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Remarkable Fractionation of the Hydrogen Isotope (δD) of Hydrocarbon during the Fast Aromatization Process: Insights from the Pyrolysis Experiments of *n*-Butylcyclohexane

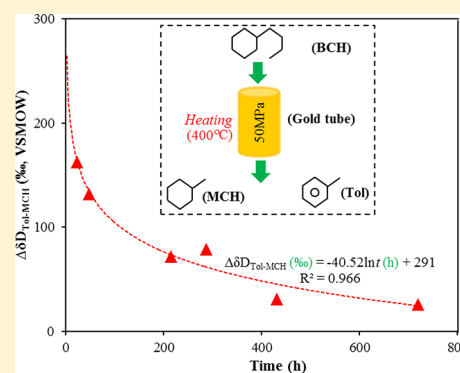
Bin Cheng,[†] Yungan Liang,^{†,‡} Jianbing Xu,^{†,‡} Qian Deng,^{†,‡} Zhiwei Wei,^{†,‡} Oluwabamise L. Faboya,[†] and Zewen Liao^{*,†}

[†]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, Guangdong 510640, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

ABSTRACT: Hydrocarbon aromatization involves the cleavage of multiple C–H bonds and the dehydrogenation of aliphatic rings, with a resultant fractionation of stable hydrogen between aromatic hydrocarbons and their counterpart precursors. Despite this understanding, there is still the paucity of studies on the hydrogen isotope (δD) fractionation of aromatic compounds and the δD fractionation characteristics during the aromatization process of hydrocarbons. In the present study, *n*-butylcyclohexane (BCH) was thermally pyrolyzed in a closed gold tube system at different time intervals to investigate the aromatization process of the monoaliphatic ring hydrocarbon. The δD evolutions of toluene (Tol) and methylcyclohexane (MCH) from the BCH pyrolysates were also examined, with the aim of studying the cleavage behavior of the C–H bond at the aliphatic ring. The results of the 24 h BCH pyrolysates showed that toluene was strongly enriched with ^2H , whereas MCH was heavily depleted, with $\Delta\delta D_{\text{Tol-MCH}}$ ($\delta D_{\text{Tol}} - \delta D_{\text{MCH}}$) being 162.3‰ [Vienna Standard Mean Ocean Water (VSMOW)]. In comparison to the initial hydrogen isotope of BCH, $\Delta\delta D_{\text{MCH-BCH}}$ and $\Delta\delta D_{\text{Tol-BCH}}$ were -46.5 and 115.8 ‰, respectively. With an increasing pyrolysis time, the degree of δD fractionation between Tol and MCH gradually mitigated. It is speculated that the dehydrogenation of the aliphatic ring started with more possibility of cracking the C– ^1H bond and then having more C– ^2H being retained in the aromatic ring at the initial stage of hydrocarbon aromatization, leading to the strong δD fractionation of the aromatic hydrocarbon. This observation is quite instructive, in that fast aromatization of the hydrocarbon caused a remarkable hydrogen isotope fractionation, which may play a significant role in the strong ^2H enrichment of aromatic hydrocarbons generated from a fast and high-temperature thermal event, such as a meteorite when passes through the atmosphere.

KEYWORDS: fast aromatization, hydrogen isotope fractionation, pyrolysis experiments, meteorite PAHs, geochemical implication



INTRODUCTION

Aromatic hydrocarbons are important organic components in source rocks, crude oil, coal, and recent sediments in the earth.¹ They generally have a high thermal stability and strong resistibility to the secondary geochemical alteration,² so that they are encoded with important geochemical information. Polycyclic aromatic hydrocarbons (PAHs) are also found in the universe outside the Earth, such as the interplanetary dust particles, the interstellar medium (ISM), and asteroidal meteorites.^{3–11} They may have special astrobiological significance¹² or be helpful in understanding organic synthesis in the universe.^{11,13}

Because living organisms are not capable of biosynthesizing aromatic compounds,¹⁴ they are generated mainly from the aromatization of hydrocarbons. A considerable number of simulated experiments have been carried out to simulate the hydrocarbon aromatization process;^{15–23} however, most of the attempts have only been to investigate the compositional

changes of the aromatic hydrocarbons.^{16–19,21–23} Again, some studies on the stable carbon isotope fractionation of aromatic hydrocarbons have also been reported in the literature,^{15,20} but very few studies have been undertaken to probe the stable hydrogen isotope fractionation during the aromatization process.

Hydrocarbon aromatization involves the cleavage of multiple C–H bonds and dehydrogenation of aliphatic rings. On the basis of the occurrence of the stable isotopes, C–H bonds generally contain four kinds of isotopic distribution patterns, including $^{12}\text{C}-^1\text{H}$, $^{12}\text{C}-^2\text{H}$, $^{13}\text{C}-^1\text{H}$, and $^{13}\text{C}-^2\text{H}$ (the chemical bonds consisting of ^{14}C and ^3H can be ignored). As a result of the kinetic isotope effect (KIE) caused by

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Table 1. Basic Geochemical Data of BCH Pyrolysates^a

group	weight (mg)	easy R_o (%)	CH/ Σ Tot	MCH/ Σ Tot	Tol/ Σ Tot	ECH/ Σ Tot	PCH/ Σ Tot	Tol/MCH	Tol/(Tol + MCH)
BCH-24h	120.6	1.47	0.27	0.35	0.07	0.17	0.14	0.20	0.17
BCH-48h	79.3	1.64	0.22	0.33	0.10	0.19	0.16	0.31	0.24
BCH-216h	41.3	2.04	0.21	0.40	0.19	0.14	0.06	0.46	0.32
BCH-288h	40.1	2.12	0.22	0.40	0.21	0.13	0.04	0.52	0.34
BCH-432h	40.1	2.24	0.23	0.37	0.28	0.10	0.02	0.77	0.44
BCH-720h	40.1	2.39	0.20	0.30	0.44	0.05	0.01	1.48	0.60

^aCH, cyclohexane; MCH, methycyclohexane; Tol, toluene; ECH, ethylcyclohexane; PCH, propylcyclohexane; and Tot, (CH + MCH + Tol + ECH + PCH).

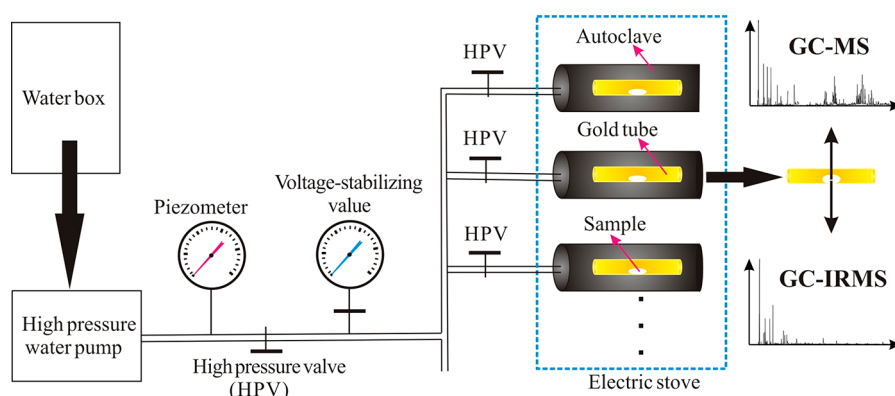


Figure 1. Schematic diagram showing the gold tube pyrolysis instrumental system.

different isotopic mass, the cleavage rate of these isotopic C–H bonds differ,^{24,25} with possible fractionation of both stable hydrogen and carbon isotopes occurring simultaneously during hydrocarbon aromatization.

The isotopic difference between ¹H and ²H is 12-fold compared to the two isotopes of carbon atom (¹²C and ¹³C); hence, it is expected theoretically that the fractionation of hydrogen isotopes will be stronger than that of carbon isotopes during aromatization. The aromatic compounds from some meteorites were recently reported to be strongly enriched with ²H (the highest one up to 1100‰) compared to their terrestrial counterparts, and this was attributed to the cold interstellar environment of the meteorites.¹¹ When meteorites pass through the earth atmosphere, they could suffer from the fast and high-temperature thermal event. It is therefore possible that the formation of PAHs may occur as a result of fast aromatization, which may influence the hydrogen isotope composition.

Toluene remains the simplest member of the aromatic family with a simple alkyl substituent. It is therefore more convenient and suitable to use toluene as a representative member of the aromatic family in studying hydrocarbon aromatization. Toluene has recently been genetically linked with methycyclohexane (MCH) based on the significant correlation between the carbon and hydrogen isotopes of both compounds in light crude oils from Tarim Basin, China.²⁶ The recent experiment in which large amounts of MCH and toluene were generated from the pyrolysis of *n*-butylcyclohexane (BCH)²² provided insight into the formation process of toluene. In the study, it was suggested that the generation of pyrolysates toluene and MCH could have taken different pathways;²⁷ nevertheless, the stable hydrogen and carbon isotope evolution of toluene or MCH could not have been influenced by the different formation routes, because the depopulation of BCH could not affect the aliphatic/aromatic

rings. Therefore, it is theoretically appropriate to believe that MCH is the direct precursor of toluene in the pyrolysates, and thus, the stable hydrogen and carbon isotope evolution of toluene and MCH can be investigated from the BCH pyrolysates.

In this present work, BCH was thermally pyrolyzed at different time intervals to investigate the hydrogen isotope fractionation between MCH and toluene under 400 °C/50 MPa.²² The cleavage behavior of different isotopic C–H bonds in the aliphatic ring and the δ D fractionation mechanism of aromatic hydrocarbon are examined. Again, we probed the consequence of hydrogen isotope fractionation during the fast aromatization process under a high-temperature thermal event.

EXPERIMENTAL SECTION

Reagents and Pyrolysis Experiments. BCH (liquid, purity of >99%) was purchased from Sigma-Aldrich. The initial hydrogen (δ D) and carbon (δ^{13} C) isotope values for BCH were $-82.2‰$ [Vienna Standard Mean Ocean Water (VSMOW)] and δ^{13} C of $-25.6‰$ [Vienna Pee Dee Belemnite (VPDB)], respectively.

Six gold tubes (length \times diameter \times thickness, $60 \times 5 \times 0.25$ mm) were employed for this experiment. The gold tubes were properly sealed at one end using an argon arc welder, while the other sides were initially left open. The tubes were then treated at 800 °C for 1 h to eliminate any organic material. The gold tubes were infused with argon for about 10 min to displace any residual air within the tubes. This was to prevent possible interference from the leftover air with the reagents because argon is chemically inert. The gold tubes were filled with varying amounts of BCH reagent using Finn timer. The open ends of the tubes were then sealed off. The amounts of BCH reagent used for each pyrolysis time are presented in Table 1.

The gold tubes were placed in stainless-steel autoclaves under a high-temperature–pressure (T – P) instrumental

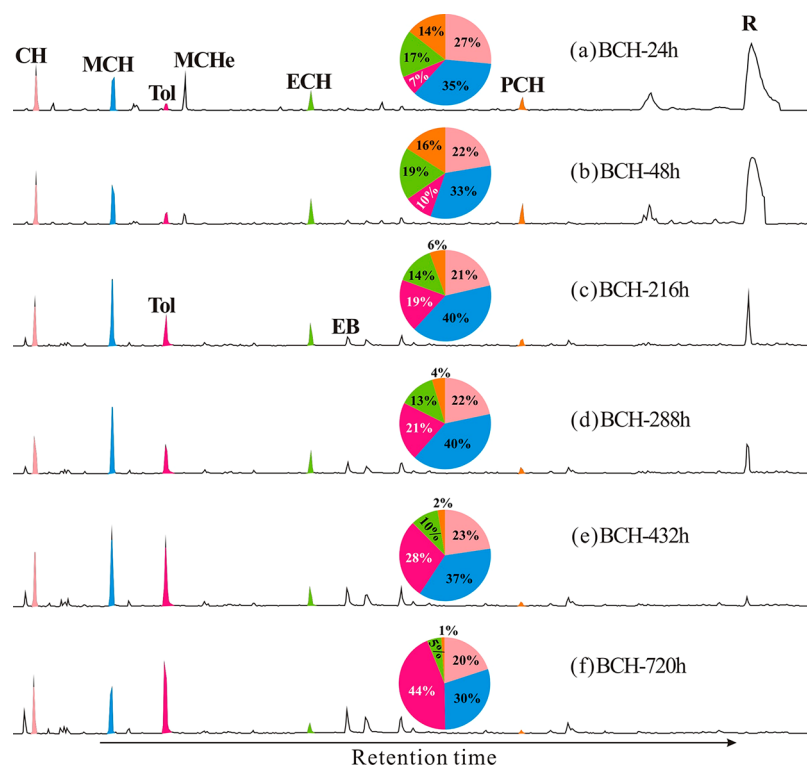


Figure 2. Distribution characteristics of BCH pyrolysates at different pyrolysis times. CH, cyclohexane; MCH, methylcyclohexane; Tol, toluene; MCHe, methylcyclohexene; ECH, ethylcyclohexane; EB, ethylbenzene; PCH, propylcyclohexane; and R, residual BCH. The embedded pie charts showed the relative contents of five compounds, including CH, MCH, Tol, ECH, and PCH.

system (Figure 1). Water was constantly added to the autoclaves to keep the pressure stable at 50 MPa. The autoclaves were heated by an electric stove from room temperature to 400 °C within 2 h, and this temperature was kept constant for the time allotted for each group. After the completion of the pyrolysis experiment, the gold tubes were cleaned outside with dichloromethane before frozen with liquid nitrogen. Each gold tube was then cut into several pieces and immediately transferred to a cell bottle (4 mL) with a certain volume of *n*-pentane solvent added to dissolve the pyrolysates.

The thermal maturation of the pyrolysates was determined using the easy R_0 (a thermal maturity index equivalent to vitrinite reflectance) method developed by Sweeney and Burnham.²⁸ The easy R_0 values obtained for different pyrolysis times are listed in Table 1.

The *n*-pentane-soluble pyrolysates were subsequently analyzed with gas chromatography–mass spectrometry (GC–MS) and gas chromatography–isotope ratio mass spectrometry (GC–IRMS).

Instrumental Analysis. The *n*-pentane-soluble pyrolysates were analyzed using a DSQ II and Thermo Fisher Trace GC Ultra combined system. The GC conditions were as follows: HP-1 ms chromatographic column (60 m × 0.32 mm × 0.25 μm film thickness) and helium as the carrier gas with a constant flow rate of 1.2 mL/min. The conditions of MS used were as follows: electron ionization mode, ion source electron energy of 70 eV, ion source temperature of 260 °C, and a mass scan range of 50–650 Da. The oven temperature ramp-up procedures were as follows: 35 °C initial temperature held for 4 min, then raised to 295 °C at a rate of 3 °C/min, and held isothermally for 20 min.

Stable carbon isotope analysis of *n*-pentane-soluble pyrolysates was performed on an Isoprime (VG) mass spectrometer combined with Agilent 6890 GC. Except for the different chromatographic column, which was a DB-5 column (30 m × 0.32 mm × 0.25 μm film thickness), the GC conditions and temperature ramp-up procedure were the same as the GC–MS analysis described above. Stable carbon and hydrogen isotope values are reported in per mil (‰) relative to the defined VPDB and VSMOW standards, respectively. Replicate analyses showed that the reproducibility of carbon and hydrogen isotope analysis was generally within ±0.5 and ±5‰, respectively. Results are reported as the average of two or three runs.

RESULTS AND DISCUSSION

Thermal Evolution of MCH and Toluene. The liquid products of BCH pyrolysis include cyclohexane, methylcyclohexane, toluene, methylcyclohexene, ethylcyclohexane, ethylbenzene, propylcyclohexane, etc. (Figure 2). These same series of compounds were reported in the experimental results of Rakotoalimanana et al.²²

With an increasing pyrolysis time, BCH was gradually cracked down and finally disappeared after 720 h of thermal pyrolysis under 400 °C/50 MPa (Figure 2). Cyclohexane and methylcyclohexane are the main products in each pyrolysis group, while methylcyclohexene could not be detected after 216 h of pyrolysis. On the contrary, increasing amounts of toluene are detected with an increasing pyrolysis time and, subsequently, the predominant product after 720 h of pyrolysis.

Figure 2 depicts the relative amounts of one-ring-containing compounds, including cyclohexane, methylcyclohexane, tol-

Table 2. Stable Hydrogen Isotope Results of MCH, MCHe, and Tol (‰)^a

sample	MCH	MCHe	Tol	$\Delta\delta D_{\text{MCH-BCH}}$	$\Delta\delta D_{\text{MCHe-BCH}}$	$\Delta\delta D_{\text{Tol-BCH}}$	$\Delta\delta D_{\text{Tol-MCH}}$
BCH-24h	-128.7	-58.4	33.6	-46.5	23.8	115.8	162.3
BCH-48h	-118.9	-41.4	12.9	-36.7	40.8	95.1	131.7
BCH-216h	-66.0		5.6	16.2		87.8	71.5
BCH-288h	-81.8		-3.2	0.4		79.0	78.6
BCH-432h	-31.3		-0.4	50.9		81.8	30.9
BCH-720h	-28.2		-2.6	54.0		79.6	25.6

^aMCH, methycyclohexane; MCHe, methylcyclohexene; and Tol, toluene.

Table 3. Stable Carbon Isotope Results of MCH, MCHe, and Tol (‰)^a

sample	MCH	MCHe	Tol	$\Delta\delta^{13}\text{C}_{\text{MCH-BCH}}$	$\Delta\delta^{13}\text{C}_{\text{MCHe-BCH}}$	$\Delta\delta^{13}\text{C}_{\text{Tol-BCH}}$	$\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$
BCH-24h	-27.0	-23.8	-28.2	-1.4	1.8	-2.6	-1.2
BCH-48h	-25.2	-20.9	-27.3	0.4	4.7	-1.7	-2.1
BCH-216h	-21.1		-23.3	4.5		2.3	-2.2
BCH-288h	-22.7		-24.0	2.9		1.6	-1.3
BCH-432h	-18.9		-22.7	6.7		2.9	-3.8
BCH-720h	-18.8		-22.8	6.8		2.8	-4.0

^aMCH, methycyclohexane; MCHe, methylcyclohexene; and Tol, toluene.

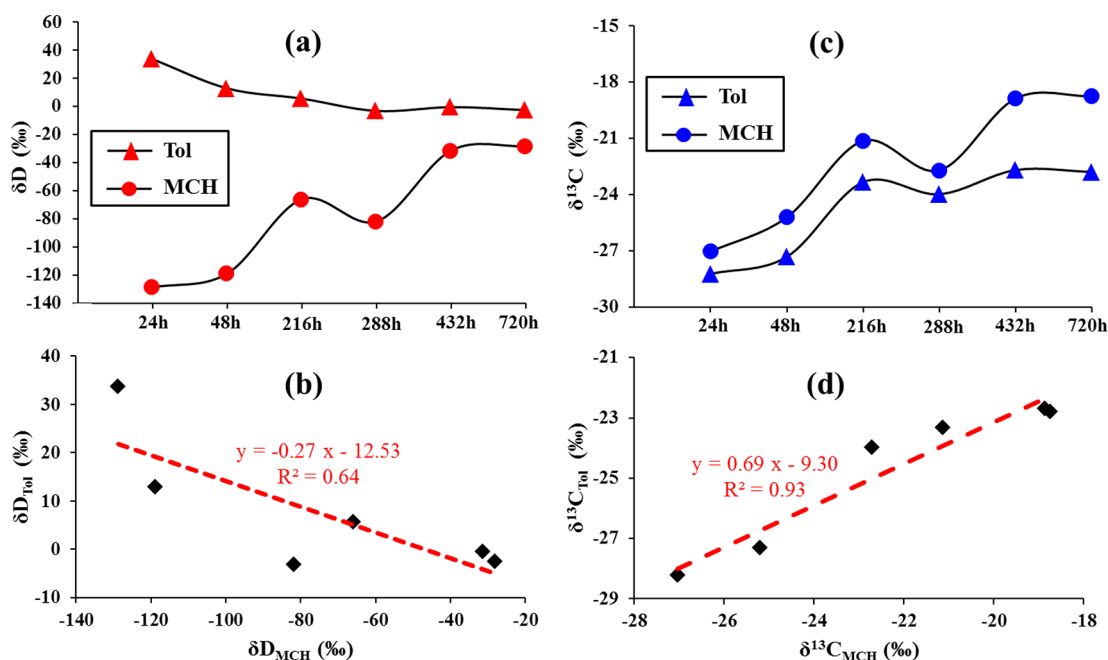


Figure 3. Evolution of stable (a) hydrogen and (b) carbon isotope of MCH and toluene with an increasing pyrolysis time and their (c) hydrogen and (d) carbon isotope correlation.

uene, ethylcyclohexane, and propylcyclohexane. Among these compounds, the relative contents of cyclohexane and methylcyclohexane range from 20 to 27% and from 30 to 40%, respectively, ethylcyclohexane ranges from 19 to 5%, and propylcyclohexane ranges from 14 to 1% with an increasing pyrolysis time, while the toluene contents increased steadily from 7 to 44%.

δD and $\delta^{13}C$ Evolution of MCH and Toluene. The results of the stable hydrogen and carbon isotope distribution of MCH and toluene from the pyrolysates are listed in Tables 2 and 3, respectively.

After 24 h of BCH pyrolysis, significant hydrogen isotope fractionations exist between toluene and MCH (Table 2). δD_{Tol} has a value of 33.6‰, while δD_{MCH} has a value of -128.7‰, with $\Delta\delta D_{\text{Tol-MCH}}$ ($\delta D_{\text{Tol}} - \delta D_{\text{MCH}}$) being high up

to 162.3‰. In comparison to the initial value of BCH, $\Delta\delta D_{\text{Tol-BCH}}$ and $\Delta\delta D_{\text{MCH-BCH}}$ have values of 115.8 and -46.5‰, respectively.

With an increasing pyrolysis time, δD_{Tol} gradually decreased from 33.6 to -2.6‰, while δD_{MCH} increased from -128.7 to -28.2‰ (Table 2 and Figure 3a). Therefore, the $\Delta\delta D_{\text{Tol-BCH}}$ value decreased from 115.8 to 79.6‰, but the $\Delta\delta D_{\text{MCH-BCH}}$ value increased from -50.9 to 54.0‰, with an increasing pyrolysis time. A negative correlation is found between toluene and MCH hydrogen isotope evolution. Linear fitting for the groups based on δD_{MCH} and δD_{Tol} data using Excel software shows a relatively weak correlation, with R^2 value of 0.64 (Figure 3b).

The stable carbon isotope fractionation of toluene and MCH is relatively low when compared to the hydrogen isotope

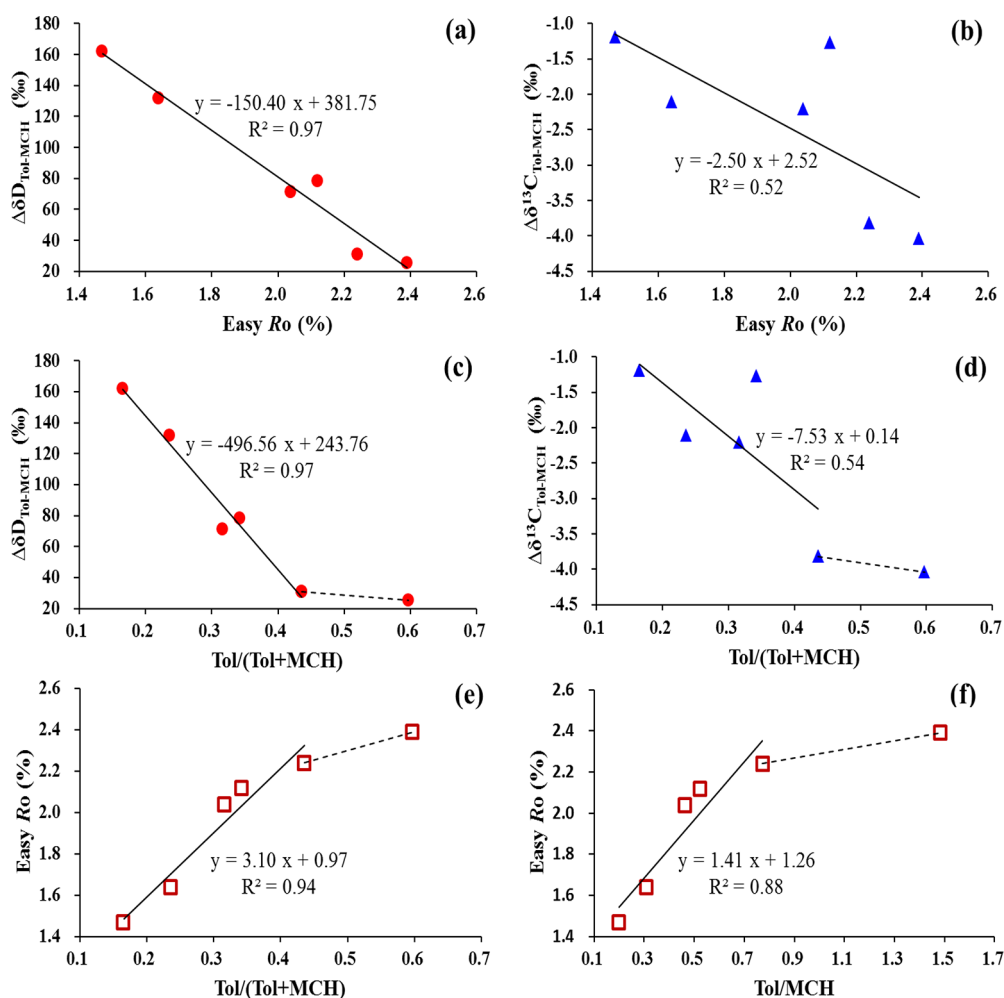


Figure 4. Correlation diagrams of (a) $\Delta\delta D_{\text{Tol-MCH}}$ –easy R_o , (b) $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ –easy R_o , (c) $\Delta\delta D_{\text{Tol-MCH}}$ –Tol/(Tol + MCH), (d) $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ –Tol/(Tol + MCH), (e) easy R_o –Tol/(Tol + MCH), and (f) easy R_o –Tol/MCH.

evolution. $\delta^{13}\text{C}$ of toluene and MCH in the 24 h pyrolysates have values of -28.2 and -27.0% , respectively (Table 3). The values of $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$, $\Delta\delta^{13}\text{C}_{\text{Tol-BCH}}$, and $\Delta\delta^{13}\text{C}_{\text{MCH-BCH}}$ are -1.2 , -2.6 , and -1.4% , respectively. The stable carbon isotope of toluene and MCH shows a similar evolutionary trend with an increasing pyrolysis time (Figure 3c). The two compounds are enriched with ^{13}C via pyrolysis time, except for 288 h pyrolysates. Toluene and MCH have $\delta^{13}\text{C}$ values of -22.8 and -18.8% , respectively, in the 720 h pyrolysates and with $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ value of -4.0% . A good positive correlation exists for their stable carbon isotope evolution with an increasing pyrolysis time, with R^2 value of 0.93 (Figure 3d).

Correlation between MCH–Toluene Isotope and Thermal Maturity Parameters. Correlation analyses between the thermal maturity parameter easy R_o and $\Delta\delta D_{\text{Tol-MCH}}$ as well as between easy R_o and $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ are shown in Figure 4. The values of $\Delta\delta D_{\text{Tol-MCH}}$ and $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ show a decreasing trend with increasing easy R_o . Fairly well negative linear correlation is observed between easy R_o and $\Delta\delta D_{\text{Tol-MCH}}$ (Figure 4a), but a poor correlation between easy R_o and $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ is noted (Figure 4b). This suggests a potential application of the $\Delta\delta D_{\text{Tol-MCH}}$ parameter in thermal maturity evaluation of reservoir oils, especially in the light crude oil reservoirs where the traditional biomarker

parameters may be invalid but where toluene and MCH can still be detected.

Panels c–f of Figures 4 show other linear correlation analyses performed for $\Delta\delta D_{\text{Tol-MCH}}$ –Tol/(Tol + MCH), $\Delta\delta^{13}\text{C}_{\text{Tol-MCH}}$ –Tol/(Tol + MCH), easy R_o –Tol/(Tol + MCH), and easy R_o –Tol/MCH. To a certain level, a relatively good linear correlation exists between $\Delta\delta D_{\text{Tol-MCH}}$ or easy R_o and the ratio Tol/(Tol + MCH), but at a higher ratio of Tol/(Tol + MCH), a weak correlation is observed (e.g., >0.44). This suggests that the ratio of Tol/(Tol + MCH) may be used as a potential parameter for appraising the thermal maturity of oil reservoirs within a reasonable scope.

Kinetic Effects of C and H Isotopes during the Aromatization Process. During the aromatization process, it is expected in theory that the cleavage of the C–H bond will cause both the hydrogen and carbon isotope fractionation of toluene as a result of KIEs with corresponding change in both the carbon and hydrogen isotopes of the intermediate product (such as MCH_e) and MCH. However, this theory is not consistent with the present experimental results, in that only the fractionation of hydrogen isotopes is observed. This may be due to the different degrees of KIEs of C and H that affect their fractionation tendencies during the aromatization process.

Hydrogen and deuterium have the largest relative mass difference of isotopes, and therefore, hydrogen isotopes have

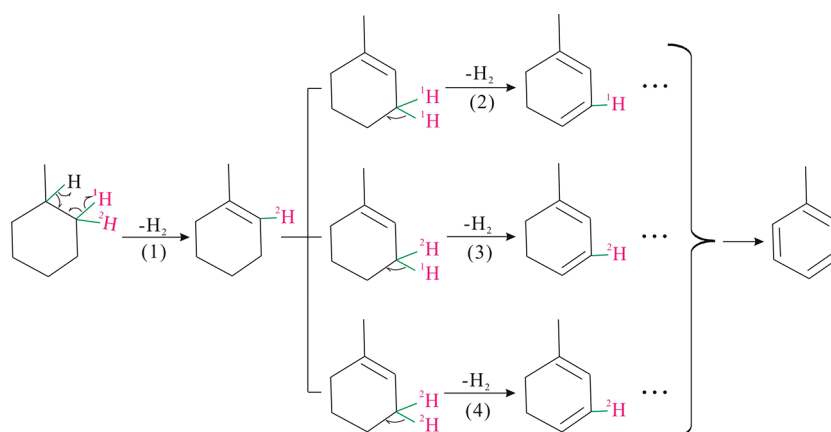


Figure 5. Schematic diagram showing the different cleavage routes of the isotopic different C–H bonds during the aromatization process.

the largest relative natural variation in their ratios.^{29,30} As a result of this large mass difference, the isotope effects of ^1H versus ^2H can have a theoretical maximum value of 18; i.e., C– ^1H bonds react 18-fold more rapidly than C– ^2H bonds.³¹ Thus, the primary KIEs of hydrogen isotopes will play a significant role during C–H bond cleavage at the aliphatic ring.

Again, the evolution trend of the stable hydrogen isotopes shows clearly that hydrogen isotope fractionation between toluene and MCH is significant during the aromatization process contrary to the carbon isotope fractionation during the aromatization of the aliphatic ring. This might be due to the small KIEs of carbon.^{32–34} The C–H cleavage had little contribution on the carbon isotope fractionation during the aromatization process of the aliphatic ring. Hence, the $\delta^{13}\text{C}$ evolutions of toluene and MCH were mainly controlled by C–C bond cleavage or formation.

δD Fractionation Mechanism in the Aromatization Process. Toluene shows more enrichment of the ^2H isotope than either MCH or initial BCH (Table 2), although this gradually diminishes with an increasing pyrolysis time (Figure 3a). The aromatization seems to have occurred prior to the end of 24 h; at this stage, toluene has a maximum value of $\delta\text{D}_{\text{Tol}}$ ($>33.6\%$). This shows that there was a strong isotopic selectivity prior to the end of 24 h, even though this occurred all through the aromatization process. The C– ^1H bonds must have first been cracked with consequent retention of more ^2H in the aromatic ring. It seems that the secondary KIE might have played a tangible role during C– ^1H cleavage, as revealed in step 1 of Figure 5 to lose two hydrogen atoms, forming the first double bond in the ring. The cleavage rate of the C– ^1H bond would increase if the other hydrogen atom bonded to the C atom is ^2H instead of ^1H .

As discussed earlier, the C atom bonded to ^1H and ^2H in the aliphatic ring will prefer to lose ^1H via the C– ^1H bond cleavage at the initial stage of hydrocarbon aromatization (e.g., step 1 of Figure 5). After the first double bond must have been formed, the other three possibilities for the C–H bond cleavage next to the double bond are illustrated in steps 2, 3, and 4 of Figure 5. Regardless of the different possibilities, toluene and its intermediates (such as MCHe) from the hydrocarbon aromatization process will retain more ^2H atoms with a consequent depletion of MCH in ^2H , which is verified by the experimental results.

At the early stage of the pyrolysis, toluene retained more ^2H atoms on the aromatic ring, such that the highest δD

fractionation effect could be observed between toluene and MCH from the 24 h pyrolysates compared to other pyrolysis time. In fact, the 12 h pyrolysis experiment on BCH was also performed, but from the 12 h pyrolysates, not enough toluene could be obtained for isotope analysis. However, from the 12 h pyrolysates, we could obtain enough MCH and detected $\delta\text{D}_{\text{MCH}}$ as -303.7% ; therefore, it is reasonable to speculate that there should be a much more remarkable δD fractionation effect between toluene and MCH prior to 24 h of pyrolysis. The δD fractionation effect will be significant for the hydrocarbon aromatization of high-temperature and fast thermal events.

Implications to the δD Composition of Meteorite PAHs. On the basis of the explanation above, a strong δD fractionation would be generated during the hydrocarbon aromatization from a fast thermal event. Consequently, studies involving the evaluation of the hydrogen isotope composition of aromatic compounds from fast thermal events, such as a meteorite passing through the atmosphere, volcanic eruption, hydrothermal alteration, forest wildfires, etc., will be of great importance.

The meteorites passing through the atmosphere experience a fast and high-temperature thermal process. The PAHs from some meteorites were recently reported to be strongly enriched in ^2H , with δD values ranging from +120 to +1100‰.¹¹ The authors inferred that the δD compositions of these PAHs are consistent with their extraterrestrial origin and that they were mainly formed in the cold interstellar environments.^{11–13} However, the carbonaceous matter in the meteorites will definitely suffer from the fast thermal alteration when passing through the atmosphere, because they will have to generally endure thousands of Celsius degrees for around 1 min. Although most of the initial meteorite mass is lost as it passes through the atmosphere by thermal evaporation, however, the fast and high-temperature thermal process will have exerted some effects on the remaining meteorite residues. Previous studies have shown that different types of hydrocarbons can be aromatized into aromatic compounds,^{15–23} even under an elevated temperature (even up to 1000 °C) within a short time.^{35–39} Thus, the hydrocarbon aromatization process could take place in the meteorites under such a high temperature during this short time interval, therefore introducing some constraints to the δD compositions of the PAHs detected in the meteorites.

The aromatization of the monoaliphatic ring hydrocarbon will bring about strong hydrogen isotope fractionation, even up to +162.3‰ ($\Delta\delta D_{\text{Tol-MCH}}$) from our 24 h pyrolysis experimental results. In Figure 6, an excellent logarithmic

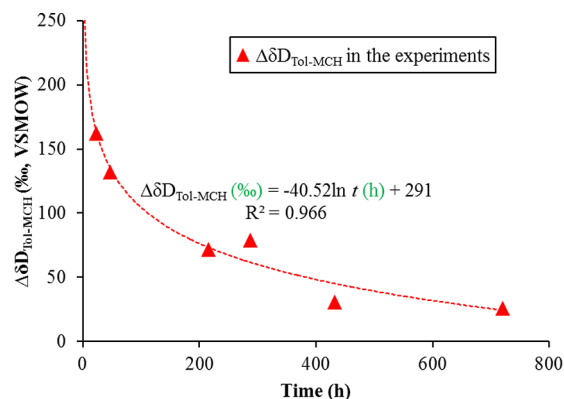


Figure 6. $\Delta\delta D_{\text{Tol-MCH}}$ evolution trend with the pyrolysis time.

relationship has been found between $\Delta\delta D_{\text{Tol-MCH}}$ values and the pyrolysis time, which suggests that, within a shorter pyrolysis time interval, the degree of hydrogen isotope fractionation between toluene and MCH could be much stronger. For example, a high δD fractionation value of +585.7‰ will be determined between toluene and MCH in 1 min according to the fitting curve in Figure 6. As stated above, δD values ranging from +120 to +1100‰ have been reported for some meteorite PAHs, if taken into account the short but strong thermal stress on the meteorite during its passing through the atmosphere; the experimental results of this work will bring some insights to the particularly positive δD composition of meteorite PAHs.

If the fast aromatization process occurred when meteorites are passing through the atmosphere, it might lead to stronger hydrogen isotope fractionation for the aromatics in meteorites and then make the PAHs remarkably enriched in deuterium. Therefore, besides the contribution from the cold interstellar environment to the hydrogen isotope composition of meteorite PAHs,¹¹ if the fast aromatization process occurred during the pass of meteorites through the atmosphere, it may

contribute its share to the strong ^2H enrichment of aromatic hydrocarbons detected in meteorites.

More δD data of the other PAHs detected from the meteorites of Murchison and LON94101 (the data from Huang et al.¹¹) are compiled into Figure 7; it can be seen that the multiple ring aromatics are generally more enriched in deuterium when compared to the one-ring aromatics. This is in accordance with the general findings that the δD fractionation is overall stronger with a higher degree of dehydrogenation of hydrocarbons. Once again, these extremely positive δD results might have been encoded with influence from the fast aromatization process that occurred as the meteorite passed through the atmosphere.

CONCLUSION

Distinct stable hydrogen isotope fractionation occurred for both toluene and MCH generated from the BCH pyrolysis. Toluene was strongly enriched with ^2H , whereas MCH was remarkably depleted in the 24 h BCH pyrolysates, with $\Delta\delta D_{\text{Tol-MCH}}$ ($\delta D_{\text{Tol}} - \delta D_{\text{MCH}}$) being 162.3‰. In comparison to the initial hydrogen isotope of BCH, $\Delta\delta D_{\text{MCH-BCH}}$ and $\Delta\delta D_{\text{Tol-BCH}}$ were -46.5 and 115.8‰, respectively, from the 24 h pyrolysates. With an increasing pyrolysis time, the degree of the hydrogen isotope fractionation between toluene and MCH gradually mitigated.

A fairly well positive correlation was found between the stable carbon isotope evolution of toluene and MCH from the pyrolysates with the increasing pyrolysis time, confirming the genetic relationship between the two compounds. The parameter $\Delta\delta D_{\text{Tol-MCH}}$ correlated fairly well with an increasing pyrolysis time, indicating its possible potential in the evaluation of thermal maturity of reservoir oils, especially in light crude oil reservoirs where the traditional biomarker parameters may be invalid but where toluene and MCH can still be detected.

An excellent logarithmic correlation was observed between $\Delta\delta D_{\text{Tol-MCH}}$ values and increasing pyrolysis time, suggesting that, in a shorter pyrolysis time interval, the degree of hydrogen isotope fractionation between toluene and MCH could be stronger. This finding will be significant in evaluating the extremely positive hydrogen isotope results of aromatics often generated from a fast and high-temperature thermal

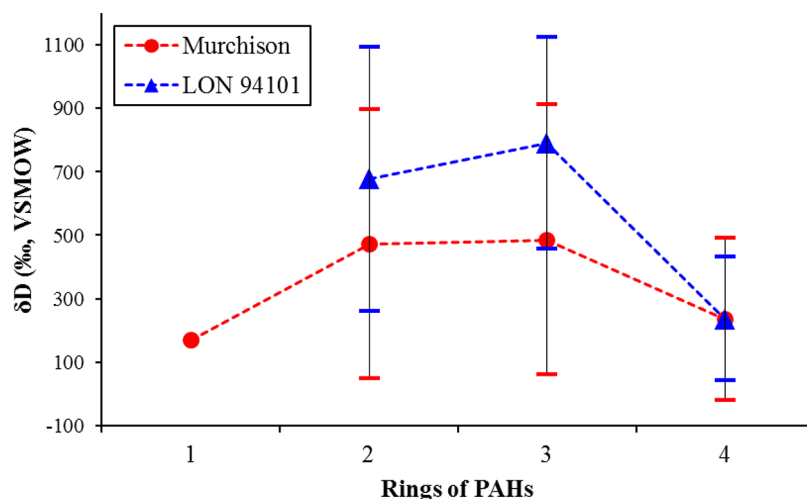


Figure 7. Variations in δD (‰, VSMOW) of PAHs as a function of ring numbers of the aromatic compounds from the meteorites (data from Huang et al.¹¹).

event, such as the passing of meteorites through the atmosphere, volcanic eruption, hydrothermal alteration, forest wildfires, etc. This kind of fast aromatization process might have brought remarkable constraints to the strong ^2H -enriched isotope compositions of the aromatics found in the meteorites of Murchison and LON94101.

AUTHOR INFORMATION

Corresponding Author

*E-mail: liaoZW@gig.ac.cn.

ORCID

Bin Cheng: [0000-0001-9327-768X](https://orcid.org/0000-0001-9327-768X)

Notes

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