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Ranking of Hydrogen Donor Reactivity by Model Acceptor and by Coal Conversion

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Abstract: Coal liquefaction processes are usually based on the thermal cleavage of activated bonds giving reactive carbon and oxygen radicals, which abstract hydrogen atoms from the donor solvents. A series of model donor solvents were used to rank their efficacy for the dissolution of Freyming coal. The transfer of hydrogen from the solvent to the coal fragments as measured by coal conversion, was examined. The ^1H nmr analysis of the reacting mixture defines the recycle index which characterizes the ability of these solvents as efficient recycle oils in coal liquefaction processes. The hydrogen donors are ranked according to their ability to convert coal to THF-soluble. A model hydrogen acceptor, benzylphenylether, was also used to rank the model donors. Ranking of hydrogen donor reactivity by coal conversion and by benzylphenylether shows a direct correlation.

Key words: Coal liquefaction, hydrogen donor, coal conversion, benzylphenylether

Introduction

The important role that hydrogen donor species play in quenching the thermally generated radical intermediates during thermal cleavage of chemical bonds in coal related structures has been studied (Meyer *et al* 1990a, b; Oviawe *et al*., 1993a,b).

Industrial processes for continous liquefaction of coal under hydrogen at high pressure and at elevated temperature (400-500°C) usually use a process-generated solvent (recycle oil) to disperse the coal in slurry. The role of the solvent is crucial to obtain steady-state usable coal-derived liquids over successive passes of the recycle oil. Solvent refining is one of the most attractive means for converting coal into liquid fuels. Various aspects of the liquefaction process have been studied extensively (Oviawe, 1989; Le-Roux *et al*., 1982; Ruixia *et al*., 2004a,b; Hong *et al*., 2003). The studies have varied widely, ranging from rate determination utilizing several types of coal related compounds such as benzyphenylether (BPE) and of donor solvents to attempt to identify the composition of specific fractions of the products.

In a previous study, it has been demonstrated that $-CH_2-$ and $-CH_2-CH_2-$ bridges connected aryl groups in coal (Benjamin *et al*., 1978). In a related study, we had earlier explored the behaviour of model acceptors to rank solvents for their effectiveness in stabilizing the radicals generated from the pyrolysis of benzylphenlether (Oviawe *et al*., 1993b)

We had earlier (Oviawe *et al*., 1989) used the benzyl and phenyloxy radicals generated thermally from benzylphenylether (BPE) to study hydrogen transfer in model hydrogen donor solvents such as tetralin (T), indane (I), 9,10-dihydrophenanthrene (DHP) and 1,2,3,4-tetrahydroquinoline (THQ).

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In this study, a related aspect of hydrogen transfer reactions is explored to determine if model acceptor experiments effectively mimic the behavior of coal in liquefaction and if so, whether they can be utilized to rank solvents for their coal liquefaction effectiveness. The direct measurement of coal conversion for model donors in this work permits comparison with model acceptor results. This study compares the results obtained using BPE with those obtained using coal to define the most efficient solvents for use in industrial processes

Materials and Methods

Materials and Solutions

Hydroaromatic substrates (1,2,3,4-tetrahydroqunoline, tetralin, indane, 9,10-dilydrophenanthrene (Aldrich 98% purity grade) and benzylphenylether (Fair Field) were used without further purification. Freyming coal was generously supplied to us by CERCHAR. Solutions were obtained as 2:1 molar mixtures of BPE with each solvent (10 and 5 millimoles, respectively) and were introduce into the microreactor.

Competition Between the Different Solvents in the Presence of Coal

Reaction of Freyming Coal with Hydroaromatic Compounds

A scheme of the micro reactor has been presented previously (Oviawe, 1989). A glass tube (volume ~10 cm^3) was fitted into the body of the reactor to avoid coking of radical products on the steel walls and to enable quantitative analysis of the products. The microautoclaves were filled with the reactants and allowed to stand in a fluidized sand bath at 400°C for 30 min in a nitrogen atmosphere while agitating at 700 cpm. The reactor and content were then cooled rapidly and opened after reducing the residual pressure (~ 8 MPa) to one atmosphere. Weight losses in the glass tube were less than 1%. The solution was divided into aliquots for ^{1}H nmr analysis. The microreactor allow both rapid heating and cooling of the reaction mixture. For each reaction with coal as substrate 0.5 g of Freyming coal ground to 200-270 mesh (53-74 μm) and dried in vacuo overnight were introduced into the micro reactor and 5 millimoles of hydroaromatic solvent were used. For each experiments with coal, the solvent was composed of the hydroaromatic substrate of interest and 1-methyl naphthalene as diluent. The % conversion of coal as a function of time is given in Table 3 (Fig. 1).

^{1}H nmr Spectroscopy

^{1}H nmr was carried out at 400 MHZ. A known quantity, Ws, of the above solution was diluted with deuterated dimethylsulphoxide (99%, CEA) for nmr analysis. The total number of moles, n_i, of each compound, I , in solution was calculated from the integrals I_i and I_r of ^{1}H signals of compound *I* and of reference r (hexamethylcyclotrisiloxane Aldrich 98%) of molecular weight Mr added to the solution in known quantity (W_r);

$$n_i = \frac{I_i}{H_i} \times \frac{H_r}{I_r} \times \frac{W_r}{M_r} \times \frac{W_t}{W_s}$$

Where H_i and H_r are the number of equivalent protons in each signal. The expected accuracy is 1-2%.

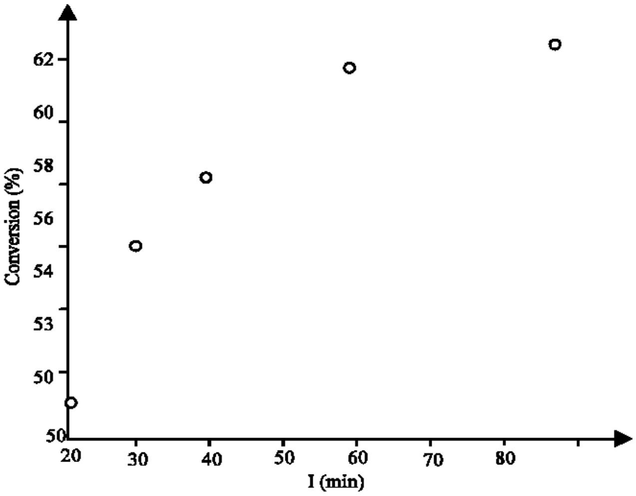


Fig. 1: Percentage conversion of coal as a function of time

Results and Discussion

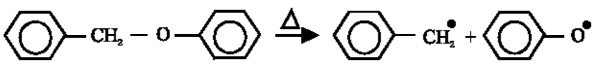
A series of four hydroaromatic solvents were used to rank their efficacy for the dissolution of freyming coal. The ranking of the model donors according to their reactivity for coal conversion is given in Table 1. The lowest donor is indane while the highest apparent donor is THQ.

In comparing the results presented in Table 1, especially taking note of the recycle index of each solvent it is clear that the best solvent for the liquefaction of coal at 400°C is DPH (RI = 0.72)

It has been widely recognized that coal liquefaction proceeds by means of pyrolytic degradation of coal molecules and the stabilization of the degraded radicals by solvent to enhance liquefaction by the solvent (Kulik *et al.*, 1980; Kuhlamann *et al.*, 1985). The solvent can also stabilize the radicals through dispersion by dissolution and solvation and hydrogen transfer (Mochida *et al.*, 1979; Curtis *et al.*, 1984). Thus, an effective solvent for the liquefaction is required to have high dissolution and hydrogen donating abilities (Mochida *et al.*, 1979). From our studies, THQ proved to be an excellent solvent. THQ and its dehydrogenated from quinoline, have high polarity which allow penetration of the coal structure and aid in dispersion of the dissolved coal. Its N-H bond is weaker than C-H bond in tetralin and in the other two solvents, thus its hydrogen donating activity is superior to those DHP, T and I .

Although the % conversion of coal using THQ is very high but the recycle index is also very low (RI = 0.38). We had earlier showed that THQ starts to decompose at a temperature of 350°C leading to the formation of degradation products such as orthotoludine (Oviawe *et al.*, 1989).

The thermal cleavage of activated bonds in BPE results in the formation of phenoxyl and benzyl radicals.



$P \rightarrow 2R^{\bullet}$

Table 1: Reactant and products issued from the liquefaction of coal in the presence of hydroaromatic solvents at 400°C (30 min)

	Moles × 10:	RI in the presence of coal	RI in the presence of BPE	Conversion of coal (%)
Tetralin initial	15.153			
Tetratlin	11.123			
.Tetralin	4.030	0.43	0.65	54.80
%. Tetralin	26.60 %			
Naphthalene	1.733			
THQ initials	15.053			
THQ	7.251			
.THQ	7.802	0.38	0.43	73.61
%.THQ	51.83			
Quinoleine	2.964			
Indane initial	16.925			
Indane	13.862	-	-	36.62
.Indane	3.063			
% Indane	23.30			
DHP initial	11.023			
DHP	4.422			
.DHP	6.601	0.72	0.83	72.32
% DHP	59.88%			
Phenanthrene	4			
	761			
Methylnapthalene Initial	14.169			
Methylnaphthalene	12.212			
.Methylnaphthalene	1.957			
% Methylnaphthalene	13.81%			

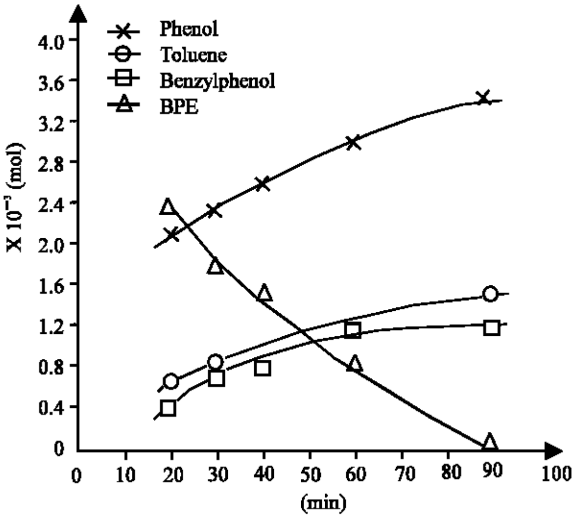


Fig. 2: Reactant and products from the thermal decomposition of BPE and hydroarmatic solvent (THQ)

These radicals are then stabilized by the hydrogen donated by the hydroaromatic solvents to form mainly phenol and toluene as the principal products. The reactants and products from the thermal decomposition of BPE in the presence of hydroaromatic solvents are given in Fig. 2. The ^{1}H nmr spectra of the reactants and products are given in Fig. 3 and 4. THQ is dehydrogenated by the radicals

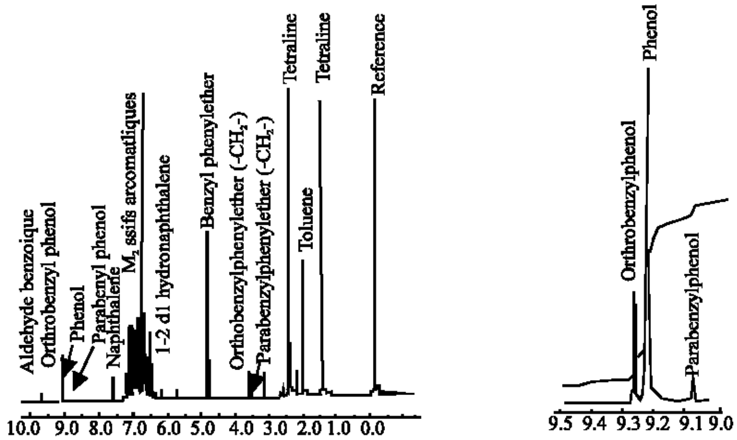


Fig. 3: Decomposition of BPE at 300° (without catalyst using tetralin (NMR Spectra)

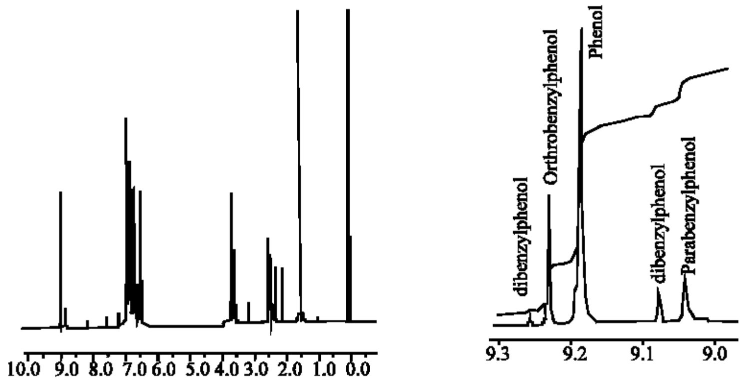
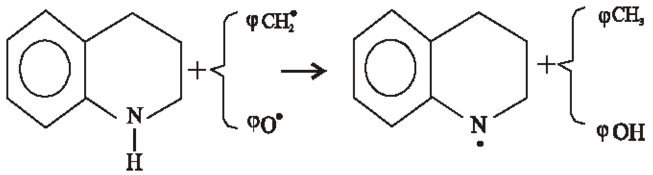


Fig. 4: Decomposition of BPE at 300°C (in the presence of a catalyst , $SaCl_2$) using tetralin

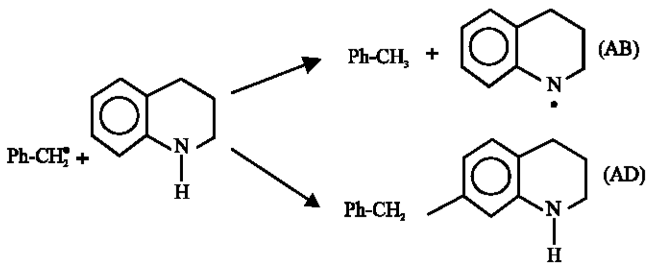
to form quinoline. Similarly, Tetralin and 9, 10-dihydrophenanthrene are dehydrogenated to naphthalene and phenanthrene respectively. Comparing Fig. 3 and 4, one finds that the presence of a catalyst, $SnCl_2$, helps to increase the liquefaction of BPE, as no trace of BPE was found at 300°C whereas there was still undecomposed BPE at the same temperature in the absence of a catalyst.

In the study using THQ to stabilize the radicals generated by the thermal decomposition of BPE, the radicals abstract the hydrogen atom attached to the nitrogen atom of THQ. Some of the benzlyl radicals then attack the nitrogen atom radical, resulting in the formation of N-benzyltetrahydroquinoline especially at the beginning of the reaction.



The radicals form at the beginning of the reaction using THQ are thus stabilized either by abstraction of hydrogen. This process is termed abstraction (AB), or are stabilized by addition to the double bonds in the aromatic ring of the solvent. This process is termed addition (AD).

$R' + AH_{2}.\ RH\ + AH'$ (AB)
$R'\ + AH_{2}\ .\ RAH_{2}'$ (AD)



These side reactions delay the dehydrogenation process of 1,2,3,4-tetrahydroquinoline to quinoline thereby resulting in poor Recycle Index (RI).

As expected, the % conversion of coal using tetralin is better than that of indane (54.80 and 36.62%, respectively). In addition, no trace of indene was detected (RI = 0). An important factor in coal liquefaction is the possibility of reusing the same solvent in successive dehydrogenation-rehydrogenation cycle (Whitehurst *et al*., 1980). This means that in each dehydrogenation step studied, the hydroaromatic solvent SH_2 is quantitatively converted to its aromatic analog S. This ideal situation is far from being reached for all the solvents considered. Thus, a performance index, the Recycle Index (RI) is defined as the ratio.

$$RI = {}^{[S]}\!/_{\Delta[SH_2]}$$

Further more, the % conversion using a non-donor solvent (1- methylnaphthalene) was the least (25.56%). If one compares these results with reference to the hydrogen donating ability of each of the solvents, it becomes more evident that DHP is the most efficient of the solvents used. The recycle index and the % conversion found in this study are practically comparable with those found in our earlier work using BPE in place of coal (Oviawe *et al*., 1993b; Oviawe, 1989).

In the experiments carried out at 400C using DHP and tetraline, DHP donates its hydrogen faster than tetralin, .[DHP]/.[T] = 2.61 against 1.33 in the presence of BPE (Table 2). The experiment with tetraline and indan at 400C show that tetralin donates its transferable hydrogen faster than indane, .[T]/.[I] = 1.98 against 1.13 in the presence of BPE. THQ was obviously excluded from this second set of experiments because of its instability above 350°C.

Comparing the ratio, .[DPH]/.[T] and .[T]/.[I] in the presence of coal and in the presence of BPE and taking critical note of the recycle index in the two cases, it is clear that the results obtained using coal is in direct agreement with those obtained using BPE. The slight difference observed may be explained by the fact that hydrogen donor content of a solvent alone may not be sufficient to completely define its effectiveness as a coal liquefaction solvent (Curtis *et al*., 1984).

The % conversion of coal is determined by the solubility of its product with hydroaromatic solvent in tetrahydrofurane (THF) according to:

Table 2: Competition between the hydroaromatic solvents in the presence of coal: concentrations of reactants and products at 400C (15 min)

Moles × 10	400C, 15 min DHP/Tetralin	400C, 15 min Tetralin/Indane
Tetratlin	3.792	3.609
. Tetralin	1.208	1.391
Dihydrophenantrene	1.842	-
. Dihydrophenantrene	3.158	-
Indane	-	4.296
. Indane	-	0.703
Naphthalene	0.511	0.634
Phenanthrene	2.183	-
RI. 0.69		-
RI. 0.43		0.46
.[DHP]/. [T	2.61	-
.[T]/. [I]	-	1.98
% .dihydrophenanthrene	63%	-
% .tetralin	24%	28%
% .Indane	-	14%

[Dihydrophenanthrene] = 5×10 moles, [Tetralin] = 5×10 moles, [Indane] = 5×10 moles, Weight of coal = 0.5 g

Table 3: Percentage conversion of coal, in the presence of tetrsalin, as a function of time at 400°C

Time	20 min	30 min	40 min	60 min	90 min
Conversion (%)	51.16	56.46	58.54	60.64	61.10

$$\%\text{Conversion of organic matter} = \frac{\text{Soluble organic matter} - \text{Insouble organic matter}}{\text{Soluble organic matter}}$$

The weight of the organic matter is calculated by subtracting the weight of ash from coal knowing that the percentage of ash in freyming coal is 5.5% and that majority of the ash is present in the residue.

For each experiment, the solvent was composed of the hydroaromatic substrate of interest and 1-methylnaphthalene as diluent. Coal conversion was measured by ash balance using THF as the wash solvent. The error obtained from duplicate analysis was generally between 1-4%.

Acknowledgement

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