Effects of Nonmethane Hydrocarbons in the Atmosphere

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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 C2H6, C3H8, C2H6, C3H8, and C4H6. 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 C4H6 could be partially effective as a chain terminator to impede catalytic removal of stratospheric O3 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 C2H6 and C2H2, 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 C2H6 and C2H2 as well as some moderately reactive (lower tropospheric lifetimes of about 5 days) NMHC: C2H6, C3H8, and C4H6. (All hydrocarbons were taken to be the normal isomer; i.e., C2H12 is $n$-C2H12.)

MODEL CALCULATIONS

Using a one-dimensional steady state model with coupled photochemistry and vertical transport, we calculated the vertical profiles of C2H6, C3H8, C2H6, C3H8, and C4H6 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 30ºN 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 CH3CCl3 of about 5 years, as compared with Singh's [1977] inferred result of (7.2 ± 1.2) years. The CI profile was obtained by assuming a total inorganic chlorine (CIX) 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 CI 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 1016 cm−3, reaction with Cl is the major loss process for the alkanes, while for C2H2 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 CI with C2H2. Lee and Rowland [1977] suggest that the reaction produces the excited C2H2C1* radical which either stabilizes to CHCl=CH or decomposes to form C2H2 and CI again. They estimate the effective rate constant for conversion of CI to CHCl=CH to be 10−18 cm3 molecule−1 s−1, which we have used in our calculations for the reaction of CI with C2H2:

\[
\text{Cl} + \text{C}_2\text{H}_2 \rightarrow \text{CHCl} = \text{CH}
\]

(R11)

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 CH4 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

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TABLE 1. Input Parameters

| Z, km | Number Density,* cm⁻² | T,* °K | K,† cm⁻³ s⁻¹ | n(OH),‡ cm⁻³ | n(Cl),§ cm⁻³ | n(O(1D)),¶ cm⁻³ | n(O²),‖ 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)     | 2.36 (-2)    | 3.06 (4)      | 3.06 (4)     |
| 18    | 2.61 (18)              | 217   | 6.46 (3)     | 5.42 (5)     | 4.09 (3)     | 7.84 (-1)      | 2.16 (6)     |
| 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)     | 7.05 (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    | 0.87 (18)              | 223   | 1.68 (4)     | 12.86        | 1.57 (4)     | 5.98           | 1.78 (7)     |
| 28    | 0.59 (17)              | 225   | 2.30 (4)     | 1.79 (6)     | 2.29 (4)     | 11.4           | 3.21 (7)     |
| 30    | 0.36 (17)              | 227   | 3.12 (4)     | 2.67 (6)     | 3.59 (4)     | 21.4           | 5.56 (7)     |
| 32    | 0.29 (17)              | 229   | 4.28 (4)     | 4.25 (6)     | 6.08 (4)     | 38.5           | 9.34 (7)     |
| 34    | 0.23 (17)              | 234   | 5.84 (4)     | 7.04 (6)     | 1.16 (5)     | 64.2           | 2.43 (8)     |
| 36    | 0.17 (17)              | 239   | 7.90 (4)     | 1.14 (7)     | 1.80 (5)     | 95.4           | 1.53 (8)     |
| 38    | 0.15 (17)              | 245   | 1.09 (5)     | 1.73 (7)     | 2.90 (5)     | 1.32 (2)       | 3.81 (8)     |
| 40    | 0.14 (17)              | 250   | 1.49 (5)     | 2.31 (7)     | 4.36 (5)     | 1.69 (2)       | 6.02 (8)     |

Read 2.63 (19) as 2.63 X 10⁻⁶

*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 CIX 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 C₇H₈, ≤0.06 ppb C₈H₁₈, and ≤0.15 ppb C₉H₂₀ as well as 0.09 ppm CO and 1.6 ppm CH₄ at Point Barrow, Alaska. Significantly higher minimum concentrations of about 4 ppb C₆H₆, 1 ppb C₇H₁₈, 1 ppb C₈H₂₀, 2 ppb C₉H₂₂, and 0.7 ppb C₁₀H₂₀ as well as 0.3 ppm CO and 1.5 ppm CH₄ 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 C₆H₆, 1 ppb C₇H₁₈, 1 ppb C₈H₂₀, 2 ppb C₉H₂₂, and 0.7 ppb C₁₀H₂₀ as well as 0.3 ppm CO and 1.5 ppm CH₄ in a nonurban area of Ohio. R. A. Rasmussen's (private communication, 1977) observations indicate background levels of about 2 ppb C₆H₆ and 0.5 ppb C₇H₁₈. 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 C₇H₈ and C₆H₆ and 0.1 ppb for C₈H₂₀, C₉H₂₀, and C₁₀H₂₀, 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 C₇H₈ than 1 ppb, our results for C₇H₈ should be multiplied by a factor of 0.1. Finally, we adopted ground level mixing ratios of 1.4 ppm for CH₄ and 0.11 ppm for CO [Ehhalt and HeMt, 1973; Seiler, 1974].

RESULTS

The calculated profiles for the standard model are presented in Figure 1. Our results indicate that detectable quantities of C₆H₆ and C₇H₈ may be present in the stratosphere. Although we know of no published data on stratospheric NMHC concentrations, upper limits (without detection) of 1 ppb C₆H₆ and C₇H₈ 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⁻³ s⁻¹) 2.6 X 10⁹ for C₆H₆, 1.8 X 10⁹ for C₇H₈, 9.3 X 10⁸ for C₈H₁₈, 1.5 X 10⁹ for C₉H₂₀, and 2.1 X 10⁹ for C₁₀H₂₂ compared with 1.0 X 10¹¹ for CH₄ and 1.3 X 10¹¹ for CO. Thus assuming 1 ppb C₆H₆ and C₇H₈ and 0.1 ppb C₈H₂₀, C₉H₂₀, and C₁₀H₂₂ at the ground, we infer a total NMHC production rate due to natural and/or anthropogenic activities of about 3 X 10¹⁴ atoms of C cm⁻³ s⁻¹ (or 94 Mton (10⁶ 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 CH₄, via

(R2) CH₄ + Cl → CH₃ + HCl
plays a major role in impeding the Cl-catalyzed destruction of O₃ [Stolarski and Cicerone, 1974]:

Cl + O₃ → ClO + O₂ (1)
ClO + O → Cl + O₂ (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, cm³ molecule⁻¹ s⁻¹ | Reference |
|----------|--------------------------------------|-----------|
| (R1) CH₄ + OH → CH₃ + H₂O | $k = 2.36 \times 10^{-11} \exp(-1710/T)$ | Davis et al. [1974] |
| (R2) CH₄ + Cl → CH₃ + HCl | $k = 2.95 \times 10^{-11} \exp(-1170/T)$ | Davis et al. [1975] |
| (R3) CH₄ + O('D) → CH₃ + OH | $k = 3.6 \times 10^{-11}$ | Hampson and Garvin [1975] |
| (R4) CH₄ + O('D) → CH₂O + H₂ | $k = 4 \times 10^{-11}$ | Hampson and Garvin [1975] |
| (R5) CH₄ + O('P) → products | $k = 3.5 \times 10^{-11} \exp(-4550/T)$ | Herron and Huie [1973] |
| (R6) C₂H₆ + Cl → C₂H₅ + HCl | $k = 1.86 \times 10^{-11} \exp(-1230/T)$ | Greiner [1970] |
| (R7) C₂H₆ + Cl → C₂H₅ + HCl | $k = 7.3 \times 10^{-11} \exp(-60/T)$ | B. Watson (personal communication, 1977) |
| (R8) C₂H₆ + O('D) → C₂H₅ + OH | $k = 6.2 \times 10^{-11}$ | Hampson and Garvin [1975] |
| (R9) C₂H₆ + O('D) → C₂H₅ + H₂O | $k = 4.1 \times 10^{-11} \exp(-3200/T)$ | Herron and Huie [1973] |
| (R10) C₂H₆ + OH → H₂O + C₂H₅ | $k = 5.3 \times 10^{-11} \exp(-1000/T)$ | Breen and Glass [1970], Fenimore and Jones [1964] |
| (R11) C₂H₅ + Cl + CHCl = CH | $k = 1 \times 10^{-12}$ | Lee and Rowland [1977] |
| (R12) C₂H₅ + O('D) → products | $k = 3 \times 10^{-13}$ | assumed |
| (R13) C₂H₅ + O('P) → products | $k = 0.5 k₄$ | assumed |
| (R14) C₂H₅ + OH → C₂H₄ + H₂O | $k = 1.2 \times 10^{-11} \exp(-675/T)$ | Greiner [1970] |
| (R15) C₂H₅ + Cl → C₂H₄ + HCl | $k = 3.2 \times 10^{-11} \exp(-340/T)$ | Trotman-Dickenson and Milne [1967] |
| (R16) C₂H₅ + O('D) → products | $k = 7 \times 10^{-13}$ | assumed |
| (R17) C₂H₅ + O('P) → products | $k = 5 \times 10^{-11} \exp(-2900/T)$ | Herron and Huie [1973] |
| (R18) C₂H₅ + OH → C₂H₄ + H₂O | $k = 1.41 \times 10^{-11} \exp(-521/T)$ | Greiner [1970] |
| (R19) C₂H₅ + Cl → C₂H₄ + HCl | $k = 1.4 \times 10^{-10} \exp(-388/T)$ | Trotman-Dickenson and Milne [1967] |
| (R20) C₂H₅ + O('D) → products | $k = 7 \times 10^{-15}$ | assumed |
| (R21) C₂H₅ + O('P) → products | $k = 1.5 \times 10^{-11} \exp(-2920/T)$ | Herron and Huie [1973] |
| (R22) C₂H₅ + OH → C₂H₄ + H₂O | $k = 6 \times 10^{-11} \exp(-820/T)$ | Greiner [1970] |
| (R23) C₂H₅ + Cl → C₂H₄ + HCl | $k = 6 \times 10^{-11} \exp(-430/T)$ | Trotman-Dickenson and Milne [1967] (based on rate for i-C₂H₅) |
| (R24) C₂H₅ + O('D) → products | $k = 7 \times 10^{-11}$ | assumed |
| (R25) C₂H₅ + O('P) → products | $k = 4.8 \times 10^{-11} \exp(-2920/T)$ | Herron and Huie [1973] |
| (R26) CO + OH → CO₂ + H | $k = 2.15 \times 10^{-11} \exp(-80/T)$ | Davis et al. [1974] |

![Fig. 1. Calculated mixing ratio profiles using the standard model. The profile of C₂H₅ is represented by the solid line and bottom abscissa, C₂H₆ by the long-dash line and bottom abscissa, C₂H₅ by the short-dash line and bottom abscissa, C₂H₆ by the dot-dash line and bottom abscissa, C₂H₅ by the dotted line and bottom abscissa, CH₄ by the open circles and top abscissa, and CO by the crosses and top abscissa.](image-url)
convert Cl to HCl, but (R11) represents a loss process for total inorganic chlorine, CIX.) 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 CH₄ for a variety of assumed OH, Cl, and K profiles is depicted in Figure 3. Note that while C₂H₈ attacks Cl at a large rate compared with CH₄ in the lower stratosphere, in the 25- to 40-km region, where Cl-catalyzed destruction of O₃ 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 CH₄ 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 C₂H₆ and C₂H₄ 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 CH₄ 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 O₃ due to Cl-catalyzed reactions is small in comparison with other loss processes. Thus our calculations indicate that for low levels of stratospheric CIX (0.1 ppb or less near 40 km), NMHC may have a small but significant effect upon the ozone chemistry near 30 km. However, for abundances of CIX 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 CIX 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 CIX 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 CIX density. On the other hand, the production of CHCl=CH by (R11) represents a net loss of CIX. Our standard model calculations yielded a column-integrated CIX loss rate via (R11) of 4 × 10⁹ cm⁻² s⁻¹, while a CIX loss rate of 6 × 10⁹ cm⁻² s⁻¹ was obtained when we reduced the tropospheric OH density by one half. These loss rates are comparable to the CIX source of about 1.3 × 10⁹ cm⁻² s⁻¹ needed to maintain the assumed stratospheric CIX 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 O₃ due to Cl-CIO catalytic...
chains to be smaller. As was noted by Lee and Rowland [1977], it is likely that O₃ 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 CIO₂ could alter our results. Using a lower limit for ΔHf(ClO₂), 84 kJ/mol [Watson, 1974], we calculate that ClO₂ 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 ClO₂ abundance, if CIO₂ 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/HO₂ 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 CH₄ [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 CH₄ oxidation chain [cf. Demerjian et al., 1974; Breen and Glass, 1970; Williamson and Hayes, 1967]. If we assume 1 ppb CH₄ and C₂H₆ at the ground and 0.1 ppb C₃H₈, C₄H₁₀, and C₅H₁₂ 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 × 10⁹ CO molecules cm⁻² s⁻¹ (or 220 Mton CO yr⁻¹). This compares with a calculated production rate from CH₄ of 1 × 10⁹ cm⁻² s⁻¹ (or 730 Mton CO yr⁻¹), a photochemical sink via (R26) of 2.3 × 10⁹ cm⁻² s⁻¹ (or 1540 Mton CO yr⁻¹), and an anthropogenic source of 9 × 10⁹ 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 C₃H₈ and C₄H₁₀, 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 C₂H₆ may act as a partially effective chain terminator to impede catalytic removal of stratospheric O₃ by Cl and CIO. 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 C₃H₈ and C₄H₁₀ and 0.1 ppb for C₅H₁₂, we obtain a total NMHC loss rate of 3 × 10⁹ atoms 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.

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