Mineral-assisted production of benzene under hydrothermal conditions: Insights from experimental studies on C₆ cyclic hydrocarbons

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Abstract

Volatile Organic Compounds (VOCs) are ubiquitously present at low but detectable concentrations in hydrothermal fluids from volcanic and geothermal systems. Although their behavior is strictly controlled by physical and chemical parameters, the mechanisms responsible for the production of most VOCs in natural environments are poorly understood. Among them, benzene, whose abundances were found to be relatively high in hydrothermal gases, can theoretically be originated from reversible catalytic reforming processes, i.e. multi-step dehydrogenation reactions, involving saturated hydrocarbons. However, this hypothesis and other hypotheses are difficult to definitively prove on the basis of compositional data obtained by natural gas discharges only. In this study, therefore, laboratory experiments were carried out to investigate the production of benzene from cyclic hydrocarbons at hydrothermal conditions, specifically 300 °C and 85 bar. The results of experiments carried out in the presence of water and selected powdered minerals, suggest that cyclohexane undergoes dehydrogenation to form benzene, with cyclohexene and cyclohexadiene as by-products, and also as likely reaction intermediates. This reaction is slow when carried out in water alone and competes with isomerization and hydration pathways. However, benzene formation was increased compared to these competing reactions in the presence of sulfide ( sphalerite and pyrite) and iron oxide (magnetite and hematite) minerals, whereas no enhancement of any reaction products was observed in the presence of quartz. The production of thiols was observed in experiments involving sphalerite and pyrite, suggesting that sulfide minerals may act both to enhance reactivity and also as reactants after dissolution. These experiments demonstrate that benzene can be effectively produced at hydrothermal conditions through dehydrogenation of saturated cyclic organic structures and highlight the crucial role played by minerals in this process.

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1. Introduction

Low-to-high temperature fluid discharges from worldwide volcanic and hydrothermal systems show the ubiquitous occurrence of Volatile Organic Compounds (VOCs), consisting of a complex mixture of different compounds mainly pertaining to the alkane, alkene and aromatic groups but also including heteroatomic constituents such as O- and S-bearing compounds and halocarbons (e.g. Capaccioni and Mangani, 2001; Capaccioni et al., 2001; Taran and Giggenbach, 2003; Schwandner et al., 2004; Tassi et al., 2005a, 2005b, 2010, 2012b; Schwandner et al., 2013; Tassi et al., 2013, 2015a,b). Recurrent patterns in the relative abundances of this multitude of compounds were found in hydrothermal/volcanic gases that originated at similar temperature and redox conditions (Capaccioni et al., 1993, 1995), suggesting a relationship between the composition of the VOCs and the physicochemical conditions at the fluid source(s). Insights into the thermodynamic properties of organic compounds (e.g. shock and Helgeson, 1990; Helgeson et al., 1998; Plyasunov and Shock, 2000, 2003) and experiments at elevated temperatures and pressures in aqueous solutions (e.g. McCollom et al., 2001; Seewald, 2001; Yang et al., 2012; Shipp et al., 2013) provide valuable insight into the behavior of VOCs in hydrothermal systems. In particular, chemical reaction pathways that can produce VOCs in volcanic/hydrothermal environments have previously been investigated.
through both (i) a theoretical approach based on thermodynamic considerations (e.g. Shipp et al., 2013 and references therein) and (ii) laboratory experiments designed to simulate hydrothermal conditions (e.g. Shipp et al., 2013 and references therein).

Experiments carried out by Seewald (1994) demonstrated the attainment of metastable equilibrium between organic compounds under hydrothermal conditions, as suggested previously on the basis of thermodynamic considerations by Shock (1990). The possible attainment of metastable equilibrium between the alkane-alkene pairs in natural fluids was confirmed by compositional data of fumarolic gases (Taran and Giggenbach, 2004). Accordingly, the relative concentrations of alkanes and alkenes have been used to give hints on the conditions prevailing in deep fluid reservoirs (e.g. Capaccioni and Mangani, 2001; Taran and Giggenbach, 2003; Capaccioni et al., 2004; Tassi et al., 2005a,b; Agusto et al., 2013). Experimental studies on chemical reactions involving organic compounds at hydrothermal conditions described stepwise pathways consisting of reversible and irreversible processes (e.g. oxidation/reduction, hydration/dehydration, carboxylation/decarboxylation) resulting in functional group interconversions, where water and minerals can act both as catalysts and also as reactants (e.g. Katritzky et al., 1996; Siskin and Katritzky, 2000; McCollom et al., 2001; McCollom and Seewald, 2003; Watanabe et al., 2004; Yang et al., 2012; McCollom, 2013; Shipp et al., 2013). Minerals commonly present in volcanic and hydrothermal environments (e.g. zeolites, smectites, sulfides) have been shown to efficiently catalyze organic reactions under hydrothermal conditions (Soma and Soma, 1989; Dale Ortego et al., 1991; Seewald, 2001, 2003; Ferris, 2005; Williams et al., 2005; Fu et al., 2008; Kaur and Kishore, 2012; Shipp et al., 2014; He et al., 2015), opening potential new insights into the chemical processes responsible for the origin of life on early Earth and astrobiology (Wächtershäuser, 1988; Russell and Martin, 2004) and perspectives in the development of new green chemistry (Shipp et al., 2014).

Benzene (C₆H₆) is one of the most abundant non-methane VOCs in volcanic/hydrothermal fluid discharges (e.g. Capaccioni et al., 2001; Taran and Giggenbach, 2003; Tassi et al., 2012b, 2013a), and is of particular interest for its impact on human health and the environment (WHO, 2000; Huff, 2007; Galbraith et al., 2010). The relatively high concentrations of benzene found in laboratory and natural hydrothermal systems have been interpreted to be a consequence of the stability of the aromatic ring over a wide range of temperature conditions (e.g. Darling, 1998; Katritzky et al., 1990; Tassi et al., 2012b). Although aromatization of methane may yield small amounts of benzene at high temperatures (Guéret et al., 1997; Holmen et al., 1995; Taran and Giggenbach, 2003), Capaccioni et al. (1993) proposed that the production of this aromatic compound in volcanic and hydrothermal environments may occur mainly through mechanisms that resemble the catalytic reforming processes used in the refining industry. These processes take place at high temperatures (700–800 K) in the presence of solid catalysts (e.g. alumina supported Pt, Pt–Re, and Pt–Ir catalysts and zeolites; Turata and Ramanathan, 2003; Rahimpour et al., 2013) and the reaction pathways include dehydrogenation, isomerization, cyclization and fragmentation, which lead to the overall conversion of alkanes to cycloalkanes, and subsequently to aromatic hydrocarbons.

While aliphatic alkanes largely dominate the composition of gases emitted from most natural systems (e.g. Capaccioni et al., 1993, 1995), the relative amounts of cyclics and aromatic compounds were found to be strongly dependent on the physicochemical conditions of the deep reservoirs. Relevant enrichments in cyclics were observed in fluids emitted from mud volcanoes (Tassi et al., 2012a; Bonini et al., 2013), while relatively high concentrations of aromatics were recognized in volcanic/hydrothermal gases (Tassi et al., 2015a,b), indicating that the conversion of cyclics to aromatics is favored by increasing temperatures.

In this study, we have investigated the mechanisms of benzene production from cyclic hydrocarbons under hydrothermal conditions in laboratory experiments carried out at 300 °C and 85 bar in the presence of different minerals typical of a hydrothermal environment, i.e. sphalerite, quartz, hematite, magnetite and pyrite. The aims were to (i) assess the efficiency of the dehydrogenation reaction for benzene production from cycloalkanes and cyclic olefins under hydrothermal conditions, and (ii) investigate the influence of specific minerals on the reactivity of organic compounds.

2. Thermodynamic considerations

The theoretical foundation for the experiments performed in the present study is discussed here on the basis of thermodynamic calculations.

Dehydrocyclization of normal alkanes to aromatics consists of (i) cyclization of normal alkanes (which in the laboratory usually requires metal catalysts), and (ii) dehydrogenation of cycloalkanes to aromatics (which in the laboratory is usually acid catalyzed), as follows:

$$C_{6}H_{14(aq)} = C_{6}H_{12(aq)} + H_{2(g)}$$

(1)

$$C_{6}H_{12(aq)} = C_{6}H_{6(g)} + 3H_{2(g)}$$

(2)

The standard state equilibrium constants for reactions (1) and (2) can be expressed as follows:

$$K_{1}^{*} = \frac{a_{C_{6}H_{12}}}{a_{C_{6}H_{14}}}$$

(3)

and

$$K_{2}^{*} = \frac{a_{C_{6}H_{6}}(f_{H_{2}})^{3}}{a_{C_{6}H_{12}}}$$

(4)

where $a$ is the activity of aqueous organic species and $f$ is the fugacity of hydrogen.

The $K_{1}^{*}$ and $K_{2}^{*}$ values at the saturated vapor pressure (PSAT), calculated using the SUPCRT database (Johnson et al., 1992), increase 3 and 15 orders of magnitude from 0 to 350 °C, respectively (Fig. 1). Both the cyclization and the dehydrogenation reactions are endothermic, and thus the stability of benzene is favored by increasing temperature. The dependence of $K_{1}^{*}$ and $K_{2}^{*}$ on hydrogen fugacity can be conveniently expressed on a log-log basis, as follows:

$$\log K_{1}^{*} = \log \frac{a_{C_{6}H_{12}}}{a_{C_{6}H_{14}}} + \log f_{H_{2}}$$

(5)

$$\log K_{2}^{*} = \log \frac{a_{C_{6}H_{6}}(f_{H_{2}})^{3}}{a_{C_{6}H_{12}}} + 3 \log f_{H_{2}}$$

(6)

At metastable equilibrium conditions, the products of both reactions (1) and (2) are thermodynamically favored by decreasing $f_{H_{2}}$ values (Fig. 2). Accordingly, field data on volcanic and hydrothermal fluids showed a positive correlation between cyclohexane/benzene ratios and $H_{2}$ contents in fumarolic discharges (Capaccioni et al., 2004).

In a hydrothermal reservoir, where redox conditions are generally controlled by the fayalite-hematite-quartz (FeO-FeO₁.₅) mineral buffer (Giggenbach, 1987), hexane and benzene production from cyclohexane, as described by reactions (1) and (2) are favored at temperatures higher than 150 °C (field D; Fig. 2). Accordingly, linear alkanes and aromatics were found to dominate the composition of the organic gas fraction in fumarolic fluids emitted from volcanic/hydrothermal systems, whereas cyclics were rarely detected (e.g. Schwandner et al., 2013; Tassi et al., 2015a,b). On the other hand, benzene hydrogenation to produce cyclohexane is favored at relatively low temperatures (field C; Fig. 2), as confirmed by the relatively high concentrations of cyclics compared to aromatics found in hydrothermal discharges fed by reservoirs having temperatures < 150 °C (Tassi et al., 2012a).

Hence, thermodynamic calculations when compared with empirical data confirm and support the hypothesis that the production of benzene
from cyclohexane through dehydrogenation is energetically favored at high temperatures, and can, and likely does occur in natural volcanic and hydrothermal environments. This suggests that experiments designed to simulate hydrothermal conditions in simplified systems should provide useful insight into the reaction pathways that may occur under specific physicochemical conditions, and into the role that minerals may have in enhancing reactivity or participating in such organic reactions.

3. Experimental procedure and analytical methods

Experiments were performed using 0.1 or 0.2 m cyclohexane (≥99.0%) and cyclohexene (≥99.9%), purchased from Sigma-Aldrich, added to water and sealed in silica glass tubes. Under the conditions of the experiment the organic reactants are soluble in aqueous media. The solvent was either (i) Ar-purged 18.2 MΩ-cm water (NANOpure® DiamondTM UV, Barnstead International) or (ii) deuterium oxide (99.9% D2O, Sigma-Aldrich). Powdered minerals were purchased from Alfa Aesar. Sphalerite (99.99% ZnS), quartz (99.5% Silicon(IV) oxide), hematite (99.5% Iron (III) oxide), magnetite (97% Iron (II, III) oxide) or pyrite (99.5% Iron (II) sulfide), were added to the samples so that the total mineral surface areas were 0.1 or 0.6 m², depending upon the experimental run. The crystal structures of the powdered minerals were confirmed by X-ray diffraction. The BET surface areas were measured as described by Shipp et al. (2014).

After adding all of the materials, the tubes were cooled using liquid nitrogen to solidify the contents and minimize reactant loss due to volatilization, and connected to a vacuum pump to evacuate the headspace (pressure < 60 mtorr). The open ends of the tubes were then sealed using a hydrogen-oxygen flame while the bottom of the tubes containing the reactants were submerged in the liquid nitrogen. The sealed tubes were placed in a pre-heated oven at 300 °C for 10 or 30 days.

After each experimental run, the glass tubes were quickly cooled by submerging in water at ambient temperature and the organic products were extracted using dichloromethane (DCM, 99.9%, Fisher Scientific) in silanized glass vials (Supelco, Inc.). The samples (organic products in DCM) were then removed from the aqueous layer and transferred to glass vials equipped with a teflon-lined septum using a disposable glass pipette.

The analysis of organic products was carried out by gas chromatography (GC; Thermo Trace GC Ultra) coupled with Quadrupole Mass Spectrometry (MS; Thermo DSQ). An aliquot (20 µL) of sample was transferred to the GC through an injection port operating at 230 °C in splitless mode. Peak separation was carried out using a TR-V1 fused silica capillary column (Thermo) and He as carrier gas at a flow rate of 1.3 mL/min in constant pressure mode. The column oven temperature was set as follows: 35 °C (hold 10 min), ramp at 5.5 °C/min to 180 °C (hold 3 min), ramp at 20 °C/min up to 230 °C (hold 6 min). The GC-MS transfer-line was set at 230 °C, the MS was operated in positive electron impact mode (EI) with an ionization energy of 70 eV, and the source was maintained at 250 °C. A mass-to-charge range from 35 to 400 m/z in full scan mode was analyzed. Retention time of the chromatographic peaks and the mass spectra were both used to identify organic compounds detected by the quadrupole detector, using the mass spectra database of the NIST05 database (NIST, 2005) for comparison. Quantitative analyses were carried out by external standard calibration procedure using Accustandard® mixtures in methanol or, alternatively, hexane solvent. Relative Standard Deviation (RSD), calculated from five replicate analyses of the standard mixtures, was <5%. The amounts of products yielded from each experiment were calculated by dividing each quantifiable product by the sum of products plus the unreacted starting material and expressed as percent abundances.

The product analysis for experiments in D2O was performed using GC–MS (Thermo Electron Trace 1300-ISQ with a TG-SQC column) with the following parameters: 1 µL split (30:1) injection, 225 °C injection port, 30 °C oven (5 min hold) with at 15 °C/min ramp to 105 °C, constant flow mode (1 mL/min with vacuum compensation), 250 °C transfer line and ion source, electron-impact ionization (70 eV) scanning 29–400 m/z 5 times per minute.

4. Experimental results

4.1. Cyclohexane experiments

As reported in Table 1, reaction of cyclohexane (0.2 m) in water at 300 °C after 10 days generated only trace amounts of benzene, cyclohexadiene and cyclohexene (0.36, 0.34 and 0.27%, respectively). No appreciable amount of deuterated cyclohexane was observed in the experiment performed at the same conditions in heavy water.
and methylcyclopentanol (0.01%). After 30 days, the products were quantitatively, with minor amounts of benzene (0.05%), cyclohexanone (0.01%).

The pathway from cyclohexane to benzene is expected to be an intermediate in the aromatization reaction (~1.3). The benzene/cyclohexene ratio (~0.2) was markedly lower than that measured in the water alone experiment (~1.3).

4.2. Cyclohexene experiments

Further experiments were carried out using cyclohexene as reactant, which is expected to be an intermediate in the aromatization reaction pathway from cyclohexane to benzene. The results are reported in Table 2. Reaction of cyclohexene in water with hematite (0.1 m2) produced benzene and cyclohexene, the former being 10 times more abundant than the latter. No cyclohexadiene or phenol were detected. A similar benzene/cyclohexene ratio (12:1) was also measured in the presence of magnetite, where cyclohexadiene was detected at very low relative amount (0.05%; Table 1). In the presence of quartz, cyclohexene was the main product, whereas cyclohexadiene and phenol were measured at very low amounts (Table 1). The benzene/cyclohexene ratio (~0.2) was markedly lower than that measured in the water alone experiment (~1.3).

5. Discussion

Benzene was produced in all of the experiments performed at 300 °C in water after only 10 days, suggesting that the aromatization of cycloalkanes and cycloalkenes could readily occur under hydrothermal conditions in natural systems, where the reactions of organic materials can occur at even higher temperatures and over longer time periods than those of the current experiments. Experiments carried out with varying reaction times, with added minerals, and using different initial compounds (cyclohexane or cyclohexene) gave different product distributions. In particular, the experimental data show that minerals can play a major role in controlling the aromatization reaction of cyclic C₆ compounds under the experimental hydrothermal conditions.

5.1. Reactions in water with no minerals

The production of small amounts of cyclohexene and cyclohexadiene from cyclohexene in water after 10 days suggests that aromatization to form benzene as a final product proceeds through a multi-step dehydrogenation mechanism, with cyclohexene and the cyclohexadiene as intermediates (Fig. 3). The production of methylcyclohexene and toluene from methylcyclohexane in water at 300 °C after 24 h (Shipp et al., 2013), may have the same origin, although in that case no diene could be detected.

Table 1

<table>
<thead>
<tr>
<th>Starting reactant</th>
<th>Molality (m)</th>
<th>0.2</th>
<th>0.2</th>
<th>0.2</th>
<th>0.1</th>
<th>0.2</th>
<th>0.2</th>
</tr>
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<td>Sphalerite</td>
<td>Sphalerite</td>
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<td></td>
<td>Formula</td>
<td>–</td>
<td>ZnS</td>
<td>ZnS</td>
<td>ZnS</td>
<td>Fe₃O₄</td>
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<td>Days</td>
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<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
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<tr>
<td>Products Cyclohexane</td>
<td>0.27</td>
<td>0.13</td>
<td>0.85</td>
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<td>1.16</td>
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<td>99.57</td>
<td>95.08</td>
<td>90.43</td>
<td>98.01</td>
<td>97.41</td>
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<tr>
<td></td>
<td>Benzene</td>
<td>0.36</td>
<td>0.23</td>
<td>2.69</td>
<td>5.91</td>
<td>1.81</td>
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<tr>
<td>Phenol</td>
<td>0.07</td>
<td>1.39</td>
<td>2.36</td>
<td>–</td>
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<td>–</td>
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Table 2

<table>
<thead>
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<td>Days</td>
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<tr>
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<tr>
<td></td>
<td>D4</td>
<td>–</td>
<td>1.39</td>
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Experiments carried out with cyclohexene at 300 °C in water did produce benzene in 10 days. However, the main products under these conditions were cyclohexanol and methylcyclopentenes, suggesting that in water alone, hydration and isomerization reactions dominate over dehydrogenation (Fig. 3). This hypothesis was confirmed by the longer timescale experiment (30 days), where methylcyclopentenes specifically dominated the products distribution.

The number of products formed from cyclohexane at 300 °C after 10 days in water was smaller than that observed with cyclohexene as reactant, pointing to a lower reactivity of cyclohexane under the experimental conditions. This suggestion is supported by the absence of deuteration of cyclohexane in the experiment performed in heavy water (Table 2). The results are consistent with those reported by Crittendon and Parsons (1994), who observed no activation of the C—H bonds in supercritical water (375 °C) after 20 min in water alone.

### Table 3

The details and results of experiments performed starting from cyclohexene at 300 °C and 85 bar are reported. The yield of each product is expressed as percent abundance with respect to the sum of quantifiable products plus unreacted starting material.

<table>
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<th>0.2</th>
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<tr>
<td>Cyclohexene</td>
<td>99.51</td>
<td>92.60</td>
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<td>Cyclohexanethiol</td>
<td>0.01</td>
<td></td>
<td></td>
<td>0.03</td>
<td>0.17</td>
<td>0.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</table>

5.2. Role of minerals

The products obtained from the reaction of cyclohexene at 300 °C in the presence of sphalerite were slightly different from those obtained in water with no minerals. In particular, in the presence of sphalerite, cyclohexadiene was not detected, presumably because of its high reactivity in the presence of this mineral (e.g. Shipp et al., 2013), rapidly converting to benzene. The detection of phenol on the other hand, confirms that some oxidation actually occurs (Fig. 3) although the detailed reaction pathways cannot be determined from the present data. In contrast to the experiments in heavy water in the absence of minerals, the extensive deuteration of cyclohexane observed in the presence of sphalerite suggests an important enhancement in the reactivity of C—H bonds. Most of the recovered deuterated cyclohexane under these conditions contained a single deuterium atom. This is consistent with

![Fig. 3](image-url)
deuteration of cyclohexane proceeding by cleavage of single C—H bonds rather than via addition of two deuteriums to cyclohexene, which would result in the incorporation of pairs of deuterium atoms from the solvent.

In laboratory experiments performed at 300 °C and 100 MPa, Shipp et al. (2014) found that the addition of sphalerite dramatically increased the kinetics of the stereoisomerization reaction of cis- and trans-1,2-dimethylcyclohexane, suggesting that the mineral efficiently acted as a catalyst through a surface-catalyzed mechanism. These observations are consistent with our current results. In analogy with the previous suggestion (Shipp et al., 2014), the active sites on the sphalerite surface presumably interact with the cyclohexane to weaken or break the C—H bond bonds via formation of a surface-bound intermediate that is able to bond to a deuterium atom derived from the solvent. Repetition of this process would be expected to result in the incorporation of a progressively increasing number of deuterium atoms (Shipp et al., 2014). Accordingly, cyclohexane incorporating up to four deuterium atoms was found in reactions in heavy water with sphalerite. A surface-catalyzed reaction mechanism was suggested by the enhanced conversion of both the cyclohexane and cyclohexene experiments with sphalerite, presumably via C—H bond cleavage, with increasing sphalerite surface area. More isomerization and hydration of cyclohexene to form methylcyclopentenes and cyclohexanol (Fig. 3), respectively, was observed at the lower sphalerite/cyclohexene ratios, since these reactions proceed even in the absence of minerals. On the other hand, aromatization of cyclohexene to benzene was observed to be the dominant reaction pathway at higher sphalerite/cyclohexene ratios, consistent with a catalytic role for sphalerite in the aromatization reaction.

However, the observation of cyclohexanethiol as a product of cyclohexene in the presence of sphalerite also suggests that the mineral can act as a reagent under the experimental conditions. Therefore, not only can sphalerite enhance the reactivity of organic compounds, but it can apparently participate in reactions of organic compounds. In fact, the presence of a sulfur-containing organic compound implies the involvement of mineral-derived dissolved sulfur in solution that can act as a reactant, perhaps in the form of H2S. The increasing production of the sulfur-bearing compound at increasing sphalerite/cyclohexene ratios for the cyclohexene experiments may be the result of increasing H2S (or increasing concentration of other soluble sulfur species) and/or the increasing number of available active sites on the sphalerite surface if the reaction is surface catalyzed.

Cyclohexanethiol production from cyclohexene was also observed in the presence of another sulfide mineral, i.e. pyrite. In the presence of pyrite, isomerization of cyclohexene to methylcyclopentenes and subsequent hydrogenation to form methylcyclopentanes was the main reaction pathway under the experimental conditions (Fig. 3). Hydration products including methylcyclopentanol and cyclohexanol were observed together with a higher yield of cyclohexanone relative to experiments involving water and sphalerite, indicating that the hydration/dehydrogenation pathway was catalyzed by pyrite. Benzene and cyclohexane were produced in similar amounts to each other, consistent with enhanced C—H bond activation similar to sphalerite. The hydrogenation of cyclohexene to the corresponding alkane is a reduction that requires a source of H2. This could be from formation of benzene (formally an oxidation) and/or from oxidation of pyrite, i.e. oxidation of sulfur to sulfate and/or successive oxidation of ferrous iron to ferric iron, as follows:

\[
\text{FeS}_2 + 8\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ + 7\text{H}_2
\]

(7)

\[
2\text{Fe}^{2+} + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2
\]

(8)

Experiments carried out in the presence of iron oxide minerals (hematite and magnetite) enhanced formation (relative to water alone) of benzene from cyclohexane. Interestingly, the benzene/cyclohexene ratios in the presence of hematite and magnetite were significantly higher than those found in the sphalerite experiments, suggesting that the iron oxides may be quite efficient in enhancing reactivity and that further work with these minerals is warranted. In contrast, experiments in the presence of quartz resulted in no evidence of enhanced reactivity compared to water alone. In fact, the quartz may have reduced the reactivity of cyclohexene, as suggested by the somewhat lower benzene/cyclohexene ratio for the experiment with quartz starting with cyclohexane and the lower yields of products from cyclohexene in the presence of quartz relative to water alone.

6. Concluding remarks

Benzene production starting with cycloalkanes is observed under hydrothermal conditions, as expected on the basis of thermodynamic calculations and prior empirical observations. The observed product distributions are consistent with a reaction pathway consisting of multi-step dehydrogenations, with cycloalkanes and cyclic dienes as intermediate products. Although further experimental work is necessary to determine the detailed reaction kinetics and to more definitively define the reaction pathways, the current data show that starting with cyclic hydrocarbons, aromatization can prevail over other reaction pathways that yield alcohols and ketones proposed by Seewald (2001). Benzene production was observed even in the absence of added minerals, as expected on thermodynamic grounds. However, minerals, in particular sulfides (sphalerite and pyrite) and iron oxides (magnetite and hematite), gave significantly higher yields of benzene and clearly enhanced reactivity. In particular, sphalerite efficiently increased the reactivity of C—H bonds, presumably via a surface-catalyzed mechanism, and also participated in organic reactions as an indirect reactant in the production of cyclohexanethiol. The latter was also produced from cyclohexene in the presence of pyrite. Finally, while quartz exhibited virtually no catalytic effect on organic reactivity, hematite and magnetite significantly enhanced the conversion of cyclohexene to benzene, even more efficiently than sphalerite.

Acknowledgements

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References


