

PHOTOCHEMISTRY OF METHANE IN THE EARTH'S EARLY ATMOSPHERE

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ABSTRACT

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A detailed model is presented of methane photochemistry in the primitive terrestrial atmosphere along with speculation about its interpretation. Steady-state CH_4 mixing ratios of 10^{-6} – 10^{-4} could have been maintained by a methane source of about $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, which is comparable to the modern biogenic methane production rate. In the absence of a source, methane would have disappeared in $< 10^4$ years, being either oxidized, or polymerized into more complex hydrocarbons. The source strength needed to maintain a steady CH_4 mixing ratio and the degree to which methane could have polymerized to form higher hydrocarbons depend upon the amount of CO_2 present in the early atmosphere. The dependence on H_2 is much weaker. Infrared absorption by methane, and especially by other hydrocarbon species, may have supplemented the greenhouse warming due to carbon dioxide. A radiative model is needed to establish this effect quantitatively. The destruction of the methane greenhouse early in the Proterozoic may have triggered the Huronian glaciation.

These calculations also suggest that atmospheres rich in both CO_2 and CH_4 may be photochemically unstable with respect to conversion to CO .

INTRODUCTION

Theoretical calculations by several investigators have led to plausible models for the composition of the Earth's primitive atmosphere (Walker, 1977; Yung and McElroy, 1979; Kasting et al., 1979; Kasting and Walker, 1981; Pinto

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et al., 1980). The model atmospheres considered in these studies consist primarily of N_2 , CO_2 and H_2O , along with smaller concentrations of H_2 and CO , and only trace amounts of O_2 . This type of weakly reducing early atmosphere is consistent with both the geological record and with the present understanding of volcanic emissions and the escape of hydrogen to space.

The factors controlling climate on the early Earth are less well understood. Models of stellar evolution predict that the ancient Sun was considerably less luminous than it is today (Newman and Rood, 1977). Since the Earth does not appear to have been extensively glaciated during the first half of its history (Frakes, 1979), several authors have suggested that the atmospheric greenhouse effect must have been substantially larger in the remote past. Sagan and Mullen (1972) originally proposed ammonia as the key primordial greenhouse constituent. However, calculations by Kuhn and Atreya (1979) and Kasting (1982) indicate that ammonia is photochemically unstable with respect to conversion to N_2 and is, therefore, unlikely to have played a major role in warming the Earth's surface.

Carbon dioxide is a more promising candidate. Owen et al. (1979) have shown that CO_2 concentrations of 100–1000 PAL (present atmospheric level) could have provided the required warming. Walker et al. (1981) have proposed a mechanism by which enhanced CO_2 levels could have been maintained in the distant past. The rate of loss of CO_2 through silicate weathering depends upon rainfall and is, therefore, likely to be a strong function of surface temperature. At global surface temperatures lower than today's, the CO_2 loss rate should decrease and more CO_2 should accumulate in the atmosphere. The Earth's climate may be effectively buffered by this mechanism, so that even relatively large decreases in solar luminosity may result in only small decreases in average surface temperature.

We suggest here, that the early greenhouse effect may have been further augmented by the presence of atmospheric methane. Donner and Ramanathan (1980) have shown that the 1.4 ppm (parts per million) of methane in today's atmosphere contribute about 1.4 K to the present globally-averaged surface temperature. The absorption due to the 7.4μ band of methane increases linearly with CH_4 concentration up to a mixing ratio of about 0.7 ppm, then more slowly above this level as the center of the band becomes saturated. Thus, methane could have made a modest contribution towards heating the early atmosphere if its mixing ratio was $> \sim 10^{-6}$. Perhaps more significantly, methane may also have polymerized in response to solar ultraviolet radiation, creating higher hydrocarbon compounds which should also have been absorbed in the infrared. If several of these compounds were each able to provide a small amount of heating, the combined effect could have been of major climatic significance. With this in mind, we have investigated the photochemical behavior of methane in the early atmosphere to determine how much CH_4 might have been present and what types of higher hydrocarbons could have been formed.

THE MODEL

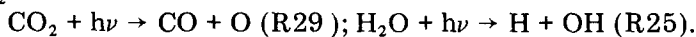
The one-dimensional photochemical model used in this study is similar to that described by Kasting (1982), except that the focus is on hydrocarbon photochemistry rather than the photochemistry of ammonia. Diffusion equations were solved simultaneously for 22 different species: O_3 , O , H_2O , OH , HO_2 , H_2O_2 , H , O_2 , H_2 , CO_2 , CO , HCO , H_2CO , CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_2H_2 , C_2H_4 , CH_3 , 3CH_2 and C_2H_5 . Another 12 species, including $O(^1D)$, 1CH_2 , excited C_2H_2 ($C_2H_2^*$), C_2H , C_2H_3 , C_3H_6 , C_4H_8 , C_3H_7 , C_4H_9 , CH_3CHO , C_2H_5CHO and C_3H_7CHO , were assumed to be in photochemical equilibrium. The equations were integrated in time-dependent fashion until a steady-state solution was approached, which typically required 10–100 years of model time. More time was required for certain ‘high CO’ cases, as will be discussed later.

The altitude grid used in the model extends from 0 to 80 km in 1 km increments. The assumed boundary conditions for most species were zero flux at the ground and at 80 km. At the top the upward fluxes of CO_2 and O_2 required to compensate for photodissociation were balanced by downward fluxes of CO and O . Constant ground-level mixing ratios were assumed for H_2O , H_2 , CO_2 and CH_4 . The tropospheric H_2O mixing ratio was fixed at values ranging from 1.5×10^{-2} at the ground to 3.8×10^{-6} at 10 km. Assumptions concerning temperature and eddy diffusion profiles, lightning production of O_2 , and rainout of H_2O_2 and H_2CO were the same as in Kasting and Walker (1981).

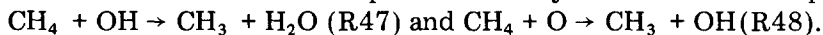
Photolysis rates were calculated for a solar zenith angle of 57.3° and then multiplied by 0.5 to approximate a diurnal average. Rayleigh scattering was treated using the method of Yung (1976). The importance of Rayleigh scattering in the context of primitive terrestrial atmospheres has been described by Kasting (1982). Its primary effect is to reduce solar ultraviolet fluxes in the lower troposphere which, for this model, means that H_2O photolysis is slowed relative to photolysis of well-mixed species such as CO_2 .

The reaction scheme describing hydrocarbon formation is based on sequences proposed by Lasaga et al. (1971), Strobel (1973), Yung and Pinto (1978), Yung and Strobel (1980) and Allen et al. (1980). Reactions (R) and rate constants are listed in Table I.

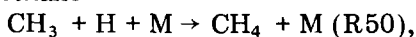
In the anaerobic atmosphere, the oxidizing radicals O and OH are produced throughout the atmosphere by photolysis at $\lambda \leq 2050 \text{ \AA}$ of CO_2 and H_2O :



These radicals initiate methane photochemistry in the lower atmosphere via



The resultant methyl radicals may react with atomic hydrogen to reform methane



or they can react with another OH or O radical to produce formaldehyde

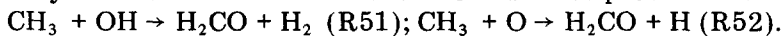


TABLE I

Reactions and rate constants

Reaction	Rate constant (cm ³ s ⁻¹)	Reference
(1) H ₂ O + O(¹ D) → OH + OH	2.3 × 10 ⁻¹⁰	JPL, 1979
(2) H ₂ + O(¹ D) → OH + H	9.9 × 10 ⁻¹¹	JPL, 1979
(3) H ₂ + O → OH + H	3.0 × 10 ⁻¹⁴ T exp (-4480/T)	Hampson and Garvin, 1977
(4) H ₂ + OH → H ₂ O + H	1.2 × 10 ⁻¹¹ exp (-2200/T)	JPL, 1979
(5) H + O ₃ → OH + O ₂	1.4 × 10 ⁻¹⁰ exp (-470/T)	JPL, 1979
(6) H + O ₂ + M → HO ₂ + M	5.5 × 10 ⁻³² (300/T) ^{1.4} [M]	JPL, 1979
(7) H + HO ₂ → H ₂ + O ₂	4.7 × 10 ⁻¹¹ (× 0.29)	Hack et al., 1978, 1979
(8) H + HO ₂ → H ₂ O + O	4.7 × 10 ⁻¹¹ (× 0.02)	Hack et al., 1978, 1979
(9) H + HO ₂ → OH + OH	4.7 × 10 ⁻¹¹ (× 0.69)	Hack et al., 1978, 1979
(10) OH + O → H + O ₂	4.0 × 10 ⁻¹¹	JPL, 1979
(11) OH + HO ₂ → H ₂ O + O ₂	4.0 × 10 ⁻¹¹	JPL, 1979
(12) OH + O ₃ → HO ₂ + O ₂	1.6 × 10 ⁻¹² exp (-940/T)	JPL, 1979
(13) HO ₂ + O → OH + O ₂	3.5 × 10 ⁻¹¹	JPL, 1979
(14) HO ₂ + O ₃ → OH + 2O ₂	1.1 × 10 ⁻¹⁴ exp (-580/T)	JPL, 1979
(15) HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	2.5 × 10 ⁻¹²	JPL, 1979
(16) H ₂ O ₂ + OH → HO ₂ + H ₂ O	1.0 × 10 ⁻¹¹ exp (-750/T)	JPL, 1979
(17) O + O + M → O ₂ + M	2.76 × 10 ⁻³⁴ exp (710/T) [M]	Campbell and Thrush, 1967
(18) O + O ₂ + M → O ₃ + M	6.2 × 10 ⁻³⁴ (300/T) ^{2.1} [M]	JPL, 1979
(19) O + O ₃ → 2O ₂	1.5 × 10 ⁻¹¹ exp (-2218/T)	JPL, 1979
(20) OH + OH → H ₂ O + O	1.0 × 10 ⁻¹¹ exp (-500/T)	Hampson and Garvin, 1977
(21) O(¹ D) + N ₂ → O + N ₂	2.0 × 10 ⁻¹¹ exp (-107/T)	JPL, 1979
(22) O(¹ D) + O ₂ → O + O ₂	2.9 × 10 ⁻¹¹ exp (-67/T)	JPL, 1979
(23) O ₂ + hν → O ₂ + O(¹ D)	J _{O₂}	Kasting et al., 1979
(24) → O + O		
(25) H ₂ O + hν → H + OH	J _{H₂O}	Kasting et al., 1979
(26) O ₃ + hν → O ₂ + O(¹ D)	J _{O₃}	Kasting et al., 1979
(27) → O ₂ + O		
(28) H ₂ O ₂ + hν → OH + OH	J _{H₂O₂}	Kasting et al., 1979
(29) CO ₂ + hν → CO + O	J _{CO₂}	Kasting et al., 1979
(30) CO + OH → CO ₂ + H	6.0 × 10 ⁻¹³ [0.25 + A[M]] / [1 + A[M]] ²	Hampson and Garvin, 1977
(31) CO + O + M → CO ₂ + M	6.5 × 10 ⁻³³ exp (-2180/T) [M]	Hampson and Garvin, 1977
(32) H + CO + M → HCO + M	2.0 × 10 ⁻³³ exp (-850/T) [M]	Baulch et al., 1976
(33) H + HCO → H ₂ + CO	1.2 × 10 ⁻¹⁰	Hochanadel et al., 1980
(34) HCO + HCO → H ₂ CO + CO	2.3 × 10 ⁻¹¹	Hochanadel et al., 1980
(35) OH + HCO → H ₂ O + CO	5.0 × 10 ⁻¹¹	Baulch et al., 1976
(36) O + HCO → H + CO ₂	1.0 × 10 ⁻¹⁰	Hampson and Garvin, 1977
(37) O + HCO → OH + CO	1.0 × 10 ⁻¹⁰	Hampson and Garvin, 1977
(38) H ₂ CO + hν → H ₂ + CO	J _{H₂CO}	Calvert et al., 1972
(39) → HCO + H		
(40) HCO + hν → H + CO	1.0 × 10 ⁻² s ⁻¹	Pinto et al., 1981
(41) H ₂ CO + H → H ₂ + HCO	2.8 × 10 ⁻¹¹ exp (-1540/T)	JPL, 1979

Table I (continued)

Reaction	Rate constant (cm ³ s ⁻¹)	Reference
(42) CO ₂ + hν → CO + O(¹ D)	J _{CO₂}	Kasting et al., 1979
(43) H + H + M → H ₂ + M	2.6 × 10 ⁻³³ exp (375/T) [M]	Liu and Donahue, 1974
(44) HCO + O ₂ → HO ₂ + CO	4.0 × 10 ⁻¹²	Reilly et al., 1978
(45) H ₂ CO + OH → H ₂ O + HCO	1.7 × 10 ⁻¹¹ exp (-100/T)	JPL, 1979
(46) H + OH + M → H ₂ O + M	6.1 × 10 ⁻²⁶ /T ² [M]	Hampson and Garvin, 1977
(47) CH ₄ + OH → CH ₃ + H ₂ O	2.4 × 10 ⁻¹² exp (-1710/T)	JPL, 1979
(48) CH ₄ + O → CH ₃ + OH	2.3 × 10 ⁻¹¹ exp (-2620/T)	Hampson and Garvin, 1977 ^m
(49) CH ₄ + O(¹ D) + CH ₃ + OH	1.3 × 10 ⁻¹⁰	JPL, 1979
(50) CH ₃ + H + M → CH ₄ + M	3.3 × 10 ⁻¹⁰ / [1 + 1/(2 × 10 ⁻¹⁹ [M])]]	Cheng and Yeh, 1977
(51) CH ₃ + OH → H ₂ CO + H ₂	1.0 × 10 ⁻¹⁰	Estimated ^b
(52) CH ₃ + O → H ₂ CO + H	1.0 × 10 ⁻¹⁰	Hampson and Garvin, 1977
(53) CH ₃ + CH ₃ + M → C ₂ H ₆ + M	Min [5.5 × 10 ⁻¹¹ ; 1.7 × 10 ⁻¹⁷ T ^{-2.3} [M]]	Van den Bergh, 1976; Troe, 1977
(54) C ₂ H ₆ + OH → C ₂ H ₅ + H ₂ O	1.86 × 10 ⁻¹¹ exp (-1230/T)	Hampson and Garvin, 1977
(55) C ₂ H ₆ + O → C ₂ H ₅ + OH	4.1 × 10 ⁻¹¹ exp (-3200/T)	Hampson and Garvin, 1977
(56) C ₂ H ₆ + O(¹ D) → C ₂ H ₅ + OH	1.3 × 10 ⁻¹⁰	Estimated ^c
(57) C ₂ H ₅ + H → CH ₃ + CH ₃	Min [1.8 × 10 ⁻¹⁰ exp (-435/T); 1.0 × 10 ⁻²⁰ T ^{-3.3} [M]]	Teng and Jones, 1972
(58) C ₂ H ₅ + OH → CH ₃ CHO + H ₂	1.0 × 10 ⁻¹⁰	Estimated ^b
(59) C ₂ H ₅ + O → CH ₃ CHO + H	1.0 × 10 ⁻¹⁰	Estimated ^b
(60) C ₂ H ₅ + CH ₃ + M → C ₃ H ₈ + M (=R53)		Benson, 1964
(61) C ₂ H ₅ + C ₂ H ₅ + M → C ₄ H ₁₀ + M (=R53)		Benson, 1964
(62) CH ₃ CHO + hν → CH ₃ + HCO	4.2 × 10 ⁻⁵ s ⁻¹	Demerjian et al., 1974
(63) C ₃ H ₈ + OH → C ₃ H ₇ + H ₂ O	1.8 × 10 ⁻¹¹ exp (-900/T)	Estimated ^d
(64) C ₃ H ₈ + O → C ₃ H ₇ + OH	1.6 × 10 ⁻¹¹ exp (-2900/T) + 2.2 × 10 ⁻¹¹ exp (-2250/T)	Hampson and Garvin, 1977
(65) C ₃ H ₈ + O(¹ D) → C ₃ H ₇ + OH	1.3 × 10 ⁻¹⁰	Estimated ^c
(66) C ₃ H ₇ + H → CH ₃ + C ₂ H ₅ (=R57)		Estimated
(67) C ₃ H ₇ + OH → C ₂ H ₅ CHO + H ₂	1.0 × 10 ⁻¹⁰	Estimated ^b
(68) C ₃ H ₇ + O → C ₂ H ₅ CHO + H	1.0 × 10 ⁻¹⁰	Estimated ^b
(69) C ₃ H ₇ + CH ₃ + M → C ₄ H ₁₀ + M (=R53)		Benson, 1964
(70) C ₂ H ₅ CHO + hν → C ₂ H ₅ + HCO	4.2 × 10 ⁻⁵ s ⁻¹	Estimated ^e
(71) C ₄ H ₁₀ + OH → C ₄ H ₉ + H ₂ O	1.76 × 10 ⁻¹¹ exp (-560/T)	Hampson and Garvin, 1977
(72) C ₄ H ₁₀ + O → C ₄ H ₉ + OH	1.6 × 10 ⁻¹¹ exp (-2900/T) + 4.4 × 10 ⁻¹¹ exp (-2250/T)	Hampson and Garvin, 1977
(73) C ₄ H ₁₀ + O(¹ D) → C ₄ H ₉ + OH	1.3 × 10 ⁻¹⁰	Estimated ^c
(74) C ₄ H ₉ + H → C ₂ H ₅ + C ₂ H ₅ (=0.5 × R57)		Estimated
(75) C ₄ H ₉ + H → C ₃ H ₇ + CH ₃ (=0.5 × R57)		Estimated
(76) C ₄ H ₉ + OH → C ₃ H ₇ CHO + H ₂	1.0 × 10 ⁻¹⁰	Estimated ^b

Table I (continued)

Reaction	Rate constant (cm ³ s ⁻¹)	Reference
(77) C ₄ H ₉ + O → C ₃ H ₇ CHO + H	1.0 × 10 ⁻¹⁰	Estimated ^b
(78) C ₃ H ₇ CHO + hν → C ₃ H ₇ + HCO	4.2 × 10 ⁻⁵ s ⁻¹	Estimated ^e
(79) CH ₄ + hν → ¹ CH ₂ + H ₂	J _{CH₄}	Mount et al., 1977
(80) C ₂ H ₆ + hν → C ₂ H ₂ + 2H ₂	J _{C₂H₆}	Mount and Moos, 1978 Strobel, 1973
(81) → C ₂ H ₄ + 2H		
(82) → CH ₄ + ¹ CH ₂		
(83) C ₃ H ₈ + hν → C ₃ H ₆ + H ₂	J _{C₃H₈} (× 0.4) ^f	Okabe and McNesby, 1962
(84) → C ₂ H ₄ + CH ₄	(× 0.3)	Calvert and Pitts, 1966
(85) → CH ₃ + C ₂ H ₅	(× 0.3)	
(86) C ₄ H ₁₀ + hν → C ₄ H ₈ + H ₂	J _{C₄H₁₀} (× 0.3) ^f	Okabe and Becker, 1963
(87) → 2C ₂ H ₄ + H ₂	(× 0.16)	Calvert and Pitts, 1966
(88) → C ₃ H ₆ + CH ₃ + H	(× 0.07)	
(89) → C ₂ H ₆ + C ₂ H ₂ + H ₂	(× 0.10)	
(90) → CH ₃ + C ₃ H ₇	(× 0.25)	
(91) → 2C ₂ H ₅	(× 0.12)	
(92) C ₂ H ₄ + hν → C ₂ H ₂ + H ₂	J _{C₂H₄}	Zelikoff and Watanabe, 1953
(93) → C ₂ H ₂ + 2H		Strobel, 1973
(94) C ₃ H ₆ + hν → C ₂ H ₂ + CH ₃ + H (=J _{C₂H₄})		Estimated
(95) C ₄ H ₈ + hν → C ₂ H ₂ + C ₂ H ₅ (=J _{C₂H₄}) + H		Estimated
(96) C ₂ H ₂ + hν → C ₂ H ₂ *	J _{C₂H₂}	Nakayama and Watanabe, 1964
(97) C ₂ H ₂ * → C ₂ H ₂ + hν	3.0 × 10 ⁵ s ⁻¹	Becker et al., 1971; Stief et al., 1965
(98) C ₂ H ₂ * → C ₂ H + H	1.0 × 10 ⁵ s ⁻¹	Takita et al., 1968, 1969; Strobel, 1973
(99) C ₂ H ₂ * + N ₂ → C ₂ H ₂ + N ₂	4.0 × 10 ⁻¹¹	Estimated ^g
(100) C ₂ H ₂ * + O ₂ → 2HCO	1.0 × 10 ⁻¹⁰	Estimated ^h
(101) ¹ CH ₂ + H ₂ → CH ₃ + H	7.0 × 10 ⁻¹²	Braun et al., 1970
(102) ¹ CH ₂ + CH ₄ → CH ₃ + CH ₃	1.9 × 10 ⁻¹²	Braun et al., 1970
(103) ¹ CH ₂ + O ₂ → H ₂ CO + O	3.0 × 10 ⁻¹¹	Laufer and Bass, 1974
(104) ¹ CH ₂ + N ₂ → ³ CH ₂ + N ₂	5.0 × 10 ⁻¹³	Bell, 1971
(105) ³ CH ₂ + H ₂ → CH ₃ + H	5.0 × 10 ⁻¹⁴	Braun et al., 1970
(106) ³ CH ₂ + CH ₄ → CH ₃ + CH ₃	5.0 × 10 ⁻¹⁴	Braun et al., 1970
(107) ³ CH ₂ + O ₂ → H ₂ CO + O	1.5 × 10 ⁻¹²	Laufer and Bass, 1974
(108) ³ CH ₂ + ³ CH ₂ → C ₂ H ₂ + 2H	5.3 × 10 ⁻¹¹	Russell and Rowland, 1979
(109) ³ CH ₂ + CH ₃ → C ₂ H ₄ + H	5.0 × 10 ⁻¹¹	Pilling and Robertson, 1975
(110) ³ CH ₂ + C ₂ H ₂ ^M → C ₃ H ₄	7.5 × 10 ⁻¹²	Laufer and Bass, 1974
(111) C ₂ H ₂ + OH → CO + CH ₃	2.0 × 10 ⁻¹² exp (-250/T)	Hampson and Garvin, 1977

Table I (continued)

Reaction	Rate constant (cm ³ s ⁻¹)	Reference
(112) C ₂ H ₂ + H + M → C ₂ H ₃ + M	Min [9.2 × 10 ⁻¹² exp(-1205/T); 10 ⁻³⁰ exp(-770/T) [M]]	Payne and Stief, 1976
(113) C ₂ H ₃ + H → C ₂ H ₂ + H ₂	7.0 × 10 ⁻¹²	Benson and Haugen, 1967
(114) C ₂ H ₃ + H ₂ → C ₂ H ₄ + H	3.0 × 10 ⁻¹³ exp(-5570/T)	Yung and Strobel, 1980
(115) C ₂ H ₃ + CH ₄ → C ₂ H ₄ + CH ₃	3.0 × 10 ⁻¹³ exp(-5370/T)	Estimated ⁱ
(116) C ₂ H ₃ + C ₂ H ₆ → C ₂ H ₄ + C ₂ H ₅	3.0 × 10 ⁻¹³ exp(-5170/T)	Estimated ⁱ
(117) C ₂ H ₄ + OH → H ₂ CO + CH ₃	2.2 × 10 ⁻¹² exp(385/T)	Hampson and Garvin, 1977
(118) C ₂ H ₄ + O → HCO + CH ₃	5.5 × 10 ⁻¹² exp(-565/T)	Hampson and Garvin, 1977
(119) C ₂ H ₄ + H + M → C ₂ H ₅ + M	Min [3.7 × 10 ⁻¹¹ exp(-1040/T); 3.0 × 10 ⁻³⁰ [M]]	Lee et al., 1978
(120) C ₃ H ₆ + OH → CH ₃ CHO + CH ₃	4.1 × 10 ⁻¹² exp(540/T)	Hampson and Garvin, 1977
(121) C ₃ H ₆ + O → 2CH ₃ + CO	4.1 × 10 ⁻¹² exp(-38/T)	Hampson and Garvin, 1977 ^h
(122) C ₃ H ₆ + H + M → C ₃ H ₇ + M	(=R119)	Estimated
(123) C ₄ H ₈ + OH → C ₂ H ₅ CHO + CH ₃	(=R120)	Estimated
(124) C ₄ H ₈ + O → CH ₃ + C ₂ H ₅ + CO	(=R121)	Estimated
(125) C ₄ H ₈ + H + M → C ₄ H ₉ + M	(=R119)	Estimated
(126) C ₂ H + O ₂ → CO + HCO	1.0 × 10 ⁻¹⁰	Estimated ^h
(127) C ₂ H + H ₂ → C ₂ H ₂ + H	3.0 × 10 ⁻¹¹ exp(-1600/T)	Estimated ⁱ
(128) C ₂ H + CH ₄ → C ₂ H ₂ + CH ₃	3.0 × 10 ⁻¹¹ exp(-1400/T)	Estimated ⁱ
(129) C ₂ H + C ₂ H ₆ → C ₂ H ₂ + C ₂ H ₅	3.0 × 10 ⁻¹¹ exp(-1200/T)	Estimated ⁱ
(130) C ₂ H + H + M → C ₂ H ₂ + M	(=R50)	Estimated
(131) C ₂ H + C ₂ H ₂ → C ₄ H ₂ + H	3.1 × 10 ⁻¹¹	Laufer and Bass, 1979
(132) C ₃ H ₄ → dust	1.0 × 10 ⁻¹⁰	Assumed ^k
(133) C ₄ H ₂ → dust	1.0 × 10 ⁻¹⁰	Assumed ^k
(134) CH ₃ + hν → ³ CH ₂ + H	5.0 × 10 ⁻⁵	Estimated ^l

^aA = 1.82 × 10⁻²⁰.

^bAssumed equal to R52.

^cAssumed equal to R49.

^dBy comparison with R54 and R71.

^eAssumed equal to R62.

^fBranching ratios assumed to be wavelength independent.

^gAssumed equal to half the rate measured by Becker et al. (1971) for quenching by H₂.

^hProducts uncertain.

ⁱBy comparison with R114, with correction for the expected difference in activation energies.

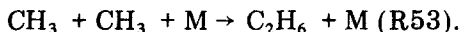
^jEstimated by Allen et al. (1980) based on results of Laufer and Bass (1979).

^kSee text.

^lBy comparison with rate estimated by Allen et al. (1980) for Titan.

^mBarassin and Combourie (1974) give 5.8 × 10⁻¹¹ exp(-4450/T).

A third possibility is recombination with another methyl radical to form ethane



Reaction R53 occurs at the high-pressure limiting rate all the way up to 80 km, so ethane can be formed efficiently throughout the model atmosphere.

Ethane, once formed, can undergo a sequence of reactions which are analogous to those of methane (R54–R61), the only essential difference being that the reaction of H with an ethyl radical



produces two methyls rather than reforming ethane. The recombination of ethyl radicals can then lead to the formation of propane and butane



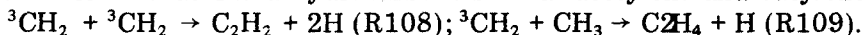
According to Benson (1964) these reactions occur at essentially the same rate as the recombination of two methyl radicals (R53). The entire sequence of higher alkanes can, presumably, be generated in this fashion, so our exclusion of species heavier than butane might be expected to cause trouble in some circumstances. The effects of cutting off the alkane sequence at $n = 4$ will be discussed in a later section. The polymerization process can also be reversed by the reaction of H with alkyl radicals, producing two smaller alkyls, as is the case for ethane.

The higher alkanes may be oxidized to form higher aldehydes in much the same way that methane is oxidized to formaldehyde. Since the C—O bonds formed in this process cannot be broken again within the atmosphere, each aldehyde molecule formed corresponds to a net loss of one methane molecule. The loss of methane via such oxidation processes must be balanced by a ground-level source of methane in order to maintain a constant CH_4 mixing ratio in the atmosphere.

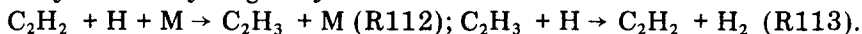
At altitudes above about 40 km methane may also be destroyed by direct photolysis



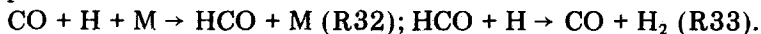
Since the photolysis of methane (and the higher alkanes) requires wavelengths shorter than 1600 Å, this process is responsible for only a small fraction of total methane destruction. The by-products of methane photolysis may react to form unsaturated hydrocarbons such as acetylene and ethylene via



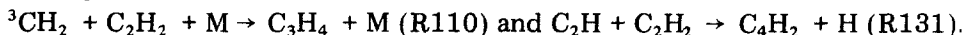
Acetylene, in particular, is potentially important because it can catalytically destroy atomic hydrogen by



In these models, however, the catalytic cycle involving CO is much more important



Acetylene can also react with different radical species to produce polyunsaturated hydrocarbon compounds. We have identified two such pathways in the model



Reaction R110 forms methylacetylene and allene in roughly a 1:2 ratio (Laufer and Bass, 1974) and is the largest source of polyunsaturated compounds in our model. Reaction 131 yields butadiene, which has been suggested as a precursor to the formation of Danielson dust on Titan (Allen et al., 1980). In this model we assume, somewhat arbitrarily, that both C_3H_4 and C_4H_2 are eventually removed from the atmosphere by conversion to some solid polymer. This assumption yields an estimate for the maximum possible loss of methane that can result from these two processes.

RESULTS

One of the difficulties in conducting a study of this kind is that the atmospheric mixing ratios of hydrogen and carbon dioxide are not known. Indeed, both H_2 and CO_2 levels are likely to have varied during ~ 2 Ga prior to the development of an oxygenic atmosphere. Reasonable values for the H_2 mixing ratio range from 10^{-5} to 10^{-3} (Kasting and Walker, 1981), while the CO_2 mixing ratio was probably between one and several hundred PAL (Owen et al., 1979; Walker et al., 1981). The calculations described here assume a range of possible mixing ratios for each of these gases.

As an initial experiment, the ground-level H_2 and CO_2 mixing ratios were fixed at 10^{-4} and 4.17×10^{-4} , respectively. (This is the equivalent of 1 PAL of CO_2 since the total atmospheric pressure is only 0.8 bars.) Calculations were performed for CH_4 mixing ratios ranging from 10^{-6} to 5×10^{-4} . Plotted in Fig. 1 are the calculated atmospheric residence time for methane and the ground-level methane source required to maintain the atmosphere in steady

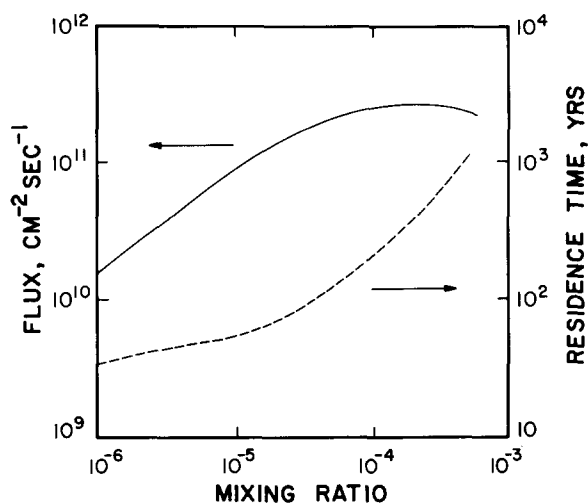


Fig. 1. Methane flux (solid curve) and atmospheric residence time (dashed curve) as a function of ground-level CH_4 mixing ratio. The assumed H_2 and CO_2 mixing ratios are 10^{-4} and 1 PAL, respectively.

state. Figure 1 illustrates several important points. First, the CH_4 residence times range from a few tens to a few thousands of years. Similar values were encountered over the entire range of different background atmospheres examined. Since a few thousand years is insignificant on a geological time scale, it is clear that only steady-state scenarios with a constant source for methane are of interest here. Second, the methane source required to maintain a CH_4 mixing ratio of several ppm is in the order of 10^{11} CH_4 molecules $\text{cm}^{-2} \text{s}^{-1}$. This figure is roughly equivalent to estimates for the present-day source of atmospheric methane (Koyama, 1963; Baker-Blocker et al., 1977; Ehhalt and Schmidt, 1978; Kasting and Donahue, 1980). We shall argue later that a source of this magnitude could have existed throughout much of the Archean. A third point — one that is considerably less certain — is the suggestion that the required methane flux reaches a maximum as the methane mixing ratio is increased above $\sim 3 \times 10^{-4}$, actually beginning to decrease for higher mixing ratios. The explanation is that interconversions among the hydrocarbon species are consuming a larger percentage of the oxidizing radicals. This phenomenon might disappear, however, in a model which included alkanes higher than $n = 4$.

Figure 2 shows altitude profiles of CO and the dominant hydrocarbon species for a methane mixing ratio $f(\text{CH}_4) = 10^{-5}$. The higher alkanes are all poorly represented, while C_2H_2 and C_2H_4 are confined almost exclusively to the upper atmosphere. A few features concerning the overall structure of the atmosphere deserve comment. First, the lower atmosphere is more highly reduced than the upper atmosphere. Second, the main photolysis paths begin with the dissociation of H_2O below 20 km, and of CO_2 above 10 km. Third, CO is much less abundant in the troposphere than in the stratosphere. Tropospherically produced OH (R25) is the main sink of this gas, via $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ (R30).

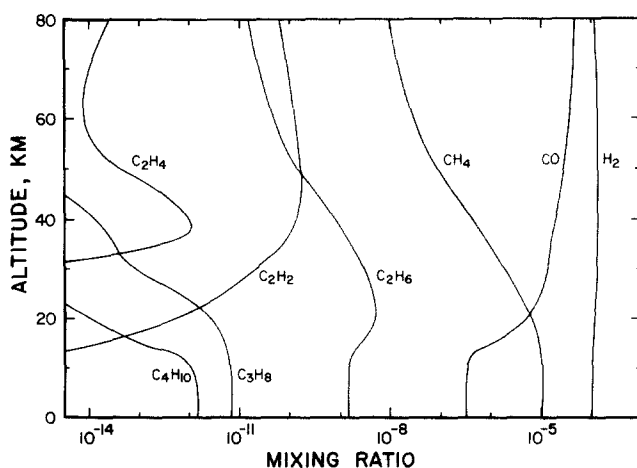


Fig. 2. Mixing ratio profiles of major reduced species at $f(\text{CH}_4) = 10^{-5}$, $f(\text{H}_2) = 10^{-4}$, and $f(\text{CO}_2) = 1$ PAL.

Figure 3 shows alkane mixing ratios for $f(\text{CH}_4) = 10^{-4}$. The alkanes have all become quite prominent and acetylene has begun to appear in the troposphere. The CO mixing ratio has also increased substantially in the troposphere, as the increasingly reduced conditions have greatly lowered the O and OH densities. Increasing CO acts to decrease H, by means of the catalytic cycle R32–R33, and thus, tends to increase the efficiency of alkane polymerization. The prediction that the tropospheric C_4H_{10} density exceeds that of C_3H_8 is an artifact of our truncated alkane sequence. In the lowest 20 km of the atmosphere shown in Fig. 3 the densities of the alkyl radicals tend to increase with increasing molecular weight. This would result, in a more complete model, in the formation of significant amounts of still higher alkanes. Our results are, therefore, not very meaningful for CH_4 mixing ratios above 10^{-4} .

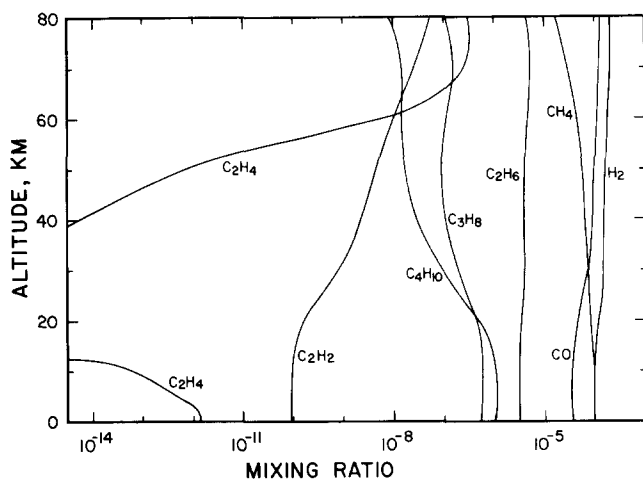


Fig. 3. The same as Fig. 2, except $f(\text{CH}_4) = 10^{-4}$.

The effects on the CO and C_2H_6 mixing ratios of varying methane mixing ratio at 1 PAL CO_2 and $f(\text{H}_2) = 10^{-4}$ are summarized in Fig. 4. All mixing ratios here refer to ground-level.

The trend towards alkane polymerization at high methane levels is accompanied by increased production of polyunsaturated hydrocarbons. Figure 5 shows column-integrated production rates for C_3H_4 and C_4H_2 as a function of methane mixing ratio. The rate of polymerization via these two channels becomes substantial at CH_4 mixing ratios near 10^{-4} , although it never exceeds a few percent of the methane oxidation rate (Fig. 1). We have not attempted to determine the subsequent fate of C_3H_4 and C_4H_2 in this model. It is conceivable, however, that they may have led to the formation of stratospheric dust in much the same fashion as has been suggested to occur in the atmosphere of Titan (Allen et al., 1980).

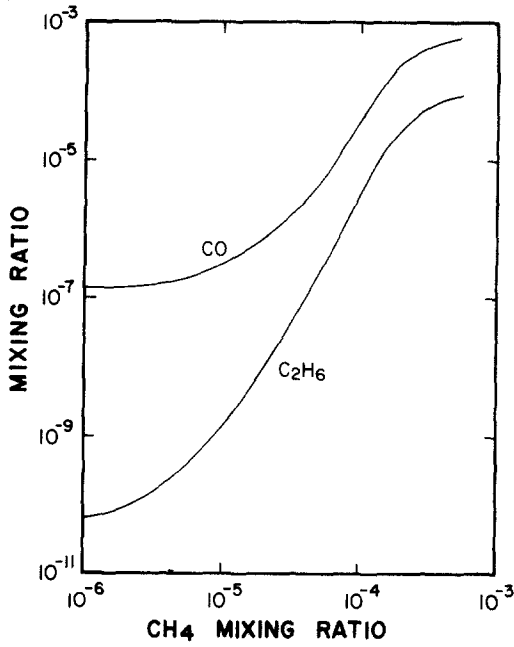


Fig. 4. Variation of CO and C_2H_6 with CH_4 mixing ratio for $f(CO_2) = 1$ PAL and $f(H_2) = 10^{-4}$.

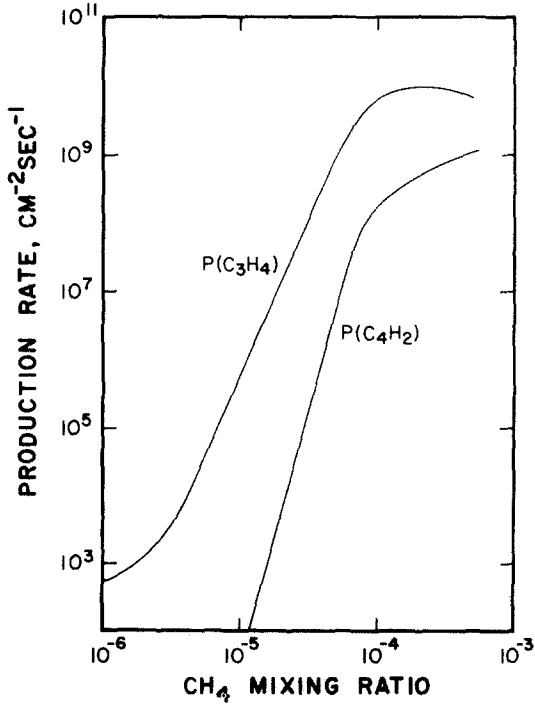


Fig. 5. Column-integrated production rates of C_3H_4 and C_4H_2 as functions of ground-level CH_4 mixing ratio. The assumed H_2 and CO_2 mixing ratios are 10^{-4} and 1 PAL, respectively.

The results presented so far correspond to an amount of CO_2 in the early atmosphere equal to today's value. We suggested earlier, though, that primitive CO_2 levels of 10–100 PAL are entirely possible, perhaps even likely. What effect would enhanced carbon dioxide levels have had upon the photochemistry of atmospheric methane?

Figure 6 shows calculated hydrocarbon mixing ratios for $f(\text{CH}_4) = 10^{-5}$, $f(\text{H}_2) = 10^{-4}$ and a CO_2 mixing ratio of 10 PAL. Comparison with Fig. 2 shows that hydrocarbon concentrations have increased dramatically: propane and butane have been enhanced by ~ 5 orders of magnitude, and ethane has become comparable to methane. The other hydrocarbons are similarly affected and, notably, so too is CO.

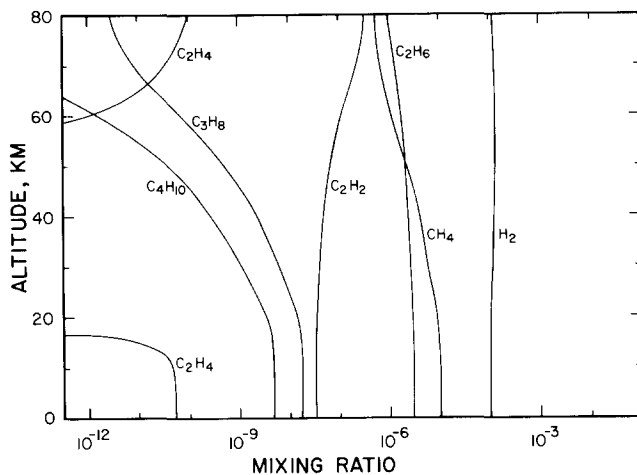


Fig. 6. Mixing ratio profiles of major reduced species at $f(\text{CH}_4) = 10^{-5}$, $f(\text{H}_2) = 10^{-4}$, and $f(\text{CO}_2) = 10$ PAL.

Figure 7 shows calculated hydrocarbon and CO mixing ratios for $f(\text{CH}_4) = 10^{-5}$ and $f(\text{H}_2) = 10^{-4}$ at 100 PAL of CO_2 . The hydrocarbons are all somewhat less abundant than at 10 PAL, but CO now constitutes $\sim 0.1\%$ of the atmosphere.

Figure 8 summarizes these results by showing the effect of varying CO_2 on CO, C_2H_6 and the required methane flux for $f(\text{H}_2) = 10^{-4}$ and $f(\text{CH}_4) = 10^{-5}$. Although the details are complex, the underlying cause of this behavior is that the increased CO_2 absorbs a larger fraction of the incident photolyzing flux, and does so higher in the atmosphere. Thus, there is more primary production of CO and O by R29, and less of H and OH by R27, and photolysis in the shielded troposphere becomes less important.

As CO_2 is increased from 1 to 10 PAL, the initial effect of reducing the rate of tropospheric water photolysis is to greatly weaken the primary atmospheric sink for CO (R30) and so CO increases. The combined effects of decreased photolytic production and increased catalytic removal by the CO cycle

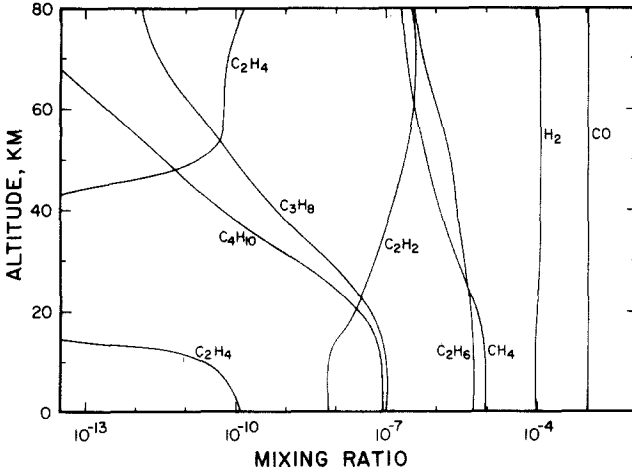


Fig. 7. The same as Fig. 6, except $f(\text{CO}_2) = 100 \text{ PAL}$.

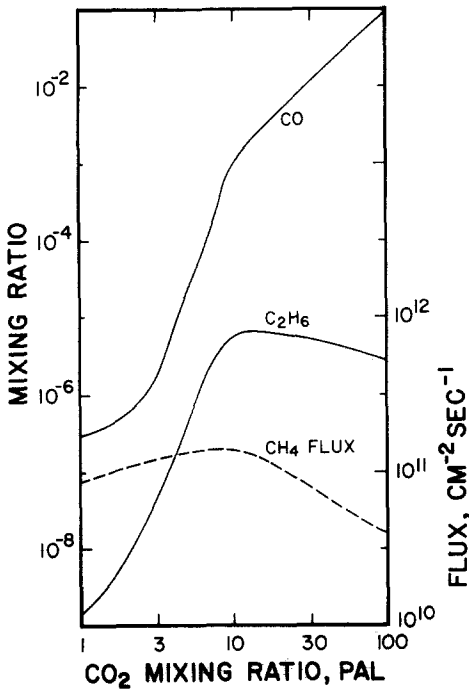
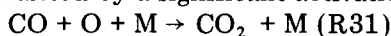


Fig. 8. Dependence on $f(\text{CO}_2)$ of $f(\text{CO})$, $f(\text{C}_2\text{H}_6)$, and the methane flux required to maintain a steady state for $f(\text{H}_2) = 10^{-4}$ and $f(\text{CH}_4) = 10^{-5}$.

(R32–33) greatly decrease tropospheric H densities. Thus, the reaction of CH_3 with itself (R53) becomes faster than the reaction of CH_3 with H (R50), so the rate of ethane formation is dramatically increased. A quirk in the alkane chemistry further favors the production of polymers. The reported re-

action rates of CH_4 with O and OH (R48 and R47) are approximately equally fast in the troposphere (see discussion of limitations below), but for the higher alkanes, the analogous reaction with O is roughly 100 times slower than the analogous reaction with OH. Hence, as decreasing rates of water photolysis and increasing mixing ratios of CO combine to reduce tropospheric OH densities, the switch to O as the dominant oxidizing radical increases the lifetimes of the higher alkanes while not seriously slowing the methyl formation rate.

At CO_2 mixing ratios above 10 PAL, water photolysis plays an almost negligible role. The basic chemistry of this atmosphere is reduced to the photolysis of CO_2 and its recombination. In the absence of an efficient means of removing CO, the relatively slow direct 3-body recombination (which is inhibited by a significant activation energy)



becomes important below about 20 km. This reduces O densities in the lower atmosphere, slowing the alkane photochemistry, as indicated by the relatively low methane flux required at 100 PAL of CO_2 .

A fairly complete set of model experiments was performed at $f(\text{H}_2) = 10^{-4}$, including $f(\text{CH}_4) = 10^{-6}$ and 10^{-5} at 1–100 PAL CO_2 , and $f(\text{CH}_4) = 10^{-4}$ at 1–10 PAL CO_2 . At 1 PAL, models with $f(\text{CH}_4) = 2.5 \times 10^{-4}$ and 5×10^{-4} were run, but these are not able to treat the alkane chemistry properly. The dependence of the required source strength on CH_4 and CO_2 mixing ratios is illustrated explicitly in Fig. 9. The contours represent the base 10 logarithm of the methane source (molecules $\text{cm}^{-2} \text{s}^{-1}$) needed to maintain the steady state. Figure 10 is a contour plot of the tropospheric ethane mixing ratio as a function of CH_4 and CO_2 mixing ratios. It illustrates regimes under which CH_4

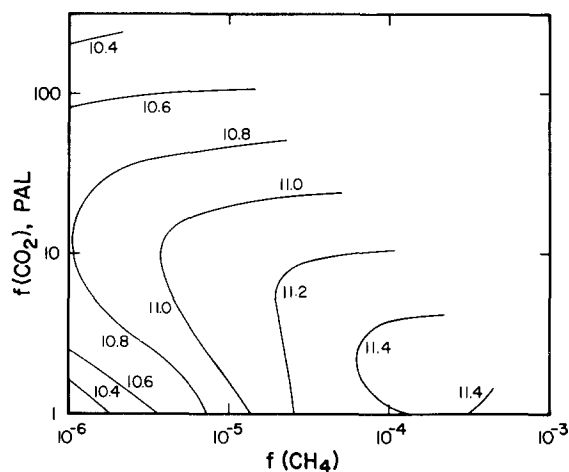


Fig. 9. Calculated ground-level methane fluxes needed to maintain the atmosphere in equilibrium for different CH_4 and CO_2 mixing ratios. Contours represent the base 10 logarithm of the required methane source in CH_4 molecules $\text{cm}^{-2} \text{s}^{-1}$. The mixing ratio of $\text{H}_2 = 10^{-4}$.

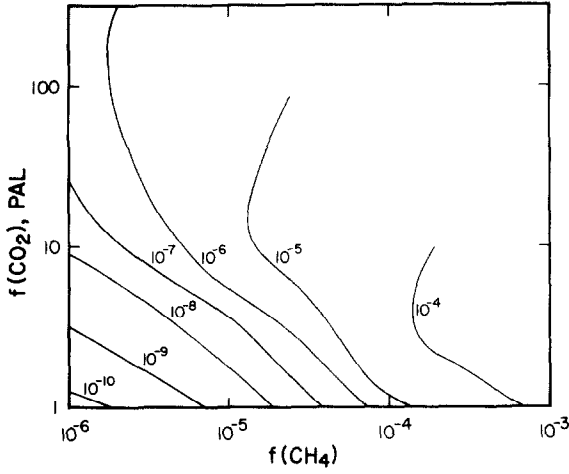


Fig. 10. Mixing ratio of C_2H_6 as a function of the mixing ratios of CO_2 and CH_4 for $f(H_2) = 10^{-4}$.

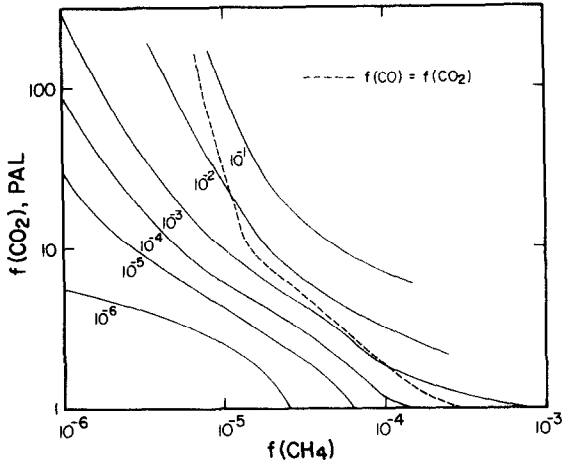


Fig. 11. Mixing ratio of CO as a function of the mixing ratios of CO_2 and CH_4 for $f(H_2) = 10^{-4}$.

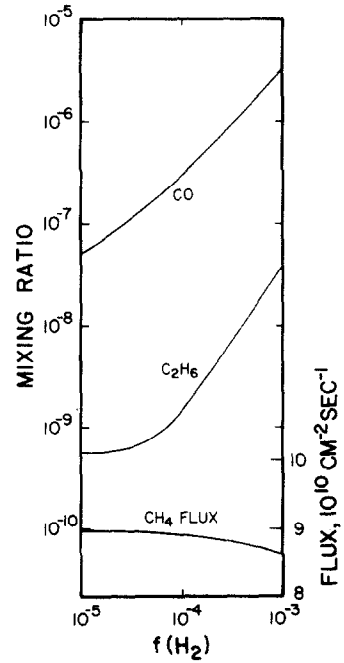


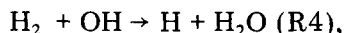
Fig. 12. Dependence on $f(H_2)$ of $f(CO)$, $f(C_2H_6)$, and the methane flux required to maintain a steady state for $f(CH_4) = 10^{-5}$ and $f(CO_2) = 1$ PAL.

and CO₂ polymerization may be expected to have been important at $f(\text{H}_2) = 10^{-4}$. In order to be effective greenhouse gases, the higher alkanes and associated hydrocarbons, aldehydes, alcohols, etc. would presumably have had to assume mixing ratios $> \sim 10^{-6}$. Thus, a substantial greenhouse effect would not be expected below and to the left of the $f(\text{C}_2\text{H}_6) = 10^{-6}$ contour.

The dependence of $f(\text{CO})$ upon CH₄ and CO₂ at $f(\text{H}_2) = 10^{-4}$ is shown in Fig. 11. The upper right hand region of the plot corresponds to conditions in which CO replaces CO₂ as the more stable carbon oxide. These atmospheres are quite reducing in character. However, at high CO mixing ratios it is possible that otherwise unimportant loss processes for CO (e.g., perhaps surface catalyzed oxidation of CO by H₂O) may act to prevent the dominance of CO. In any event, the question of the stability of CO₂ in the early terrestrial atmosphere requires more consideration.

Figure 12 shows the effect of varying the H₂ mixing ratio from 10^{-5} to 10^{-3} for $f(\text{CH}_4) = 10^{-5}$ and CO₂ = 1 PAL. Both CO and C₂H₆ increase with increasing H₂, but neither increases as rapidly or nonlinearly as when CH₄ or CO₂ are varied. The change in the required methane flux is very small indeed.

These effects are relatively easy to understand. Molecular hydrogen reacts with OH

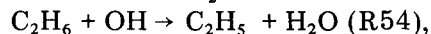


so increased H₂ decreases OH densities. Since CO is removed by OH



$f(\text{CO})$ should increase linearly with $f(\text{H}_2)$, as is the case in Fig. 12.

Ethane presents a more complex problem, since both its production and its loss are affected by changes in H₂ concentrations. The dominant loss process for ethane at all H₂ levels is the reaction with OH



so it can be expected that C₂H₆ concentrations should vary linearly with $f(\text{H}_2)$, all other things being equal. However, the ethane production rate depends on CH₃ concentrations and these, in turn, are affected by the densities of H and OH. At low H₂ levels, CH₃ production stems largely from the reaction of CH₄ with OH (R47). This tends to counteract the OH dependence of the loss rate, with the result that the ethane concentration is nearly independent of $f(\text{H}_2)$. At high H₂ levels, the CO catalytic cycle (R32–R33) tends to reduce H densities, which results in a slower rate of destruction of methyl radicals via the reaction of CH₃ with H (R50). The C₂H₆ production rate is enhanced and so the ethane concentration increases faster than linearly with increasing $f(\text{H}_2)$.

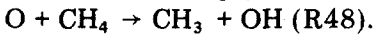
The required methane flux is almost independent of H₂, because methane is oxidized almost exclusively in the stratosphere, by reactions with atomic oxygen (R48 and R57). The reaction of H₂ with O (R3) is very slow, and does not compete effectively for O atoms at the hydrogen mixing ratios considered here.

Although we have not made a systematic evaluation of the effects of varying H_2 at all CH_4 and CO_2 levels, we expect that at higher CO_2 levels, variations in H_2 would be even less important than they are at 1 PAL, since OH becomes a less important species that is effectively dominated by reaction with abundant CO. For H_2 to have a major effect would require enough H_2 to force reaction with O. This would require both $f(H_2) \geq 10^3 f(CH_4)$ and $f(H_2) \geq 30 f(CO)$ for the C-H-O atmospheres considered here.

LIMITATIONS OF THE MODEL

Obviously, considerable uncertainty arises in this calculation because of incomplete knowledge of hydrocarbon photochemistry. Our results are probably most secure at low methane and CO_2 levels, where the primary photochemical pathway for methane is the relatively well understood process of oxidation to formaldehyde. At higher methane levels one of the chief problems is a poor understanding of the production and loss processes for acetylene. In this model we have minimized the importance of acetylene by including a number of speculative loss processes (R100, R110, R114–116 and R131) and only relatively well-known production processes. Consequently, C_2H_2 concentrations remain relatively low, even at high methane mixing ratios. The result is that the atomic hydrogen catalytic destruction cycle involving C_2H_2 (R112 and R113) is less effective than that involving CO (R32 and R33). Since lowered atomic hydrogen densities result in higher polymerization rates, our model is very sensitive to both of these cycles. An earlier version of this model, which did not include as many loss processes for acetylene, exhibited higher C_2H_2 concentrations and a more rapid onset of polymerization at high methane levels.

In general, uncertainty in an individual reaction rate does not pose a major problem — the exception is



A much slower rate for R48 has been reported by Barassin and Combourie (1974). This rate strongly affects the details of the chemistry; in particular (for the case where $f(H_2) = 10^{-4}$, $f(CH_4) = 10^{-5}$, and $f(CO_2) = 1$ PAL), the slower rate causes larger tropospheric O densities, and hence delays the onset of hydrocarbon polymerization as a function of methane mixing ratio. The methane sustaining flux is also reduced by a factor of ~ 2 ; the flux calculations are much less sensitive to details of the chemistry, since the CH_4 loss rate is largely a function of photon flux.

Another factor which would affect these results would be a change in the eddy diffusion profile. We have used the present-day profile from Hunten (1975), which assumes a very small value for the eddy diffusion coefficient in the lower stratosphere. In the absence of a temperature inversion due to ozone, the early atmosphere may have been more turbulent in this region.

This would result in increased downward transport of C_2H_2 and CO and, consequently, in reduced atomic hydrogen concentrations in the troposphere. Thus, again, the degree of methane polymerization could have been greater than we have calculated here.

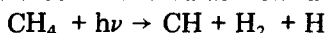
Another major problem with this model is the exclusion of alkanes of greater molecular weight than butane. If the rate of the three-body recombination remains unchanged for the higher alkyl radicals, the production of pentane, hexane and still higher alkanes cannot be ignored in atmospheres containing large amounts of CH_4 or CO_2 . The situation is difficult to analyze because it is not clear where the polymerization process would stop. In a study of the primitive Martian atmosphere, Yung and Pinto (1978) predicted that alkanes heavier than heptane would condense to liquid form at temperatures expected to prevail on the Martian surface. The warmer surface temperature on the primitive Earth would prevent condensation until much higher molecular weights were attained. It may be that alkane mist would have condensed out of the colder regions of the stratosphere and then evaporated as it descended into the relatively warm troposphere. However, such speculation is probably premature at this time, due to uncertainty concerning the formation rates of the higher hydrocarbon species. Here we can only point out two expected effects of higher alkane formation on our results. First, by providing additional loss processes for C_3H_7 and C_4H_9 , such reactions should tend to restore the normal ordering of alkane concentrations, whereby the densities decrease with increasing molecular weight. Second, oxidation and possibly condensation of higher alkanes would have constituted an additional drain on atmospheric methane, so the required methane source strength at high CH_4 and CO_2 levels may have been greater than we have calculated here.

The large CO concentrations predicted by our model at high CH_4 and CO_2 mixing ratios may be unrealistic. Possibly, CO could have been reduced to CH_4 by catalytic processes occurring at the Earth's surface or in oceans. This reaction is favored thermodynamically, but requires a mechanism for breaking the C—O bond. Direct photolysis of CO requires wavelengths shorter than 1100 Å and could only occur high up in the atmosphere, but alternative gas phase pathways may exist. Bar-Nun and Chang (1983) recently reported methane and other hydrocarbons among the products formed by 1849 Å irradiation of a gaseous mixture of CO and H_2O . The mechanism and efficiency of CH_4 formation remains unclear. Additional study of this system would be of interest because of its implications for the composition of the primitive atmosphere.

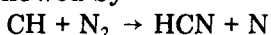
The steady-state CO/ CO_2 ratio is quite sensitive to tropospheric photolysis rates and the assumed water vapor profile. An earlier version of this model that did not include Rayleigh scattering predicted much smaller amounts of CO at high CO_2 and CH_4 mixing ratios, due to a more rapid rate of hydroxyl formation by photolysis of water vapor. The hydrocarbon chemistry considered here may well have produced aerosols similar to those observed on

Titan, so the scattering optical depth of the atmosphere may have been much greater than assumed here.

Finally, due to our neglect of nitrogen chemistry, the present model overlooks the production of hydrogen cyanide — a compound of special interest to biochemists studying the origin of life. Hydrogen cyanide could have been formed at altitudes above 40 km by



followed by



About 7% of methane photolysis reactions yield CH radicals (Gorden and Ausloos, 1967), which react with N_2 at a rate of between 7.3×10^{-14} (Braun et al., 1967) and 1×10^{-12} (Bosnali and Perner, 1971). Hydrogen cyanide, like CH_4 , photolyzes only at very short wavelengths (Huebner and Carpenter, 1979), so most of the HCN produced at high altitudes could have survived long enough to be transported down into the lower atmosphere. Current studies of HCN in the atmosphere of Titan (Hanel et al., 1981) should shed more light on the photochemistry of this important molecule.

TENTATIVE LIMITS ON METHANE IN THE ARCHEAN ATMOSPHERE

We have shown that methane would have been an ephemeral constituent of an anaerobic primitive atmosphere of the kind considered here and could have remained in the atmosphere for geologically significant periods of time only if there was a continuous supply. Our calculations show that a source strength of about 10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$ or larger would have been needed to sustain methane mixing ratios of 10^{-6} , the lowest value likely to be of climatic significance.

The present-day flux of methane to the atmosphere has been estimated as about 10^{14} moles y^{-1} or 3.75×10^{11} molecules $\text{cm}^{-2} \text{s}^{-1}$ (Koyama, 1963; Baker-Blocker et al., 1977; Ehhalt and Schmidt, 1978; Kasting and Donahue, 1980). This flux is almost entirely of biogenic origin, being a product of methanogenic bacteria that derive energy mainly from the reaction



(Wolfe, 1971; Deuser et al., 1973; Zeikus and Winfrey, 1976; Dacey and Klug, 1979). The hydrogen and carbon dioxide are products of microbial fermentation of organic matter in anaerobic environments (Gray and Gest, 1965)



Walker (1980a) has pointed out that much of the present day biogenic methane may be oxidized by microorganisms in overlying aerobic waters before reaching the atmosphere; with allowance for this loss, the total source of microbial methane today might be $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

The total rate of photosynthetic fixation of carbon today is 2.6×10^{13} atoms $\text{cm}^{-2} \text{ s}^{-1}$ using the tabulation of Holland (1978), so ~4% of current

productivity is converted into methane (Watson et al., 1978). On the anaerobic Earth, the fraction of organic carbon recycled as methane would presumably have been higher, but the productivity might well have been lower. The present day marine productivity of 1.1×10^{13} atoms $\text{cm}^{-2} \text{s}^{-1}$ might be a more plausible estimate of productivity during the Archean. A still more plausible estimate might be obtained by excluding open ocean productivity for reasons that have been discussed by Knoll (1979) and Walker (1978). The resulting estimate of a globally averaged carbon flux today of 2.7×10^{12} atoms $\text{cm}^{-2} \text{s}^{-1}$ is derived from the figures quoted by Koblentz-Mishke et al. (1970) for in-shore and neritic waters. Such waters may, of course, have been rare on the Archean Earth.

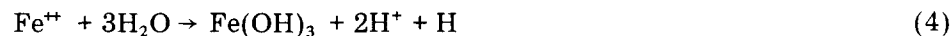
Undoubted evidence of life extends back to 3.5 Ga ago (Walter et al., 1980), and isotopic evidence for the activity of methanogenic bacteria as long ago as 2.7 Ga has also been reported (Schoell and Wellmer, 1981; Hayes, 1983). Nor is the antiquity of the methanogens in doubt (Woese and Fox, 1977). Therefore, it seems possible that microorganisms on the Archean Earth might have generated a methane flux approaching 10^{12} molecules $\text{cm}^{-2} \text{s}^{-1}$, depending on the fraction of fixed carbon converted into methane.

Possibly tighter constraints on the problem can be set by considering the oxidation–reduction balance of the atmosphere and ocean combined. The atmospheres we have described would have been losing hydrogen to space at a rate that can be estimated as

$$F(\text{H}) = 4 \times 10^{13} [2f(\text{H}_2) + 2f(\text{H}_2\text{O}) + 4f(\text{CH}_4)] \text{ atoms cm}^{-2} \text{ s}^{-1} \quad (3)$$

where $f(\text{H}_2\text{O}) = 3.8 \times 10^{-6}$ is the mixing ratio of water vapor in the stratosphere, and $f(\text{H}_2)$ and $f(\text{CH}_4)$ are the mixing ratios of hydrogen and methane at the ground (Hunten, 1973; Hunten and Donahue, 1976; Walker, 1977; Kasting et al., 1979; Kasting and Walker, 1981). This loss of reducing power to space must have at least been balanced by a supply of reducing power to the atmosphere and ocean, or the world would have become aerobic (see discussion below). Evidence for a predominantly reducing atmosphere and ocean in the Archean has been summarized most recently by Walker et al. (1983).

The present-day flux of reduced volcanic and metamorphic gases to the atmosphere has been estimated by Kasting and Walker (1981) as equivalent to 8×10^8 H atoms $\text{cm}^{-2} \text{s}^{-1}$. The potential flux of divalent iron released by terrestrial weathering might be as large as 8×10^{10} Fe atoms $\text{cm}^{-2} \text{s}^{-1}$ (Kasting and Walker, 1981), equivalent to 8×10^{10} H atoms $\text{cm}^{-2} \text{s}^{-1}$ by way of the schematic reaction



We are aware of no estimate of the total flux of reduced species provided by submarine weathering today. This flux must be considerably less than the flux of oxygen into the deep sea, for otherwise the deep sea would be anoxic. Using numbers presented by Broecker (1974) we calculate an upper limit on

the submarine weathering flux equivalent to 4×10^{12} H atoms $\text{cm}^{-2} \text{s}^{-1}$. These estimates are all highly uncertain and their applicability to the distant past is even more uncertain, but we conclude that methane mixing ratios in the range 10^{-4} – 10^{-6} are not obviously inconsistent with the maintenance of anaerobic conditions in the atmosphere and ocean. Such mixing ratios could have been sustained by a sufficiently abundant source of reduced iron in solution and a flourishing microbiota, including photoautotrophs, fermenting heterotrophs and methanogens. Oxidation–reduction balance could have been maintained by oxidation of the iron, either directly by the photoautotrophs (Walker, 1980a) or by reaction with photosynthetic oxygen

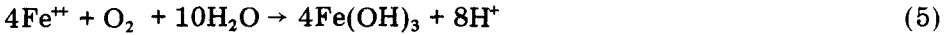


Figure 13 illustrates a hypothetical biogeochemical cycle of methane and hydrogen under Archean conditions. The methane generated by methanogens was oxidized photochemically in the atmosphere to carbon dioxide and hydrogen. These products then flowed back into the ocean to be converted by biological activity into methane and water. The steady loss of hydrogen from the top of the atmosphere was balanced by the oxidation of a fraction of the flux of reduced minerals passing through the ocean in solution.

Our results, summarized in Fig. 9, allow some estimates to be made of the relative magnitudes of the fluxes and concentrations in this cycle. Suppose, for example, that the methane flux was close to the modern value, $\sim 1.5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$, and that the CO_2 mixing ratio was about 10 PAL. According to Fig. 9 the methane mixing ratio would have been about 3×10^{-5} . Using the piston velocity approach (Broecker, 1974) we calculate that an average supersaturation of methane in surface seawater by a factor of ~ 3 would have

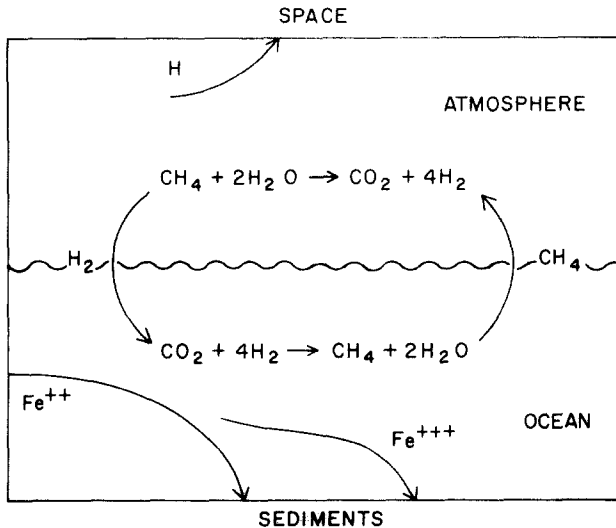


Fig. 13. Possible biogeochemical cycles of methane and hydrogen during the Archean era.

provided the necessary flux. The return flux of hydrogen would have required an atmospheric hydrogen partial pressure larger by 5×10^{-4} atmospheres than the partial pressure in solution equilibrium with surface seawater (Walker, 1980b). Modern methanogens can apparently hold hydrogen partial pressures down to 3×10^{-4} atmospheres (Hungate, 1967; Wolin, 1976) and photosynthetic bacteria can probably lower hydrogen even further (Walker, 1980c), so the atmospheric partial pressure of hydrogen was not likely to have exceeded 8×10^{-4} atmospheres.

With a hydrogen mixing ratio of 8×10^{-4} , a methane mixing ratio of 3×10^{-5} , and a stratospheric water vapor mixing ratio of 3.8×10^{-6} , the hydrogen escape flux would have been 10^{11} atoms $\text{cm}^{-2} \text{s}^{-1}$ according to eq. 3. This expression probably overestimates the escape flux at high hydrogen partial pressures (Kasting and Walker, 1981) so the required rate of supply of reducing power to atmosphere and ocean would have been smaller than 10^{11} $\text{cm}^{-2} \text{s}^{-1}$. From the point of view of biogeochemical cycles we find no obvious defect in the hypothesis that methane mixing ratios exceeding 10^{-6} could have been sustained in the Archean atmosphere by methanogenic bacteria.

We have already noted the possible climatic impact of the greenhouse effect due to this much methane and the hydrocarbon products of its photochemical destruction. Accumulation of abundant free oxygen in the atmosphere in the Early Proterozoic may have lowered the concentrations of methane and other hydrocarbons in the atmosphere, causing a global climatic cooling (Walker et al., 1983). The Early Proterozoic glaciogenic rocks of the Huronian sequence in Canada are underlain by sedimentary rocks that appear to have been deposited under reducing conditions and are overlain by rocks that appear to have been deposited under oxidizing conditions (Roscoe, 1969, 1973).

Turning to the possible abundance of methane in the prebiological atmosphere, abiotic sources of methane are likely to have been quite small (with the possible exception of a CO rich atmosphere, as discussed above) after the initial period of Earth accretion, dissipation of the solar nebula, and differentiation of the Earth into core, mantle and crust. The present oxidation state of the Earth's upper mantle is such that the fraction of total carbon released as methane by volcanoes and metamorphic reactions is much less than that released as carbon dioxide or carbon monoxide. An estimate for the present-day release rate of carbon monoxide is 2×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ (Kasting and Walker, 1981). Thus, even if the early rate of release of volcanic and metamorphic gases were 10–100 times higher than at present, the amount of methane released is hardly likely to have been enough to maintain a methane mixing ratio as high as 10^{-6} . Since the segregation of the core very probably occurred during the course of Earth accretion (Stevenson, 1983), there is no reason to believe that volcanic and metamorphic gases on the early Earth were richer in methane than they are today (Holland, 1962).

Mid-ocean hot springs provide a potentially important source of abiotic methane, especially in light of evidence for much stronger interaction be-

tween seawater and mantle in the Archean (Veizer, 1976, 1979; Veizer and Jansen, 1979). The present-day rate of supply of methane by mid-ocean ridge hot springs has been estimated at $1.6 \times 10^8 \text{ m}^3 \text{ y}^{-1}$ (Welhan and Craig, 1979; Craig and Lupton, 1980), equivalent to a flux of 3×10^7 molecules $\text{cm}^{-2} \text{ s}^{-1}$. Unless this mid-ocean source of methane were 1,000 times larger on the Archean Earth it could not have yielded methane mixing ratios in the atmosphere as high as 10^{-6} . As discussed in the previous section, methane may have been generated photochemically in an atmosphere rich in H_2O and CO . The magnitude of the source will remain uncertain until more is known about the reaction mechanisms involved.

These findings can be summarized in a very tentative history of atmospheric methane. Any primordial methane accumulated during the course of Earth accretion would have been dissipated by photochemical reactions in the atmosphere in a geologically short period of time after the segregation of the core. Abiotic sources of methane are not likely to have been large enough to sustain methane mixing ratios as high as 10^{-6} , the threshold for a possible methane greenhouse, with a CO -rich atmosphere being a possible exception. After the origin of life an increasing biogenic source of methane may have driven methane mixing ratios well above 10^{-6} . The rise of atmospheric oxygen in the early Proterozoic may have led to more rapid photochemical destruction of methane, lowering the methane mixing ratio to approximately its present value of 1.4×10^{-6} . Indeed, the methane mixing ratio may have dropped briefly to much lower values due to rapid photochemical oxidation processes in mildly oxidizing atmospheres (Kasting and Donahue, 1980).

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