Effects of iron-containing minerals on hydrothermal reactions of ketones

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Abstract

Hydrothermal organic transformations occurring in geochemical processes are influenced by the surrounding environments including rocks and minerals. This work is focused on the effects of five common minerals on reactions of a model ketone substrate, dibenzylketone (DBK), in an experimental hydrothermal system. Ketones play a central role in many hydrothermal organic functional group transformations, such as those converting hydrocarbons to oxygenated compounds; however, how these minerals control the hydrothermal chemistry of ketones is poorly understood. Under the hydrothermal conditions of 300 °C and 70 MPa for up to 168 h, we observed that, while quartz (SiO_2) and corundum (Al_2O_3) had no detectable effect on the hydrothermal reactions of DBK, iron-containing minerals, such as hematite (Fe_2O_3), magnetite (Fe_3O_4), and troilite (synthetic FeS), accelerated the reaction of DBK by up to an order of magnitude. We observed that fragmentation products, such as toluene and bibenzyl, dominated in the presence of hematite or magnetite, while use of troilite gave primarily the reduction products, e.g., 1, 3-diphenyl-propane and 1, 3-diphenyl-2-propanol. The roles of the three iron minerals in these transformations were further explored by (1) control experiments with various mineral surface areas, (2) measuring H_2 in hydrothermal solutions, and (3) determining hydrogen balance among the organic products. These results suggest the reactions catalyzed by iron oxides (hematite and magnetite) are promoted mainly by the mineral surfaces, whereas the sulfide mineral (troilite) facilitated the reduction of ketone in the reaction solution. Therefore, this work not only provides a useful chemical approach to study and uncover complicated hydrothermal organic-mineral interactions, but also fosters a mechanistic understanding of ketone reactions in the deep carbon cycle.
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Keywords: Hydrothermal; Iron minerals; Ketones; Organic geochemistry; Deep carbon cycle

1. INTRODUCTION

The hydrothermal chemistry of organic compounds influences a wide range of critical geochemical processes, including the degradation and transport of organic matter in sedimentary systems (Seewald, 2003), the formation of oil and gas reservoirs (Head et al., 2003; Larter et al., 2003; Jones et al., 2008), and the metabolic cycles of microbes in subsurface environments (Head et al., 2003; Hondt et al., 2004; Simoneit et al., 2004; Hinrichs et al., 2006; Horsfield et al., 2006; McCollom and Seewald, 2007; Mason et al., 2010; Shock and Canovas, 2010; McDermott et al., 2015). A variety of organic compounds have been detected and identified in deep-ocean hydrothermal fluid samples (Cruse and Seewald, 2006; Proskurowski

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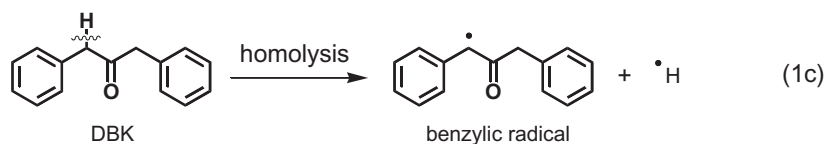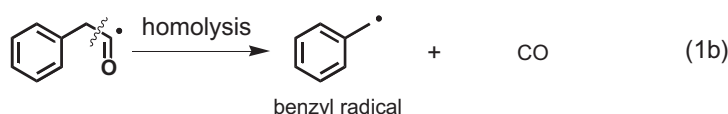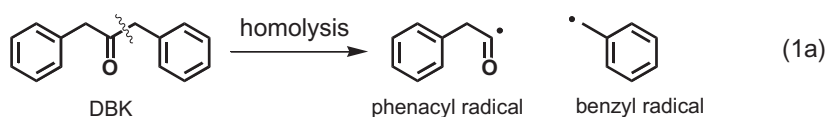*E-mail address:* zimingyang@oakland.edu (Z. Yang).

et al., 2008; Konn et al., 2009; McCollom et al., 2015), and the chemistry of a large number of organic structures under hydrothermal conditions has been studied (Bell and Palmer, 1994; Andersson and Holm, 2000; Akiya and Savage, 2001; Cody et al., 2001; Katritzky et al., 2001; McCollom and Seewald, 2003a,b; Savage, 1999; Watanabe et al., 2004). In particular, thermodynamic properties and predictive models have been constructed for organic molecules in hydrothermal solutions at the gas–liquid phase equilibrium (Helgeson et al., 1998, 2009; LaRowe and Dick, 2012; LaRowe and Helgeson, 2006; Plyasunov and Shock, 2000, 2003; Shock, 1995; Shock and Helgeson, 1990; Sverjensky et al., 2014). In the past decade attempts have been made to systematically study the chemistry of various organic functional groups in aqueous media at elevated temperatures and pressures (McCollom and Seewald, 2007; Yang et al., 2012; Shipp et al., 2013; Shock et al., 2013; Shipp et al., 2014; Yang et al., 2014, 2015), in order to provide stepping-stones for understanding hydrothermal organic geochemistry mechanistically.

Geochemical processes involving organic carbon take place not in pure aqueous solution, but with gases and electrolytes, variable pH, and most importantly, inorganic materials such as rocks and minerals. It has been suggested for decades that minerals can, and perhaps should, influence organic hydrothermal reactivity (Jurg and Eisma, 1964; Simoneit, 1992; Seewald, 2001). There have been impressive reports of the ways in which naturally occurring inorganic substrates exhibit significantly different reactivity and stability under hydrothermal conditions (Leif and Simoneit, 2000; Cody et al., 2001; Seewald, 2001; Foustoukos and Seyfried, 2004; Fu et al., 2008; Williams et al., 2011; Shipp et al., 2014). Among these studies, many employ iron-containing mineral assemblages to control variables such as oxidation state, pH, and dissolved anions in hydrothermal solutions (Andersson and Holm, 2000; McCollom, 2013; McCollom and Seewald, 2003a; Reeves et al., 2012; Seewald, 1994, 2001). For example, Seewald (Seewald, 2001) used pyrite-pyrrhotite-magnetite, hematite-magnetite, and hematite-magnetite-pyrite assemblages to regulate the activities of dissolved H_2 and H_2S in hydrothermal water; Reeves et al. (Reeves et al., 2012)

used the pyrite-pyrrhotite-magnetite assemblage to provide a redox-buffered hydrothermal environment for C_1-C_5 n-alkanes at 323 °C and 350 bar; and McCollom (McCollom, 2013) studied hydrothermal transformations of amino acids using the hematite-magnetite-pyrite and pyrite-pyrrhotite-magnetite assemblages. The roles of these mineral mixtures have been suggested either as catalysts in promoting mineral surface reactions or as reagents in altering solution properties such as ionic strength, pH, and dissolved metal and sulfur species (McCollom, 2013).

While mineral assemblages have the advantage of regulating hydrothermal fluid chemistry, understanding the contribution of each individual mineral and identifying the hydrothermal organic-mineral reaction mechanisms remain quite limited. To expand our understanding, we initiated a study to identify the influence of separate minerals on the hydrothermal chemistry of ketones. In a previous study, the reaction pathways and mechanisms of a model ketone, dibenzylketone (DBK), were systematically studied in pure hydrothermal water at 300 °C (Yang et al., 2012, 2014). This work summarizes the first experimental results from DBK hydrothermal reactions with common iron-containing minerals, including hematite (Fe_2O_3), magnetite (Fe_3O_4), and troilite (synthetic FeS). For comparison, the effects of non-iron minerals, such as corundum (Al_2O_3) and quartz (SiO_2), were also investigated.

The ketone functional group (C=O) was chosen for study because it occupies a central position in the reaction path that links alkanes and carboxylic acids (Fig. 1, revised from Seewald, 2003). One of the most critical roles that ketones may play is to form carboxylic acids by breaking a carbon–carbon (C—C) bond. DBK is a useful model ketone because it has a benzylic position that allows relatively facile C—C bond fragmentation. A detailed analysis of the hydrothermal products revealed extensive C—C bond cleavage in DBK at hydrothermal conditions; although, it is noteworthy that carboxylic acids were not detected in H_2O alone (Yang et al., 2012). Many of the observed products were associated with radical coupling reactions, in which pairs of radicals were generated through a homolytic C—C cleavage in DBK molecules (Eq. (1a)).