

## IRON CARBONYL CATALYZED REDUCTIONS OF MODEL COAL CONSTITUENTS UNDER WATER GAS SHIFT CONDITIONS

Thomas J. Lynch, Mahmoud Banah, Herbert D. Kaesz

Department of Chemistry and Biochemistry  
University of California, Los Angeles, CA 90024  
and

Clifford R. Porter  
Pentanyl Technologies, Inc., 11728 Highway 93, Boulder, CO 80303

### INTRODUCTION

Liquefaction and heteroatom removal are of importance in adapting coal into fuels and chemical feedstocks which now depend on petroleum. Soluble reagents and catalysts are needed to deal with coal solids. Iron pentacarbonyl has been found to be an economically viable reagent and/or catalyst for up-grading coal; studies of its use in desulfurization and hydrogenation have been reported (1). In fundamental studies at UCLA our objective is to elucidate the reactivity of iron carbonyl under water gas shift (WGS) conditions towards organic substrates that model coal structure. Our work is paralleled by similar studies using a variety of other metal carbonyls, (2) and is preceded by studies of Wender and Orchin and their co-workers using cobalt carbonyl (3,4).

### EXPERIMENTAL

Glass reaction vessels, fitted to a 0.3 L copper lined autoclave or a 0.1 L stainless steel autoclave were used for all studies. Reactions were analyzed by extracting the glass liner contents with  $\text{CCl}_4$ , drying with  $\text{MgSO}_4$  and removing solvent on a rotary evaporator. Characterization was performed by IR, GC,  $^1\text{H}$  and  $^{13}\text{C}$  NMR and mass spectral methods. Gas sampling above the reaction mixture shows both  $\text{H}_2$  and  $\text{CO}_2$  (by gas chromatography) indicating that the water gas shift reaction had taken place. Control experiments in which no iron complex was present were performed for all reported reactions. Acridine is the only compound that is significantly hydrogenated under the control conditions; the other substrates are unaffected unless iron carbonyl is also present.

### RESULTS AND DISCUSSION

Reactions in methanol, water and base under carbon monoxide pressure were initially performed at  $150^\circ\text{C}$  to optimize the iron carbonyl catalyzed water gas shift reaction (5,6) see Table I. Nitrogen heterocycles are readily hydrogenated under these conditions. Quinoline, 1, is 100% hydrogenated in the nitrogen-containing ring. Isoquinoline, 3, is both hydrogenated and N-formylated to 4 (7), similarly in 100% yield. Hydrogenation of only one of the two nitrogen containing rings of the phenanthrolines, is

Table I. Reductions with Iron Carbonyl Catalyzed Water Gas Shift System

<u>Substrate</u>	<u>Product</u>	<u>yield<sup>a,b</sup></u>
Quinoline <u>1</u>	<u>2</u>	100%
Isoquinoline <u>3</u>	<u>4</u>	100%
Acridine <u>5</u>	<u>6</u>	100%
4,7-phenanthroline <u>7</u>	<u>8</u>	75%
1,10-phenanthroline <u>9</u>	<u>10</u>	50%
anthracene <u>11</u>	<u>12</u>	25%

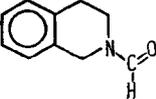
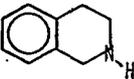
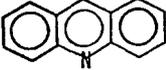
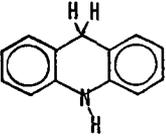
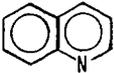
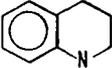
<sup>a</sup>Reaction conditions are as follows: 150°C, 42 kgcm<sup>-2</sup>, 15 h in CH<sub>3</sub>OH (75 ml) H<sub>2</sub>O (25 ml) KOH (4.8 g), substrate (5.0 mmol) and Fe(CO)<sub>5</sub> (2.5 mmol).

<sup>b</sup>Under the above conditions but without Fe(CO)<sub>5</sub>, no reactions are observed.

observed. The yield of 10 is significantly reduced since it forms iron complexes as indicated by a brightly colored aqueous phase partially characterized by  $^1\text{H}$  NMR of acetone- $d_6$  extracts. Anthracene is relatively unreactive under these conditions. We have however found ways in which its hydrogenation may be significantly increased, see below. Compounds which we found to be unaffected at  $150^\circ\text{C}$  are naphthalene, phenanthrene, dibenzyl, anisole, diphenyl ether and dibenzthiophene.

In light of the 100% yields observed in the conversions of 1, 3 and 5 these reactions were performed using catalytic amounts of iron carbonyl; the results are listed in Table II. At  $150^\circ\text{C}$ , 22 and 24 molar equivalents each of 3 and 5, respectively, are hydrogenated. At slightly higher temperatures,  $\text{Fe}(\text{CO})_5$  catalyzes the hydrogenation of 1 with an activity of 43 turnovers.

TABLE II  
REDUCTIONS OF NITROGEN CONTAINING HETEROCYCLES  
USING CATALYTIC AMOUNTS OF  $\text{Fe}(\text{CO})_5$

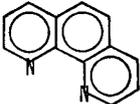
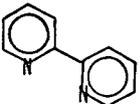
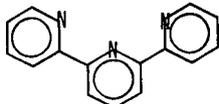
SUBSTRATE	RATIO <sup>A</sup>	T/ $^\circ\text{C}$	PRODUCT AND TN <sup>B</sup>
	55 : 1	150	 (22)
"	55 : 1	300	<div style="display: flex; align-items: center;"> <div style="font-size: 3em; margin-right: 10px;">}</div> <div style="text-align: center;"> <p>"</p>  </div> <div style="margin-left: 10px;">(21)</div> </div>
	28 : 1	150	 (24)
	250 : 1	180	 (43)

A) RATIO OF SUBSTRATE TO  $\text{Fe}(\text{CO})_5$

B) MOL OF PROD./ MOL OF  $\text{Fe}(\text{CO})_5$

Reactions were next undertaken at 300 °C to parallel coal liquefactions which are observed in higher yield at the higher temperature (8). Using catalytic amounts of  $\text{Fe}(\text{CO})_5$ , isoquinoline is again N-formylated and hydrogenated with a total of 35 turnovers (Table II). Dibenzothiophene, on the other hand, remains unreactive. Other studies at 300 °C are summarized in Table III. The first entry shows that anthracene, when treated by itself is less converted (19%) than it was at 150 °C. It occurred to us that some of the constituents in coal, itself, might affect the catalytic properties of  $\text{Fe}(\text{CO})_5$ . We therefore carried out experiments in which the reduction of anthracene was investigated in the presence of the substances listed in the next four entries in Table III. With these a greater degree of conversion of anthracene to 12 is observed. The

TABLE III  
NITROGEN HETEROCYCLES ENHANCING THE HYDROGENATION OF ANTHRACENE  
TO 9,10-DIHYDROANTHRACENE, 1, AT 300°C. <sup>A</sup>

HETEROCYCLE	YIELD OF <u>1</u> / MOL $\text{Fe}(\text{CO})_5$
NONE	19%
	25%
	37%
	62%
	296% (461%) <sup>B</sup>

A) REACTION CONDITIONS AT 300°C :  $\text{CO}$ , 70  $\text{kgcm}^{-2}$ , 1 H IN  $\text{H}_2\text{O}$  (2.5 ML),  $\text{KOH}$  (2.8g), SUBSTRATE (3.0 MMOL), HETEROCYCLE (3.0 MMOL) AND  $\text{Fe}(\text{CO})_5$  (3.0 MMOL).

B)  $\text{CO}$ ,  $\text{H}_2\text{O}$  AND  $\text{KOH}$  AS ABOVE BUT WITH PHASE TRANSFER CATALYST ADDED:  $\text{Me}_4\text{NCl}$  (1.5 MMOL); OTHER CONSTITUENTS,  $\text{Fe}(\text{CO})_5$  (1.5 MMOL); TERPYRIDINE (1.5 MMOL); ANTHRACENE (15 MMOL).

nitrogen heterocycles are thus beneficial to reductions catalyzed by iron pentacarbonyl while quinoline and phenanthroline are themselves undergoing conversion to partially hydrogenated (and/or N-formylated) products. Notably, the nitrogen heterocycles phenanthroline, dipyridyl and terpyridyl which may participate as chelating ligands on iron were more effective for hydrogenation of anthracene than quinoline.

The effect on the reduction of anthracene of a phase transfer catalyst added either by itself or together with dipyridyl is summarized in Table IV. In such additions, dramatic increases are observed in the reduction. Such results at 300°C contrast the work of Alper and co-workers who at room temperature observed no benefit of a phase transfer agent in the reduction of aromatic nitro compounds by  $\text{Fe}(\text{CO})_5$  (or  $\text{Fe}_2(\text{CO})_9$ ) (9). The presence of tetrabutylammonium iodide increases the yield of 9,10-dihydroanthracene 44 times. Combining  $\text{Bu}_4\text{NI}$  and dipyridyl with  $\text{Fe}(\text{CO})_5$ , gives the greatest reduction of anthracene, 17.1 turnovers.

The role of the phase transfer catalysts is most likely to increase the base concentration in the vicinity of the iron catalyst and further, to solubilize the anionic iron intermediates in the organic phase. The last entry in Table IV represents an experiment where the tetraalkylammonium phase transfer catalyst and the base are combined in the form of  $\text{Me}_4\text{NOH}$ . With this reagent the product yield is comparable to that originally achieved with 42 equivalents of  $\text{KOH}$ .

TABLE IV  
EFFECT OF PHASE TRANSFER AGENTS AND  
PHASE TRANSFER AGENTS WITH DIPYRIDYL FOR ENHANCING THE  
HYDROGENATION OF ANTHRACENE TO 9,10-DIHYDROANTHRACENE, 1<sup>A</sup>

PHASE TRANSFER AGENT	TURN- OVER <sup>B</sup>	TURNOVER w/DIPYRIDYL
NONE	0.32	0.62
$\text{Me}_4\text{NCl}$	1.0	3.0
$\text{BzEt}_3\text{NCl}$	-	1.3
$\text{Bu}_4\text{NI}$	14.2	17.1
<hr/>		
$\text{Me}_4\text{NOH}^C$	0.54	

<sup>A</sup>CONDITIONS AS BEFORE AT 300°C

<sup>B</sup>MMOL OF 1/MMOL OF  $\text{Fe}(\text{CO})_5$

<sup>C</sup> $\text{KOH}$  EXCLUDED FROM THIS REACTION.

Some preliminary experiments to elucidate the principal catalyst species in solution and mechanistic features of the reductions were undertaken. To determine the principle iron carbonyl species at reaction conditions, aliquots were withdrawn from the autoclave at 175° C. IR spectra of these obtained within 3 min of sampling indicate that  $\text{HFe}(\text{CO})_4$  is the principal iron carbonyl species (10).

Since the principal species may not be the catalytically active species some other possible candidate complexes were tested as catalysts; these are shown in Table V. All proved inferior to  $\text{Fe}(\text{CO})_5$  even in the presence of dipyriddy. Of special significance is that cluster compounds, which are known to constitute thermal degradation products of metal carbonyls, were equally less effective as the loaded forms of the catalyst than iron pentacarbonyl.

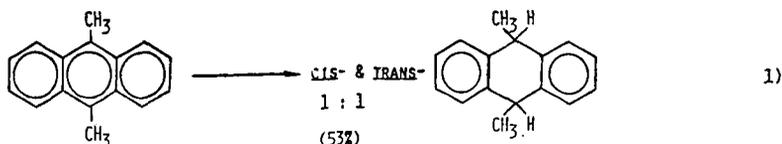
TABLE V  
COMPARISON OF IRON(0) COMPLEXES FOR THE  
HYDROGENATION OF ANTHRACENE TO 9,10-DIHYDROANTHRACENE,  $\frac{1}{2}$ <sup>A</sup>

COMPLEX	TURN-OVER <sup>B</sup>	TURNOVER W/DIPYRIDYL
$\text{Fe}(\text{CO})_5$	14.2	17.1
$\text{Fe}(\text{COT})(\text{CO})_3$	7.1	
$\text{Fe}_3(\text{CO})_{12}$		3.4
$(\text{Et}_3\text{NH})[\text{HFe}_3(\text{CO})_{11}]$		11.2

A CONDITIONS AS BEFORE AT 300°C

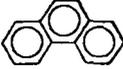
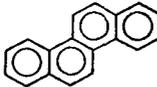
B MOL EQUIV OF  $\frac{1}{2}$ /EQUIV OF IRON(0)

Finally, we tested dimethylantracene to elucidate whether a *cis*-concerted addition or some other process were taking place in the hydrogenation (11). Our results are shown in reaction 1.



We observe a 48%:52% mixture of the cis and trans isomers suggesting that either an electron transfer or hydrogen atom transfer is the initial step of reduction. The reduction potentials of a number of the compounds studied and their ability to be reduced under iron carbonyl catalyzed WGS conditions is shown in Table VI. A correlation is seen among these data, (12), supporting an electron transfer process as the initial step in the reduction of the aromatics.

TABLE VI  
CORRELATION OF HYDROGENATIONS UNDER  $\text{Fe}(\text{CO})_5$  CATALYZED  
WGSR WITH  $E_{1/2}$  vs SCE

<u>SUBSTRATE</u>	<u><math>E_{1/2}</math></u> /V	
	PYRIDINE	-2.52 NOT REDUCED
	NAPHTHALENE	-2.50 "
	PHENANTHRENE	-2.45 "
	CHRYSENE	-2.32 "
	PYRENE	-2.11 "
	ANTHRACENE	-1.94 REDUCED IN MIDDLE RING
	QUINOLINE	-1.14 REDUCED IN NITROGEN-CONTAINING RING
	1,10-PHENANTHROLINE	1.06 "

## CONCLUSION

Iron pentacarbonyl catalyzes the hydrogenation of nitrogen heterocycles regioselectively in the nitrogen containing ring and anthracene is hydrogenated in the middle ring under water gas shift conditions above 150 °C. Chelating nitrogen heterocycles activate the  $\text{Fe}(\text{CO})_5$  toward anthracene hydrogenation. Phase transfer catalysts also have a pronounced enhancement effect on all reductions. There is thus high potential in use of iron pentacarbonyl in hydrogenations when activated by appropriate synergistic agents. Preliminary studies suggest that these reductions proceed by an initial electron transfer process from  $\text{HFe}(\text{CO})_4$ .

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