

Thermodynamic Study on the Formation, Decomposition and Oxidation Of Methane in the Soil Atmosphere

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Abstract

Through the use of thermodynamic relationships, the Gibbs free energy change of 12 reactions describing methane (CH₄) formation, decomposition and oxidation was calculated for various sets of environmental conditions comparable to those of soil. The calculations showed that the possibility of CH₄ formation out of formic acid and acetic acid was enhanced by a low CO₂ fugacity. At similar CO₂ fugacities, the CH₄ stability area when produced out of acetic acid was greater than out of formic acid, indicating that much more conditions are in favour for formation of that gas out of acetic acid than out of formic acid. Low O₂ fugacity enhances CH₄ formation out of methanol. While, high H₂ fugacity enhances CH₄ formation out of CO₂. Simple decomposition of the environmentally active CH₄ to lesser active ones (C₂H₆, C₃H₈, C₂H₄ and C₂H₂) was enhanced by a low H₂ fugacity. At similar H₂ fugacity, the stability area of C₂H₆ and C₂H₂ was larger than that of C₃H₈ and C₂H₄. Hence, more easier formation of C₃H₈ and C₂H₄ out of CH₄ can be expected. Methane is unstable and can easily be oxidized to CO₂ in the presence of even very small amounts of O₂ (10⁻²⁷ Pa), NO₃⁻ or Fe³⁺ (10⁻⁹M). In contrast, some CH₄ can be formed in the presence of SO₄²⁻ at relatively higher activity (10⁻⁶M).

Key words: Methane cycle, Gaseous hydrocarbons, Soil atmosphere, Thermodynamics, Gibbs free energy.

Introduction

Methane (CH₄) is one of the principle greenhouse gases, second only to CO₂ as an anthropogenic source of greenhouse gases responsible for global warming. Although CH₄ concentration in the atmosphere is minute (1.75ppmv, Dlugokencky *et al.*, 2003), it is very effective in trapping heat (Wigley, 1989). Methane global warming potential is 32 times higher than that of CO₂ for a 100 years time-scale (OTA, 1991 and Al-Sheikh, 2004). However, implications of the recent fluctuations in the growth rate of tropospheric CH₄ was noticed (Isobel *et al.*, 2002). Indeed, CH₄ cycle is less well understood than CO₂ cycle.

Methane formation is mainly biological as a result of organic matter (e.g. simple acids, alcohols,...) degradation under O₂ restricted conditions. It is believed that methane producing bacteria are energetically limited by the availability of their substrates H₂ and acetate (Zinder, 1990, Achtnich *et al.*, 1995). The global annual CH₄ emission

is estimated at 500 ton-gram per year with an uncertainty of 10 to 20% (IAEA, 1992). Beside its important emission from rice paddies, projections for the year 2100 suggest that due to an increased population and waste generation, landfills will become a major source of atmospheric CH₄ (Kreileman and Bouwman, 1994).

Simple decomposition of CH₄ to less environmentally active hydrocarbons (e.g. ethane and propane) is possible under strong reducing (restricted aeration) conditions (El-Sebaay, 1986). It can also transform to ethylene (Van Cleemput and El-Sebaay 1985) which can cause crop damage when present in the plant rhizosphere at even 1ppmv.

Oxidation of CH₄ seems to be the most important sink process especially in agricultural soils (Chan and Parkin, 2001) and landfills (Bogner, 1992, Boeckx and Van Cleemput, 1996) as compared with the forest and prairie soils. In china, mid-season aeration of rice fields (to oxidize CH₄) is a widely accepted

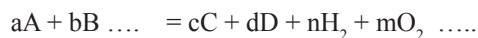
agricultural practice (Cai *et al.*, 1999). In agricultural soils, mineral redox species play a role in mitigating CH₄ emission. The time until the onset of CH₄ production and the magnitude of CH₄ production are usually a function of the amount of easily degradable organic substances and reducible iron and sulfate (Gaunt *et al.*, 1997, Yao and Conrad, 1999, Moller *et al.*, 2004). It was, however, stated by Yao and Conrad (1999) that many details of the events leading to CH₄ production remain unclear.

For a better understanding of methane cycle, and in order to describe and predict the possibilities of methane formation, decomposition and oxidation under specified sets of environmental conditions, the Gibbs free reaction energy concept was used, and information on the spontaneity of different reactions was obtained.

Procedure of calculation

The mode of calculation and subsequent interpretation was based on the use of the Gibbs free reaction energy change (ΔG_r). A negative ΔG_r value indicates that equilibrium is situated at the right of the equation, so that spontaneous change occurs. A positive ΔG_r value shows that the equilibrium is situated at the left, so that the reactant(s) remains stable.

The ΔG_r values of 12 reactions were calculated using the Gibbs free standard formation energy (ΔG_f^0), and the activities of the participating compounds according to the following formula, related to the general reaction:



$$\Delta G_r = \Delta G_r^0 + RT \ln \frac{(C)^c (D)^d (H_2)^n (O_2)^m \dots}{(A)^a (B)^b \dots}$$

in which,

$$\Delta G_r^0 = \sum \Delta G_f^0 (\text{products}) - \sum \Delta G_f^0 (\text{reactants})$$

$$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}, T = 298\text{k}$$

The Gibbs free standard formation energy of the different used compounds are listed in Table 1. The studied reactions of methane formation, decomposition and oxidation and their calculated ΔG_r^0 values are shown in Table 2. Because formation, decomposition and oxidation of methane in soils are mainly biological, it was thought more realistic to

calculate free reaction energy changes (ΔG_r) for real biological conditions instead of unit activity of the reactants and the reaction products.

Therefore, ΔG_r values for each of the 12 reactions were calculated, taking into account the respective ΔG_r^0 values and a set of variable activities of the participating compounds. Fugacities of the gas species were expressed in Pascal (Pa), and the activities of the liquid dissolved species were expressed in Molarity (M). The activities of the variables (reactants and products) varied as follows:

for the gaseous hydrocarbons (CH₄, C₂H₆, C₃H₈, C₂H₄ and C₂H₂):

between 10³ and 10⁻¹⁵ Pa,

For the organic compounds in solution (HCOOH, CH₃COOH, CH₃OH):

between 10⁻² and 10⁻²⁰ M,

For O₂: between 0.2 × 10⁵ (level in air atmosphere) and 10⁻²⁷ Pa,

For H₂: between 10³ and 10⁻²⁷ Pa,

For CO₂: (as product) between 0.03 × 10³ (level in air atmosphere) and 5 × 10³ Pa,

(as reactant) between 10³ and 10⁻¹⁵ Pa,

For N₂: between 10⁻¹ and 10⁻⁵ Pa,

For H⁺, HS⁻, NO₃⁻, SO₄²⁻, Fe³⁺ and Fe²⁺: between 10⁻⁶ and 10⁻⁹ M.

With this range of activities, all possible conditions which can occur in soils were covered. It should be taken in mind that the data obtained from the thermodynamic calculations do not give any answer on questions concerning the velocity of reaching the equilibrium. Enzymatic or chemical catalytic actions might importantly influence the reaction rate.

Results and discussion

The results of the calculations of the ΔG_r values as a function of the activity of the participating reaction compounds are presented in cubes. The axes represent the activities of the reactant(s) and the reaction product(s). Each cube is divided up into two parts by a dotted plane (the plane of equilibrium, where $\Delta G_r = 0$). The lower part represents the area in which the reactant remains stable ($\Delta G_r > 0$). The upper part represents the area wherein the product remains stable ($\Delta G_r < 0$), under the particular reaction conditions. The

studied reactions and their ΔG_r^0 values are organized in three groups as shown in Table 2. Each group will be discussed separately.

Formation of methane

It is well accepted that simple decomposition products of soil organic matter and plant root exudates (e.g. simple acids, alcohols, etc.) are the main precursors for the methane produced in soil. The chemical formation of CH_4 out of $HCOOH$, CH_3COOH , CH_3OH and CO_2 was investigated under different activities of the participating compounds of each studied reaction.

Figure 1a and 1b show the stability area of the formed CH_4 out of formic acid and acetic acid at different CO_2 fugacities. It can be seen that for a fixed CH_4 fugacity, the lower the CO_2 fugacity, the more easily $HCOOH$ or CH_3COOH is transformed into CH_4 . This means that when CO_2 is low in soil, formic acid as well as acetic acid (if present in soil) can spontaneously transform into CH_4 . However, the conditions of CH_4 formation are not very much influenced by CO_2 fugacity and only at very low $HCOOH$, and CH_3COOH activity it remains stable. This can be seen clearly from the slope of equilibrium plane in both figures. In that sense, Allen et al. (2003)

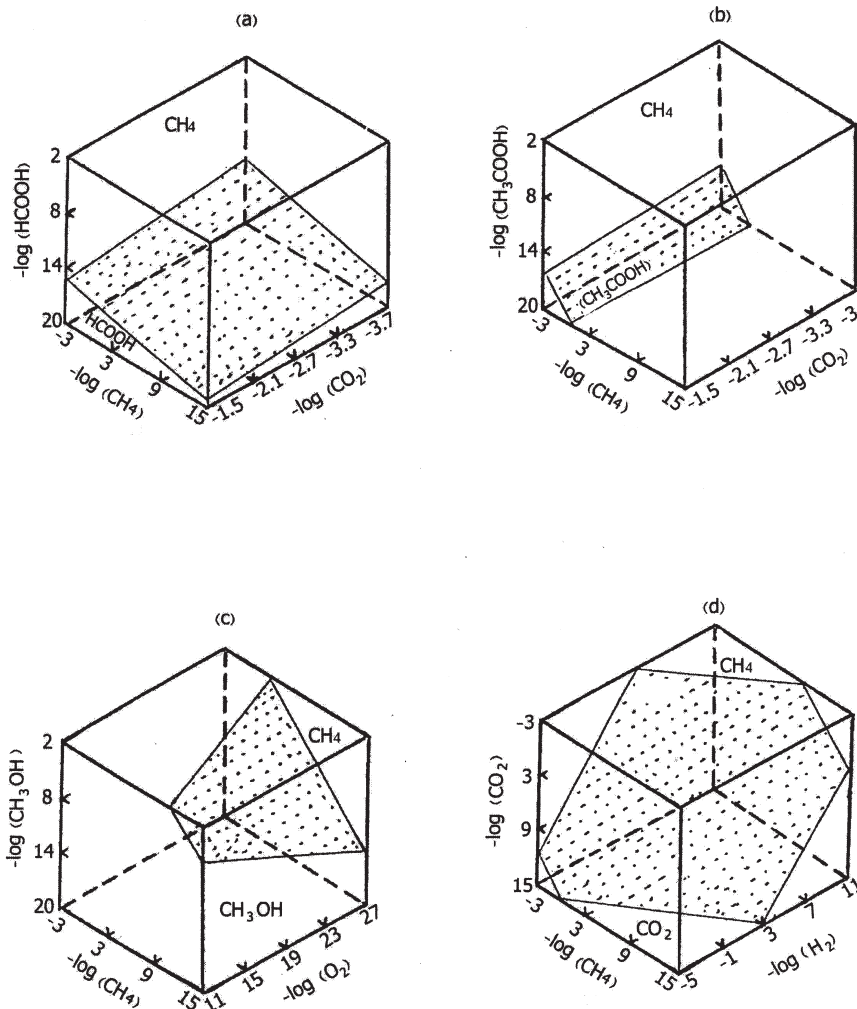


Fig 1. Stability area of methane formed out of (a) formic acid, (b) acetic acid, (c) methanol and (d) carbon dioxide.

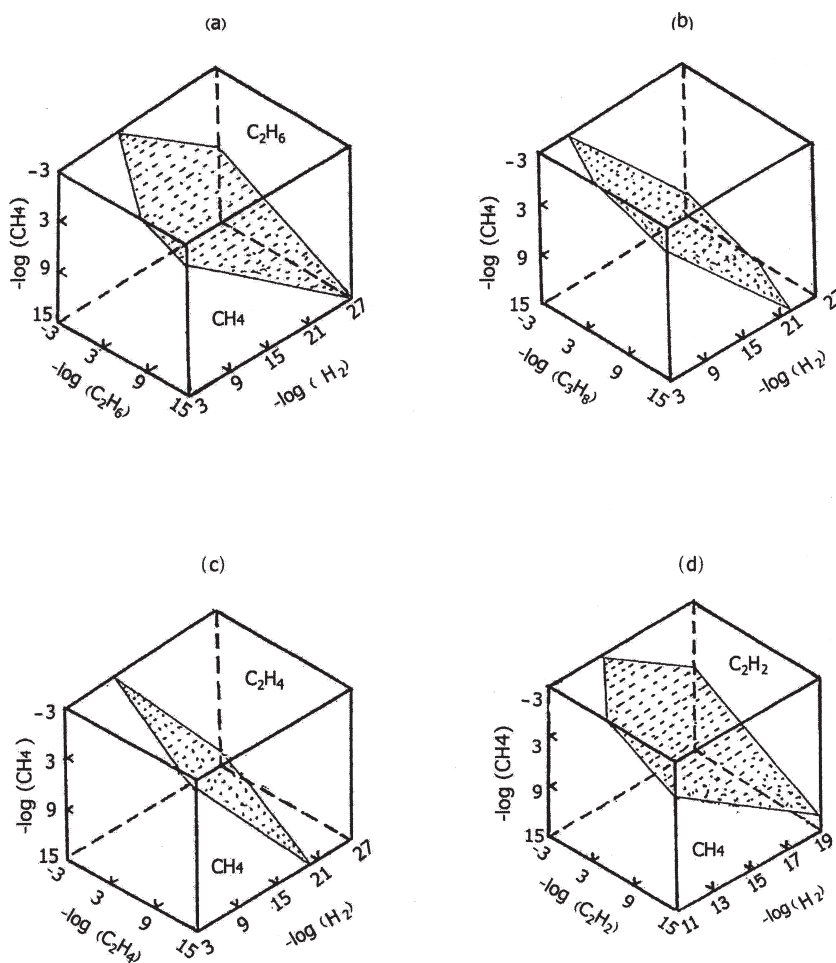


Fig 2. Stability area of (a) ethane, (b) propane, (c) ethylene and (d) acetylene formed out of methane.

contributed the high increase in CH_4 production at 71 days after rice planting to the increase in acetate production in soil. Also, Achtnich *et al.* (1995) declared that methanogenic bacteria are energetically limited by the availability of their substrates H_2 and acetate. Comparison between figures 1a and 1b shows that at the same CO_2 fugacity, the CH_4 stability area when produced out of acetic acid was greater than when produced out of formic acid. This indicates that when both acids have an equal opportunity to form CH_4 , much more conditions are in favour for formation of that gas out of acetic acid than out of formic acid. In addition, if the reactions 1 and 2 (table 2) have the opportunity to occur simultaneously, the reaction with the lowest ΔGr should be the one

continuing to equilibrium. This means that, for a fixed CO_2 fugacity, HCOOH will be the main reactant (least stable) at equilibrium followed by CH_3COOH .

Figure 1c presents the stability area of CH_4 when produced out of methanol at different O_2 fugacities. It can be seen that the lower O_2 fugacity and the fugacity of CH_4 , the easier methanol can be transformed. Out of O_2 fugacity scale, it is clear that the CH_4 stability area is small. Methane was only clearly stable when O_2 fugacity dropped to a very low value (1011- Pa and lower). This gives some proof of the sensitivity of CH_4 towards O_2 .

Formation of CH_4 out of CO_2 at different H_2 fugacities is presented in figure 1d. Out of this figure it can be seen that the higher H_2 fugacity the

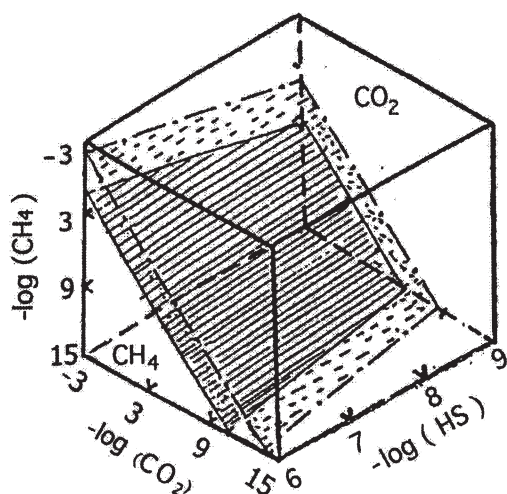


Fig 3. Stability area of carbon dioxide formed out of methane at 10^{-6} (-) and 10^{-9} (.....) M sulfate.

easier CO_2 is transformed into CH_4 . This means that when H_2 is formed in soil (e.g. after flooding and attaining very low redox potential values), CO_2 in the soil can spontaneously transform into CH_4 . This result coincided with the result of Conrad (1999) who mentioned that during energy generation methanogenes can reduce CO_2 with H_2 to form CH_4 . In addition, out of H_2 fugacity scale, CH_4 showed a large stability area. Also, CH_4 formation can occur spontaneously even at very low CO_2 fugacity (10^{-13} Pa and lower) and H_2 fugacity (10^{-11} Pa and lower).

Decomposition of methane

Under certain conditions, CH_4 can simply decompose to form other gaseous hydrocarbons and H_2 . Hence, the stability of C_2H_6 , C_3H_8 , C_2H_4 and C_2H_2 formed out of CH_4 at different H_2 fugacities was investigated and shown in figures 2a, 2b, 2c and 2d. Out of these figures, it can be seen that the lower the H_2 fugacity, the higher the possibility of CH_4 decomposition is. The stability area of the various produced hydrocarbons is different. Out of H_2 fugacity scale, one can notice that the stability area of C_2H_2 and C_2H_6 was larger than that of C_3H_8 and C_2H_4 . This means that at relatively high H_2 fugacity (e.g. higher than 10^{-3} Pa) when these gases have an equal opportunity of formation out of CH_4 , a more easier formation of C_3H_8 and C_2H_4 can be expected. In

Table 1. Heat of formation of the reactions components^a.

Name	Symbol	State	$\Delta G^{\circ r}$ (kJ mol ⁻¹ at 298°k)
methane	CH_4	gaseous	- 50.79 ^b
ethane	C_2H_6	gaseous	- 32.89 ^b
propane	C_3H_8	gaseous	- 107.15 ^b
ethylene	C_2H_4	gaseous	- 68.12 ^b
acetylene	C_2H_2	gaseous	- 204.20 ^b
formic acid	HCOOH	aqueous	- 361.41 ^b
acetic acid	CH_3COOH	aqueous	- 389.53 ^b
methanol	CH_3OH	aqueous	- 175.44 ^b
carbon dioxide	CO_2	gaseous	- 394.38 ^b
oxygen	O_2	gaseous	0 ^c
hydrogen	H_2	gaseous	0 ^c
nitrogen	N_2	gaseous	0 ^c
hydrogen ion	H^+	aqueous	0 ^c
hydrogen sulfide ion	HS^-	aqueous	+ 12.55 ^c
iron (II) ion	Fe^{2+}	aqueous	- 84.94 ^c
iron (III) ion	Fe^{3+}	aqueous	- 10.54 ^c
nitrate ion	NO_3^-	aqueous	- 110.46 ^c
sulfate ion	SO_4^{2-}	aqueous	- 741.99 ^c
water	H_2O	liquid	-237.19 ^c

^a : converted from kcal mol⁻¹ (given in the reference) to kJ mol⁻¹ (SI unit), where 1 cal = 4.18J.

^b : Karapet Yants and Karapet Yants (1970)

^c : Krauskopf (1967).

other words, the stability area of C_2H_2 and C_2H_6 is the highest followed by C_3H_8 and C_2H_4 indicating a higher likelihood for transformation of CH_4 towards C_3H_8 and C_2H_4 than towards C_2H_2 and C_2H_6 . This leads to form environmentally less active gases (i.e. C_3H_8 and C_2H_4) out of environmentally harmful one (i.e. CH_4) as was mentioned by Van Cleemput and El-Sebaay (1985). Moreover, if the reactions 5, 6, 7 and 8 (table 2) have the opportunity to occur simultaneously, the reaction with the lowest ΔG_r value should be the one continuing to equilibrium. It means that for a fixed H_2 fugacity, C_3H_8 will be the main product (most stable) at equilibrium. Removing that particular reaction from the list of the four reactions and repeating the same calculation procedure allows to establish a chain of decreasing stability ($\text{C}_2\text{H}_4 > \text{C}_2\text{H}_6 > \text{C}_2\text{H}_2$).

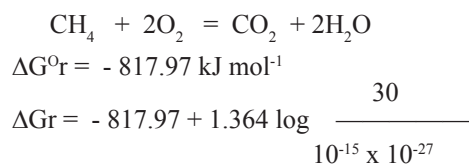
Oxidation of methane

Although addition of oxidized compounds (e.g. fertilizers) such as nitrate to soil is known to hold up

Table 2. Gibbs free energy of methane formation, decomposition and oxidation reactions.

Reaction No.	Considered Reactions	ΔG_r^0 (kJ mol ⁻¹) at 2980k
A.	<i>Formation:</i>	
1.	out of formic acid: $\text{HCOOH} = \frac{1}{4}\text{CH}_4 + \frac{3}{4}\text{CO}_2 + \frac{1}{2}\text{H}_2\text{O}$	- 65.68
2.	out of acetic acid: $\text{CH}_3\text{COOH} = \text{CH}_4 + \text{CO}_2$	- 55.65
3.	out of methanol: $\text{CH}_3\text{OH} = \text{CH}_4 + \frac{1}{2}\text{O}_2$	+ 124.92
4.	out of carbon dioxide: $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$	- 130.79
B.	<i>Decomposition</i>	
5.	to ethane: $\text{CH}_4 = \frac{1}{2}\text{C}_2\text{H}_6 + \frac{1}{2}\text{H}_2$	+ 34.35
6.	to propane: $\text{CH}_4 = \frac{1}{3}\text{C}_3\text{H}_8 + \frac{2}{3}\text{H}_2$	+ 15.08
7.	to ethylene: $\text{CH}_4 = \frac{1}{2}\text{C}_2\text{H}_4 + \text{H}_2$	+ 84.85
8.	to acetylene: $\text{CH}_4 = \frac{1}{2}\text{C}_2\text{H}_2 + \text{H}_2$	+ 115.39
C.	<i>Oxidation</i>	
9.	by oxygen: $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$	- 817.97
10.	by nitrate: $\text{CH}_4 + \frac{8}{5}\text{NO}_3^- + \frac{8}{5}\text{H}^+ = \text{CO}_2 + \frac{4}{5}\text{N}_2 + \frac{14}{5}\text{H}_2\text{O}$	- 830.99
11.	by sulfate: $\text{CH}_4 + \text{SO}_4^{2-} + \text{H}^+ = \text{CO}_2 + \text{HS}^- + 2\text{H}_2\text{O}$	- 63.43
12.	by iron (III): $\text{CH}_4 + 8\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{CO}_2 + 8\text{Fe}^{2+} + 8\text{H}^+$	- 464.34

the redox potential to drop down upon the creation of anaerobic conditions (e.g. flooding) which suppress CH_4 production, it is still not clear whether this suppression is due to a lower production or due to oxidation of the formed CH_4 . Therefore, the stability of CH_4 was investigated in the presence of different activities of O_2 , NO_3^- , SO_4^{2-} and Fe^{3+} together with different activities of the participating compounds of each reaction (no. 9, 10, 11 and 12, table 2). The ΔG_r of reactions 9, 10 and 12 were all negative at the most extreme values of activities. This indicates that CH_4 was unstable in the presence of even a very small amount of O_2 (10^{-27} Pa). This is illustrated for reaction 9 as follows:



$$\Delta G_r = -758.67 \text{ kJ mol}^{-1}$$

To have equilibrium between CH_4 and 10^{-27} Pa O_2 , we need a fugacity of CH_4 of only 10^{-544} Pa. This is extremely small as compared to the background value in the atmosphere (1.75 ppmv or 0.175 Pa) as reported by Dlugokencky *et al.* (2003). Hence, it should be concluded that the equilibrium of reaction 9 is situated to the right. So, CH_4 is not stable in the presence of O_2 . This coincided with the results obtained by many authors (Chan and Parkin, 2001; Borjesson *et al.*, 2001; Conrad, 1999; Boeckx and Van Cleemput 1996). It also emphasized the importance of mid-season aeration of rice fields which is a widely accepted practice in China (Cai *et al.*, 1999). The calculated results of reactions 10 and 12 showed that (at pH 7) ΔG_r values are all negative. This means that CH_4 in both reactions was not stable in the presence of NO_3^- and Fe^{3+} even at very low activities (10^{-9} M), indicating that CH_4 is oxidized to CO_2 . In the presence of SO_4^{2-} , however, at activities of 10^{-6} and 10^{-9} M CH_4 was formed at pH7. This is illustrated in figure 3. This figure shows that for a certain sulfate activity and by decreasing the HS^- activity, the oxidation possibility of the CH_4 was enhanced. The oxidation possibility increased by increasing the sulfate activity. Indeed, in recent experimental results of Gauci *et al.* (2004) as well as early results of Cappenberg (1975), Martens and Berner (1974), the presence of CH_4 has been observed in conjunction with sulfide. Also, El-Sebaay (1986) found that O_2 and NO_3^- but not SO_4^{2-}

inhibited CH_4 production out of soils. The different effect on CH_4 stability of O_2 , NO_3^- and Fe^{3+} on one hand and of SO_4^{2-} on the other hand can already be seen in the ΔG_r^0 values given in Table 2 when considering unit activity of the participating compounds. The lowest (negative) ΔG_r^0 values were found for O_2 and NO_3^- . They were less negative for Fe^{3+} and much less for SO_4^{2-} . The results, however, do not give information on how fast the oxidation occurs.

It can be concluded that agricultural practices related to soil aeration such as ploughing or mid-season aeration of rice fields play a key role in determining CH_4 balance in soils. Calculations declared that under restricted aeration CH_4 can decompose to less environmentally active gases (e.g. C_3H_8 , C_2H_6

and C_2H_2). While, under well aerated conditions and/or in the presence of chemical fertilizers containing nitrate, iron (III) and to some extent sulfate, CH_4 is unstable and can easily be oxidized to CO_2 which is less effective than CH_4 in trapping heat. It is worth to mention that much research has been carried out on CH_4 production out of different environments, but little attention has been given to the mitigation practice processes which need to be more intensively investigated in the future.

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دراسة تكوين وانحلال وأكسدة الميثان في هواء التربة بالاستعانة بأسس الديناميكا الحرارية

عبد الملك بن عبد الرحمن آل الشيخ
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الملخص

بالاستعانة بأسس الديناميكا الحرارية Thermodynamics تم حساب التغيرات في طاقة جيبس الحرة لعدد 12 تفاعل تصف تكوين وانحلال وأكسدة غاز الميثان تحت ظروف بيئية إفتراضية تماثل تلك المتواجدة بالتربة.

أوضحت النتائج المحسوبة أن وجود غازات مثل ثاني أكسيد الكربون والهيدروجين والأكسجين بتركيزات معينة (كما في الترب المغمورة) ووجود مركبات أكسدة مثل أيونات النترات والحديد الثلاثي والكبريتات (كما في الأسمدة الكيماوية التي تضاف للتربة) لها دور أساسي في (أ) تكوين الميثان (الضار بالبيئة) من الأحماض العضوية البسيطة التي تنتج من تحلل المواد العضوية أو الناتجة من إفرازات الجذور مثل حمض الأستيك وحمض الفورميك، (ب) انحلال الميثان إلى غازات هيدروكربونية أقل إضراراً بالبيئة مثل الايثان والبروبان والإستيلين، (ج) أكسدة الميثان إلى ثاني أكسيد الكربون الأقل من الميثان في الاحتفاظ بالحرارة والمشاركة فيما يعرف بظاهرة البيت الزجاجي (Greenhouse).

أظهرت الدراسة أنه تحت ظروف مماثلة من ثاني أكسيد الكربون يكون الميثان الناتج من حمض الاستيك أكبر من الناتج من حمض الفورميك. كما تشجع التركيزات المنخفضة من الأكسجين على إنتاج الميثان من كحول الميثانول. بينما تساعد التركيزات العالية من الهيدروجين على تحول ثاني أكسيد الكربون إلى ميثان.

أوضحت النتائج إمكانية تحلل الميثان (تحت الظروف المفترضة) إلى غازات هيدروكربونية أخرى - وأن هذا التحلل يزداد عند التركيزات المنخفضة من الهيدروجين. كما أن تحلله إلى البروبان والإيثيلين أسهل من تحلله إلى الإيثان والإستيلين.

أظهرت الدراسة أن الميثان غير ثابت ويتحول إلى ثاني أكسيد كربون في وجود تركيزات منخفضة جداً من الأكسجين (10^{-27} باسكال) وكذلك في وجود تركيزات منخفضة جداً من أيونات النترات والحديد الثلاثي (10^{-9} مولر). بينما يمكن أن يتكون في وجود تركيزات مرتفعة نسبياً من أيونات الكبريتات (10^{-6} مولر). وقد أظهرت النتائج المحسوبة توافقاً كبيراً مع النتائج العملية التي قام بها آخرون خاصة في حالات تكوين الميثان. وتوصي الدراسة بمزيد من الاهتمام بالعمليات الزراعية التي تزيد من تحلل وأكسدة الميثان بغرض تقليل المنطلق منه إلى الهواء الجوي.

من الإهتمام بالعمليات الزراعية التي تزيد من تحلل وأكسدة الميثان بغرض تقليل المنطلق منه إلى الهواء الجوي.