of 2.3×10^{11} cm^{-2} s^{-1} (or 1540 Mton CO yr^{-1}), and an anthropogenic source of 9×10^{10} cm^{-2} s^{-1} (or 640 Mton CO yr^{-1}) [*Seiler*, 1974]. However, our calculated CO production rate from the oxidation of NMHC is uncertain owing to the lack of detailed observations of the ambient concentrations of these species. Furthermore, heterogeneous loss processes may block the photooxidation of NMHC and thereby prevent the release of CO.

CONCLUSION

Our calculations (Figure 1) imply that measurable quantities of relatively unreactive NMHC, especially C_2H_6 and C_2H_2, may be present in the upper troposphere and stratosphere. Nevertheless, our results indicate that NMHC are not likely to have a large impact on the background photochemistry of the troposphere and stratosphere, although local effects near source regions are probable. In view of the many uncertainties in the photochemistry of the lower atmosphere, our findings support the present-day practice of many modelers who neglect NMHC in their calculations. However, we have found that if CHCl=CH is stable in the lower stratosphere, then C_2H_2 may act as a partially effective chain terminator to impede catalytic removal of stratospheric O_3 by Cl and ClO. Interestingly, Cl atoms at levels predicted to exist in the present-day lower stratosphere might comprise the major stratospheric sink of NMHC.

Assuming ground level mixing ratios of 1 ppb for C_2H_6 and C_2H_2 and 0.1 ppb for C_3H_8, C_4H_{10}, and C_5H_{12}, we obtain a total NMHC loss rate of 3×10^{10} atoms C cm^{-2} s^{-1}, which could conceivably result in the production of 200 Mton CO yr^{-1}. More detailed measurements of NMHC levels in various environments are needed to refine this estimate.

Acknowledgments. This work was supported in part by the National Aeronautics and Space Administration under grant NSG-1363 (to W.L.C.) and grant NSG-7187 (to R.J.C.) and by the National Science Foundation under grant ATM74-11478 A05 (to R.J.C.).

REFERENCES

Breen, J. E., and G. P. Glass, The reaction of the hydroxyl radical with acetylene, *Int. J. Chem. Kinet.*, *3*, 145–153, 1970.

Cavanaugh, L. A., C. F. Schadt, and E. Robinson, Atmospheric hydrocarbon and carbon monoxide measurements at Point Barrow, Alaska, *Environ. Sci. Technol.*, *3*, 251–257, 1969.

Chameides, W. L., and D. H. Stedman, Tropospheric ozone: Coupling transport and photochemistry, *J. Geophys. Res.*, *82*, 1787–1794, 1977.

Chameides, W. L., S. C. Liu, and R. J. Cicerone, Possible variations in atmospheric methane, *J. Geophys. Res.*, *82*, 1795–1798, 1977.

Cicerone, R. J., D. H. Stedman, and R. S. Stolarski, Estimate of late 1974 stratospheric concentration of gaseous chlorine compounds (ClX), *Geophys. Res. Lett.*, *2*, 219–222, 1975.

Crutzen, P. J., Photochemical reactions initiated by and influencing ozone in unpolluted tropospheric air, *Tellus*, *26*, 47–57, 1974.

Davis, D. D., S. Fisher, and R. Schiff, Flash photolysis–resonance fluorescence kinetics study: Temperature dependence of the reactions $OH + CO \rightarrow CO_2 + H$ and $OH + CH_4 \rightarrow H_2O + CH_3$, *J. Chem. Phys.*, *61*, 2213–2219, 1974.

Davis, D. D., R. L. Schiff, U. Machado, and R. T. Watson, Absolute rate constants for elementary reactions of atmospheric importance: Results from the University of Maryland's gas kinetics laboratory, *Rep. 2*, Univ. of Md., College Park, 1975.

Demerjian, K. L., J. A. Kerr, and J. G. Calvert, The mechanism of photochemical smog formation, *Advan. Environ. Sci. Technol.*, *4*, 1–262, 1974.

Ehhalt, D. H., and L. E. Heidt, The concentration of molecular H_2 and CH_4 in the stratosphere, *Pure Appl. Geophys.*, *106-108*, 1352–1360, 1973.

Fenimore, C. P., and G. W. Jones, Rate of destruction of acetylene in flame gases, *J. Chem. Phys.*, *41*, 1887–1889, 1964.

Greiner, N. R., Hydroxyl radical kinetics by kinetic spectroscopy, 6, Reactions with alkanes in the range 300–500°K, *J. Chem. Phys.*, *53*, 1070–1076, 1970.

Grenda, R. N., and H. W. Goldstein, Nonurban measurements of methane and ethane under varying atmospheric conditions, *J. Geophys. Res.*, *82*, in press, 1977.

Hampson, R. F., and D. Garvin (Eds.), Chemical kinetic and photochemical data for modeling atmospheric chemistry, *NBS Tech. Note 866*, 113 pp., Nat. Bur. of Stand., Gaithersburg, Md., 1975.

Herron, J. T., and R. E. Huie, Rate constants for the reactions of atomic oxygen (O^3P) with organic compounds in the gas phase, *J. Phys. Chem. Ref. Data*, *2*, 467–518, 1973.

Hunten, D. M., Vertical transport in atmospheres, in *Atmospheres of Earth and Planets*, edited by B. M. McCormac, pp. 59–72, D. Reidel, Hingham, Mass., 1975.

Lee, F. S. C., and F. S. Rowland, The reaction of chlorine atoms with acetylene and their possible stratospheric significance, submitted to *J. Chem. Phys.*, 1977.

Levy, H., Normal atmosphere: Large radical and formaldehyde concentrations predicted, *Science*, *173*, 141–143, 1971.

Levy, H., Photochemistry of the lower troposphere, *Planet. Space Sci.*, *20*, 919–935, 1972.

Liu, S. C., T. M. Donahue, R. J. Cicerone, and W. L. Chameides,

Effect of water vapor on the destruction of ozone in the stratosphere perturbed by ClX or NO_x pollutants, *J. Geophys. Res., 81,* 3111–3118, 1976.

McConnell, J. C., M. B. McElroy, and S. C. Wofsy, Natural sources of atmospheric CO, *Nature, 233,* 187–188, 1971.

Research Triangle Institute, Investigation of ozone and ozone precursor concentrations at non-urban locations in the eastern United States, *Publ. EPA-450/3-74-034,* U.S. Environ. Prot. Agency, Washington, D. C., 1974.

Rowland, F. S., and M. J. Molina, Chlorofluoromethanes in the environment, *Rev. Geophys. Space Phys., 13,* 1–35, 1975.

Seiler, W., The cycle of atmospheric CO, *Tellus, 26,* 117–135, 1974.

Singh, H. B., Atmospheric halocarbons, *Geophys. Res. Lett., 4,* 101–104, 1977.

Stolarski, R. S., and R. J. Cicerone, Stratospheric chlorine: A possible sink for ozone, *Can. J. Chem., 52,* 1610–1615, 1974.

Sze, N. D., Anthropogenic CO emissions: Implications for the atmospheric CO-OH-CH_4 cycle, *Science, 195,* 673–675, 1977.

Trotman-Dickenson, A. F., and G. S. Milne, *Tables of Bimolecular Gas Reactions, NSRDS-NBS9,* National Bureau of Standards, Gaithersburg, Md., 1967.

Watson, R. T., Rate constants of ClO_x of atmospheric interest, *Chem. Kinet. Data Surv. VIII, NBSIR 74-516,* Nat. Bur. of Stand., Gaithersburg, Md., June 1974.

Weinstock, B., Carbon monoxide: Residence time in the atmosphere, *Science, 166,* 224–225, 1969.

Went, F. W., Organic matter in the atmosphere, and its possible relation to petroleum formation, *Proc. Nat. Acad. Sci., 46,* 212–221, 1960.

Williamson, D. G., and K. D. Bayes, The reaction of C_2O with oxygen and nitric oxide, *J. Amer. Chem. Soc., 89,* 3390–3396, 1967.

Wofsy, S. C., Interactions of CH_4 and CO in the earth's atmosphere, *Annu. Rev. Earth Planet. Sci., 4,* 441–469, 1976.

Wofsy, S. C., J. C. McConnell, and M. B. McElroy, Atmospheric CH_4, CO, and CO_2, *J. Geophys. Res., 77,* 4477–4493, 1972.

(Received March 24, 1977;
revised August 25, 1977;
accepted September 9, 1977.)