Thermodynamics and kinetics of reactions between C₁–C₃ hydrocarbons and calcium sulfate in deep carbonate reservoirs

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Organic-inorganic reactions during thermochemical sulfate reduction (TSR) are the main cause for the destruction of hydrocarbons in deep carbonate sediments. In this paper, thermal simulation experiments on C₁–C₃ hydrocarbons and solid calcium sulfate were carried out using an autoclave operated at high temperature and high pressure. The gas and solid products were characterized by advanced analytical methods including microcoulometry, gas chromatography and FT-IR. The kinetics and thermodynamics were investigated on the basis of the experimental data, and the results showed that the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate can proceed spontaneously in the laboratory to produce H₂S, H₂O, and CaCO₃ as the main products. From the kinetic calculation, it is found that these three reactions are zero order reactions with activation energies of 152.9 kJ/mol, 131.0 kJ/mol and 120.6 kJ/mol, respectively. When extrapolated to geological temperatures, the time needed to reach 50% conversion at the temperature of 200°C for the reaction between CH₄ and CaSO₄ is 1.44 million years.

Keywords: TSR, thermal simulation experiments, C₁–C₃ hydrocarbons, solid calcium sulfate, kinetics and thermodynamics

INTRODUCTION

In recent years, much work on the destruction of oil and gas in carbonate rocks has been carried out (Machel, 1987; Sassen and Moore, 1988; Leventhal, 1990; Cai *et al.*, 2003). Hydrocarbons are thermodynamically unstable in the presence of sulfate in deep carbonate sediments (Anisimov, 1978; Hutcheon *et al.*, 1995) and thermochemical sulfate reduction (TSR) will occur resulting in the disappearance of hydrocarbons. Previous work (Machel *et al.*, 1995; Worden and Smalley, 1996; Machel, 1998) has shown that TSR is a common reaction in geological sediments at temperatures ranging from 100°C to 200°C. Hydrocarbons including branched or n-alkanes, cyclic and mono-aromatic species in the gasoline range participate in TSR and the sulfate is almost always derived from gypsum or anhydrite (Kiyosu, 1980; Hill, 1990; Leventhal, 1990; Alonso-Azcarate *et al.*, 2001). H₂S and carbonate are the main products of the reaction of hydrocarbons with sulfate (Toland, 1960; Claypool and Mancini, 1989; Machel, 2001). However, there are few simulation studies that hydrocarbons have been demonstrated to be the organic reactant with the solid calcium sulfate (Machel, 2001).

The major component of natural gas from deep carbonate sediments is methane, although ethane and propane also occur in natural gas from some basins (Manzano *et al.*, 1997; Snowdon, 2001). Therefore, thermal simulation experiments for the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate were carried out to investigate the TSR process. The gas and solid products were characterized by microcoulometry, gas chromatography and FT-IR methods, and based on the experiment results, the kinetics and thermodynamics were investigated.

EXPERIMENTAL

Apparatus

Thermal simulation experiments for the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate were carried out using an autoclave operated at high temperature and high pressure. The autoclave is a vertical reactor made of a stainless-steel tubing with a volume of 200 ml. The sample basket is a quartz glass cylinder with a height of 40 mm and diameter of 20 mm. CaSO₄ powder was added to the basket and placed in the reactor. The reactor was evacuated, and then charged with methane, ethane or propane at a given pressure.

Experimental conditions and analytical methods

The reaction of CH₄, C₂H₆ and solid CaSO₄ were carried out with the initial pressure of 6 MPa at room temperature. The reactor was directly heated to 400°C and

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then heated by a program control to the final temperatures. For the reaction between CH_4 and CaSO_4 , the final temperatures were 550°C, 600°C, 650°C, 670°C and 700°C, and the heating times were 166 h, 120 h, 66 h, 60 h and 50 h, respectively. For the reaction between C_2H_6 and CaSO_4 , the final temperatures were 450°C, 480°C, 510°C, 540°C, 570°C and 600°C and the heating times were 78 h, 72 h, 66 h, 60 h, 54 h and 48 h, respectively. For the reaction between C_3H_8 and CaSO_4 , the initial pressure was the saturated vapor pressure of propane at room temperature and the reactor was heated under the same time/temperature regimes as the reaction between C_2H_6 and CaSO_4 .

During the simulation experiments, the weight of solid reactant and solid product was measured by an electronic balance. The properties of the products were characterized by microcoulometry, gas chromatography and FT-IR methods.

Microcoulometry To determine the H_2S concentration of the gaseous products, a WK-2B microcoulometer was used. The entrance temperature of the furnace was 500°C and exit temperature was 850°C. The temperature of the gasification zone was 60°C. The flow rates of air, nitrogen, and sample gas were 40 ml/min, 160 ml/min, and 30 ml/min, respectively.

Gas chromatography A Hewlett-Packard 6890 gas chromatograph equipped with a TCD detector was used. GC was performed using five packed columns: two silica columns (3.05 m $\times$ 3.2 mm), one Porapak Q column (1.83 m $\times$ 3.2 mm), and two Chromosorb Paw columns coated with 20% sebaconitrile (0.61 m $\times$ 3.2 mm, 9.15 m $\times$ 3.2 mm). The temperatures of detector and the oven were 200°C and 50°C, respectively. Nitrogen was used as a carrier gas at a flow-rate of 17 ml/min.

FT-IR All spectra were recorded from 4000 cm^{-1} to 400 cm^{-1} using a Nicolet FT-IR spectrometer. Each spectrum gives the averaged value of 32 scans with a spectral resolution of 4 cm^{-1} .

KINETIC MODEL AND THE METHOD OF GEOLOGICAL APPLICATION

According to reaction theory, the kinetic equation is

$$\frac{dx}{dt} = k(1-x)^n. \quad (1)$$

Where x is reaction conversion, t is reaction time, k is the reaction rate constant, n is reaction order, and dx/dt is reaction rate. The reaction rate constant can be expressed as

$$k = Ae^{-E_a/RT}. \quad (2)$$

Where A is the apparent frequency factor, E_a is apparent activation energy, R is the gas constant, and T is absolute temperature.

Equation (1) can be substituted by Eq. (2) to yield

$$\frac{dx}{dt} = Ae^{-E_a/RT}(1-x)^n. \quad (3)$$

The reaction order can be regarded as zero for the reactions of hydrocarbon with sulfate, which will be proved in the kinetics section of results and discussion. β is defined as the heating rate, that is,

$$\beta = \frac{dT}{dt},$$

then

$$\frac{dx}{dT} = \frac{A}{\beta} e^{-E_a/RT}. \quad (4)$$

The integration of (4) gives the following equation:

$$x = \frac{ART^2}{\beta(E_a + 2RT)} e^{-E_a/RT}. \quad (5)$$

Taking the nature logarithm of both sides of Eq. (5) gives

$$\ln \left[\frac{x\beta}{T^2} \right] = \ln \frac{AR}{(E_a + 2RT)} - \frac{E_a}{RT}. \quad (6)$$

By using the linear regression of $\ln[x\beta/T^2]$ vs. $1/T$ in Eq. (6), the apparent activation energy E_a and apparent frequency factor A can be determined by the slope and intercept of the regressed line respectively.

Based on these kinetic parameters, the reaction rate constant k and time needed to reach 50% conversion at geological temperatures can be calculated using Eqs. (1) and (2).

RESULTS AND DISCUSSION

Analysis of the reaction products

Because TSR is a very slow process under geologic temperatures (100–200°C), it is necessary to increase the simulation temperature in the laboratory. In addition, there are many other factors that affect the rate of TSR in natural environments, for example, temperature, pressure, water medium, component of the mineral phase, composition of the hydrocarbons, and the catalysts etc. Conse-

Table 1. The gas composition (v%) from the GC for the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate

	H ₂	CO ₂	C ₃ H ₈	C ₃ H ₆	n-C ₄ H ₁₀	i-C ₄ H ₁₀	CH ₄	C ₂ H ₆	C ₂ H ₄
CH ₄ -CaSO ₄	5.578	1.110	—	—	—	—	93.196	0.155	—
C ₂ H ₆ -CaSO ₄	2.732	0.459	0.161	0.029	0.072	0.006	85.358	11.095	0.086
C ₃ H ₈ -CaSO ₄	4.620	1.512	3.814	0.051	0.016	0.016	86.435	3.793	0.102

quently, the precise simulation conditions are important for understanding the TSR process. It is difficult to detect the products after reaction at temperatures of less than 400°C in the laboratory and the critical temperature of water is 374°C. Therefore, the simulation experiments have to be carried out without the water medium. The reactor was directly heated to 400°C and then further heated by a programmed temperature with different heating rates.

For the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate, the concentration of hydrogen sulfide was 1558 ml/m³, 1642 ml/m³ and 16893 ml/m³ at a temperature of 600°C, respectively. The gas composition from the GC is shown in Table 1.

The FT-IR spectrum of the solid product for the reaction between CH₄ and CaSO₄ at a temperature of 650°C is shown in Fig. 1, which also includes the spectra of the solid product for the reactions of C₂H₆-CaSO₄ and C₃H₈-CaSO₄ at a temperature of 550°C. FT-IR spectra of the calcium carbonate and calcium sulfate are given in Fig. 2. The left spectrum of Fig. 2 shows that the peaks at 1418.77 cm⁻¹, 877.85 cm⁻¹ and 714.85 cm⁻¹ are the vibrational band of the carbonic acid radical. The appearance of a peak at 1418.77 cm⁻¹ can be explained by the formation of carbonate. The right spectrum of Fig. 2 shows that the vibrational bands of hydroxy result in the peaks at 3547.32 cm⁻¹ and 1688.96 cm⁻¹, while the vibrational bands of sulfate occur at 1117.70 cm⁻¹, 463.55 cm⁻¹, 669.70 cm⁻¹ and 600.87 cm⁻¹. Comparing these with the peaks in Fig. 1, it can be concluded that the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate have been carried out to produce calcium carbonate and water (Wen *et al.*, 1989; Pejov and Petruševski, 2001; Svetozar *et al.*, 2002; Wang *et al.*, 2004).

Some black material was observed in the products for the reactions of C₂H₆-CaSO₄ and C₃H₈-CaSO₄. After calcination at high temperature (>700°C), the black material becomes white. Correlated with the gas composition in Table 1, it is apparent that C₂H₆ and C₃H₈ were subject to further thermo-cracking to produce gas and organic carbon. Therefore, the black deposit probably corresponds to be coke.

Based on the simulation experiments, the reactions of C₁–C₃ hydrocarbons with solid calcium sulfate can proceed at a temperature of 450–700°C. According to the

literature on hydrocarbon generation, the vitrinite reflectance of source rocks is 2.0–3.0% at temperatures of 450–700°C, which correspond to the temperatures of 160–200°C in geological settings. (Burnham and Sweeney, 1989; Cheng *et al.*, 1996; Huang, 1996; Schenk and Dieckmann, 2004). Therefore, it seems likely that the reactions of hydrocarbons with sulfate take place in deeply buried carbonate sediments.

Thermodynamics

It is important to calculate the thermodynamic parameters to know whether the organic and inorganic reactants participate in TSR under geologically relevant conditions. In this paper, the thermodynamics for the reactions of C₁–C₃ hydrocarbons with calcium sulfate were investigated. The reactions involved in the systems are as follows:

The thermodynamic data (Dean, 1991; Helgeson *et al.*, 1998) are listed in Table 2. Using the data in Table 2, the Gibbs free energy of the reactions at different temperatures was calculated and is shown in Table 3.

The reactions can proceed spontaneously because Gibbs free energy is negative. The absolute value of Gibbs free energy of the three reactions increases with increasing temperature, implying that the reactions are more favorable at higher temperature. Comparison of the Gibbs free energies of three reactions indicates that the reaction between C₃H₈ and CaSO₄ has the highest value while the reaction between CH₄ and CaSO₄ has the lowest value. Because the absolute value of Gibbs free energy represents the reaction probability, the reaction between CH₄ and CaSO₄ proceeds with the most difficulty.

Kinetics

The simulation experiments have demonstrated that hydrogen sulfide is the gaseous product of three reactions. Because H₂S is corrosive, it reacts with the autoclave wall

(a)

(b)

(c)

Fig. 1. (a) The FT-IR spectrum for the solid products of the reaction between CH_4 and CaSO_4 at 650°C , (b) the FT-IR spectrum for the solid products of the reaction between C_2H_6 and CaSO_4 at 550°C , (c) the FT-IR spectrum for the solid products of the reaction between C_3H_8 and CaSO_4 at 550°C .

(a)

(b)

Fig. 2. (a) The FT-IR spectrum for calcium carbonate, (b) the FT-IR spectrum for calcium sulfate.

and it is therefore difficult to accurately measure the H_2S concentration in the gas phase.

In the kinetic model for the reaction between CH_4 and CaSO_4 , the molar conversion was calculated from the weight change of the solid product and reactant. The conversions are 1.45%, 2.55%, 3.70%, 6.42%, 10.99% at temperatures of 550°C , 600°C , 650°C , 670°C and 700°C , respectively.

The molar conversion for the reactions of C_2H_6 , C_3H_8 and CaSO_4 can be determined by subtracting organic carbon content from the weight change of solid product and reactant. The conversions at the different temperatures for the reaction between C_2H_6 and CaSO_4 are 0.54%, 1.68%, 2.13%, 2.63%, 2.17% and 12.50%, respectively. For the reaction between C_3H_8 and CaSO_4 , the conversions are 0.48%, 1.48%, 2.73%, 3.97%, 5.15% and 7.98%, respectively.

Table 2. The thermodynamic data of C₁–C₃ hydrocarbons and calcium

Species	$\Delta_f H_m^\circ$ kJ·mol ⁻¹	$\Delta_f G_m^\circ$ kJ·mol ⁻¹	S_m° J·mol ⁻¹ ·K ⁻¹	$C_{p,m}^\circ$ J·mol ⁻¹ ·K ⁻¹		
				a	b × 10 ³	c × 10 ⁶
CH ₄ (g)	-74.81	-50.72	188.0	14.15	74.50	-17.99
C ₂ H ₆ (g)	-84.68	-32.8	219.6	9.401	159.83	-46.23
C ₃ H ₈ (g)	-103.8	-23.4	270.0	10.08	239.30	-73.358
CaSO ₄ (s)	-1434.11	-1321.85	106.69	70.21	98.70	0.01
CaCO ₃ (s)	-1206.80	-1128.80	92.9	4.36	358.00	-300.00
H ₂ S(g)	-20.6	-33.6	205.8	26.71	23.87	-5.06
H ₂ O(l)	-285.83	-237.13	69.91	29.16	14.49	-2.02
C(s)	0	0	5.74	0.11	38.94	-17.39

$$C_{p,m} = a + bT + cT^2.$$

Table 3. The Gibbs free energy of the reaction for C₁–C₃ hydrocarbons and CaSO₄. The different Gibbs free energies at different temperatures were for the reaction of CH₄ and CaSO₄, C₂H₆ and CaSO₄, C₃H₈ and CaSO₄, respectively.

Temperature/K	298.15	523.15	573.15	623.15	673.15	723.15	773.15	823.15	873.15	923.15
$\Delta_r G_m^\circ$ /kJ·mol ⁻¹	-26.96	-45.277	-49.588	-53.934	-58.288	-62.622	-66.905	-71.106	-75.195	-79.138
	-83.72	-123.06	-132.10	-141.19	-150.27	-159.33	-168.35	-177.30	-186.17	-194.94
	-131.96	-192.75	-206.63	-220.54	-234.44	-248.30	-262.08	-275.76	-289.32	-302.73

Table 4. The linear regression coefficients for the reactions of C₁–C₃ hydrocarbons and CaSO₄

	0	0.2	0.4	0.6	0.8	1.0
Regression coefficients for the reaction between CH ₄ and CaSO ₄	0.9925	0.9880	0.9834	0.9788	0.9743	0.9707
Regression coefficients for the reaction between C ₂ H ₆ and CaSO ₄	0.9792	0.9760	0.9715	0.9680	0.9642	0.9607
Regression coefficients for the reaction between C ₃ H ₈ and CaSO ₄	0.9811	0.9778	0.9742	0.9710	0.9675	0.9642

When using the kinetic model, the reaction order should first be determined. From Eq. (3), letting $dT/dt = \beta$ and taking ln of both sides yields

$$\ln \left[\frac{dx}{dT} \frac{\beta}{(1-x)^n} \right] = \ln A - \frac{E_a}{RT}. \quad (10)$$

Based on the conversions at different temperatures, and taking different n values (0–1), the linear regression coefficients of lines for

$$\ln \left[\frac{dx}{dT} \frac{\beta}{(1-x)^n} \right] \text{ vs. } \frac{1}{T}$$

can be drawn. When the linear regression coefficient is closest to 1, the corresponding value of n is the reaction order (Kiranas *et al.*, 1997; Li, 2000). The linear regression coefficients for the reaction between CH₄ and CaSO₄

are listed in Table 4, and it can be concluded that the reaction order is zero. Moreover, the reaction orders of the reactions of C₂H₆, C₃H₈ and CaSO₄ also appear to be zero (see Table 4).

By using linear regression of $\ln[x\beta/T^2]$ vs. $1/T$ in Eq. (6), the apparent activation energy E_a and apparent frequency factor A for the reactions of C₁–C₃ hydrocarbons and solid calcium sulfate can be determined by the slope and intercept of regressed line in Fig. 3. The linear regression coefficients of lines for three reactions are 0.996, 0.982 and 0.986, respectively. The resulting kinetic parameters are shown in Table 5 and the reaction between CH₄ and CaSO₄ has the highest activation energy. It is proved that the S-O bands in sulfate are very strong and difficult to break, and methane is the most stable organic reactant in TSR process.

Geological application

The reaction rate constant, k , and time needed to reach 50% conversion for the reaction of C₁–C₃ hydrocarbons

Table 5. Kinetic parameters for the reactions of C_1 – C_3 hydrocarbons and $CaSO_4$

	E (kJ/mol)	A (sec ⁻¹)
The reaction between CH_4 and $CaSO_4$	152.919	1.162×10^3
The reaction between C_2H_6 and $CaSO_4$	130.953	3.06×10^2
The reaction between C_3H_8 and $CaSO_4$	120.582	5.79×10

Table 6. The values of k and reaction time of 50% conversion for the reaction of C_1 – C_3 hydrocarbons and $CaSO_4$. The different values at different temperatures were for the reaction of CH_4 and $CaSO_4$, C_2H_6 and $CaSO_4$, C_3H_8 and $CaSO_4$, respectively.

Temperature (K)	Rate constant k (sec ⁻¹)	Time (year)
323.15	3.12×10^{-21}	9.90×10^{13}
	2.07×10^{-19}	1.06×10^{11}
	1.87×10^{-18}	1.18×10^{10}
373.15	1.52×10^{-18}	4.82×10^{10}
	1.43×10^{-16}	1.54×10^8
	7.63×10^{-16}	2.88×10^7
423.15	4.50×10^{-15}	1.42×10^8
	2.09×10^{-14}	1.05×10^6
	7.54×10^{-14}	2.92×10^5
473.15	4.55×10^{-13}	1.44×10^6
	1.07×10^{-12}	2.06×10^4
	2.82×10^{-12}	7.79×10^3

Fig. 3. (a) The regression line for the reaction between CH_4 and $CaSO_4$, (b) the regression line for the reaction between C_2H_6 and $CaSO_4$, (c) the regression line for the reaction between C_3H_8 and $CaSO_4$. By using linear regression of vs., the apparent activation energy E_a and apparent frequency factor A can be determined by the slope and intercept of regressed line.

and solid calcium sulfate at geological temperatures is determined using Eqs. (1) and (2). The results are listed in Table 6. When extrapolated to the geological environment, the reaction rate is so slow that a long time is required to reach 50% conversion. For example, 1.44 million years will be necessary for 50% conversion for the reaction between CH_4 and $CaSO_4$ system at a temperature of 200°C. Because of a slow reaction rate, thermochemical sulfate reduction is a kinetically controlled process in deep carbonate reservoirs.

Comparison of the kinetic results with other work

Some work has been carried out for the kinetics of TSR (Kiyosu, 1980; Trudinger *et al.*, 1985; Kiyosu and Krouse, 1990; Goldhaber and Orr, 1995; Bildstein *et al.*, 2001; Gorshkov *et al.*, 2001; Machel, 2001). Kiyosu referred that the reaction order of TSR is first according to the experiments between sulfate and glucose and the activation energy range is 140–208 kJ/mol. Gorshkov found that the reaction order for the formation of H_2S is zero based on the experimental results. Trudinger, Goldhaber

and Orr indicated that TSR process could be performed in lab only at temperatures in excess of 175°C and that geological reaction rate could be measured only above 250°C. Goldhaber and Orr also determined that typical sour gas reservoirs may form in a few million years. Bildstein pointed out there are some control steps in the TSR process to affect the reaction rate.

In this paper, according to the experiment results, the reactions of C₁–C₃ hydrocarbons with solid calcium sulfate are zero order reactions with activation energies of 152.9 kJ/mol, 131.0 kJ/mol and 120.6 kJ/mol, respectively. When extrapolated to geological temperatures, the time needed to reach 50% conversion at the temperature of 200°C for the reaction between CH₄ and CaSO₄ is 1.44 million years. Moreover, we have proved that methane is the most stable organic reactant in TSR process, which is a kinetically controlled process. These results can be compared with those reported in previous work.

CONCLUSIONS

Simulation experiments show that hydrogen sulfide, calcium carbonate and water are the main products from the reaction of C₁–C₃ hydrocarbons with solid calcium sulfate. It is demonstrated that the reaction of C₁–C₃ hydrocarbons with solid calcium sulfate can proceed in deep carbonate sediments.

Thermodynamic calculations have been performed to investigate the possibility of the reactions. It is found that the reactions carry out spontaneously and increasing temperature is favorable. A kinetic model was developed from the experimental data and the kinetic parameters were determined. It is shown that the reaction between CH₄ and CaSO₄ has the highest activation energy while that between C₃H₈ and CaSO₄ has the lowest activation energy. When extrapolated to the temperature of the geological environment, the time needed to reach 50% conversion at a temperature of 200°C is 1.44 million years. TSR is a kinetically controlled process in deep carbonate reservoirs.

Investigation of the TSR process is important for explaining hydrocarbon destruction in deep carbonate environments. TSR is complex in natural environments and further research on this subject will be necessary.

Nomenclature

$\Delta_f H_m^\circ$:	standard enthalpies of formation
$\Delta_f G_m^\circ$:	standard Gibbs energy of formation
S_m° :	standard entropy
$C_{p,m}^\circ$:	heat capacity
$\Delta_r G_m^\circ$:	standard reaction Gibbs energy
a, b, c:	parameters for heat capacity
E_a :	apparent activation energy, kJ·mol ⁻¹
A:	apparent frequency factor, sec ⁻¹
R:	gas constant, 8.314 J·mol ⁻¹ ·K ⁻¹

n:	reaction order
k:	reaction rate constant
T:	reaction temperature, K
t:	reaction time, s
x:	reaction conversion
dx/dt:	reaction rate
β:	heating rate

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