Estimation of the Reaction Rate for the Formation of CH$_3$O from H + H$_2$CO: Implications for Chemistry in the Solar System$^1$

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It is argued that the formation of the methoxy radical (CH$_3$O) from H + H$_2$CO may play an essential role in the reduction of CO to CH$_4$. The rate coefficient for this reaction has been estimated using the approximate theory of J. Troe (1977a, J. Chem. Phys. 66, 4745) and transition state theory. We briefly discuss the implications of this reaction for the chemistry of CO in the solar nebula, for interpreting the laboratory experiments of A. Bar-Nun and A. Shaviv (1975, Icarus 24, 197) and A. Bar-Nun and S. Chang (1983, J. Geophys. Res. 88, 6662) and for organic synthesis in the prebiotic terrestrial atmosphere.

INTRODUCTION

The simplest carbon compounds, present in the terrestrial and planetary atmospheres, exhibit a wide range of oxidation states, carbon dioxide and methane being respectively the most oxidized and the most reduced forms of carbon. Table I summarizes our current knowledge of the major carbon species in the terrestrial and planetary atmospheres.

The question arises as to the origin of and the interconversion among the carbon species. The presence of carbon monoxide in the atmospheres of Mars and Venus is readily explained as the product of CO$_2$ photodissociation (McElroy and Donahue 1972, Yung and DeMore 1982). A major source of CO in the terrestrial troposphere is the oxidation of CH$_4$, which is produced biologically (Levy 1971, Wofsy et al. 1972, Wofsy 1976). CO and CO$_2$ on Titan are derived from the oxidation of CH$_4$ by oxygen brought into the atmosphere in the form of H$_2$O in micrometeoroids (Samuelson et al. 1983, Yung et al. 1984). The origin of CO on Jupiter and Saturn is controversial at present. Although it is agreed that the oxidation of CH$_4$ is the ultimate source, theories differ on whether the oxidation takes place in the deep atmosphere (Prinn and Barshay 1977, Fegley and Prinn 1985) or in the stratosphere (Prather et al. 1978, Strobel and Yung 1979).

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It is clear from the above brief discussion that some of the most interesting chemistry in the Solar System involves changes in the oxidation state of the simple carbon species. The chemical pathways for the conversion of CH₄ to CO and CO₂ are for the most part known (see for example Wofsy 1976, Yung et al. 1984). The reverse process, the reduction of CO to CH₄, is, however, poorly understood. This is surprising in view of the importance of the reduction process in the chemistry of the Solar System (Prinn and Barshay 1977, Lewis and Prinn 1980, Prinn and Fegley 1981, Fegley and Prinn 1985, 1986). In this article we investigate the chemical kinetics of a hitherto unsuspected reaction which may play a crucial role in the hydrogenation of CO. The implications of this reaction for chemistry in the Solar System are briefly discussed.

THE WORK OF PRINN AND B ARSHAY

Prinn and Barshay (1977), in a fundamental paper on CO in the atmosphere of Jupi-
ingle bond between C and O. For instance in CH$_3$OH the single bond between C and OH is only 89 kcal/mole (Calvert and Pitts 1966). Thus, removing a single-bonded oxygen from carbon would be easy. The more difficult step must lie in the conversion of the double bond into a single bond. But, as we show, there may be a surprise. The conversion of the C═O double bond into a C—O single bond could be easier than previously thought.

Consider the reaction of a hydrogen atom with formaldehyde,

$$H + H_2CO \rightarrow \text{products.} \quad (5)$$

This reaction has been extensively studied in the laboratory (Baldwin and Cowe 1962, Westenberg and deHaas 1972, Ridley et al. 1972, Klemm 1979, Dean et al. 1980). The rate coefficient according to Klemm (1979) is

$$k_5 = 3.3 \times 10^{-11} \exp(-1835/T) \text{ cm}^3 \text{ sec}^{-1},$$

and there is generally good agreement between the values reported by the different groups. The products of (5) have not been determined, but it is most likely that the incident hydrogen atom abstracts a hydrogen atom from H$_2$CO,

$$H + H_2CO \rightarrow H_2 + HCO$$

$$\Delta H = -13.6 \text{ kcal/mole.} \quad (6)$$

According to Harding and Schatz's (1982) ab initio calculation, (6) is indeed the dominant channel of (5). This theoretical work also correctly predicts the value of $k_5$ (see next section).

It is of interest to consider the possibility of an addition channel for (5). If the hydrogen atom is added to the carbon atom, this leads to the formation of the methoxy radical

$$H + H_2CO + M \rightarrow CH_3O + M. \quad (7)$$

If, however, the hydrogen atom is added to the oxygen atom, the hydroxymethyl radical is formed,

$$H + H_2CO + M \rightarrow CH_2OH + M. \quad (8)$$

The two channels are not necessarily exclusive since CH$_3$O may isomerize to CH$_2$OH,

$$\text{CH}_3O \rightarrow \text{CH}_2OH$$

$$\Delta H = -5 \text{ kcal/mole} \quad (9)$$

(Saebo et al. 1983). Note that in either case the carbonyl bond is broken, and the oxygen atom is now attached to the carbon atom via a single bond. Also, according to Dunning et al. (1984), (8) is negligible compared with (7) because the reaction has a higher activation energy barrier. So for simplicity we shall restrict our interest to (7).

The methoxy radical produced by (7) has the structure

\[
\begin{array}{c}
\text{H} \\
\text{H} \text{—C—O.} \\
\text{H}
\end{array}
\]

and is isoelectronic to the radical C$_2$H$_5$. It can readily abstract an H atom to form CH$_3$OH,

$$\text{CH}_3O + H_2 \rightarrow \text{CH}_3OH + H \quad (10)$$

$$\text{CH}_3O + \text{CH}_4 \rightarrow \text{CH}_3OH + \text{CH}_3 \quad (11)$$

$$\text{CH}_3O + \text{H}_2CO \rightarrow \text{CH}_3OH + \text{HCO.} \quad (12)$$

Methanol can be attacked by H atoms,

$$\text{CH}_3OH + H \rightarrow \text{CH}_3 + \text{H}_2O, \quad (13)$$

followed by

$$\text{CH}_3 + H + M \rightarrow \text{CH}_4 + M. \quad (14)$$

If we add up (7), (10), (13), and (14), we obtain the net result (see Appendix A for details)

$$\text{H}_2CO + 2H + H_2 \rightarrow \text{CH}_4 + \text{H}_2O. \quad (15)$$

There are alternatives to (15) obtained by choosing (11) or (12) instead of (10), but the result is the same: hydrogenation of formaldehyde to methane. We have thus produced the net effect of the Prinn and Barshay schemes (1)–(3) by a two-stage mechanism, the first stage being the formation of the intermediate CH$_3$O by (7), and the second stage being the elimination of
REACTION RATE FOR CH$_3$0 519

The ideas outlined here seem to have been first considered by De-Grat and Calvert (1967), but were not pursued further due to the lack of quantitative data on (7). The greatest uncertainty in the new scheme is the rate-limiting step (7). Since (7) has never been measured, we shall attempt to estimate the rate coefficient theoretically.

COMPUTATION OF THE REACTION RATE OF
H + H$_2$CO + M $\rightarrow$ CH$_3$O + M

The approach we adopt is first to study the reverse reaction

$$\text{CH}_3\text{O} + M \rightarrow \text{H} + \text{H}_2\text{CO} + M \quad (16)$$

and then deduce $k_7$ using the relation

$$K_{eq} = k_{16}/k_7, \quad (17)$$

where $K_{eq}$ is the equilibrium constant for the chemical system

$$\text{CH}_3\text{O} \leftrightarrow \text{H} + \text{H}_2\text{CO}. \quad (18)$$

An estimate of the rate constant for (16) can be made using Troe’s (1977a,b, 1979) simplified theory of unimolecular dissociation. In the low-pressure limit, the collision rate constant can be calculated from the expression

$$k_{16}^0 = MZ_{LJ} \frac{\rho_{vib,h}(E_0)kT}{Q_{vib}} \exp\left(\frac{E_0}{kT}\right) \times F_{anh} F_e F_{rot} F_{rot,int} \beta,$$

with

$Z_{LJ}$ = Leonard–Jones collision frequency,

$Q_{vib}$ = the vibrational partition function,

$\rho_{vib,h}(E_0)$ = the harmonic oscillator density of states,

$F_{anh}$ = the anharmonicity factor for Morse oscillators,

$F_e$ = the energy dependence factor,

$F_{rot}$ = the rotational factor,

$F_{rot,int}$ = the internal rotation factor, and

$\beta$ = collision efficiency.

The mathematical expression for each of the factors has been provided by Troe (1977a,b) (see also application of Troe’s theory for computing rate coefficients of interest to planetary atmospheres, Laufer et al. 1983). Employing (18) for computing $k_{16}^0$ requires as input both the energetics of the chemical system and CH$_3$O structural data (i.e., bond lengths and vibrational frequencies). Note that $k_{16}^0$ is extremely sensitive to the system energetics which are represented schematically in Fig. 1. The experimentally obtained value for $E_0$ is $29 \pm 1/5$ kcal/mole (Westbrook and Dryer 1979, Tsuboi and Hashimoto 1981); the value for $\Delta H$ is $25 \pm 3$ kcal/mole (Engelking et al. 1978, Batt and McCulloch 1976). The inferred activation energy $E_A$ is $4 \pm 4$ kcal/mole. These values are in marked disagreement with theoretical calculations performed by Dunning et al. (1984) and C. Meilius (private communication, 1985): $E_0 = 24 \pm 2$ kcal/mole, $\Delta H = 17 \pm 2$ kcal/mole, from which one infers $E_A = 7 \pm 4$ kcal/mole. Since the theoretical calculations are likely to underestimate the CH$_3$O heat of formation due to inadequate compensation for electron-pair interactions (L. B. Harding, private communication, 1986), we consider the experimental data to be more reliable. However, we shall carry out computations using both sets of data in order to assess the impact of this uncertainty on our results. The input parameters needed for calculating the various physical factors in (18) are taken from Adams (1985). The equilibrium constant, $K_{eq}$, is calculated.
TABLE I

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>( k_{16} ) (sec(^{-1}))</th>
<th>( K_{eq} ) (cm(^{-3}))</th>
<th>( k_7 ) (cm(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 7.2 \times 10^{-11} )</td>
<td>( 4.8 \times 10^{6} )</td>
<td>( 1.5 \times 10^{-17} )</td>
</tr>
<tr>
<td>600</td>
<td>( 7.0 \times 10^{-1} )</td>
<td>( 3.8 \times 10^{15} )</td>
<td>( 1.8 \times 10^{-16} )</td>
</tr>
<tr>
<td>900</td>
<td>( 7.3 \times 10^{2} )</td>
<td>( 4.6 \times 10^{18} )</td>
<td>( 1.5 \times 10^{-16} )</td>
</tr>
<tr>
<td>1200</td>
<td>( 1.4 \times 10^{4} )</td>
<td>( 1.7 \times 10^{20} )</td>
<td>( 7.8 \times 10^{-17} )</td>
</tr>
</tbody>
</table>

(a) Computations performed using experimental data

(b) Computations performed using theoretical data

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>( k_{16} ) (sec(^{-1}))</th>
<th>( K_{eq} ) (cm(^{-3}))</th>
<th>( k_7 ) (cm(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 2.9 \times 10^{-7} )</td>
<td>( 2.9 \times 10^{12} )</td>
<td>( 9.8 \times 10^{-20} )</td>
</tr>
<tr>
<td>600</td>
<td>( 4.6 \times 10^{1} )</td>
<td>( 3.0 \times 10^{18} )</td>
<td>( 1.5 \times 10^{-17} )</td>
</tr>
<tr>
<td>900</td>
<td>( 1.1 \times 10^{4} )</td>
<td>( 4.0 \times 10^{20} )</td>
<td>( 2.8 \times 10^{-17} )</td>
</tr>
<tr>
<td>1200</td>
<td>( 1.1 \times 10^{5} )</td>
<td>( 4.9 \times 10^{21} )</td>
<td>( 2.2 \times 10^{-17} )</td>
</tr>
</tbody>
</table>

At the high-pressure limit, the rate coefficient for (16) can be computed using the transition state theory,

\[
k_{16}^\infty = \frac{kT}{h} \frac{Q_vQ_j}{Q_v^*Q_j^*} \exp(-E_0/kT),
\]

where \( Q_v \) and \( Q_j \) denote the partition functions for CH\(_3\)O, and \( Q_v^* \) and \( Q_j^* \) are the corresponding partition functions for the transition state (i.e., excited CH\(_3\)O). The other symbols in (19) have their usual meaning and will not be elaborated here (see, for example, Robinson and Holbrook 1972). As a first approximation the ratio of the partition functions can be set to unity in (19). This assumption is valid especially at high temperatures since the decomposition of CH\(_3\)O involves primarily the C—H stretching motion and is relatively uncoupled from other modes of motion. This fact implies that relatively few degrees of freedom are affected in going from stable CH\(_3\)O to excited CH\(_3\)O. With this simplifying assumption, the values of \( k_{16}^\infty \) are computed according to (19) and summarized in Table III.

We shall make a brief comparison of our results with those obtained using \textit{ab initio} calculations. The most complete study of the reaction, H + H\(_2\)CO, is due to Harding and Schatz (1982). However, the predicted heat of formation of CH\(_3\)O was in conflict with the experimental value. By making an empirical adjustment in the energetics of the system, the authors obtained results for the abstraction branch (6) that are in excellent agreement with experimental studies. The same group (Dunning et al. 1984) have also performed computations for the addition branch (7). Their results for 10 and 760 Torr are shown in Fig. 2, along with our own results. At 10 Torr our result, \( k_7^\infty \), is in reasonable agreement with curve A. The difference may be attributed to differences in the estimates of the excited CH\(_3\)O structural parameters. In the high-pressure limit, our result, \( k_7^\infty \) computed for infinite pressure, is expected to be higher than curve B, which refers to 760 Torr. However, at low temperature our treatment is oversimplified. Inclusion of the effects due to the higher density of rotational levels in the excited CH\(_3\)O would tend to increase the computed value of \( k_7^\infty \). Hence, the somewhat large discrepancy between \( k_7^\infty \) and curve B at low temperature can be understood.

TABLE III

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>( k_{16}^\infty ) (sec(^{-1}))</th>
<th>( k_7^\infty ) (cm(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 6.4 \times 10^{-9} )</td>
<td>( 1.4 \times 10^{-15} )</td>
</tr>
<tr>
<td>600</td>
<td>( 4.0 \times 10^{2} )</td>
<td>( 1.0 \times 10^{-13} )</td>
</tr>
<tr>
<td>900</td>
<td>( 1.9 \times 10^{6} )</td>
<td>( 4.0 \times 10^{-13} )</td>
</tr>
<tr>
<td>1200</td>
<td>( 2.8 \times 10^{8} )</td>
<td>( 1.6 \times 10^{-12} )</td>
</tr>
</tbody>
</table>

(a) Computations performed using experimental data

(b) Computations performed using theoretical data

<table>
<thead>
<tr>
<th>T (°K)</th>
<th>( k_{16}^\infty ) (sec(^{-1}))</th>
<th>( k_7^\infty ) (cm(^3) sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 2.7 \times 10^{-5} )</td>
<td>( 9.1 \times 10^{-18} )</td>
</tr>
<tr>
<td>600</td>
<td>( 2.6 \times 10^{4} )</td>
<td>( 8.9 \times 10^{-15} )</td>
</tr>
<tr>
<td>900</td>
<td>( 3.0 \times 10^{7} )</td>
<td>( 7.6 \times 10^{-14} )</td>
</tr>
<tr>
<td>1200</td>
<td>( 1.1 \times 10^{9} )</td>
<td>( 2.2 \times 10^{-13} )</td>
</tr>
</tbody>
</table>

Note. The appropriate values of \( K_{eq} \) are the same as those in Table II and are not shown here.
REACTION RATE FOR CH₃O

from Prinn and Barshay (1977) \(k_1 = 3.8 \times 10^{-25} \text{ cm}^3 \text{ sec}^{-1}, [\text{H}_3] = 2.4 \times 10^{21} \text{ cm}^{-3}, \) and \([\text{H}_2\text{CO}]/[\text{CO}] = 3.9 \times 10^{-4}\), we obtain
\[
\tau_{\text{chem}} = 2.8 \times 10^6 \text{ sec}.
\]

From the condition of quenching, \(\tau_{\text{chem}} = \tau_{\text{conv}}\), we deduce \(K = 2 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}\).

These values of \(\tau_{\text{chem}}\) and \(K\) are identical to those reported by Prinn and Barshay (1977).

If we now take (7) as the rate limiting step for the destruction of CO, the chemical lifetime is
\[
\tau_{\text{chem}} = \frac{[\text{CO}]}{k_7[H][\text{H}_2\text{CO}]}.
\]

Taking the value of the rate coefficient at 1 bar based on curve B in Fig. 2, \(k_7 = 3 \times 10^{-14} \text{ cm}^3 \text{ sec}^{-1}\), and \([\text{H}] = 3 \times 10^{11} \text{ cm}^{-3}\) from Prinn and Barshay (1977), we obtain \(\tau_{\text{chem}} = 2.9 \times 10^5\) and \(K = 2 \times 10^8 \text{ cm}^2 \text{ sec}^{-1}\). These values differ from those obtained by Prinn and Barshay (1977) by an order of magnitude. Since \(P = 300\) bars, it is more realistic to use \(k_7\) in Fig. 2. Taking \(k_7 = 4 \times 10^{-13} \text{ cm}^3 \text{ sec}^{-1}\), we obtain \(\tau_{\text{chem}} = 2.2 \times 10^4 \text{ sec}\) and \(K = 2.7 \times 10^{10} \text{ cm}^2 \text{ sec}^{-1}\). The discrepancy between our results and those of Prinn and Barshay (1977) is now two orders of magnitude. Unfortunately the results quoted here are subject to large uncertainties. R. G. Prinn and B. Fegley (1987, private communication) pointed out that the formation of CH₃O by (7) may not be the rate-limiting step for the destruction of CO, because thermal decomposition (16) may severely limit the stability of CH₃O. Based on arguments elaborated in Appendix A we estimate a preferred value for the efficiency factor for the conversion of CH₃O to CH₃OH (and subsequently to CH₄), \(f = 0.55\). However, a smaller value \(f = 0.14\) is not ruled out. The time constants estimated here must all be increased by a factor \(1/f\). Hence, the discrepancy between our results and those of Prinn and Barshay (1977) could be reduced to within an order of magnitude.

**IMPLICATIONS FOR CO IN THE JOVIAN ATMOSPHERE**

According to Prinn and Barshay (1977), CO is produced in the deep atmosphere of Jupiter by thermoequilibrium chemistry between CH₄ and H₂O and transported to the tropopause by very rapid upward mixing. To account for the observed abundance of CO (see Table I), the quenching must take place at about \(T = 1064^\circ\text{K}\) and \(P = 350\) bars (the corresponding H₂ number density is about \(2.4 \times 10^{21} \text{ cm}^{-3}\)). The chemical time constant for CO according to (1) is
\[
\tau_{\text{chem}} = \frac{[\text{CO}]}{k_1[H_2][\text{H}_2\text{CO}]}.
\]

where \([X]\) denotes the concentration of species \(X\) in molecules \(\text{cm}^{-3}\). The transport time due to convection may be parameterized by
\[
\tau_{\text{conv}} = H^2/K,
\]

where \(H\) is the atmospheric scale height (=240 km) and \(K\) is the eddy diffusion coefficient, whose value remains to be determined. Using appropriate values taken
The purpose of this discussion is to point out the potential importance of (7) for the chemistry of CO on Jupiter. Obviously the same argument can be applied also to Saturn and Uranus. However, a satisfactory treatment of the implications of (7) for the chemistry and dynamics of the Jovian atmosphere must address the issue of the observed depletion of H₂O and an independent estimate of the magnitude of the eddy diffusion coefficient (Bjoraker 1985, Bjoraker et al. 1986, Lunine and Hunten 1987). This will not be further discussed here.

REEVALUATION OF THE EXPERIMENTS OF BAR-NUN AND SHAVIV

Bar-Nun and Shaviv (1975) performed a series of experiments on the conversion of CO and H₂ to hydrocarbons. The mixture of either 1% CO with 9% H₂ or 0.1% CO with 20% H₂ was shock heated in an Ar atmosphere to temperatures between 1600 and 3600°K. Following the heat pulse, during which some CO was hydrogenated to hydrocarbons, the gas was quenched and its composition was subsequently analyzed using gas chromatography. An analysis of the results of the experiments (Bar-Nun and Podolak 1985) suggests that the reaction for destroying CO has an apparent activation energy of 23 kcal/mole, which is considerably lower than the value 72.4 kcal/mole given by (1). Furthermore, an estimate of the chemical lifetime of CO at 1064°K based on an extrapolation of the observed data (Bar-Nun and Podolak 1985) yields a time constant that is six orders of magnitude shorter than that obtained by Prinn and Barshay (1977).

The Bar-Nun and Shaviv experiments cannot be understood using the Prinn–Barshay scheme (1). The lower apparent activation energy is consistent with a radical–molecule reaction such as (7) but not with a molecule–molecule reaction such as (1) as the rate-limiting step. However, the chemical lifetime of CO deduced by Bar-Nun and Podolak (1985) is not predicted by our mechanism. It is possible that the rate coefficient k₇ could be larger than our conservative estimate, but it would be difficult to justify an adjustment of k₇ by four to five orders of magnitude in order to account for the experiments. There may be an unknown mechanism that is even more efficient than our scheme. So until a thorough analysis of the experiments is performed, we shall regard these results as circumstantial evidence that (1) is inadequate, but not as support of our mechanism.

REEVALUATION OF THE EXPERIMENT OF BAR-NUN AND CHANG

Bar-Nun and Chang (1983) showed that the gas-phase photolysis of H₂O at 1849 Å in the presence of CO could lead to the production of a variety of organic compounds including C₁–C₃ hydrocarbons, alcohols, aldehydes, acetone, and acetic acid. The results are generally in agreement with those obtained in previous experiments (Hubbard et al. 1971, Bar-Nun and Hatman 1978), and provide firm evidence for the hydrogenation of CO to highly reduced carbon species. In proposing a mechanism for explaining the results of their experiments, the authors recognized that the crucial step is the reduction of H₂CO. They invoked a four-centered disproportionation reaction between photolytically excited H₂CO and H₂CO,

\[ \text{H}_2\text{CO}^* + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{CO}. \]

This reaction has been reported to occur at 15°K in a solid matrix of formaldehyde, but has never been studied in the gas phase. We consider this chemical path as improbable. Our mechanism, consisting of (7), (12), (13), (14) and other similar reactions, is much more attractive and can provide a natural explanation of the large yields of CH₃OH and CH₄ in the experiments. However, quantitative modeling of the experimental results is beyond the scope of this paper and will not be pursued here (see Wen et al. 1987).
REACTION RATE FOR CH₃O

IMPLICATION FOR ORGANIC SYNTHESIS IN THE PREBIOTIC TERRESTRIAL ATMOSPHERE

The major form of carbon in the primitive atmosphere was most probably CO₂ (Kasting et al. 1984). The photochemistry of CO₂ should be similar to that prevailing in the atmosphere of Mars and Venus today (see, for example, Yung and DeMore 1982), in which the photolysis of CO₂ occurs readily

\[ \text{CO}_2 + \text{hv} \rightarrow \text{CO} + \text{O}. \]

A preliminary model of the H₂–O₂–CO₂ chemistry has been explored by Pinto et al. (1980). The authors proposed two chemical schemes which could be stoichiometrically represented as

\[ 2\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO} + \text{CO}_2 \]

and

\[ \text{CO}_2 + 2\text{H}_2 \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}, \]

and should be compared with photosynthesis,

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO} + \text{O}_2. \]

It can be seen that our proposed schemes resemble prototypes of photosynthesis. Outgassed volatiles contain a small fraction of reduced compounds even today (Holland, 1978, 1984) in the form of H₂, CO, and H₂S. It has been implicitly assumed by earlier workers that the reduced material was lost solely by escape of H₂ from the exosphere. Pinto et al. (1980) explored a more interesting alternative—that the reduced material could lead to the production of organic carbon, H₂CO,

With the aid of (7), it is obvious that H₂CO can be further reduced to CH₃O and ultimately to CH₃OH by reactions such as

\[ \text{CH}_3\text{O} + \text{HCO} \rightarrow \text{CH}_3\text{OH} + \text{CO} \]

\[ \text{CH}_3\text{O} + \text{H}_2\text{CO} \rightarrow \text{CH}_3\text{OH} + \text{HCO}. \]

Destruction of CH₃OH by (13) or by photolysis,

\[ \text{CH}_3\text{OH} + \text{hv} \rightarrow \text{CH}_3 + \text{OH}, \]

leads to the production of CH₃ radicals, from which CH₄ and other simple hydrocarbons can be synthesized. A quantitative assessment of the impact of (7) on organic synthesis in the primitive atmosphere will be carried out in a separate paper (Wen et al. 1987).

CONCLUSION

We have identified a two-stage mechanism for the reduction of CO to CH₄ via the formation of the methoxy radical. The rate coefficient for the crucial addition branch of the H + H₂CO reaction has been estimated using the standard Troe theory and the transition-state theory. The results compare favorably with those obtained independently by Dunning et al. (1984) using ab initio quantum mechanical calculations. However, we should regard these calculations as order of magnitude estimates and not as quantitative predictions. It is unfortunate that this important reaction has never been identified in the laboratory, but given our estimates for the rate coefficient it should be possible to design kinetics experiments and measure the branching ratio between the abstraction channel (6) and the additional channel (7).

The formation of the CH₃O radical may have profound consequences for the destruction of CO in the deep atmosphere of Jupiter and synthesis of organic compounds in the prebiotic terrestrial atmosphere. In addition, the bulb experiments (Bar-Nun and Chang 1983) on the hydrogenation of CO are inexplicable in terms of conventional gas-phase kinetics. Our work provides insight into these experiments and we intend to quantitatively simulate the results of these experiments.

APPENDIX A

EFFICIENCIES FOR CONVERSION OF CH₃O TO CH₃OH AND CH₃OH TO CH₄ IN THE ATMOSPHERE OF JUPITER

After a CH₃O molecule is formed by (7), there is competition between the backward reaction,
**TABLE AI**

**LIST OF SOME SIMPLE REACTIONS WHICH ABSTRACT HYDROGEN ATOMS FROM CH₄ AND H₂**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate constant, $k$ (cm³ sec⁻¹)</th>
<th>$k(T = 1064°K)$ (cm³ sec⁻¹)</th>
<th>$\Delta H^\circ$ (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1 C₂H + CH₄ → C₂H₂ + CH₃</td>
<td>$3.0 \times 10^{-12}$</td>
<td>$2.4 \times 10^{-12}$</td>
<td>-21.8</td>
</tr>
<tr>
<td>A2 OH + CH₄→ H₂O + CH₃</td>
<td>$3.2 \times 10^{-19}$ $T^{2.4 - 1064°K}$</td>
<td>$8.0 \times 10^{-13}$</td>
<td>-15.0</td>
</tr>
<tr>
<td>A3 CH₃O + CH₄ → CH₄OH + CH₃</td>
<td>$2.6 \times 10^{-15}$ $T^{3.4 - 40°K}$</td>
<td>$4.0 \times 10^{-15}$</td>
<td>3.1</td>
</tr>
<tr>
<td>A4 C₂H₅ + CH₄→ C₂H₆ + CH₃</td>
<td>$1.4 \times 10^{-15}$ $T^{3.4 - 40°K}$</td>
<td>$1.3 \times 10^{-15}$</td>
<td>5.5</td>
</tr>
<tr>
<td>A5 C₂H + H₂→ C₂H₂ + H</td>
<td>$1.9 \times 10^{-13}$ $T^{3.4 - 40°K}$</td>
<td>$4.9 \times 10^{-13}$</td>
<td>-21.9</td>
</tr>
<tr>
<td>A6 OH + H₂</td>
<td>$1.1 \times 10^{-17}$</td>
<td>$T^{3.4 - 40°K}$</td>
<td>-15.1</td>
</tr>
<tr>
<td>A7 CH₃O + H₂→ CH₄OH + H</td>
<td>5.1 $T^{3.4 - 40°K}$</td>
<td>7.4 $T^{3.4 - 40°K}$</td>
<td>5.4</td>
</tr>
</tbody>
</table>

Note. * Enthalpy change for reaction. All data taken from Benson (1976) at 300°K except the heat of formation of CH₃O, which is assumed to be 1.1 kcal/mole.

CH₃O + M→ H₂CO + H + M, (16)

and the reaction leading to the formation of CH₃OH,

CH₃O + H₂→ CH₃OH + H. (10)

Let us define the fraction of CH₃O that is eventually converted into CH₃OH as the efficiency factor,

$$f = \frac{k_{10}[H_2]}{k_{10}[H_2] + k_{16}^\infty}.$$  

Since $k_{10}$ has not been measured, it must be estimated on the basis of analogy with other reactions listed in Table AI. Comparison of the rate constants for (A1)–(A4) with those of (A5)–(A7) suggest that abstraction reactions involving H₂ are about two to six times faster than the corresponding reactions involving CH₄ (unless otherwise stated, all rate coefficients are evaluated at 1064°K). Comparison between $k_{A3}$ and $k_{A4}$ suggests that CH₃O is about three times as reactive toward CH₄ as C₂H₅. On the basis of this type of reasoning we conclude that $k_{10} = 1.5 \times 10^{-14}$ cm³ sec⁻¹ ($k_{10}/k_{A3} = 3$, $k_{10}/k_{A7} = 2$) represents the best estimate. Therefore, for the conditions for Jupiter described in the text, we have $k_{10}[H_2] = 3.6 \times 10^7$ sec⁻¹, $k_{16}^\infty = 2.9 \times 10^7$ sec⁻¹ (from Table III,a), and hence

$$f = 0.55.$$  

A somewhat lower value of $f$ is obtained if we take $k_{16}^\infty = 2.2 \times 10^8$ sec⁻¹ (Table III,b) computed using theoretical data. (This value is close to $3.7 \times 10^8$ sec⁻¹, derived using the expression quoted in Tsang and Hampson 1986.) In this case, the estimated value of the efficiency factor is

$$f = 0.14.$$  

We have assumed in the text that the primary fate of CH₃OH on Jupiter is

CH₃OH + H→ CH₃ + H₂O, (13)

followed by

CH₃ + H + M→ CH₄ + M, (14)

or

CH₃ + H₂→ CH₄ + H. (A8)

While the predominance of (14) and (A8) on Jupiter is obvious, the predominance of (13) is not. The competing reactions are

CH₃OH + H→ CH₂OH + H₂, (A9)

and

CH₃OH + H→ CH₃O + H₂. (A10)

The most likely fate of CH₂OH is reacting with H₂ and H,

CH₂OH + H₂→ CH₃OH + H, (A11)

CH₂OH + H→ CH₃OH*→ CH₃ + OH. (A12)

We note that the net result of (A9) and (A11) is a do-nothing cycle. Reaction (A12) is based on analogy with the reaction

C₂H₅ + H→ C₂H₆*→ 2CH₃ (A13)

(Teng and Jones 1972). The net result of (A9) and (A12) is the formation of CH₃, as in (13). We consider (A10) unlikely and
should be much slower than (13) since the bond energies for CH₃O—H and CH₃—OH are 100 and 89 kcal/mole, respectively (Calvert and Pitts 1966). On the basis of these arguments we conclude that the efficiency of conversion of CH₃OH to CH₄ on Jupiter should be close to unity.

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