ELSEVIER

Journal of Hazardous Materials B126 (2005) 149–157

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Catalytic hydrogenation of polycyclic aromatic hydrocarbons over palladium/γ-Al_2O_3 under mild conditions

Tao Yuan, William D. Marshall *

Department of Food Science and Agricultural Chemistry, Macdonald Campus of McGill University, 21,111 Lakeshore Road, Ste-Anne-de-Bellevue, Qué., Canada H9X 3V9

Received 24 March 2005; received in revised form 1 June 2005; accepted 15 June 2005
Available online 8 August 2005

Abstract

As a prelude to the optimization of a continuous decontamination system, catalytic hydrogenations of selected tri-, tetra- and penta-cyclic aromatic hydrocarbon compounds over commercial alumina supported palladium were investigated under mild conditions (∼90 °C/0.42 MPa H_2) and interpreted in the light of reports from the literature. Acenaphthylene, acenaphthene, anthracene, phenanthrene, chrysene and benzo[α]pyrene were hydrogenated, virtually completely, to saturated polycyclic hydrocarbon compounds with no appreciable evidence of carbon–carbon bond rearrangement during equilibration. With comparable operating conditions, triphenylene was only partially hydrogenated; the central ring remained unsaturated. The effects of reaction temperature, time of equilibration and supporting gases on hydrogenation were evaluated. Whereas near-critical CO_2 had no perceptible influence on rate/course of the reaction, nitrogen decreased the reaction rate somewhat.

Keywords: Polyaromatic hydrocarbons (PAHs); Hydrogenation; Detoxification; Soil remediation

1. Introduction

The polycyclic aromatic hydrocarbons (PAHs) represent a class of organic compounds that consist of two or more fused aromatic rings. Representatives of this class of toxicant can be detected in almost all components of our environment [1]. They are components of coal tar, creosote and crude oil, and are formed by the incomplete combustion of organic materials and as by-products of heat assisted industrial processing. Because of their carcinogenic and mutagenic properties, PAHs have long been regarded as environmental priority pollutants [2] that require metabolic activation to electrophilic intermediates [3–5] and subsequent covalent adduct formation with cellular DNA to elicit their adverse biological activity [6,7]. Although several different activation pathways have been identified, strong evidence points to the prominent role of bay- and fjord-region dihydrodiol epoxides as ultimate mutagenic and carcinogenic metabolites [8] of PAH compounds.

1.1. Hydrogenations of fused rings

The partial saturation of fused ring aromatic compounds does not suffer from as dramatic a loss of resonance stabilization as do mono-ring compounds so that the hydrogenation of naphthalene to 1,2-dihydronaphthalene is exothermic. This accounts for the more facile hydrogenation of polyaromatic hydrocarbon compounds relative to single ring aromatic systems. For high H_2 pressure (1200 psi), homogeneous hydrogenations (100 °C), relative to benzene conversion to cyclohexane (=1) the rates for naphthalene ($C_{10}H_8$) hydrogenation to tetralin ($C_{10}H_{12}$) was 7 whereas subsequent hydrogenation of tetralin to decalin ($C_{10}H_{18}$) was 0.35. Similarly, the relative rate of anthracene ($C_{14}H_{10}$) hydrogenation to tetrahydroanthracene ($C_{14}H_{14}$) was 21 and subsequent hydrogenation to octahydroanthracene was determined to be 3. Hydrogenation of phenanthrene

* Corresponding author. Tel.: +1 514 398 7921; fax: +1 514 398 7977.
E-mail address: william.marshall@mcgill.ca (W.D. Marshall).

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.06.022

($C_{14}H_{10}$) to sym-tetrahydrophenanthrene ($C_{14}H_{14}$) was 1.3 or to asymmetric tetrahydrophenanthrene was 0.7 [9].

There has been extensive research on the catalytic hydroprocessing of lower molecular weight PAHs (predominantly anthracene and phenanthrene) [10–14]. The product distribution of PAHs hydrogenation is highly dependent on catalyst type, temperature and solvent. Hydrogenation processes are believed to be stepwise but intermediates with partially hydrogenated rings are often not detected [15]. For heterogeneous hydrogenation of tri-cyclic substrates, reduction was seen to occur in a ring by ring manner. Phenanthrene, in a series of equilibria, was hydrogenated sequentially to tetra- to octa- and finally to perhydrophenanthrene. The secondary hydrogenation of dihydrophenanthrene was not observed; instead, dehydrogenation to phenanthrene was the major product [16]. Similarly, dihydroanthracene was considered to be equilibrated with anthracene that was hydrogenated, in stepwise fashion, to tetrahydro- to sym- or asymmetric octahydro- and to perhydroanthracene. For hydroaromatics, the temperature above which dehydrogenation was favoured over hydrogenation, decreased with increasing number of fused ring. For phenanthrene, the crossover temperature was determined to be ∼400 °C [17].

The intramolecular rearrangement of hydroaromatic compounds can take two forms corresponding to processes of ring contraction (ex. tetrahydrophenanthrene to its methylcyclopentanic isomer over sulfided Ni-Mo/Al_2O_3 at 430 °C [18]) or the process of ring shift (interconversion of anthracene derivatives and phenanthrene derivatives) that has been observed in the presence of a variety of catalysts at 200–300 °C, [19] in acid at 482 °C [20], thermally induced equilibration [21] or in the presence of $AlCl_3$ [22].

1.2. Supercritical CO_2 as a reaction medium

The use of mixtures of molecular hydrogen with supercritical carbon dioxide ($scCO_2$) as a medium to perform hydrogenation possesses several attractive properties. The use of $scCO_2$ has often been considered to be an ideal phase because of its mild critical properties (T_C = 31 °C, P_C = 7.4 MPa), non-toxicity, non-flammability, modest cost and a lack of restrictive regulations. Molecular hydrogen is completely miscible in near-critical CO_2 [23], and can result in a very high initial rate of reaction – up to 1400 mol of formic acid have been produced from CO_2 per mol of catalyst per hour [24]. The same reaction under identical conditions but in liquid organic solvents is much slower principally the results of decreased diffusion rates and the limited solubility of H_2 in most organic solvents. Solvent polarity of the reaction medium can be fine tuned with ease in the near-critical region (generally 1.05–1.2 T_C [25]) by simply changing the pressure. To achieve suitable substrate solubility, the reaction medium can be modified by adding an inert co-solvent. As an example, acetonitrile can be volume expanded several fold with dense-phase CO_2 in which this solvent is totally miscible. Moreover, the reactants/products can be separated readily from the reaction medium by pressure reduction. Because aromatic hydrogenations are highly exothermic [26], reaction is favoured and selectivities can be increased by operation at lower temperatures yet for hydrogenations on a larger scale some means of heat dissipation can become necessary. The heat capacities of $scCO_2$ can also be pressure-tuned to be more liquid-like [27] and to minimize product hold up. For porous solid catalysts product, selectivity can also be optimized to mitigate pore-diffusion limitations and the accumulation of coke-forming precursors that can inactivate catalytic sites. Catalytic inactivation has been reported during hydrogenations over Pt^0/Al_2O_3 in near-critical CO_2 [28] that might have resulted from the possible formation of one or more possible surface species including formates, carbonates and/or CO in the presence of $CO_2 + H_2$. Several insightful reviews [29–31] have been published recently.

The contamination of soil with PAHs can result from atmospheric fallout, coking and petroleum refining/upgrading wastes, tar and asphalt waste particles, waste disposal and sludge [32] where they are recalcitrant. Despite the fact that PAHs can be biodegraded, their persistence in soil, as measured in terms of half-life, can exceed eight years [33]. Our previous research [34,35] on catalytic hydrodechlorination of pentachlorophenol (PCP), octachloronaphthalene, decachlorobiphenyl and subsequent reduction of phenol, naphthalene or biphenyl by hydrogenation over selected transition metals had demonstrated that palladium on gamma-alumina was the most active of the catalysts evaluated.

As a prelude to the development/optimization of procedures for the continuous detoxification of PAH contaminated particulate matter (soil or sediment) by extraction with supercritical carbon dioxide, the objective of the current study was to investigate the hydrogenation of selected 3–5 fused ring PAHs under mild temperatures and pressures. It was anticipated that with these conditions, hydrogenation (rather than dehydrogenation) would predominate and that hydrocracking reactions and/or rearrangements would be minimized.

2. Experimental

2.1. Chemicals

Acenaphthylene, acenaphthene, anthracene, phenanthrene, triphenylene, chrysene and benzo[α]pyrene, (Fig. 1) all ACS Reagent grade, were obtained from Sigma–Aldrich Co., Oakville, ON. Pure hydrogen gas was purchased from MEGS, Montréal, QC, Pd^0/γ-Al_2O_3 (5%, w/w) was purchased from Alfa-Aesar, Ward Hill, MA, USA (catalog number 11713), and organic solvents were obtained from Fisher Scientific, Ottawa, Ont.

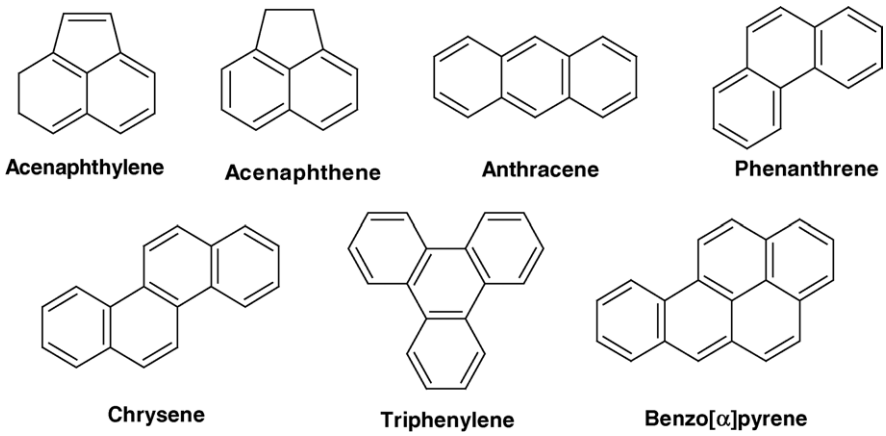

Fig. 1. Structures of selected polyaromatic hydrocarbons (PAHs).

2.2. Reactor and operation

The stainless steel (ss) reactor consisted of a 50 ml, high pressure cylindrical vessel with a demountable top that had been modified with the addition of two ss tubes (1/16 in. i.d.) that served as gas inlet and outlet. The tubes were each terminated with a high pressure needle valve. In operation, substrate (0.5 mg), hexane (1 ml), catalyst (25 mg) and a teflon-coated magnetic stirring bar was added to the vessel and then the vessel was equilibrated in a water bath at the desired operating temperature of the experiment. Pure H_2 gas (0.42 MPa) was added and the reaction was continued for 0.5–6 h. To terminate the reaction, the pressure was released through a silica capillary restrictor (50 μm i.d. × ∼25 cm) into an organic trapping solvent. The trapped reaction products were combined with organic washes from the reaction vessel and monitored by gas chromatography (GC)–MS and –FID.

2.3. GC analysis

GC–MS was performed on a Varian model 3900 gas chromatograph fitted with a model 8400 autosampler and a model 2100T ion trap detector. The DB-5 capillary column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) was eluted with helium at 1.0 ml min^{-1}. After an initial hold for 1 min at 50 °C, the column temperature was ramped, at 10 °C min^{-1} to 300 °C, and held for a further 3 min prior to cool down. The temperature of the injector, transfer line and detector were maintained at 250, 250 and 150 °C, respectively. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the National Institue of Standards and Technology (NIST) or the Saturn mass spectral libraries and corroborated, when available, by co-chromatography with authentic standard. Quantitation of the sample was performed on a Hewlett-Packard Model 5890 gas chromatograph with FID under the identical chromatographic conditions.

3. Results and discussion

3.1. Rationale for the selection of the experimental approach

It was anticipated that PAH contaminated soil might be remediated by extraction with supercritical carbon dioxide. The process would be more attractive if the toxicants were to be detoxified during the extraction process. We have optimized procedures for the detoxification of chlorinated aromatics (PCBs and chlorinated phenols) in $scCO_2$ by hydrodechlorination over bimetallic mixtures (Ag^0/Fe^0, Pd^0/Fe^0, Pd^0/Mg^0) [34] or noble metal catalyst (Pd^0/γ-Al_2O_3, Pt^0/γ-Al_2O_3 or $Ni^0/SiO_2/Al_2O_3$) [35]. Yet extractions do not mobilise only chlorinated aromatics – other classes of non-polar toxicants would be equally susceptible to extraction. It was anticipated that PAH compounds could be detoxified by dearomatization if hydrogen was included in the $scCO_2$ mobile phase.

An advantage of the $scCO_2$ approach would be the complete miscibility of hydrogen gas with this fluid. It was desired to mimic processing in near- or $scCO_2$ with gaseous organic solvent (hexane) as the reaction medium. In consequence, trials were performed in the presence of a large excess of catalyst in a hexane–hydrogen atmosphere. The low operating pressure (0.42 MPa) was anticipated to be sufficient to assure an appreciable hexane liquid phase at all operating temperatures, so that the reaction mixture was stirred vigorously to minimize diffusion limitations.

3.2. Anthracene hydrogenation

The influence of reaction temperature (50–90 °C) was evaluated for the hydrogenation of 0.5 mg (2.8 μmol) anthracene over 25 mg Pd^0/γ-Al_2O_3 during 30 min (Table 1 which summarizes the means ± one relative standard deviation (R.S.D.) of three replicate trials). After this time, the anthracene (Fig. 1) had been hydrogenated virtually

Table 1
Product distributions (mol% + R.S.D.) that resulted from anthracene (0.5 mg, 2.80 μmol) hydrogenation at various temperatures in the presence of Pd^0/γ-Al_2O_3 (25 mg)/H_2 (0.42 MPa), during 0.5 h

Product	50 °C	60 °C	70 °C	80 °C	90 °C
Anthracene, dodecahydro,	0.12 ± 75.3	1.5 ± 55.8	N.D.[a]	N.D.	N.D.
Anthracene, octahydro[b], 1	14.8 ± 2.6	8.2 ± 20.5	N.D.	N.D.	N.D.
Anthracene, octahydro, 2	14.6 ± 12.3	2.4 ± 32.8	N.D.	N.D.	N.D.
Anthracene, octahydro, 3	57.4 ± 3.0	40.4 ± 5.6	5.3 ± 19.0	N.D.	N.D.
Anthracene, octahydro, 4	Trace[c]	Trace	N.D.	N.D.	N.D.
Anthracene,1,2,3,4-tetrahydro,	Trace	Trace	Trace	N.D.	N.D.
Anthracene, tetradecahydro[b], 1	0.50 ± 30.2	9.6 ± 13.0	27.1 ± 3.8	37.0 ± 2.7	36.4 ± 5.7
Anthracene, tetradecahydro, 2	N.D.	N.D.	Trace[b]	Trace	Trace
Anthracene, tetradecahydro, 3	1.6 ± 59.3	18.4 ± 11.1	53.4 ± 4.3	68.8 ± 4.2	60.2 ± 2.2
Anthracene, tetradecahydro, 4	N.D.	N.D.	Trace	Trace	Trace
Anthracene, tetradecahydro, 5	0.10 ± 45.4	1.7 ± 21.3	7.8 ± 11.7	6.6 ± 32.8	5.8 ± 6.8
Anthracene, tetradecahydro, 6	N.D.	0.92 ± 13.8	1.5 ± 2.2	1.9 ± 26.0	1.7 ± 13.2
Recovery (%)	89.2 ± 4.5	83.2 ± 3.0	95.1 ± 4.8	114.3 ± 6.4	104.1 ± 3.1

[a] N.D., none detected.
[b] Anthracene, octahydro, compounds 1–4 and tetradecahydro, compounds 1–6 are listed in order of elution under the chromatographic conditions of the experiment.
[c] Trace (less than the limit of quantitation, 0.05 mol%).

completely at the higher operating temperatures, but partially hydrogenated intermediates were detected in the product mixtures from reactions at 50–70 °C. The products were 1,2,3,4-tetrahydroanthracene (present in trace quantity at lower reaction temperatures), octahydroanthracene (four isomers detected) and tetradecahydroanthracene (six isomer detected). Products of hydrocracking that might have included alkyl-naphthalenes or their reduced congeners alkyl-tetralins or -decalins [36] were not detected. Neither were there any products of mass greater than 192.3 (perhydroanthracene). Hydrogenation at 80 or 90 °C resulted in complete hydrogenation to tetradecahydroanthracene of which two isomers dominated (Table 1). None of the mass spectra of intermediates or products were characterized by a prominent fragment (or base peak) corresponding to the loss of 15 atomic mass units (amu) from the molecular ion which suggested that ring contraction (to form methylcyclopentane derivatives) did not contribute to the distribution of products. The mixture of isomer of perhydrogenated compounds was somewhat troubling in that only five configurational isomers of perhydroanthracene are known compounds [37]. It seems possible that the sixth isomer resulted from an intramolecular isomerization to form a hydrogenated phenanthrene specie. The octahydro isomer mixture apparently contained both symmetric and asymmetric species as evidenced by fragments corresponding to the loss of 43 and 57 amu from the molecular ion and indicated the presence of two fused saturated rings [16] and must have come from asymmetric isomers. The mass spectra of other peaks contained fragments corresponding to *m*/*e* 28 amu characteristic of a saturated ring fused with an aromatic ring [16] and are presumed to have come from symmetrical octahydro isomers. It seems possible that the traces of the fourth isomer (in order of elution) corresponded to symmetrical octahydrohydrophenanthrene. The recovery of products was judged to be acceptable given the fact that quantitation was based on the FID response to the substrate rather than to each of the products.

Extended reaction times (1 or 2 h) was assessed at 70 °C (Table 2). After 1 h, all the substrate had been transformed to perhydroanthracene species. Hydrogenation for a further 1 h did not change the distribution of products perceptibly. The same two tetradecahydroanthracene isomers dominated the distribution. For extended reaction with these conditions, hydrogenation was complete, virtually all the substrate was accounted for among the products and no evidence hydrocracking or addition product formation was obtained. At 90 °C, complete anthracene hydrogenation was observed after 20 min and in contrast, the absence of catalyst resulted in the production of only traces (∼0.9 mol%, Table 2) of tetrahydro specie. When chromatographically homogeneous octahydroanthracene served as substrate, the same six isomers of perhydro species were observed as the only reaction products after 20 min at 90 °C/0.42 MPa H_2 (data not shown).

3.3. Phenanthrene, acenaphthene or acenaphthalene hydrogenation

As was observed for anthracene, phenanthrene hydrogenation, at 90 °C, 0.42 MPa H_2, over Pd^0/γ-Al_2O_3 catalyst was virtually complete within 20 min (Table 3). Five tetradecahydrophenanthrene isomers were detected, three of which had formed in appreciable quantities. Six structural isomers have been reported for perhydrophenanthrene [38]. Two octahydrophenanthrene isomers that had formed after 10 min of hydrogenation had disappeared in the subsequent sampling times.

As anticipated, the hydrogenation (90 °C, 0.42 MPa H_2) of a mixture of acenaphthylene (75%) and acenaphthene (20%) to totally hydrogenated products dodecahydroacenaphthylene (five isomers detected, Table 4) proved to be appreciably more facile than the two other three fused ring

Table 2
Product distribution (mol% + R.S.D.) that resulted from anthracene (0.5 mg, 2.8 μmol) in H_2 (0.42 MPa) in the presence/absence of 25 mg Pd^0/γ-Al_2O_3 catalyst for 1–2 h at 70 °C or 10–30 min at 90 °C

Products	1 h (70 °C)	2 h (70 °C)	10 min (90 °C)	20 min (90 °C)	30 min (90 °C, no catalyst)
Anthracene	N.D.[a]	N.D.	N.D.	N.D.	88.2 ± 4.0
Anthracene, dodecahydro,	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene, octahydro, 1	N.D.	N.D.	0.26 ± 110.6	N.D.	N.D.
Anthracene, octahydro, 2	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene, octahydro, 3	N.D.	N.D.	2.2 ± 108.7	N.D.	N.D.
Anthracene, octahydro, 4	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene, tetradecahydro, 1	31.0 ± 9.0	32.7 ± 6.9	33.8 ± 9.1	39.6 ± 7.0	N.D.
Anthracene, tetradecahydro, 2	Trace[b]	Trace	Trace	Trace	N.D.
Anthracene, tetradecahydro, 3	64.2 ± 7.8	62.2 ± 14.6	54.0 ± 11.3	65.7 ± 5.6	N.D.
Anthracene, tetradecahydro, 4	Trace	Trace	Trace	Trace	N.D.
Anthracene, tetradecahydro, 5	7.4 ± 23.7	7.2 ± 6.3	5.1 ± 22.6	6.6 ± 4.5	N.D.
Anthracene, tetradecahydro, 6	2.0 ± 21.7	1.9 ± 26.4	1.4 ± 35.7	2.0 ± 3.5	N.D.
Anthracene, 1,2,3,4-tetrahydro	N.D.	N.D.	N.D.	N.D.	0.88 ± 33.8
Recovery (%)	104.6 ± 5.7	104.0 ± 11.3	96.6 ± 7.9	114.5 ± 5.9	89.0 ± 3.9

[a] N.D., none detected.
[b] Trace (less than limit of quantitation, 0.05 mol%).

Table 3
Distributions of products (mol% ± R.S.D.) that resulted from phenanthrene (0.5 mg, 2.80 μmol) in H_2 atmosphere (0.42 MPa) at 90 °C in the presence/absence of 25 mg Pd^0/γ-Al_2O_3 catalyst for 10–30 min

Products	10 min	20 min	30 min	30 min (no catalyst)
Phenanthrene	0.91 ± 11.4	N.D.[a]	N.D.	98.7 ± 7.6
Phenanthrene, octahydro-, 1	<0.30	N.D.	N.D.	N.D.
Phenanthrene, octahydro-, 2	20.0 ± 3.2	N.D.	N.D.	N.D.
Phenanthrene, tetradecahydro-, 1	16.1 ± 3.7	29.6 ± 5.5	29.0 ± 5.9	N.D.
Phenanthrene, tetradecahydro-, 2	15.4 ± 3.1	27.9 ± 3.1	25.7 ± 4.2	N.D.
Phenanthrene, tetradecahydro-, 3	31.1 ± 2.8	56.8 ± 3.3	51.5 ± 4.9	N.D.
Phenanthrene, tetradecahydro-, 4	1.0 ± 7.6	1.7 ± 30.6	1.6 ± 12.1	N.D.
Phenanthrene, tetradecahydro-, 5	1.1 ± 11.2	2.1 ± 8.9	2.0 ± 16.5	N.D.
Perhydrophenanthrene isomers	64.7			
Recovery (mol%)	85.6 ± 2.6	118.2 ± 2.7	109.8 ± 5.0	98.7 ± 7.6

Results based on phenanthrene calibration.
[a] N.D., none detected.

systems (anthracene and phenanthrene). On the basis of bond length considerations, acenaphthalene can best be described as a naphthalene weakly conjugated with an outer double bond. The protons on C(1) and C(2) of the outer double bond resonate at lower field than the aromatic protons of the naphthalene moiety and from neutron activation experiments, the C(1)–C(2) bond is longer than a normal double bond which may reflect the strain imposed by the naphthalene framework

Table 4
Products distribution (mol% ± R.S.D.) that resulted from the of acenaphthylene 0.5 mg (3.9 μmol) and 0.13 mg (0.87 μmol) acenaphthene at 90 °C, H_2 (0.42 MPa) in the presence/absence of 25 mg Pd^0/γ-Al_2O_3 for 3–30 min

Products	3 min	5 min	15 min	30 min (no catalyst)
Acenaphthylene	N.D.	N.D.	N.D.	12.6 ± 63.5
Acenaphthene	N.D.	N.D.	N.D.	96.3 ± 5.2
Acenaphthylene, decahydro 1	19.7 ± 10.3	N.D.[a]	N.D.	N.D.
Acenaphthylene, decahydro 2	2.7 ± 6.2	N.D.	N.D.	N.D.
Acenaphthylene, dodecahydro[b] 1	33.1 ± 11.4	60.82 ± 3.2	64.71 ± 3.3	N.D.
Acenaphthylene, dodecahydro 2	3.70 ± 6.4	6.79 ± 52.2	9.20 ± 121.2	N.D.
Acenaphthylene, dodecahydro 3	27.6 ± 10.2	34.04 ± 2.9	31.8 ± 28.6	N.D.
Acenaphthylene, dodecahydro 4	N.D.	12.21 ± 5.9	11.92 ± 3.2	N.D.
Acenaphthylene, dodecahydro 5	4.20 ± 11.2	5.15 ± 1.8	5.16 ± 4. 8	N.D.
Acenaphthylene, hexahydro	19.73 ± 8.1	N.D.	N.D.	3.0 ± 5.1
Recovery (%)	110.9 ± 8.6	119.0 ± 2.5	122.8 ± 2.3	111.8 ± 7.2

Quantitation was based on calibration with acenaphthylene.
[a] N.D., none detected.
[b] Isomers of perhydroacenaphylene are listed in order of increasing chromatographic retention.

on the double bond [39]. Furthermore, it is known that the resonance energy (RE) for acenaphthalene is only slightly higher than the RE for naphthalene [40] indicating that the aromatic character comes mainly from the naphthalene moiety. The hydrogenation process was essentially complete within 5 min. After 3 min of reaction, partially hydrogenated products decahydro- (two isomers) and hexahydroacenaphthylene were detected. Presumably, the two isomers of the decahydro-species corresponded to *cis* and *trans* ring junctions within the two saturated rings; the hexahydro species presumably was 1,2,2a,3,4,5-hexahydroacenaphthalene [41] and the increased reaction rate reflected the increased strain inherent in the tri-cyclic 6:6:5 fused ring system.

3.4. Chrysene or triphenylene hydrogenation

Chrysene and triphenylene were selected for evaluation as representatives of tetra-cyclic aromatic compounds. For chrysene, the same hydrogenation conditions (90 °C/0.42 MPa H_2), resulted in complete hydrogenated to octadecahydrochrysenes (seven isomers detected) in 1.5 h. Two dodecahydrochrysene isomers, that were detected after 1 h of reaction, were absent after 1.5 h of hydrogenation and only perhydrochrysene was observed (Table 5A). Presumably the two isomers of dodecahydro-intermediate corresponded to products in which either a terminal ring or an internal ring remained unsaturated. Of the two dodecahydrochrysene isomers, the structure with an internal aromatic ring has been reported to result in formation of a prominent propyl fragment (M-43) as well as a pronounced ethylenic fragment (M-28) [18]. The other isomer was characterized by a prominent M-82 fragment and the absence of an ethylenic fragment. After 1 h, the ratio of the isomer with the internal aromatic ring relative to the isomer with a terminal aromatic ring was ∼3 to 1.

By contrast, triphenylene was hydrogenated less efficiently (Table 5B). The main product was dodecahydrotriphenylene ($C_{18}H_{24}$) which accumulated rapidly within the reaction mixture. Only a single isomer was detected, which presumably was the structure with the central ring unsaturated and other three peripheral rings hydrogenated. There was a trace (0.08 mol%) of completely hydrogenated product octadecahydrotriphenylene after 0.5 h that increased gradually to ∼17% over 6 h. The decreased rate of hydrogenation of the internal ring is thought to arise from the puckered peripheral rings that impede access of intermediate to the catalyst surface active site. It is also generally accepted that hydrogenation of substituted benzene rings is appreciably slower than the hydrogenation of polycyclic systems but in this case, the decrease in rate is more dramatic than for the other systems described above. The apparent recovery of excess substrate (>100 mol%, Table 5B) is considered to reflect the fact that quantitation was performed with triphenylene rather than with hydrogenated product(s) for lack of an appropriate standards. The presumption that FID response to product can be approximated by FID response to substrate was not realized in this system.

3.5. Benzo[α]pyrene hydrogenation

Arbitrarily, benzo[α]pyrene ($C_{20}H_{12}$) was chosen to represent penta-cyclic fused ring systems. This substrate was completely hydrogenated to fully saturated products (eicosahydrobenzo[α]pyrene, $C_{20}H_{32}$, 12 isomers detected, six of which were dominant). For shorter reaction times (0.5 or 2 h) at 90 °C, partially hydrogenated products tetradecahydrobenzo[α]pyrene ($C_{20}H_{26}$) were detected (eight isomers) that decreased with extended reaction to form the perhydrogenated products. No other partially hydrogenated intermediates were observed in the trials at 90 °C (Table 6) and no hydrogenation was evident, after 2 h, in the absence of catalyst (data not shown). Moderate increases in temperature caused appreciable changes in the product distribution so that for extended reaction time (4 h), dehy-

Table 5
Distribution of products (mol% ± R.S.D.[a]) that resulted from the hydrogenation of tetra-cyclic ring compounds, chrysene (0.5 mg) or triphenylene (0.5 mg) in H_2 (0.42 MPa) in the presence/absence of 25 mg Pd^0/γ-Al_2O_3 catalyst for 1–6 h at at 90 °C

Products	30 min	1 h	1.5 h	2 h	6 h	2 h (no catalyst)
A						
Chrysene	N.P.[b]	N.D.[c]	N.D.	N.P.	N.P.	91.9 ± 5.9
Chrysene, decahydro	N.P.	13.2 ± 26.6	N.D.	N.P.	N.P.	N.D.
Chrysene, octadecahydro	N.P.	94.3 ± 8.3	106.0 ± 6.2	N.P.	N.P.	N.D.
Recovery (%)	N.P.	107.6 ± 5.2	106.0 ± 6.2	N.P.	N.P.	91.9 ± 5.9
B						
Triphenylene	N.D.	N.P.	N.P.	N.D.	N.D.	95.7 ± 3.8
Triphenylene, dodecahydro	124.6 ± 20.6	N.P.	N.P.	134.4 ± 11.6	104.7 ± 10.1	N.D.
Triphenylene, octadecahydro	0.08	N.P.	N.P.	15.0 ± 37.5	17.2 ± 6.7	N.D.
Recovery (%)	124.6 ± 20.6	N.P.	N.P.	149.4 ± 11.4	121.9 ± 9.5	95.7 ± 3.8

Quantitation was based on A, chrysene or B, triphenylene calibration.
[a] R.S.D., one relative standard deviation based on three replicate trials.
[b] N.P., not performed.
[c] N.D., none detected.

Table 6
Distribution of products (mol%) of benzo[α]pyrene (0.5 mg, 2.0 μmol) hydrogenation in H_2 (0.42 MPa) at 90 °C in the presence/absence of 25 mg Pd^0/γ-Al_2O_3 catalyst for 0.5–4 h

Temperature (°C)/time (h)	Eicosahydro	Tetradeca	Dodeca	Deca	Octa	∑ products
90/0.5	8	74	N.D.[a]	N.D.	N.D.	82
90/2	70	12	N.D.	N.D.	N.D.	82
90/4	113	N.D.	N.D.	N.D.	N.D.	113
120/0.5	6	93	N.D.	1	N.D.	100
120/2	7	91	N.D.	2	N.D.	100
120/4	16	62	N.D.	1	N.D.	79
150/0.5	1	80	N.D.	19	N.D.	100
150/2	2	64	0.6	32	2	101
150/4	10	61	1	28	N.D.	100
200/0.5	3	85	2	8	3	101
200/2	3	12	5	24	56	100
200/4	9	84	1	5	0.6	99
250/0.5	N.D.	85	1	12	1	99
250/2	N.D.	4	1	11	83	99
250/4	N.D.	0.5	7	50	42	97

Results were based on calibration with benzo[α]pyrene.
[a] N.D., none detected.

drogenation became increasingly favoured. At 120, 150 or 200 °C tetradecahydro products dominated the product mixture and at 250 °C, decahydro isomers dominated. Thus, complete hydrogenation was favoured by lower temperature and an extended reaction time.

3.6. Hydrogenation of phenanthrene in admixture with carbon dioxide or nitrogen

A final series of experiments evaluated the influence of carbon dioxide on the rate/course of phenanthrene hydrogenation in the presence of excess H_2 (0.42 MPa) at 90 °C (Table 7). The reaction mixture was over-pressured with CO_2 (to 0.42–24.1 MPa) or N_2 (to 10.3 MPa) and hydrogenated at 90 °C for 10 min. Whereas increased pressure caused somewhat less efficient trapping of products, the fraction of totally hydrogenated products (perhydrophenanthrenes) among the product mixture remained constant. Thus, the presence of added CO_2 had no perceptible influence on the rate/course of the hydrogenation. In previous studies of the hydrodechlorination (HDC) of pentachlorophenol with this catalyst, it had been observed that rates of overall reaction, HDC plus dearomatization, were reduced somewhat by the presence of supercritical carbon dioxide [35]. It is considered that the active surface sites for hydrodechlorination and for hydrogenation/dearomatization are different. Seemingly, the hydrogenation site(s) were not influenced by added CO_2 but surprisingly, the presence of N_2 (10.3 MPa) caused the rate (but not the course) of hydrogenation to be decreased for this substrate.

Table 7
Recoveries (mol% ± R.S.D.[a]) from the hydrogenation of phenanthrene (0.5 mg) at 90 °C over Pd^0/γ-Al_2O_3 (25 mg) in H_2 (0.42 MPa) that had been over-pressured with CO_2 (to 0.42–24.1 MPa) or N_2 (to 10.3 MPa)

Products	CO_2 (MPa)					N_2 (MPa)
	0.42	3.4	10.3	17.2	24.1	10.3
Phenanthrene, tetradecahydro- 1	12.8 ± 19.5	14.7 ± 4.6	10.0 ± 24.0	9.0 ± 3.4	10.3 ± 4.2	9.9 ± 2.9
Phenanthrene, tetradecahydro- 2	14.3 ± 14.8	15.5 ± 1.0	11.6 ± 13.9	9.8 ± 2.4	10.9 ± 4.9	10.4 ± 6.0
Phenanthrene, tetradecahydro- 3	23.7 ± 15.0	26.7 ± 1.0	21.7 ± 11.3	13.6 ± 6.5	16.0 ± 6.7	14.1 ± 7.6
Phenanthrene, tetradecahydro- 4	7.6 ± 5.4	7.5 ± 5.4	7.7 ± 2.7	7.3 ± 5.4	7.4 ± 3.5	7.2 ± 1.9
Phenanthrene, tetradecahydro- 5	8.7 ± 4.2	9.4 ± 0.9	8.2 ± 2.6	8.3 ± 2.0	8.6 ± 3.7	7.4 ± 2.3
Subtotal	67.0 ± 10.4	73.7 ± 1.1	59.3 ± 5.6	48.2 ± 3.0	53.1 ± 4.2	49.0 ± 3.5
Phenanthrene, octahydro- 1	10.2 ± 6.8	9.9 ± 2.9	11.1 ± 8.9	10.9 ± 5.3	10.2 ± 10.2	15.6 ± 16.0
Phenanthrene, octahydro- 2	33.7 ± 14.8	32.3 ± 14.3	17.0 ± 2.1	16.3 ± 2.9	17.3 ± 4.6	44.4 ± 2.7
Subtotal	43.9 ± 12.1	42.1 ± 10.3	28.1 ± 4.8	17.3 ± 4.6	27.5 ± 6.4	60.0 ± 6.1
Total	110.9 ± 2.2	115.9 ± 4.4	87.4 ± 2.2	75.3 ± 3.2	80.6 ± 4.5	109.0 ± 4.9
Ratio (perhydro/total)	60.0 ± 8.7	63.7 ± 3.4	67.8 ± 3.3	63.9 ± 0.4	65.9 ± 1.6	44.9 ± 1.5

[a] R.S.D., one relative standard deviation based on three replicate trials.

4. Conclusion

At moderate temperature, the catalytic hydrogenation of lower molecular weight PAH compounds over palladium was highly selective and efficient. PAHs were readily reduced to saturated hydrocarbons without hydrocracking to form alkylated hydrocycle(s). The greater the number of fused rings in the substrate, the longer the reaction time needed to achieve complete hydrogenation. Apparently, the terminal rings of the substrates were hydrogenated more rapidly than the interior ring(s) and substituted benzenic intermediates were hydrogenated more slowly than their polyaromatic substrates. At higher temperature, partial hydrogenation was increasingly favoured. None the less, the toxicities of even partially hydrogenated intermediates can be anticipated to be reduced appreciably relative to their polyaromatic substrates. However, during soil remediation, noble metal catalysts are prone to poisoning and masking of active sites by volatile compounds of sulfur, chlorine, silicon, phosphorus and heavy metals.

Acknowledgement

Financial support from the Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

References

[1] A. Bjørseth (Ed.), Handbook of Polycyclic Aromatic Hydrocarbons, Marcel Dekker, Inc., New York, 1983.
[2] L.H. Keith, W.A. Telliard, ES&T Special Report: Priority pollutants: I-a perspective view, Environ. Sci. Technol. 13 (1979) 416–423.
[3] D.R. Thakker, H. Yagi, W. Levin, A.W. Wood, A.H. Conney, D.M. Jerina, Polycyclic aromatic hydrocarbons: metabolic activation to ultimate carcinogens, in: M.W. Anders (Ed.), Bioactivation of Foreign Compounds, Academic Press, New York, 1985, pp. 142–177.
[4] E.L. Cavalieri, E.G. Rogan, The approach to understanding aromatic hydrocarbon carcinogenesis. The central role of radical cations in metabolic activation, Pharmacol. Ther. 55 (1992) 183–199.
[5] D.H. Phillips, P.I. Grover, Polycyclic hydrocarbon activation: bay regions and beyond, Drug Metab. Rev. 26 (1994) 443–467.
[6] J. Szeliga, A. Dripple, DNA adduct formation by polycyclic aromatic hydrocarbon dihydrodiol epoxides, Chem. Res. Toxicol. 11 (1998) 1–11.
[7] B. Jernström, A. Gräslund, Covalent binding of benzo[a]pyrene 7,8-dihydrodiol 9,10-epoxides to DNA: molecular structures, induced mutations and biological consequences, Biophys. Chem. 49 (1994) 185–199.
[8] P.G. Wislocki, A.H.Y. Lu, Carcinogenicity of proximate and ultimate carcinogens of polycyclic aromatic hydrocarbons, in: S.K. Yang, D.B. Silverman (Eds.), Hydrocarbon Carcinogenesis: Structure–Activity Relationships, CRC Press, Boca Raton, FL, 1994, pp. 1–58.
[9] I.P. Rothwell, A new generation of homogeneous arene hydrogenation catalysts, Chem. Commun. (1997) 1331–1338.
[10] S.S. Salim, A.T. Bell, Effects of Lewis acid catalysts on the hydrogenation and cracking of three-ring aromatic and hydroaromatic structures related to coal, Fuel 63 (1984) 469–476.
[11] C.M. Lee, C.N. Satterfield, Effect of ammonia on the hydrogenation of phenanthrene during the hydrodenitrogenation of quinoline, Energy Fuel 7 (1993) 978–980.
[12] H.M. Feder, J. Halpern, Mechanism of the cobalt carbonyl-catalyzed homogeneous hydrogenation of aromatic hydrocarbons, J. Am. Chem. Soc. 97 (1975) 7186–7188.
[13] M.J. Girgis, B.C. Gates, Catalytic hydroprocessing of simulated heavy coal liquids. 1. Reactivities of aromatic hydrocarbons and sulfur and oxygen heterocyclic compounds, Ind. Eng. Chem. Res. 33 (1994) 1098.
[14] R.N. Landau, S.C. Korré, M. Neurock, M.T. Kline, in: M.T. Oballa, S.S. Shih (Eds.), Catalytic Hydroprocessing of Petroleum Distillates, Marcel Dekker, New York, 1994, pp. 421–432.
[15] C. Schuth, M. Reinhard, Hydrodechlorination and hydrogenation of aromatic compounds over palladium on alumina in hydrogen-saturated water, Appl. Catal. B: Environ. 18 (1998) 215–221.
[16] S.C. Korré, M.T. Kline, R.J. Quann, Polynuclear aromatic hydrocarbons hydrogenation. 1. experimental reaction pathways and kinetics, Ind. Eng. Chem. Res. 34 (1995) 101–107.
[17] R.P. Dutta, H.H. Schobert, Hydrogenation/dehydrogenation of polycyclic aromatic hydrocarbons using ammonium tetrathiomolybdate as catalyst precursor, Catal. Today 31 (1996) 65–77.
[18] J.-L. Lemberton, M. Guisnet, Phenanthrene hydroconversion as a potential test reaction for the hydrogenating and cracking properties of coal hydroliquefaction catalysts, Appl. Catal. 13 (1984) 181–192.
[19] W.-C. Lai, C. Song, A. van-Duin, J.W. de Leeuw, Ring-shift isomerization of sym-octahydrophenanthrene into sym-octahydroanthracene. Effects of zeolite catalysts and equilibrium compositions, Catal. Today 31 (1996) 145–161.
[20] B.R. Cook, S.G. Colgrove, Anthracene isomerization over amorphous silica-alumina: a novel hydrogen transfer reaction, Prepr. Am. Chem. Soc. Div. Petrol. Chem. 39 (1994) 372–378.
[21] C.J. Pope, W.A. Peters, J.B. Howard, Thermodynamic driving forces for PAH isomerization and growth during thermal treatment of polluted soils, J. Hazard. Mater. B79 (2000) 189–208.
[22] S.D. Kong, C.Y. Lee, B.R. Yoo, M.E. Lee, H.N. Jung, Friedel-Crafts type alkylation of 1,2,3,4,5,6,7,8-octahydroanthracene with vinylchlorosilanes: synthesis of mono, bis[2-(chlorosilyl)ethyl]-1,2,3,4,5,6,7,8-octahydroanthracenes, Bull. Korean Chem. Soc. 23 (2002) 1213.
[23] C.Y. Tsang, W.B. Street, Phase equilibriums in the hydrogen/carbon dioxide system at temperatures from 220 to 290 K and pressures to 172 MPa, Chem. Eng. Sci. 36 (1981) 993–1000.
[24] P.G. Jessop, T. Ikarlya, R. Noyori, Homogeneous catalytic hydrogenation of supercritical carbon dioxide, Nature (London) 368 (1994) 231–233.
[25] B. Subramaniam, C.J. Lyon, V. Arunajatesan, Environmentally benign multiphase catalysis with dense phase carbon dioxide, Appl. Catal. B: Environ. 37 (2002) 279–292.
[26] C. Song, Designing sulfur-resistant, noble-metal hydrotreating catalysts, CHEMTECH 29 (1999) 26–30.
[27] V. Arunajatesan, B. Subramaniam, K.W. Hutchenson, F.E. Herkes, Fixed-bed hydrogenation of organic compounds in supercritical carbon dioxide, Chem. Eng. Sci. 56 (2001) 1363–1389.
[28] B. Minder, T. Mallat, K.H. Pickel, K. Steiner, A. Baiker, Enantioselective hydrogenation of ethyl pyruvate in supercritical fluids, Catal. Lett. 34 (1995) 1–9.
[29] P.E. Savage, S. Gopalan, T.I. Mizan, C.J. Martino, E.E. Brock, Reactions at supercritical conditions: applications and fundamentals, AIChE 41 (1995) 1723–1778.
[30] A. Baiker, Supercritical fluids in heterogeneous catalysis, Chem. Rev. 99 (1999) 453–473.
[31] B. Subramaniam, Enhancing the stability of porous catalysts with supercritical reaction media, Appl. Catal. A. Gen. 212 (2001) 199–213.
[32] A. Germain, F. Perron, R. Van Collie, PAHs in the Environment: fate, ecotoxicity and regulations: assessment report on PAHs under

the Canadian environmental protection act priority substance list, Environment Canada, Quebec Region, Montreal, Quebec, 1993, 104 pp.
[33] S.R. Wild, M.L. Berrow, K.C. Jones, The persistence of polynuclear aromatic hydrocarbons (PAHs) in sewage sludge amended agricultural soils, Environ. Pollut. 72 (1991) 141–157.
[34] Q. Wu, T. Yuan, W.D. Marshall, Approaches to soil remediation with green procedures, in: A.S. Gopalan, C.M. Wai, H.K. Jacobs (Eds.), Supercritical Carbon Dioxide; Separations and Processes ACS Symposium Series 860, American Chemical Society, Washington, DC, 2003, pp. 172–186.
[35] T. Yuan, A. Majid, W.D. Marshall, Detoxification of aryl-organochlorine compounds by catalytic reduction in supercritical carbon dioxide, Green Chem. 5 (2003) 25–29.
[36] J.-L. Lemberton, M. Guisnet, Phenanthrene hydroconversion as a potential test reaction for the hydrogenating and cracking properties of coal hydroliquefaction catalysts, Appl. Catal. 13 (1984) 181–192.
[37] R.L. Clarke, The preparation of trans-anti-trans-perhydroanthracene, J. Am. Chem. Soc. 83 (1961) 965–968.
[38] N.L. Allinger, B.J. Gorden, I.J. Tyminski, M.T. Wuesthoff, Conformational analysis. LXX. Perhydrophenanthrenes, J. Org. Chem. 67 (1971) 739.
[39] R.A. Wood, T.R. Welberry, A.D. Rae, Crystal structure of acenaphthylene at 80 K by neutron diffraction, J. Chem. Soc. Perkin Trans. 2 (1985) 451–456.
[40] J.P. Gastmans, A.F. Gastmans, M.H.M. Ferraz, Study of aromaticity by Hueckel theory, Tetrahydron 33 (1977) 2205–2213.
[41] J.S. Yu, B.C. Ankianiec, I.P. Rothwell, M.T. Nguyen, All-cis catalytic hydrogenation of polynuclear aromatic hydrocarbons by Group 5 metal aryl oxide compounds, J. Am. Chem. Soc. 114 (1992) 1927–1929.