Quarterly Report 9/1/90

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TITLE: Novel technique for Coal Pyrolysis and Hydrogenation Product Analysis

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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 118 nm wavelength, but additional compound selectivity is achievable by tuning the wavelength of the photo-ionization source in the VUV. Resonant four wave mixing techniques in Hg vapor will allow near continuous tuning from about 126 to 106 nm.

WORK DONE AND CONCLUSIONS: This report covers the first year of the three year grant period. A microjet reactor coupled to a VUV photoionization time-of-flight mass spectrometer was used to obtain species measurements for high temperature pyrolysis of several of the targeted species including butadiene, ethyl acetylene, methyl acetylene, allene, acetylene and cyclopentadiene. Cyclopentadiene was chosen because it is obtained from the distillates produced in carbonization of coal. Calibrations of species profiles during the pyrolysis of ethyl acetylene at 2 ms residence time and various temperatures have been given in previous reports and papers describing this work appear in *The Journal of Physical Chemistry*, Vol. 94 (1990) and *Combustion Science and Technology*, Vol. 70, pp. 187 (1990). Data from the allene and methyl acetylene pyrolysis experiments has been analyzed and will be presented at the AIChE annual meeting in November, 1990. An abstract of the talk is attached to this report.

Our initial work on an empirically based calibration for VUV photoionization based on photoelectron spectra data in the literature is promising. 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.

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In this project year we have also developed and tested a dual ionization source using VUV photoionization coupled with laser-driven pulsed electron impact ionization. This allows MS-MS data with one MS and is useful for characterization of hydrocarbon unknowns (paper attached).

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: This research is innovative, offering a relatively new technique with significantly improved performance for the mass detection of $> C1$ 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 have obtained kinetic data for the pyrolysis of several of the targeted species including butadiene, ethyl acetylene, methyl acetylene, acetylene and cyclopentadiene. Data analysis and calibration were completed in the first half of the project year for the pyrolysis of ethyl acetylene. 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 the allene form of benzene. Analysis of the cyclopentadiene system will be carried out next followed by a comparison of butadiene and ethyl acetylene data.

This project year included the construction and testing of a new VUV-MS system. We have upgraded the data acquisition capabilities of the system to allow for real-time tuning. This grant does not include funds for the improvement of the equipment so we are looking to other sources for this support. 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 press in *Review of Scientific Instruments*. A final preprint of the paper is attached to this report.
2. Pyrolysis of allene and methyl acetylene and identification of higher molecular weight products. Higher hydrocarbon production was found to occur at lower reaction temperatures for allene and reaction pathway analysis showed that the allene form of C_3H_4 likely plays a role in benzene formation. An abstract of the talk to be presented at the 1990 AIChE annual meeting in Chicago is attached.
3. Pyrolysis of ethyl acetylene and butadiene and identification of products including radicals using VUV (118 nm) photoionization MS.
4. Further development of correlations for VUV photoionization yields based on PES data.

ARTICLES AND PRESENTATIONS

Boyle, J., Pfefferle, L., Gulcicek, E., Colson, S., *Review of Scientific Instruments*, in press (1990).

Boyle, J., Pfefferle, L., Gulcicek, E., Colson, S., *Combustion Science and Technology*, Vol. 70, pp. 187 (1990).

Boyle, J., Pfefferle, L., "VUV Photoionization Study of Higher Hydrocarbon Production During the Pyrolysis of Methyl Acetylene and Allene" to be presented AICHE Annual meeting 1990

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