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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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Quarterly Report
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High Temperature Infrared Analysis of Cyclic Olefins

The goal of this research is to develop a methodology for analyzing the reactivity of cyclic olefins in situ in a high temperature and high pressure infrared cell. Cyclic olefins, such as 1,4,5,8-tetrahydronaphthalene (isotetralin) and 1,4,5,8,9,10-hexahydroanthracene (HHA), are highly reactive donor compounds that readily donate their hydrogen to coal and model acceptors when heated to temperatures of 200 °C and above. These donors are active donors in the low severity liquefaction of coal at 350 °C as shown in the research performed in this project. The infrared studies are being perfomed in a high temperature infrared cell that was obtained from AABSPEC. Modifications to that cell have been made and have been reported in previous progress reports.

The research performed during this quarter, April to June 1995, focused on high temperature infrared analysis. A literature survey was undertaken involving high temperature infrared analysis and is included in this report. Also, the Fourier transform infrared spectrometer was upgraded with a new computer and operating system last quarter. These improvements were required because the high temperature cell requires a very small sample and better analysis and quantitative software packages were required in order to analyze the high temperature samples. Difficulties arose in the installation process and delayed research on this project for a substantial portion of the quarter. Additional time was required to learn how to operate the new windows-based software and the new software packages. Considerable time was invested in learning how to interface the new software and computer configuration with the infrared spectrometer. The previous data obtained was then converted to the MS-DOS format so that comparisons with previously performed spectra could be made.

The AABSPEC high temperature cell had previously been taken to a temperature of 90 °C; however, not much temperature control was displayed during that experiment. The temperature had been set for 50 °C and had risen very quickly to 90 °C when the heat to the cell was turned off. To circumvent a repeat of the last experiment and to gain more control over the temperature rise, the temperature controller parameters were adjusted to allow for a slower temperature rise. n-Hexadecane, a solvent often used in coal liquefaction reactions was added to the cell and the temperature was raised to 175 °C. Since the FTIR was not operational, high temperature spectra could not be taken. A higher temperature was not used because the autoignition temperature of n-hexadecane is 205 °C. Some effort was directed to loading the n-hexadecane into the AABSPEC cell in an oxygen free environment using a glove box. This work will be continued next quarter.

Literature Review: Infrared Spectroscopy at Elevated Temperatures and Pressures

Introduction

The literature is replete with examples of IR experimentation at elevated temperatures and pressures. IR spectra have been recorded at temperatures well in excess 2000 °C and pressures in the gigabars. This review focuses on experimentation at temperatures up to about 500 °C and pressures less than 2000 psi. Unfortunately, most of the work at high temperature was done at atmospheric pressure, while most of the high pressure studies were conducted at room temperature. Examples of combined high temperature and high pressure studies are relatively rare. This is largely due to the fact that combined high temperature/high pressure studies require highly specialized cells. Usually these cells had to be designed by the investigator and were necessarily very specific to a single application. Increasing interest in combined high temperature/high pressure IR techniques has led to the development of commercial cells designed to be of more general applicability. A broad range of topics in chemical infrared spectroscopy has been opened to investigation. The advent of FTIR in the 1970's provided a powerful tool for the in situ study of chemical reactions. This paper provides a brief overview of some of the more noteworthy developments in the field of high temperature/high pressure IR spectroscopy. Numerous references are provided, many of which provide additional literature citations. In addition, some of the more prominent effects of elevated temperatures and pressures on the appearance of IR spectra which have been documented are presented.

The problem of combining high temperatures with high pressures is a formidable one, because the strength of materials falls off rapidly with increasing temperature. The greatest success has been achieved by the use of internal heaters, the pressure vessels themselves being kept near room temperature[1]. When it is desirable to obtain spectra above room temperature, as a rule, special cells must be constructed. The different ways in which they may be built is limited only by the particular application and the imagination of the spectroscopist. Obviously many variations are possible, a great number and variety have been described in the literature[2,3]. All have a common purpose, i.e., to place a sample of material to be studied in a closed system where it can be heated, where it can be exposed to a known pressure, and where its infrared spectrum can be obtained[4].

Applications to Vapor Phase Spectroscopy

When it is necessary to obtain a vapor spectrum of a material of low volatility, long path cells are employed. The cells are heated to increase the vapor pressure of a the molecules under study. This application presents little difficulty, because gas cells under pressure are easily heated[5]. It is extremely important to carefully control both temperature and pressure when performing any quantitative analysis upon gas phase species. Absorption band intensities, widths, and areas are dependent upon both of the parameters. In fact, the absorptivity of a component in terms of its partial pressure may be a function of the total pressure of the sample.

The infrared absorption spectrum of a gas at low pressure consists of narrow bands corresponding to transitions between individual vibration-rotation energy levels. The distribution of molecules in the various rotational and vibrational energy levels follows the Boltzmann distribution, which is a function of temperature. As the temperature increases, the population of the molecules in the higher-energy states increases, and the contours of the vibration-rotation band change accordingly. In addition, more frequent collisions induce broadening of the absorption bands, which does not necessarily correlate linearly with concentration.

As the total pressure of a vapor phase sample is increased, the number of molecular collisions per unit time increases. The molecule cannot rotate freely during these collisions, and if its rotational energy changes by absorption of radiation, one or both of the energy levels involved are displaced. The actual result in measurement terms is that the average absorption band is widened with an apparent increase in intensity. This phenomenon is known as pressure broadening, and its effect must be taken into account during calibration by recording all standards at the same total pressure[6].

Applications to Liquid Phase Spectroscopy

The production of spectra of materials in solution at elevated temperatures is a more difficult problem. Nearly all solvents having useful infrared transmission are volatile, hence cannot be heated much above their (usually low) atmospheric boiling point without keeping them at elevated pressure. This is not generally considered a simple extension of IR sampling technique and had received far less attention in the literature. One class of relatively nonvolatile solvents, which have reasonably good infrared transmission, is the higher molecular weight alkanes. If heavier alkanes are used as solvent, a sealed cell can be heated to 200 °C without a great increase in pressure.

An additional problem arises because the exact temperature in a cell is hard to estimate without direct measurement, for it takes a surprisingly long time for a thin liquid film between two salt plates to come to thermal equilibrium. Temperature measured near the salt windows, or even in one of the windows, will not necessarily be that of the solution of liquid inside the cell. Standard thermocouples will not fit into a 0.1 millimeter space between salt plates. One design to overcome this difficulty incorporated a short length of thin (0.001 inch diameter) nickel wire run though the cell - in a hole in one salt window and out the other - for use as a resistance thermometer. Wire this thin did not impede liquid flow through the cell and blocked only a trivial amount of infrared radiation. The resistance thermometer was made to be one arm of a Wheatstone bridge circuit and temperatures inside the cell accurate to 0.2 °C were easily measured. This device proved useful in the study of absorption bands in solution as a function of temperature. Both absorption peak height and integrated intensity appeared to be sensitive functions of temperature - much more sensitive than can be accounted for by simple cubical thermal expansion of liquids. For example, the absorbances of certain CS_2 absorption bands decreased by about 6% when heated from 27 °C to 36 °C, whereas thermal expansion of the CS_2

solvent over this temperature range would have accounted for only about 1 % of this difference. This should serve as a warning: careful attention must be given to thermostating solutions when quantitative analysis is being done. No really satisfactory explanation of this phenomenon has been advanced. It is a subject that deserves further study[7].

Free rotation usually disappears in the liquid phase and is replaced by vibrational motion within the cage formed by the surrounding solvent molecules. Rotational fine structure occurring in the gas phase disappears and a single peak, usually symmetrical in shape, is produced[8]. The absorption spectrum of a compressed substance can often provide useful and direct information about the nature of the interaction forces between its molecules and about the possible internal distortions of the molecules caused by applied external pressure. An extreme instance of the effect of intermolecular interaction is seen in the large difference which usually exists between the spectrum of a liquid and that of the corresponding rarefied gas. Oxygen provides a good example of this; it is blue in the liquid and solid forms but is a colorless gas at room temperature and one atmosphere pressure. It is interesting to consider what happens to the absorption spectrum of gaseous oxygen as its density approaches that of the liquid. Investigators found that gaseous oxygen becomes blue at pressure of several hundred atmospheres, and its absorption spectra then contains a number of diffuse bands which are characteristic of liquid oxygen but not of gas. It was also observed that the absorption coefficients increased more rapidly than the density of the gas[9].

In the liquid phase, as in the gaseous, pressure may change the absorption spectrum of a system either by altering the equilibrium between different molecular species or by modifying the surroundings and internal structures of the existing molecules. The first effect is usually large and easy to interpret; the second is small, and because of the complex nature of molecular interactions in liquids, more difficult to interpret. Investigations with water, methyl alcohol, anyl alcohol, and toluene at pressures up to 8000 atmospheres revealed no discernible differences in their absorption bands in the near infrared as compared to spectra obtained at ambient pressure[10]. It is thought unlikely that pressures below 2000 psi would have any noticeable effect on the spectra of hydrocarbon liquids.

Any well constructed liquid cell may be made the basis of a hot cell, provided some care is given to the sealing of the filling ports. Because of the pressure generated in an enclosed heated liquid, possibly above its critical temperature, the cell windows must be well polished to a high degree of flatness and tightly clamped up if the seal to the spacer is to withstand the working conditions[11]. The best results for quantitative measurements are obtained if the cell is not moved after the introduction of the first sample, in which case sampling should be a flow-through method. The reason for this is that sample cell positioning is difficult to reproduce accurately. When this flow-through method is not possible, the cell should fit snugly into its holder to protect against any motion[12]. A number of manufacturers produce commercial models of liquid cells incorporating these design criteria, notably Harrick, Spectra-Tech, and AABSPEC.

Recent Research

The practical realization of the combination of high temperature and high pressure infrared analysis is very difficult. In practice, cells suitable for high-pressure experiments have limitations in their temperature range. Conversely, high temperature cells more often than not are not able to operate at reasonably high pressures. Nevertheless, in recent years some authors have made significant progress in this area[13]. An interesting approach to solving the problem of obtaining spectra of liquids at elevated temperatures and pressures is that of Rossiter[14]. The difficulty arises because the hot liquid must be in contact with the cell window. The material of the window loses mechanical strength as the temperature is increased and its ability to withstand pressure is lost. This is a particularly severe problem with the types of materials which give good wide range transmission in the mid-infrared spectral region, such as ZnS and ZnSe. This problem has been overcome by using two sets of windows, an internal set which is in contact with the sample, and an external set which is separated from the internal windows by a gas pressurization chamber. The gas chamber can be pressurized to eliminate the pressure differential across the internal windows, although the paper by Rossiter did not indicate how the internal pressure was measured. The external windows are provided with cooling coils to keep them at a temperature which allows them to maintain their mechanical strength. This experimental design is thought by Rossiter to hold great promise for the future of high temperature/high pressure infrared spectroscopy.

The new cell designs have made it possible to extend virtually all of the techniques used in infrared spectroscopy to elevated temperatures and pressures, including FTIR, Attenuated Total Reflectance, Diffuse Reflectance, Emission Spectroscopy, Photoacoustic Spectroscopy, Specular Reflectance, Large Angle Reflectance, and even IR hyphenated techniques like GC-IR. Research is currently underway in such diverse areas as homogeneous and heterogeneous catalysts, chemisorption and physical absorption of gases on metal or powder surfaces, water absorption on a hydrated silica surface, pyrolysis products, phase transitions in crystalline forms, polymers, coatings, fuels and lubricants, fatty acid chromatography, to name just a few. Future research and development promises to extend virtually every aspect of infrared spectroscopy to elevated temperatures and pressures.

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Future Work

A great deal more training in the use of Windows and the new software packages is anticipated, for it seems that even simple things (like getting the plotter to work) turn into multiple man-hour tasks. It will be necessary (for reproducibility) to convert old files obtained in Nicolet format to MS-DOS format for comparison to spectra obtained using the new computer system. Then a suitable solvent or series of solvents must be found in order to extend the useful range of the FTIR to elevated temperatures. The absorbance versus concentration behavior of aromatics and cyclic olefins will be investigated. In particular, spectra will be obtained of naphthalene, decalin, tetralin, and isotetralin at incrementally increased temperatures up to 350 °C. If time permits, spectra will be obtained at combined elevated temperatures and pressures using a nitrogen or hydrogen blanket. It may be necessary to use the partial least-squares and/or the deconvolution package from Nicolet to obtain absorbance versus concentration curves.

A Plan for Obtaining High Temperature Spectra

1. Convert old files from Nicolet format to MS-DOS format.
2. Save MS-DOS files to a floppy diskette.
3. Obtain room temperature spectra for comparison to old spectra.
4. Obtain elevated temperature spectra for comparison to old elevated temperature spectra.
5. Find a suitable solvent (or series of solvents) for work at elevated temperatures - IR transparent, not too volatile, reasonably safe.
6. Determine the vapor pressure of said solvents at temperatures up to 350 °C in case the outer chamber needs to be pressurized.

7. Obtain spectra of neat solvent.

8. Compare to library spectra.

9. Perform solubility studies of naphthalene, decalin, tetralin, and isotetralin.

10. Obtain spectra of naphthalene, decalin, tetralin, and isotetralin solutions at elevated temperatures in 50 °C increments.

11. Obtain spectra at combined elevated temperatures and elevated pressures using a nitrogen or hydrogen blanket.

Other Research Activities

In addition to the infrared studies and literature review, the first manuscript that was submitted to *Energy and Fuels* for review was received from the reviewers and the manuscript is being revised. The second manuscript involving the hydrogen donation by hexahydroanthracene at low severity conditions was not worked on this quarter, but the work will resume next quarter.