NOTE

A comparative experimental study on gas generation from saturated and aromatic hydrocarbons isolated from a Cambrian oil in Tarim basin

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The saturated and aromatic hydrocarbons isolated from a Cambrian oil (TZ62well) in the central Tarim basin were pyrolyzed in sealed gold tubes to investigate how the gases generated from them would vary in compositions of constituents and their carbon isotopes. The results illustrate that the gases from the cracking of saturates are much drier and more enriched in ¹²C than the gases from the cracking of aromatics at the same levels of thermal maturity. The dryness index of the gases (defined as the volume percentage of C₁ to C₁₋₅) from the cracking of saturates ranges from 26.2% to 90.6% whereas it is never lower than 60.6% for the gases from the cracking of aromatics throughout the experiment. The methane from the saturates shows a larger carbon isotope change, ranging from -54.8‰ to -35.5‰, than the methane from the aromatics whose carbon isotopes range from -37.4‰ to -32.2‰ throughout the experiment. The above experimental observations indicate that the cracking of crude oils with different bulk compositions could produce gases that have distinct constituents and carbon isotopic compositions.

Keywords: oil cracking, saturates, aromatics, pyrolysis experiment, natural gas, carbon isotopes

INTRODUCTION

The crude oil generated by the thermal transformation of sedimentary organic matter can be further cracked to form hydrocarbon gases and pyrobitumen at more severe thermal stress (Tissot *et al.*, 1987). The accumulation of gases associated with oil cracking has been well documented in many basins (Prinzhofer and Huc, 1995; Lewan, 2002; Isaken, 2004; Zhao *et al.*, 2005; Ma *et al.*, 2007; Tian *et al.*, 2007; Mancini *et al.*, 2008). Numerous experiments have been performed on crude oils to investigate their thermal stability and cracking mechanisms (Ungerer *et al.*, 1988; Behar *et al.*, 1991; Horsfield *et al.*, 1992; Pepper and Dodd, 1995; Schenk *et al.*, 1997; Tsuzuki *et al.*, 1999; Huang and Otten, 2001; Hill *et al.*, 2003; Tang *et al.*, 2005). However, crude oil is a complex mixture of various compounds that can be classified into saturates, aromatics, resins and asphaltens. The bulk composition of crude oil may vary significantly due to source rock types, maturity and genetic and/or post genetic proc-

esses, such as biodegradation and migration fractionation. Therefore, the general observations of oil cracking obtained from the pyrolysis of whole oil samples can not be reliably extrapolated to all geological conditions when the bulk composition of crude oil varies significantly in different basins.

In recent years, many authors have conducted a series of pyrolysis experiments on various compounds, including aromatics (Behar *et al.*, 1999; Lorant *et al.*, 2000; Darouich *et al.*, 2006a, b), saturates (Jackson *et al.*, 1995; Behar and Vandenbrouck, 1996; Burnham *et al.*, 1997; McKinney *et al.*, 1998; Zhang *et al.*, 2008) and even NSO compounds (Behar *et al.*, 2008), to investigate their individual thermal stability and gas potentials. Based on the results of model compounds, Vandenbrouck *et al.* (1999) attempted to use a compositional kinetic model to simulate petroleum formation and cracking in the North Sea. More recently, Behar *et al.* (2008) presented a more detailed compositional kinetic model of oil cracking based on extensive pyrolysis data on crude oil. However, most of the aforementioned studies are focused on the thermal stability of various compounds, and little attention has been paid to the chemical, especially the carbon isotopic compositions of the generated gases. In the present study,

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we pyrolyzed the saturated and aromatic hydrocarbons isolated from a Cambrian oil from the Tarim basin in order to illustrate how the resulting generated gases would vary in constituent and their carbon isotopic compositions. The resulting experimental observations may be helpful for understanding the chemical compositions of gases from the secondary cracking of crude oil.

SAMPLES AND METHODS

Sample preparation

A crude oil sample was collected from the Silurian reservoirs of well TZ62 in the central Tarim basin. The biomarkers in the crude oil show its Cambrian origin (Xiao *et al.*, 2005). The crude oil was first treated with approximately 40-fold volumes of *n*-hexane for 24 hr to precipitate the asphaltenes. Then, the saturated and aromatic hydrocarbons were isolated from deasphalted crude oils by using column chromatography as described in Fowler *et al.*, (1995). Briefly, a clean and dried glass column (50 cm in length and 15 mm internal diameter) was packed sequentially with pre-activated alumina (80–200 mesh) and silica gel (80–200 mesh) (3:1, w/w). During the packing the column was constantly tapped by a rubber stick to ensure that the alumina and silica gel are compacted tightly. The deasphalted crude oil was introduced into the top of the column to produce a concentrated band (Bastow *et al.*, 1998). *n*-Hexane and *n*-Hexane/dichloromethane (1:1, v/v) were then used to elute saturated and aromatic hydrocarbons, respectively.

Pyrolysis experiment

The pyrolysis experiments were conducted in sealed gold tubes using a method described widely in the literatures (Hill *et al.*, 2003; Tang *et al.*, 2005; Pan *et al.*, 2006; Zhang *et al.*, 2008). In summary, an appropriate amount of sample (approximate 80–15 mg from low temperature to high temperature) was injected into a number of gold tubes (40 mm in length, 3 mm internal diameter and 0.2 mm in wall thickness) that were pre-welded at one end. Once loaded, the open end of each gold tube was purged with argon gas to displace the air in the tube before being pressed in a vise to create an initial seal, which was subsequently welded in an atmosphere of argon gas. The sealed gold tubes were then loaded into the stainless steel pressure vessels that were connected together to maintain a uniform pressure among them. The final pressure was adjusted and maintained at 50 MPa by pumping water in or out of vessels during the experiment. The temperature, measured by a thermocouple placed within an empty vessel with an accuracy of $\pm 1^\circ\text{C}$, was first raised from the room temperature to 250°C within 12 h and then programmed to 600°C at a heating rate of 20°C/h . During the experiments the pressure error was ± 1 MPa.

Gas chemistry and stable carbon isotope analysis

Before chemical analysis, every gold tube was cleaned using dichloromethane solvent and placed into a vacuum collector interfaced to a HP 5890 II gas chromatograph. The gold tube was pierced by a steel needle attached to the vacuum collector into which the gas was released. After 30 s equilibration time, the valve was switched to channel the gas into the gas chromatograph. The gaseous hydrocarbons (C_{1-5}) were quantified using an external standard. The GC employed a Poraplot Q capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) and helium as carrier gas. The oven temperature for the hydrocarbon gas analysis was initially held at 70°C for 6 min, ramped from 70 to 130°C at 15°C/min , from 130 to 180°C at 25°C/min , and then held at 180°C for 4 min.

The carbon isotope compositions of hydrocarbon gases were measured on a Delta ^{Plus} XL gas chromatograph-isotope ratio mass spectrometer (GC-IRMS). The GC was equipped with a Poraplot Q capillary column ($30\text{ m} \times 0.32\text{ mm} \times 0.25\text{ }\mu\text{m}$). Helium was used as carrier gas. The samples were injected at an initial temperature of 50°C (held for 3 min), after which the oven was heated to 190°C at a rate of 15°C/min and held for 15 min. The carbon isotope ratios for individual gaseous hydrocarbons were calculated using CO_2 as a reference gas that was automatically introduced into the IRMS at the beginning and end of each analysis. The carbon isotopic value of CO_2 reference gas was calibrated by NBS 22 oil as a reference material using element analysis (ThermoQuest Flash EA1112 Series), combined with isotope ratio mass spectrum (Delta ^{Plus} XL). In addition, a standard mixture of gaseous hydrocarbons ($\text{C}_1\text{--C}_4$), with known isotope compositions calibrated by our laboratory, was used daily to test the performance of the instrument. At least two measurements were performed for each gas sample to confirm the analytical errors were less than ± 0.3 (‰, PDB).

Bulk stable carbon isotope analysis

The bulk carbon isotopes of saturates and aromatics were measured on a ThermoQuest Flash EA1112 Series C N elemental analyzer linked to a Finnigan Delta ^{Plus} XL Isotope Ratio Mass Spectrometer (IRMS) via a Finnigan MAT ConFlo III unit. The samples were combusted under a flow of helium and oxygen in an oxidation tube at 900°C and the element of carbon was converted CO_2 gas that was introduced into IRMS for measurement. The CO_2 reference gas was calibrated against NBS 22 oil standard and a working standard (black carbon) was measured prior to, during and after each batch of samples to monitor the accuracy of measurement with the EA-IRMS system.

Fig. 1. A plot showing the total hydrocarbon gas yields from the pyrolysis of saturated and aromatic hydrocarbons at a heating rate of 20°C/h.

RESULTS AND DISCUSSIONS

Gas yield

The constituent and their carbon isotopic compositions of gases generated by the pyrolysis of saturated and aromatic hydrocarbons are listed in Table 1. The aromatics produce larger quantities of hydrocarbon gases than the saturates at temperatures of 435°C ($Ro = 1.22\%$) or lower, after which the quantity of C_{1-5} gases from the cracking of saturates is far higher than that of the aromatics (Fig. 1). At the maximum temperature of 600°C ($Ro = 3.88\%$) the yield of C_{1-5} gases from the cracking of saturates is 729 mL/g whereas the yield from the cracking of aromatics is only 401 mL/g (Fig. 1). The gas potential for saturates is nearly two times higher than that of the aromatics because the saturates are more enriched in hydrogen than the aromatics. During the pyrolysis experiment, the yield of methane increases continuously with temperature due to its extremely high thermal stability (Fig. 2a). This indicates that the methane can be obtained as a stable product. However, the wet gases (C_2-C_5) reach their maximum yield, and then, they are cracked at more severe thermal stress (Figs. 2b–d). This illustrates that the wet gases (C_2-C_5) are intermediate products whose yields are controlled by their relative rates of generation and cracking in a closed system. Their yields will continue to increase and reach a maximum value at the temperature where the generation and cracking rates balance, after which the yields will be observed to decline due to the predominance of cracking over generation. In the present study, the balance temperatures for ethane and propane are approximately 525°C ($Ro = 2.56\%$) and 495°C ($Ro = 2.04\%$), respectively (Table 1, Fig. 2).

Constituents in gases

The experimental pyrolysis of crude oil in a closed

Table 1 The selected chemical and carbon isotopic compositions of gaseous pyrolysisates from the cracking of saturates and aromatics in sealed gold tubes

Temp. (°C)	EasyRo* (%)	Saturated hydrocarbons						Aromatic hydrocarbons									
		Gas yield (mL/g)			Dryness (%)	Carbon isotopes (‰)			Gas yield (mL/g)			Dryness (%)	Carbon isotopes (‰)				
		C ₁	C ₂	C ₃		C ₄ -C ₅	C ₁	C ₂	C ₃	C ₁	C ₂		C ₃	C ₄ -C ₅			
408	0.95	2.19	1.64	1.78	1.48	30.87	-54.8	-41.7	-38.1	21.55	6.97	3.83	2.28	62.22	-37.6	-31.3	-30.8
420	1.06	4.83	3.50	3.48	2.74	33.20	-54.4	-41.5	-37.9	25.16	8.67	4.96	2.73	60.61	-39.9	-32.1	-30.9
435	1.22	9.67	7.56	8.12	10.90	26.69	-51.9	-41.2	-36.9	34.91	11.40	6.54	4.36	61.02	-38.9	-32.0	-30.8
450	1.39	34.55	28.11	30.03	32.67	27.56	-50.3	-38.1	-34.7	nd**	nd	nd	nd	nd	nd	nd	nd
465	1.59	72.63	55.72	56.17	57.41	30.02	-47.5	-36.2	-32.5	93.92	28.40	17.16	10.81	62.50	-37.5	-31.6	-30.1
480.1	1.81	124.41	85.31	73.55	57.17	36.54	-46.2	-33.8	-30.1	122.71	36.94	21.53	12.25	63.44	-37.0	-30.8	-28.6
495	2.04	186.49	105.78	82.48	36.81	45.31	-44.3	-30.3	-26.2	157.10	45.12	23.16	8.76	67.10	-36.1	-29.1	-26.0
510	2.3	270.92	129.79	75.08	22.63	54.36	-42.9	-29.2	-23.6	183.68	49.84	20.08	4.72	71.11	-35.6	-27.3	-22.4
525	2.56	346.68	134.93	56.02	10.95	63.20	-40.7	-26.2	-18.3	222.89	51.00	16.02	2.33	76.27	-34.4	-26.0	-17.5
540	2.84	444.90	131.62	28.70	3.91	73.04	-40.0	-23.8	-11.2	259.30	48.20	9.64	0.50	81.63	-34.1	-22.5	nd
560	3.21	541.48	112.64	11.42	1.32	81.20	-38.3	-20.6	nd	307.50	42.06	2.46	0.12	87.32	-33.4	-18.6	nd
580	3.56	611.06	89.27	2.72	0.30	86.88	-35.9	-17.2	nd	344.80	30.43	0.54	0.03	91.75	-33.0	-15.6	nd
600	3.88	660.50	66.48	1.59	0.16	90.64	-35.5	-15.5	nd	377.62	23.17	0.31	0.01	94.14	-32.2	-13.1	nd

*The EasyRo was calculated by the model of Sweeney and Burnham (1990) using the thermal schemes of pyrolysis in this study.

**nd: no data.

Fig. 2. Plots showing the yields of methane, ethane, propane and C_{4-5} component from the pyrolysis of saturated and aromatic hydrocarbons at a heating rate of 20°C/h .

system produces gases dominated by C_{2-5} wet gases while the natural gas usually contains more than 60% methane (Mango, 2001; Hill *et al.*, 2003). Several mechanisms have been suggested to explain this inconsistency, including catalytic intervention (Mango and Hightower, 1997), gas fractionation during expulsion (Inan, 2000), fractionation during migration (Price and Schoell, 1995; Snowden, 2001) and accumulation efficiency (Michels *et al.*, 2002). Others have proposed specific precursors to methane, including methyl naphthalenes (van Aarssen *et al.*, 1999) and phenanthrenes (McNeil and BeMent, 1996). The present study shows that the chemical composition of gases depends significantly on the precursors of gases. Before appreciable cracking of ethane and propane, the gases evolved from the saturates are dominated by the wet gases and the gas dryness (defined as the volume percentage of C_1 to C_1-C_5) is as low as 26.7% at 435°C (Fig. 3). With the cracking of wet gases the methane gradually becomes dominant and the dryness reaches a value of 90.6% at 600°C . These observations are consistent with those obtained from the pyrolysis of single saturated compounds at similar conditions (Jackson *et al.*,

1995; Zhang *et al.*, 2008). However, the situation is quite different for the gases from the aromatics (Fig. 3), where gas dryness never lower than 60% during the experiments. The largest differences in dryness for the gases from the saturates and aromatics is up to 35% at a temperature of 435°C ($Ro = 1.22\%$).

This result illustrates that the chemical composition of gases from oil cracking is partly controlled by the bulk composition of crude oils. The high concentration of methane for gases from aromatics can be partly explained by the demethylation reactions that occur widely in aromatics and high maturity source rocks (McNeil and BeMent, 1996; Behar *et al.*, 1999, 2002; Lorant *et al.*, 2000; Darouich *et al.*, 2006a). For example, the alkyl-aromatics cleave preferentially under thermal stress at the position between the first (α) and second carbon (β) atoms as shown in Fig. 4. The products would then be $-\text{CH}_2\cdot$ (the black dot shows a free radical), attached to the aromatic system, and a chain radical $\text{R}\cdot$, one carbon shorter than the original chain. The $\text{R}\cdot$, being in a highly aromatic atmosphere, would be expected to migrate to another aromatic system, where it would become attached,

Fig. 3. The changes in gas Dryness with increasing thermal stress for the two different samples.

Fig. 4. Sketch reactions illustrating the formation of methane from demethylation of alkyl-aromatics (modified from McNeil and BeMent, 1996 and see details in Smith and Savage, 1992).

making another alkyl-on-aromatic structure and liberating a hydrogen atom. The $\text{-CH}_2\cdot$ could acquire the liberated hydrogen atom, or it could abstract a hydrogen atom from any alkyl group in the vicinity. The result would be a methyl group attached to an aromatic system. Then, the methyl-aromatics lose the methyl groups to produce methane by a series of hydrogen transfer reactions (Fig. 4) (Smith and Savage, 1992; McNeil and BeMent, 1996). However, the gas generation from saturates are mainly related to the progressive cracking of high molecular weight saturates to low molecular weight saturates and the direct formation of methane by demethylation from a long, straight carbon chain is minor (Jackson *et al.*, 1995; McKinney *et al.*, 1998; Behar and Vandenbroucke, 1996; Hill *et al.*, 2003).

Carbon isotopes

The bulk carbon isotopic compositions ($\delta^{13}\text{C}$) of saturates and aromatics are measured to be -28.6‰ and -28.3‰ respectively and those values of methane, ethane and propane from the pyrolysis of saturates and aromatics are listed in Table 1 and compared in Fig. 5. For the methane evolved from the saturates, the lightest $\delta^{13}\text{C}$

Fig. 5. Plots showing the changes in methane carbon isotope compositions with temperature for the gases from the two different samples pyrolyzed at 20°C/h .

measured is -54.8‰ at 408°C ($R_o = 0.95\%$) and the heaviest value of -35.5‰ occurs at 600°C ($R_o = 3.88\%$) (Table 1, Fig. 5a). The carbon isotopic change observed during the pyrolysis experiment is 19.3‰ . The methane from the aromatics, however, shows a smaller carbon isotopic change with $\delta^{13}\text{C}$ ranging from the lightest value of -39.9‰ to the heaviest value of -32.2‰ (Table 1, Fig.

Fig. 6. A plot showing how the mixing of methane derived from saturates and aromatics results in a carbon isotope reversal during the early stage of thermal maturity. The Actual yield and Assumed yield denote that the carbon isotope of mixed methane was calculated based on the actual and assumed yields of methane from saturates and aromatics, respectively See details in text.

5a). Generally, the methane from the saturates is more enriched in ^{12}C than the methane from the aromatics at the same thermal stress levels. The largest difference of 18.4‰ occurs at 408°C ($R_o = 0.95\%$), after which the difference becomes smaller with increasing thermal stress. At the temperature of 600°C, the difference is about 3.3‰ (Fig. 5a).

Paralleling the methane $\delta^{13}\text{C}$, both ethane and propane from the aromatics are more enriched in ^{13}C than those from the saturates at the same thermal maturity levels (Figs. 5b and 5c). At lower temperatures the differences in $\delta^{13}\text{C}$ are larger than at the higher temperatures. For example the difference in ethane $\delta^{13}\text{C}$ between the two samples is about 10.5‰ at 408°C ($R_o = 0.95\%$). With increasing temperature the differences become smaller and nearly negligible (less than 0.48–2.4 per mil) as the maturity approaches 2.5% R_o for ethane and 2% R_o for propane (Fig. 5b). It is worth noting that the $\delta^{13}\text{C}$ of ethane and propane for both samples become extremely enriched in ^{13}C with respect to their initial $\delta^{13}\text{C}$ when they begin to crack (Table 1, Figs. 5b and 5c). They are finally heavier than the saturate and aromatic fractions of the starting oil at maturity around 2.2% R_o for saturate and 2% R_o for aromatics. This trend also was reported by other authors (Lorant *et al.*, 1998; Zhang *et al.*, 2008). In some cases this also occurs in sedimentary basins. For example, James (1983) suggested that the relatively heavy $\delta^{13}\text{C}$ values of ethane and propane in the Delaware-Val Verde basin were probably caused by secondary cracking. More recently, Tilley and Muehlenbachs (2006) reported the cracking of ethane and propane in the Gething Formation in the western Canadian sedimentary basin. The residual gases have

unusually heavy $\delta^{13}\text{C}$ values ($\delta^{13}\text{C}_{[1]} = -34\text{‰}$, $\delta^{13}\text{C}_{[2]} = -13\text{‰}$, and $\delta^{13}\text{C}_{[3]} = 0\text{‰}$). Therefore the $\delta^{13}\text{C}$ values of ethane and propane could be used to determine the maximum thermal stress they have experienced.

It is well accepted that the gases thermally derived from organic matters usually become enriched in ^{13}C with increasing thermal maturity. In many pyrolysis experiments, however, an obvious reversal in the carbon isotopes of gaseous hydrocarbons often occurs at the early stage of methane generation (Lorant *et al.*, 1998; Tang *et al.*, 2000; Cramer *et al.*, 2001; Hill *et al.*, 2003; Tian *et al.*, 2007). This indicates that the carbon isotope of methane first become enriched in ^{12}C and then in ^{13}C with increasing thermal maturities. One explanation for this phenomenon is hypothesizing two or more precursors for gas generation with different isotopic compositions (Smith *et al.*, 1985; Tang and Jenden, 1998). Our experimental results support this hypothesis. The $\delta^{13}\text{C}$ value of methane from aromatics has a reversal of 2.3‰ between 408°C and 420°C, while that of methane from saturates shows no reversal in the present experimental conditions. When the methane from saturates and aromatics are mixed at a ratio of 3:1 (i.e., methane produced by 3 pieces of saturates and 1 piece of aromatics), the reversal in methane carbon isotope becomes more obvious, with a difference of 3.5‰ between 408°C and 420°C (Fig. 6). This indicates that even if there is no reversal in the $\delta^{13}\text{C}$ of methane from aromatics and saturates, the mixing of methane from saturates and aromatics might result in a reversal in methane $\delta^{13}\text{C}$ values. This can be explained by the fact that the methane yield from aromatics is much higher than that from saturates in early stages of maturation (Table 1 and Fig. 2). If we assume that both the saturates and aromatics produce the same quantity of methane at the same levels of thermal maturity, the mixing of methane at a ratio of 3:1 would only lead to a minor reversal of 0.2‰ in $\delta^{13}\text{C}$ values (Fig. 6). This illustrates that the reversal in methane $\delta^{13}\text{C}$ is controlled not only by the carbon isotope difference of distinct gases, but also their difference in yields. Therefore, the actual carbon isotope reversal with thermal maturity in geological conditions could vary significantly due to variations in precursors of gases and their gas potentials.

CONCLUSIONS

The pyrolysis of saturates and aromatics isolated from a Cambrian oil illustrates that the gases from the cracking of saturates are much drier and more enriched in ^{12}C than the gases from the cracking of aromatics at equivalent thermal maturity levels. The dryness of the gases from the cracking of saturates ranges from 26.2% to 90.6% whereas it is never lower than 60.6% for the gases from the cracking of aromatics during the whole experiment.

The methane evolved from the saturated hydrocarbons shows a larger carbon isotope variation, ranging from -54.8‰ to -35.5‰ , than the methane from the aromatics whose carbon isotopes range from -39.9‰ to -32.2‰ throughout the experiment. The maximum difference in methane carbon isotope composition between the two gases is up to 17.2‰ at the lowest pyrolysis temperature and this difference becomes smaller with increasing temperatures (only 3.3‰ at the temperature of 600°C). Our pyrolysis observations indicate that the cracking of crude oils can be one of the most crucial reactions for the generation of gases, in which the constituents and carbon isotope compositions are clearly different.

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