

THERMAL CHEMISTRY PATHWAYS OF 1-NAPHTHOL

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Previously we have reported our investigations of the thermal chemistry pathways of a number of ether systems under coal conversion like conditions. (1-4). In our studies on naphthalene methyl ether pyrolysis (4), we distinguished three major reaction pathways at 400°C (750°F): O-C alkyl cleavage yielding naphthols and R-H after hydrogen abstraction, an isomerization pathway of the starting ethers and a rearrangement pathway involving initial alkyl C-H hydrogen abstraction. Cleavage of the O-C bond is the most important pathway in this system.

We showed that the decomposition kinetics of the 1-naphthalene methyl ether was faster than that of the 2-isomer and that both naphthalene ethers were thermally more reactive than anisole (Table I). The product slates for the ethers are listed in Table II.

Figure 1 depicts four possible pathways to form naphthalene from 1-naphthalene methyl ether. One way which appeared particularly attractive was hydrodeoxygenation of naphthol. In this study we pursue that question by investigating the high temperature chemistry of 1-naphthol under coal conversion like conditions.

1-Naphthol was heated to 450°C (840°F) in a 30 cc batch autoclave under an initial room temperature pressure of 500 psi (3.5 MPa) of hydrogen. At reaction temperatures, the total pressure of the system rose to ~1000 psi. As shown in Figure 2, under our (largely) gas phase reaction conditions, the major products are naphthalene and tetralin. Other products identified included 1-tetralone and 1-tetralol. The presence of these two C₁₀ oxygenates is consistent with the results of Poutsma and Dyer (5) who studied the thermal chemistry of 1-naphthol without any external hydrogen. Their work was carried out at 400°C (750°F), a temperature where 1-naphthol exists largely in the liquid phase. In their hydrogen starved system, only a 2% yield of naphthalene was obtained, comparable to our naphthalene yields from the thermolysis of the naphthalene methyl ethers (Table II).

Figure 2 shows that the yield of the hydroaromatic, tetralin, diminishes with time while that of naphthalene grows as a function of time. This is consistent with a continuing hydrogen demand from unreacted naphthol and other hydrogen deficient systems (i.e., radicals, 1-tetralone and 1-tetralol) slowly dehydrogenating tetralin to naphthalene.

Under thermal conditions where Poutsma and Dyer (5) show about 33% conversion, the major products are dinaphthylfuran (53%), 1-tetralone (18%), tetralin (3%) and naphthalene (2%). Under hydrogen at similar levels of conversion (39%), we found tetralin (35%), naphthalene (28%), and 1-tetralone (10%), with only 5% dimeric and higher molecular weight species. Clearly with moderate pressure hydrogen, even without any added catalyst, the dimerization

or "growth" pathway so damaging to high oil yields from coal pyrolyses is superseded by reduction of the hydroxyl-containing ring. We calculate a rate constant for the disappearance of 1-naphthol to be $2.2 \times 10^{-3} \text{ sec}^{-1}$ at 450°C under hydrogen and $1.3 \times 10^{-4} \text{ sec}^{-1}$ at 400°C without added hydrogen.

Scheme I provides a series of thermal steps which can account for the initial generation of phenolics, then aromatics, and finally hydroaromatics under moderate hydrogen pressure. We begin with aryl alkyl ethers, moieties determined to be important reactive components in lignins (6) and in low rank coals (7). In contrast, when the naphthol is generated without external sources of hydrogen, the dominant pathway is one of condensation to make a dimeric furan (5). Since in a coal system, there will be some available hydrogen (native to the coal) even a pyrolysis will lead to the formation of some aromatic and hydroaromatic compounds as secondary reaction products following the initial ether cleavage pathway to phenols.

Experimental

1-Naphthol (Aldrich) was used as received (capillary gc analysis showed a purity >99%). The six batch reactors employed were constructed of 316 stainless steel and have previously been described in detail (8). Each reactor was charged with 2.0g of 1-naphthol and 500 psi (3.5 MPa) of hydrogen, attached to a rack and together plunged into a preheated fluidized sand bath and moderately agitated. Heatup times are on the order of 1.5 minutes. Individual reactors were removed from the hot sand bath at various times and rapidly quenched by plunging them into a water bath. Product analysis was by capillary gc. Use of an external standard (n-hexadecane) permitted identification of >90% by weight of the charged material.

Summary

1-Naphthol thermolysis was studied at 450°C (840°F) under moderate hydrogen pressure of ~1000 psi at reaction temperatures. The surprising result is the marked difference from earlier results reported on thermolysis of 1-naphthol under nitrogen: whereas the condensed products, dinaphthylfuran and 1-tetralone are dominant under nitrogen; in the hydrogen case tetralin and naphthalene are the most important products. This change in reaction product is accounted for by a new, competitive reaction pathway provided to the system by the molecular hydrogen.

References

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3. R. H. Schlosberg, P. F. Szajowski, G. D. Dupre, J. A. Danik, A. Kurs, T. R. Ashe, and W. N. Olmstead, *Ibid.*, **63**, 690 (1983).
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6. See, e.g., K. Freudenberg, *Ann. Rev. Biochem.*, **8**, 88 (1983).
7. R. Liotta, *J. Amer. Chem. Soc.*, **103**, 1735 (1981).
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Table I
 UNIMOLECULAR DECOMPOSITION RATES
 FOR METHYL ARYL ETHERS

Batch Autoclaves, 3.5 MPa N₂, 0.1 Hr Residence Time

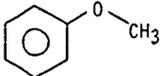
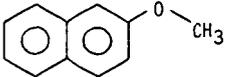
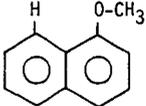
Ether	% Recovered Ether @ T=0.1 Hr <u>450°C</u>	k(hr ⁻¹)		
		<u>400°C</u>	<u>450°C</u>	
	Anisole	91	-	0.94
	2-Methoxy-Naphthalene	71±2	0.5	4.1
	1-Methoxy-Naphthalene	33±3	1.4	12

Table II

NAPHTHYL METHYL ETHER PYROLYSIS RESULTS

Batch Autoclave, 0.1 Hr. Residence Time, N₂

% in Liquids by GC Analysis

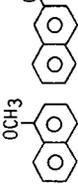
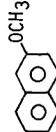
Reactant	Temperature (°C)								
	400	tr	89 ± 2	-	3 ± 1	-	1 ± 0.3	-	0.6 ± 0.2
	450	4	33	13	5 ± 1	tr	3	-	12
	400	-	-	96 ± 2	-	0.2 ± 0.1	-	-	-
	450	3	9	71	0.2	1	-	2	tr

Figure 1

POSSIBLE PATHWAYS TO NAPHTHALENE

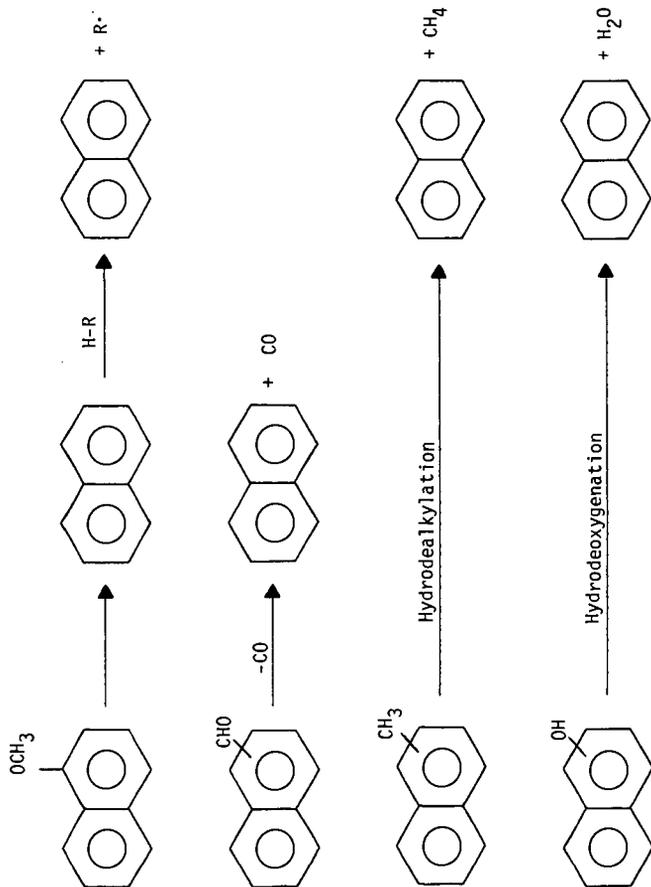


Figure 2

α -NAPHTHOL CONVERSION
450°C./500 psi H₂

