Natural catalytic activity in a marine shale for generating natural gas

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Many organic-rich rocks are major sources of oil and gas in sedimentary basins presumably through high-temperature thermal cracking. This view was brought into question with recent reports of marine shales generating catalytic gas in the laboratory at 50°C, 300°C below thermal-cracking temperatures. Gas forms under natural conditions without artificial stimulation. Compositions of methane, ethane and propane are near thermodynamic equilibrium \((2C_2H_6 = CH_4 + C_3H_8)\) mirroring those in natural deposits. It is significant because thermal cracking can neither generate hydrocarbons at equilibrium nor can it bring them to equilibrium over geological time. Thus, catalysis must be the source of equilibrium in natural gas habitats and in marine shales. There is experimental evidence for metathesis \((2C_n \leftrightarrow C_{n-1} + C_{n+1})\) as the catalytic path to equilibrium. However, it is without example in contemporary catalysis, and therefore, calls for extraordinary empirical support. Here, we report independent and unequivocal evidence of natural catalytic activity in a marine shale linking metathesis and thermodynamic equilibrium. A Cretaceous Mowry shale catalysed the dimerization of propylene \((C_3H_6)\) to methyl cyclopentane \((\text{MCP}, C_6H_{12})\) and \(n\)-hexane \((n-C_6; C_6H_{14})\) at 50°C in greater than 99 per cent selectivity. Propylene increased the rate of \(n\)-C\(_6\) generation by a factor of 100 with 100 per cent selectivity to the straight-chain hexane \((n-C_6)\). Propylene also suppressed the generation of all hydrocarbons except cyclopentane, MCP and \(n\)-C\(_6\). The ratio MCP/\(n\)-C\(_6\), which swung chaotically between 1 and 25 before propylene addition, was rendered invariant with propylene addition \((R^2 = 0.99; \text{MCP/}n\text{-}C_6 = 1.20 \pm 0.034 \text{s.d.})\). These uniquely catalytic reactions confirm natural catalytic activity in this shale. It appears to be ‘palaeoactivity’ possibly conceived in early diagenesis and sustained over geological time.

**Keywords:** metathesis; catalysis; olefin condensation; palaeoactivity; low-temperature gas; natural gas

1. Introduction

It is broadly accepted that thermal cracking is the primary source of non-biogenic natural gas (Tissot & Welte 1984; Hunt 1995; Peters et al. 2005), and laboratory pyrolysis experiments are often cited to support this

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theory (Behar et al. 1992; Waples 2000; Lewan & Ruble 2002; Erdman & Horsfield 2006; Lewan et al. 2008). An alternative catalytic path has been discounted primarily because there has been no convincing evidence of natural activity in carbonaceous sedimentary rocks, and the possibility seemed remote (Lewan et al. 2008).

There is now substantial evidence of natural catalytic activity in marine shales. Gas is generated at ambient temperatures under natural conditions without artificial stimulation (Mango & Jarvie 2009a, 2010). Methane, ethane and propane are generated near thermodynamic equilibrium (Mango & Jarvie 2009b) duplicating their molecular compositions in natural gas (Mango et al. 2009). Gas metathesis \( (2C_n \leftrightarrow C_{n-1} + C_{n+1}) \) appears to be the path to equilibrium (Mango & Jarvie 2010) although its source and nature are unclear.

Natural catalytic activity is not in itself surprising, however. Catalysis in petroleum generation has been the subject of speculation for over half a century (Frost 1945; Grim 1947). Natural activity exists in acidic clay minerals (Goldstein 1983; Kissin 1987, 1990) and is generally associated with biomarker isomerization and diamondoid formation, for example (Wingert 1992; Dahl et al. 1999; Peters et al. 2005). Natural catalysts could also play a role in metastable equilibria in hydrothermal systems (Helgeson et al. 1993; Seewald 1994, 2003).

Gas metathesis stands out because it is without example (Mango & Jarvie 2010). Olefins metathesis is well known (Gault 1981; Pines 1981; Cotton et al. 1999) but there are no reports of a similar catalytic process involving saturated hydrocarbons. The possibility that a natural catalyst might do so therefore invites close attention.

Catalyst-specific reactions are diagnostic of catalytic activity. We selected propylene \( (C_3H_6) \) as a probe in our experiments because of its thermal stability, sensitivity to catalytic action and its ability to generate different products in the presence of different catalysts. Acid catalysts, for example, dimerize propylene with skeletal isomerization giving essentially all possible \( C_6 \) olefin isomers (Pines 1981). Low-valent transition metals (LVTMs), on the other hand, dimerize propylene to specific olefins: for example, \( n \)-hexenes and 2-methylpentenes to the exclusion of the 3-methylpentenes (Pines 1981).

The facile conversion of propylene to specific products at ambient temperatures is, therefore, definitive evidence of catalytic activity with implications on the nature of the catalyst (Gault 1981; Pines 1981; Cotton et al. 1999). It is used here to probe the natural catalytic activity in a Cretaceous Mowry shale that had previously shown metathetic activity at low temperatures (Mango & Jarvie 2010).

Transition metals often promote catalytic action through unsaturated intermediates, olefins in particular, and we speculated that they could be intermediates in the generation of gas in marine shales (Mango & Jarvie 2009b, 2010). Higher hydrocarbons could shed hydrogen to the shale forming olefin intermediates, which then split (fission) to lighter hydrocarbons as indicated in reaction (1.1) \( ([\ ] \text{ symbolizes an open site (a metal), } [C_n] \text{ symbolizes a mono-unsaturated hydrocarbon } C_nH_{2m} \text{ bonded to it, and } m \text{ and } n \text{ are integers indicating the number of carbon atoms in the olefin}) \)

\[
[C_n] + [\ ] \rightarrow [C_{n-m}] + [C_m].
\] (1.1)
Conversion to gas consumes hydrogen, \([C_n]\), and regenerates open sites \([\ ]\) (reaction (1.2)), where \([H_2]\) denotes hydrogen in kerogen in some unspecified form

\[
[C_n] + [H_2] \rightarrow C_nH_{2n+2} + 2[ ].
\]  

Continued generation should exhaust the shale of occupied sites, \([C_n]\), and maximize open catalytic sites \([\ ]\). Our strategy was to regenerate \([C_n]\) by adding olefins to an exhausted shale as shown in reaction (1.3)

\[
[ ] + C_nH_{2n} \rightarrow [C_n].
\]  

\([C_n]\) could metathesize to higher and lower olefins (Pines 1981), or fuse to higher olefins \([C_{2n}]\) (the reverse of reaction (1.1) (Pines 1981; Cotton et al. 1999), ultimately generating higher hydrocarbons.

2. Results

A Cretaceous Mowry shale was heated isothermally (100°C) for 19 h with hydrocarbon products removed every hour and analysed for compositions of \(C_1\text{–}C_6\). Initial rates of generation (19 \(\mu\)g \(C_1\text{–}C_6\) g\(^{-1}\) h\(^{-1}\)) fell sharply with time to about 3 per cent of original activity after 11 h. Assuming that the sample was exhausted in \([C_n]\), about 470 \(\mu\)g propylene was then injected into the reactor and heating resumed with hourly removal and analysis of gas.

Table 1 shows the distribution of hourly rates (\(\mu\)g g\(^{-1}\) h\(^{-1}\)) for the hydrocarbons generated over 19 h at 100°C. Figure 1 shows rates of \(C_6\) hydrocarbon generation over time. \(C_1\text{–}C_6\) rates of generation increased by a factor of 7 with propylene addition (figure 1 and table 1). A total of 0.24 \(\mu\)mol \(C_1\text{–}C_6\) was generated before propylene addition and 0.25 \(\mu\)mol later, but the product was almost exclusively \(n\)-hexane (\(n\)-C\(_6\)) and methyl cyclopentane (MCP). They averaged 63 per cent of total \(C_1\text{–}C_6\) product before propylene addition and 99 per cent after. The generation of other hexanes (isohexanes and cyclohexane) was suppressed by propylene, and all \(C_1\text{–}C_5\) hydrocarbons, with the exception of cyclopentane (CP), were also suppressed (table 1). Figure 2 shows a strong correlation \((R^2 = 0.99)\) between MCP and \(n\)-C\(_6\) (\(\mu\)g g\(^{-1}\) h\(^{-1}\)) after addition of propylene, and a much weaker correlation prior to propylene addition.

Duplicate experiments in figure 3 show chaotic fluctuations in MCP/\(n\)-C\(_6\) before the addition of olefin and their disappearance later.

We obtained similar results with propylene addition at 50°C. After 7 h at 100°C (no propylene), the rate of generation was 3.3 \(\mu\)g \(C_1\text{–}C_6\) g\(^{-1}\) h\(^{-1}\). MCP was 6 vol. % of the \(C_1\text{–}C_6\) hydrocarbons and \(n\)-C\(_6\) was 15 per cent. With propylene addition at 50°C, the rate fell slightly (2.7 \(\mu\)g \(C_1\text{–}C_6\) g\(^{-1}\) h\(^{-1}\)), but MCP was now 55 per cent of the generated hydrocarbons and \(n\)-C\(_6\) was 45 per cent, with the two hydrocarbons constituting greater than 99 per cent of total product.

3. Discussion

Mowry shale was generating 0.02 \(\mu\)g \(n\)-C\(_6\) g\(^{-1}\) h\(^{-1}\) after 11 h of heating at 100°C. The rate increased by a factor of 100 with the addition of propylene (table 1). All \(C_1\text{–}C_6\) hydrocarbons with the exception of CP, MCP and \(n\)-C\(_6\) disappeared with
Figure 1. Rates of C₆ hydrocarbon generation, Mowry shale, 100°C. Hours 1 and 2 (19 and 13 μg g⁻¹ h⁻¹, respectively) are not included in this figure because initial products could contain desorbed pre-existing hydrocarbons, although our analysis indicates that it would be minor (Mango & Jarvie 2009a,b). Filled square, n-hexane; filled triangle, methyl cyclopentane; filled circle, other hexanes.

Table 1. The effect of propylene addition (hour 12) on hydrocarbon generation (μg g⁻¹ h⁻¹) over time, Mowry shale, 100°C.

<table>
<thead>
<tr>
<th>time (h)</th>
<th>C₁–C₂</th>
<th>C₄a</th>
<th>C₅a</th>
<th>MCP</th>
<th>MPsa</th>
<th>n-C₆</th>
<th>Sum</th>
</tr>
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<tr>
<td>1</td>
<td>0.036</td>
<td>1.400</td>
<td>4.402</td>
<td>4.920</td>
<td>5.627</td>
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<td>2</td>
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<td>2.307</td>
<td>5.369</td>
<td>3.288</td>
<td>1.332</td>
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<td>0.157</td>
<td>0.472</td>
<td>0.697</td>
<td>0.841</td>
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<tr>
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<td>0.039</td>
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<tr>
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<td>1.159</td>
<td>0.041</td>
<td>0.977</td>
<td>2.18</td>
</tr>
</tbody>
</table>

aC₄ includes isobutane and n-butane. C₅ includes the isopentanes, n-pentane and cyclopentane. Cyclopentane dominated the pentanes between hours 11 and 19. Methyl pentanes (MPs) include cyclohexane, 2-methylpentane and 3-methylpentane. Zeros denote concentrations below analytical detection.

the addition of C₃H₆. Propylene addition to Bakken shale and Marcellus shale under the same conditions did not generate MCP and n-C₆. MCP and n-C₆ were therefore generated from C₃H₆ fusion catalysed by Mowry shale as opposed to some spurious source of activity induced under experimental conditions.

A catalyst’s capacity to shape the course of reaction, often referred to as ‘selectivity’, is perhaps the most significant characteristic of a catalytic process. Mowry shale exhibited three examples of selectivity in propylene dimerization: (i) it suppressed the generation of specific hydrocarbons (C₁–C₅, cyclohexane and isohexanes); (ii) promoted the generation of specific hydrocarbons (MCP and n-C₆), and (iii) generated the straight-chain hexane (n-C₆) to the exclusion of the branched-chain hexanes.

As far as we know, 100 per cent selectivity to the straight-chain hydrocarbon in the dimerization of propylene is unprecedented in thermal reactions and without any example in catalysis. Acid catalysis is unlikely because it generates branched hydrocarbons almost exclusively (Pines 1981). Free radicals are also unlikely because secondary radicals, the likely intermediates, would preferentially generate 2-methyl pentyl radicals and therefore branched hydrocarbons. There are no reports of free radical reactions converting propylene to n-butylene selectively that we know of. A variety of metals catalyse the polymerization of propylene to branched polymers and LVTM, nickel in particular, dimerize propylene to 2-methylpenene, n-hexene and 2,3-dimethylbutene (Pines 1981). 3-Methylnpentene is rarely produced in nickel catalysis.

Any property that is clearly not a property of a corresponding thermal reaction is a distinguishing property of a catalytic reaction. Chaotic oscillations are a case in point (Eiswirth 1993; Pismen et al. 1998; Cirak et al. 2003). The oscillations in figure 3 are a characteristic of low-temperature gas generation noted before
Figure 3. Fluctuations in MCP/\(n\)-C\(_6\) over time in duplicate experiments, Mowry shale, 100°C. The lower panel is from the data in table 1 and figure 1. A duplicate experiment is shown in the upper panel. Yield (C\(_1\)–C\(_6\)) for the reaction in the upper panel was 23 mg (3–11 h), and 15 mg (12–19 h). Yield (C\(_1\)–C\(_6\)) for the reaction in the lower panel was 11 mg (3–11 h), and 22 mg (12–19 h). Broken lines with filled circle, before propylene addition; solid lines with filled square, after propylene addition.

(Mango & Jarvie 2009a,b, 2010). Thermal reactions do not oscillate over time, and first-order kinetics should not generate gas in episodes (Mango & Jarvie 2009a) or the chaotic fluctuations in MCP/\(n\)-C\(_6\) shown in figure 3.

The transition from chaotic oscillations to invariance shown in figure 3 suggests the creation of a new and stable path to MCP and \(n\)-C\(_6\). Propylene brought order to a chaotic system. It suggests pair-wise generation of MCP and \(n\)-C\(_6\) through a C\(_6\) intermediate as the only source of these hydrocarbons after addition of olefin (reaction (3.1))

\[
2[C_3] \rightarrow [C_6] \rightarrow \text{MCH} + n\text{-C}_6. \quad (3.1)
\]
This is consistent with propylene filling the open catalytic sites in Mowry shale ([ ]), thus generating high concentrations of \([C_3]\), high concentrations of \([C_6]\) through fusion and a single path to MCP and \(n\)-C\(_6\) (reaction (3.1)). The system’s instability prior to olefin addition (figure 3) might reflect hydrogen fluctuations, since hydrogen plays a key role in gas generation (reaction (1.2)). Propylene could be delivering hydrogen and stability to a hydrogen-deficient catalyst through degradation (Mango & Jarvie 2009a, 2010).

We propose two possibilities for propylene dimerization to \(n\)-C\(_6\) and MCP. In the first (figure 4), propylene sheds hydrogen forming \(bis-\pi\)-allyl-metal intermediates, common in transition metal catalysis (Cotton et al. 1999). These dimerize to 1,5-hexadienes, a reaction similar to nickel-catalysed dimerization of butadiene, a reaction that is believed to proceed through a \(\pi\)-allyl intermediate (Cotton et al. 1999). The scheme accounts for the preservation of linear structure in \(n\)-C\(_6\), and there is precedence for 1,5-hexadiene–metal complexes interconverting MCP and \(n\)-C\(_6\) (Gault 1981).

In a second possibility (figure 5), propylene condenses to 2-methyl-4-ethylmetallocyclobutane through metathesis (Pines 1981, p. 264), which then rearranges to 2-methylmetallocyclohexane (Gault 1981), possibly the intermediate \([C_6]\) in reaction (3.1). Neither scheme is hydrogen-balanced. We assume a source of hydrogen through degradation (Mango & Jarvie 2009a, 2010). \(n\)-C\(_6\) generation consumes hydrogen while MCP generation is hydrogen-neutral.

Propylene is converted to MCP and \(n\)-C\(_6\) in the presence of Mowry shale in a catalytic reaction rarely seen in laboratory experiments. It suppresses the generation of all hydrocarbons except CP, \(n\)-C\(_6\) and MCP (table 1) and renders the MCP/\(n\)-C\(_6\) ratio invariant over time (figures 2 and 3). This is consistent with \([C_3]\) saturation through reaction (1.3) and fusion of \([C_3]\) as the path to \(n\)-C\(_6\) and MCP (figures 3 and 4).
The results clearly establish catalytic activity in Mowry shale. Thermal dimerization of propylene at ambient temperatures is not a possibility. The only questions are the catalyst and its history. A number of factors point to LVTM. Partially filled $d$ orbitals would account for the high activity in our experiments (Nørskov 1982; Somorjai 1994). Nonlinear kinetics (Mango & Jarvie 2009a) resemble chaotic chemical reactions on transition metal surfaces (Eiswirth 1993; Pismen et al. 1998; Cirak et al. 2003). Oxygen poisoning (Mango & Jarvie 2009a) is a characteristic of LVTM, Co and Ni in particular (Toyoshima & Somorjai 1979). There is substantial laboratory evidence of reduced Ni and Co oxides converting oil to a gas indistinguishable from natural gas in molecular and isotopic compositions (Mango et al. 1994; Mango 1996; Mango & Hightower 1997; Mango & Elrod 1999; Mango 2000). Reports of metastable equilibria between hydrocarbons, water and authigenic mineral assemblages (Helgeson et al. 1993; Seewald 1994, 2003) may involve catalytic assistance.

Chemotrophic and phototrophic micro-organisms could be a source of LVTM and thus the natural activity in these shales. They contain low-valent nickel and iron in their hydrogenase enzymes (Montet et al. 1998). Dead chemotrophic and phototrophic organisms would carry residual hydrogenase enzymes into sediments during organic deposition. The metals, preserved in low-valent states during diagenesis, could be the active agents in these shales. Whatever the catalyst’s origin, it is a ‘palaeocatalyst’ that has had geologic time to reach its final active state and is unique in this regard.

Two questions deserve comment here. The first is the extraordinary nature of Mowry activity compared with the other shales. We do not think that the differences are in degree. Mowry shale generates gas compositions that are quite different from those generated by Floyd shale (Mississippian) and New Albany shale (Devonian/Lower Mississippian, e.g. Mango & Jarvie 2010). The fact that propylene had little effect on Bakken shale (Upper Devonian/Lower Mississippian) and Marcellus shale (Devonian) may also be reflecting unique properties of Mowry shale. These distinctions better fit differences in catalyst compositions rather than differences in catalyst concentrations.
The second has to do with the high levels of activity observed. All shales have exhibited some level of activity, and they have varied broadly (Mango et al. 2009; Mango & Jarvie 2010). However, conversion rates are all high on a geological time scale. Rates of catalytic gas generation projected to geological time would predict far more gas than is currently seen in petroleum basins. Thus, what constrains catalytic gas generation is the more important question than what promotes it. We suspect two factors. The first is mass transport, which is discussed elsewhere (Mango & Jarvie 2009b). The second, perhaps the more important, is pressure. Since most catalytic processes are equilibrium systems, and this one is no exception (Mango et al. 2009), there could be a critical gas pressure that suppresses the rates of gas generation. This would mean that generation in closed vessels would continue to a critical pressure, then stop. Generation in open vessels, where gas pressures never reach critical, could continue to completion.

4. Experimental

The Mowry shale, sample preparation and product analysis are described elsewhere (Mango & Jarvie 2009a,b). Reactions were carried out in argon in 5 ml glass vials fitted with septa. Charged vials were heated at 100°C for periods of 1 h over 19 h. Two millilitre gas samples were withdrawn hourly and replaced with argon through two needles inserted into the vial through the septum. Reagent grade propylene (greater than 99%) of 470 μg (approx. 1 ml gas) was injected after 11 h of heating, the mixture hand-shaken, and heating resumed. Product compositions (μg g⁻¹ h⁻¹) in the 2 ml samples withdrawn hourly are tabulated in table 1.

Duplicate experiments were carried out using low-activity Bakken shale (Upper Devonian/Lower Mississippian, 3039 m, Williston Basin, ND) and Marcellus shale (Devonian, 2350 m, Appalachian Basin, West Virginia). Bakken: total organic carbon (Leco) = 2.7%; Rock-Eval: S1 = 3.6 mg hydrocarbons g⁻¹ rock; S2 = 7.35 mg hydrocarbon g⁻¹ rock; T_max = 436°C. Marcellus: total organic carbon (Leco) = 6.22%; Rock-Eval: S1 = 0.15 mg hydrocarbon g⁻¹ rock; S2 = 0.35 mg hydrocarbon g⁻¹ rock; S3 = 0.15 mg carbon dioxide g⁻¹ rock; T_max = 524°C. Both shales had generated less than 0.02 μg C₄–C₆ g⁻¹ h⁻¹ in our standard test for hydrocarbon-generation capacity (100°C, 1 h). Propylene addition at 100°C had no detectable effect on product distributions and showed no evidence of MCP or n-C₆ generation.

5. Conclusions

— A cretaceous Mowry shale exhibits natural catalytic activity in the dimerization of propylene at ambient temperatures.
— The active catalysts are probably LVTM. The catalytic fusion of propylene to n-C₆ to the exclusion of branched C₆, although rare, strongly suggests catalysis by LVTM (Pines 1981).
— Natural catalytic activity is probably a major source of natural gas. Mowry shale generates gas at thermodynamic equilibrium (Mango & Jarvie 2010), and converts heavier hydrocarbons (wet gas) to methane (dry gas).

at ambient temperatures (Mango & Jarvie 2009b). Because the same shale exhibits natural catalytic activity in the dimerization of propylene under the same conditions, natural catalysis is the probable source of gas at equilibrium and methane enrichment, two outstanding properties of natural gas that thermal-cracking cannot explain (Mango 2001; Mango et al. 2009).

References


