

Organic geochemistry paper

CARBON CATALYSED HYDROGEN EXCHANGE IN PETROLEUM SOURCE ROCKS

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ABSTRACT

Hydrogen exchange of carbon –bound hydrogen has been observed when alkenes, saturated and aromatic hydrocarbons were heated at moderate temperatures on carbonaceous surfaces (activated carbon and coal). Isomerization of alkenes and formation of hydrogenated/dehydrogenated products from the saturated and aromatic reactants resulted.

A suite of crude oils have been analysed and the relative abundances of structurally related hydrocarbons compared. The consistent relationships between hydrocarbons in crude oils that are chemically related by hydrogenation/dehydrogenation processes suggest that a hydrogen exchange process similar to that demonstrated in laboratory experiments occurs during crude oil formation in sediments

1. Introduction

The probable involvement of catalysis in sedimentary reactions has been made to account for the predominance of methane in natural gas (Shock, 1994; Mango and Hightower, 1994; Mango, 2001) however evidence for the nature of such catalysts is lacking. Although most of the discussion about sedimentary catalysis has centred on methane formation other reactions occur in sediments that are usually catalysed when undertaken in the laboratory. One such reaction type is hydrogen exchange (hydrogenation and dehydrogenation).

Evidence that hydrocarbons undergo hydrogen exchange in sediments during petroleum formation has been provided by both isotope and molecular studies.

Changes in hydrogen isotope ratios of components in terrestrially sourced petroleum systems (Schimmelmann et al., 2004, Sessions et al., 2004) showed that extensive C-

bond H exchange occurred during chemical genesis from precursor compounds. Maturity also plays a significant role in the extent to which H- exchange takes place with specific compound types (Dawson et al., 2005). A knowledge of the cause of these reactions, and their mechanism, is fundamental to our understanding of the formation of petroleum in sediments.

Relationships observed between structurally related compound types has also indicated the possibility of hydrogen exchange. The report by Williams et al., 1988 of unusually high abundances of alkylaromatic and alkylparaffin compounds with common carbon skeletons in some crude oils led to their suggestion that inter-conversion of the aromatic and saturated ring systems might have occurred but they favoured an explanation involving a common alkylation process.### add comment about alkylnaphthalenes, alkylphenanthrenes and chrysenes and co-occurrence with partially hydrogenated cpds##

Although reactions involving hydrogen with hydrocarbons such as hydrogenation are commonly carried out in the laboratory with molecular hydrogen it is less common to use a hydrocarbon as the source of hydrogen. However reactions of this type using heterogeneous catalysts are well-documented (Johnstone et al., 1985). Results from laboratory reactions suggest that if hydrogen exchange between hydrocarbons occurs in sediments it is probable that a catalyst is involved.

In this paper we report evidence for the catalysis of hydrogen exchange between aromatic and saturated ring systems on carbon- rich surfaces (activated carbon and coal) in laboratory experiments down to 170⁰C.Evidence that these reactions have also occurred in petroleum source rocks was provided by linear relationships of hydrogenation /dehydrogenation compound pairs from a suite of crude oils.

We have failed to uncover publication of hydrogenation/dehydrogenation on carbon surfaces at the low temperatures reported here, in fact reaction temperatures above 400⁰C are common. Carbon as a catalyst appears to have been largely ignored as most chemists have traditionally used more effective catalysts such as sulphur, selenium or metals to promote these reactions at much lower temperatures in laboratory experiments.

We have used compounds representing the carbon ring systems of naphthalene (tetralin and decalin) and biphenyl (cyclohexylbenzene and bicyclohexyl) because these compounds are##### ubiquitous constituents of petroleum SR and crude oils bit more about methyl and dimethyl derivatives ### readily analysed constituents of crude oils (Alexander et al., 1994; Hunt, 1995) and these structural types are reported to undergo heterogeneous catalytic hydrogen exchange reactions (Johnstone et al., 1985, Poutsma, 2002). They also show that the reaction type of interest is not restricted to a single structural type.

2.Experimental

Reference compounds were purchased from commercial suppliers: bicyclohexyl(Aldrich), cyclohexylbenzene(), decalin(), tetralin(Merck). ???????????

Activated carbon ???????????

Sealed tube heating experiments were carried out in glass tubes deactivated with dichlorodimethylsilane(Aldrich) after soaking in hydrochloric acid. After

flushing the reactants with nitrogen gas the tubes were sealed under vacuum before heating in a thermostat.##### In atypical experiment----- Duplicate experiments ##### The reaction products were extracted with dichloromethane and separated into fractions by column chromatography (Bastow et al., 2003). Blank experiments without carbon were undertaken in parallel.

====copy GS-MS conditions from KP----- Collie coal ????????????

Relative abundance data used for compound ratios was calculated from peak areas in mass chromatograms using m/z -(bicyclohexyl), ---(biphenyl), ---(cyclohexylbenzene), ---(decalin), ----(tetralin) ????????????

3. Results and discussion

A simple hydrogen exchange reaction of hydrocarbons involves isomerisation of carbon-carbon double bonds. This reaction type was investigated by heating 1-octadecene on activated carbon at 170⁰C. A chromatogram of the products is shown in Figure 1. The group of peaks were shown to represent octadecenes as the hydrogenated product contained only octadecane. The number of peaks in this chromatogram appear to exceed the number of double-bond positional isomers indicating that both E and Z stereoisomers are also present.

Isomerization of double bonds on carbon surfaces is of fundamental importance for our understanding of geochemical processes. Not only are hydrocarbon structural processes involved but also changes in the isotopic composition of carbon bound hydrogen. The double-bond isomerisation processes reported here have been observed in our laboratory using other compound types and will be the subject of other publications.

Hydrogen exchange reactions have also been investigated using saturated and aromatic hydrocarbons. The reactants selected were bicyclohexyl and tetralin not only because they are constituents of crude oil but also because they represent compounds with carbon skeletons that occur in both the saturated and aromatic fractions of petroleum. Chromatograms of the products obtained after heating these compounds on activated carbon at different temperatures are shown in Figure 2. Both compounds show progressive hydrogen loss to form the very stable aromatized structures biphenyl and naphthalene. Evidence that hydrogen addition as well as dehydrogenation occurs on the catalyst is shown by the presence of isomeric decalins in the reaction product from experiments with tetralin.

Analysis of a group of crude oils from the Carnarvon Basin of Western Australia for the saturated and aromatic hydrocarbons used in the laboratory experiments provided data suggesting that the carbon catalysed hydrogen exchange reactions have also occurred under natural conditions in sediments. The crude oils with a range of maturities as measured by aromatic maturity parameters (van Aarsen et

al., 2000).are shown in Table 1. Plots of some key compound ratios are shown in Figure 3. The linear relationships between parameters involving hydrogen exchange on a common carbon skeleton ie hydrogenation /dehydrogenation reactions is strong evidence that these reaction systems have occurred during crude oil formation.

1. Conclusions

Hydrogen exchange involving a straight chain alkene, saturated cyclic and aromatic hydrocarbons has been demonstrated to be catalysed on carbon surfaces, The consistent relationships between hydrocarbons in crude oils that are chemically related by hydrogenation/dehydrogenation processes suggest that a hydrogen exchange process similar to that demonstrated in laboratory experiments occurs during crude oil formation in sediments.

Acknowledgements

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