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High Temperature Pyrolysis Mechanisms of Coal Model Compounds

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Work Performed Under Contract No.: DE-FC21-87MC24207

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
West Virginia University
Department of Chemistry
Morgantown, West Virginia

DISCLAIMER

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High-Temperature Pyrolysis Mechanisms of Coal Model Compounds

by
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Abstract

The degradation of the carboxylic acid group has been examined with respect to potential pretreatment strategies for fossil fuel conversion processes. In one potential pretreatment strategy involving cation exchange of the carboxylic acid group, a series of benzoic acid and stearic acid salts have been chosen to model the "tight" carboxylic acids of immature fossil fuel feedstocks and have been pyrolyzed with an entrained flow reactor. Our preliminary results indicate that Group I and II salts yield primarily the parent acid. Benzoate salts also yield small amounts of benzene while the stearic acid salts give no other detectable products. In contrast, zinc stearate gives a series of hydrocarbon products including octene and dodecene, indicating that extensive conversion of the parent compound to low MW products has been accomplished.

In two alternative treatment strategies, esterification and anhydride preparation have also been accomplished with these compounds being subjected to the entrained flow reactor conditions. The benzoate esters give a number of products, such as benzaldehyde, benzene, and low MW gases. The formation of these compounds is extremely dependent on pyrolysis conditions and alkoxy chain length. Long alkoxy chain benzoate esters produce low MW gas with subsequent formation of the parent acid at temperatures below 500° C while higher pyrolysis temperatures give low MW gases with amounts of benzaldehyde and benzene. Benzoic anhydrides, mixed and symmetric, also produce benzene and a series of aldehydes when exposed to entrained flow pyrolysis. Aldehyde selectivity may be controlled to some extent in these reactions through the use of mixed anhydrides as the pyrolysis substrate.

A xenon flashlamp and an entrained flow reactor have been used to heat organic substrates to varying temperatures using different heating rates. Ultrarapid flashlamp pyrolysis (heating rate>10^5°C/s) has been performed on bibenzyl (**BB**), 1,6- diphenylhexane (**DPH**), and 1,4-dibenzoylbutane (**DBB**). Acetylene is the primary flashlamp product from these compounds. **DPH** also yields a significant amount of ethylene while **DBB** yields a small percentage of benzaldehyde. These results contrast with slower heating rates and more traditional pyrolyses of the same substrates. For example, traditional pyrolysis of **BB** yields products which are easily explained by cleavage of the central C- C bond to yield benzyl radicals. Since the ultrarapid pyrolysis products differ from those observed with traditional heating techniques and differ from the products formed photochemically, the flashlamp pyrolysis products are attributed to high temperature thermal activation.

Acknowledgements

We gratefully acknowledge the assistance of Lawerence J. Shadle (Morgantown Energy Technology Center) in obtaining the use of the flashlamp pyrolysis equipment.

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EXECUTIVE SUMMARY

Coal and oil shale model compounds containing tight carboxylic acid groups have been subjected to pyrolysis conditions using both a flashlamp reactor and an entrained flow reactor. Complete product analyses of the reactions of several compounds with these units have been completed. Pyrolyses of several cation exchanged metal salts show that Group I and II salts (*i.e.*,Li, Na, K, Ca, Ba) lead to no significant increase in conversion of these tight carboxylic acid groups. In sharp contrast, $Zn(OH)_2$ pretreatments lead to significant conversion at dramatically lower temperatures. Alternative strategies for facile removal of carboxylic acid functional groups were examined. Esterification is limited by the chain length of the reacting chain. Anhydride formation shows utility for removing aryl carboxylic acids, depending on structural features which are not yet fully understood. Studies using flashlamp pyrolysis to achieve different heating rates show that the products derived from ultrarapid flashlamp pyrolysis are of thermal origin and not from photochemical origin.

INTRODUCTION

In recent years a variety of studies have been initiated in an effort to examine pretreatment processing and ultrarapid heating as a means for the more efficient conversion of fossil fuel feedstocks. The past studies have examined the mass losses of coal and oil shale from various pyrolysis conditions. Our experimental design was to utilize compounds of known composition. This strategy would allow for easy product identification and a quantitation of the products originating from a given functional group. With this strategy we can investigate the chemical mechanisms leading to low MW products from the pyrolysis of fossil fuel feedstocks.

PURPOSE

The objective of this research was to investigate the chemical mechanisms that take place in a fluidized bed reactor which lead to lower MW products. These mechanisms have been studied utilizing model compounds with known composition and functionality and have been specifically chosen to represent those functional groups within coal and oil shale that cause difficult conversion problems. These chemical reactions are evaluated for successful pretreatment by analyzing the products, reaction temperature requirements, and activity of any pretreatment catalyst.

BACKGROUND

A variety of studies, in a laboratory effort to emulate high heating rate and industrial pretreatment process conditions, have shown that changes in the heating rate of fossil fuel substrates and addition of metals (*i.e.*, potassium, sodium) can dramatically change the relative products formed in a given pyrolysis process.

The use of pretreatment strategies has recently emerged as a method to convert pyrolytically stable functional groups to low MW products. Such strategies could provide a means for enhancing the conversion of various fossil fuel feedstocks to low MW products. Similarly, metal catalysts have been shown to be effective for inducing the conversion of fossil fuels to economically useful products. The catalytic behavior of these metals, however, has not been specifically addressed with respect to the conversion of organic carbon to low MW products.

Organic acids (*i.e.*, carboxylic acids) present a very difficult conversion problem. These acids require large amounts of thermal energy to react to form converted products and usually appear as unwanted products from a given pyrolysis process.[1] Solomon has classified the carboxylic acids as "tight" or "loose" acids with respect to the amount of energy necessary for their elimination.[1] In most cases, temperatures greater than 750°C are needed to convert this functional group. Since the acid group requires large amounts of energy for its conversion, pretreatment may allow these reactions to occur at much lower temperatures. Our potential pretreatment strategy is to exchange the carboxylic acid proton for a metal. This strategy has shown

limited success as a catalytic treatment in TGA studies.[2-6] The explanations for this activity have only considered the properties of the metal (e.g., metal oxide bond strength of the char[2], metal oxide bond strength of the fuel[3,4], and the base character of the metal oxide[5,6]) to be important to the reactions occurring upon pyrolysis. An alternative pretreatment strategy involves chemical derivatization to effect bond cleavage in a different bond than would be broken under normal pyrolysis of the carboxylic acid. Conversion of carboxylic acids to anhydrides was suggested by the chemical similarity to peptide syntheses where specific leaving groups can be selected to leave at a given time or temperature.

The heating rate of various compounds has also been shown to be an important variable affecting the distribution of products from a conversion process. A preferred technique for generating the fastest heating conditions utilizes conversion of high intensity light into thermal energy in an appropriate substrate. Granger and Ladner[7] were the first to show that enhanced yields of low MW gases are obtained from ultrarapid flashlamp pyrolysis. In an independent study, Calkins[8] observed that flashlamp pyrolysis of Pittsburgh #8 coal at >700°C produces low MW hydrocarbons such as acetylene, ethylene, and propene, while entrained flow pyrolyses produces only aromatic compounds containing polymethylene chains. Vastola[9] and Hanson[10] have shown that a high intensity laser (*i.e.*, ruby or CO_2 lasers) may also be used as a pyrolysis source for a range of medium volatile bitumunous, high volatile bituminous, and high volatile anthracite coals and oil shales, yielding low MW hydrocarbon gases with some amounts of napthalene, benzene, and toluene among other liquid/solid products being produced. These studies demonstrate that different products are obtained when using ultrarapid flashlamp pyrolysis conditions and using traditional pyrolysis techniques. A critical question in these studies concerns the origins of reactivity. Since the laboratory test is designed to evaluate rapid thermal heating, the use of light energy may play a complicating and unwanted role by initiating photochemical reactions. Studies here have been undertaken to prove that the observed reactivity originates from thermal and not photochemical origins.

METHODOLOGY

Melting points were determined on a Laboratory Devices Mel- Temp apparatus and were uncorrected. Gas-liquid chromatographic analyses were conducted on a Hewlett-Packard Model 5890A GLC equipped with a 10 m 5% phenylmethylsilicone or a Carbowax 20M Megabore column. HPLC was performed on a Waters Associates Protein Peptides I system capable of gradient elution and using UV detection at 245 nm. GC/MS were measured with a Finnigan Model 4021 quadrapole mass spectrometer equipped with a Model 9610 data reduction system for comparison of mass spectra to those of authentic samples. IR spectra were recorded on a Mattheson Cygnus 100 FTIR spectrophotometer. ^{1}H NMR spectra (δ (ppm) and J (hertz)) were measured in $CDCl_3$ with TMS as an internal standard on a Varian EM-360 or a JOEL GX-270 spectrometer.

Flashlamp Sample Preparation: 3 g of presized 23 μm graphite particles and 1 g of the organic substrate were placed in a round bottom flask containing 30 mL of anhydrous ether. The ether was slowly removed *in vacuo* with stirring on a rotary evaporator to ensure a uniform sample distribution. Replicate analyses by GC and HPLC showed that the amount of material on a given amount of graphite was uniform within experimental error. The treated graphite was dried in an oven at 110°C for 24 h prior to flashlamp irradiation.

Flashlamp Pyrolyses: These experiments were performed on a xenon flashlamp reactor capable of heating rates to 10^5°C/s.[11-13] The temperature profiles of various graphite samples having different particle sizes have been analyzed extensively by direct measurements using two-wavelength optical pyrometry.[14] The temperatures as a function of time of unreactive graphite particles are understood exactly through the XELAMP model. The

time/temperature profiles for reactive fuel substrates are reasonably modeled by this computational method and depend upon a variety of factors such as the heat capacity of the substrate, the chemical reactions occurring in the particle, the vaporization rates of the particle, etc. Quantization of the gas yield is determined by the rise in pressure of the system after the lamp is flashed while qualitative and quantitative analysis of the gas yields of each product are obtained by direct injection of a 100 μL volume of gas sample into a GC/MS system calibrated for the gases determined to be present in the mixture.

Entrained Flow Pyrolysis: The entrained flow reactor is composed of a Lindberg Model 55085-A tube furnace capable of maximum temperatures of 800°C. A quartz tube packed with uniform 1 mm quartz beads provides the reactive hot zone within the furnace. Products are collected first in a room temperature trap, followed by two liquid nitrogen temperature traps. This trapping system provides for the separation of solid and high boiling liquid species from the low boiling and gaseous products. Based upon computational and pressure rise/decay measurements, the residence time for the substrate in the hot zone is approximately 2.5 s. This allows ample time for the starting material to reach the furnace's temperature maximum. A typical experiment involves 20 mTorr vacuum sublimation through the furnace hot zone. The pyrolysis material is collected in the trap system and immediately analyzed by GC and HPLC.

Preparation of Materials: Bibenzyl, benzoic anhydride, ethyl stearate, methyl benzoate, ethyl benzoate, and 1,4-dibenzoylbutane were purchased from Aldrich Chemical and used without further purification. 1,6-Diphenylhexane was prepared from 1,4-dibenzoylbutane utilizing a Wolff-Kishner reduction in the manner of Sweeting and Wilshire.[15] The crude 1,6-diphenylhexane was purified via silica gel column chromatography using hexane/ethyl acetate elution, followed by vacuum distillation. The mixed benzoic acid anhydrides (aceticbenzoic anhydride, trimethylaceticbenzoic anhydride) were prepared from the sodium benzoate salt and the proper acid chloride. A typical preparation involves dissolving 1 equivalent of acid chloride in THF (dry). To this solution is added 150 μL of pyridine. A suspension of 1 equivalent of pre-dried sodium benzoate in THF is then added dropwise. The resulting solution is allowed to stir at room temperature for 12 h. The solution is filtered with Celite and the filter cake washed several times with cold hexane. The filtrate is concentrated and the resulting oil may be further purified by vacuum distillation at 0°C to afford the mixed anhydride. The mixed anhydrides should be used immediately or frozen to protect against rapid diproportionation to the symmetric analogues.

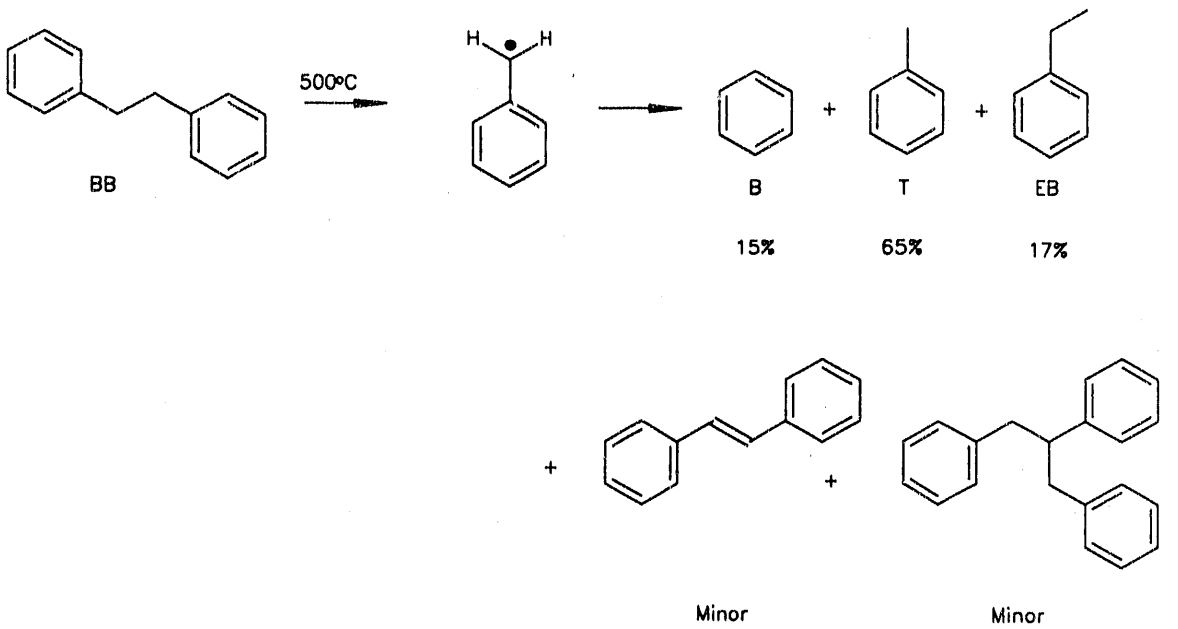
Li, Na, K, Ca, Ba, Zn, and Fe salts of stearic and benzoic acid were prepared by dissolving the acid in a small amount of hot deionized water. A solution of the appropriate metal hydride was added until the acidic solution became neutral or just alkaline. The water was then evaporated and the resulting salt dried under vacuum.

RESULTS AND DISCUSSION

Bibenzyl: The traditional pyrolysis reaction pathway of bibenzyl is well known and yields toluene, stilbene, and benzene with relatively small amounts of radical coupling and disproportionation products depending upon the exact conditions used (note eq. (1)).[16]

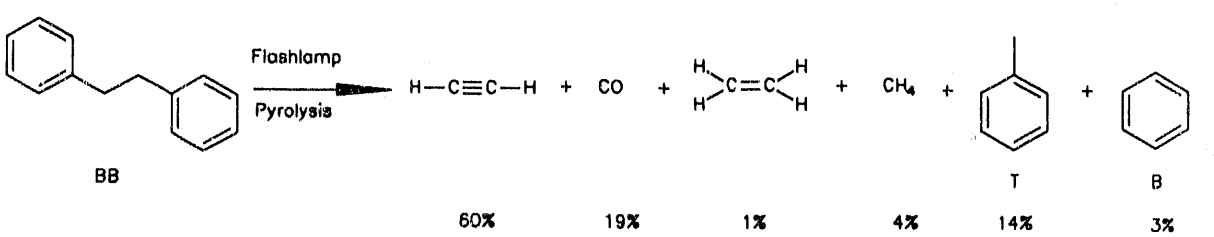
In our laboratory, using slower heating rates, we have verified that pyrolysis of bibenzyl (**BB**) yields a product distribution similar to that reported by other workers (*vide supra*) with toluene (**T**), ethylbenzene (**EB**), and benzene (**B**) being the major products. Photochemical reactions give similar results. In strong contrast to these low heating rate pyrolysis results is the product distribution obtained from pyrolysis using the

(1)



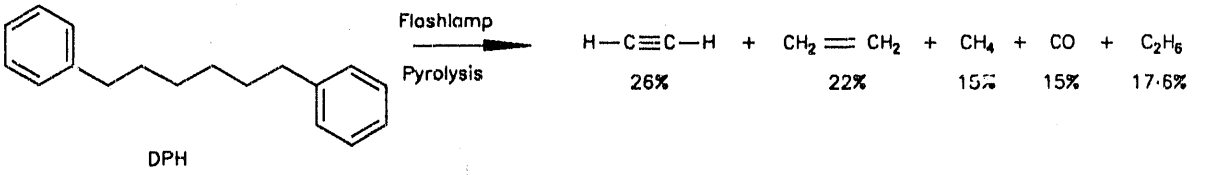
flashlamp reactor. As seen in eq (2), the major product is C_2H_2 with minor amounts (relative to the amount of C_2H_2) of CO, toluene, and benzene being produced upon flashlamp irradiation.

(2)



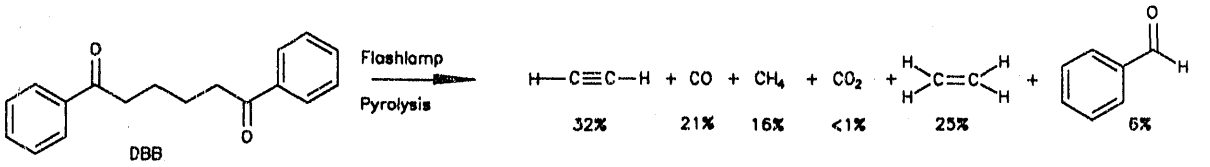
1,6-Diphenylhexane: 1,6-Diphenylhexane (**DPH**) has been shown previously to yield toluene, styrene, and benzene at 700°C.[15] In our laboratory, no reaction was observed for pyrolysis at 650°C. In contrast to both of the low temperature pyrolysis results, ultrarapid pyrolysis results in a reaction yielding predominantly C_2H_2 and C_2H_4 (eq (3)). No photochemical reactivity is observed for this compound.

(3)



1,4-Dibenzoylbutane: Thermolysis of **DBB** in our entrained flow reactor at 650°C yielded only starting material, indicating no reaction at this temperature. However, C_2H_2, C_2H_4, and CO are formed during the ultrarapid flashlamp pyrolysis of this substrate as shown in eq (4). Photochemical reactions gave distinctive products which were not the same as those obtained by ultrarapid pyrolysis.

(4)



Li, Na, K, Ba, and Ca Salts of Benzoic and Stearic Acid: These salts were exposed to entrained flow reaction conditions of 500°-650°C. All compounds in this series gave significant tar formation which was confined to the central portion of the reactor where the furnace is at its temperature maximum. Small amounts of liquid were trapped in the liquid nitrogen traps from the pyrolysis of the benzoate species which was identified to be benzene. Other products included minor amounts of the parent acid and recovered starting material. The amount of benzene produced did not vary with metal component but became slightly larger with increased pyrolysis temperatures (See Table I).

Table I
Benzene Isolated from Group I Benzoates

Benzoate	% Benzene Recovered
Li	8.2
Na	9.0
K	8.6
Ca	7.1
Ba	8.8

These results suggest that large amounts of thermal activation energy are necessary for the elimination of the acids functionalized to Group I salts. The Group I series showed no apparent periodic effects in the pyrolysis of the benzoic and stearic acid salts, with no increase in conversion throughout a given period.

Transition Metal Stearates: Zinc stearate was used as an entrained flow substrate in the temperature range of 400-650°C. This compound was initially pyrolyzed at 650°C yielding a variety of alkene products (*i.e.*, 1-hexene, 2-octene, 1-dodecene, 1-heptadecene with a significant amount of tar formation. An inorganic material was also produced in this pyrolysis and has been tentatively identified as zinc oxide. The pyrolysis of this compound was also performed at 650, 500, and 400°C. Tar formation is significantly smaller at lower temperatures. At 400°C nearly 91% of the total starting organic mass is accounted for by the trapped alkene and short chain aldehyde products.

The pyrolysis reactions of zinc stearate differ greatly from the pyrolyses of stearic acid and the Group I salts. Stearic acid is completely unreactive at 650°C and is recovered unchanged from the entrained flow pyrolysis. The Group I salts give primarily the parent acid as a product with high temperature requirements for reaction.

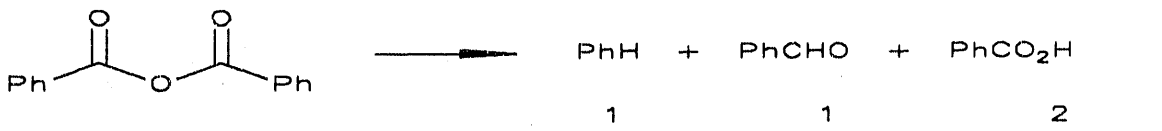
In sharp contrast to the zinc stearate experiments are the pyrolysis results of iron stearate. This compound was exposed to pyrolysis temperatures of 300-650°C. No low MW products were formed. However, products of mass C_{37} or greater were observed along with significant tar formation even at lower temperatures.

Ester Pyrolysis: Ethyl stearate was pyrolyzed in the temperature range of 300-500°C in the entrained flow reactor. A solid was trapped which was identified to be stearic acid. The same product was formed in all experiments within the given temperature range. A large amount of gas was also produced which was later identified to be ethylene. Ethyl stearate pyrolysis at temperatures greater than 500°C gave several new products such as stearyl aldehyde and ethanol. Ethyl stearate was also subjected to ultrarapid flashlamp pyrolysis at 1.40 J/cm^2 and yielded only low MW gases, *i.e.*, methane, ethane, ethylene, and CO_2. Methane was observed to be the major gaseous product from these reactions. Ethyl benzoate reacted in a similar manner as ethyl stearate. In the temperature range of 400-500°C, ethyl benzoate reacts to give benzoic acid and ethylene. Above 500°C, this compound also gives small amounts of benzaldehyde and ethanol. In sharp contrast to these results is product distribution observed from the pyrolysis of methyl benzoate. At low temperature pyrolysis conditions (<500°C), methyl benzoate is completely unreactive while at higher temperature pyrolyses, benzaldehyde, benzene, methanol, and methane are produced. These results show a significant dependence upon the alkoxy chain length. For C_2 and greater alkoxy fragments, the major reaction pathway proceeds through a known thermolytic process (*i.e.*, Chugaev rearrangement[16]) while smaller alkoxy fragments are unreactive at low temperature but give fragmentation products as the pyrolysis temperature is increased.

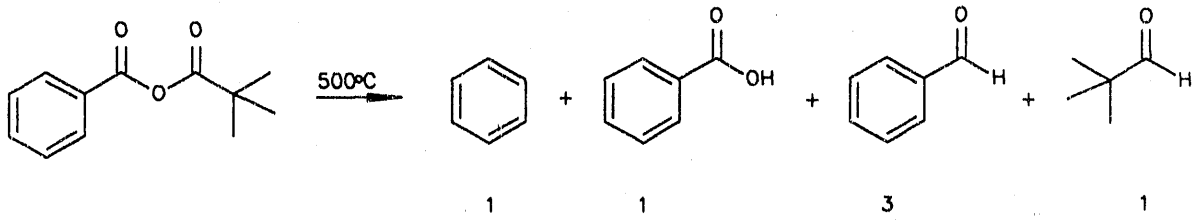
Anhydride Pyrolysis: Benzoic anhydride was subjected to entrained flow pyrolysis conditions with temperatures greater than 400°C. The product distribution at all temperatures was similar with the formation of benzene, benzaldehyde, and benzoic acid (eq (5)). The ratio of products from these pyrolyses was found to be 1:1:2, respectively. It should also be noted that a significant amount of gaseous material was collected and tentatively identified as CO_2. The mass balance in this experiment was 97.2%. This is an excellent mass balance, if one assumes that the gaseous material is indeed CO_2. Although the amount of benzoic acid is somewhat greater than expected (based on the amount of benzaldehyde which is formed), the relative rates of decarboxylation of the benzoyl radical and the rate of decarbonylation of the aldehyde radical may be different and lead to the observed products. Since these products were the expected pyrolysis products, we were encouraged to attempt the pyrolysis of additional model compounds in an attempt to develop carboxylic acid pretreatments.

Trimethylacetic benzoic anhydride (**TMABA**) was pyrolyzed in our entrained

(5)

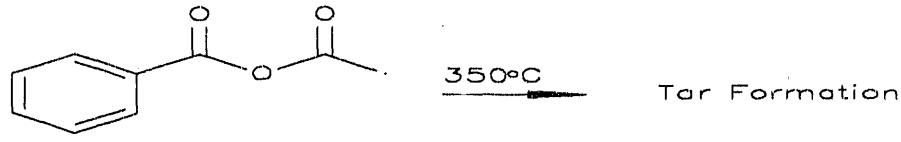


(6)



flow reactor at varying temperatures. This compound gave a series of cleavage products at 500°C. Analysis of the products showed benzene, benzoic acid, benzaldehyde, and trimethylacetaldehyde in the relative quantities of 1:1:3:1 (eq (6)). When pyrolyzed at lower temperatures, **TMABA** reacts in an identical manner. The cleavage of the carboxylic acid is signaled by the appearance of benzene and benzaldehyde in the product mixture. These results were encouraging, since we broke the desired carboxylic acid group. However, significant problems remained for potential pretreatment strategies. First, the selectivity was rather poor, with only a 3:1 ratio of the desired pathway being observed. Second, this synthesis of the starting materials was rather difficult. The difficulty in synthesizing this model compound made it highly unlikely that significant conversions to this functionality could be achieved in coal or other fossil fuel substrates where a large number of variables is present to prevent the desired derivitization. With these problems in mind, we attempted the synthesis of other anhydrides which may result in the desired carboxylic acid cleavage.

(7)



Acetic benzoic anhydride was chosen because of the large decrease in the steric requirements for reaction, leading to a facile synthesis. Interestingly, this compound reacts in a very different manner (eq (7)). In contrast to **TMABA**, acetic benzoic anhydride is very sensitive to temperature, water, and air. When pyrolyzed at low temperatures (*i.e.*, <350°C), acetic benzoic anhydride yields no low molecular weight products which could be identified. Significantly, a large amount of tar and polymeric material was formed. Previous interpretations of acetic benzoic anhydride have postulated that a ketene intermediate is responsible for the observed lack of low molecular weight products. The time allowed for this project did not permit further identification of this material. The results of this reaction show a significant selectivity for the bond cleavage reaction giving a benzaldehyde radical and a trimethylacetyl radical which proceed to the observed products.

These results suggest a potentially viable treatment for arylcarboxylate functional groups in low temperature pyrolyses. By controlling the structure of the mixed anhydride, the arylcarboxylate functional group can be selectively degraded. To date, the exact nature of the arylcarboxylate pretreatment has not been optimized to yield a viable pretreatment strategy.

CONCLUSION

Group I pretreated acids show no conversion enhancement. These species may require temperatures greater than those utilized in this study or higher than are economically feasible to be effective.

Low MW products may be formed from zinc hydroxide pretreated feedstocks. The presence of the zinc center at an acid group greatly enhances the elimination of the carboxylic acid functional group, resulting in low MW alkene products at greatly reduced pyrolysis temperatures. Low MW products may also be formed from ester pretreatments as described by the well known Chugaev reaction.

Pretreatment strategies aimed at producing an anhydride provide an alternative strategy that shows promise. Mixed anhydrides, such as trimethylaceticbenzoic anhydride, give selective bond cleavage products which show an effective elimination of the original carboxylate group. In contrast, mixed anhydrides possessing α-hydrogen atoms appear to give polymeric products derived from ketenes.

Effectively altering the heating rate of reaction also provides a successful means of fossil fuel feedstock conversion. The results described above for ultrarapid pyrolysis conditions conclusively demonstrate that the reactions of these model compounds using the flashlamp reactor cannot be attributed to thermal reactions 500-700°C or to photochemical reactions. The products observed here clearly correspond to reactions of molecules having a huge internal energy content, consistent with the computer generated model which predicts temperatures of ca. 2000°C for these conditions. These results will appear in an article in the March/April issue of *Energy and Fuel*.[17]

Increasing the temperature and heating rate of the process provides for a dramatic change in the product distribution yielding primarily low MW hydrocarbon gases with loss of the long chain polymethylene aromatics.

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