

METHANE AND ETHANE GENERATION FROM OIL CRACKING : FIRST ISOTOPIC MODELLING BASED ON ^{13}C LABELLED COMPOUNDS

Luc FUSETTI¹, Françoise BEHAR¹, Kliti GRICE² and Sylvie DERENNE³

1. IFP, Geochemistry Department, 1 & 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France.
2. Stable Isotope and Biogeochemistry Group, Centre for Applied Organic Geochemistry, Curtin University of Technology, Kent Street, WA6845 Perth, Australia.
3. LCBOP, UMR 7618 BioEMCo CNRS/ENSCP, 11 rue P. M. Curie, 75231 Paris cedex 05, France.

Recent papers have demonstrated that aromatic hydrocarbons are less stable than saturated ones during thermal cracking (Behar and Vandembroucke, 1996; Behar et al., 1999 and 2002, Dominé et al., 2002). Therefore the focus of the present work includes a molecular and kinetic isotopic study of secondary methane and ethane generated from aromatic compounds present in the low-molecular-weight fraction ($\text{C}_6\text{-C}_{14}$) of petroleum found in high pressure and high temperature (HP-HT) reservoirs. In addition the kinetic scheme will illustrate the isotopic fractionations taking place at temperatures ranging from 160°C to 220°C over several millions of years.

More than 200 isothermal pyrolysis experiments in gold sealed tubes have been carried out at three temperatures ranging from 395 to 450°C for periods of several hours to several months. As shown with some examples in the table below, attention has been paid to mass balances using different fractions, such as a gaseous fraction ($\text{C}_1\text{-C}_4$), a pentane extract ($\text{C}_6\text{-C}_{14}$ and $\text{C}_{15}\text{-C}_{20}$), a DCM extract (C_{20+}) and the residue, in order to get a better constrained isotopic model. A complete kinetic study on 10 non-labelled compounds has been performed first in order to establish the kinetic scheme for methane and ethane generation. These compounds include 2-ethyltoluene and 3-ethyltoluene, 3-ethylorthoxylyene and 4-ethylorthoxylyene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene, 1,2,4,5-tetramethylbenzene, 1-methylnaphthalene, 1,5-dimethylnaphthalene and 2,4,5-trimethylnaphthalene. These components indeed represent the overall composition of the $\text{C}_6\text{-C}_{14}$ aromatic fraction of a typical oil and also represent different group positions, chain lengths, ring substitutions and ring effects. The influence of the previous factors was quantified by calculating activation energies (E_a) and frequency factors (A) for methane and ethane generation, using an Arrhenius plot.

In addition, an extensive isotopic study has been carried out in order to get a holistic mass balance for the $^{13}\text{C}/^{12}\text{C}$ of the different fractions. Important carbon isotope fractionations were observed in ethane and methane at different temperatures and various pyrolysis times. For example 5.6 and 7.5‰ enrichments were observed for methane and ethane, respectively

for 2-ethyltoluene when the pyrolysis time was increased from 10 to 432 hours at a temperature of 450°C. A 14.3‰ enrichment was observed for methane generated from 1,2,4-trimethylbenzene under similar conditions.

Syntheses of aromatic compounds, with a ^{13}C label in specific positions, have also been carried out successfully allowing us to study the carbon isotope fractionations occurring during methane and ethane generation. Indeed, a mixture of each labelled compound with its non-labelled counterpart, in order to start from a reasonable $\delta^{13}\text{C}$ value, will be pyrolysed and run through the above analytical protocol.

The results of the present study should lead to the first kinetic model of carbon isotope fractionation during methane and ethane generation from a given oil cracked under conditions met in high pressure and high temperature reservoirs.

| Compound | 2ET | 124TMB | 124TMB | 124TMB |
|---|------------|------------|------------|------------|
| Conditions | 395°C/144h | 395°C/144h | 450°C/10h | 450°C/50h |
| C ₁ | 0.33 | 0.15 | 0.23 | 6.3 |
| C ₂ | 0.37 | 0.014 | 0 | 0.33 |
| C ₆ -C ₁₄ | 90 | 92 | 91 | 65 |
| C ₁₅ -C ₂₀ | 1.9 | 1.7 | 3.6 | 13 |
| C ₂₀₊ | 2.5 | 2.5 | 2.6 | 2.9 |
| Residue | 0 | 0 | 0 | 7.1 |
| Sum | 95 | 96 | 97 | 95 |
| $\delta^{13}\text{C}$ (Compound) | in process | in process | in process | in process |
| $\delta^{13}\text{C}$ (C ₁) | -38.6 | -41.1 | -47.1 | -35.6 |
| $\delta^{13}\text{C}$ (C ₂) | -37.5 | ND | ND | ND |
| $\delta^{13}\text{C}$ (C ₆ -C ₁₄) | in process | in process | in process | in process |
| $\delta^{13}\text{C}$ (C ₁₅ -C ₂₀) | -29.4 | -29.7 | -27.1 | -29.4 |
| $\delta^{13}\text{C}$ (C ₂₀₊) | -27.5 | -27.9 | -27.6 | -28.2 |
| $\delta^{13}\text{C}$ (Residue) | ND | ND | ND | -29.5 |

Table 1. Mass balances (% of initial charge) and $\delta^{13}\text{C}$ (‰) obtained during some closed system pyrolysis experiments of 2-ethyltoluene (2ET) and 1,2,4-trimethylbenzene (124TMB).

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