

ytterbium-ligand adducts. The consistency of the results obtained at low ytterbium/ligand ratios with those at higher ratios over the entire range investigated supports this assumption. (2) Although the nature of the interacting lanthanide reagent species cannot be unequivocally established nor critically inferred from these results, it seems likely that a large contribution from partially dissociated species, i.e., $\text{Yb}(\text{fod})_2^+$ or $\text{Yb}(\text{fod})_2^{2+}$ is present. The low polarity solvent does not favor dissociation of the shift reagent but the strong binding ability of the lariat ethers could surely enhance the stability of the dissociated species, perhaps even that of Yb^{3+} . This kind of ligand displacement reaction as opposed to the more common ligand number expansion, although unprecedented, would explain the relatively large LIS values of the side-arm carbon atoms. If the interacting species were $\text{Yb}(\text{fod})_3$, it would be sterically difficult for the side-arm donor groups to interact with the lanthanide metal center. Further studies are currently underway to establish the nature of the interacting lanthanide reagent species with the lariat ethers.

Conclusions

The use of lanthanide shift reagents provides some insight into the structures of lanthanide ion complexes with lariat ethers. Ytterbium complexation by ligands 1 and 2 was studied by this novel approach. LIS data clearly indicate that the substitution position of the methoxy group in the benzene ring is the key to side-arm participation in the interaction with the ytterbium cation. In this way, our results demonstrate binding cooperativity in the case of the *o*-methoxy lariat (structure 1) while no such side-arm-ring cooperativity is evident for the *p*-methoxy lariat (structure 2). However, in both ligands, the crown macroring is, as expected, the main complexation site.

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Pyrolysis Studies of Organic Oxygenates. 5. Thermal Chemistry Pathways of 1-Naphthol under Hydrogen

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Previously we have investigated the thermal chemistry pathways of a number of ether systems under coal conversion like conditions.¹⁻⁴ In our studies on the pyrolysis of naphthalene methyl ethers⁴ we identified three major pathways at 400 °C: O-C alkyl cleavage yielding naphthols and R-H upon hydrogen abstraction, an H-C alkyl ab-

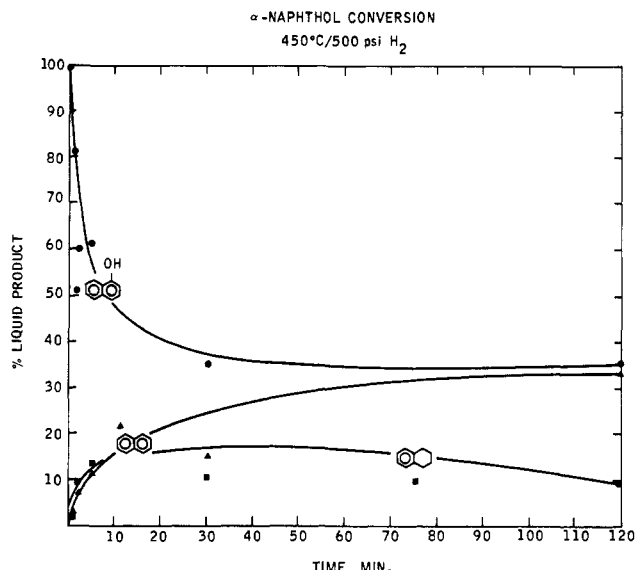


Figure 1.

straction/rearrangement pathway, and an isomerization pathway. The O-C alkyl cleavage is the most important thermal chemistry pathway.

In this paper we continue reporting our results on the thermal chemistry of reactive oxygenates representative of those species believed important in low-rank coals or coal conversion products. Here, we pursue the O-C alkyl cleavage pathway seen for ethers, to try to understand the important secondary reactions of the aryl alkyl ether system. In particular, we have studied 1-naphthol pyrolysis under coal conversion like conditions.

1-Naphthol was heated to 450 °C in a 30-cm³ batch miniautoclave under an initial room temperature pressure of 3.5 MPa (500 psi) hydrogen. The pressure at reaction temperature was ~1000 psi. As shown in Figure 1, under our (largely) gas-phase conditions, the major products are naphthalene and tetralin. Other products identified include 1-tetralone and 1-tetralol. The presence of these two oxygenates is consistent with the results of Poutsma and Dyer⁵ who studied 1-naphthol thermal chemistry without any external hydrogen at a temperature of 400 °C (where 1-naphthol exists largely in the liquid phase). Poutsma and Dyer showed only a 2% yield of naphthalene in a hydrogen starved system. This level of naphthalene is comparable to our yields of naphthalene from the thermal chemistry of naphthalene methyl ethers under an inert atmosphere.⁴

The tetralin yield diminishes with time (Figure 1) and that of naphthalene increases with time. This is consistent with hydrogen demand from unreacted naphthol and other hydrogen-starved systems (e.g., radicals, 1-tetralone, etc.) slowly dehydrogenating tetralin to naphthalene. At the moderate level of hydrogen pressure employed along with the high temperature of the experiments, hydrogen demand from the system appears to outstrip the ability of molecular hydrogen to replenish the hydroaromatic.

Under thermal conditions where Poutsma and Dyer⁵ show about 33% conversion (75 min at 400 °C, no hydrogen), the major products are dinaphthylfuran (53%), 1-tetralone (18%), naphthalene (2%), and tetralin (3%). Under reaction conditions of 450 °C and 1000 psi of hydrogen at 39% conversion, we found tetralin (35%), naphthalene (28%), and 1-tetralone (10%) with 5% dimeric and higher molecular weight species. Clearly under

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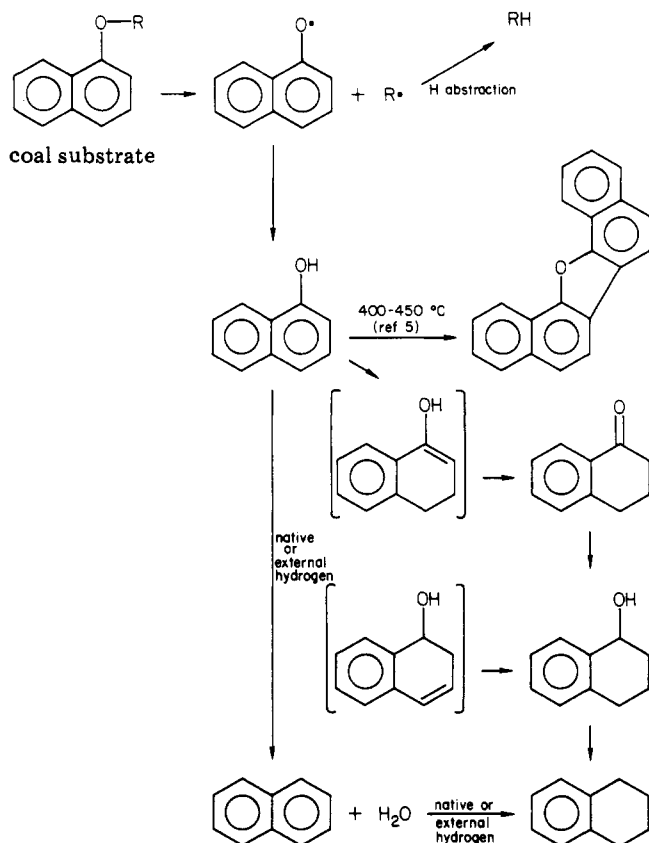
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Scheme I. Proposed Sequential Conversion of Coal's Native Ethers to Aromatic and Hydroaromatic Hydrocarbons



our moderate hydrogen pressure conditions, the pathway proposed by Poutsma and Dyer⁵ is superseded by reduction of the hydroxyl-containing ring. We calculate a rate constant (for the disappearance of 1-naphthol) of $2.2 \times 10^{-3} \text{ s}^{-1}$ at 450 °C under hydrogen vs. a rate constant of $1.3 \times 10^{-4} \text{ s}^{-1}$ determined at 400 °C without added hydrogen. The dramatic movement of our product slate to two-ring (vs. five-ring) and naphthoaromatics (vs. oxygenates) using 1000 psi of hydrogen and no catalyst is a surprising result.

Scheme I provides a series of thermal steps which can account for the initial generation of phenolics, then aromatics, and finally hydroaromatics under hydrothermal conditions starting from alkyl aryl ether moieties (functionalities determined to be important for lignins⁶ and for low-rank coals⁷). In contrast, when the naphthol is generated without external sources of hydrogen, the dominant pathway, even at 400 °C, 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 under an inert atmosphere will lead to some formation of aromatic and hydroaromatic compounds following the initial ether conversion to phenols. This interpretation is consistent with a report by Collins that 1-naphthol-¹⁴C plus Illinois No. 6 coal at 400 °C for 20 h gave some small amount of naphthalene-¹⁴C.⁸

Experimental Section

1-Naphthol (Aldrich) was used as received (capillary GC analysis showed 1-naphthol purity of >99%). The six batch reactors employed were constructed of 316 stainless

steel and have been described in detail.⁹ The reactors were each charged with 2.0 g of 1-naphthol and 3.5 MPa of H₂ (500 psi), held on a rack, and plunged into a preheated fluidized sand bath and moderately agitated. Individual reactors were removed from the hot sand bath at various times and rapidly cooled by plunging them into a water bath. Product analyses were carried out by capillary GC. Use of an external standard (hexadecane) allowed identification of >90% by weight of charged material.

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Conjugate Addition-Cycloacylation of Acetylenic Diesters: Synthesis of Highly Functionalized Cyclopentenones

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Intramolecular trapping of anionic species generated by conjugate additions to unsaturated carbonyl compounds have recently provided some interesting new reaction sequences.¹⁻³ The majority of these reactions have involved 1,4-additions to α,β -ethylenic ketones and esters. Since nucleophilic conjugate additions to α,β -acetylenic esters followed by intermolecular capture of the intermediate anionic species have provided a wealth of useful methods for acyclic olefin synthesis,⁴⁻¹¹ we felt that intramolecular capture of the anion could serve to generate highly functionalized and substituted cyclic olefins. This report describes a conjugate addition-cycloacylation sequence on 1,6-hex-2-yne diol esters 1.

In order that the conjugate addition-cycloacylation might be attempted, we first required a short, efficient method for preparation of the acetylenic diester substrates and two sequences were tested (eq 1). Alkylation of the dianion¹² of isobutyric acid with propargyl bromide provided acetylenic acid 2. Treatment of acetylene 2 with *n*-butyllithium (2 equiv) followed by quenching with CO₂,

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