

FREE RADICAL CHAIN REACTIONS OF BITUMEN RESIDUE

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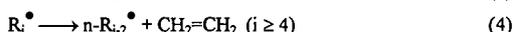
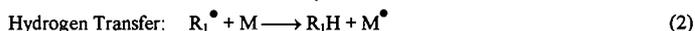
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ABSTRACT

The mechanism of residue cracking was probed by diluting Athabasca bitumen with a solvent capable of accepting free radicals: 1-methyl naphthalene. The dilute solution was cracked at 400°C and 13.8 MPa hydrogen pressure. In the presence of a free radical chain reaction, this solvent would reduce the rate of cracking and give characteristic bi-naphthyl products due to recombination of radicals. Both of these trends were verified by comparing conversion of residue and liquid phase composition to data from control experiments. We conclude that the residue fraction of bitumen cracks by the same type of mechanism as lighter hydrocarbons, i.e. chain reactions involving free radical intermediates. Similar experiments under coking conditions suggest that free radical chain reactions are also important for coke formation.

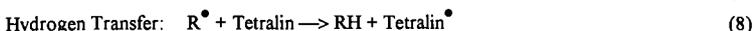
INTRODUCTION

Free radicals are formed during pyrolysis reactions due to the breakage of covalent bonds, and essentially all mechanisms for thermal cracking involve the formation and reaction of radical species. The unpaired electron in these radicals makes these highly reactive, unless the unpaired electron is stabilized, as in high viscosity pitches or in coke residues. Rice and Hertzfeld (1934) recognized that free radicals were the active intermediates in thermal cracking of n-alkanes. The main steps of the chain reaction are as follows:



where M and M[•] are the parent alkane and the parent radical, R_i[•] and R₁H are the methyl or ethyl radical and the corresponding alkane, R₂[•] is the methyl, ethyl or higher primary alkyl radical, R_i[•] is the butyl or higher radical and R_p[•] and R_s[•] are the primary and secondary pentyl or higher radicals. The simple model of Hertzfeld and Rice (1934) has been continuously expanded to allow detailed molecular modeling of ethylene cracking furnaces (Hillewaert et al., 1988). Free radical chain reactions are also observed in a variety of alkyl-aromatic and alkyl-cycloaromatic compounds. Of the thermal reaction mechanisms reviewed by Poutsma (1990), for example, all compounds with aliphatic side chains or rings with a least two carbons followed a free radical chain reaction. The predominant mechanism for thermal cracking reactions of alkanes, alkylaromatics, cycloalkanes, ethers and thioethers is free radical chain reactions.

Application of a free radical chain mechanism to a complex hydrocarbon mixture, such as coal or bitumen, is much more difficult. The reactants and products are poorly defined, and direct observation of radical species *in situ* can be obscured by highly stabilized radicals. Mechanisms proposed for thermal cracking of these complex mixtures have normally invoked free radicals as intermediates, but the crucial role of chain reactions has often been ignored. The most common type of reaction that is amenable to manipulation is hydrogen transfer, either from a hydrogen donor species such as tetralin or from molecular hydrogen. One the earliest mechanisms suggested for the role of donor solvents in coal liquefaction was proposed by Curran et al. (1967):



where M is the coal extract and R[•] is a general radical species. This mechanism spawned the idea of *capping of free radicals*. The role of hydrogen sources (donor solvents and molecular hydrogen) is to stabilize the reactive radical species, thereby giving stabilized molecular products.

The only cracking reaction in the sequence of reactions (7) through (11) is the initiation step. In fact, this reaction scheme lacks a propagation step that involves cracking. Each breakage of a carbon-carbon bond requires an initiation reaction.

Thermodynamics are clearly against this view of thermal reaction chemistry. Homolytic cleavage of a stable carbon-carbon bond requires an activation energy larger than the bond dissociation energy, or approximately 345.6 kJ/mole at 25°C. Actual activation energies for initiation reactions of alkanes consistent with this value, with reported values in the range 213 - 398 kJ/mol. In contrast, the propagation steps of a chain reaction face a much lower energy barrier. The β -scission reaction (equation 3) has an activation energy of 125 - 146 kJ/mol, while hydrogen abstraction has an energy of 46 - 71 kJ/mol. The chain reaction proceeds because the initial radical species turn over hundred or thousands of times to give many moles of cracked products per mole of initiation reactions. In contrast, the radical capping model has a chain length of unity. Observed rates of conversion by thermal cracking in the liquid phase are much higher than would be expected on the basis of scission of carbon-carbon bonds, i.e. initiation reactions only.

The concept of capping of radicals appears widely in the fuel science literature, to explain the reactions of coal liquids and other materials such as bitumens (for example, Sanford, 1994). The literature presents a paradox: model compounds follow free radical chain reactions as long as 2-carbon or longer aliphatic groups are present, while complex mixtures are presumed to generate radicals which are capped by donated hydrogen. Radical species are used to explain both processes, but one has a chain reaction and the other doesn't. A limited number of crossover studies have used insights into chain reaction mechanisms to explain observations of cracking kinetics (Thomas et al., 1989), or proposed new propagation steps for heavy hydrocarbons such as radical hydrogen transfer (McMillen et al., 1987).

Two barriers have likely prevented wider acceptance of the importance of chain reaction in thermal cracking of mixtures of heavy hydrocarbons. First, the chain reaction mechanisms are more complex, and lack the attractive simplicity of the radical capping mechanism. Second, the existence of chain reactions is difficult to prove in complex reaction mixtures. Compounds which are capable of trapping free radicals are routinely used in organic chemistry, however, such compounds are unstable at the temperatures of over 400°C typical of thermal cracking. The toluene carrier technique, developed by Swarcz (1949) to measure bond dissociation energies, offers one method of determining the significance of chain reactions. Homolytic scission of an alkyl-benzene is a slow step due to the high energy requirement: decomposes



In the presence of a large excess of toluene, the radicals will react with the toluene rather than abstracting hydrogen from the parent alkyl benzene. Abstraction of hydrogen from toluene generates a stabilized benzyl radical, therefore, the reaction is fast in comparison to initiation:



The formation of benzyl radicals diverts the chain reaction away from the parent compound, so that β -scission is suppressed. In the very dilute case, cracking of the parent compound proceeds at the rate of the initiation reaction, thereby giving an estimate of the bond dissociation energy.

Khorasheh and Gray (1993) reacted n-hexadecane in a variety of aromatic solvents in dilute solution in the liquid phase. Formation of solvent radicals was indicated by two observations; first the rate of cracking of n-hexadecane was reduced by the addition of solvent, and second the solvent radicals reacted with each other to give dimerized products. Cracking in benzene formed biphenyl, while cracking in toluene and ethylbenzene gave alkyl-diphenyl methanes and diphenyl ethanes. In general, therefore, we would expect dilution in a solvent capable of forming radicals to slow the rate of cracking by diverting the chain reaction, and to form solvent dimers.

Another important free radical reaction in vacuum residues is coking. Usually attributed to some combination of condensation reactions and phase behavior, coke formation may begin with dimerization or polymerization of residue molecules. Although cracking is favored at temperatures over 400°C, addition reactions have been observed in the liquid phase at these temperatures. For example, Khorasheh and Gray (1993) observed significant formation of addition products in the cracking of n-hexadecane in the liquid phase. The toluene carrier technique would prevent the interaction of residue radicals with other species, and thereby block any dimerization reactions.

The purpose of this study was to apply the toluene carrier technique to liquid-phase thermal cracking of vacuum residues, to verify the role of free radical chain reactions in both cracking and coking reactions.

EXPERIMENTAL

The solvent 1-methylnaphthalene (1-MN) was selected as a less volatile analog to toluene to serve as a radical acceptor in the liquid phase. Like toluene, 1-MN would form relatively stable benzyl radicals upon loss of a hydrogen to a radical. Athabasca vacuum residue (424°C+) was blended with 1-MN to give a 17 weight% solution, for an approximate molar concentration of 1.2%. The solution of residue was reacted in a 500 mL batch reactor (Parr) under hydrogen at 400°C and 13.8 MPa. The solution was degassed by pressurizing with nitrogen, purging the gas, then pressurizing twice with hydrogen and purging each time. The reactor was then pressurized for a final time at a hydrogen pressure just below the amount required to achieve 13.7 MPa at reaction temperature. As the reaction temperature was approached additional hydrogen was added to the reactor to bring it to the final pressure. The reaction time was 1hr, measured from the time that the final temperature was achieved. Two control experiments were also conducted: reaction of solvent only to determine the background yield of dimer products in the absence of residue, and reaction of residue only to determine conversion in the absence of solvent. Reaction conditions were similar for coking, except that the reaction time was only 30 min, and the atmosphere was nitrogen at an initial cold pressure of 101 kPa.

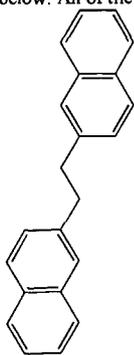
The reactor products were separated first by spinning band distillation, to remove components boiling below 343°C, particularly the solvent. Several batches of material from the spinning band distillation were then combined to give enough sample for determination of the vacuum residue by ASTM D-1160 distillation. The liquid products were also analyzed by gas chromatography using a 30 m HP-1 capillary column in a Hewlett Packard 5890 GC equipped with a flame ionization detector. Individual peaks were identified by GC-MS.

RESULTS AND DISCUSSION

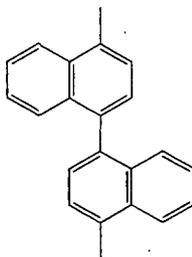
The conversion of the residue fraction with and without dilution in 1-MN is shown in Table 1. The mean conversion without solvent was 48.6%, but the conversion in dilute solution was much more variable, ranging from 1.5% to 41.6%. The distillation data from one batch of residue reacted in 1-MN (data not shown) were anomalous in giving half the amount of gas oil compared to the other experiments, therefore, the results were excluded. The remaining experiments with 1-MN diluent were more variable than without 1-MN, giving a mean conversion of 35.7%. In replicate experiments, therefore, the addition of 1-MN as a radical acceptor reduced the conversion of the residue fraction, consistent with a chain reaction mechanism.

Each set of five experiments with 1-MN diluent was pooled, then distilled. Spinning band distillation to remove of the large volume of solvent was followed by a single vacuum distillation to determine the amount of unconverted residue. This sample handling was the most likely source of variability. Other possible causes, such as variations in solvent purity, batch to batch variation in time-temperature history, sensitization by trace oxygen in the reactor or the catalytic effects of the reactor walls would all tend to average out from run to run due to the pooling of products from five reactor experiments.

Reaction of 1-MN without residue gave a series of dimers, illustrated in Figure 1. Structures of two of the compounds were identified by GC-MS, as compounds I and II shown below. All of the GC peaks in Figure 1 had the same molecular weight of 282.



I 2,2'-(1,2-ethanediyl)bis-naphthalene



II 4,4'-dimethyl-1,1'-binaphthyl

The formation of a series of termination products, including I and II, was consistent with reaction of the various resonance forms of the methyl naphthyl radicals that would form from 1-MN.

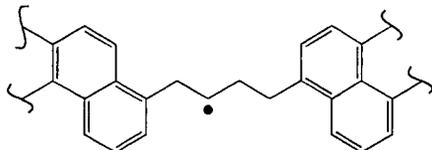
When the solvent was reacted in the presence of residue, the total concentration of termination products increased by a factor of 5.88, taking into account the interfering signals from the cracked products of the residue (Table 2). The concentration of compound I was the largest in most samples, and its concentration was increased by a factor of 3.64 when the solvent was reacted in the presence of residue (Table 3). This increase in the concentration of products from

the solvent clearly shows that radicals were transferred from the bitumen to the solvent by hydrogen abstraction, and that the cracking of the residue sensitized the solvent for free radical reactions.

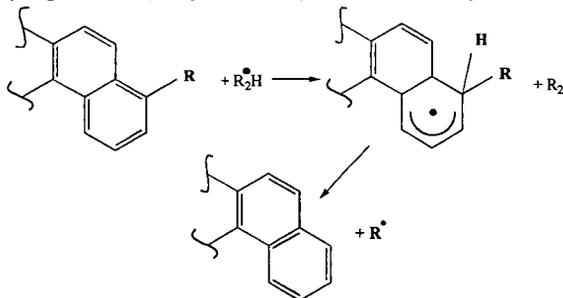
The experimental data were, therefore, consistent with both predictions of the effect of adding a free radical acceptor to the residue; reduced cracking of the residue due to the transfer of radical species to the solvent, and a concomitant increase in dimers formed from the solvent. These data can only be interpreted in light of a chain reaction mechanism for the cracking of the residue. As a non-donor compound, 1-MN should have had no effect on the rate of cracking had the radical capping mechanism been in effect.

When 1-MN was added to residue under coking conditions (i.e. a nitrogen atmosphere) the yield of coke decreased from 0.011 g coke/g feed residue to 0.022 g/g. The coke product was separated by diluting the product in methylene chloride and filtering through a 0.22 μm filter, therefore, the solids recovered would include clays and mineral solids from the feed oil. The determination was in triplicate. The concentration of termination products from the solvent in the presence of residue increased by a factor of 2.05 relative to solvent alone reacted under nitrogen. These results suggest that coking is also suppressed by addition of a radical acceptor, but further work is required at higher coke yields to verify the trend.

The main gap in the radical capping model is the lack of propagation steps that result in breakage of carbon-carbon bonds. The β -scission reaction is the most reasonable candidate in petroleum and bitumen residue materials, which contain an abundance of aliphatic carbon-carbon bonds in side chains and in bridges between aromatic clusters. A radical such as the following hypothetical structure:



can undergo β -scission to form an olefin and benzyl-type radical. The benzyl radical would then either abstract a hydrogen from another residue molecule (eqn 2) or isomerize (eqn 5) or terminate (eqn 6). Strong aryl-alkyl C-C bonds may crack by mechanisms such as the radical hydrogen transfer (RHT) mechanism (McMillen et al., 1987), an alternate propagation step:



(14)

Although the RHT mechanism remains controversial, it is consistent with some important experimental observations (Savage, 1995) and it provides for continuation of a chain reaction once a radical is formed by homolytic bond cleavage.

CONCLUSIONS

1. Residue conversion was more variable when diluted with 1-MN, but always lower than without dilution.
2. Residue cracking increased the concentration of termination products from 1-MN, consistent with and increase in radical concentration.
3. Experimental data were consistent with a free radical chain mechanism

ACKNOWLEDGMENTS

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REFERENCES

- Curran, George P.; Struck, R.T.; Gorin, E. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 166-173.
 Khorasheh, F.; Gray, M.R. *Ind. Eng. Chem. Res.* **1993**, *32*, 1864-1876.
 McMillen, D.F.; Malhotra, R.; Chang, S.-J.; Ogier, W.C.; Nigenda, S.E.; Fleming, R.H. *Fuel* **1987**, *66*, 1610-1619.

- Poutsma, M.L. *Energy Fuels* 1990, 4, 113-131.
 Rice, F.O.; Herzfeld, K.F. *J. Am. Chem. Soc.* 1934, 56(1), 284 - 289.
 Sanford, E.C. *Ind. Eng. Chem. Res.* 1994, 33, 109-117.
 Savage, P.E. *Energy Fuels* 1995, 9, 590-598.
 Szwarc, M. *J. Chem. Phys.* 1949, 17, 421-435.
 Thomas, M.; Fixari, B.; Le Perche, P.; Princi, Y.; Lena, L. *Fuel* 1989, 68, 318-322.

Table 1. Conversion of the Residue Fraction with Hydrogen Atmosphere

Experiment Type and #	# of Reactor Expts Mixed	Conversion of Residue, %	Average
Undiluted Residue Series A	2	50.3 %	
Undiluted Residue Series B	2	48.6 %	
Undiluted Residue Series C	2	46.9 %	48.6%
Residue in 1-MN Series D	5	26.8 %	
Residue in 1-MN Series E	5	38.9 %	
Residue in 1-MN Series F	5	41.6 %	35.7%

Table 2. Ratio of Termination Products From Residue in 1-Methyl Naphthalene Experiments to Pure 1-Methyl Naphthalene Experiments

Rxn Description and Series	# of Reactor Expts Mixed	Termination Products, g/g (n=2)	Mean Concentration	Correction for Residue Contribution	Ratio of Residue in 1-MN to Pure 1-MN
Pure 1-MN (Series G)	1	0.320 E-3	0.224 E-3	1.32 E-3	5.88
Pure 1-MN (Series H)	1	0.128 E-3	g/g 1-MN		
Residue in 1-MN (D)	5	1.23 E-3	1.63 E-3		
Residue in 1-MN (F)	5	2.03 E-3	g/g Mixture		
Correction for Background signal for Residue					
Undiluted Residue (A)	2	0.461 E-3		g/g 1-MN	
Undiluted Residue (C)	2	0.597 E-3	0.535 E-3		
Undiluted Residue (5)	2	0.548 E-3	g/g Mixture		

Table 3. Ratio of Diphenyl Ethane Found in Residue in 1-Methyl Naphthalene Experiments to Pure 1-Methyl Naphthalene Experiments

Reaction Description	Series Number	# of Reactor Expts Mixed	Termination Products in Sample g/g (n=2)	Termination Products in Sample Mean	Ratio of Residue in 1-MN to Pure 1-MN
Pure 1-MN	1	1	1.33 E-4	0.902 E-4	3.64
Pure 1-MN	4	1	0.473 E-4	g/g 1-MN	
Residue in 1-MN	1	5	1.93 E-4	3.29 E-4	
Residue in 1-MN	4	5	3.52 E-4	g/g 1-MN	

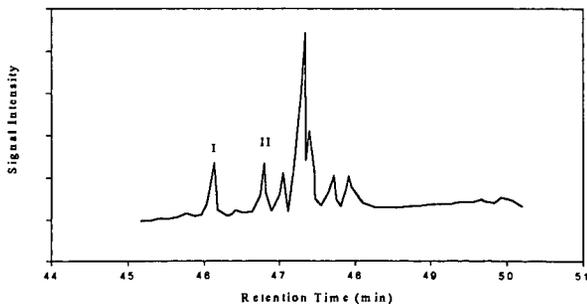


Figure 1. Chromatogram of Termination Products