

REACTIONS OF THE COAL CLEAVING REAGENT, PYRIDINE HYDRIODIDE,  
WITH ETHERS AND ESTERS

David H. Buchanan, A. Mei-Ying Chen and James N. O. Sy

Department of Chemistry, Eastern Illinois University,  
Charleston, IL 61920, U.S.A.

INTRODUCTION

Mayo reported(1,2,3) efforts to break cross-links in coal under mild conditions, by treating a toluene insoluble, pyridine soluble (TIPS) fraction of Illinois No.6 coal with pyridine hydriodide (Py-HI) in pyridine, at room temperature, for six days. The hydroxyl content of the product increased, the molecular weight (VPO, GPC) decreased and iodine was incorporated. Lithium iodide in pyridine showed a similar effect. Treatment of TIPS with sodium in liquid ammonia quenched by  $\text{NH}_4\text{Cl}$  also increased the hydroxyl content but the decrease in molecular weight was less than with Py-HI. Treatment of the sodium/ammonia products with Py-HI further reduced the molecular weight. The suggestion is that these reagents are cleaving similar, if not identical, functional groups in coal.

Sodium in liquid ammonia cleaves ethers in coal(4,5), most likely diaryl or aryl-benzyl but not alkyl-aryl or dialkyl ethers, by a radical anion mechanism.(6)

This study was undertaken to determine if ether or ester groups of types which may be present in coal are cleaved by Py-HI or LiI in pyridine, at moderate temperatures, to produce phenols. Py-HBr(7) cleaves alkyl-naphthyl ethers above 230°, but low temperature cleavage reactions with Py-HI have not been reported. Lithium iodide demethylates 2-methoxynaphthalene in refluxing collidine (172°).(8)

Mono-functional ethers or esters treated with Py-HI or LiI in the presence and absence of coal fractions, solvents, sulfides and radical sources are unreactive at low temperatures but alkoxy groups ortho to an aromatic carboxyl group are cleaved.

EXPERIMENTAL

Pyridine hydriodide was prepared in 78% yield by passing HI gas into a dry toluene solution of pyridine and recrystallizing the solid product from methanol. The following compounds were synthesized by standard methods and have physical constants in agreement with literature values: Benzyl phenyl ether (I), 2-naphthyl-methyl-2-naphthyl ether (II), 1-naphthylmethyl-1-naphthyl ether (III), cyclohexyl phenyl ether (IV), phenyl phenethyl ether (V), and 1-naphthyl benzoate (VI). Other model compounds were reagent grade commercial products, checked for purity by HPLC and NMR, and used without further purification.

Pyridine was distilled from barium oxide under nitrogen before use. Reactions were usually conducted on a .1-10 mmole scale (.02-3M), under nitrogen. Products were isolated from pyridine solutions by quenching with aqueous acid followed by extraction and quantitative analysis using either gas chromatography (12% FFAP column) or HPLC ( $\text{C}_{18}$  reverse phase column). The reported yields (or recoveries) are reproducible within  $\pm 3\%$  absolute. Fractions of an Illinois No. 5 coal (PSOC-252) from the Penn State Coal Data Bank were isolated by the methods of Mayo. For experiments in which ethers and Py-HI were mixed with coal fractions, an aspirator vacuum was applied and broken with nitrogen several times to speed up the swelling or dissolution of the fraction and diffusion of reagents into the coal network.

REACTIONS WITHOUT SOLVENT

As expected from Royer's work(7), the following compounds were cleaved by excess Py-HI in an evacuated, sealed tube at 210° for 45 hrs: Anisole, (I), (IV), (V) and

methyl benzoate. From the ether reactions, phenol was isolated; from the ester, benzoic acid. Only trace amounts of alkyl iodides were found since they react with HI at 210° to yield the observed hydrocarbons. These results show the ethers to behave normally and also indicate that the reactivity of Py-HI is slightly greater than that of Py-HBr, as expected for cleavage by nucleophilic substitution. At 196° and 25 hours, Py-HI converted 2-methoxy benzoic acid to a complex mixture of products including several ring iodinated species (mass spec).

#### REACTIONS IN SOLUTION

As expected, 2-naphthylmethyl-2-naphthyl ether (II) is cleaved by refluxing 57% aqueous HI to yield 2-naphthol. However, at temperatures of 50 to 115°, for up to seven days, Py-HI did not cleave the monofunctional aromatic ethers or esters listed in Table 1 in either wet or dry pyridine, acetonitrile or ethanol. The addition of radical initiators, AIBN or benzoyl peroxide, did not produce cleavage, nor did FeS, FeS<sub>2</sub>, or FeCl<sub>2</sub> added to mimic mineral matter in coal. Added diphenyl sulfide also had no effect.

Ethers (I) and (II) were mixed with Py-HI and TIPS or extracted coal, in pyridine, under nitrogen for up to seven days at 55 or 115°. No cleavage products were detected by HPLC (2% detection limit) and ether (II) was recovered from the coal in high yield.

#### HYDROGEN BONDED ETHERS

Recent data from Larsen(9) and Gethner(10) indicate that ether oxygen in coal may already be protonated and perhaps activated toward iodide attack. Larsen showed that all hydroxyl groups in coal can be derivatized with bis(tri-n-butyltin)oxide and that each introduced tin atom is within hydrogen bonding distance of another heteroatom. Elemental composition requires that this atom be oxygen. Gethner's FTIR study of D<sub>2</sub>O exchanged coal shows that all phenolic hydroxyl groups in Illinois No.6 coal are hydrogen bonded, suggesting that the geometry seen in Larsen's tin derivative is also present in coal itself.

We propose that these results can be explained by structure (VII) in which ether oxygen within a coal cross-link is hydrogen bonded to a phenolic hydroxyl group which is also covalently linked to part of the network. Such ethers may be activated toward iodide attack in pyridine solution where simple ethers would not react.

If a structure such as (VII) were present in TIPS, would it activate the ether toward cleavage by iodide? To answer this, we used 2-methoxy phenol, 2-phenylmethoxy phenol and several alkoxy substituted benzoic acids as model ethers for reactions with Py-HI, LiI and KI in pyridine, acetonitrile and DMSO and found that both 2-methoxy and 2-ethoxy benzoic acid are cleaved by sources of iodide ion in pyridine at 85-115° to produce salicylic acid. The two phenols and the 4-methoxy and 2-phenoxy benzoic acids are inert under these conditions. Results are summarized in Table 2.

The substituted benzoic acids were chosen as compounds in which the effect of internal hydrogen bonding on ether cleavage could be conveniently tested and these results do not imply that ethers cleaved in coal are ortho to carboxylic acids. These results do show that Py-HI and LiI can cleave alkyl-aryl ethers in pyridine if the ether oxygen can be protonated by intramolecular hydrogen bonding. Intramolecular hydrogen bonding in 2-methoxy benzoic acid has been demonstrated in the concentration range of our experiments, conditions where benzoic and 2-methyl benzoic acids are largely dimeric.(11)

Based on fluorescence studies, Ware and co-workers(12) concluded that the carboxyl proton of 3-hydroxy-2-naphthoic acid hydrogen bonds to added pyridine, in toluene solution, without complete ionization of the O-H bond. This implies that the acid proton is available for activating an adjacent ether, possibly as in structure (VIII).

If structures such as (VIII) are present in pyridine solution, and provide conditions sufficient for cleavage, then the reactions with KI and LiI are rationalized. The failure of 4-methoxy benzoic acid to react suggests that electronic effects through the ring are not responsible for the reactions of the ortho isomers. Although kinetics have not been determined, the reaction order methyl>ethyl>>phenyl is consistent with cleavage via nucleophilic substitution on carbon.

The failure of 2-methoxy phenol and 2-phenylmethoxy phenol to react is a problem, since the hydrogen bond in structures such as (VII) must come from hydroxyl rather than carboxyl to be consistent with Larsen's and Gethner's data. Perhaps the geometry for strong internal hydrogen bonding in the model phenols is not appropriate (five versus six membered ring) or the electronic effect of one oxygen inhibits activation of the adjacent oxygen-carbon bond. Studies of other substituted phenols are currently in progress.

#### SUMMARY

Pyridine hydriodide and lithium iodide, in pyridine, dealkylate 2-methoxy and 2-ethoxy, but not 4-methoxy benzoic acids at 115°. These results plus the reports of Mayo et al (1,2,3) allow, but do not require, the conclusion that iodide reagents cleave ethers in coal. Based upon the behavior of these and other model compounds, we believe that any ethers in coal cleaved by LiI or Py-HI in pyridine must have structures which provide intramolecular hydrogen bonding to the ether oxygen to activate the oxygen-carbon bond toward attack by iodide ion. Gethner's and Larsen's recent results indicate that ethers in coal may meet this requirement.

#### ACKNOWLEDGEMENTS

Financial support from the Illinois Coal Research Board and the Faculty Research Council of Eastern Illinois University, plus laboratory assistance from Ken Osborne and Alan Wilcox, is gratefully acknowledged.

#### REFERENCES

1. Mayo, F.R., Buchanan, D.H. and Pavelka, L.A., Fuel Division, Am. Chem. Soc., Preprints, 1980, 25, No. 2, 182
2. Mayo, F.R., Buchanan, D.H., Pavelka, L.A. and Hirschon, A.S., Manuscript submitted to Fuel
3. Mayo, F.R., Hirschon, A.S., Zevely, J.S., Sundback, K., Fuel Division, Am. Chem. Soc., Preprints, 1983, 28, No. 5, 253
4. Lazarov, L. and Angelova, G., Fuel, 1968, 47, 333
5. Alemany, L.B. and Stock, L.M., Fuel, 1981, 60, 1002
6. Burwell, R.L., Chem. Rev., 1954, 54, 615
7. Royer, R., Buisson, J.P. and Demerseman, P., Bull. Soc. Chim. Fr., 1971, 4362
8. Harrison, I.T., Chem Comm., 1969, 616
9. Larsen, J.W., Nadar, P.A., Mohammadi, M. and Montano, P.A., Fuel, 1982, 61, 889
10. Gethner, J.S., Fuel, 1982, 61, 1273
11. Miller, K.J., J. Chem. and Eng. Data, 1976, 21, 308
12. Ware, W.R., Shukla, P.R., Sullivan, P.J. and Bremphis, R.V., J. Chem. Phys., 1971, 55, 4048

Table 1 Starting material recovery from reactions of Py-HI with model ethers or esters

Compound <sup>a</sup>	Solvent	Catalyst	Time	Temp (°C)	% Recovery <sup>b</sup>
I	Py	None, Ext Coal TIPS	5hr-7d	55-80	89-93
I	Py, CH <sub>3</sub> CN	AIBN, (PhCOO) <sub>2</sub>	1-2d	70-95	87-94
II	Py	FeS, FeS <sub>2</sub> , Ph <sub>2</sub> S Ext Coal, H <sub>2</sub> O, FeCl <sub>2</sub>	3-7d	90-115	94-100
II <sup>c</sup>	Py	None	5d	90	98
II	CH <sub>3</sub> CN	None	5d	78	94
III	Py	None	3d	115	100
IV, V	CH <sub>3</sub> CN	None	1, 3d	81	93, 94
VI	Py	None	3d	115	96
Anisole	Py, EtOH	None	5-6hr	Reflux	92-93
Methyl Benzoate	CH <sub>3</sub> CN	None	10hr	81	93

a Identified in Experimental Section

b No cleavage products detected (<2%)

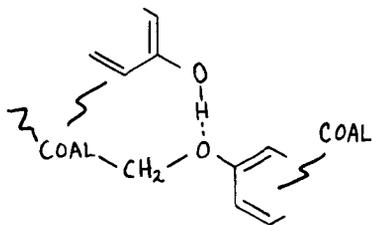
c LiI-H<sub>2</sub>O in place of Py-HI

Table 2 Reaction of substituted benzoic acids or phenols with iodide salts

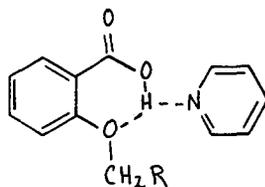
Substituent	Reagent	Solvent	Temp <sup>a</sup> (°C)	% Acid Product	% Ether Recovered
Benzoic Acids					
2-methoxy	Py-HI	Py	85	10	80
2-methoxy	Py-HI	Py	115	81	14
2-methoxy	LiI-H <sub>2</sub> O	Py	85	54	44
2-methoxy	KI	Py	115	58	33
2-methoxy	Py-HI	CH <sub>3</sub> CN	75	-- <sup>b</sup>	99
2-methoxy	Py-HI	DMSO	75	--	94
2-ethoxy	Py-HI	Py	115	18	84
2-phenoxy	Py-HI	Py	115	--	100
2-phenoxy	LiI-H <sub>2</sub> O	Py	90	--	94
4-methoxy	Py-HI	Py	115	--	96
Phenols					
2-methoxy phenol	Py-HI	Py	115	--	100
2-phenylmethoxy phenol	Py-HI	Py	115	--	100

a Reaction time 3 days

b No cleavage products detected (<2%)



Structure (VII)



Structure (VIII)