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Quarterly Report 3/1/91

TITLE: Novel Technique for Coal Pyrolysis and Hydrogenation Product Analysis

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GRANT NO.: DE-FG22-89PC89767

OBJECTIVE: The overall objective of this study is to establish vacuum ultraviolet photoionization-MS and VUV pulsed EI-MS as useful tools for a simpler and more accurate direct mass spectrometric measurement of a broad range of hydrocarbon compounds in complex mixtures for ultimate application to the study of the kinetics of coal hydrogenation and pyrolysis processes. The VUV-MS technique allows ionization of a broad range of species with minimal fragmentation. Many compounds of interest can be detected with the initial wavelength used (118 nm), but additional compound selectivity is achievable by tuning the wavelength of the photo-ionization source in the VUV. Techniques for semicontinuous scanning in the VUV are also being investigated to allow for compound selectivity and verification of calibration schemes.

WORK DONE AND CONCLUSIONS: This report covers the second quarter of the second year of the three-year grant period. In the second project year, we are concentrating on the pyrolysis of C₆ and C₇ compounds starting with cyclohexane benzene and toluene in order to develop the VUV-MS technique for compounds more representative of those in coal pyrolysis applications. In the first two quarters of the current project year, we have carried out the pyrolysis and oxidative pyrolysis of cyclohexane and toluene and mixtures of these compounds in a microflow reactor. Figures 1 and 2 show mass spectra for cyclohexane pyrolysis and cyclohexane/toluene pyrolysis at 1400 K and 2 ms residence time. The first step in cyclohexane pyrolysis is ring rupture to hexene. The hexene goes through rapid decomposition or, in the case of the hexane/toluene mixture, is also depleted by methyl addition to ultimately form mass 100. The methyl and methane radicals are formed through toluene pyrolysis to phenyl and methyl radicals. Thus mixture data yields insight into pyrolysis of pure compounds because you can titrate species that either are the same mass as the parent fuel or that are important mechanistically but never reach high steady-state concentrations. Mixture data also provides cross checks on species calibrations through reaction rate analysis. Figures 3 and 4 show mass spectra taken during the oxidative pyrolysis of cyclohexane and cyclohexane/toluene for the same conditions as Figures 1 and 2. Note that for these oxidative pyrolysis conditions an important pathway for toluene loss is a reaction with oxygen to form benzaldehyde. Conversion

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of cyclohexane is near complete in both cases and conversion of toluene increases in oxidative case. The ratio of the mass 100 peak (methyl substituted hexene) peak to the mass 106 peak (benzaldehyde and $\text{O-C}_2\text{H}_5$) is an indication of the increased role of the benzyl pathway in the oxidative case. This can also be seen in the higher hydrocarbon products in each case. In nonoxidative pyrolysis the higher hydrocarbons observed are condensed ring structures (e.g. masses 120, 178, 202). In oxidative pyrolysis, however, the most predominant higher hydrocarbons are those with C_1 bridges (e.g. masses 169, 194).

We are also continuing work on an empirically based calibration for VUV photoionization based on photoelectron spectra data in the literature. Various compounds tested show 10 -20% photoionization yield per band above the ionization threshold. Because of this initial success, we are searching for additional photoelectron spectra data to extend the scope of these correlations for as many species as possible.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This research is innovative, offering a relatively new technique with significantly improved performance for the mass detection of $> \text{C}_1$ hydrocarbons in mixtures. This technique would facilitate the scientific investigation of coal upgrading processes such as pyrolysis and hydrogenation by allowing accurate direct analysis of both stable and intermediate reaction products. The on-line, non-destructive nature of the VUV-MS technique facilitates data collection and analysis, allowing more experiments to be run with greater analysis accuracy, greatly improving the database and allowing more confident prediction of reaction pathways.

PLANS FOR THE COMING PERIOD: We are currently preparing a paper contrasting higher hydrocarbon growth mechanisms during the pyrolysis of allene and methyl acetylene. This work clarifies the role of C_3H_4 in the growth of higher hydrocarbon compounds and benzene in a combustion environment. In the first quarter we began pyrolysis experiments of C_6 hydrocarbons. Cyclohexane was chosen for the initial species tested because of an expected greater tendency to fragment at 118 nm than other compounds we have used in the past. In this quarter we extended this to study pyrolysis and oxidative pyrolysis of cyclohexane and toluene, as well as mixtures of these species. This work will continue in the third and fourth quarters with benzene and substituted C_5 ring compounds added to the study.

We are investigating alternatives for generating VUV photons in semicontinuous scanning configuration. Tripling in Hg vapor was tested, but a more attractive alternative (with more uniform tripling efficiency) might involve a four-way difference frequency mixing procedure using a second color UV light at 193 nm. For this procedure we would require the purchase of an excimer laser. This grant does not include funds for the upgrading of the equipment, so we are looking to other sources to purchase this equipment. Work on an empirically based calibration for prediction of VUV photoionization yields based on photoelectron spectra data is also continuing.

HIGHLIGHT ACCOMPLISHMENTS

1. Development and testing of a dual ionization source using VUV photoionization coupled with laser-driven pulsed electron impact ionization was carried out. This allows MS-MS data with one MS and is useful for characterization of hydrocarbon unknowns. A paper describing this technique is in print (2/91) in *Review of Scientific Instruments*. A reprint of the paper is attached to this report.

2. Higher hydrocarbon production was found to occur at lower reaction temperatures for allene than methyl acetylene. Reaction pathway analysis showed that the allene form of C_3H_4 likely plays a role in benzene formation. The first reaction product at low temperatures is mass 80 (an allene dimer), and this species can react with allene to form a substituted C_6 ring compound. This results in substantial higher hydrocarbon growth at relatively low temperatures and allene conversions.

3. Further development of correlations for VUV photoionization yields based on PES data is continuing.

ARTICLES AND PRESENTATIONS

Boyle, J., Pfefferle, L., Gulcicek, E., Colson, S., "Laser-driven electron ionization for a VUV photoionization time-of-flight mass spectrometer," *Review of Scientific Instruments*, **62**(2), February, 1991*.

*Reprint ~~attached~~ *not included*.

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Figure #1:

Cyclohexane Pyrolysis

1400K, 2ms

Figure #2:

Cyclohexane/Toluene Pyrolysis

Figure #3

Cyclohexane Oxidative Pyrolysis

1400K, 2ms

Figure #4

Cyclohexane/Toluene Oxidative Pyrolysis

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