# δD EVOLUTIONS OF TOLUENE AND METHYLCYCLOHEXANE FROM THE THERMAL PYROLYSATES OF *N*-BUTYLCYCLOHEXANE

Bin Cheng[1], Yungan Liang[1,2], Jianbing Xu[1,2], Qian Deng[1,2], Zhiwei Wei[1,2], Zewen Liao[1,*]

[1]*Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, China*
[2]*University of Chinese Academy of Sciences, China*
*(* corresponding author: liaozw@gig.ac.cn)*

Toluene (Tol) is one of the main compounds in light crude oil reservoirs, which was considered to be genetically linked with methyl cyclohexane (MCH) in crude oils based on the significant correlation ship between their carbon and hydrogen isotopes (Liang et al., 2018). Studies on the stable hydrogen isotope fractionation of aromatic compounds during their aromatization are important in understanding the formation and evolution mechanism of aromatic compounds in oil reservoirs. In this work *n*-butylcyclohexane (BCH, with δD of −82.2‰ and $\delta^{13}C$ of −25.6‰) was thermally pyrolysed under 400 °C/50 MPa for various time intervals (Table 1), to study the δD evolution of the toluene and methylcyclohexane from the pyrolysates of BCH.

The pyrolysis products of BCH included cyclohexane, methylcyclohexane, toluene, methylcyclohexene, ethylcyclohexane, ethylbenzene, propylcyclohexane, and so on, more details can be found from Cheng et al. (2018 ). With the increasing pyrolysis time, the BCH was gradually cracked and finally disappeared after 720h thermal pyrolysis. The toluene and methylcyclohexane were the main products in each pyrolysis groups, whereas more and more toluene was detected with the increasing pyrolysis time and even became the predominant product after 720h pyrolysis. Distinct δD fractionation occurred in both toluene and MCH generated from the BCH pyrolysis. The toluene was strongly enriched whereas MCH remarkably depleted in $^2H$ in the 24h BCH pyrolysates, with $\Delta\delta D_{Tol-MCH}$ ($\delta D_{Tol} - \delta D_{MCH}$) being 162.3‰ (Table 1). With the increasing pyrolysis time, the degree of the hydrogen isotope fractionation was gradually mitigated between toluene and MCH. Fairly well positive correlation was found for the stable carbon isotope evolution between toluene and MCH from the pyrolysates with the increasing pyrolysis time, as that these two compounds are genetically from the same precursor, which may be also true even in light crude oil reservoirs.

**Table 1.** Geochemical data of MCH and toluene from the thermal pyrolysates of BCH.

| Samples | Easy *R*o (%) | Tol/ MCH | Tol/ (Tol+MCH) | Stable hydrogen isotope (‰) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | MCH | Tol | $\Delta\delta D_{Tol-MCH}$ | $\Delta\delta D_{MCH-BCH}$ | $\Delta\delta D_{Tol-BCH}$ |
| BCH−24h | 1.47 | 0.20 | 0.17 | −128.7 | 33.6 | 162.3 | −46.5 | 115.8 |
| BCH−48h | 1.64 | 0.31 | 0.24 | −118.9 | 12.9 | 131.7 | −36.7 | 95.1 |
| BCH−216h | 2.04 | 0.46 | 0.32 | −66.0 | 5.6 | 71.5 | 16.2 | 87.8 |
| BCH−288h | 2.12 | 0.52 | 0.34 | −81.8 | −3.2 | 78.6 | 0.4 | 79.0 |
| BCH−432h | 2.24 | 0.77 | 0.44 | −31.3 | −0.4 | 30.9 | 50.9 | 81.8 |
| BCH−720h | 2.39 | 1.48 | 0.60 | −28.2 | −2.6 | 25.6 | 54.0 | 79.6 |

Correlation analyses between the thermal maturity parameter Easy *R*o and $\Delta\delta D_{Tol-MCH}$, as well as the Easy *R*o and $\Delta\delta^{13}C_{Tol-MCH}$, were showed in Fig. 1. Fairly well negative linear correlation was observed between the Easy *R*o and $\Delta\delta D_{Tol-MCH}$ (Fig. 1a), but poor correlation

between the Easy *R*o and $\Delta\delta^{13}C_{Tol-MCH}$ (Fig. 1b). It seems that the parameter of $\Delta\delta D_{Tol-MCH}$ has a potential application for the thermal maturity evaluation in oil reservoirs, especially applicable in the light crude oil reservoirs where the traditional biomarker parameters may be invalid but the toluene and MCH are liable to detect. Some other linear correlation analyses were done in Fig. 4c–f, including the $\Delta\delta D_{Tol-MCH}$ − Tol/(Tol+MCH), $\Delta\delta^{13}C_{Tol-MCH}$ − Tol/(Tol+MCH), the Easy *R*o − Tol/(Tol+MCH) and the Easy *R*o − Tol/MCH. These correlation diagrams indicated that the $\Delta\delta D_{Tol-MCH}$ or Easy *R*o had a fairly good linear correlation with the concentration ratio of Tol/(Tol+MCH) in a reasonable scope, but poor correlation with higher ratio of Tol/(Tol+MCH) (e.g. > 0.44). It indicated that the ratio of Tol/(Tol+MCH) in oil reservoirs may be used as a potential parameter to evaluate the thermal maturity level within a reasonable scope.

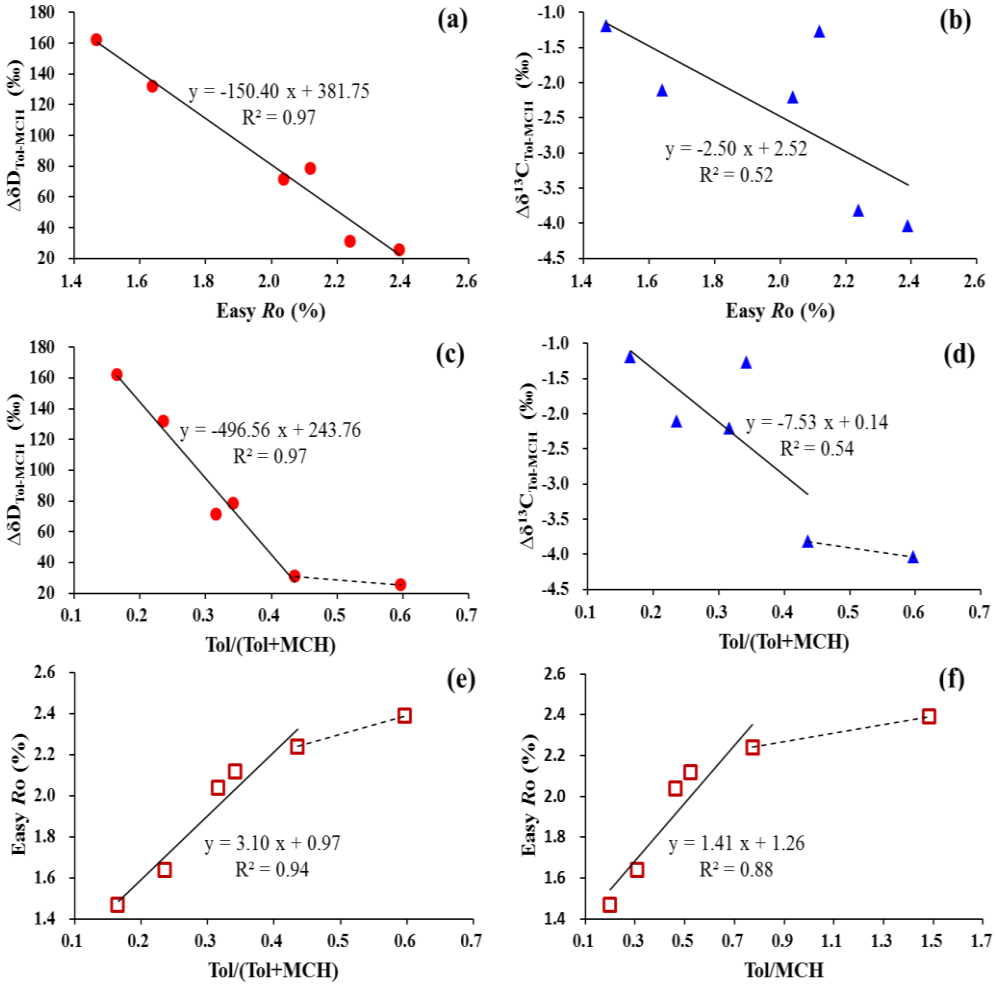


**Fig. 1.** Diagrams of $\Delta\delta D_{Tol-MCH}$ − Easy *R*o (a), $\Delta\delta^{13}C_{Tol-MCH}$ − Easy *R*o (b), $\Delta\delta D_{Tol-MCH}$ − Tol/(Tol+MCH) (c), $\Delta\delta^{13}C_{Tol-MCH}$ − Tol/(Tol+MCH) (d), Easy *R*o − Tol/(Tol+MCH) (e) and Easy *R*o − Tol/MCH (f).

## References

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