INVESTIGATION OF THE ROLE OF ETHER GROUPS DURING COAL LIQUEFACTION

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A considerable effort has been made in recent years to further the understanding of the structure of coal and to achieve a fundamental understanding of the mechanism of coal liquefaction. Many models have been put forth to explain or correlate data obtained from liquefaction experiments. In most of these studies, species are lumped or grouped by similarity in for example distillation properties (1) or solubility characteristics (2). However, the mechanism of coal liquefaction depends not only on operating parameters such as nature of the donor solvent, temperature and pressure but also on the characteristics and rank of the feed coal. Consequently, kinetic models based on the above lumped parameters may not apply to different processes or for different feed coals.

Neavel's view that the initial chemical reactions involve homolysis to yield free radicals which are capped by hydrogen from the donor solvent or hydroaromatic structures in the coal (3), has been generally accepted. The presence of labile linkages, such as ether groups, in the lattice networks would presumabily hasten the comminution of the coal matrix. However, the importance of ethers in this role has been demonstrated (4-10), but has not been conclusively established. The presence of ether bonds in coal has been inferred from alkali metal reduction studies (11-13) in which the products were considerably more soluble in pyridine, were of a lower molecular weight and were of a higher phenolic content. Siskin and Aczel (9) carried out a parallel study on coal pyrolysates and model compounds. By selectively blocking existing hydroxyl groups, they were able to determine the hydroxyl groups which were generated by ether cleavage during pyrolysis.

We intend to present additional evidence as to the importance of ether cleavage during the early stages of coal liquefaction through a comparison of different kinetic analyses.

EXPERIMENTAL

Detailed information on the experimental procedure were described previously (8). Characteristics of the coals studied are listed in Table 1. The liquefaction experiments were conducted with the use of tubing bomb reactors heated in a fluidized bed sand bath. Basically, coal was heated to temperatures between 350 and 425°C for up to 60 minutes in the presence of tetralin under a hydrogen atmosphere. Following each experiment, the products were dispersed in a large excess of hexane. The hexane - insoluble material was filtered, washed and dried. An aliquot was extracted with THF in a Soxhlet apparatus, and the total conversion to soluble material and gases was calculated from the weight of insoluble residue.

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Direct oxygen determinations were conducted on the coals and the hexane - insoluble products by using the pyrolysis mode of the Carlo Erba Elemental Analyzer. The measured oxygen contents of the hexane - insolubles were recalculated as a percentage of the dry coal. This total oxygen was subdivided into two components, hydroxyl and unaccounted oxygen, since the amount and changes

$$O_T = O_{OH} + O \text{ unaccounted} \qquad 1)$$

in the carbonyl groups during liquefaction are small (5). Hydroxyl concentrations of the various samples were determined by acetylation. All of the results reported are averages of duplicate values.

BACKGROUND AND THEORETICAL DEVELOPMENT

We had previously noted that the rate of conversion of the western coal (PSOC-521) was slower than those of the Interior (PSOC-767) and Eastern Province (PSOC-757) coals. Sample data are given in Table 2. The Wyoming coal was also inferred to have the highest concentration of ether groups (7.7 O/100 C atoms) for the three coals studied (8). If ether cleavage is an important process in the early stages of liquefaction, this coal should perform well. That it does not could be accounted for if in this coal, the ethers constitute multiple crosslinks, a majority of which have to be cleaved in order to generate soluble products, or if the ether links for this coal are stable and do not react or are relatively slowly cleaved under the conditions used. A more sophisticated kinetic approach will now be presented, which takes account of the complex nature of coal liquefaction.

This approach is an adaptation of that of Szladow and Given (14) in which the theoretical analysis assumes many parallel reactions in a complex reacting mixture. Golikeri and Luss (15) were the first to establish a method for determining the apparent activation energies, E', in systems comprising many parallel first order reactions whose activation energies may be temperature and conversion dependent. Since concentrations are based on molarity rather than mass, the generation of activation energies has little meaning for systems such as coal liquefaction. Szladow and Given (14) extended this treatment for the case where the total mass as opposed to the total number of moles is known for the reacting system. It was shown that E' can be derived at various conversion levels of x using equation 2).

$$\frac{d \ln t_x}{d\,(1/T)} = \frac{E_a}{R} \qquad 2)$$

t_x = time needed to achieve a specific level of conversion

E_a = the weighted mean of the activation energy at a specific level of conversion.

Using this approach, apparent activation energies were generated for conversion to THF solubles and for removal of unaccounted oxygen.

RESULTS AND DISCUSSION

Since the unaccounted O is determined by difference, all errors incurred throughout the dtermination of total oxygen and O as OH end up in this term. Plots of unaccounted O removal versus time were adjusted to account for the nonisothermality of the first two minutes and for the presence of unconvertible ethers, i.e. benzologues of furan. Shown in figure 1 is a representative plot for the Wyoming coal. The coordinates were adjusted in the following manner:

$$\% \text{ O unaccounted removed} = \frac{O_i - O_o}{O_m - O_o} \times 100 \qquad 3)$$

where

O_i = unaccounted oxygen removed at residence time, t_i

O_o = unaccounted oxygen removed at t_i = 2 minutes

O_m = maximum unaccounted oxygen removed; that is, that part of the unaccounted O that in principle could be removed at infinite reaction time. (Highly unreactive oxygen, as in furans, is excluded).

By defining O_m in this manner, as oppose to O ($t = \infty$), those O functionalities that may be generated by retrogressive reactions, such as condensation reactions, can be ignored. Since unaccounted O removal was found to be linearly related to generation of THF-solubles (8), O_m was obtained from an extrapolation of a least squares fit of the data to C_m. C_m is defined as the sum of the reactive macerals plus one third of the inert macerals less fusinite.

The apparent activation energy, E', for different conversion/removal levels was determined using equation 2 and figure 1. The logarithm of the time needed to attain specific levels of removal of unaccounted O was plotted against the reciprocal of temperature. From the slopes of these lines (E'/R), the activation energies were determined. The values for the three coals are plotted against the level of unaccounted O removed in figure 2. Error bars reported as the standard deviation of the slopes of these plots are also included. It should be noted that E' increases with level of unaccounted O removal. This is consistent with the behavior of reacting mixtures; namely, the more reactive species are preferentially consumed leaving behind the more refractory compounds.

Apparent activation energies were generated in an analogous manner for conversion of the three coals to THF - soluble material. The values for E' are plotted against level of conversion in figure 3. The associated error bars are based on a 90% confidence level. It should be noted that the large errors are reflective in both cases of fewer data points available at higher levels of conversion, as well as the uncertainty in contact time measurement.

It is striking that for any one coal, the plots of conversion against activation energies for production of THF-solubles, and for removal of unaccounted oxygen are closely similar (within the limits of experimental error). The implication seems to be that it is primarily ether cleavage processes that determine the magnitudes of the activation energies for the reactions generating THF-solubles.

In light of the estimates of maximum numbers of ethers cleaved in the three coals (8), as well as their activation energies at different conversion levels, it appears that the basis for the Wyoming coal's slower conversion is the need to cleave a greater number of labile bonds to generate a specific level of conversion to soluble products. The "ethers" in both the Wyoming coal (PSOC-521) and the Ohio coal (PSOC-757) exhibit a wide range of activation energies that are paralleled by their activation energies for conversion to THF-solubles. The Oklahoma coal (PSOC-767) contained the fewest "ethers" (4.1 O/100 C atoms), and also the range of activation energies for cleavage of these was least over the level considered. Furthermore, the change in activation energy for overall conversion was also least for this coal.

In view of previous studies (6, 9, 10, 16, 17) the unaccounted O lost during the early stages of coal liquefaction is probably from structures analogous to phenyl - benzyl and dibenzyl ethers. Under conditions of greater severity additional species may be removed or even added. Phenols present (18) or generated in the products may enhance the cleavage of diaryl ethers. The small magnitudes of the activation energies at low levels of conversion at first sight seem surprising. However, Anthony et al. (19) have shown that in the complex set of parallel reactions occurring during the rapid devolatilization of coal, the overall temperature coefficient for the whole set of reactions can be low, and, in fact, lower than the activation energy for any pure component of the reaction mixture decomposing on its own. In view of the possibility that coals contain a fairly high concentration of physically trapped molecules (20), the processes involved in liquefaction may include activated diffusion out of the macromolecular network. However, this cannot be proven from the activation energy data presented here.

CONCLUSIONS

Since the Wyoming coal (PSOC-521) has a slower conversion in-spite of its higher number of cleavable ethers (8) and its comparably low activation energy for conversion to THF-solubles and for un-accounted O removal, it is inferred that this coal is extensively cross-linked by ether linkages.

Similar changes in activation energies were obtained with level of total conversion and extent of unaccounted O removal for any one coal up to more than 50% conversion. Since the removal of unaccounted O consists of ether cleavage, we infer that ether cleavage continues to be important, not only in the earliest stages of coal liquefaction.

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TABLE 1

Characteristics of Coals Used

PSOC No.	757	767	521
State	Ohio	Oklahoma	Wyoming
Seam	Ohio No. 4	(unnamed)	Rock Springs No. 7
ASTM rank class	HVB	HVA	HVC
C (wt.%, dmmf)	81.3	82.1	79.0
H (wt.%, dmmf)	5.3	5.6	5.2
O (wt.%, dmmf)	9.3	8.4	13.8
S, total (wt.%, dry basis)	3.39	3.55	0.78
Maceral composition (%)			
Vitrinites	75.7	91.5	94.2
Exinites	8.0	2.1	1.0
Inertinites	16.4	6.4	4.8
Mean maximum reflectance of vitrinite (%)	0.50	0.54	0.52
Mineral matter (direct by LTA)(wt.%)	7.92	5.69	4.72

[a]Includes 5.4% semifusinite and 7.3% micrinite.

TABLE 2

Time Needed to Attain Specific Level of Conversion

	Level of Conversion	
PSOC No.	50% of dmmf reactive macerals at 400°C	75% of dmmf reactive macerals at 425°C
521	18.6	44
757	8.0	6.6
767	7.5	7.4

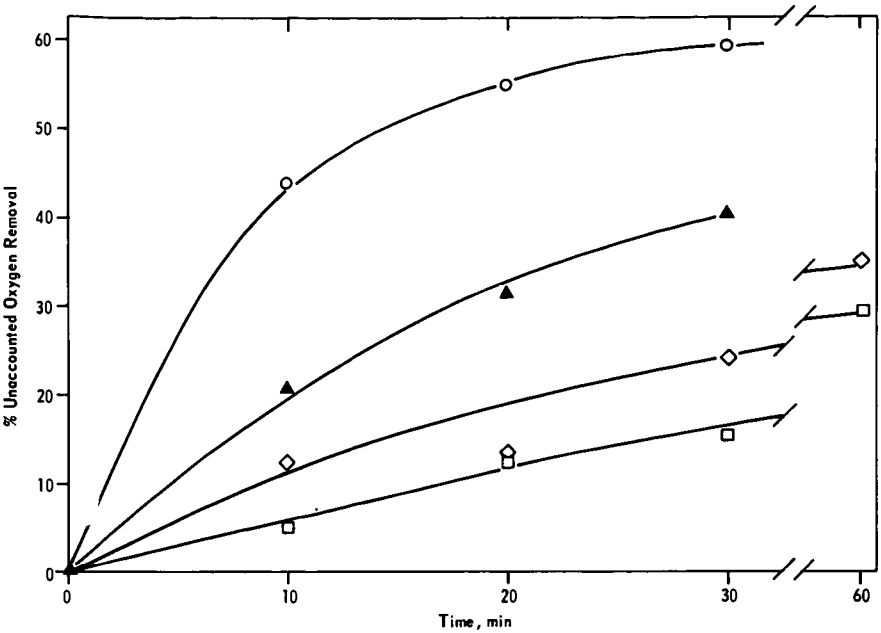

Figure 1. REMOVAL OF UNACCOUNTED OXYGEN FROM WYOMING COAL AS A FUNCTION OF TIME (with transformed coordinates)
○ 425°C ▲ 400°C ◇ 370°C □ 350°C

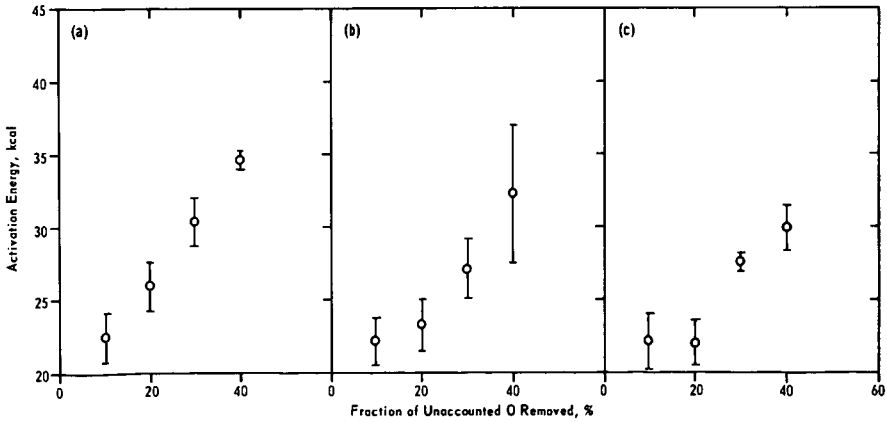

Figure 2. "ACTIVATION" ENERGIES FOR THREE COALS AT DIFFERENT LEVELS OF REMOVAL OF UNACCOUNTED OXYGEN
(a) PSOC-521; (b) PSOC-757; (c) PSOC-767

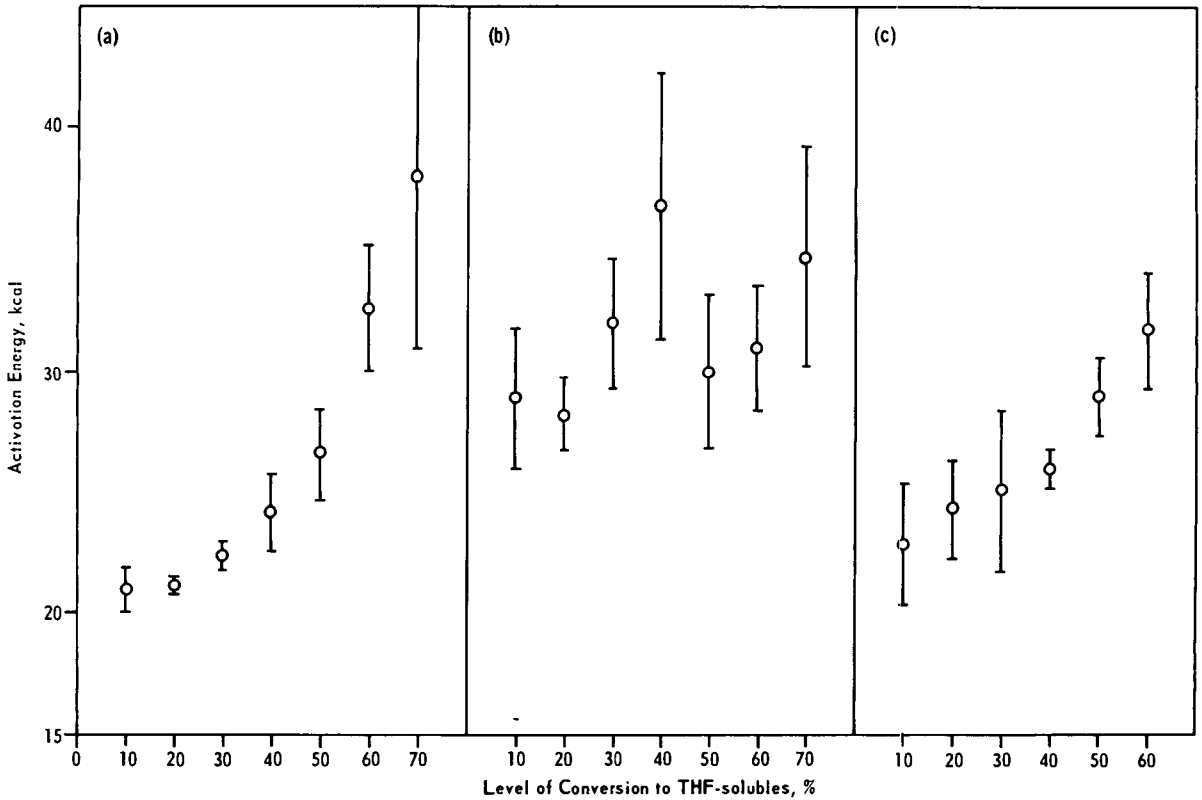

Figure 3. "ACTIVATION" ENERGIES FOR THREE COALS AT DIFFERENT LEVELS OF CONVERSION
(a) PSOC–757; (b) PSOC–767; (c) PSOC–521