DOE/PC/91281--T21

Low Severity Coal Liquefaction Promoted by Cyclic Olefins

Grant No. DE-FG22-91-PC-91281

Quarterly Report
January to March 1996

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DISCLAIMER

Acknowledgments

The research of Jeffrey Snelling is sincerely appreciated. The technical support of Joe Aderholdt, Henry Cobb, and Michael Hornsby is appreciated by all of us. The word processing performed by Melanie Butcher is gratefully acknowledged.

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High Temperature Infrared Analysis of Cyclic Olefins

Introduction

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 performed 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 useful temperature range of the high temperature infrared cell has been extended to 230 °C through the use of a high-boiling perfluorocarbon solvent. The solvent used was an Air Products and Chemicals Company proprietary product, trade named Multifluor APF-240. Solubilities of aromatics and cyclic olefins were quite low in APF-240, usually less than 0.1 wt% at room temperature, but were found to be a strong function of temperature, increasing markedly when the mixtures were heated to 65 °C. Spectra were initially obtained of n-hexadecane and naphthalene at temperatures of 65, 100, 125, 150, 175, 200 and 230 °C. In addition, the stability of decalin, tetralin, and isotetralin at these elevated temperatures was also evaluated.

Previous studies had shown that naphthalene was quite stable at temperatures up to 230 °C, but a more definitive stability study was conducted to confirm this observation. Stability studies also confirmed the non-reactivity of decalin and tetralin at elevated temperatures up to 230 °C. High temperature FTIR analysis of isotetralin showed that isotetralin reacted at temperatures of 100 °C and higher to 230 °C. This quarter, the reaction product spectrum was analyzed to determine the primary product.

Experimental

A persistent problem of noisy FTIR spectra obtained at high temperatures was addressed early in Winter quarter, 1996. The optics were aligned which gave a noticeable reduction in the noise level. Some degradation in the system optics caused by normal wear and tear is also apparent in the spectrometer. This degradation, coupled with the minimum scan speed and highest possible resolution (2 cm^{-1}), may have been pushing the equipment to its limits. For this reason, the resolution was reduced to 4 cm^{-1} and a considerable reduction in the noise level resulted. The change to 4 cm^{-1} should not affect the quality of the data since none of the peaks to be resolved are less than 4 cm^{-1} apart.

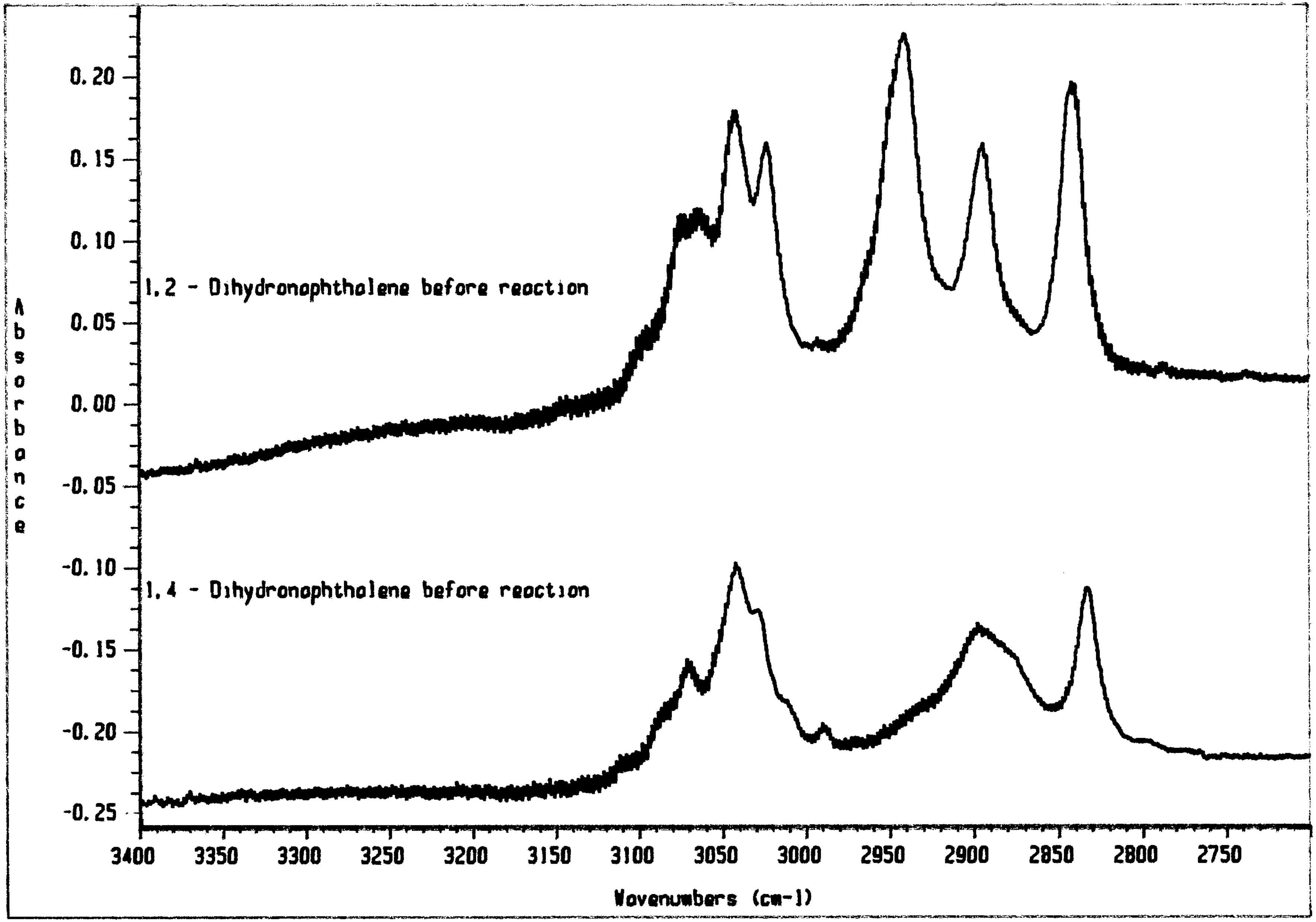
Research Performed During this Quarter

1,2- and 1,4-Dihydronaphthalene Stability Studies

Since 1,2- and 1,4-dihydronaphthalene are likely to be intermediates or even end products in the reaction of isotetralin, they were subjected to the same stability tests as were naphthalene, decalin, tetralin and isotetralin. The stability studies consisted of increasing the temperature of the samples from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding the initial temperature and each intermediate temperature constant for thirty minutes. Scans were obtained before and after each step, and a scan was taken every thirty minutes at the final temperature for a period of three to four hours.

These studies indicate that 1,2-dihydronaphthalene is stable at temperatures up to 230°C but 1,4-dihydronaphthalene reacts. Figure 1 presents the spectra of the two dihydronaphthalene isomers

Figur1 . Sp1ctra of ,2 - Dihydronaphthal1n1 and ,4 - Dihydronaphthal1n1 at 65 °C



before reaction. By comparing the scans of the 1,4-dihydronaphthalene (1,4-DHN) reaction product and 1,2-dihydronaphthalene (1,2 DHN) on the same plot (see Figure 2), the 1,4-DHN reaction product is readily identified as 1,2-DHN. This result will be confirmed by gas chromatographic analysis that is planned for next quarter.

Since isotetralin was reactive at 230 °C, additional studies were conducted with the final temperature being reduced to 200 °C, 150 °C and 100 °C. These reactions were performed to determine the degree of reactivity of the isotetralin at different temperatures.

Spectral Interpretation

A substantial amount of effort this quarter went into spectral interpretation of the high temperature spectra. Initial investigations indicated poor correlation of experimental scans with literature data. It was suspected that there may be some solvent shift effects caused by the presence of the perfluorocarbon solvent as compared to the neat compounds presented in the literature. In hopes of more precisely duplicating the carbon-hydrogen stretch positions, a simpler compound was chosen for experimental scanning. Benzene was chosen for the aromatic C-H stretches (see Figure 3). The scan for benzene compared quite favorably with the literature spectrum, with the major peak frequencies all being within 2 to 3 cm^{-1} of the literature values, which is within the current experimental resolution of 4 cm^{-1}. Upon closer inspection, it was determined that the IR peaks obtained from naphthalene, decalin, tetralin and isotetralin at high temperatures were also in good agreement with literature data. In fact, the peak absorbance matched so closely that there was very little solvent shifting effect.

It should be noted that benzene, with only one type of aromatic hydrogen, gives rise to three peaks in the C-H stretching region (see Figure 3), whereas naphthalene, with two distinct types of

Figure 2. Comparison of Spectra from Reaction Product form 1,4 - Dihydronaphthalene to 1,2 - Dihydronaphthalene

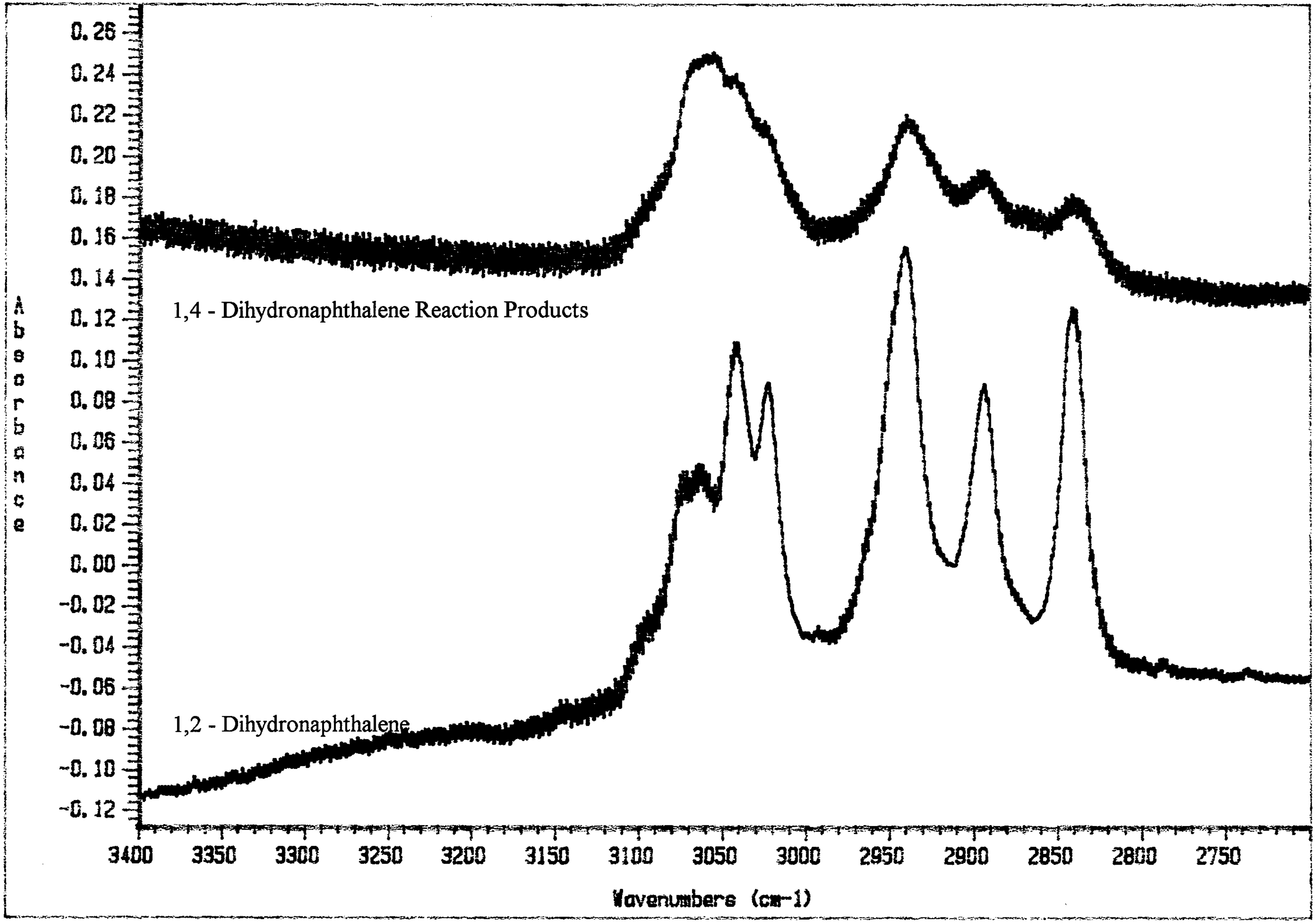
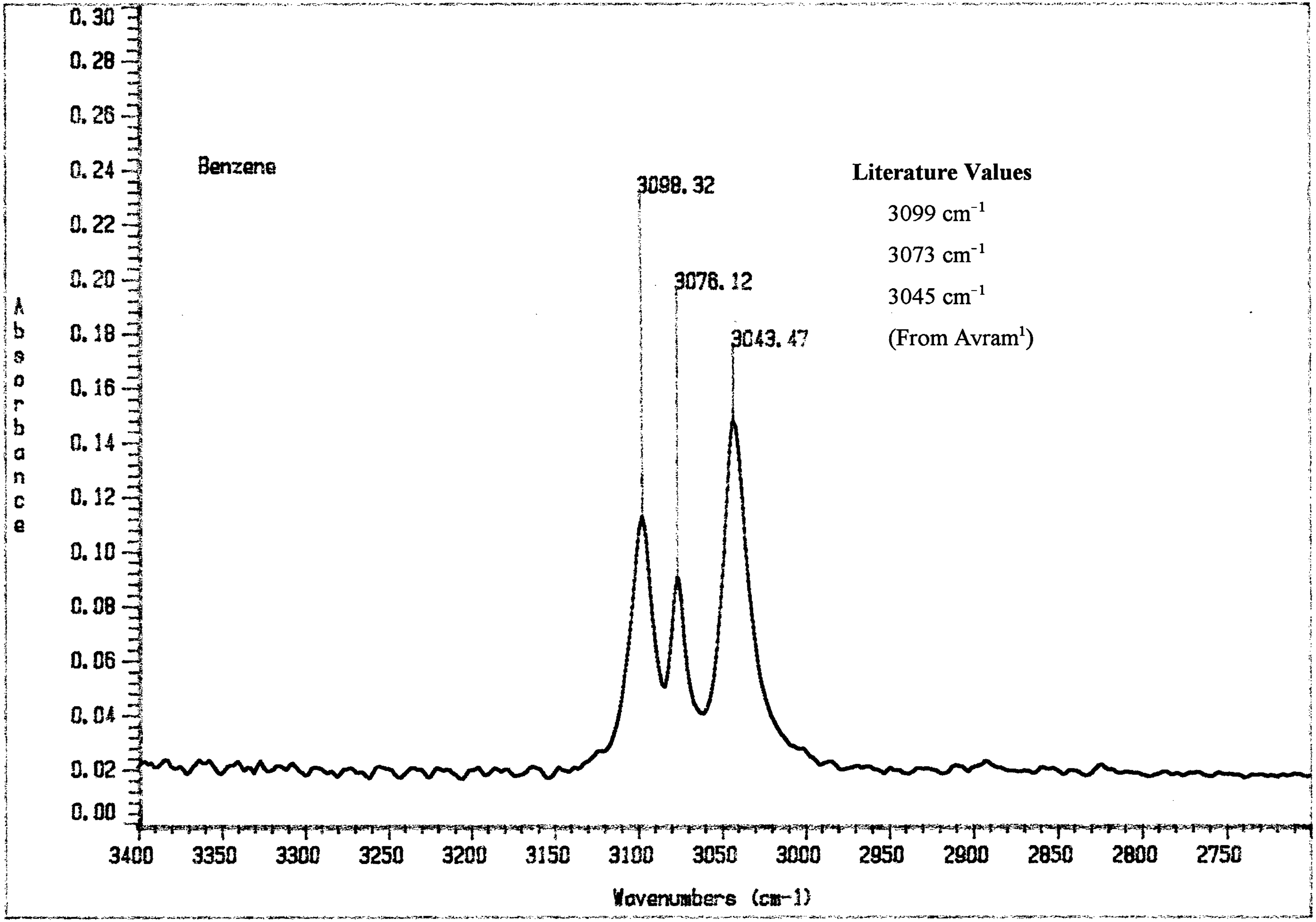


Figure 3. Spectrum of Benzene in Perfluorinated Hydrocarbon Solvent



Literature Values

3099 cm^{-1}

3073 cm^{-1}

3045 cm^{-1}

(From Avram[1])

aromatic hydrogens, gives rise to only two major peaks (see Figure 4). The presence of the fused ring in naphthalene restricts the vibrational modes available to C-H stretching, thus reducing the number of major peaks. It should also be noted that assignment of peaks to particular vibrational modes in this region is extremely difficult.[2] Fortunately, assignment of peaks to vibrational modes is not necessary for the identification of reaction products.

Reaction of Isotetralin

As noted in the quarterly report for Fall, 1995, at high temperature conditions of 100 to 230 °C tetralin is stable showing no changes in the FRIR spectra whereas isotetralin reacts. By comparing the scans of the isotetralin reaction products and tetralin (see Figure 5), the major reaction product obtained from isotetralin is tetralin. A spectral subtraction routine was employed in connection with this determination (see Figure 6). The subtraction of tetralin from the isotetralin reaction products leaves very little of any other compound, confirming that the major product is tetralin. This result will be further confirmed by GC analysis. If there are any by-products such as 1,2- or 1,4-dihydronaphthalene, or any unreacted isotetralin, this too could be confirmed by GC analysis.

High Pressure Work

The modifications required to introduce a high pressure gas blanket over the liquid in the FTIR sample cell have been completed. These modifications will allow for spectra to be obtained at combined elevated temperatures and pressures. Next quarter, research is planned in which the isotetralin reaction will be performed under a H_2 blanket.

Figure 4. Naphthalene Spectrum

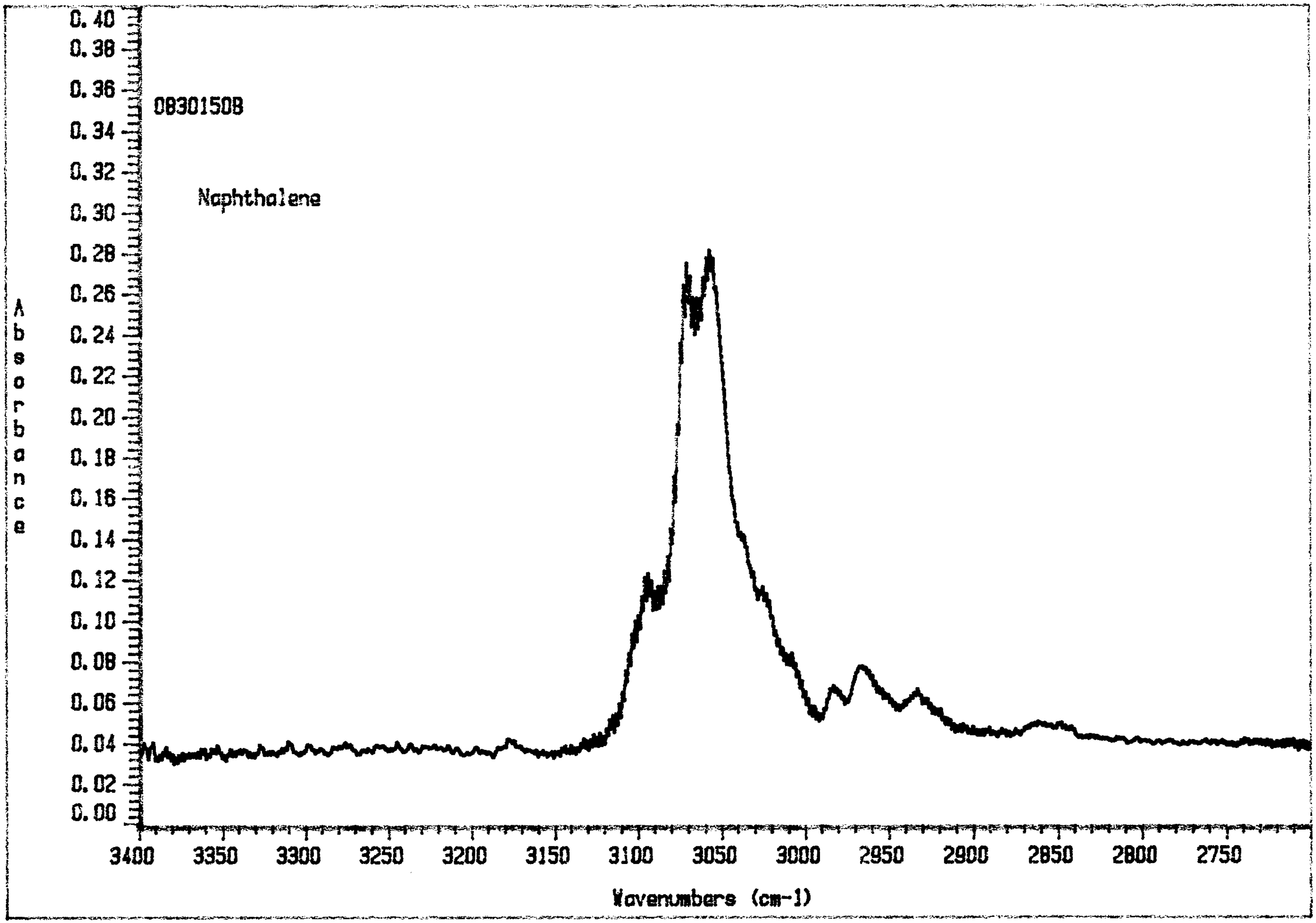


Figure 5. Comparison of Spectra from the Reaction Products From Isotetralin to Tetralin

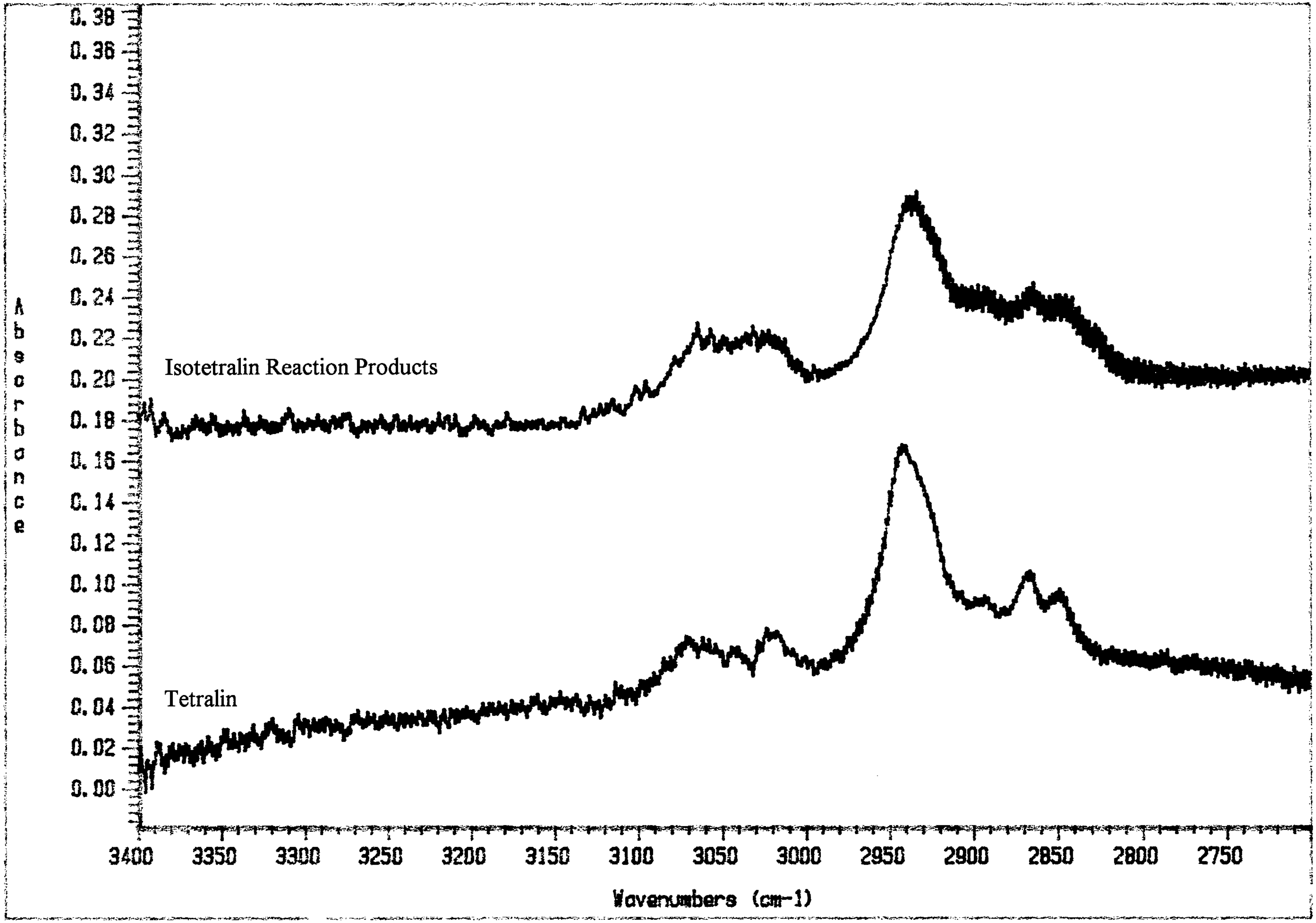
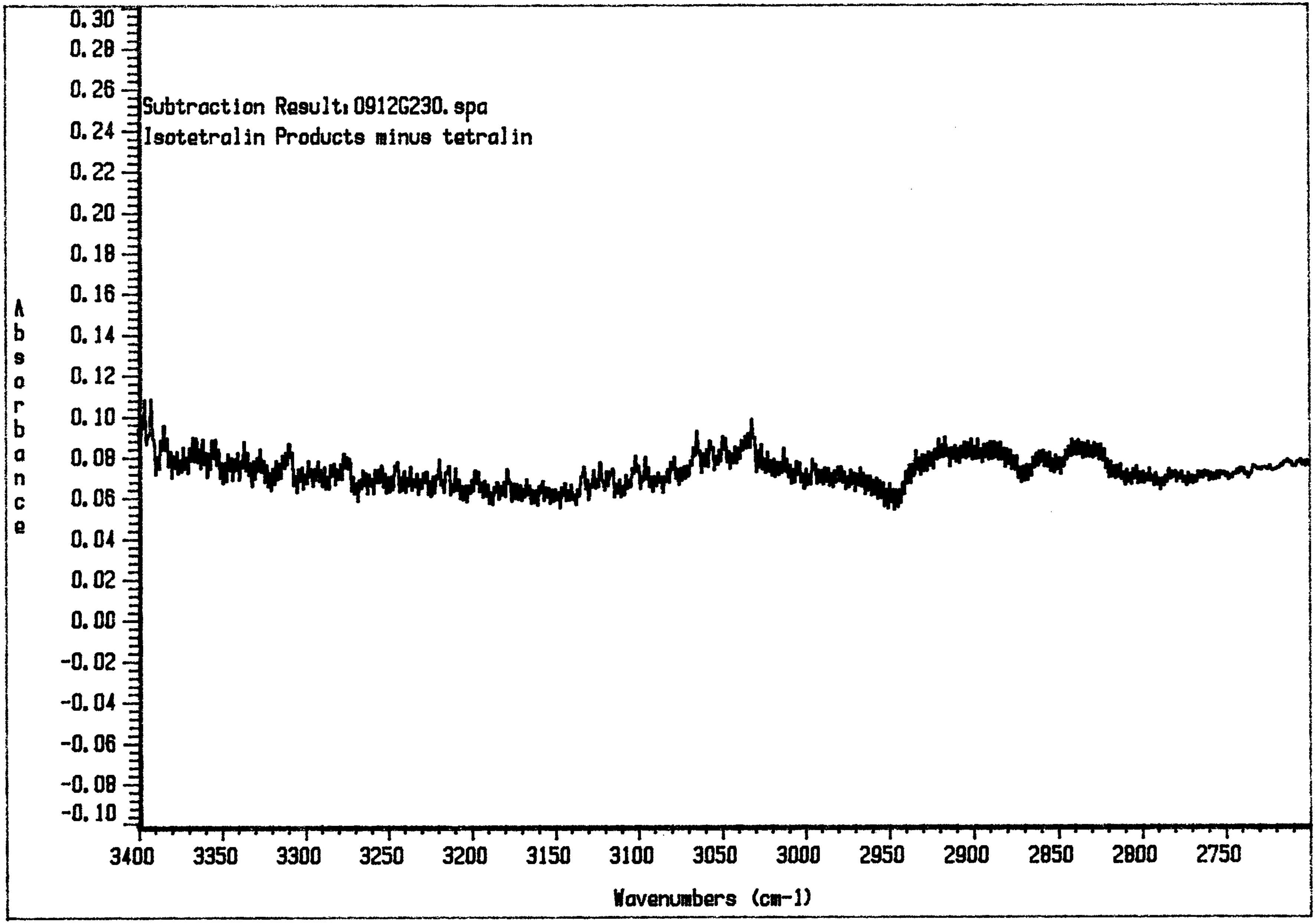


Figure 6. Subtraction Spectrum of Isotetalin Reaction Product from Tetralin



Future Work

In order to obtain spectra at elevated pressures, a system is being designed to apply pressure to both the internal sample chamber and external inert gas pressurization chamber of the AABSPEC cell. Such a design must necessarily incorporate safety features such as over-pressure relief valves. The stability studies using naphthalene, decalin, tetralin, isotetralin, 1,4-DHN and 1,2-DHN will be extended to 500 psi and 230°C using Air Products Multifluor APF-240, as solvent.

Gas chromatographic analysis will be used to confirm the identity of the products of the stability tests. The stability studies will be further extended to 350°C and 500 psi using a perfluoroether obtained from DuPont. The linear region of the absorbance versus concentration curves at elevated temperatures and pressures will be determined. It may be necessary to use the least squares and/or deconvolution software packages in connection with this determination. The kinetics of the reaction of isotetralin at elevated temperatures and pressures will be determined.

References

1. Avram, M., *Infrared Spectroscopy,* Wiley-Interscience, New York, N.Y., 1972, p. 200
2. Avram, M., op. cit., p. 203.

M98004035

Report Number (14) DOE/PC/91281--T21

Publ. Date (11) [199605]

Sponsor Code (18) DOE, XF

UC Category (19) UC-900, DOE/ER

DOE