

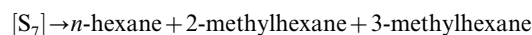
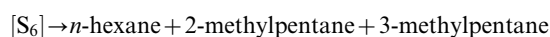
Carbon isotopic evidence for the catalytic origin of light hydrocarbons

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The molecular proportionality between C₆ and C₇ isomers reported recently (F. D. Mango, *Geochim. Cosmochim. Acta*, 2000, **64**, 1265; ref. 1) is probably the strongest evidence for catalysis yet published. It implicates two cyclopropane-like precursors, [S₆] and [S₇] (where S denotes any substrate), of similar structures, each yielding three isomers along similar kinetic pathways:



This view is supported here by the carbon isotope ratios of these isomers in 36 oils from Western Canada (M. J. Whiticar and L. R. Snowdon, *Org. Geochem.*, 1999, **30**, 1127; ref. 2). They exhibit strong correlations in δ¹³C, consistent with their being formed in triads through isotopically indistinguishable precursors. These results add significantly to the growing body of evidence supporting catalysis.

Introduction

There can be little doubt that light hydrocarbons (C₁–C₉) can be produced thermally from decomposing hydrocarbons in sedimentary rocks.³ Although other pathways have always seemed possible (e.g., catalysis^{4,5}), they were rarely given serious consideration until it became clear that (a) ordinary hydrocarbons should remain stable under the time–temperature conditions typically seen in sedimentary rocks,^{6–9} and (b) thermal cracking in the laboratory does not produce a gas resembling natural gas.^{8,10–16} Catalysis gained additional recognition in 1987 when an invariance in isoheptanes was disclosed.¹⁷ That work introduced steady-state kinetics as a critical, if not necessary, element to light hydrocarbons (LH) genesis, thereby undermining thermal cracking as the sole explanation.

Catalysis by acidic clay minerals^{18–20} and reduced transition metals²¹ were offered as alternative sources of LHs. However, only the latter has reproduced the composition of natural gas in the laboratory.^{22–25} LHs exhibit a striking molecular proportionality consistent with a catalytic origin through cyclopropane-like intermediates,¹ a mechanism independently supported elsewhere.^{26,27} An isotopic analysis of these same hydrocarbons is reported here. The data used are from Whiticar and Snowdon² who reported the molecular and isotopic compositions for 26 LHs in 42 oils and condensates from Western Canada.

Results and discussion

Assume that hexane and heptane isomers originate as suggested by Mango¹ and illustrated in Fig. 1.

If the kinetic pathways [S₆] → [n-C₆ + 2-MP + 3-MP] and [S₇] → [n-C₇ + 2-MH + 3-MH] are energetically similar, as would be the case in Fig. 1 for example, then the following proportionality obtains:

$$[(n-C_6)(MHs)]/[(MPs)(n-C_7)] = \alpha \quad (1)$$

(where MHs = 2-methylhexane + 3-methylhexane; MPs = 2-methylpentane + 3-methylpentane).

The LH in crude oils obey eqn. (1) to a remarkable degree. Fig. 2 shows the correlation between [(n-C₆)(MHs)] and [(MPs)(n-C₇)] in concentrations of wt.% total oil (r² = 0.99; ref. 1). α is tightly constrained to a mean of 0.75 with a standard deviation (s) of 0.20 (mean centered), significantly below those of the ratios composing α: s = 0.42 for (n-C₆/n-C₇), 0.46 for (n-C₆/MPs), 0.51 for (n-C₆/MHs), and 0.41 for (MPs/MHs). Moreover, the variability of α is unique to its particular

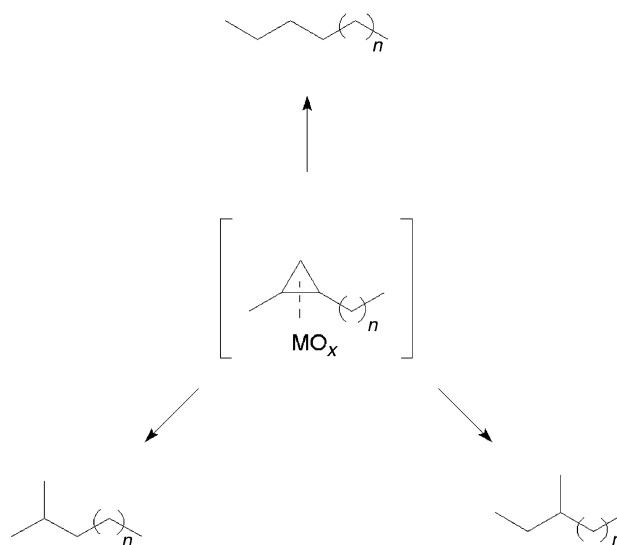


Fig. 1 A kinetic scheme for catalytic isomerization through a cyclopropane-reduced metal oxide intermediate: [S₆] (n = 1), and [S₇] (n = 2); Fig. 1 of Mango.¹ [S] is a cyclopropyl–transition metal complex formed from some substrate S. The actual structure of [S] is unspecified and should not be inferred from the figure (see Mango¹ for discussion). Cyclopropanes may or may not exist as distinct entities. However, their inclusion as distinct entities coordinated to a catalytic site best illustrates the hypothetical process where three isomers are kinetically linked to a common intermediate.

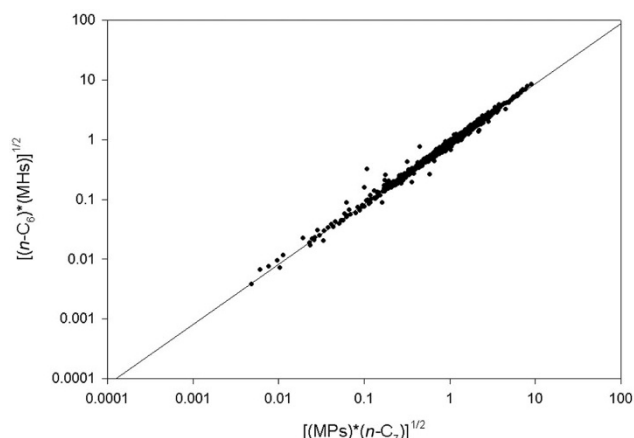


Fig. 2 A plot of $[(n-C_6) \cdot (MHs)]^{1/2}$ vs. $[(MPs) \cdot (n-C_7)]^{1/2}$ for 900 crude oils; Fig. 2 in Mango (ref. 1). MHs = (2-MH + 3-MH); MPs = (2-MP + 3-MP). Concentrations are in wt.% total oil. The data are plotted as square root to constrain the scale to average concentrations. The line is the linear regression line: intercept = -0.068; slope = 1.01; $r^2 = 0.991$. Mean for the ratio $[(n-C_6) \cdot (MHs)] / [(MPs) \cdot (n-C_7)] = 0.75 \pm 0.31s$. Mean-centered $s = 0.20$.

combination of product functions. Its s of 0.20 increases by a factor of four in $[(MPs)(MHs)] / [(n-C_6)(n-C_7)]$ and by a factor of almost five in $[(n-C_7)(MHs)] / [(n-C_6)(MPs)]$ (ref. 1). Thus, at all concentrations, $[(n-C_6)(MHs)]$ and $[(MPs)(n-C_7)]$ express a

strong and significant correlation in crude oils, perhaps the strongest yet disclosed among LHs, while α remains nearly constant.

This relationship establishes a genetic link between $[n-C_6 + 2-MP + 3-MP]$ and $[n-C_7 + 2-MH + 3-MH]$ pointing to *structurally similar* precursors. It would be reinforced if it could also be shown that the six LH reflect *isotopically similar* precursors. Although $\delta^{13}C$ for $[S_6]$ and $[S_7]$ cannot be measured directly, they can be calculated from the weighted sums:

$$\delta^{13}C([S_6]) = a\delta^{13}C(2-MP) + b\delta^{13}C(3-MP) + c\delta^{13}C(n-C_6) \quad (2)$$

$$\delta^{13}C([S_7]) = d\delta^{13}C(2-MP) + e\delta^{13}C(3-MP) + f\delta^{13}C(n-C_6) \quad (3)$$

(where a , b and c (d , e , and f) are the molecular fractions of the respective isomers; $a + b + c = 1$, and $d + e + f = 1$). Thus, $\delta^{13}C$'s for $[S_6]$ and $[S_7]$ can be calculated from the $\delta^{13}C$'s and molecular fractions of the six isomers.

Whiticar and Snowdon² published this data for the LH in 42 oils from Western Canada. Table 1 was constructed from their data. It contains 36 of their oils, including all with sufficient data to calculate $\delta^{13}C$ ($[S_6]$) and $\delta^{13}C$ ($[S_7]$) except for two, possibly altered oils. Fig. 3 shows $[S_6]$ to be isotopically indistinguishable from $[S_7]$. The mean for $\delta^{13}C$ ($[S_6]$)/ $\delta^{13}C$ ($[S_7]$) = $1.00 \pm 0.024s$, which is within the experimental error reported for this data ($\pm 0.5s$).

Table 1 Light hydrocarbon data taken from Whiticar and Snowdon.² $\delta^{13}C$ values are averages of multiple analyses. $\delta^{13}C$ $[C_6]$ and $\delta^{13}C$ $[C_7]$ (the last two columns) were calculated from eqn. (2) and eqn. (3), respectively with coefficients a , b and c calculated from the respective C_6 concentrations normalized to 1 and coefficients d , e , and f calculated from the respective C_7 concentrations normalized to 1. The amount of 2-MP (in %) was taken from column five of Whiticar-Snowdon's Table 3 labeled 3DMC4 incorrectly. Six oils in Whiticar-Snowdon's set of 42 oils were excluded from this set: Brazeau PA was excluded because of possible thermochemical sulfate reduction (TSR), Fusilier was not included because of low n -alkanes and thus possible biodegradation. Four other oils were excluded because they did not contain the full suite of data required to calculate $\delta^{13}C$ $[C_6]$ and $\delta^{13}C$ $[C_7]$: Brazeau River F, Chester, Foothills 8, and Manyberries

	2MP (%)	3MP (%)	nC6 (%)	$\delta^{13}C$ 2MP	$\delta^{13}C$ 3MP	$\delta^{13}C$ nC6	2MH (%)	3MH (%)	nC7 (%)	$\delta^{13}C$ 2MH	$\delta^{13}C$ 3MH	$\delta^{13}C$ nC7	$\delta^{13}C$ [C6]	$\delta^{13}C$ [C7]
Blueberry	5.48	3.89	4.13	-28.3	-27.45	-28.1	8.09	7.08	3.42	-26.65	-27.9	-28.9	-27.9939	-27.5400
Bonanza	6.27	4.56	4.94	-29.03	-29.4	-30	3.3	5.67	2.86	-28.9	-29.47	-30.8	-29.4408	-29.6325
Brazeau C	4.49	3.29	3.26	-27.9	-25.7	-29.7	2.53	4.16	2.3	-26.6	-26.8	-30.5	-27.7759	-27.6903
Brazeau D	1.67	1.28	3.49	-26.8	-25	-29	3.25	4.3	10.09	-26.2	-26.8	-29.9	-27.6345	-28.4626
Brazeau M	4.72	3.28	2.44	-24.6	-24.25	-26.5	5.52	4.58	1.45	-24.2	-25.3	-27.2	-24.9341	-25.0128
Brazeau Y	2.39	1.75	3.79	-21.8	-21.9	-23.7	6.92	5.56	11.16	-21.6	-23.5	-24.8	-22.7301	-23.5575
Cecil	5.58	4.18	2.86	-28.6	-27.6	-29.4	3.95	6.35	2.26	-26.5	-27.9	-29.5	-28.4501	-27.7476
Cherhill	6.34	4.98	3.91	-27.5	-26.3	-28.8	3.93	7.22	3.46	-25.6	-26.55	-29.1	-27.4414	-26.8984
C. del Bonita	8.78	5.95	6.41	-27.2	-26.7	-28.4	9.91	5.49	1.72	-26.3	-27.2	-29	-27.4231	-26.8599
Dunvegan	2.9	1.88	6.34	-25.1	-24.8	-26	4.02	4.01	12.91	-24	-26.1	-26.7	-25.5624	-26.0668
Foothills 12	3.7	2.37	7.57	-25.1	-23.8	-25.4	6.21	5.06	12.62	-24.2	-25.9	-26.5	-25.0406	-25.7751
Glenevis	8.89	6.06	5.86	-27.5	-26.85	-28.1	5.44	6.36	2.53	-25.55	-27.2	-28.5	-27.4797	-26.8031
Home 34	3.64	2.33	6.95	-25.3	-25.3	-25.9	6.1	4.84	11.38	-24.9	-26.3	-27	-25.6228	-26.2743
Hutch	6.12	5.59	1.78	-26.7	-25.9	-27.1	4.09	7.16	1.21	-23.9	-25.6	-27.4	-26.4213	-25.2168
Loon	3.4	2.82	1.75	-27.4	-25.6	-29.3	2.51	4.33	1.49	-25.3	-26.25	-29.5	-27.1803	-26.5451
Lousana	4.62	4.22	1.95	-28.7	-26.3	-30.1	1.6	3.64	1.03	-26.2	-27.1	-30.7	-28.0144	-26.4617
Medicine River	5.14	3.58	4.2	-25.55	-24.95	-25.7	5.04	5.71	3.41	-24.2	-26.15	-26.55	-25.4325	-25.5523
Miracle 1	6.05	3.73	9.54	-26	-25.2	-26.4	6.44	5.03	9.01	-24.7	-26.1	-27	-26.0431	-26.0557
Moose Mtm	4.92	3.93	6.42	-24.55	-23.85	-25.85	9.64	6.34	6.74	-23.85	-23.9	-25.9	-24.9164	-24.4721
Moose Mtm 2	3.77	2.89	8.24	-24.7	-23	-25.3	7.17	4.71	13.38	-23.2	-23.6	-25.8	-24.7021	-24.6518
Otter	4.22	2.98	6.7	-27.8	-26.1	-29.7	1.97	4.66	9.65	-26	-26.7	-29.9	-28.3514	-28.5121
Plato	5.26	4.11	2.88	-25.9	-25.5	-26.9	4.19	5.49	1.11	-23.9	-25.8	-27.4	-26.0009	-25.2268
Provost	5.21	3.68	3.61	-25.9	-26	-26	4.92	5.5	2.59	-24.4	-26.2	-26.9	-25.9583	-25.6586
Rainbow 1	5.49	4.09	8.5	-25.55	-24	-27.75	5.15	7.1	14.13	-23.9	-24.2	-28.9	-26.2337	-26.6589
Rainbow 2	3.85	3.3	6.36	-26.9	-25.2	-29.3	5.05	7.48	14.11	-24.3	-24.7	-28.4	-27.6146	-26.5839
Redwater	3.55	2.8	4.78	-27.5	-25.8	-29	3.11	4.68	8.05	-25.6	-26.4	-29.9	-27.7165	-28.0217
Rycroft	4.15	2.83	7.1	-27.05	-26.01	-29.15	3.78	4.92	11.89	-27.25	-28.9	-30.95	-27.8999	-29.7809
S. Eureka	4.91	3.23	7.48	-26.5	-26	-27.15	5.48	4.81	9.22	-24.85	-26.5	-27.95	-26.7079	-26.7218
Sage Creek	0.64	0.56	0.97	-25.15	-25.25	-24.9	5.56	4.77	8.8	-23.2	-25.55	-25.55	-25.0641	-24.8670
Sylvan Lake	6	4.21	4.03	-25.9	-25.8	-25.8	2.13	5.29	2.19	-24.25	-25.3	-25.55	-25.8421	-25.1242
Turner Valley	0.78	0.66	1.26	-23.3	-22.8	-24.05	4.88	5.78	7.53	-22.7	-24.1	-25.4	-23.5278	-24.2626
Virginia Hills	4.71	3.51	7.86	-24.9	-24.3	-26.9	8.27	6.44	7.19	-24.55	-25.35	-28.1	-25.7466	-25.9508
Wainwright	6.19	4.19	3.19	-25.7	-25.6	-26	5.76	6.78	1.69	-23.8	-25.8	-26.5	-25.7396	-25.0736
Wallesden Gr.	5.05	3.83	4.37	-26.5	-25.8	-27.7	4.62	5.7	2.91	-24.7	-26.3	-27.9	-26.6934	-26.0932
Wembley	5.44	3.38	6.71	-29.7	-28.5	-30.4	4.93	6.04	6.14	-28.1	-28.9	-30.8	-29.7413	-29.3513
Zama	4.71	3.06	7.66	-25.9	-25.3	-28	5.19	6.74	15.43	-23.4	-24.8	-28.8	-26.8235	-26.7903

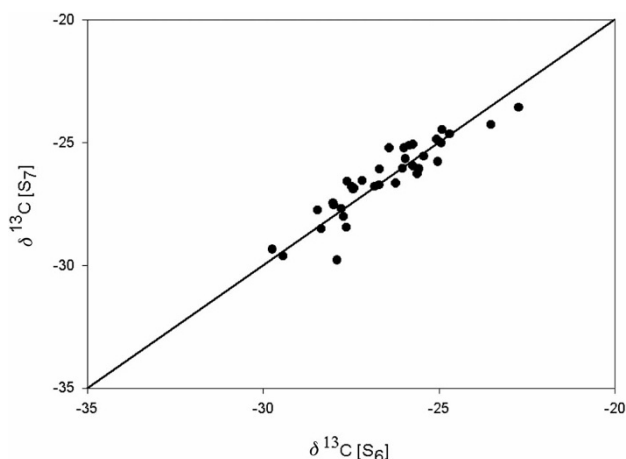


Fig. 3 A plot of carbon isotope ratios (‰) for presumed intermediates [S₆] and [S₇], where $\delta^{13}\text{C} ([S_6]) = a \delta^{13}\text{C} (2\text{-MP}) + b \delta^{13}\text{C} (3\text{-MP}) + c \delta^{13}\text{C} (n\text{-C}_6)$ and $\delta^{13}\text{C} ([S_7]) = d \delta^{13}\text{C} (2\text{-MH}) + e \delta^{13}\text{C} (3\text{-MH}) + f \delta^{13}\text{C} (n\text{-C}_7)$. Data shown in Table 2. The reported analytical error for $\delta^{13}\text{C}$'s is $\pm 0.5\text{‰}$ s (ref. 2). The mean for $\delta^{13}\text{C} ([S_6]) / \delta^{13}\text{C} ([S_7]) = 1.00 \pm 0.02s$. For the linear regression, $r^2 = 0.83$, slope = 0.90 and intercept = -2.48.

Fig. 2 (ref. 1) provides molecular evidence for structurally similar precursors, like the hypothetical intermediates [S₆] and [S₇] in Fig. 1. Fig. 3 is consistent with this, implicating isotopically indistinguishable precursors. Whiticar and Snowdon² came to a similar conclusion: "these isotopic distributions among isomers are strong evidence suggesting that the formation of these gasoline-range hydrocarbons is intricately linked to the isotopic signature of the precursor molecules from which they are derived".

Fig. 3 does not exclude the conventional view that LH are thermal descendents of higher isoprenoids and *n*-alkanes (ref. 28). But it is difficult to explain the two correlations (Fig. 2 and 3) by this mechanism. They suggest a catalytic agent guiding the course of reaction through structurally similar intermediates. Irrespective of how these six LH might originate (catalytically or thermally), however, their molecular and isotopic correlations establish a genetic link (\leftrightarrow) between *n*-alkanes and isoalkanes that traverses carbon number and is fundamental to the origin of LH:



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