

ON THE NATURE OF HYDROAROMATIC HYDROGEN IN MODEL COMPOUNDS AND IN COAL

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Keywords: Catalytic Dehydrogenation, Hydroaromatic Hydrogen, Hydrogen Evolution/Transfer

ABSTRACT

The catalytic dehydrogenation of coal to yield molecular hydrogen using palladium on a support has been investigated by several workers. However, little has been reported on elucidation of the nature of the dehydrogenation reaction, the ease of removal of hydroaromatic hydrogen from different structural components or the effects of solvents of different boiling points, reduction potentials, hydrogen transfer ability, or the mechanism of hydrogen removal. The present study used model hydroaromatic compounds to gain information on the ease of catalytic removal of hydrogen either as H₂ or to a hydrogen acceptor. The course of the dehydrogenation of a number of model compounds was found to involve hydrogen transfer to intermediates, some of which have been identified. A mechanism for the palladium-catalyzed removal of hydrogen is proposed. The use of a hydrogen acceptor has permitted use of low-boiling solvents so as to minimize side reactions. Catalytic dehydrogenation, in addition to gaining information on hydrogen transfer to coal from hydroaromatic compounds, promises to be a valuable analytical technique to determine the amount and nature of hydroaromatic hydrogen in coal, recycle oils and heavy petroleum residues.

INTRODUCTION

The sources of hydrogen in direct coal liquefaction are molecular hydrogen and hydrogen in hydroaromatic structures in added solvents, recycle oils or in coal itself. It is important to have a measure of donatable hydrogen atoms available in hydroaromatic structures in coal and in oils derived from coal. Few efforts have been directed towards developing a direct method for determination of the nature and reactivity of hydroaromatic hydrogen that exists in coal. It is generally accepted that the main hydrogen sources in coal liquefaction are hydroaromatic structures containing two or more cyclic rings. Hydroaromatics may contain two available hydrogen atoms as in 9,10-dihydroanthracene (9,10-DHA), four as in a tetrahydroanthracene (THA), six as in a corresponding hexahydro compound (HHA) or eight as in an octahydroanthracene (OHA). Determination of the relative rates of hydrogen donation of hydroaromatics in recycle solvents is of particular important in achieving insights into the chemistry of coal liquefaction.

¹H-NMR and ¹³C-NMR⁽¹⁾ techniques have been used for the evaluation of hydroaromatic hydrogen. This approach can be applied to distillate fractions, but the residual material gives diffuse spectra and analysis becomes uncertain.

Reggel and coworkers^[2,3] studied the catalytic dehydrogenation of coal using a 5% Pd/CaCO₃ catalyst at the boiling point of a solvent. They found the compound phenanthridine (b.p. 350 °C), an excellent coal solvent, to be the most useful vehicle. It appeared that solvents with low reduction potentials were better than vehicles of higher reduction potentials in the removal of hydrogen from coal. With this technique, Reggel et al. concluded that high rank coals contain considerable hydroaromatic hydrogen with a maximum of about 40 atoms of hydrogen removed per 100 carbon atoms at coals of about 76% carbon (maf). Much of their work was aimed at studying coal structure and it was suggested that lignite and subbituminous coal contain substituted benzene rings with few hydroaromatic structures.

Heredy et al^[4] felt that the use of high boiling solvents such as phenanthridine, which is also a polar solvent, might tend to adduction and condensation reactions leading to an incorrect measurement of hydroaromatic hydrogen.

The objectives of the present work are to study the catalytic dehydrogenation of model compounds and to relate the results to the catalytic dehydrogenation of coal, recycle solvents and liquefaction residues and to determine the fate of hydroaromatic hydrogen during these reactions. Kinetic analysis and the search for possible mechanistic pathways in catalytic dehydrogenation are also important aims of this research. In addition, these studies promise to shed light on the interchange and transfer of hydrogen involved between aromatic and hydroaromatic structures during coal liquefaction. It is hoped that an analytic method for determination and differentiation of hydroaromatic hydrogen will emerge from this research together with difficult to obtain information on the fate of hydrogen atoms attached to polynuclear systems during the liquefaction of coal.

We first investigated the effect of various high boiling solvents on the catalytic dehydrogenation of a number of model hydroaromatic compounds containing trinuclear polycyclic rings. Removal of hydrogen appears to be affected by both the boiling point of the vehicle and its reduction potential. We then found that solvents that boil as low as 245 °C could be used in the catalytic dehydrogenation of these model compounds if we added a good hydrogen acceptor such as stilbene. This unsaturated compound readily accepts hydrogen atoms to form bibenzyl under our typical catalytic dehydrogenation conditions.

EXPERIMENTAL

The dehydrogenation system is designed to provide for automatic data recording. Reactions were carried out in a three-necked flask at atmospheric pressure. The palladium catalyst was reduced with flowing hydrogen at 150°C for one hour prior to reaction. After the flask was cooled to room temperature under hydrogen, the model compound and vehicle were charged into the flask containing an Alnico stirring bar. The system was purged with He for 20 minutes and the flask then fitted with a mantle and heated. Evolved gases from the reaction were taken from the middle neck and collected over mercury in a burette. The mercury level used to maintain the pressure was controlled by a bulb mounted on a slide mechanism, by which the mercury level in both the bulb and burette were equalized. The level was recorded automatically, thus providing a continuous recording of the gas volume within the burette. The yield of hydrogen evolved was calculated from the difference of hydrogen evolved from the dehydrogenation of the model compound and a blank run. The hydrogen yield is expressed as the percentage of the theoretical available hydroaromatic hydrogen in the model compound. For example, the theoretical amount of hydroaromatic hydrogen in 9,10-DHA (2 atoms of hydrogen per molecule)

is 140.8 cc/gram, measured at 25 °C and 740 mm of Hg. In the presence of stilbene, a hydrogen acceptor, hydroaromatic hydrogen was mostly transferred to the hydrogen acceptor rather than evolved as hydrogen gas. The amount of hydrogen transferred was measured from the amount of bibenzyl formed.

Gas samples were removed from the sample port and analyzed by GC(Hewlett Packard 5880A). The residues were analyzed by GC and by GC-MS(The GC is a HP-5890 series II and the mass spectrometer is a HP-5970 series selective detector). Organic chemicals were obtained from Aldrich Chemical Inc.; catalysts were obtained from Strem Chemical Co. and from the Engelhard Corp.(Pd/CaCO₃, Pd/C).

RESULTS AND DISCUSSION

Effect of Boiling Point and Reduction Potentials on Hydrogen Evolution

Thermodynamically; high temperature and low pressure favor dehydrogenation; coal liquefaction, therefore, requires high hydrogen pressure. Reggel et al. postulated that the reduction potential, the energy required to accept an electron of the solvent, is of importance in catalytic dehydrogenation. This is borne out by the data obtained from catalytic dehydrogenation of 9,10-DHA with several vehicles. Pyrene, with a high boiling point (393 °C) and a comparatively low reduction potential(-1.56V) gives 95.1 percent of the theoretical yield of molecular hydrogen. p-Terphenyl, b.p. 383°C, but with a high reduction potential gives only 82.1% of H₂. Phenanthridine and anthracene, with lower boiling points and low reduction potentials, give high H₂ yields. Comparison of the use of phenanthrene and anthracene, molecular isomers, as vehicles is quite dramatic. The lowest H₂ evolution occurs with phenanthrene which boils only 3°C below anthracene but has a significantly higher reduction potential. This effect, the relative importance of boiling point and reduction potential of solvents on catalytic dehydrogenation, bears further investigation.

Dehydrogenation of 9,10-DHA with Various Solvents in the Presence of Stilbene, a Hydrogen Acceptor

The suggestion that use of a high-boiling solvent, indeed a nitrogen-containing vehicle, could lead to side reactions, may well be valid. We found that we could use low-boiling solvents in the presence of a hydrogen acceptor and the following experiments used stilbene as the hydrogen acceptor. Interestingly, depending on the vehicle, some hydrogen was evolved as molecular H₂ while some hydrogen was transferred to stilbene to form bibenzyl. The results are summarized in Table 2.

Initial experiments were carried out with two high boiling solvents (p-terphenyl and pyrene)which tended to yield more H₂ as gas than that transferred to the acceptor. Examination of the results reveals that the ratio of hydrogen evolution and hydrogen transfer may also depend on both temperature and reduction potential.

Experiments were then carried out with quinaldine (b.p. 248°C, reduction potential -1.50V) and 2-methylnaphthalene (b.p. 243°C, reduction potential -1.98V). Similar results were obtained with both solvents. 2-Methylnaphthalene is a good electron transfer agent and this probably is responsible for its effectiveness. With these low-boiling vehicles, hydrogen transfer to stilbene is the main step in the catalytic dehydrogenation of 9,10-DHA.

Also shown in Table 2, the surface area of the Pd support had essentially no effect. The reduced Pd on carbon catalyst, with a surface area of 1000 m²/g, gave the same or slightly higher amounts of hydrogen removal from 9,10-DHA as did reduced Pd on CaCO₃ (surface area

of 12m²/g).

An experiment with biphenyl (b.p. 255°C), a good electron transfer agent, resulted in 87% of the hydrogen in 9,10-DHA being transferred to stilbene with only 2.3% evolved as H₂ gas.

It is important that the palladium be in its lowest oxidation state; exposure of the catalyst to air affects the dehydrogenation deleteriously.

It is interesting to note that when 9,10-DHA is catalytically dehydrogenated in the presence of half the equivalent of stilbene, half the hydroaromatic hydrogen in 9,10-DHA is transferred to stilbene, half is evolved as gas (Table 2). It was observed that hydrogen evolution occurred after the stilbene was hydrogenated, indicating that hydrogen transfer to stilbene is preferred over H₂ gas evolution under these conditions.

Characterization of Hydrogen Transfer Mechanism of Hydroaromatics

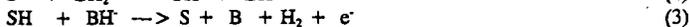
Several hydroaromatic compounds were dehydrogenated in the presence of stilbene with quinaldine as the vehicle in an attempt to elucidate the mechanism of hydrogen transfer. Dehydrogenation of 9,10-DHA gives only anthracene and hydrogen; it is unlikely that intermediate polynuclears are involved.

The model compound 1,4,5,8,9,10-hexahydroanthracene (HHA) is neither an aromatic nor a hydroaromatic compound. It does not contain an aromatic ring but has four isolated double bonds. But catalytic dehydrogenation of this compound in quinaldine in the presence of stilbene yields the hydroaromatic compounds 9,10-DHA, 1,2,3,4-tetrahydroanthracene (THA) and 1,2,3,4,5,6,7,8-octahydroanthracene (OHA) as well as bibenzyl formed by addition of hydrogen to the stilbene. As shown in Figure 1, the concentration of HHA decreases rapidly as the reaction proceeds. The yield of THA increases to a maximum after 5 minutes and decreases thereafter; it is then maintained at very low concentrations. The initial formation rate of OHA is very slow and then increases to a maximum value as the concentration of THA decreases; its concentration then falls slowly to a constant value. As for 9,10-DHA, its concentration increases smoothly at first and reaches a maximum in 10 minutes, following the maximum observed for THA by 5 minutes. The hydrogen transfer rate to stilbene is higher than the rate of formation of anthracene, particularly in the initial stages. It is noteworthy that the concentration of anthracene increases significantly after 10 minutes, when the concentrations of the hydroaromatics begins to drop, suggesting that the precursor of THA is a key intermediate through which both OHA and DHA are produced.

When the hydroaromatic, OHA, was dehydrogenated in the presence of stilbene, its concentration slowly decreased with time. After 40 minutes, only 10% of hydrogen was transferred and 15% of THA was formed. No 9,10-DHA was formed and only trace amounts of anthracene were detected. This indicates that OHA is a relatively poor hydrogen donor compared with THA and DHA. This is in keeping with the recent findings of Bate and Harrison⁽⁶⁾ who found, that for coal dissolution, the type of donor present may be more important than the total hydrogen donor content. The dehydrogenation of a mixture of DHA, HHA and OHA was carried out to compare hydrogen transfer rates of these model compounds (Figure 2).

On the Mechanism of Catalytic Dehydrogenation

Based on the above results, a mechanism of catalytic dehydrogenation and hydrogen transfer is proposed to explain the reaction pathways involved in dehydrogenation of these model compounds. The basic dehydrogenation pathway presented is based mostly on results of the dehydrogenation of 9,10-DHA both in the presence and in the absence of a hydrogen acceptor. S, BH₂, and B refer to vehicle, 9,10-DHA, and anthracene respectively.



It is assumed that the dehydrogenation step in the mechanism (eq.3) is rate controlling. A kinetic model expression based on this mechanism proposed describes the experimental curve of hydrogen evolved versus time very well. Further information is needed to improve this model and to apply it to the dehydrogenation of other substances containing hydroaromatic structures.

In the presence of a hydrogen acceptor, stilbene, a similar reaction pathway is involved, where the reduced solvent transfers hydrogen to adsorbed stilbene rather than further reacting with the $BH^{\cdot-}$ intermediate to evolve hydrogen to gas phase.

CONCLUSIONS

For vehicles boiling above 340 °C, both boiling point and reduction potential of the solvent employed appear to influence the palladium-catalyzed dehydrogenation of model polynuclear hydroaromatic compounds to yield gaseous hydrogen. For certain solvents that boil about 100 °C lower (245 °C or so), the palladium-catalyzed dehydrogenation of the same compounds occurs readily in the presence of a good hydrogen acceptor such as stilbene. Depending on the model hydroaromatic compound and reaction conditions, hydroaromatic hydrogen may be evolved as molecular hydrogen or be transferred to the hydrogen acceptor. With lower boiling vehicles, addition reactions are minimized with selective removal of hydroaromatic hydrogen.

A pathway for palladium-catalyzed dehydrogenation is proposed. The first step involves transfer of an electron from zerovalent palladium to the solvent. The solvent then remove a proton from the hydroaromatic compound. The slow step is the removal of hydrogen from reduced solvent.

The mechanism of removal of different hydroaromatic hydrogens may occur through various intermolecular transfers. There is a need to quantify not only total hydroaromatic content in coal and recycle solvents but also to determine the contributions from individual types of hydroaromatic compounds.

ACKNOWLEDGEMENT

The authors acknowledge the financial support from U.S. Department of Energy under Contract No. DE-PS22-89PC89998.

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Table 1. Dehydrogenation of 9,10-DHA with Pd/C in the Presence of Various Solvent

Polynuclear Aromatics	B.P. °C	Reduction Potential, -V	Dehydrogenation, H ₂ yield, cc	Blank, H ₂ , cc	Theoretical H ₂ yield, %
Phenanthridine	348	1.58	28.9	1.1	98.3
Phenanthrene	337	1.90	24.7	2.0	80.5
Pyrene	393	1.56	29.8	3.0	95.1
p-Terphenyl	383	2.01	26.4	3.2	82.1
Anthracene	340	1.46	27.0	1.1	91.8

Table 2. Dehydrogenation of 9,10-DHA with Pd/C in the Presence of a Hydrogen Acceptor

Catalyst	Vehicle Reduction Potential and B.P.	Feed		H ₂ Evolved, %	Bibenzyl %
		DHA, g	Stilbene, g		
Pd/C	p-Terphenyl 2.01, 383°C	0.2	0.2	79.7	20.3
Pd/C	Pyrene 1.56, 393°C	0.2	0.2	61.3	38.7
NONE	Phenanthridine 1.58, 348°C	0.2	0.2	11.1	16.5
NONE	o-Terphenyl 1.90, 337°C	0.2	0.2	1.0	9.1
Pd/C	Quinaldine 1.50, 248°C	0.2	0.2	2.7	92.5
Pd/CaCO ₃	Quinaldine 1.50, 248°C	0.2	0.2	14.5	74.0
Pd/C	2-Methylnaphthalene 1.96, 243°C	0.2	0.2	5.5	93.4
Pd/CaCO ₃	2-Methylnaphthalene 1.96, 243°C	0.2	0.2	8.8	90.4
Pd/CaCO ₃	Biphenyl 2.18, 255°C	0.2	0.2	2.3	87.2
Pd/C	Quinaldine 1.50, 248°C	0.3	0.15	50	50

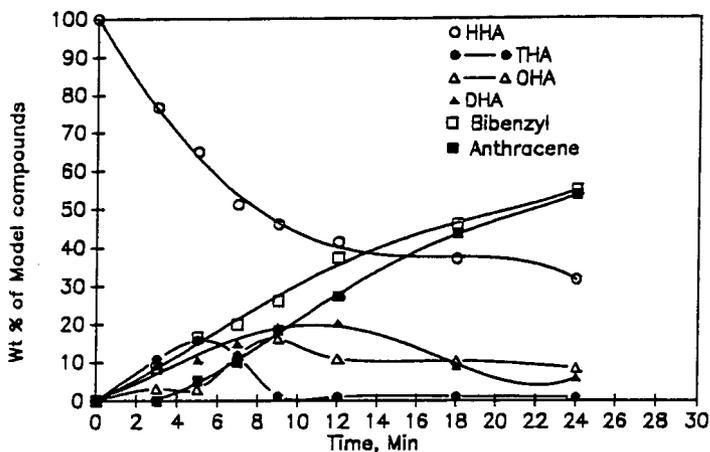


Figure 1. Dehydrogenation of HHA with Pd/CaCO₃, quinaldine as vehicle in presence of stilbene as a hydrogen acceptor.

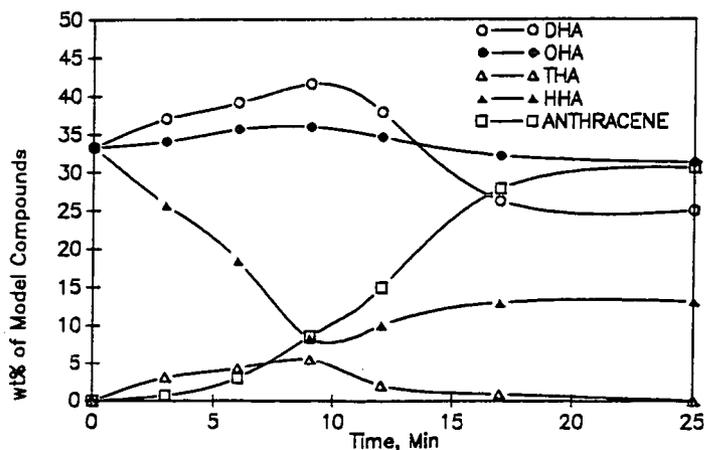


Figure 2. Dehydrogenation of mixture of model compounds on 0.5g reduced Pd/CaCO₃ with quinaldine as vehicle in presence of stilbene as a hydrogen acceptor.