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NOVEL CATALYTIC METHODS FOR HETEROATOM
REMOVAL IN COAL LIQUIDS UPGRADING

Quarterly Report for the Period March 1, 1983—June 1, 1984

By
Richard M. Laine
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Work Performed Under Contract FG22-83PC60781

SRI International
Menlo Park, California

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NOVEL CATALYTIC METHODS FOR HETEROATOM REMOVAL IN COAL LIQUIDS UPGRADING

Quarterly Report No. 3
For the Period March 1, 1983 through June 1, 1984

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ABSTRACT

The goal of this project is to optimize the reaction conditions for upgrading coal liquids. The research effort is divided into three tasks. Our results for this quarter are summarized below:

Task 1: Last quarter we found that H_2S aides in the HDN process. During this quarter, we have undertaken an H_2S concentration study on this reaction and found a direct correlation between the amount of added H_2S and the reduction in nitrogen content. We will submit the results of this study to Fuel as a communication (see Appendix A). For comparison, we also used H_2O and Na_2S as additives; however, neither appears to be as effective as H_2S in the HDN process.

Also, during this quarter we submitted to Fuel two manuscripts on the interactions of H_2S with coal and coal models. These manuscripts are attached as Appendices B and C.

Task 2: We initiated syntheses of some organometallic molybdenum cluster complexes $[\text{Mo}_2(\text{OAc})_4]$ and cluster complexes $\text{Mo}_2(\text{allyl})_4$ and have reacted these complexes with an alumina support. Preliminary tests reveal that these complexes have, as expected, less hydrogenation activity than the activated CoMo catalyst. However, we have not yet tested them for HDN activities. We have submitted a paper on the mechanism of the HDN process with the CoMo catalyst to the Journal of Molecular Catalysis. The manuscript is attached as Appendix D.

Task 3: We began experiments on the addition of added Bronsted acids (C_3FCOOH) to the reaction system. So far, the results have been promising and indicate a direct correlation between the amount of added acid and the amount of HDN activity.

INTRODUCTION

Coal is an abundant energy source. However, for it to be used in place of petroleum, it first must be liquefied and demineralized, and the heteroatoms must be removed. Generally, this process is done in two stages. In the first stage, a coal recycle-solvent is used to liquify and demineralize the coal, and in the second stage the coal liquid is hydrotreated to lower the molecular weight and to remove the heteroatoms. It is more beneficial to work in two stages because not only are the optimum conditions different for each step, but the mineral matter will poison the hydrodenitrogenation (HDN), desulfurization (HDS), and deoxygenation (HDO) catalysis.

The purpose of this work is to optimize the conditions for the second stage of the coal liquefaction scheme: the catalytic removal of sulfur, nitrogen, and oxygen (written in order of increasing difficulty). The removal of oxygen is important to increase in fuel value of the coal liquid, whereas the removal of nitrogen and sulfur is important for two reasons: (1) nitrogen and sulfur are a source of pollution and (2) they will poison reforming catalysts used in further upgrading of coal liquids. Nitrogen and oxygen are the most difficult to remove and require the most consumption of hydrogen. The ultimate goal of this work is the removal of the heteroatoms with the minimum amount of hydrogen and with the lowest possible temperatures and pressures.

The possible mechanisms for the HDN reactions of quinoline^{1,2} are shown in Figure 1. As seen in this figure, there are two routes for the denitrogenation of quinoline. The thermodynamically favored reaction pathway, which is shown in the heavy line, requires three more moles of hydrogen than does the unfavored pathway. Because hydrogen is expensive, any catalyst that would cause the denitrogenation to go through the second pathway would greatly reduce the cost of hydrotreatment. Furthermore, the fuel value of the liquid would be increased. Also, any systems that would allow the HDN and HDS processes

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FIGURE 1 QUINOLINE HDN REACTION NETWORK

to proceed at lower temperatures and pressures would also decrease the cost of the upgrading as well as the lifetime of the catalyst by decreasing coking.

SRI International is exploring a novel approach for the catalytic hydrogenitrogenation (HDN) and perhaps the hydrodeoxygenation (HDO) of coal-derived liquids. Our approach is divided into three tasks:

- Task 1. Develop an understanding of how very strong nucleophiles, such as H_2S , NaSH , and Na_2S (and corresponding selenides), interact with coal liquids under catalysis conditions.
- Task 2. Synthesize novel, high activity, highly dispersed, "surface-confined" catalysts based on very reactive organometallic molybdenum cluster complexes for comparison with commercially available HDN and HDO catalysts.
- Task 3. Develop an understanding of the effects of added Bronsted and Lewis acids (or added acid sites on the catalyst support) on the effectiveness of the catalyst systems developed in Task 2. Also briefly explore the effects of fluoride impregnation of the supports and the addition of Fe, Co, and Ni compounds on HDN and HDO.

TASK 1: INTERACTION OF NUCLEOPHILES WITH COAL LIQUIDS

This quarter we extended our baseline studies with H_2S , and for comparison we conducted experiments using H_2O and Na_2S additives. We also determined the dependence of the HDN process on the concentration of H_2S . (A more detailed discussion of our results with H_2S is presented in Appendix A.) The products of these reactions were analyzed in terms of elemental analyses, H_2 consumption, and IR and NMR spectroscopy. The results of the reaction with H_2S are shown in Table 1, and those with Na_2S and H_2O are shown in Table 2.

Experimental Procedures

The experimental procedures were discussed in Quarterly Report 2 and are also described in Appendix A of this report. Sodium sulfide (Na_2S) was obtained from Alfa.

Results and Discussion

Treatment of SRC-II with $\text{H}_2\text{S}/\text{H}_2$ and 1% Sulfided CoMo Catalyst

The data from these reactions are listed in Table 1. In runs 1 through 6 we treated 50 g of the coal liquid with a 1% sulfided catalyst concentration. Runs 1 and 2 used only H_2 , run 3 was with a 5-mol% $\text{H}_2\text{S}/\text{H}_2$ mixture, run 4 with a 7.5-mol% $\text{H}_2\text{S}/\text{H}_2$ mixture, and runs 5 and 6 with a 10-mol% $\text{H}_2\text{S}/\text{H}_2$ mixture. As shown in Figure 1 of Appendix A, there is a direct and beneficial correlation between the amount of HDN activity and the amount of added H_2S .

Treatment of SRC-II with Na_2S and 1% Sulfided CoMo Catalyst

To determine the difference between sulfur added as $\text{S}^{=}$ and H_2S , we treated the SRC-II liquid with Na_2S . The molar amount of Na_2S was identical to that of H_2S in 10 mol% $\text{H}_2\text{S}/\text{H}_2$. As shown in Table 2 the

Table 1
EFFECT OF H₂S ON CATALYSIS^a

Run	% H ₂ S	Gas	% C	% H	% N	% S	% R	H/C	% H _{alip}	% C _{alip}	H ₂ Consumption, mmol/g SRC
SRC-II	--	--	86.72	8.75	0.92	0.23	3.36	1.20	66	32	--
1	0	H ₂	88.19	9.54	0.75	0.037	1.48	1.29	71	38	4.5
2	0	H ₂	86.65	9.24	0.72	--	--	1.27	--	--	4.2
3	2.9	H ₂ S/H ₂	87.81	9.32	0.67	--	--	1.26	--	--	4.9
4	4.3	H ₂ S/H ₂	86.75	9.23	0.61	--	--	1.27	--	--	4.9
5	5.7	H ₂ S/H ₂	86.95	8.88	0.58	0.12	3.47	1.23	72	40	4.3
6	5.7	H ₂ S/H ₂	87.02	9.01	0.54	--	--	1.23	--	--	4.7

^aReactions with 1% sulfided catalyst at 400°C for 1 h with 1200 psig of hydrogen (or H₂S/H₂).

extent of hydrogen uptake was less (by 2 mmol/g SRC-II) with Na_2S (run 7) than in a typical run (run 1) the nitrogen contents of the SRC-II liquid products from the two runs were similar. In contrast, when 10 mol% $\text{H}_2\text{S}/\text{H}_2$ was used, the final nitrogen content was lower (0.56% average of runs 5 and 6). Also, in the Na_2S run there appeared to be incorporation of sodium in the product.

Treatment of SRC-II with H_2O and 1% Sulfided CoMo Catalyst

We also treated the SRC-II liquid with H_2O to determine the difference between H_2O and H_2S as additives. As shown in Table 2, the nitrogen content (0.75%) of the SRC-II liquid product of the H_2O run was similar to that of the baseline H_2 run.

Table 2
EFFECT OF ADDITIVE ON CATALYSIS^a

Run	Additive (wt%)	% C	% H	% N	% S	H/C	% H _{alip}	% C _{alip}	H ₂ Consumption, mmol/g SRC
SRC-II	--	86.72	8.75	0.92	0.23	1.20	66	32	--
1	H ₂	88.19	9.54	0.75	0.037	1.29	71	38	4.5
5	H ₂ S(5.7%)/H ₂	86.95	8.88	0.58	0.12	1.23	72	40	4.3
7	Na ₂ S(13%)/H ₂	83.72	8.44	0.72	0.18	1.20	73	38	2.5
8	H ₂ O(5%)/H ₂	87.84	9.38	0.75	--	1.27	72	38	4.9
9	TFA(4%)/H ₂	87.68	9.16	0.63	--	1.24	70	37	5.3
10	TFA(4%)/H ₂	87.14	9.15	0.65	--	1.25	--	--	--
11	TFA(8%)/H ₂	87.22	9.16	0.53	0.14% F	1.25	--	--	4.2
12	TFA(4%)/H ₂ S(5.7%)/H ₂	86.77	9.26	0.54	--	1.27	72	35	4.9
13	TFA(4%)/H ₂ S(5.7%)/H ₂	87.55	9.01	0.51	--	1.23	--	--	4.9

^aReactions with 1% sulfided catalyst at 400°C for 1 h with 1200 psig of hydrogen (or H₂S/H₂).

TASK 2: SYNTHESIS AND REACTIONS OF CATALYSTS

The principal goal of Task 2 is to develop and compare high activity, highly dispersed, "surface-confined" catalysts based on organometallic molybdenum cluster complexes for comparison with commercially available HDN and HDO catalysts. The available literature suggests that the manner in which the metal is dispersed on the support is important both in terms of the reactivity and the lifetime of the catalyst.³ Metals that are highly dispersed on the support tend to be more reactive and less susceptible to sintering.

Experimental Procedures and Materials

Materials

$\text{Mo}_2(\text{OAc})_4$ and $\text{Mo}_2(\text{allyl})_4$ were synthesized as described in Quarterly Report 2. H_2S was obtained from Matheson. H_2 and an H_2S (10%) gas mixture were obtained from Liquid Carbonic. The γ -aluminum oxide (Al_2O_3) A-201 HSA was obtained from Kaiser and was ground to 60-200 mesh, calcined at 600°C for 24 h, and stored under N_2 in a dry box. Quinoline, tetrahydroquinoline, n-undecane, and n-hexadecane were obtained from Aldrich. Both quinoline and tetrahydroquinoline were distilled from CaH_2 under N_2 before use. We obtained n-Dodecane from Shell.

Analytical Procedures

Product analyses were determined on an HP-5708 GC with a 15-m DB-1 capillary column or an HP-5880 GC with a 4.6-m 10% OV-17 on a Chromosorb G column. GC-mass spectral analyses were obtained using an LKB-9000 or Ribermag R 10 10 C mass spectrometer.

Kinetic Studies

The procedures for the kinetic studies for the hydrogenation of quinoline are described in Appendix D.

Treatment of $\gamma\text{-Al}_2\text{O}_3$ with H_2S

A sample of $\gamma\text{-Al}_2\text{O}_3$, which was ground 60-200 mesh, but not calcined, was heated to 500°C under flowing H_2S (10%)/ H_2 for 12 h. The material (sulfur content 0.17%) was stored under N_2 .

Preparation of Supported Catalysts

$\text{Mo}_2(\text{OAc})_4$ on $\gamma\text{-Al}_2\text{O}_3$. $\text{Mo}_2(\text{OAc})_4$ (1.08 g) and calcined $\gamma\text{-Al}_2\text{O}_3$ (3.77 g) were ground under N_2 with a mortar and pestle to give a 10-wt% molybdenum content (Compound I). We are now attempting to use two methods to determine the best way to activate this complex; (1) A portion of the supported material is heated under vacuum at 300°C for 4 h to give a black material (Compound II) and (2) a portion of the supported material is treated with flowing H_2S (10%)/ H_2 for 24 h at 200°C to give a blue-black material (Compound III).

$\text{Mo}_2(\text{allyl})_4$ on $\gamma\text{-Al}_2\text{O}_3$. $\text{Mo}_2(\text{allyl})_4$ (0.085 g, 0.24 mmol) was dissolved in 40 mL of dry degassed hexane to give a dark-green solution. Calcined alumina (1.00 g) was added to the stirred solution. The solution turned colorless after 0.5 h. A pale brown precipitate (Compound IV) was recovered by filtration, washed with hexane, and dried in vacuum. Yield: 1.06 g.

Results and Discussion

So far we have tested the hydrogenation activities of only compounds I, II, and IV. These compounds are relatively inactive as hydrogenation catalysts compared with the CoMo catalyst. These results are expected because the hydrogenation properties of CoMo are attributed to the cobalt. We will test the HDN activities of these compounds during the next quarter.

TASK 3: INTERACTIONS OF ACIDS WITH COAL LIQUIDS

The objective of Task 3 is to develop an understanding of the effects of added Bronsted and Lewis acids on the effectiveness of the catalyst system. During this quarter we briefly explored the use of an added Bronsted acid, trifluoroacetic acid (TFA), to the sulfided CoMo catalyst. We found that the addition of TFA to the reaction mixture has a beneficial effect and that a direct correlation exists between the amount of added acid and the amount of nitrogen in the reaction product.

Experimental Procedures

The experimental procedures have already been discussed. Trifluoroacetic acid (TFA) was obtained from Aldrich.

Results and Discussion

Treatment of SRC-II with TFA and 1% Sulfided Catalyst

As seen in Table 2, when we added 4 wt% of TFA to the standard reaction (1% catalyst, 400°C 1 h, 1200 psig H₂), the nitrogen content of the SRC-II product in runs 9 (0.63%) and 10 (0.65%) was less than the nitrogen content of 0.75 when no acid or H₂S was added. Furthermore, when we doubled the acid concentration to 8 wt% the nitrogen content decreased to 0.53% (run 11). When we combined the addition of 4 wt% of TFA with 1200 psig of H₂S (10%)/H₂, the final nitrogen content was 0.54% (run 12).

Except for the changes in nitrogen content, the NMR, IR, and elemental analyses all of these reaction products are similar. The fluorine content in run 2 was 0.14%, indicating only a small amount of fluorine incorporation. The gas analyses of the acid runs shows CO₂ and CHF₃, indicating the decomposition of the TFA.

In conclusion, it appears that the addition of acid aids in the HDN process; however, because the acid decomposes, it is difficult to determine at what stage the acid aids in the HDN. Furthermore, in the experiment with both H_2S and TFA, it is also difficult to determine which additive is effective or if both act simultaneously.

SUMMARY AND FUTURE WORK

We have seen from our results in Tasks 1 and 3 that both hydrogen sulfide and trifluoroacetic acid aid in the HDN process. Although the HDN enhancement resulting from the addition of trifluoroacetic acid is most likely due to its acidic properties, it is difficult at this time to determine at what step in the HDN process that the acceleration occurs. Furthermore, we cannot determine at this time if the enhancement of H_2S is due to its acidic or nucleophilic properties or a combination of both effects. We will address these questions in our future work. We also plan to test the catalysts prepared under Task 2.

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APPENDIX A

CATALYTIC HYDRODENITROGENATION OF AN SRC-II COAL LIQUID.
EFFECT OF HYDROGEN SULFIDE

CATALYTIC HYDRODENITROGENATION OF AN SRC-II COAL LIQUID.
EFFECT OF HYDROGEN SULFIDE

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Introduction

The most expensive part of the hydrotreating process for coal liquids is hydrodenitrogenation (HDN). Any reaction procedures that aid in removing nitrogen without adding cost will help make coal a competitive energy source. Bhide et al.¹ Satterfield,^{2,3} and others have demonstrated that H₂S accelerates the catalytic HDN of quinoline; however, the exact reasons for this acceleration have never been clear.

We have recently suggested, based on mechanistic studies of HDN, that H₂S could enhance HDN in coal liquids because of its acidic and/or nucleophilic properties.⁴ We report here some preliminary results on the effects of H₂S on the catalytic HDN of an SRC-II coal liquid.

Experimental Procedures and Materials

SRC-II middle distillate was obtained from Pittsburg and Midway Mining Co. SRC pilot plant at Fort Lewis, Washington. The cobalt-molybdenum catalyst, HT-400 (3 wt% CoO, 15.1 wt% MoO₃, on Al₂O₃) was obtained from Harshaw Chemical Company. Hydrogen sulfide (H₂S) was obtained from Matheson. Hydrogen (H₂), nitrogen (N₂), and an H₂S(10%)/H₂ gas mixture were obtained from Liquid Carbonic.

Apparatus

Hydrogenation reactions were performed in a 300-mL Autoclave Engineers (AE) Magnedrive stirred reactor, heated with a 1000-W electric furnace (AE). The temperature was controlled with a model CP temperature controller (AE). The autoclave was connected through a sample gas vent to a Carle Series S gas chromatograph (GC) adapted by Carle to analyze C₁-C₃, H₂, O₂, N₂, and H₂S. For gas analyses, the autoclave was vented into a 1-mL sample injection port of the GC.

Analytical Procedures

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL FX 90Q spectrometer. NMR samples were prepared by mixing one part by weight of coal liquid with two parts of CDCl_3 . The conditions for obtaining the ^{13}C NMR spectra were as follows. Samples were made 0.025 M in $\text{Cr}(\text{AcAc})_3$. The pulse width was 6 μs and pulse delay 15 s. The NNE option (heterodecoupling with no Nuclear Overhauser enhancement) was chosen for quantitative ^{13}C analyses.

The infrared (IR) spectra were obtained on a Perkin-Elmer 281 spectrophotometer. Elemental analyses were obtained from Galbraith Laboratories.

Catalyst Preparation

The HT-400 catalyst was ground and sieved to obtain a 60- to 200-mesh powder. The catalyst was activated at 400°C in a flowing mixture of H_2S (10%) in H_2 for 24 h, then stored in a Vacuum Atmospheres, Dri-box under N_2 . (Before the catalyst was sulfided, it was dried for 1 h in air, pretreated with $\text{H}_2\text{S}/\text{H}_2$ mixture for 1 h at room temperature, then slowly heated to 400°C over a 2-h period). Anal.: Mo, 7.8%; S, 7.75%; empirical formula: $\text{Co}_4\text{S}_9(\text{MoS}_{2.1})_4$.

Standard Reaction Procedures

The autoclave was filled under N_2 with the desired quantity of activated catalyst and SRC-II liquid. The reactor was then purged and charged with 1200 psi of H_2 (or $\text{H}_2/\text{H}_2\text{S}$). For those reactions using H_2S only, the following procedure was used: A tared 20-mL minireactor was purged and filled with H_2S to the desired weight. The minireactor was then connected to the 300-mL autoclave and the system was purged with N_2 . The 300-mL reactor was cooled with dry ice, and the H_2S was condensed into the autoclave.

The system was heated to 400°C over a 40-min period and maintained at 400°C for 1 h, at which time the heating furnace was removed. When the reactor had cooled to room temperature, GC analyses were performed

on the product gases. The liquid products were removed and filtered through a medium-pore filter to remove the catalyst.

Results and Discussion

Treatment of SRC-II with Hydrogen Sulfide

The data from the reactions of H_2S or $\text{H}_2\text{S}/\text{H}_2$ with the SRC-II liquid are shown in Table 1. When the SRC-II was treated with H_2S alone, we observed some evolution of gases (1.96 mmol gas/g coal liquid) due to H_2 , ethane, and propane. The NMR data indicate that the fraction of aliphatic hydrogen and carbon decreased from 0.66 to 0.60 (± 0.02) and 0.32 to 0.30 (± 0.01), respectively, and the H/C ratio decreased from 1.20 to 1.15 (± 0.02) from the original SRC-II liquid. In contrast, the treatment of the coal liquid with the $\text{H}_2\text{S}/\text{H}_2$ mixture resulted in essentially no change from the original. The IR spectra of these reaction products are similar to that of the original liquid and show no absorptions in the region of 2550 to 2600 cm^{-1} where we expected to see SH stretches. Elemental analyses of the products from the H_2S and $\text{H}_2\text{S}/\text{H}_2$ reactions showed no sulfur incorporation nor any decrease in nitrogen content (within error limits of analysis). Thus, we see that in the absence of catalyst, the SRC liquid is not effected by $\text{H}_2\text{S}/\text{H}_2$ and is slightly dehydrogenated by H_2S .

Treatment of SRC-II with Sulfided Catalyst

The data from the reactions of sulfided catalysts with the SRC-II liquid are shown in Table 2.

In experiments 3 through 5 we treated 50 g of the coal liquid using a 1% sulfided catalyst concentration. Experiment 3 was performed with H_2 , 4 with the 10 mol% $\text{H}_2\text{S}/\text{H}_2$ mixture, and experiments 3 and 4 were performed with 5.0 and 7.5 mol% $\text{H}_2\text{S}/\text{H}_2$, respectively.

As seen in Table 2, the addition of H_2S to the reaction mixture does not have a dramatic effect on the hydrogen uptake or on the aliphatic ratios (by NMR). Nor were there significant differences in the IR spectra of the products from the runs. However, as seen from the

Table 1. Reactions with H₂S at 400°C for 1 h

<u>Experiment^a</u>	<u>% H₂S^b</u>	<u>gas</u>	<u>%N</u>	<u>%S</u>	<u>H/C</u>	<u>%H_{aliph}</u>	<u>%C_{aliph}</u>
SRC-II	--	--	0.92	0.23	1.20	66	32
1	18.5	H ₂ S	1.00	0.54	1.16	60	30
2	5.7	H ₂ S(10%)/H ₂ ^c	0.92	0.43	1.21	67	33

^aAverage of two runs.

^bwt% of H₂S in coal liquid.

^c1200 psig initial pressure.

Table 2. Reactions with 1% Sulfided Catalyst at 400°C for 1 h
with 1200 psig of H₂ (or H₂S/H₂)

<u>Experiment</u>	<u>%H₂S^a</u>	<u>Gas</u>	<u>%N</u>	<u>%S</u>	<u>H/C</u>	<u>%H_{alip}</u>	<u>%C_{alip}</u>
3 ^b	0	H ₂	0.74	0.037	1.28	71	38
4	2.9	H ₂ S(5%)/H ₂	0.67	--	1.26	--	--
5	4.3	H ₂ S(7.5%)/H ₂	0.61	--	1.27	--	--
6 ^b	5.7	H ₂ S(10%)/H ₂	0.56	0.12	1.23	72	40

^awt% of H₂S in coal liquid.

^bAverage of two runs.

elemental analyses of these products, the nitrogen content 0.74 (experiment 3) in the baseline run with H_2 decreased to 0.56% (experiment 4) in the H_2S/H_2 run. Figure 1 shows that as the H_2S concentration increases the nitrogen concentration decreases.

Conclusions

In concurrence with our predictions, the addition of H_2S under coal liquid upgrading conditions aids in the HDN process. Note that Bhinde et al.¹ and Satterfield^{2,3} observed that free H_2S significantly enhanced HDN in model studies with quinoline. We are currently attempting to further validate these observations by studying of the effects of other nucleophiles and acids on HDN of coal liquids.

Figure 1
EFFECT OF H_2S ON HDN*

*1h reaction of SRC-II liquid at 400°C with 1%
sulfided CoMo catalyst and 1200 psig H_2S/H_2

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APPENDIX B

THE CHEMISTRY OF HYDROGEN SULFIDE UNDER COAL LIQUEFACTION CONDITIONS.

1. MODELING HYDROGEN TRANSFER CATALYSIS

THE CHEMISTRY OF HYDROGEN SULFIDE UNDER COAL LIQUEFACTION CONDITIONS.

1. MODELING HYDROGEN TRANSFER CATALYSIS

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ABSTRACT

The work reported here represents our initial attempts to develop a complete kinetic and mechanistic understanding of the reaction chemistry of H_2S under coal liquefaction conditions using both model systems and coal. We find that hydrogen sulfide promotes/catalyzes the transfer of hydrogen from tetralin to 2-hydroxyquinoline (2-HOQ). The presence of H_2S can increase the rate of hydrogen transfer from tetralin to 2-HOQ by a factor of ten compared with the same reaction run in the absence of H_2S . The energy of activation for hydrogen transfer was found to decrease by approximately 5 kcal/mole in the presence of H_2S . The presence of H_2S was also found to promote loss of oxygen from 2-HOQ to form small amounts of quinoline. No evidence of C-C or C-N bond cleavage in 2-HOQ was noted under any of the reaction conditions studied. These results suggest that the presence of H_2S reduces the temperatures necessary to promote effective hydrogen transfer from tetralin by 50°-75°C. Moreover, they imply that similar effects occur in H_2S -promoted coal liquefaction.

INTRODUCTION

The fact that hydrogen sulfide (H_2S) promotes coal liquefaction has been known for a long time.¹⁻⁸ A number of groups, including those of Stenberg,¹⁻⁴ Appel,^{5,6} and Baldwin,⁷ have described research aimed at delineating the parameters of H_2S promoted coal liquefaction. In addition, Stenberg has described preliminary efforts to explore the reaction chemistry of H_2S with model compounds under conditions that simulate those occurring during coal liquefaction.^{3,4} For these promotional effects to be used to their fullest advantage, more such efforts, especially detailed efforts, are needed to identify the exact mechanisms by which H_2S functions to promote coal liquefaction.

Reliance on the published literature on the organic chemistry of H_2S to explain the mechanisms by which H_2S functions under coal liquefaction conditions seems, at best, to have only partial value. It is rare^{9,10} to find a study that attempts to look at the high temperature organic chemistry of H_2S . Furthermore, it may be foolhardy to extrapolate several hundred degrees to draw mechanistic analogies. Consequently, we have attempted to develop a complete kinetic and mechanistic understanding of the reaction chemistry of H_2S under coal liquefaction conditions using both model systems and coal.¹¹ It is hoped that our studies will complement those already in progress.

On the basis of the recent work of the above cited groups and to some extent on the low temperature organic chemistry of H_2S , it appears that H_2S promotes coal liquefaction because it can catalyze transfer of hydrogen from hydrogen donors to coal, it can aid in hydrocracking, and because it is a strong nucleophile, it may aid in removing oxygen and nitrogen from coal materials.¹⁻⁹ To study these various effects separately, it was necessary to: (1) choose a model compound in which several reactive pathways were available and that has functionalities expected of a coal compound and (2) choose sets of reaction conditions

that permit the various reaction pathways to be studied separately if they are observed to proceed simultaneously.

For example, in studies of H_2S promoted cleavage of model linkages in diphenylmethane (C-C) and in N,N-dimethylaniline (C-N) at 450°C and 425°C respectively, Stenberg et al.^{2,4} report that although hydrogen sulfide is involved, elemental sulfur cannot be ruled out as an active species in the cleavage reactions. In fact, they suggest that at 450°C reaction (1) may be important.

Moreover, they find that added sulfur enhances the rate of reaction.

In the work described below, we have tried to avoid potential complications and have been rewarded with preliminary kinetic results of value in developing an understanding of the high temperature chemistry of H_2S .

EXPERIMENTAL

Reagents

2-Hydroxyquinoline was obtained from Eastman Kodak and used without further purification. 1,2,3,4-Tetrahydronaphthalene (tetralin) was obtained from Aldrich and was distilled from lithium aluminum hydride under nitrogen before use. Hydrogen sulfide (H_2S) was obtained from Matheson. Hydrogen (H_2), nitrogen (N_2), and an H_2S (10%) in H_2 gas mixture were obtained from Liquid Carbonic.

Apparatus

Reaction vessels were 3/8-in. OD, 316 SS tubes with a 5.0-mL volume. The tubes were fitted with caps and fittings (C.P. Parker) and a pressure valve (10k psig, Autoclave Engineers).

Standard Reaction

The reaction vessel was filled under nitrogen with tetralin (90 mole %) and 2-HOQ (10 mole %). For those reactions using H_2S , the vessel was purged by two pressurization/depressurization cycles with 10% $\text{H}_2\text{S}/\text{H}_2$ mixture and then the desired amount of $\text{H}_2\text{S}/\text{H}_2$ was added. Hydrogen was added as necessary so that the total pressure was 1200 psig. The vessel was then heated to the reaction temperature (usually 400°C) for the desired time in a fluidized sandbath. Following reaction, the vessel was cooled with liquid nitrogen, vented, and opened. The contents were then washed into a flask with tetrahydrofuran.

Analytical Procedures

Quantitative analyses were obtained using a Hewlett-Packard 5711 gas chromatograph (GC) with either a 3.2 m x 0.625 cm glass column packed with 10% OV 17 on Gas Chromorb Q or a 25-m dimethylsilicone fluid capillary column. n-Dodecane was used as an internal standard. GC-mass

spectral (GC/MS) analyses were obtained using an LKB-9000 or a Ribermag R 10 10 C mass spectrometer.

RESULTS

As part of a screening study to choose useful model compounds for the kinetic studies, we examined the reactivities of a few model compounds with H_2S and tetralin at 400°C including 6-methyl-2-hydroxyquinoline (6-methyl-2-pyridone), para-hydroxydiphenylether (para-phenoxy phenol) and 2-hydroxyquinoline (2-HOQ). Of these, only 2-HOQ reacts cleanly, reaction (2), at moderate rates and represents the most

kinetically viable compound for study under coal liquefaction conditions. At 400°C , we find no evidence for the formation of sulfur deposits and experienced no anomalies in our kinetic analyses. The fact that the major reaction is the hydrogenation of 2-HOQ to dihydro-2-hydroxyquinoline (H_2HOQ) provides us with the unique opportunity to study H_2S as a hydrogen transfer catalyst under coal liquefaction conditions. As a minor product of the reaction, we also see the presence of quinoline. Thus, we observe H_2S to promote deoxygenation.

Tables 1 and 2 contain data for the reaction rate studies of 2-HOQ as a function of reaction time at 400°C . Baseline data, obtained in the

[Insert Tables 1 and 2]

absence of H_2S , are shown in Table 1. Table 2 contains the data from the runs made with added H_2S (5 wt%). The results, as plotted in Figure 1, are linear and suggest that in both cases these reactions follow

[Insert Figure 1]

pseudo-first-order kinetics.

Tables 3 and 4 contain data for the 2-HOQ hydrogenation rate studies conducted as a function of reaction temperature (30-minute

[Insert Tables 3 and 4]

reaction times) for baseline runs and with added H_2S (5 wt%). The pseudo-first-order rate constants for the 2-HOQ reaction temperature studies are listed in Table 5. Arrhenius plots of these data, shown in

[Insert Table 5]

Figure 2, give an E_a for the tetralin/2-HOQ hydrogenation baseline case of 33.8 (± 4) kcal/mole and an E_a for the H_2S promoted reactions of 29.8 (± 3) kcal/mole. Figure 3 plots the percent conversion of 2-HOQ to dihydro-2-HOQ and to quinoline as a function of temperature.

[Insert Figures 2 and 3]

The effect of H_2S concentration on rates of reaction is plotted in Figure 4. We see from this plot that the reaction rate accelerates rapidly as the H_2S concentration increases to $\sim 5\%$ and then increases at a much slower rate at higher concentrations.

[Insert Figure 4]

DISCUSSION

The data in Tables 1 and 2 and the slopes of the plots in Figure 1 show that the hydrogenation of 2-HOQ proceeds at rates approximately ten times faster in the presence of H_2S than in its absence. Stated in another way, these results demonstrate that, for a given rate of 2-HOQ hydrogenation, the H_2S catalyzed reaction proceeds at 50°–75°C lower temperature than in its absence. A similar observation can be made concerning the rates of 2-HOQ deoxygenation. Deoxygenation in the presence of H_2S proceeds at rates obtainable only at temperatures 75° to 100°C higher in its absence.

The evidence points to H_2S acting as an effective hydrogen transfer catalyst. The ~ 5-kcal difference in activation energies is what one would expect based on H_2S functioning as a catalyst. Basically, the difference in E_a can be interpreted to mean that H_2S has reduced the activation energy required to promote the rate-limiting step or that the overall reaction now has a different rate-limiting step. If the latter is true, an argument can be made that H_2S changes the reaction mechanism by which hydrogen transfer occurs.

These conclusions are supported by the rapid rise in hydrogen transfer activity observed in Figure 4 as the H_2S concentration increases to 5% H_2S and the rapid falloff in the rate of increase observed past 5%. These results are what might be expected if H_2S were to act catalytically to change the rate-limiting steps occurring in hydrogen transfer from tetralin to 2-HOQ or to change the hydrogen transfer mechanism. Unfortunately, the differences between the two possibilities are not discernable at present and only further documentation will provide a definitive answer to the question. The most important observation that can be made is that similar falloffs are found to occur in H_2S promoted coal liquefaction (see following paper), thus providing a correlation between the model system studies performed here and H_2S promoted coal liquefaction.

H₂S also promotes catalytic deoxygenation at much higher rates than obtainable using tetralin alone. The fact that deoxygenation occurs at all in the absence of H₂S (although at much higher temperatures) suggests that H₂S may not promote deoxygenation by nucleophilic displacement of the oxygen moiety.¹² It may catalytically generate the species responsible for deoxygenation. This ties in with the fact that in no instances do we see any direct evidence for sulfur incorporation into the model compound or the solvent under any conditions studied here.

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Table 1. Reaction of 2-HOQ with tetralin at 400°C as a function of time. (values recorded are in mol% of total products)

Time (min)	30	60	80	100	120
Tetralin	88.6	89.3	89.3	89.1	89.1
Napthalene	0.6	0.7	0.5	0.9	0.9
Dihydro-2-HOQ	0.3	0.6	0.3	0.6	0.8
2-HOQ	9.7	9.4	9.3	9.1	8.5

Table 2. Reaction of 2-HOQ with tetralin and H₂S at 400°C as a function of time. (values recorded are in mol% of total products, H₂S added as 5 wt%)

Time (min)	15	30	45	60
Tetralin	89.4	88.9	89.1	88.9
Napthalene	0.7	0.9	0.9	0.9
Quinoline	-	0.2	0.3	0.5
Dihydro-2-HOQ	2.1	2.5	3.4	4.5
2-HOQ	7.8	7.3	6.1	4.5

Table 3. Reaction of 2-HOQ with tetralin for 30 min as a function of reaction temperature (values recorded are in mol% of total products)

	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>500°C</u>
Tetralin	88.6	88.6	88.7	83.2
Napthalene	0.6	0.9	1.3	6.7
Quinoline	-	-	-	0.4
Dihydro-2-HOQ	0.3	0.9	1.5	5.5
2-HOQ	9.7	9.0	8.5	4.1

Table 4. Reaction of 2-HOQ with tetralin and 5 wt% H₂S for 30 min as a function of reaction temperature. (values recorded are in mol% of total products)

	<u>350°C</u>	<u>375°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>
Tetralin	89.6	89.4	89.0	89.0	88.8
Napthalene	0.4	0.6	1.0	1.0	1.2
Quinoline	-	-	0.2	0.4	0.8
Dihydro-2-HOQ	0.5	0.9	2.5	3.8	7.5
2-HOQ	9.5	8.8	7.3	5.7	1.8

Table 5. Pseudo-first order rate constants for 2-HOQ reactions as a function of temperature with and without added H_2S .
(values recorded are in sec^{-1})

	<u>350°C</u>	<u>375°C</u>	<u>400°C</u>	<u>425°C</u>	<u>450°C</u>	<u>500°C</u>
$k_{\text{blank}}(\times 10^5)$	-	-	1.7	5.9	9.0	50
$k_{\text{H}_2\text{S}}(\times 10^5)$	2.9	7.1	17	31	95	-

FIGURE 1 2-HOQ CONVERSION AT 400°C AS A FUNCTION OF TIME

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FIGURE 2 PLOT OF $\ln k_{\text{OBS}}$ AGAINST $1/T$ FOR THE REACTION OF 2-HOQ WITH TETRALIN

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FIGURE 3 2-HOQ CONVERSIONS AS A FUNCTION OF TEMPERATURE

JA-327583-131

FIGURE 4 2-HOQ CONVERSION AT 400°C FOR 1 h AS A FUNCTION OF H_2S CONCENTRATION

APPENDIX C

THE CHEMISTRY OF HYDROGEN SULFIDE UNDER COAL LIQUEFACTION CONDITIONS.

2. THE SYNERGISTIC EFFECTS OF H_2S AND THE MIXED-SOLVENT SYSTEM
TETRALIN AND TETRAHYDROQUINOLINE ON LIQUEFACTION OF A MODERATELY
REACTIVE COAL

THE CHEMISTRY OF HYDROGEN SULFIDE UNDER COAL LIQUEFACTION
CONDITIONS. 2. THE SYNERGISTIC EFFECTS OF H_2S AND
THE MIXED-SOLVENT SYSTEM TETRALIN AND TETRAHYDROQUINOLINE ON
LIQUEFACTION OF A MODERATELY REACTIVE COAL

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ABSTRACT

In an effort to correlate our recent studies on the effects of hydrogen sulfide (H_2S) catalyzed hydrogenation of a model compound with H_2S -promoted coal liquefaction under conventional liquefaction conditions, we evaluated the role of H_2S in the hydrogen transfer and liquefaction of coal. In addition, we evaluated the effects of using tetrahydroquinoline (THQ) as an H-donor solvent for coal liquefaction based on recent reports of its efficacy in promoting high conversions under mild conditions. Thus, we have undertaken a preliminary study to evaluate the effects of mixed solvents and added H_2S on the overall conversions of a moderately reactive Wyodak-2 coal as defined by tetrahydrofuran (THF) solubility. Conversion efficiencies were measured as a function of time and of H_2S concentration in the H_2S /THQ solvent system. The specific solvent systems studied included tetralin and mixtures of tetralin and THQ, with and without H_2S .

In all cases, coal conversion was enhanced by the presence of H_2S and/or THQ relative to the baseline case using tetralin alone. Conversion as a function of THQ concentration was also determined. The relative abilities of the various combinations to effect conversion are as follows: tetralin < 5 wt% THQ/tetralin < 3 wt% H_2S /tetralin < 10 wt% THQ/tetralin = 20 wt% THQ/tetralin < 3 wt % H_2S /20 wt% THQ/tetralin. From these results, we conclude that both H_2S and THQ operate

synergistically to provide enhanced yields of high-quality coal liquids. The relationships between conversion, H_2S concentration, and nitrogen incorporation are discussed.

INTRODUCTION

A number of researchers¹⁻⁶ have recently described H-donor coal liquefaction processes based on the H-donor solvent, tetrahydroquinoline (THQ), that provide extremely high liquefaction conversions under relatively mild conditions. For example, in a typical run with Belle Ayr coal and with THQ as the H-donor solvent (conditions = 1 h, 1000 psig of H₂, 425°C), the coal liquids produced were 100% THF soluble and 55% heptane soluble.^{4,5} By comparison, when tetralin was used as solvent, under identical conditions, the resultant coal liquids were only 85% THF soluble and 50% heptane soluble. Unfortunately, during the liquefaction process large amounts of THQ becomes incorporated in the coal liquids. Attempts to distill these liquids give much lower distillate yields than those obtained in the runs using tetralin alone.⁵ Studies with model compounds equation (1) have demonstrated that THQ and its partially dehydrogenated derivative equation (2) dihydroquinoline (DHQ) incorporate electrophiles and nucleophiles through reaction with coal, as illustrated in equations (1) and (2).^{7,8}

Electrophiles RXH X=NH-, O-, S-

In reaction (1), THQ, acting as a nucleophile, reacts with a coal electrophile to become incorporated in the coal molecule. In reaction (2), DHQ, which is a very reactive electrophile, reacts with a coal

nucleophile and thus becomes incorporated in a coal molecule. Reaction (3) provides the typical example of the reactivity of these two species:

The THQ dimer, 1, and its partially dehydrogenated derivatives are common products found in most liquefaction studies run with THQ as the H-donor solvent or co-solvent.^{7,8}

In parallel but unrelated studies, Stenberg and co-workers,⁹⁻¹² Appell and co-workers,¹³⁻¹⁴ Baldwin and Vinciguerra,¹⁵ and others^{16,17} demonstrated the beneficial influence sulfur compounds, particularly H₂S, have on the liquefaction of a variety of coals. For example, liquefaction studies of Big Brown, Texas, lignites (400°C, 2600 psig 1:1 H₂:CO, 54 kg/day) show that, with H₂S, the products are approximately 20% gases, 35% distillates, and 30% SRL.¹⁰ Much the same product distributions and conversions are found in the absence of H₂S, but only if the liquefaction temperature is raised to 460°C. Based on reaction studies of H₂S with various coals and model compounds, Stenberg et al. ascribe the enhancements obtained in liquefaction performed with H₂S to its ability to act as a hydrogen donor and a hydrocracking agent. Also, because H₂S is a strong nucleophile, it can displace oxygen from oxygen-containing coal molecules.^{9-12,18}

It is this latter fact, when coupled with our hypotheses on H₂S promoted hydrodenitrogenation,^{19,20} that suggested that a liquefaction system based on both THQ and H₂S could take advantage of the best aspects of both systems and diminish or eliminate the negative aspects of the THQ liquefaction system. Our rationale was that H₂S, especially as HS⁻, is an exceptionally strong nucleophile and as such, should compete successfully with THQ for coal electrophiles, thus reducing the chances for THQ incorporation in coal via reaction (1). In addition, H₂S should compete with coal nucleophiles for DHQ, thus preventing

incorporation via reaction (2). We envisioned that, coincidentally, THQ's basicity could promote the formation of HS^- , thereby creating a potential synergy for coal liquefaction.

The work described below is a preliminary effort designed to test the effects of melding the two systems to obtain an improved liquefaction process that uses the best aspects of both THQ and H_2S promoted coal liquefaction. A further motivation for these studies is our interest in correlating the high temperature organic chemistry of H_2S on coal model compounds, as described in the preceding paper, with the organic reaction chemistry of H_2S on coal and coal liquids, especially as it pertains to the chemistry obtained in the presence of heterogeneous hydrotreating catalysts.

EXPERIMENTAL

Reagents

1,2,3,4-Tetrahydronaphthalene (tetralin) and 1,2,3,4-tetrahydroquinoline (THQ) were obtained from Aldrich. Hydrogen sulfide (H_2S) was obtained from Matheson. Hydrogen (H_2), nitrogen (N_2), and a 10% $\text{H}_2\text{S}/\text{H}_2$ gas mixture were obtained from Liquid Carbonic.

Preparation of Coal

Wyodak-2 was supplied by the Electric Power Research Institute, Inc., as a coarse powder stored under water. The coal was separated from the water and dried at room temperature under vacuum (<0.1 mm) for 24 hours. The coal was ground and sieved under nitrogen to 60-325 mesh. Analysis: C, 63.61; H, 4.74; N, 0.57; S, 1.13; ash, 5%. In all handling procedures, coal and coal liquids were kept under nitrogen or vacuum.

Apparatus

Reaction vessels were 3/8-in. OD, 316 SS tubes with a 5.0-mL volume and were capped with C. P. Parker fittings. The tubes had a 1/8-in. SS tube welded perpendicular to the tube, which was connected to a pressure valve (10k psig, Autoclave Engineers).

Standard Reaction

The reaction vessel was filled under nitrogen with 0.50 g of coal and 1.0 g of either tetralin or a THQ/tetralin mixture. The vessel was sealed, purged, and filled with either H_2 or the desired amount of $\text{H}_2\text{S}/\text{H}_2$. For those reactions with an excess amount of H_2S , the tared reaction vessel was filled with pure H_2S and then filled with H_2 . Hydrogen was added as necessary so that the total pressure was 1200 psig. The reaction vessel was then heated to 400°C for the desired time in a fluidized sand bath. Following reaction, the vessel was cooled with liquid nitrogen, vented, and opened. The contents were then washed

into a flask with tetrahydrofuran (THF). The coal and coal liquids were filtered through a medium porosity fritted filter, washed with THF, and separated into THF soluble and THF insoluble portions. The THF and H-donor solvent were carefully removed from the soluble portion. The insoluble and soluble portions were dried at 76°C under vacuum for 24 h and 48 h, respectively.

RESULTS AND DISCUSSION

Liquefaction Studies

Our initial efforts were to establish baseline reactivities, using coal liquefaction in tetralin/400°C as the base case. The results of these studies are shown in run 1 of Table 1. The three most pertinent

[Insert Table 1]

standards used in evaluating the results of the various studies are the extent of solubilization, the quality of the coal liquids produced, and the nitrogen content of the coal liquids produced.

Coal conversion is defined by the carbon content of the residual insolubles. This can be taken to be a lower limit because of the likelihood that some solvent becomes incorporated in the residual insolubles. Thus, at the low end (tetralin), conversions are approximately 44%, and at the high end (20% H₂S/20% THQ + 80% tetralin), conversions are at least 75%.

The quality of the coal liquids can be defined as the weight average molecular weight of the coal liquids as measured by FIMS (field ionization mass spectral) analyses and by nitrogen content. In general, the weight average molecular weights for all the coal liquids run from ~ 420 to ~ 490. Within the framework of the sample preparation procedures and the analytical technique, these values can be considered quite similar. Because it is difficult to compare the liquid products where there may be both physical and chemical incorporation of solvents,

as well as losses due to volatile products, we rely on the carbon content of the insoluble coal residue as a measure of coal conversion.

Table 1 tabulates the effects of H_2S concentration on coal conversion with tetralin as the H-donor solvent at $400^\circ C$. The effects of adding THQ to tetralin in the absence of H_2S are recorded in Table 2. The addition of 3 wt% H_2S to tetralin increases the coal

[Insert Table 2]

conversion from 44% to 54% which is comparable to the conversion with 20% THQ/tetralin. At 20% H_2S , the conversion increased considerably over that with 20% THQ/tetralin.

As the amount of THQ is varied from 5% to 10% to 20%, the extent of the conversion does not change significantly; however, in each case conversion is considerably more than when THQ is not used. In addition, we observe that the nitrogen content of the insoluble residue is similar, although the nitrogen content of the soluble portions increases with increasing THQ concentration. This is partly because of the difficulty in removing physically bound THQ (see below).

The important observation here is that one does not need exceptionally large amounts of THQ to obtain the measurable enhancements in conversion. The fact that these enhancements do not change significantly on increasing the THQ concentration four-fold (from 5% to 20%) suggests that THQ's role in promoting liquefaction may not be that of a more active H-donor, but rather that of a base or a hydrogen transfer catalyst or both.

Comparing the H_2S promoted liquefaction results with those from the THQ studies does not allow us to determine whether H_2S and THQ function in the same manner. That is, are the same bonds being broken in both instances? If THQ acts as does H_2S (see preceding paper) to catalyze hydrogen transfer, then the addition of H_2S to the THQ/tetralin mixture should not induce higher conversions because the relative rates of conversion appear similar for both liquefaction processes. In fact,

addition of H_2S to the mixed-solvent system does result in a significant increase in conversion as shown in Table 3. These results are presented graphically in Figure 1.

[Insert Table 3 and Figure 1]

Correlations with the Modeling Studies

The initial indications of these studies are that there is a correlation between the results of the modeling studies performed in the previous paper and those reported here. The primary point of similarity is the relative improvement in reaction rates/liquefaction enhancements that are observed as the relative concentrations of H_2S are increased. As noted by other researchers,¹⁵ the amounts of H_2S needed to provide substantial improvements in the liquefaction process are relatively small. Furthermore, there is a rapid falloff in the rate of improvement as the quantities of H_2S are increased (see Table 4). This falloff is

[Insert Table 4]

observed in both the model studies and the liquefaction studies and could be interpreted to mean that H_2S functions mainly as a catalyst to promote hydrogen transfer; however, our results are still too preliminary to verify or deny this possibility. It is important to note that under no instances do we observe incorporation of sulfur into model compounds or coal liquids as would be expected if catalysis occurs.

Quality of the Coal Liquids

Figures 2 and 3 are FIMS analyses of the coal liquids from the 15-min tetralin and 15-min 3% H_2S /20% THQ/tetralin runs corrected for ^{13}C . The tetralin run gave 44% minimum conversion, whereas the H_2S /THQ run gave a 71% minimum conversion. As can be seen, the weight average molecular weights are essentially similar, and the overall distribution of products is much the same.²¹ These FIMS plots also show the presence of remaining tetralin (mw = 132), naphthalene (mw = 128), THQ (mw = 133), quinoline (mw = 129), the THQ dimer (mw = 264), and partially dehydrogenated dimer (mw = 262).

[Insert Figures 2 and 3]

Qualitatively, the coal liquids obtained from the H₂S studies are superior to those obtained using tetralin alone in that they are free flowing liquids at the drying temperature (76°C) whereas those obtained from the tetralin are tarry solids and difficult to handle. The general conclusion is that the quality of the coal liquids deriving from the H₂S/20% THQ/tetralin system is at least as good as that obtained from the tetralin alone. Moreover, considering that the conversions are at least 20% higher in the mixed-solvent system and give the same quality liquids, it must be concluded from these preliminary studies that the H₂S/THQ/ tetralin system is a superior liquefaction system.

The problem of nitrogen incorporation remains to be solved; however, it is clear that a part of this problem may be just inefficient removal of the solvent. A further solution to this problem is to reduce the quantity of THQ used. We have demonstrated that THQ content can be reduced to 5% without significant decrease in overall conversions. Similar results have been briefly reported in an earlier study.²²

With regard to our proposal that H₂S could prevent THQ incorporation in coal, we have some preliminary FIMS data that suggest that it does prevent incorporation; unfortunately, the data are insufficient to draw decisive conclusions.

In future work, we hope to improve the H₂S/THQ/tetralin system sufficiently to promote complete liquefaction at times even shorter than 15 min and with concomitant reduction in THQ incorporation.

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Table 1. H₂S concentration study with tetralin
at 400°C for 15 min. liquefaction yields
as a function of the solubility
(based on carbon content)*

	<u>0% H₂S</u>	<u>3% H₂S</u>	<u>20% H₂S</u>
THF insoluble	56	46	33
THF soluble	42	54	83
Conversion based on carbon remaining	44	54	67

*Reference 21.

Table 2. THQ/tetralin concentration study at 400°C for 15 min.
liquefaction yields as a function of the solubility
(based on carbon content)*,†

	% THQ/Tetralin			
	<u>0</u>	<u>5</u>	<u>10</u>	<u>20</u>
THF insoluble	56	44	38	41
% N	0.63	0.85	0.85	0.86
THF soluble	42	46	58	63
% N	0.40	1.39	1.59	2.30
Conversion based on carbon remaining	44	56	62	59

*Yields corrected for nitrogen incorporation.

†Reference 21.

Table 3. Comparison of the THQ/tetralin/H₂S system with the H₂S/THQ/tetralin system as a function of time.
(based on carbon content)*

<u>Solvent</u>	<u>7.5 min (%)</u>	<u>15 min (%)</u>
THQ/Tetralin/H ₂ S		
THF Insoluble	40	29
% N	1.07	0.99
THF Soluble	93	61
% N	2.61	2.23
Conversion based on carbon remaining	60	71
THQ/Tetralin		
THF insoluble	44	41
% N	1.18	0.76
THF soluble	82	78
% N	2.48	2.16
Conversion based on carbon remaining	56	59

*Yields corrected for nitrogen incorporation
†Reference 21

Table 4. H₂S concentration study with 20% THQ/tetralin at 400°C for 15 min. liquefaction yields as a function of THF solubility (based on carbon content)*,†

	<u>0% H₂S</u>	<u>3% H₂S</u>	<u>23% H₂S</u>
THF insoluble	41	29	25
% N	0.86	0.99	1.0
THF soluble	78	61	95
% N	2.16	2.23	1.93
Conversion based on Carbon Remaining	59	71	75

*Yields corrected for nitrogen incorporation.
†Reference 21.

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FIGURE 1 EFFECT OF H_2S ON CONVERSION OF COAL AT $400^\circ C$
FOR 15 min. IN TETRALIN AND IN 20% THQ/TETRALIN

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FIGURE 2 TETRALIN CORRECTED FOR ^{13}C
Reaction time: 15 min

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FIGURE 3 TETRALIN/THQ/H₂S CORRECTED FOR ¹³C
Reaction time: 15 min

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Appendix D

THE INTERACTIONS OF QUINOLINE AND TETRAHYDROQUINOLINE WITH CATALYSTS.
MODELING HETEROGENEOUS CATALYSTS WITH HOMOGENEOUS CATALYSTS.

THE INTERACTIONS OF QUINOLINE AND TETRAHYDROQUINOLINE
WITH CATALYSTS. MODELING HETEROGENEOUS CATALYSTS
WITH HOMOGENEOUS CATALYSTS. 4.¹

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ABSTRACT

The literature on the catalytic hydrodenitrogenation (HDN) of petroleum, coal, shale oil and tar sands is replete with examples of studies on the reactions of HDN catalysts with model compounds such as pyridine, indole or quinoline. Despite these extensive and often informative studies, to date, the exact mechanism(s) by which nitrogen heterocycles interact with the catalyst surface to undergo first hydrogenation and then ring cleavage and loss of ammonia remains a mystery. The present study attempts to develop a reasonable picture of how nitrogen heterocycles interact with HDN catalysts and undergo HDN through the exploration of the stoichiometric and catalytic reactions of these heterocycles with homogeneous catalysts. We present here studies on the reactions of quinoline (Q) and tetrahydroquinoline (THQ) with $\text{Os}_3(\text{CO})_{12}$ that provide information concerning how these species bind to metals and undergo hydrogenation and dehydrogenation.

INTRODUCTION

There is extensive literature devoted to the subject of catalytic hydrodenitrogenation (HDN) of petroleum, coal, shale oil and tar sands.³⁻¹⁰ This literature is replete with examples of studies on the reactions of HDN catalysts with model compounds such as pyridine,⁴ indole⁵ or quinoline.⁶⁻¹⁰ For example, studies of heterogeneously catalyzed HDN of the prototypical model compounds, quinoline and tetrahydroquinoline (THQ), provide the reaction network shown in Figure 1.^{6,7}

These careful studies have generated all the necessary rate constants and thermodynamic information to evaluate the HDN process, as it applies to quinoline, from a chemical engineering standpoint. Thus, the thermodynamically preferred reaction pathway for HDN of quinoline, as depicted in Figure 1, is the heavily lined pathway.⁶⁻¹⁰ The preferred pathway, in terms of hydrogen expenditure and quality of product, is the pathway that promotes HDN without hydrogenating the second aromatic ring; the unemphasized pathway in Figure 1.

[Insert Figure 1]

Currently, HDN costs account for ~ 80% of the hydrotreating costs associated with refining petroleum. Consequently, there is a considerable economic driving force associated with reducing hydrogen consumption in HDN through development of better catalysts; catalysts that promote HDN via the latter pathway.

Despite the extensive and informative HDN studies already in the literature, to date, the exact mechanism(s) by which nitrogen heterocycles interact with the catalyst surface to undergo first hydrogenation and then C-N bond/ring cleavage and loss of ammonia remains a mystery. The motivating force for the work described below comes from the rationale that studies leading to the elucidation of these mechanisms may make it possible to design better HDN catalysts.

Results and Discussion

Our initial approach to identifying the mechanisms operative in catalytic hydrogenation and in the C-N bond cleavage processes of heteroaromatic species is to explore the reactions of quinoline and THQ with a number of organometallic compounds. Our intent is to establish; (1) whether or not the reactions of quinoline/THQ with organometallic species can be compared with those observed for quinoline/THQ with a standard HDN catalyst; and, (2) if these comparisons will allow us to draw mechanistic analogies between the two systems. We have previously used such comparisons to propose a comprehensive picture of the mechanistic processes that occur in heterogeneously catalyzed HDN.^{1,11,12} This proposal serves as a guideline for the research reported here.

Our preliminary work has centered on studies of the stoichiometric and catalytic reactions of $\text{Os}_3(\text{CO})_{12}$ or $\text{H}_2\text{Os}_3(\text{CO})_{10}$ with quinoline (Q) and THQ. We chose to study the stoichiometric reactions of Q/THQ with these osmium clusters predicated on our interest in preparing stable organometallic complexes of reactants (Q and H_2/D_2), products (THQ) and

Compounds 1 and 2, which were first prepared by Yin and Deeming,¹⁴ have, for the first time, been characterized structurally as shown in Figure 2.

[Insert Figure 2]

Complexes 3-5, were characterized via, mass spectroscopy, ^1H and ^{13}C NMR, elemental analysis and IR. These characterizations, supported by the structures shown in Figure 2, allow us to propose the following structures for 3-5.

[Insert Figure 3]

Visual examination of these compounds quickly leads to the pertinent observation that activation of a C-H bond α to nitrogen in both the heteroaromatic ring in Q and the heterocyclic rings of THQ and piperidine has accrued. This is a common feature of cyclic amine osmium chemistry. In fact, oxidative addition of C-H bonds α to nitrogen in heteroaromatic rings occurs as a general phenomena in both molecular

organometallic chemistry and heterogeneous metal chemistry.¹⁴⁻¹⁷ A second important observation is that we have finally isolated and characterized saturated nitrogen containing metallocycles, 4 and 5, resembling those we have previously proposed to form during catalytic C-H activation/D for H exchange on tertiary amines; and, during catalytic C-N bond cleavage in the transalkylation reaction and in HDN.^{1,11,18,19} In this instance, the metalloazocycles are four membered rings rather than the three membered rings we proposed; however, the intermediacy of three membered rings in the formation of the metalloazocyclobutanes cannot be ruled out. A third observation is that the osmium clusters catalyze the dehydrogenation of THQ (see below and experimental) to form complexes of Q,⁶⁻¹⁰ reactions (2) and (3). Because catalytic dehydrogenation of THQ occurs in CoMo catalyzed HDN of Q,⁶⁻¹⁰ this observation provides an indication that the osmium system can be used to model some aspects of CoMo catalyzed HDN. This is particularly important in view of the work of Fish et al.^{20,21} In their pioneering HDN modeling studies on rhodium catalyzed hydrogenation of Q, they were able to observe selective hydrogenation of Q to THQ; however, they were unable to obtain catalytic dehydrogenation of THQ.

All of these observations permit us to draw conclusions concerning the mechanisms of Q hydrogenation under HDN conditions when considered in conjunction with the following hydrogenation and deuterium labeling experiments.

Catalytic Hydrogenation of Quinoline

We have briefly explored the kinetics of osmium and CoMo catalyzed

hydrogenation of Q to THQ, reaction (5), in order to develop

Catalyst = $\text{Os}_3(\text{CO})_{12}$, $\text{H}_2\text{Os}_3(\text{CO})_{10}$, CoMo

an understanding of the mechanisms involved and to be able to compare the two catalysts. The search for a suitable solvent for the kinetic studies lead to the results shown in Table 1. Of the three solvents

[Insert Table 1]

tested, THF provides the highest reaction rates with the least complications. For the reactions carried out in heptane, the catalysts were found to form insoluble species, after extended reaction times (24h), tentatively identified (by IR) to be the higher cluster, $\text{H}_4\text{Os}_4(\text{CO})_{12}$. For the reactions carried out in MeOH, anomalous products were observed to form resulting from methylation of the THQ. Only in THF were the osmium catalysts found to be completely soluble and produce THQ free of side products. Even in THF the catalyst activities diminish after significant conversions (~ 60%). A plausible explanation for this observation is that the catalyst is converted to a less active form e.g. 2 (vide infra). Consequently, we have relied on initial rates and deuteration studies to develop a mechanistic picture of osmium catalyzed hydrogenation. In our preliminary rate studies, we have evaluated the hydrogenation activity of $\text{H}_2\text{Os}_3(\text{CO})_{12}$, reaction (5), as a function of catalyst concentration. The results of this study, plotted in Figure 4,

indicate that the rate of Q hydrogenation exhibits a first order

[Insert Figure 4]

dependence on $\text{H}_2\text{Os}_3(\text{CO})_{12}$ concentration which in turn signifies that the nuclearity of the catalyst is maintained under the reaction conditions. Therefore, the trinuclear cluster complexes, 1-4, isolated from the stoichiometric reactions are reasonable intermediates in the Q hydrogenation/dehydrogenation equilibria.

We have begun studies of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ hydrogenation rates as a function of hydrogen pressure. Our results indicate that there is an apparent dependence on H_2 pressure; however, our data are incomplete, at present, thus limiting what can be said concerning the involvement of H_2 in the hydrogenation reaction mechanisms. However, it is clear that H_2 activation occurs prior to or as part of the slow step in the catalytic cycle.

In parallel with our hydrogenation studies, we have explored the use of D_2 to provide labelling information of value in identifying various steps in the hydrogenation/dehydrogenation cycles. Through the use of deuterium NMR, we find that considerable deuterium becomes catalytically and regioselectively incorporated in both Q and THQ. The regioselectivity of $\text{H}_2\text{Os}_3(\text{CO})_{10}$ and CoMo catalyzed deuterium incorporation in both Q and THQ are shown in Figure 5.

[Insert Figure 5]

The deuteration results shown in Figure 5 are a measure of the various catalyst-substrate interactions. These results suggest that

there are quite a few similarities and some contrasts between the homogeneous osmium catalyst and the heterogeneous CoMo catalyst. The specific differences that are immediately noticeable are the relatively higher amounts of deuterium incorporated at the 2 position in THQ by osmium in comparison with CoMo and conversely the higher amounts of deuterium incorporated by CoMo at the 3 position. Reasonable mechanistic explanations for these results require an examination of the similarities.

The similarities are more numerous and must be separated into three areas: deuteration that precedes hydrogenation, that which occurs during hydrogenation and that which occurs in THQ. The last area was explored separately by studying the reactions of THQ with both catalysts in the presence of D_2 , and the absence of Q. Under these conditions deuterium incorporates as shown in Figure 6.

[Insert Figure 6]

Both catalysts incorporate deuterium into the aromatic ring at positions ortho and para to the nitrogen as might be expected for C-H activation/D for H exchange in an activated aromatic ring (THQ is an aniline derivative). Aromatic C-H activation is an expected product in osmium reactions,¹⁴ but it's not clear what one would expect from a metal sulfide hydrogenation catalyst. In fact, it's not clear just which metal, either cobalt or molybdenum, is responsible for what catalytic actions in the hydrogenation step given that there is a continuing controversy about the physical interactions or lack of interactions between the two metals. Although cobalt is generally

considered to be the species responsible for hydrogenation, in view of Topsoe's recent suggestions that the two metals form strong chemical interactions at the active site, it is possible that a bimetallic catalyst site is responsible for hydrogenation.^{22,23}

In the osmium reactions with THQ under D_2 , the 2 and 3 positions on ring are also equally deuterated. This observation is valuable for three reasons, first because it implicates compound 4 as the first intermediate in THQ dehydrogenation; second, based on the principle of microscopically reversibility it implicates compound 4 as the last step in the hydrogenation of Q; and third, because dehydrogenation was not complete, it suggests the existence of another intermediate.

This intermediate, which we have not been able to isolate, provides us with a clear idea of the complete, step by step catalytic cycle again based on the principle of microscopic reversibility. Although, the compound was not isolated, the selectivity of the deuteration suggests that both the 2 and 3 positions are activated simultaneously. This result would readily obtain if compound 4 or a similar species were to react further to form a π -allyl complex, eg 6.

6

In this light, analysis of the pattern of osmium catalyzed deuterium incorporation in the unreacted Q provides a picture of the mechanism of quinoline hydrogenation. Most of the deuterium is incorporated at the 2 position in quinoline, but some is incorporated at the 4 position. Incorporation at both positions could arise from competing 1,2 and 1,4 hydrogenation followed by ring inversion at the nitrogen and reductive elimination, reactions (6) and (7):

However, the THQ deuteration experiments indicate that there is no significant difference between the amounts of deuterium incorporated at the 2 and 3 positions. If reductive elimination from the 1,2 hydrogenation intermediate [the reverse of reaction (6)] were facile, then one would expect to see significantly more deuterium in the 2 position than in the 3 position in THQ. Furthermore, the small amounts of deuteration at the 4 position suggest (see below) that 1,4 addition is occurring. If this process proceeds via the same initial complex

that gives 1,2 addition then the ratio of deuterium at the 4 position to that at the 2 position in both Q and THQ should remain constant over time. In fact, the ratio is not constant, increasing steadily as the reaction proceeds. Consequently, deuterium incorporation proceeds by intermediates such as 1 and 2 where C-H activation of the heteroaromatic ring occurs, reactions (8) and (9):

This idea receives further support from the observation that 2 is not an intermediate in the hydrogenation catalytic cycle. If 2 is used as the catalyst species under hydrogenation conditions identical to those used with either $\text{Os}_3(\text{CO})_{12}$ or $\text{H}_2\text{Os}_3(\text{CO})_{10}$ (see Table 1), then hydrogenation of Q to THQ is observed; however, the rate of reaction is one-third that observed with $\text{H}_2\text{Os}_3(\text{CO})_{10}$. Thus, 2 cannot be an active intermediate in the catalytic cycle.²⁴ From these observations and the work of Muetterties and others,^{14-17,25} we conclude that deuterium incorporation at the 2 position occurs via intermediates such as 1 and 2 rather than by 1,2 hydrogenation. Finally, we can conclude that the presence of more than one deuterium at the 2 position of THQ results from prior deuterium incorporation at the 2 position on Q.

The appearance of small amounts of deuterium in the 4 position must

proceed via a reversible 1,4 addition/elimination process; although this is not a particularly favorable process. This conclusion is based on the principle of microscopic reversibility. That is, if dehydrogenation proceeds via compounds 4 and 6, then the next logical step backwards must be the formation of compound 7. 7 must be the last step in the catalytic dehydrogenation cycle and therefore the first step in the hydrogenation pathway. We can then propose a complete picture of osmium catalyzed quinoline hydrogenation/THQ dehydrogenation as shown in Scheme 1.

Scheme 1

In the case of CoMo catalyzed hydrogenation of quinoline, the analysis is much the same. The observation, in the THQ deuteration experiments, of only trace amounts of deuterium at all the positions in the heterocyclic ring does not permit significant discussion about the dehydrogenation mechanism; however, it does indicate that the process leading to extensive D for H exchange at the 3 position in THQ must occur during the hydrogenation of Q and not through THQ-catalyst interactions.

Although, only small amounts of deuterium are incorporated in Q during the CoMo catalyzed deuteration of Q; the incorporation is quite specific. The majority of the deuterium is found at the 3 position with lesser amounts at the 2 and 4 positions. We conclude that deuterium incorporation at the 2 position is likely to proceed by way of a quinoline C-H activation process akin to that observed in the osmium case (as in compounds 1 and 2) rather than via 1,2 hydrogenation, in

order to readily account for deuteration at the 3 and 4 positions both in the Q and in THQ. The evidence implicates a 1,4 hydrogenation process as the pathway for incorporation at these positions.

The rationale for these statements comes from considering the possible steps in the catalytic cycle that will account for all of the observations in the deuteration experiments. For example, the C-H activation/D for H exchange that occurs at the 3 position, leading to the 3,3-dideuterio THQ product, must occur during hydrogenation and must proceed by way of an intermediate or intermediates that allow changes in the stereochemistry of the catalyst vis a vis the face of the partially hydrogenated heterocycle. Furthermore, this same process must allow for reversible hydrogenation/dehydrogenation to provide pathways for the deuteration of the 3 and 4 positions in Q.

The apparently exclusive 1,4 hydrogenation process that occurs in the osmium catalyzed quinoline hydrogenation also appears to occur in the CoMo process. This conclusion is supported by the observation that deuterium incorporates in the 4 position in Q. The deuterium experiments suggest that the difference between the two catalytic systems lies in reactivity of the resulting intermediates. In the osmium system, we propose the straight forward formation of a π -allyl-like complex that rapidly hydrogenates selectively to give active, coordinately unsaturated catalyst and THQ. In the CoMo case, the formation of a true π -allyl complex may not be possible and it is at this juncture that we envision a reversible stepwise hydrogenation process wherein the stereochemistry of the catalyst-heterocycle interaction can be lost. The process that leads to multiple

incorporation at the 3 position is unclear at present; however, based on the known organic chemistry of enamines we can suggest the reversible process shown in (10) where -XH is either a metal hydride shown as the second step in Scheme 2 where D-X is either metal hydride or a sulfhydryl group.

The complete mechanistic picture of CoMo catalyzed hydrogenation of Q as presently understood is illustrated in Scheme 2.

SCHEME 2

Conclusions

These mechanistic interpretations are far from definitive, they require further refinement; however, they do provide a preliminary picture of the catalyst-substrate interactions that occur during the HDN process. We will expand upon this picture in future publications.

EXPERIMENTAL SECTION

GENERAL METHODS:

Both quinoline and tetrahydroquinoline were purchased from Aldrich and distilled from CaH_2 under N_2 prior to use. THF was dried and deoxygenated by distillation from sodium benzophenone ketyl under N_2 immediately before use. Methanol was used as received from Mallinkrodt. n-Heptane, n-octane and n-undecane of 99% purity were used as received from Aldrich. Catalyst precursors were either purchased from Strem Chemicals and used as received, or synthesized according to published methods. Hence, $\text{Os}_3(\text{CO})_{12}$ was prepared from OsO_4 by the method of Johnson and Lewis,²⁶ and $\text{H}_2\text{Os}_3(\text{CO})_{10}$ was prepared from $\text{Os}_3(\text{CO})_{12}$ by the method of Knox, Koepke, Andrews, and Kaesz.²⁷

ANALYTICAL PROCEDURES

Product analyses for all the kinetic studies were performed on a Hewlett Packard 5710A GC equipped with FID and modified for use with 25 m dimethylsilicone capillary column. Chromatograms were collected and integrated on a Hewlett Packard 5880A GC terminal using n-undecane as an internal standard. Infrared spectra were obtained using a Perkin-Elmer 281 IR spectrophotometer. NMR spectra were recorded on a JOEL FX90Q equipped with a 5 mm broad band probe. GC-Mass Spectral analyses were performed using an LKB-9000 or Ribermag R 10 10 C mass spectrometer.

CATALYST PREPARATION

The commercial cobalt-molybdenum catalyst manufactured by Harshaw

and used in these studies was HT-400 E 1/8 and consisted of 3% CoO and 15.1% MoO₃ by weight supported on 1/8 inch extruded Al₂O₃. This catalyst was ground to 60-200 mesh, and sulfided by heating from room temperature to 400°C in 2 hours and then maintaining the temperature at 400°C for an additional 24 hours while blanketing the catalyst with a slow flow (ca 1-2 ml/min) of 10% H₂S - 90% H₂. Analysis provided the following stoichiometry Co₄S₉(MoS_{2.1})₈.

KINETIC STUDIES

All kinetic reactions were carried out in a 45 ml Parr screw cap bomb equipped with a gas inlet and pressure gauge. In a typical kinetic run, a 10 ml solution containing reactants ([cat] = $0.7-3 \times 10^{-3}$ M, [quinoline] = 0.305 M for osmium complexes; or 10-50 mg of CoMo catalyst, [quinoline] = 0.305 M for CoMo reactions) and a magnetic stirbar were placed in a quartz liner which had been soaked for at least 12 hours in concentrated H₂SO₄-(NH₄)₂S₂O₈ to remove trace metals. The liner containing solution, was sealed in the bomb (total volume with liner, 34 ml) and flushed 5 times with at least 700 psi H₂ or N₂. After the final flush cycle the bomb was pressurized to the desired level, generally [H₂] = 600 psi, and placed in an oil bath maintained at the appropriate temperature $\pm 1^\circ\text{C}$, usually 90° or 145°. Periodically, aliquots were removed by cooling the bomb to room temperature, releasing the pressure and removing 0.1-0.3 mL of solution. The run was resumed by repeating the initial pressurization procedure. Progress of the reaction was monitored by GC as described above in the analytical procedures. In this manner 5 to 9 points were collected during the

first 10-20% of the reaction. Initial reaction rates were calculated assuming pseudo zero-order reaction conditions. Mass balance was checked by comparing the area of the internal standard with sum of the areas of products and reactants and was found to agree within 5% even at > 90% conversion.

Deuterium Incorporation

Deuterium incorporation experiments were carried out using the same techniques and reaction conditions as the kinetic runs with the following modifications.

Each run was purged with N_2 prior to pressurization to 125 psi with D_2 . In the studies of the reduction of quinoline, the reactions were quenched at selected times yielding conversions of quinoline to tetrahydroquinoline of 3%-85%. When tetrahydroquinoline was used as the substrate the solution was heated approximately 15 h. The contents of the bomb were concentrated under reduced pressure. Initially, the quinoline and tetrahydroquinoline were separated on a silica gel column eluting with 15:85 Et_2O :Pet Ether (30-60) and the 2H -NMR spectrum of each product was collected in cyclohexane. Once the deuterium resonances were assigned, NMR spectra were collected without separating the products. Integration of the deuterium resonances gave the relative amounts of deuterium incorporation at each site on the deuterated Q and THQ.

Catalytic Dehydrogenation of THQ

A THF solution of $H_2Os_3(CO)_{10}$ (1.5×10^{-3} M) and THQ (.24 M) was placed in a bomb, purged 5 times with N_2 and pressurized with 250 psi of

N₂. The bomb was placed in an oil bath at 145°C. Periodically, aliquots were removed from the bomb and the products were analyzed by GC as previously described. Initially, the solution contained 1.2% quinoline as an impurity in the starting THQ. However, dehydrogenation was observed as the amount of quinoline increased gradually with time. Hence, after 22 h the solution contained 3.0% quinoline, after 93 h 4.2%, and after 166 h 6.3%. The reaction mixture remained homogeneous throughout the run.

A solution containing 271 mg Os₃(CO)₁₂ (.3 mmol), and .6 ml THQ (4.8 mmol), dissolved in 50 mL octane was heated to 145°C in a sealed tube for 40 h. The solvent was removed under reduced pressure and most of the excess THQ was removed by drying in a vacuum (10⁻³ mm) for 8 h. The products were separated by preparative TLC on silica, eluting twice with hexane. The yields of H₂(η²-C₉H₆)₂Os₃(CO)₈ and H₂(η²-C₉H₁₀)₂Os₃(CO)₈ were 94 mg (30%) and 18 mg (6%) respectively.

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Table 1

RATE OF HYDROGENATION OF QUINOLINE BY VARIOUS CATALYSTS^a

Catalyst	Solvent	Temp °C	Turnover Frequency hr ⁻¹
CoMo	Heptane	145	6.5 ^b
Os ₃ (CO) ₁₂	Heptane	145	50
H(C ₉ H ₆ N)Os ₃ (CO) ₁₀	Heptane	145	26
H ₂ Os ₃ (CO) ₁₀	Heptane	145	70
H ₂ Os ₃ (CO) ₁₀	MeOH	145	87
H ₂ Os ₃ (CO) ₁₀	THF	90	11

^a[Catalyst] = 0.7 - 3.0 x 10⁻³ M; [Quinoline] = 0.305 M; [H₂] = 600 psi.

^bBased on total metal.

JA-G2G2-1

FIGURE 1 QUINOLINE HDN REACTION NETWORK

Figure 2

4

3

5

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FIGURE 3

FIGURE 4 DEPENDENCE OF RATE OF APPEARANCE OF THQ ON $\text{H}_2\text{O}_3(\text{CO})_{10}$

FIGURE 5

FIGURE 6

SCHEME 1