

PARTICIPATION OF HYDROGEN IN THE HYDROGENOLYSIS AND HYDROGENATION
OF COAL-RELATED MODEL COMPOUNDS CATALYZED BY ZINC HALIDES

T. J. Fredrick and A. T. Bell

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
and
Department of Chemical Engineering
University of California, Berkeley, CA 94720

INTRODUCTION

Model compound studies have recently been performed to help elucidate the types of reactions which occur during the liquefaction of coal in presence of $ZnCl_2(1-5)$. These investigations have shown that $ZnCl_2$ will catalyze the cleavage of ether, sulfide, and aliphatic bridges between aromatic centers and the hydrogenation of fused ring aromatics. It has also been demonstrated that the reactivity of a given structure can be strongly affected by the composition of substituents present on the aromatic nuclei. The purposes of the present work were to identify the role of molecular hydrogen in the hydrogenolysis and hydrogenation of coal-related model compounds and to demonstrate the differences in the ability of $ZnCl_2$, $ZnBr_2$, and ZnI_2 to activate H_2 .

EXPERIMENTAL

Apparatus

Reactions were carried out in a 300-cm³ stirred, stainless-steel autoclave fitted with a glass liner to facilitate introduction of reactants and removal of products. The pressure and temperature within the autoclave were monitored continuously. For most of the experiments described in this paper, the solvent and catalyst were preheated to reaction temperature within the autoclave. The reactant, dissolved in a small amount of solvent, was then injected into the autoclave from a small pressure vessel. Samples of the liquid products were withdrawn at prescribed times during the course of a run.

Materials

Model compounds were obtained commercially. These materials were dried but not purified before use. Benzene and cyclohexane, used as solvents, were dried by refluxing over a sodium-benzophenone mixture and then distilled under dry N_2 .

The $ZnCl_2$, $ZnBr_2$ and ZnI_2 were dried in a vacuum oven overnight at 105°C and then stored in an N_2 -purged dry box. Weighing of the catalyst and transfer into the glass liner was also carried out in the dry box.

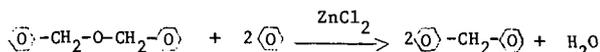
Product Analysis

The liquid products were analyzed by gas chromatography. Product identification was established by gas chromatography/mass spectrometry.

RESULTS AND DISCUSSION

Cleavage of Ether Linkages

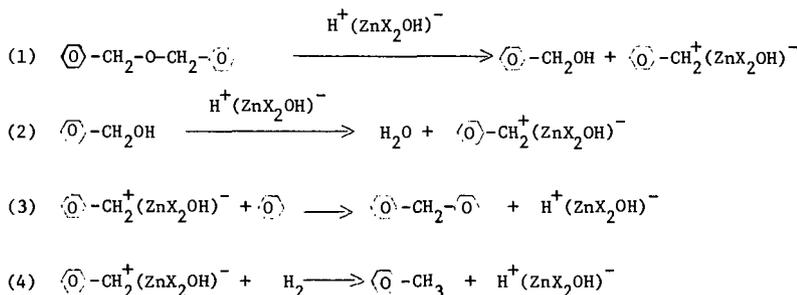
The effects of hydrogen partial pressure and catalyst composition on the hydrogenolysis of dibenzyl ether in benzene solution are listed in Table I. It is observed that in the presence of $ZnCl_2$, diphenyl methane is the principal product formed and that the extent of reaction is unaffected by the presence or absence of molecular hydrogen. These results indicate that the overall reaction can be written as follows:



and that the hydrogen required for the formation of water derives from the benzene. As a result, molecular hydrogen does not appear to be essential for the progress of the reaction.

Table I shows that the catalytic activity of zinc halides decreases in the order $ZnCl_2 > ZnBr_2 > ZnI_2$. It is also seen that in the presence of $ZnBr_2$ and ZnI_2 , toluene is produced in addition to diphenyl methane. Moreover, while the extent of dibenzyl ether conversion is unaffected by the partial pressure of H_2 , the selectivity to toluene increases in direct proportion to the H_2 partial pressure. These results suggest that $ZnBr_2$ and in particular ZnI_2 are more effective in activating H_2 than $ZnCl_2$, but that even in an activated state hydrogen does not affect the rate of consumption of dibenzyl ether. However, once activated hydrogen becomes effective in the formation of toluene.

The accumulated evidence suggests that the hydrogenolysis of dibenzyl ether may proceed via the following sequence of steps

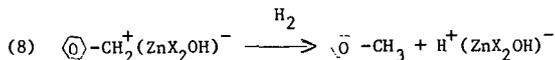
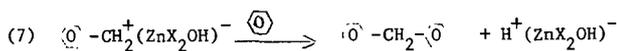
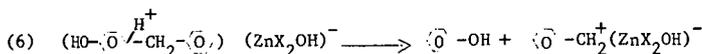
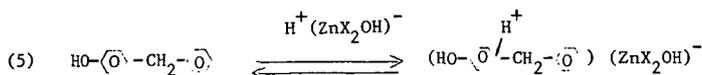


Studies in which the ratio of H_2O to ZnX_2 were varied clearly demonstrate that the active form of the catalyst is a Brønsted acid, $H^+(ZnX_2OH)^-$. Cleavage of the ether is initiated by protonation of the ether and the rate of this reaction is affected by the composition of the zinc halide. The nature of the final reaction products is dictated by reactions 3 and 4 and the ratio of the rate coefficients associated with these reactions is determined by the catalyst composition.

Cleavage of Aliphatic Linkages

The hydrogenolysis of 4-hydroxydiphenyl methane (4HDM) and 1-benzyl-naphthalene (1BN) in benzene solution were studied to establish the effects of hydrogen partial pressure and catalyst composition on the cleavage of aliphatic linkages between aromatic nuclei. In the presence of zinc halide catalyst, 4HDM reacts to form phenol, diphenyl methane, and toluene. As shown in Table II, the hydrogen partial pressure has no effect on the conversion of 4HDM but the selectivity to toluene increases with the hydrogen partial pressure. The catalytic activity in this instance decreases in the order $ZnBr_2 > ZnCl_2 > ZnI_2$, and the selectivity to toluene increases in the order $ZnBr_2 > ZnCl_2 > ZnI_2$. The reaction of 1BN produces naphthalene, diphenyl methane and toluene. The effects of hydrogen partial pressure and catalyst composition on the reactions of this compound are similar to those for 4HDM.

The reaction products obtained from 4HDM and 1BN and the kinetics by which these reactants are converted to products (2) can be explained on the basis of the following mechanism:

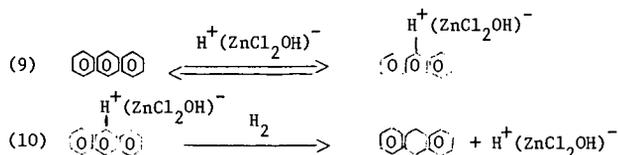


As in the case of the cleavage of ether linkages, reaction is initiated by protonation of the reactant. The primary difference is that this step is reversible and cleavage of the aliphatic linkages occurs in a subsequent rate limiting 1 step. The distribution of final products is governed by reactions 7 and 8.

Hydrogenation of Condensed Aromatics

Studies of the hydrogenation of fused-ring aromatics catalyzed by $ZnCl_2$ have shown (5) that 1-naphthol and anthracene undergo extensive reaction. The influence of hydrogen partial pressure on the extent of reaction and the distribution of products formed is shown in Table III. It is apparent that in the absence of hydrogen both reactants are converted extensively to tar via Scholl condensation. In the presence of hydrogen, 1-naphthol is hydrogenated to 1,2,3,4-tetrahydro-1-naphthol which then undergoes dehydration to form dihydronaphthalene. The latter compound is very reactive (5), undergoing hydrogenation to form tetralin and dehydrogenation to form naphthalene. The hydrogenation of anthracene produces primarily dihydroanthracene and smaller amounts of tetrahydroanthracene and octahydroanthracene.

The hydrogenation of both reactants is believed to proceed by sequential protonation and hydride addition, as exemplified by the first stages of anthracene hydrogenation shown below.



The formation of tetrahydro- and octahydroanthracene is assumed to involve a repetition of steps similar to reactions 9 and 10.

CONCLUSIONS

The following conclusions may be drawn from the present study:

- Zinc halide catalysts are active in their Bronsted acid form, e.g., $\text{H}^+(\text{ZnX}_2\text{OH})^-$.
- Cleavage of ether and aliphatic linkages between aromatic nuclei is indicated by protonation of the substrate and is unaffected by the presence of molecular hydrogen.
- Hydrogen transfer to benzylic groups liberated by the cleavage of dibenzyl ether, 4HDM and LBN and the selectivity for forming toluene from these reactants depends on the nature of the halide used.
- The hydrogenation of fused-ring aromatics involves molecular hydrogen and appears to proceed via sequential protonation and hydride transfer.

REFERENCES

1. D. P. Mobley and A. T. Bell, Fuel 58, 661 (1979).
2. N. D. Taylor and A. T. Bell, Fuel 59, 499 (1980).
3. D. P. Mobley and A. T. Bell, Fuel 59, 499 (1980).
4. D. P. Mobley and A. T. Bell, J. Cat. 64, 494 (1980).
5. S. S. Salim, Ph.D. Thesis, Department of Chemical Engineering, University of California, Berkeley, CA, 1980.

ACKNOWLEDGMENT

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy.

Table I. Effects of H₂ Pressure and Catalyst Composition on the Reaction of Dibenzyl Ether

Catalyst	H ₂ Press. (atm) ^a	Ether Conversion (%) ^b	Toluene	Product Yield ^c Diphenyl Methane	Other
ZnCl ₂	35(N ₂)	81.3	0	88.0	10.2
ZnCl ₂	34	84.5	0	88.4	12.7
ZnCl ₂	82	79.0	0	88.4	9.1
ZnBr ₂	34	22.2	1.8	55.5	45.0
ZnI ₂	31	12.0	9.2	45.6	61.0
ZnI ₂	82	6.0	30.2	31.3	42.2

Reaction conditions: T = 225°C; Benzene = 80 cm³; Dibenzyl Ether ZnX₂ = 4.0 mole/mole.

^aAt reaction temperature.

^bFollowing 30 min of reaction.

^cBased on moles of dibenzyl ether reacted

^dBenzyl alcohol, benzyl halide and dibenzyl benzenes.

Table II. Effects of H₂ Pressure and Catalyst Composition on the Reactions of 4HDM and 1BN

Reactant	Catalyst	H ₂ Press. (atm) ^a	Reactant Conversion (%) ^b	Toluene	Product Yield ^c Diphenyl methane
4HDM	ZnCl ₂	37	27.1	5.4	38.2
4HDM	ZnCl ₂	71	27.9	10.5	30.0
4HDM	ZnBr ₂	44	62.2	3.4	42.0
4HDM	ZnI ₂	37	12.6	27.9	20.2
4HDM	ZnI ₂	68	13.7	49.9	13.7
1BN	ZnCl ₂	44	16.8	12.9	35.2
1BN	ZnCl ₂	68	17.4	20.3	31.7
1BN	ZnBr ₂	81	22.7	6.9	51.8
1BN	ZnI ₂	51	13.4	37.3	26.7

Reaction conditions: T = 325°C; Benzene = 80 cm³; 4HDM/ZnX₂ = 40 mole/mole; 1BN/ZnX₂ = 1.0 mole/mole

^aAt reaction temperature.

^bFollowing 2 hr of reaction.

^cBased on moles of dibenzyl ether reacted.

Table III. Effects of Gas Composition on the Reactions of 1-Naphthol and Anthracene

Products from 1 - Naphthol	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylbenzenes	0.1	-
tetralin	14.0	0.1
dihydronaphthalene	2.1	0.2
naphthalene	3.4	1.6
1-tetralene	3.5	1.6
1,2,3,4 -tetrahydro-1-naphthol	0.1	trace
5,6,7,8 -tetrahydro-1-naphthol	2.1	trace
2-naphthol	-	0.5
tar	-	77.0
Products from Anthracene	H ₂ Conversion ^a (%)	N ₂ Conversion ^a (%)
alkylnaphthalenes	0.4	-
octahydroanthracene	3.2	-
tetrahydroanthracene	13.0	trace
dihydroanthracene	51.0	0.9
tar	-	94.0

Reaction conditions: T = 325°C; P = 107 atm; Cyclohexane = 50 cm³; 1 - naphthol / ZnCl₂ = 1.85 mole/mole
Anthracene/ZnCl₂ = 1.85 mole/mole

^aFollowing 1 hr of reaction.