

# HYDROGENATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SUPERCRITICAL CARBON DIOXIDE

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## ABSTRACT

The hydrogenation of phenanthrene catalyzed by rhodium supported on carbon (Rh/C) in supercritical carbon dioxide (scCO<sub>2</sub>) was studied. Our results show that at 1:1 catalyst-to-substrate ratio it is difficult to obtain complete conversion of phenanthrene to hydrogenated products. An increase in catalyst to a 2:1 ratio showed almost quantitative conversion to hydrogenated products, with a slight increase in hydrogen pressure from 1300 psi to 1500 psi. The fully hydrogenated product, perhydrophenanthrene, was obtained in equilibrium with other products at 46% in four hours.

A series of group five transition metal hydrido complexes featuring aryloxy ligands will be synthesized and tested as hydrogenation catalysts for phenanthrene and the rates of reaction will be compared with those heterogeneous systems that have been tested in scCO<sub>2</sub>.

## INTRODUCTION

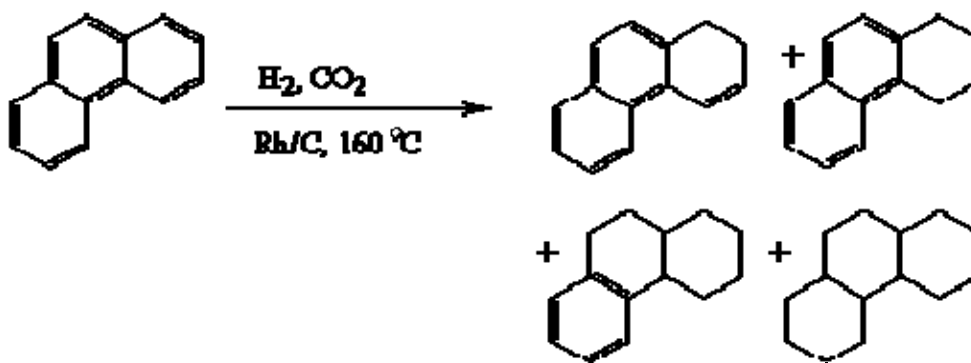
Heterogeneous catalyzed hydrogenation of aromatics is a well-developed and active field of chemistry,<sup>[1]</sup> and is rapidly gaining importance for a range of applications in the petroleum industry. Many easily recoverable petroleum resources have been exploited to date, and it is predicted that approximately 50 years of these easily extractable resources remain in the Athabasca oil sands of Alberta, Canada. However, the bitumen deposits in these oil sands are considered to contain upwards of 1.7 trillion barrels of oil reserves.<sup>[2]</sup>

For this reason, bitumen upgrading technologies must be improved so that the material can be extracted in an economically feasible fashion. Bitumen consists largely of polycyclic aromatic hydrocarbons (PAHs) that have the potential to be upgraded into synthetically useful materials. The efficient upgrading of these compounds will result in the elimination of many of the waste materials from the extraction of bitumen. The energy requirements for extraction of bitumen and its upgrading are high, so it is now imperative to find new methods for extraction and upgrading of PAHs from bitumen.

It has been proposed that the use of supercritical fluids (SCFs) for the extraction of PAHs from bitumen will lead to reduced energy requirements as well as major reductions in greenhouse gas emissions. Optimal hydrotreating processes use a temperature of 379 °C for the conversion of aromatics;<sup>[3]</sup> however, scCO<sub>2</sub> has a critical temperature (T<sub>c</sub>) of 31 °C. By using scCO<sub>2</sub> the potential exists to lower the energy requirement of the upgrading process. Our recent studies using scCO<sub>2</sub> have shown that a range of aromatic compounds can be

hydrogenated using Rh/C as a catalyst at remarkably mild temperatures and pressures. The conversion of phenanthrene to its hydrogenated products (Figure 1) is reported here.

In addition to heterogeneous hydrogenation catalysts there are many well-known homogeneous hydrogenation catalyst systems; however, these are generally only effective for the hydrogenation of olefins<sup>[4]</sup>. There are only a few homogeneous catalysts that demonstrate the ability to catalyze the hydrogenation of aromatic substrates. Some middle and later transition metal complexes have demonstrated the ability to hydrogenate aromatic rings<sup>[5]</sup>, but there is some ambiguity as to whether the active species are truly homogeneous<sup>[1]</sup>. On the other hand, a series of group 5 hydrido complexes featuring aryloxo ligands has been developed; these have demonstrated the ability to hydrogenate naphthalene, anthracene and phenanthrene in good yield in cyclohexane at 80 °C and 1200 psi of H<sub>2</sub>.<sup>[4]</sup> We are working toward the synthesis of [Ta(OC<sub>6</sub>H<sub>3</sub>-Pr<sup>i</sup><sub>2</sub>-2,6)<sub>2</sub>(Cl)(H)<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub>] and will test its ability to hydrogenate phenanthrene for comparison with the results obtained for the heterogeneous hydrogenation by supported Rh/C in scCO<sub>2</sub>.



**Figure 1: Reaction scheme for the hydrogenation of phenanthrene.**

## METHODS AND MATERIALS

Supercritical reactions were carried out in a 25 mL stainless steel reactor. The substrate (phenanthrene; 98%), and the supported catalyst (Rh, 5 wt% (dry) on carbon, wet; Degussa type G106B/W, reduced) was obtained from Aldrich. The reactor was charged with the substrate and catalyst, and the vessel was heated to the desired temperature at which point H<sub>2</sub> gas was added. The reactor was then pressurized with CO<sub>2</sub>. Products were isolated by filtration and analyzed by a 7890A Agilent gas chromatograph in tandem with a 5975C mass spectrometer (GC/MS).

## RESULTS

Results of the hydrogenation reactions using Rh/C in scCO<sub>2</sub> are presented in Table 1. The temperature of 160 °C had been optimized from previous work in the McGrady group. It is evident from Table 1 that the catalyst-to-substrate ratio plays a crucial role in the yield of hydrogenated products. Reactions 5, 6, 7 and 8 were performed for 2, 4, 8 and 16 h

respectively, using a 2:1 (w/w) catalyst-to-substrate ratio and 1500 psi of H<sub>2</sub> gas. Conversion to hydrogenated products in scCO<sub>2</sub> was >97 % with significant yields of the fully hydrogenated perhydrophenanthrene being observed. At a 1:1 ratio (reactions 1, 2, 3 and 4) a lower hydrogen pressure led to higher yields of products; however the fully hydrogenated product was not observed under these conditions.

Table 1: Heterogeneous hydrogenation of phenanthrene using Rh/C at varying times and H<sub>2</sub> pressure in scCO<sub>2</sub> at 160 °C.

Rxn	Catalyst (mg)	Substrate (mg)	Time (hours)	P H <sub>2</sub> (psi)	P CO <sub>2</sub> (psi)	% Conversion to products*	% Fully Hydrogenated*
1	15	15	4	900	2350	9.7	0
2	15	15	8	900	2350	3.2	0
3	25	25	4	900	2350	83.2	0
4	25	25	4	1300	2500	17.1	0
5	50	25	2	1500	2400	99.0	11.4
6	50	25	4	1500	2400	97.8	46.5
7	50	25	8	1500	2500	97.9	36.8
8	50	25	16	1500	2500	49.3	0.6

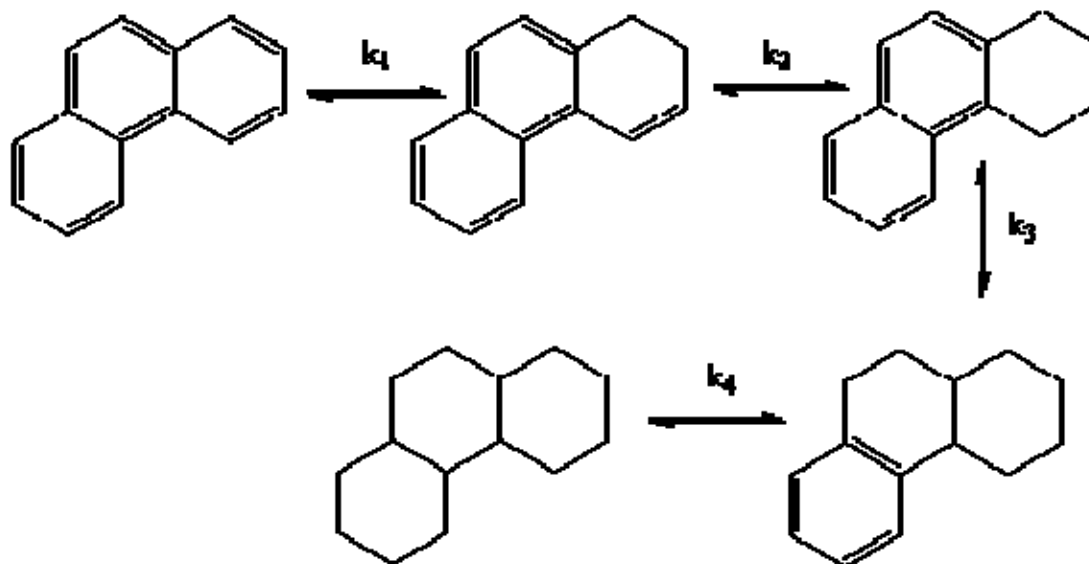
\*analyzed by GC/MS

## CONCLUSIONS

The results in Table 1 reveal a time dependence that implies the existence of an equilibrium that controls the formation of hydrogenated products (Figure 2). It has been previously reported that hydrogenation reactions of PAHs are reversible and exothermic, and complete conversion is often not feasible because of thermodynamic equilibrium limitations<sup>[6]</sup>. Reactions 5, 6, 7 and 8 were carried out for periods between 2 and 16 h, and near-quantitative conversion to products was observed with the exception of 8; however, after 4 h the highest proportion of fully hydrogenated perhydrophenanthrene was observed. We intend to explore these observations further and to monitor the reaction in real time so that equilibrium constants for these reaction parameters can be determined.

Investigations into other heterogeneous catalysts for hydrogenation and ring-opening of phenanthrene and other PAHs are currently underway. This is important due to the inability of noble metal catalysts to withstand poisoning by sulfur<sup>[7]</sup>. In order for these catalysts and CO<sub>2</sub> to be used in commercial processes they must be able to withstand the conditions of the process.

A series of group 5 transition metal hydrido complexes featuring aryloxy ligands will be synthesized and tested as hydrogenation catalysts for phenanthrene. Previous work has demonstrated the ability of these homogeneous catalysts to hydrogenate a range of polycyclic aromatic hydrocarbons in conventional solvents<sup>[4]</sup>. Once synthesized, the rates of reaction will be compared with those heterogeneous systems that have been tested in scCO<sub>2</sub>.



**Figure 2: Equilibrium between phenanthrene starting material and the formation of products during hydrogenation.**

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