LOW SEVERITY COAL LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

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ABSTRACT

The development of the donor solvent technology for coal liquefaction has drawn a good deal of attention over the last three decades. The search for better hydrogen donors led investigators to a class of compounds known as cyclic olefins. Cyclic olefins are analogues of the conventional hydroaromatic donor species but do not contain aromatic rings. The cyclic olefins are highly reactive compounds which readily release their hydrogen at temperatures of 200 °C or higher. Considerable effort has been expended toward understanding the process of hydrogen donation. Most of this work was conducted in bomb reactors, with product analysis being carried out after the reaction was complete. Efforts directed towards fundamental studies of these reactions *in situ* are rare. The current work employs a high temperature and high pressure infrared cell to monitor *in situ* the concentrations of reactants and products during hydrogen release from hydrogen donor compounds.

The hydrogen release reactions were studied using FTIR solution spectroscopy. High boiling perfluorocarbons were used as solvents for this work. The reactions were ultimately studied at low severity coal liquefaction conditions, i.e., 350 °C and 35 bars hydrogen. The compounds of interest to this study are the cyclic olefin isotetralin and its potential products under the conditions of hydrogenation, viz. decalin, and dehydrogenation, viz. 1,4-dihydronaphthalene and 1,2-dihydronaphthalene. Tetralin is also of interest because of the potential for isomerization of isotetralin to tetralin.

Naphthalene, tetralin and decalin were found to be stable at temperatures up to 350 °C. 1,2-Dihydronaphthalene was found to be reactive at temperatures of 250 °C and above.

1,4-Dihydronaphthalene was found to be reactive at temperatures of 230 ^{o}C and above. Isotetralin was found to be reactive at temperatures of 150 ^{o}C and above. The end products from these reactions were primarily naphthalene and tetralin. There appeared to be a temperature dependent competition between the mechanisms of dehydrogenation and hydrogenation, or in the case of isotetralin, between dehydrogenation (hydrogen release) and isomerization to tetralin (no hydrogen release). Temperatures of 230 ^{o}C and lower tended to favor the release of hydrogen from isotetralin, whereas temperatures of 250 ℃ and higher resulted in more of the isotetralin isomerizing to tetralin.

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The hydrogen release reactions were studied using FTIR solution spectroscopy. High boiling perfluorocarbons were used as solvents for this work. The compounds of interest to this study are the cyclic olefin isotetralin and its potential products under the conditions of hydrogenation, viz. decalin, and dehydrogenation, viz. 1,4-dihydronaphthalene and 1,2-dihydronaphthalene. Tetralin is also of interest because of the potential for isomerization of isotetralin to tetralin. The reactions were studied initially at 230 °C under ambient pressure. Because of the high reactivity of isotetralin, isotetralin was also subjected to the ambient pressure stability study at the lower

temperatures of 200 °C, 150 °C and 100 °C. The 230 °C testing was extended to 35 bars nitrogen pressure and to 35 bars hydrogen pressure for all the compounds. Ultimately the reactions were studied at low severity coal liquefaction conditions, i.e., 350 °C and 35 bars hydrogen.

Naphthalene, tetralin and decalin were found to be stable at temperatures up to 350 °C. 1,2-Dihydronaphthalene was found to be reactive at temperatures of 250 °C and above. 1,4-Dihydronaphthalene was found to be reactive at temperatures of 230 °C and above. Isotetralin was found to be reactive at temperatures of 150 °C and above. The end products from these reactions were primarily naphthalene and tetralin. There appeared to be a temperature dependent competition between the mechanisms of dehydrogenation and hydrogenation, or in the case of isotetralin, between dehydrogenation (hydrogen release) and isomerization to tetralin (no hydrogen release). Temperatures of 230 °C and lower tended to favor the release of hydrogen from isotetralin, whereas temperatures of 250 °C and higher resulted in more of the isotetralin isomerizing to tetralin.

CHAPTER I

Introduction

Coal has been used as an energy source for thousands of years.[1.1,2] Coal powered the industrial revolution in England, continental Europe and the United States. Coal was the predominant transportation fuel during the days of the steam locomotive. Destructive distillation, or carbonization of coal for the production of coke for the rapidly expanding steel industry also produced liquids and gases. Coal gas lamps lit the streets from London, England to Montgomery, Alabama. Coal liquids provided raw materials to a growing dyestuffs and chemicals industry, but little attention was paid to their potential for use as fuels. The first significant production of liquid fuels from coal was by Berthelot [1.3] in 1869. Although originally designed to run on coal gas [1.4], the internal combustion engine ultimately placed a heavy premium on liquid fuels. Demand soon exceeded supply. Because of ease of processing and favorable economics, petroleum feedstocks were much more suited for conversion to liquid fuels than was coal. The countries which controlled (what was then considered vast) domestic, colonial or imperialistic petroleum reserves, *e.g.*, the United States, England, France and the Netherlands, turned to oil as the primary source for liquid fuels. Petroleum replaced coal as the prime provider of strategic and transportation fuels, as well as energy for industrial and home use. Those countries without petroleum resources, notably

Germany, that had any hope of maintaining a competitive industrialized economy were faced with becoming major importers or developing alternate routes to liquid fuels. Accordingly, Germany was the first to develop technologies for the conversion of coal to liquid fuels, an effort for which Bergius was awarded the Nobel Prize in 1931.[1.5] This work culminated in the production of 100,000 barrels per day of liquid fuels for the German war effort in the early 1940's.[1.6]

By this time, American consumption of petroleum as fuels and as raw materials for plastics and other chemicals manufacturing had grown tremendously. The next two decades saw increasing reliance on imported oil. As early as the 1950's, oil companies were warning of the dwindling supply of domestic reserves and the need to develop alternative energy sources. But largely because of the complacency of the American public, the U.S. government and business sectors failed to initiate the mobilization of resources that could safeguard America's energy future and start America on the path to energy independence. The crisis of the Arab oil embargo of 1973 alerted America and all the oil importing nations to the potential for even graver disasters. In the hopes of averting future crises, the government subsidized research in alternative fuels technologies, coal liquefaction being one of them.

Numerous coal liquefaction technologies have been developed over the last three decades. Basically, three reactions are necessary to convert solid coal into liquid fuels: (1) the chemical bonds in the coal matrix must be ruptured to yield smaller, lighter fragments; (2) hydrogen must be added, since coal is hydrogen deficient compared to hydrocarbon fuels; and (3) the removal of heteroatoms, deashing and upgrading of coal liquids to useable fuels is involved in any liquefaction process.

Hydrogen may be added either directly or indirectly. In indirect hydrogenation, the coal is gasified by thermal decomposition in the presence of steam and oxygen. The resulting gases are then catalytically converted to a mixture of hydrocarbon liquids *via* a Fischer-Tropsch synthesis. In direct hydrogenation, gaseous hydrogen is added directly to the coal in the presence of a catalyst at high temperature, or hydrogen is transferred to the coal by a suitable hydrogen containing donor solvent. A typical donor solvent is the hydroaromatic species 1,2,3,4-tetrahydronaphthalene, also known as tetralin. When tetralin donates hydrogen to coal derived liquids, naphthalene is formed. The naphthalene in the coal derived liquids is hydrogenated back to tetralin in a hydrotreater. The donor solvent is separated from the mixture and recycled to the coal unit. Both the regeneration of the solvent and the hydrogen transfer from solvent to coal liquids proceed at substantially lower temperatures than the indirect and gaseous hydrogenation processes. This lower temperature operation offers several advantages. Along with reduced energy costs, lower temperature operation allows for highly specialized reactor system components to be replaced with less expensive “off the shelf” items. Less make gas is produced, the gases being less desirable economically than the liquid fuels. Also, less char is produced. Not only is char undesirable as a product, but it tends to cause coking of the catalysts in the upgrading units downstream.

Since energy expenditure represents a major cost in liquefaction processes, development of the donor solvent technology has drawn a good deal of attention. The search for better hydrogen donors led investigators to a class of compounds known as cyclic olefins. Cyclic olefins are analogues of the conventional hydroaromatic donor species but do not contain aromatic rings. The cyclic olefins are highly reactive compounds which readily release their hydrogen at temperatures of 200 °C or higher. For example, 1,4,5,8-tetrahydronaphthalene, also known as isotetralin, has been shown to be a substantially better hydrogen donor than tetralin under typical coal liquefaction conditions.[1,7-12]

Considerable effort has been expended toward understanding the process of hydrogen donation. Most of this work was conducted in bomb reactors, with product analysis being carried out after the reaction was complete. Efforts directed towards fundamental studies of these reactions in progress are rare. Because hydrocarbons absorb in the mid-infrared region, infrared spectroscopy is a useful technique to follow the course of hydrogen donation reactions. The course of hydrogen donation reactions could be followed *in situ* if the concentrations of reactants and products could be measured. The goal of this research is to develop a methodology to study the release of hydrogen from cyclic olefins in a high temperature and high pressure infrared cell.

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CHAPTER II

Infrared Spectroscopy at Elevated Temperatures and Pressures

A Literature Review

This chapter provides a brief history of the development of infrared cells for use at elevated temperatures and pressures. The mechanical problems associated with combining high temperatures and high pressures are discussed in some detail. The effects of temperature and pressure on the appearance of spectra are also examined. Some examples of the numerous applications in which these cells have been employed are presented. A brief description of the cell chosen for the current work is given.

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 of 2000 ^{o}C and pressures into the gigabars. This review focuses on experimentation at temperatures up to about 500 ^{o}C and pressures less than 140 bars. 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 section 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.

Background

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.[2.1] 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.[2.2,3] 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.[2.4]

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 the molecules under study. This application presents little difficulty, because gas cells under pressure are easily heated.[2.5] It is extremely important to control both temperature and pressure carefully when performing any quantitative analysis upon gas phase species. Absorption band intensities, widths, and areas are dependent upon both of these 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.[2.6]

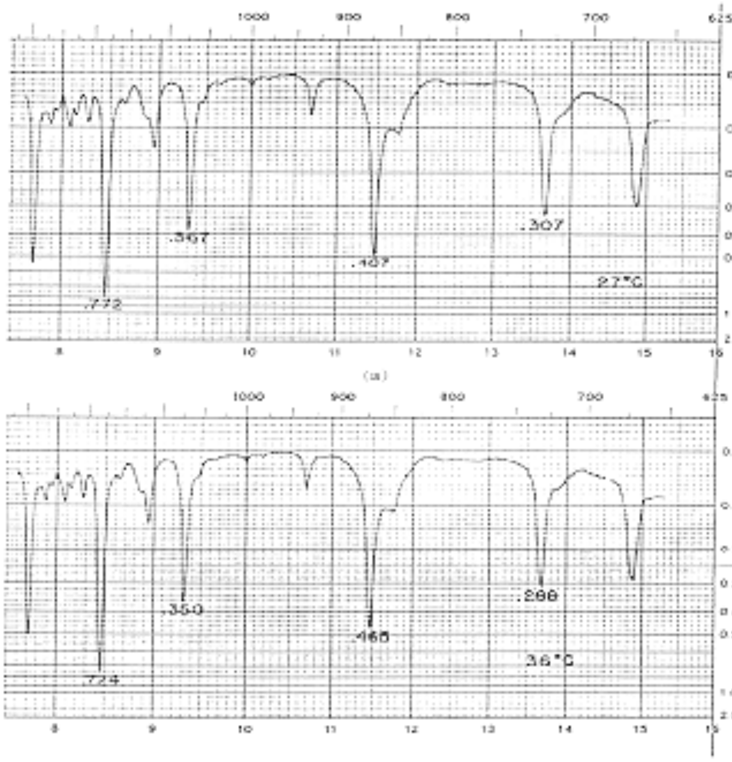
Applications to Liquid Phase Spectroscopy

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, and, hence, cannot be heated much above their (usually low) atmospheric boiling point unless they are kept at elevated pressure. This is not generally considered a simple extension of IR sampling technique and has 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 a solvent, it is not difficult to heat a sealed cell to 200 ^{o}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 or 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 (0.025 mm diameter) nickel wire run through 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. An example is shown in Figure 2-1; it can be seen that the absorbances of certain absorption bands have decreased by about 6%, 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.[2.7]

Free rotation usually disappears in the liquid phase and is replaced by librational 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.[2.8] 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

Figure 2-1



(a)

(b)

Spectrum of a 3% solution of 2,4,5-trichlorophenol in CS_2, (a) at 27°C and (b) at 36°C.

spectrum of gaseous oxygen as its density approaches that of the liquid. Investigators found that gaseous oxygen becomes blue at pressures of several hundred atmospheres, and its absorption spectra then contains a number of diffuse bands which are characteristic of liquid oxygen but not of the gas. It was also observed that the absorption coefficients increased more rapidly than the density of the gas.[2.9]

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, amyl alcohol, and toluene at pressures up to 8000 bars revealed no discernible differences in their absorption bands in the near infrared as compared to spectra obtained at ambient pressure.[2.10] It is thought unlikely that pressures below 140 bars would have any noticeable effect on the spectra of hydrocarbon liquids.

Any well-constructed liquid cell may be made the basis of a heated 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.[2.11] 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.[2.12] A number of manufacturers produce commercial models of liquid cells incorporating these design criteria, notably Harrick, Spectra-Tech and Aabspec.

Cell Design

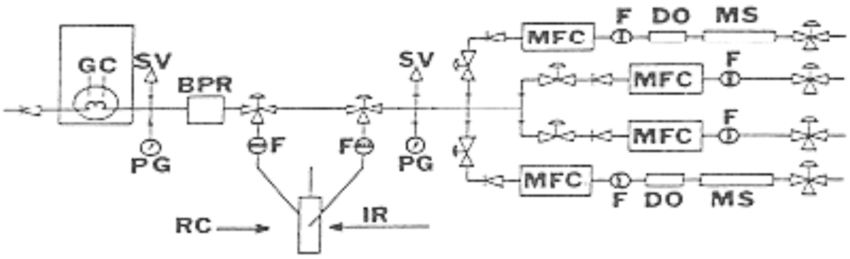
The practical realization of the combination of high temperature and high pressure is very difficult. In practice, cells suitable for high-pressure experiments have limitations in their temperature range. Conversely, high temperature cells more often than not are not able to operate at reasonably high pressures. Nevertheless, significant progress has been made in this area, and a number of articles describing cells designed for obtaining infrared spectra at elevated temperatures and pressures have appeared in the literature.[2.13] The earliest designs, such as those described by Noack [2.14], and Tinker and Morris [2.15], employed a cell for the study of reactions carried out in a separate reactor. Essentially, these systems consisted of an autoclave with an IR cell located downstream for the analysis of reaction products. Since it is often desirable to do *in situ* studies of chemical reactions at elevated temperatures and pressures, several designs have been described in which the cell itself acts as the reactor. The cell developed by Penninger [2.16] is of the flow type and is primarily designed for chemical engineering purposes, *e.g.*, *in situ* infrared recording of chemical reactions in gas-liquid systems, mixing characteristics of reactors under actual reaction conditions, and sensor device of an automatic reactor control system. This type of application is an extension of the earlier cell designs which were directed more towards pure chemistry. Since the window material and the metal-window seal present the most serious problems in the construction and use of a high pressure spectroscopic cell [2.17], a substantial portion of the effort in the development of these cells went into improving the window seals.[2.18]

Whyman [2.19] provides an excellent review of the history of the development of infrared cells for use at elevated temperatures and pressures. In 1972, the details of only two or three such cells had been presented throughout the world. Over the next 15 years, many such cells were described and this technique became part of the traditional armory of physical methods, particularly in industrial laboratories. The reason for industrial interest is quite simply that it is essentially the only currently (1987) available spectroscopic technique for *in situ* monitoring of the species present under actual working conditions of pressure and temperature. It can, therefore, provide information which is directly relevant to industrial processes. Clearly the use of such a method provides a significant advance over the traditional method of withdrawal of samples from high pressure - high temperature vessels followed by analysis under ambient conditions.[2.20] The advent of Fourier transform instrumentation has considerably simplified the technique both in terms of enhancement of overall sensitivity and in terms of ease of operation when remote control is necessary. Commercial cells for the investigation of liquids, gases and solids under high pressures and temperatures are now available.

The cells described can be used to study a batch reaction or incorporated into a continuous flow system. One such design for catalytic studies in gas flow systems as described by Lavalley[2.21] is shown in Figure 2-2. The entire high pressure system is built directly on the FTIR spectrometer. The design is typical of flow systems for use with IR spectroscopy, and basically consists of high pressure gas cylinders which contain the reactant gases, mass flow controllers, a junction where the gases mix and flow through the IR cell which serves as the reactor, and a back pressure regulator. This particular design also incorporates a downstream gas chromatograph. The flow system can also be used to study the reactions of liquids or slurries, or liquids on a solid catalyst disc or catalyst particles.

Figure 2-2

Flow System with FTIR Spectrometer



MFC	Mass flow controller
DO	Deoxygen trap
MS	Molecular sieve trap
F	Filter
PG	Pressure gauge
SV	Safety valve
RC	Reactor cell
BPR	Back pressure regulator
GC	Gas chromatography

Of particular interest to the current work is the study of liquids under pressures of gases. Spectroscopic cells which have been described for the measurement of spectra of liquids and/or solids under pressures of gases have generally been used for the study of catalytic reactions and the identification of reaction intermediates under process conditions. Whyman[2.22] provides a detailed description of three different designs, designated A, B and C respectively.

Type A includes those cells which are self contained units, such as an autoclave fitted with windows, and which can be stirred and heated. Thus chemical reactions can be monitored continuously from start to finish without perturbing the system, *i.e.*, a truly *in situ* experiment.

In the Type B cell design, the IR cell and autoclave are separate components which are operated in conjunction with each other. Thus, reacting solutions from the autoclave are circulated through the IR cell by means of either gravity or a pump.

Type C cells are closely related to those of Type B but have been designed specifically as flow cells for the study of liquid/solid (or gas/liquid/solid and gas/solid) systems and the examination of heterogeneous catalysts under working conditions. The cell described by Penninger[2.23] represents the latest in a series of developments in spectroscopic cells which were initially designed for the study of homogeneous catalysts.[2.24-27] The Penninger cell is a versatile piece of equipment which may be used for the study of either liquid-solid catalyst interactions (with or without dissolved gas) or gas-solid systems.

An interesting approach to solving the problem of obtaining spectra of liquids at elevated temperatures and pressures is that of Rossiter.[2.28] 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 an internal window and a pair of external windows. The internal window is in contact with the sample, while the external windows are separated from the internal window by a gas pressurization chamber. The gas chamber can be pressurized to eliminate the pressure differential across the internal window. 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 under way in such diverse areas as homogeneous and heterogeneous catalysis, chemisorption and physical adsorption 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 decomposition, superconductors, supercritical fluid extraction, and supercritical fluid chromatography, to name just a few. Future research and development promises to extend virtually every aspect of infrared spectroscopy to elevated temperatures and pressures.

Of direct interest to the current work, the cell designed by Rossiter has been used to obtain solution spectra of lauric acid in carbon tetrachloride at 260 °C and 60 bars.[2.28] The spectra of jet fuel at high temperature and pressure is also presented in this paper. This cell should be well suited to the purpose of following the reaction of isotetralin at low severity coal liquefaction conditions. It should also be suited, with some modifications, to the study of heterogeneous catalyst systems.

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CHAPTER III

Experimental Methods

This chapter provides a brief description of the chemicals, apparatuses and procedures used in this research. Additional details on the apparatuses and procedures employed may be found in the appendices.

I. Chemicals

Table 3.1 presents the chemicals used in this research.

Table 3.1

Compound	Purity	Source
Naphthalene	99+%	Aldrich
cis-Decalin	99 %	Aldrich
trans-Decalin	99 %	Aldrich
Tetralin	99 %	Aldrich
Isotetralin	92 %	Prepared in our lab
1,2-Dihydronaphthalene	94 %	Wiley
1,4-Dihydronaphthalene	89 %	Wiley

Benzene	HPLC grade	Fisher
Cyclohexane	99 %	Aldrich
Cyclohexene	99 %	Aldrich
Carbon tetrachloride	Spectranalyzed	Fisher
n-Hexadecane	99 %	Aldrich
APF-240™	99+%	Air Products
Krytox™ GPL-107	99+%	DuPont
Perfluorohexane	99 %	3M
Methylnonafluorobutyl Ether (HFE)	99 %	3M
Diphenylmethane	99 %	Aldrich

APF-240™ is an Air Products and Chemicals Company trade name for perfluorodiisopropyldecalin. APF-240™ has a boiling point of 240 °C. Krytox™ is a general purpose lubricant manufactured by DuPont. It is a perfluoropolyalkyl ether with a boiling point over 450 °C. It exhibits very little thermal degradation at 350 °C, and thus was thought to be suitable for use as a solvent in the higher temperature portion of this work. Perfluorohexane and HFE were used as solvents for Krytox™.

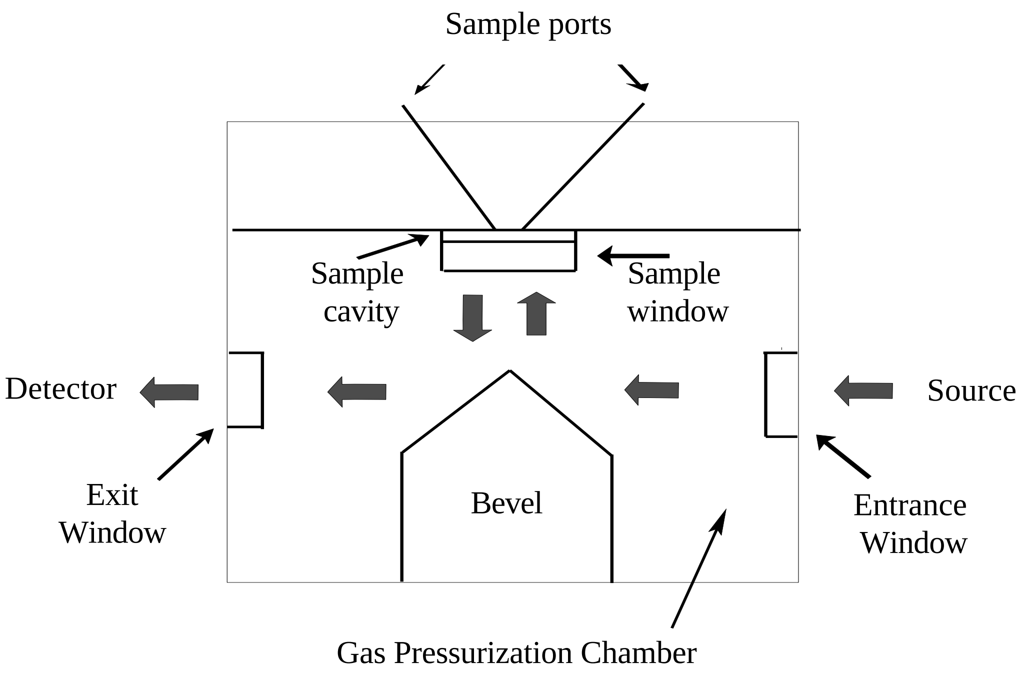
II. Apparatus

The infrared spectrometer employed in this research was a Nicolet 5SXC FTIR spectrometer with an OMNIC™ software package. A continuous nitrogen purge was maintained to reduce atmospheric moisture and carbon dioxide in the instrument which might have interfered with test results. The infrared cell used was an experimental design developed by AABSPEC Corporation, and designated as model # RA4000-EXP Reflecting Flow Cell. It can be used in continuous flow through or static mode, but in this research was used only as a batch reactor. The cell is capable of operating at temperatures up to 425 ℃ and pressures of 140 bars. It employs three ZnS salt windows, one is in contact with the sample and necessarily at the same temperature as the sample. The other two salt windows are housed in the walls of the gas pressurization chamber and are cooled by externally circulating liquid. The pressure in the gas pressurization chamber can be adjusted externally, thus insuring zero pressure differential across the heated sample window. The atmosphere in the gas pressurization chamber can be the same as or different from the atmosphere above the sample. The pathlength for infrared radiation through the sample is determined by the width of the polytetrafluoroethylene (PTFE) spacer, which was 0.5 mm thick. The sample cavity was cylindrical in shape with the spacer forming the cylinder wall and the salt window forming one flat end. The other end is formed by an interior wall of the stainless steel cell. This end is drilled with an entry and an exit port for the introduction and removal of solutions. The reactor volume is heated by means of an electrical resistor in a brass block mounted to the cell. A thermocouple port is drilled into the cell very close to the sample cavity to provide accurate temperature measurement during operation. The heater and thermocouple were connected to a microprocessor to allow for process control during operation.

The infrared radiation is admitted through the inlet window of the gas pressurization chamber. The IR beam strikes a stainless steel bevel where it is deflected through the sample window and into the sample cavity. The beam then reflects off the stainless steel wall and out through the sample window. Thus the effective pathlength is roughly twice the spacer thickness, or 1.0 mm. The radiation returns to the opposite face of the bevel and is reflected out through the exit salt window to the detector. Transmission-like spectra were obtained which compared very closely with spectra generated using conventional transmission cells. Figure 3-1 presents a sketch of the radiation path through the cell. Appendix A provides a schematic of the cell construction. Rossiter, who designed the cell, provides a detailed description of the function and operation of the cell.[3.1]

Figure 3-1

Path of Infrared Radiation through the Cell



III. Procedure

I. To obtain solution spectra, it was necessary to find a solvent which was transparent to infrared radiation in the range of interest and was a suitably good solvent for naphthalene, decalin and tetralin. Isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene were not used in this determination because of their high cost and limited availability. Carbon tetrachloride was chosen because of its transparency in the region of interest and good solubility characteristics, and also because of the absence of any C-H stretches which might have interfered with C-H stretches in the samples under study.

ii. The appropriate concentrations of hydrocarbons in carbon tetrachloride were determined which would give absorbance values less than or equal to one. The samples were scanned in the region from 4000 cm^{-1} to 400 cm^{-1}, but the region of interest to this study is only from 3400 cm^{-1} to 2700 cm^{-1}. Appendix B provides a detailed description of the routine used to obtain FTIR spectra.

iii. The spectra of naphthalene, decalin and tetralin in carbon tetrachloride were obtained in replicate to insure reproducibility.

iv. The experimental spectra were compared to library spectra to insure the FTIR was functioning properly.

v. A solvent was chosen to extend the useful range of the AABSPEC cell to 230 ^{o}C. The solvent chosen was perfluoro-diisopropyldecalin, marketed by Air Products and Chemicals Company under the trade name APF-240™. The boiling point of APF-240™ is 240 ^{o}C. It is suitably transparent to infrared radiation in the range of interest to this study. It contains less than 1 ppm residual hydrogen, so no interference from C-H stretches was expected.

vi. The linear range of absorbance versus concentration was determined for solutions of decalin, tetralin and naphthalene in carbon tetrachloride using the AABSPEC cell.

vii. The temperature dependence of the absorbance was determined by placing naphthalene, decalin and tetralin in APF-240™ in a sealed cell, then scanning the samples at 65 °C, 100 °C , 150 °C, 200 °C and 230 °C. The PTFE spacer which determined the pathlength was held in place by a stainless steel plug and o-ring assembly on the opposite side of the salt window. Also, the outer edges of the spacer contacted the stainless steel body of the cell. Any lengthening of the pathlength due to a temperature increase would thus be caused by an expansion of the stainless steel cell. The linear expansivity of steel is 0.136×10^{-4}/ °C. Over a temperature interval of 165 °C, the expansion calculated was only 0.22%. The pathlength was assumed to be constant.

Stability Studies, 65 °C to 230 °C

In order to investigate the reactivities of naphthalene, decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene at elevated temperatures, a routine for obtaining high temperature spectra was developed. The details of this procedure are described in Appendix B. Solutions of naphthalene, cis-decalin, tetralin, isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene in APF-240™ were all subjected to the stability test described under conditions of ambient pressure (sealed cell, no atmosphere present), 35 bars nitrogen blanket, and 35 bars hydrogen blanket. The progress of the reactions were monitored *in situ* by scanning every 30 minutes. Peaks which were characteristic of reactive starting materials diminished while peaks of products grew, although in many cases these peaks overlapped. The spectral addition and subtraction routines provided with the OMNIC™ software were employed to generate synthetic FTIR scans in an attempt to match as closely as possible the reacting mixture scan as the reaction proceeded. After the final scan, the product was allowed to cool and removed from the cell for GC analysis. Due to the small reactor volume, the reactor contents cooled about 50 °C in the first minute, and were cool enough to remove from the cell in about five minutes.

Stability Studies, 250 °C to 350 °C

Two modifications to the cell were necessary in order to extend the testing to 350 °C. The PTFE spacer which forms the cylindrical wall of the sample cavity was replaced with a higher temperature material. The cell manufacturer provided Grafoil™ spacers for this purpose. Grafoil™ is a flexible graphite material manufactured by Union Carbide Corporation. Also, the Viton™ rubber o-ring which forms the seal between the sample cavity and the gas pressurization chamber was replaced with a higher temperature material. The cell manufacturer recommended a Kalrez™ o-ring for this purpose. Kalrez™ is a perfluoroelastomer manufactured by DuPont Dow Elastomers.

GC Analysis of Reactants and Products

Gas chromatographic analysis was used to confirm the final product concentrations determined by FTIR. Both the reactants and the product mixtures were injected into a Varian 3400 series gas chromatograph with a 60 m x 0.32 mm I.D. J&W Scientific capillary column with a 0.25 micron film thickness of a Durabond™ DB-5 stationary phase. Helium gas was used as the carrier and compounds were detected by flame ionization detection. Retention times of reactants and potential products were determined using solutions prepared from stock. Relative concentrations were determined from the ratio of the peak area counts as the response factors for the compounds under study are known to be close to unity.[3.2] Diphenylmethane was used as an internal standard. Table 3.2 summarizes the gas chromatographic analysis parameters.

Table 3.2

The instrumental parameters were:

Instrument:	Varian 3400 Gas Chromatograph
Column:	J & W Scientific 60 m x 0.32 mm ID
Injection port temperature:	300 °C
FID detector temperature:	315 °C
Initial column temperature:	65 °C
Final column temperature:	150 °C
Initial column hold time:	12 minutes
Program rate:	2.5 °C/min
Phase:	DB-5
Film thickness:	0.25 micron
Carrier gas:	Helium

REFERENCES

3.1 Rossiter, Valentine J., “Taking the Spectroscopy of Fluids Beyond the Limits - Advances in Sampling at High Temperatures and Pressures”, *Spectroscopy,* **10(6)**, 18 (1995)

3.2 Kim, Honggon, *Catalytic Activity of Organometallic Molybdenum, Nickel and Vanadium in Coprocessing*, Ph.D. Dissertation, Auburn University, Auburn, Alabama, 1991, p. 259

CHAPTER IV

Infrared Spectroscopy at Elevated Temperatures and Pressures

Applications to the Study of the Release of Hydrogen From Isotetralin

This chapter provides a detailed description of the development of an FTIR spectroscopic method for studying the release of hydrogen from isotetralin at elevated temperatures and pressures. A brief introduction to the fundamentals of absorption spectrometry is presented, followed by a detailed discussion of the application of these fundamentals to the current work. The development of this analytical method is an ongoing process, and at the time of publication of this document the method is far from being a routine procedure. Amendments were made to the method as the results of initial experimentation were obtained. These amendments are discussed in Chapter V.

Fundamentals of Absorption Spectrometry

The analytical determination of a solute in a solvent is dependent upon the relationship between the absorbance of the solute at a particular wavelength and the concentration of the solute in solution. This relationship is governed by Beer’s Law, usually expressed as

$$\mathbf{A = abc,} \qquad \text{Eq 4.1}$$

where A = the absorption at a given wavelength,

a = the absorptivity of the solute at the given wavelength,

b = the pathlength the radiation traverses through the sample, and

c = the concentration of the solute in the solvent, usually expressed in terms of mass (or moles) of solute per volume of solution.

In infrared spectrometry, it is customary to express the wavelength in terms of wavenumber, where the wavenumber in reciprocal centimeters (cm^{-1}) is obtained by dividing 10,000 by the wavelength in microns.

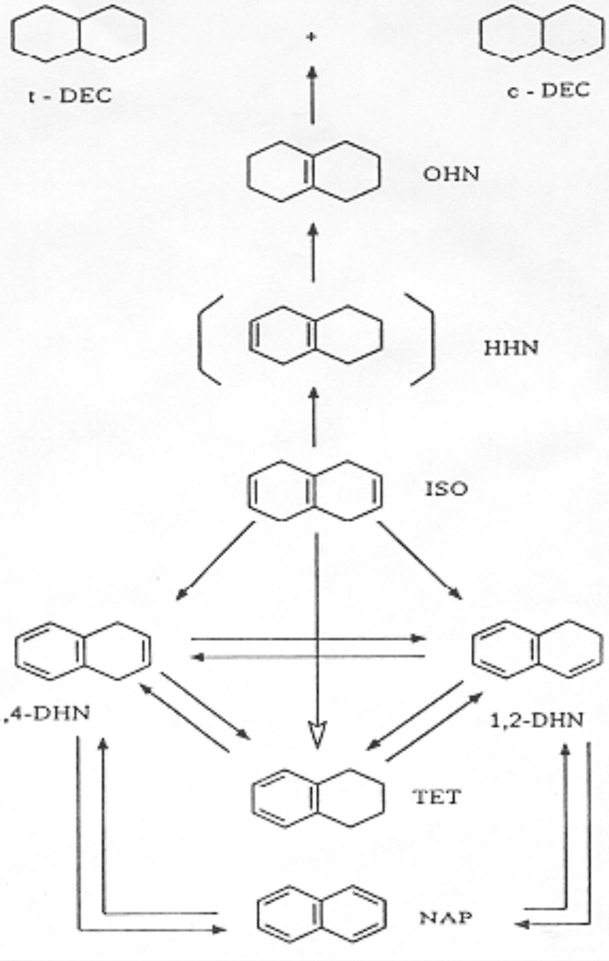
Some Room Temperature Preliminaries

The compounds of interest to this study are isotetralin and its potential products under conditions of hydrogenation or dehydrogenation. These are naphthalene (NAP), 1,2-dihydronaphthalene (1,2-DHN), 1,4-dihydronaphthalene (1,4-DHN) and decalin (DEC). Tetralin (TET) is also of interest, because of the potential for isomerization of isotetralin to tetralin while maintaining the fused ring structure. Figure 4-1 presents a proposed reaction pathway for isotetralin.[4.1] Hexahydronaphthalene (HHN) and octahydronaphthalene (OHN) are likely intermediates but were not present at sufficiently high concentrations to be detected by FTIR or GC as used in this study.

Because of its high reactivity, isotetralin has been used as a starting material in the synthesis of a wide variety of compounds. Numerous articles describing studies in which isotetralin was a reactant have appeared in the literature over the last thirty years. In particular, a number of studies of the hydrogen donating ability of isotetralin were found. Curtis, Guin and Kwon[4.2] showed that isotetralin has a much greater capacity to

Figure 4-1

FIGURE 1: REACTION PATHWAY FOR ISOTETRALIN.



donate hydrogen to coal than does its hydroaromatic analog, namely tetralin. Bedell and Curtis[4.1,3-5] showed that both isotetralin and the three ring cyclic olefin 1,4,5,8,9,10-hexahydroanthracene (HHA) release much more hydrogen than their conventional hydroaromatic analogs, both with and without coal present. Japanese researchers found that HHA suppresses the formation of insoluble matter and decreases the extent of retrogressive reactions in coal conversion.[4.6] Further research indicated that coal undergoes either retrogressive reactions or dissolution reactions depending on the hydrogen donor ability of the solvent used.[4.7] Using aromatics as acceptors, Wang and Curtis[4.8] compared the hydrogen donor ability of cyclic olefins, hydroaromatics, and cycloalkanes which were derived from resids by a modified Birch method. The studies by Curtis *et al*., Bedell *et al.* and Wang *et al*. were predecessors to the current work.

Assignment of Peaks to Absorbing Species

The first step in assigning peaks to absorbing species was to determine the wavelength where the molecules demonstrated their strongest absorbances. Naphthalene, cis-decalin, trans-decalin and tetralin were chosen for this determination. Isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene were excluded from this determination because of their high cost and limited availability. In addition, benzene, cyclohexane and cyclohexene were scanned to aid in the determination of the peak locations for aromatic stretches, cyclic paraffinic stretches and cyclic olefinic stretches, respectively. The structures of these single ring compounds are simpler than the structures of their fused ring analogues, and in general, should give rise to less complicated spectra in which the stretches are more readily identifiable.

Polyatomic molecules give rise to a host of absorption peaks which are characteristic of the molecules. All of the compounds in this study show characteristic absorption peaks in the range from 3400 cm^{-1} to 2700 cm^{-1}. In this region, peaks above 3000 cm^{-1} result from aromatic, heteroaromatic, acetylenic or olefinic stretching.[4.9] For the compounds used in this study, this is limited to aromatic or olefinic stretching. The peaks between 3000 cm^{-1} and 2700 cm^{-1} are associated with aliphatic stretches.[4.10]

Figures 4-2 through 4-7 present carbon tetrachloride solution spectra of cis-decalin, cyclohexane, naphthalene, benzene, cyclohexene and tetralin, respectively, with the locations of the major absorbance peaks labeled. The location of the absorbance peaks in cis-decalin and trans-decalin were the same, and for this reason, only the spectra of cis-decalin is presented. The location of the cyclic paraffinic stretches in cyclohexane and decalin are within 6 cm^{-1}. In fact, the peaks are so well characterized that they have been assigned to definite vibrational modes of the molecules. The peak around 2852 cm^{-1} is characteristic of the symmetric methylene stretch, while the peak near 2920 cm^{-1} is characteristic of the asymmetric methylene stretch.[4.10] This type of direct comparison was not available in the case of the aromatics, however. Benzene, in which all the carbon-hydrogen bonds are in the same environment, gives rise to three peaks in the region from 3400 cm^{-1} to 2700 cm^{-1}, whereas naphthalene, which has two distinct types of carbon-hydrogen bond environments, gives rise to only two. The fused ring structure limits the number of vibrational modes available to naphthalene in this region of the spectrum. Cyclohexene gives rise to only one peak in the olefinic/aromatic region, but the presence of the double bond complicates the spectra in the aliphatic region.

Figure 4-2

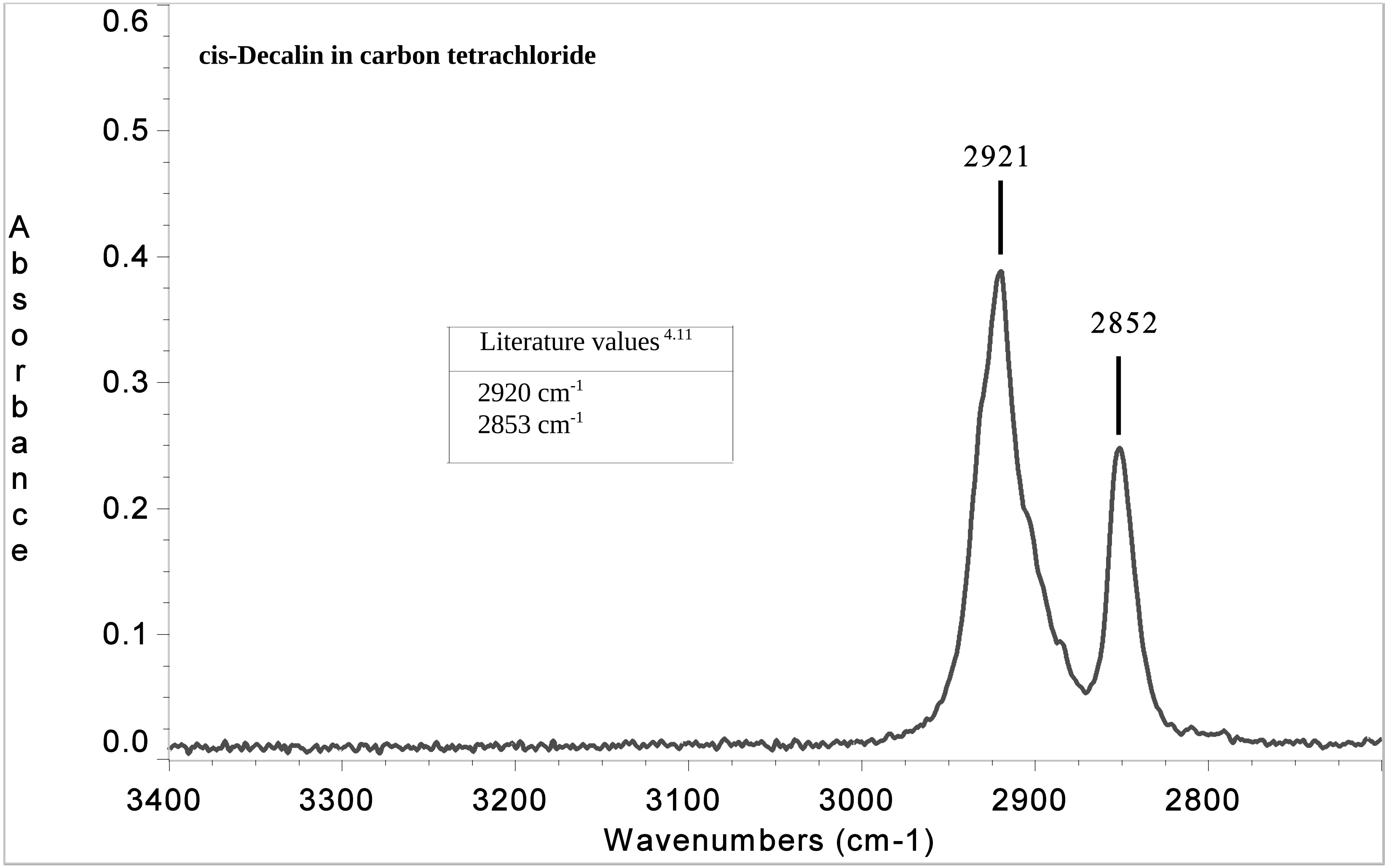

cis-Decalin in carbon tetrachloride
2921
2852
Literature values 4.11
2920 cm-1
2853 cm-1
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-3

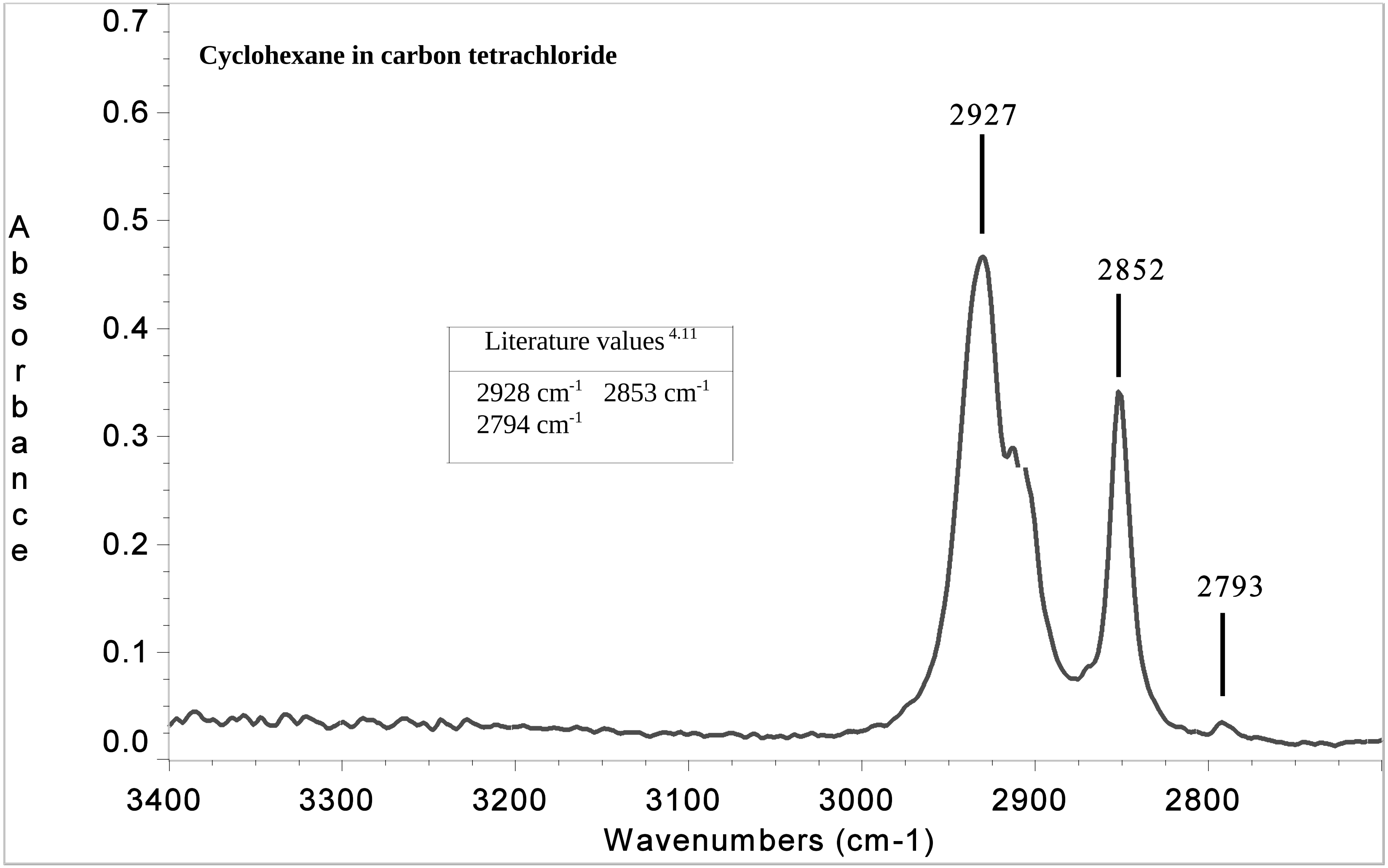

Cyclohexane in carbon tetrachloride
2927
2852
2793
Literature values 4.11
2928 cm-1 2853 cm-1
2794 cm-1
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-4

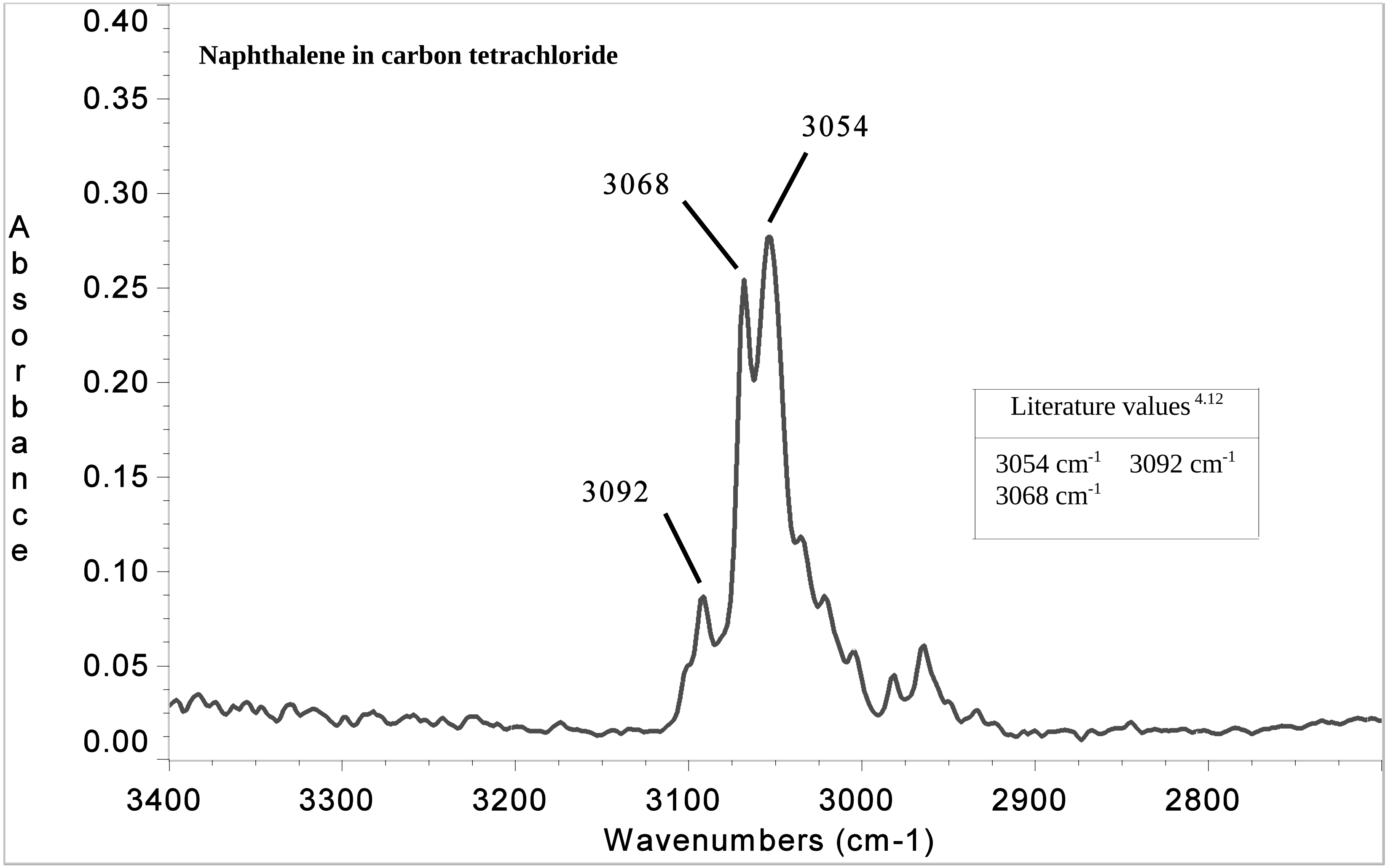

Naphthalene in carbon tetrachloride
3054
3068
3092
Literature values 4.12
3054 cm-1
3092 cm-1
3068 cm-1
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-5

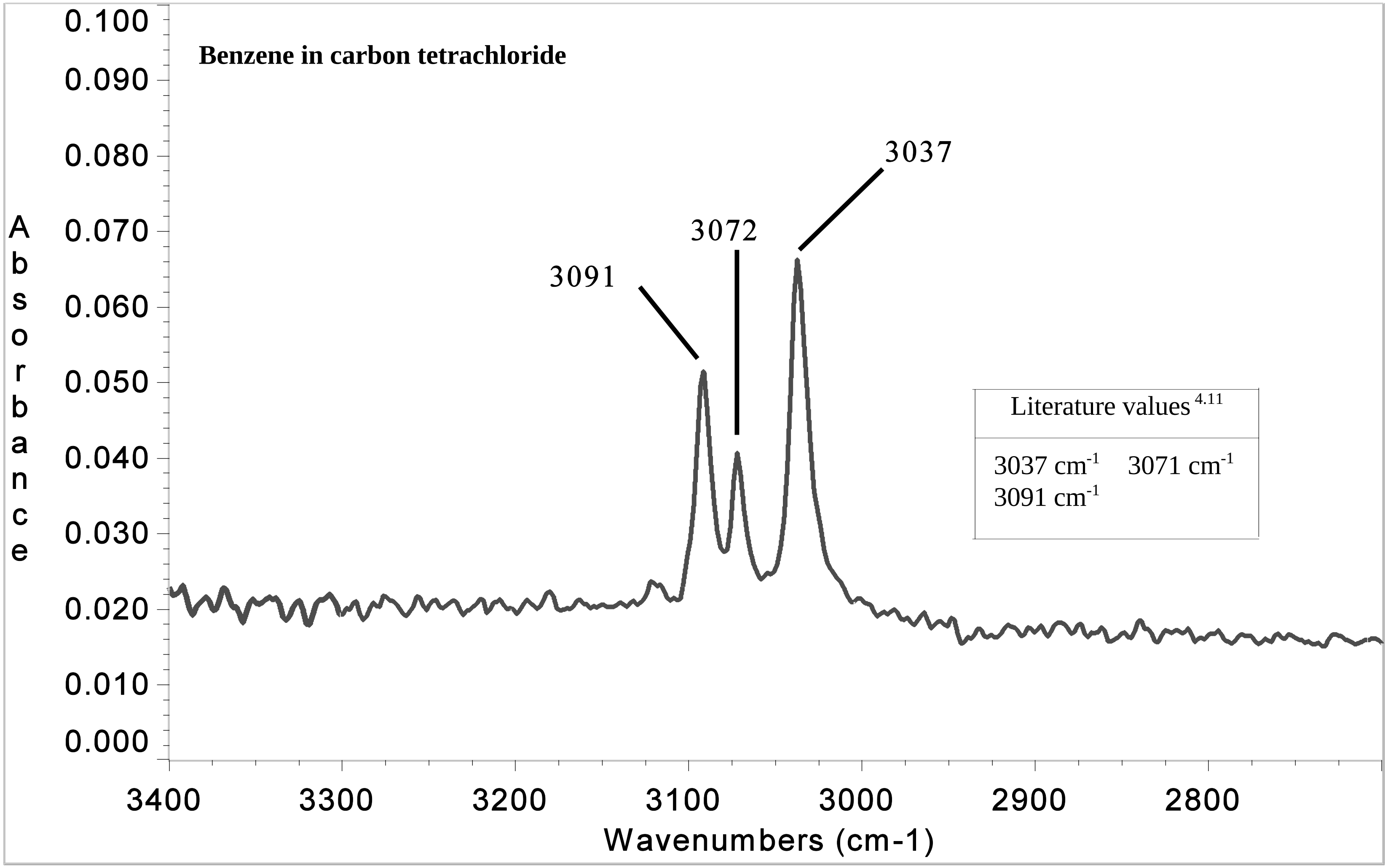

Benzene in carbon tetrachloride
3037
3072
3091
Literature values [4.11]
3037 cm^{-1}
3071 cm^{-1}
3091 cm^{-1}
Absorbance
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-6

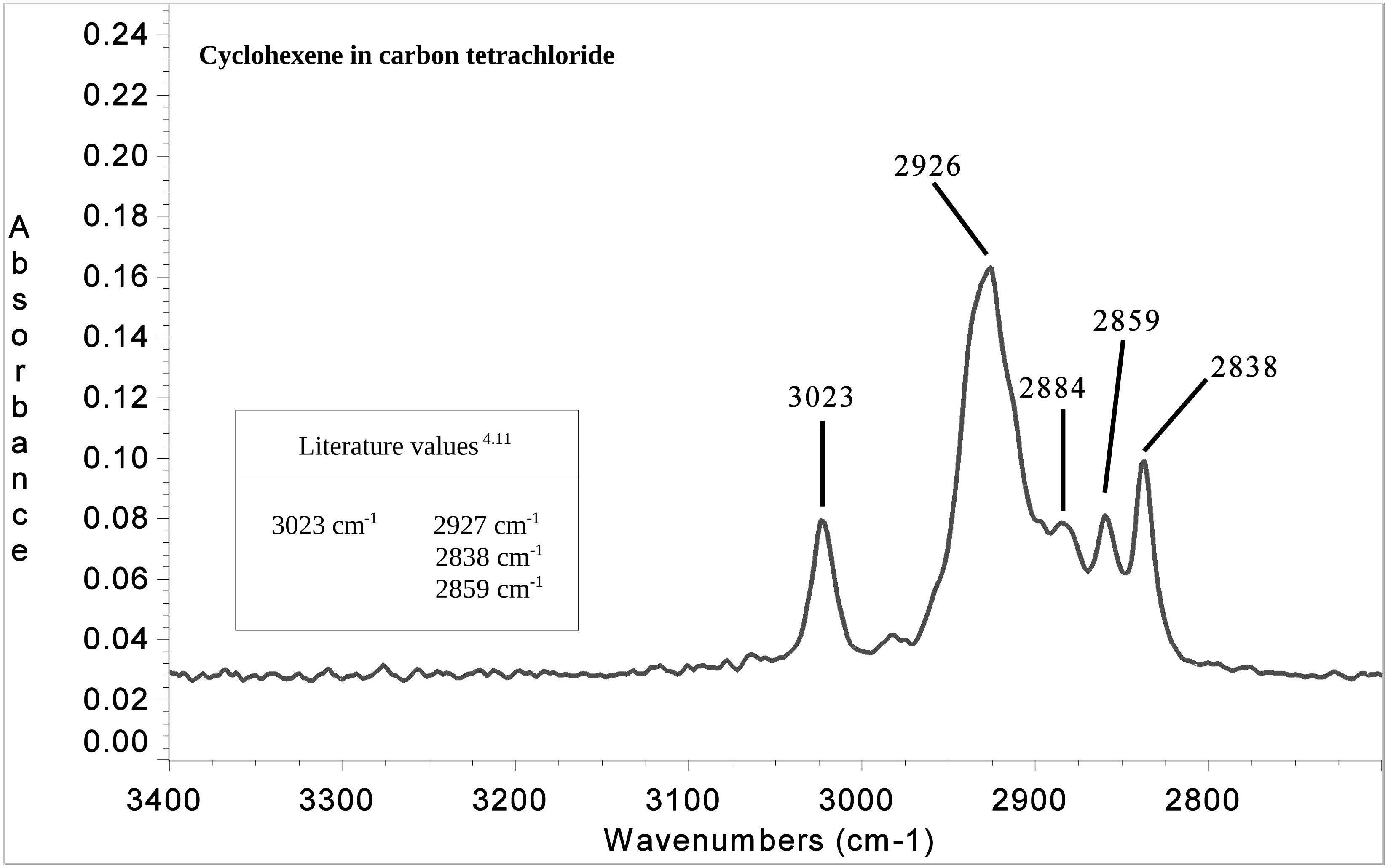
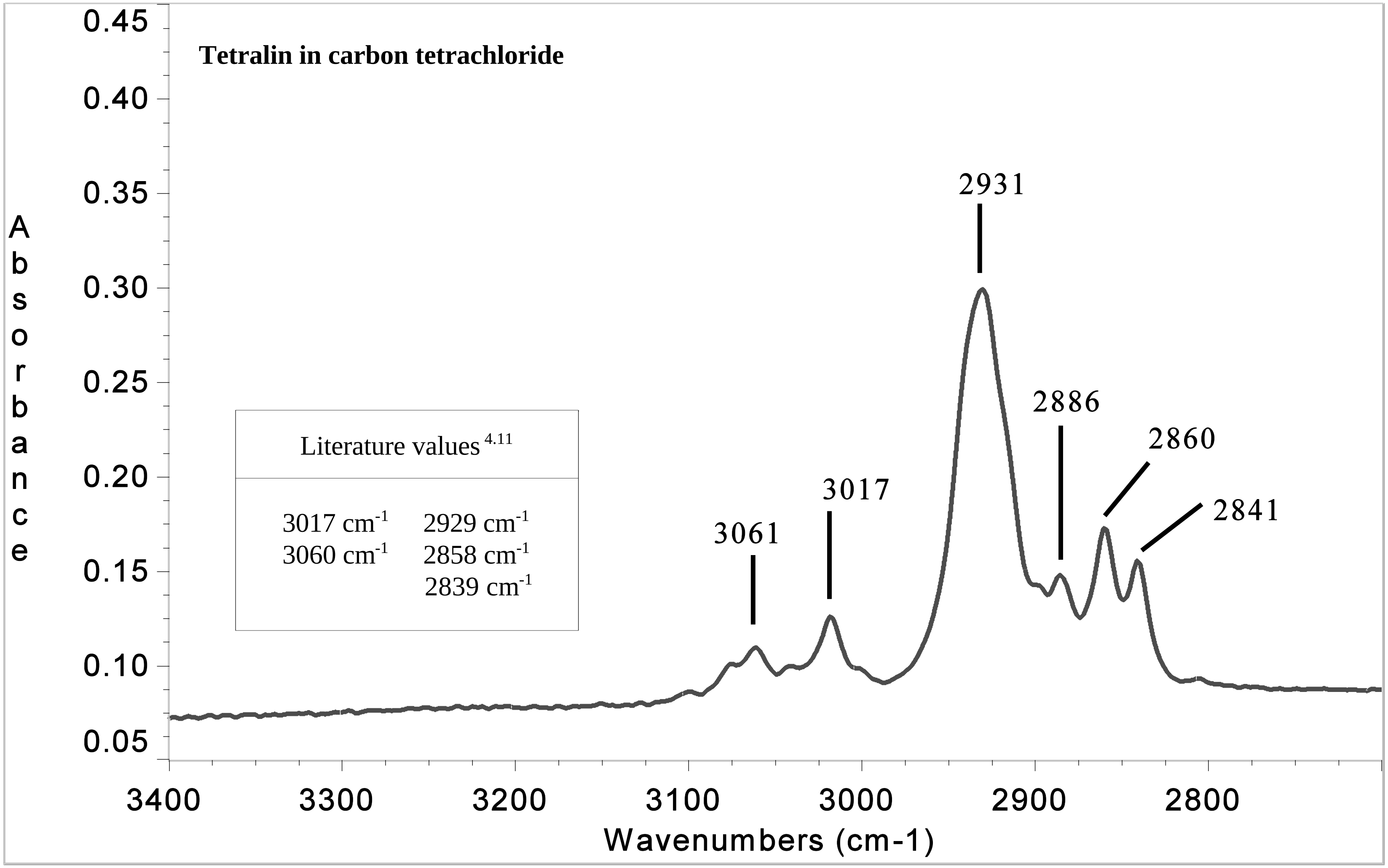

Cyclohexene in carbon tetrachloride
Absorbance
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3023
2926
2884
2859
2838
Literature values 4.11
3023 cm-1
2927 cm-1
2838 cm-1
2859 cm-1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-7


Tetralin in carbon tetrachloride
Literature values [4.11]
3017 cm^{-1}
3060 cm^{-1}
2929 cm^{-1}
2858 cm^{-1}
2839 cm^{-1}
3061
3017
2931
2886
2860
2841
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Cyclohexane gives rise to two peaks in the aliphatic region, whereas cyclohexene gives rise to four. The spectrum of tetralin in the aliphatic region is quite similar to the spectrum of cyclohexene, all four peaks being within one to six cm^{-1} of their locations in the spectrum of cyclohexene. Tetralin gives rise to two peaks in the aromatic/olefinic region.

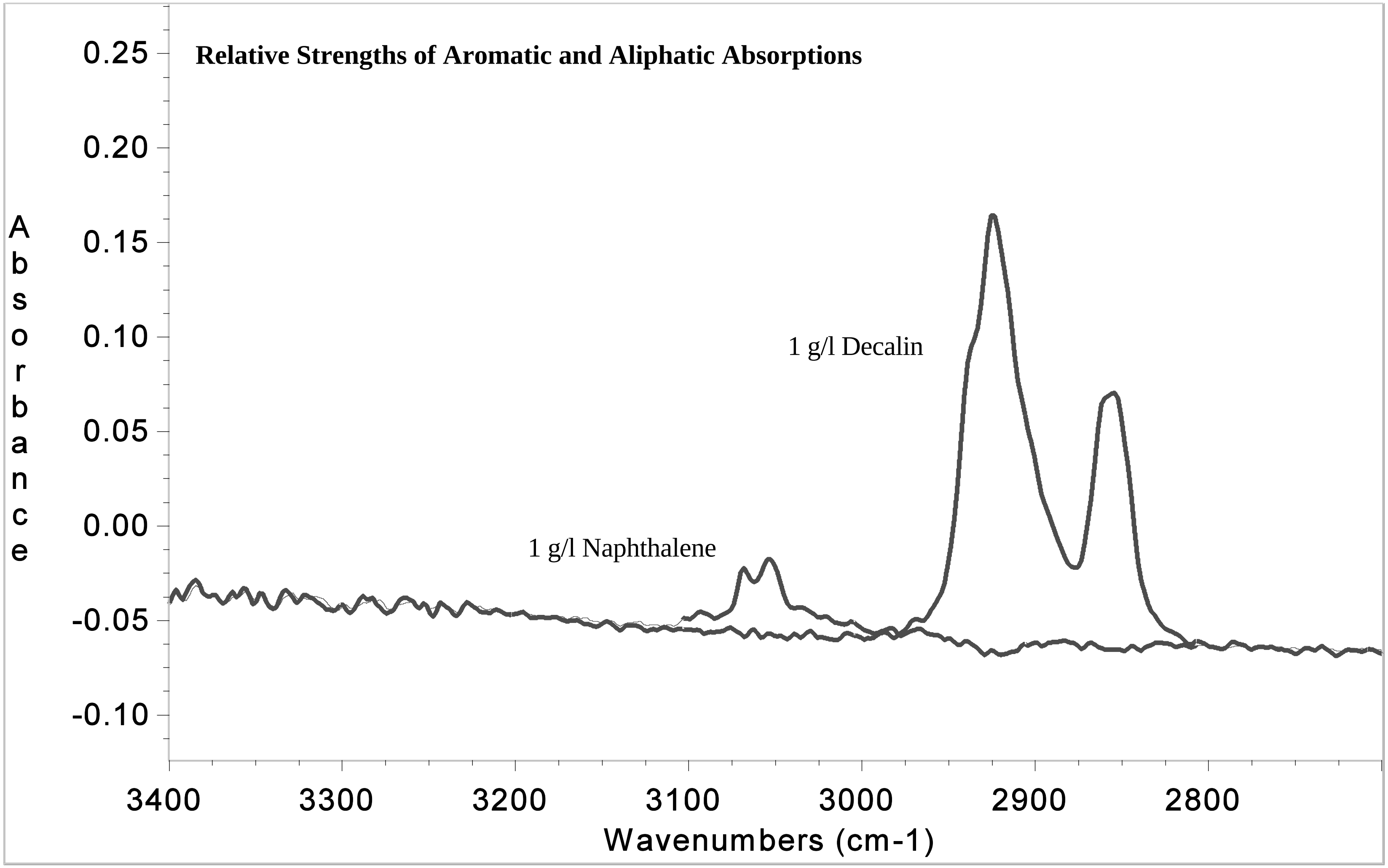
The next step was the comparison of experimental spectra with library spectra to verify the accuracy of the spectrometer. The comparison with library spectra was very good. In the case of benzene, none of the peak locations varied by more than 1 cm^{-1} from the values presented in the Merck FT-IR Atlas.[4.11] The other compounds gave similar results. Most of the experimental peak locations varied by less than one cm^{-1} from the literature values, and none of the experimental peak locations varied by more than three cm^{-1} from literature values. This is less than the resolving power of the instrument as used in this study, which was 4 cm^{-1}.

It should be noted at this time that the assignment of peak locations to definite vibrational modes available to a complex molecule is an exceedingly difficult task.[4.13] Fortunately, this type of assignment is not necessary to assigning characteristic peaks to compounds. A detailed assignment of peak locations to compounds in carbon tetrachloride solution was not performed because of the potential for solvent shifting effects when the higher temperature solvents were employed.

Relative Strengths of Absorbing Species

Figure 4-8 shows that, at identical concentrations, the absorbance peak heights for decalin are much higher than those for naphthalene. This is consistent with the well

Figure 4-8


Relative Strengths of Aromatic and Aliphatic Absorptions
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
1 g/l Decalin
1 g/l Naphthalene
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

established fact that aliphatic compounds are much stronger absorbers than aromatic compounds are. The ratio of the height of the most prominent peak in decalin to the height of the most prominent peak in naphthalene is about six to one. The decalin:tetralin hydrogen ratio is 18:8, and this could only account for a little more than half of the increase in peak height. Moreover, in tetralin, which has twice as many aliphatic hydrogens as it has aromatic hydrogens, the peak height ratio is about four to one. The implication to this study is that increases in aromaticity (peaks above 3000 cm^{-1}) as hydroaromatics and cyclic olefins dehydrogenate will be more difficult to observe than decreases in aliphaticity (below 3000 cm^{-1}).

Linear Region of the Absorbance versus Concentration Curves

It is generally desirable in absorption spectrometry work and particularly desirable in the present study to work in the linear region of the Beer's law curve. Beer's law, rearranged to the form

$$\mathbf{A/c = ab,} \qquad \text{Eq. 4.2}$$

predicts a linear response so long as the absorptivity and pathlength are constant. However, Beer's law is a simplification, and usually only applies over a narrow range of concentrations, dependent on the experimental conditions. The simplest way to determine the linear region of the Beer's law curve is to measure the absorbances of solutions of known concentration over two or three orders of magnitude and plot the result. This determination was performed for naphthalene, decalin and tetralin in carbon tetrachloride. Isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene were not employed because of their high cost and limited availability. It was thought that the linear region for these compounds would be somewhere between the extremes represented by naphthalene and decalin. Figure 4-9 presents the absorbance versus concentration data for tetralin, showing the non-linear region above about 1.2 g/l. Figure 4-10 presents the low concentration data with the concentration axis expanded ten times. From this plot it was determined that the linear region of the absorbance versus concentration curve for tetralin was from about 0.05 g/l to about 1 g/l. At concentrations less than 0.05 g/l, the signal to noise ratio was too small for accurate determination of absorbance peak heights. Figure 4-11 presents the data for decalin, which is roughly the same as that for tetralin. Figure 4-12 presents the data for naphthalene. The lessened absorbances associated with aromaticity in naphthalene extended the linear region of the absorbance versus concentration curve above the upper limit of concentration found for decalin and tetralin. However, at the concentrations in the lower part of the linear region for decalin and tetralin, the absorbance of naphthalene is so small as to be almost undetectable by FTIR under the experimental conditions used in this work. Again, the linear region of the absorbance versus concentration curves for isotetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene was thought to be intermediate between the two extremes represented by decalin and naphthalene, since these compounds contain methylene groups and double bonds and/or aromatics.

Figure 4-9

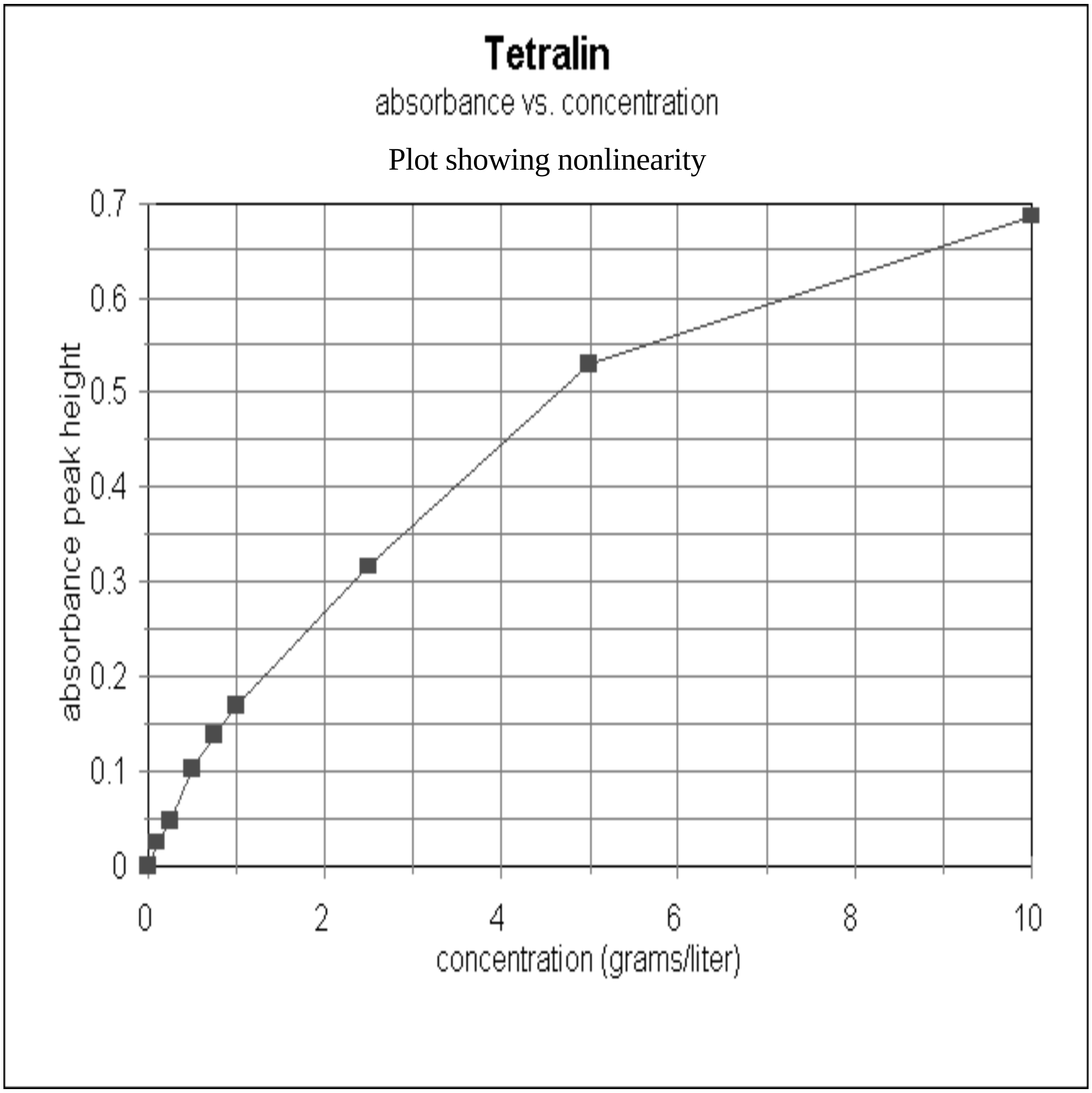

Tetralin
absorbance vs. concentration
Plot showing nonlinearity
absorbance peak height
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
10
concentration (grams/liter)

Figure 4-10

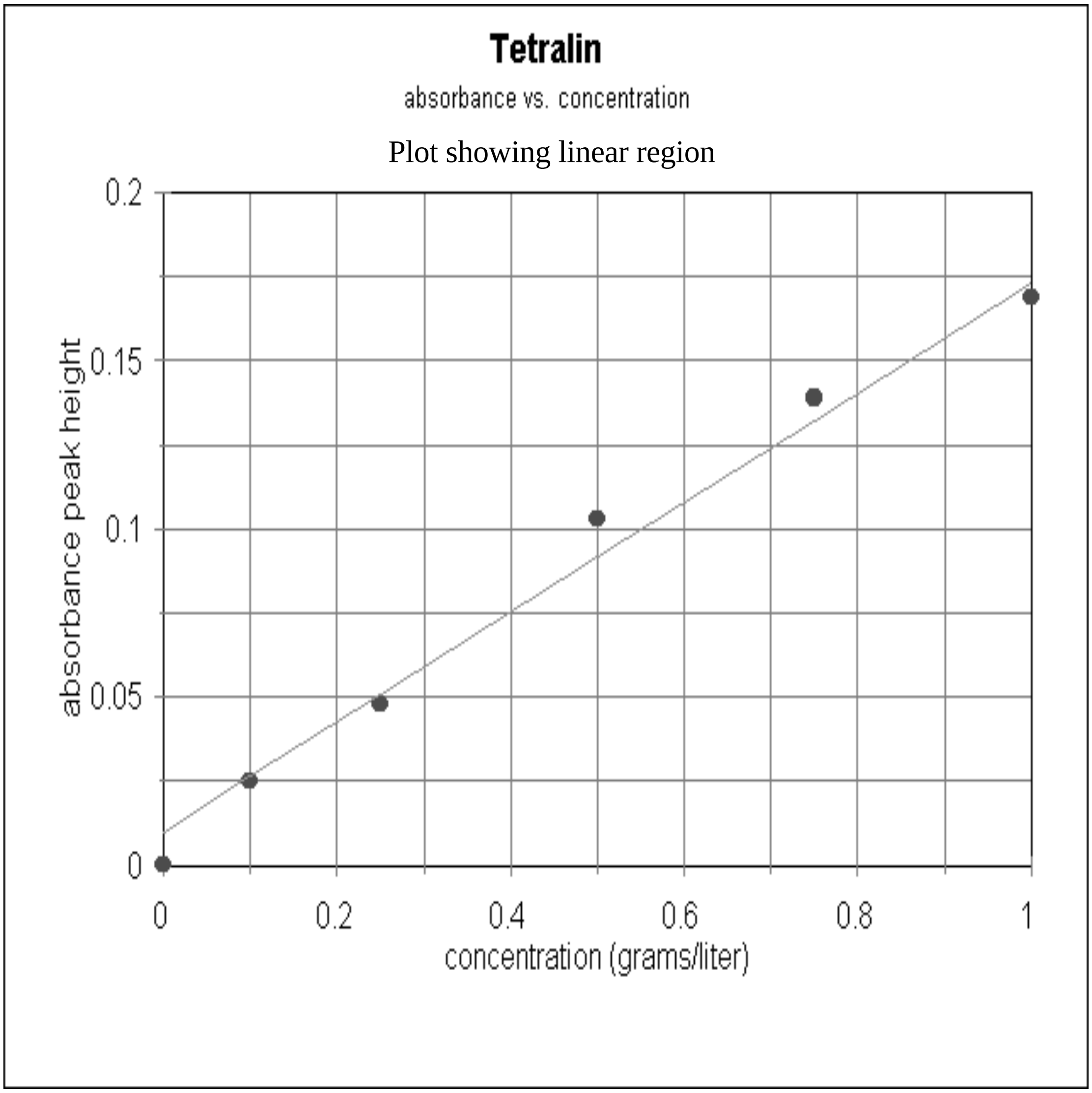

Tetralin
absorbance vs. concentration
Plot showing linear region
absorbance peak height
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
concentration (grams/liter)

Figure 4-11

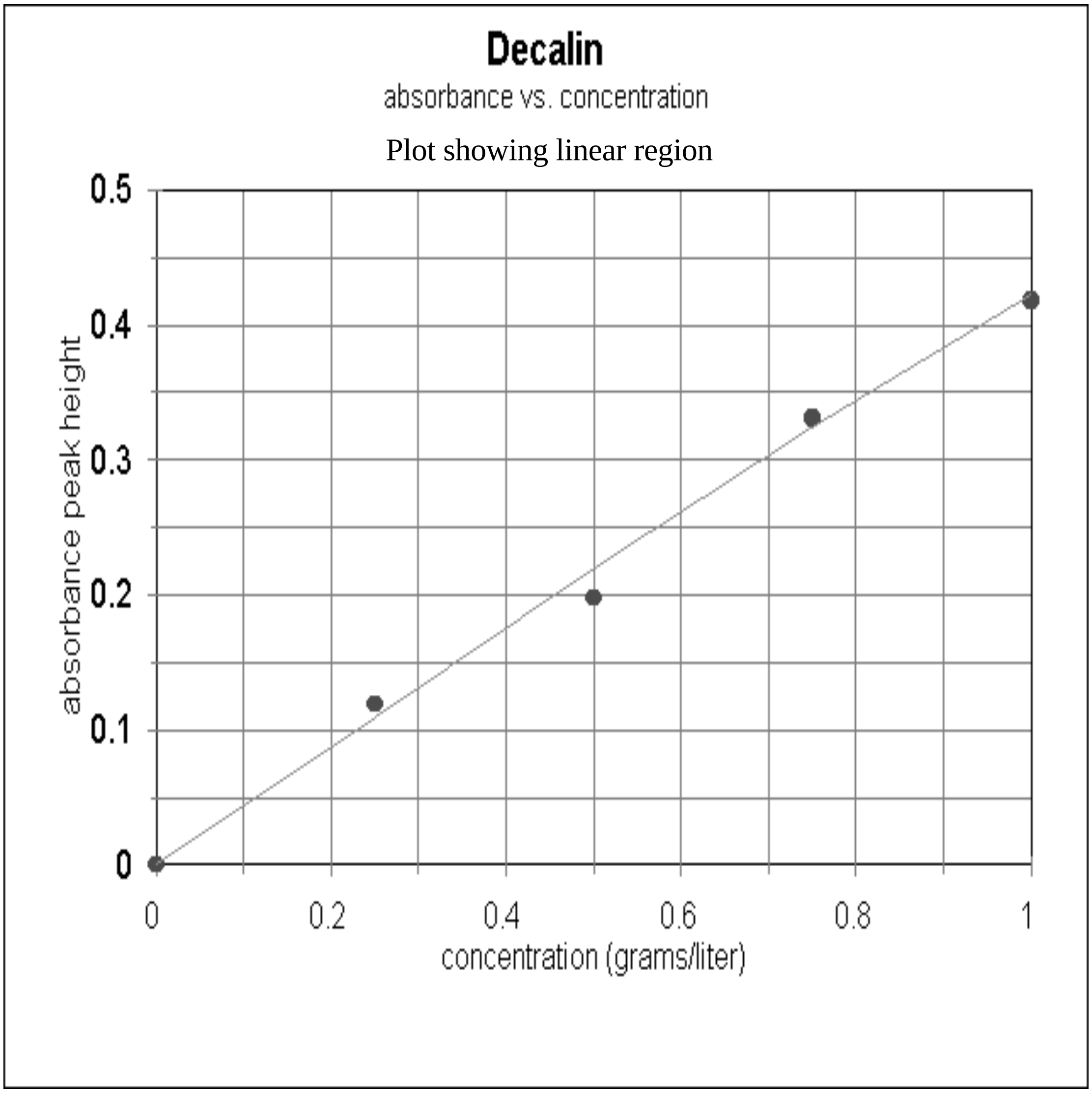
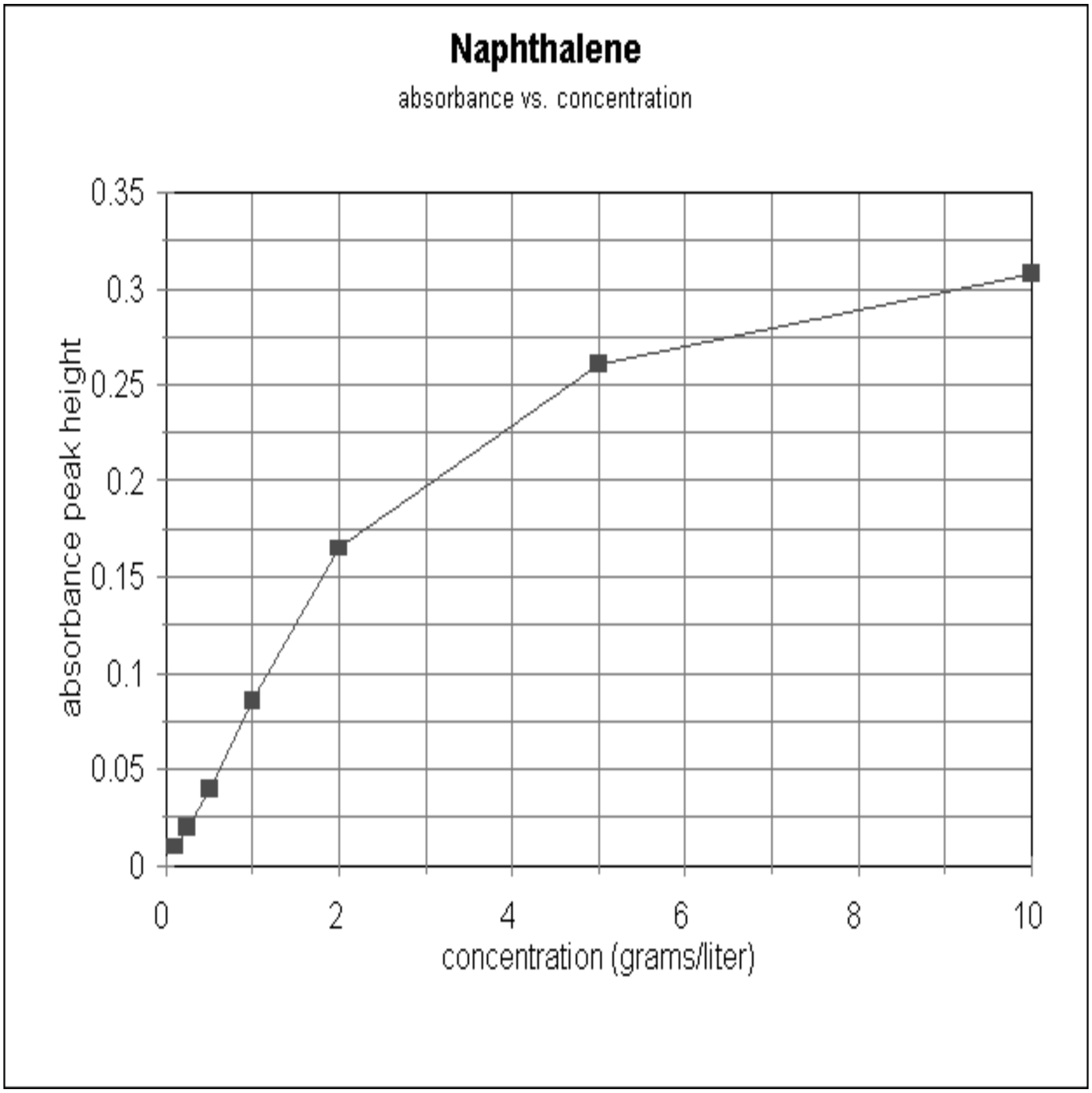

Decalin
absorbance vs. concentration
Plot showing linear region
absorbance peak height
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
concentration (grams/liter)

Figure 4-12


Naphthalene
absorbance vs. concentration
absorbance peak height
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
2
4
6
8
10
concentration (grams/liter)

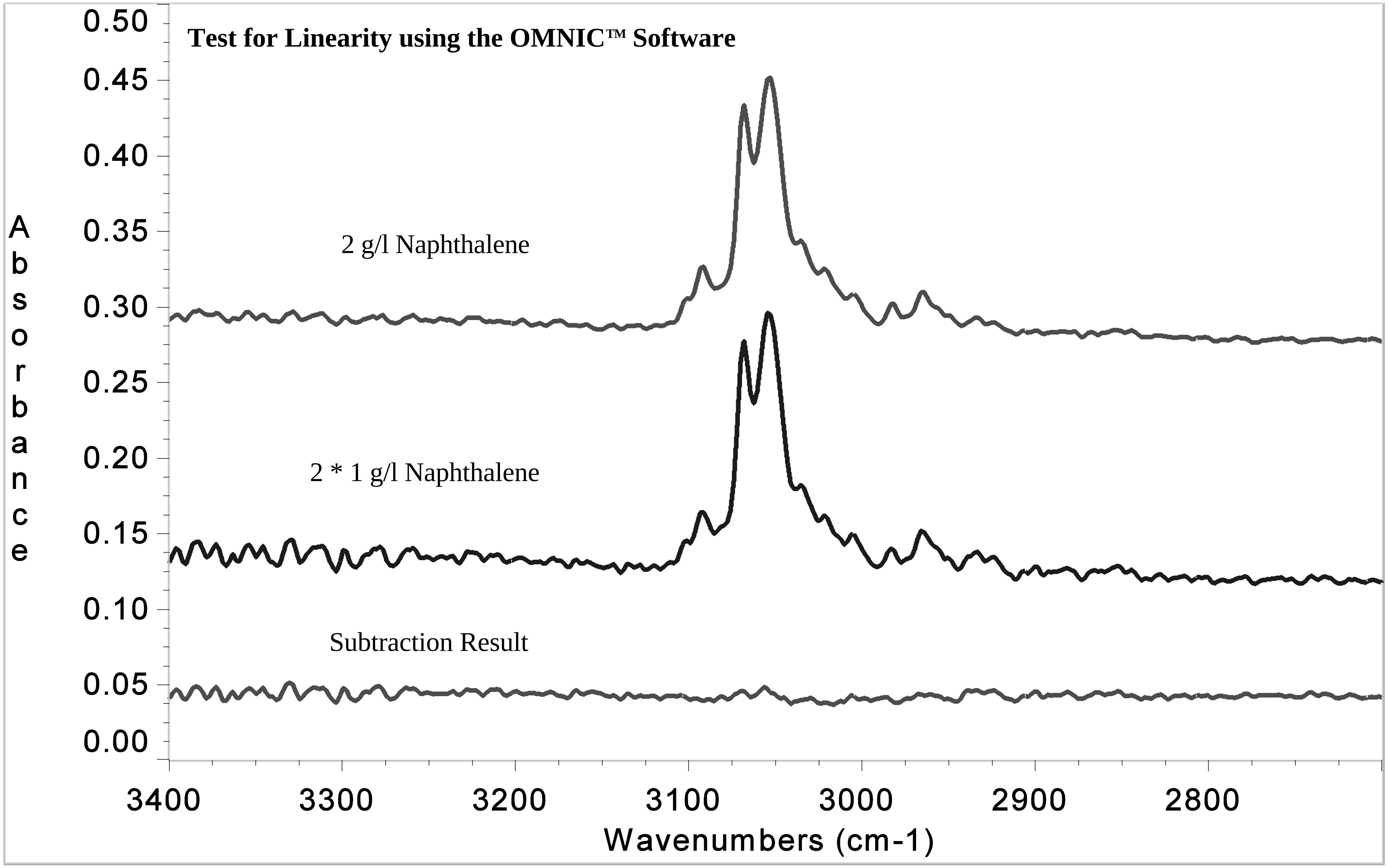
Test for Linearity using the Nicolet Software

The Nicolet software package for the FTIR spectrometer provided a check to insure that operation was in the linear region of the absorbance versus concentration curve. The software provides for the comparison of two spectra, either visually or by spectral subtraction. For example, a spectrum of a naphthalene solution of known concentration was multiplied by two using the multiplication routine in the software package. This spectrum was then compared to the spectrum of a naphthalene solution which was twice as concentrated as the first. The scans should be identical if operation was in the linear region of the absorbance versus concentration curve. Figure 4-13 presents the scan of a 1 g/l naphthalene solution multiplied by two, and the scan of a 2 g/l naphthalene solution. The spectral subtraction result is also presented. Visual inspection indicated very close agreement, and the spectral subtraction routine left only a straight line, *i.e.*, no peaks appeared in the subtraction result which were above the noise level.

The Extension to 230 °C

Solvents which show good transparency in the mid-infrared region and good solubility of hydrocarbons, *e.g.*, carbon disulfide and carbon tetrachloride, are typically low boiling and cannot be used at high temperatures without the application of pressure. Even with applied pressure, these types of solvents could be in the two phase region or supercritical region at the temperatures involved in this work. Since this would not have been acceptable for the current work, a high boiling solvent with good transparency in the mid-infrared had to be found.

Figure 4-13


Test for Linearity using the OMNIC™ Software
2 g/l Naphthalene
2 * 1 g/l Naphthalene
Subtraction Result
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

As noted in Chapter II, the higher molecular weight alkanes are relatively nonvolatile and have reasonably good infrared transmission. If heavier alkanes are used as solvent, it is not difficult to heat a sealed cell to 200 °C without a great increase in pressure. Accordingly, n-hexadecane was the first solvent chosen for the high temperature work. The compounds in this study were readily soluble in n-hexadecane. n-Hexadecane showed good transparency in the aromatic/olefinic region, but obscured the solute stretches in the aliphatic region. Since aliphatic absorption strengths are much greater than aromatic/olefinic absorption strengths, it was essential to be able to monitor changes in the aliphatic peak heights. The use of n-hexadecane as solvent was abandoned and the search for a suitable high temperature solvent for this study continued.

Perfluorocarbon Media

The search for a suitable solvent led eventually to perfluorocarbon media. The use of perfluorocarbon media as solvents for chemical reactions is not new. Numerous investigators have studied the use of perfluorocarbons to replace ozone-depleting chlorinated solvents. Carbon tetrachloride, for years the solvent of choice for industrial chlorinations, is typical of the many ozone-depleting solvents whose use is being phased out by international agreement.[4.14] Perfluorocarbons have been used as reaction media for esterifications, transesterifications and polymerizations[4.15], flash photolysis[4.16], brominations[4.17], fluorinations[4.18] and photooxidations.[4.19] Of more direct interest to the current study, Kaufman *et al.*, used perfluorocarbon media to study coal liquefaction reactions.[4.20,21] The objective of these studies was to separate the physical effects of dissolution of the coal from the effects of chemical reaction. It was not the purpose of these studies to follow the progress of the reaction using spectrometric techniques. One study which did employ spectrometric techniques to observe hydrocarbons in perfluorocarbon media was by Hlkida *et al.*[4.22] Near ultraviolet and visible absorption spectra were obtained for a number of aromatic radical cations including 1,2-dihydronaphthalene in gamma-irradiated perfluoro-matrices at liquid nitrogen temperatures. Infrared spectroscopy has been used to monitor residual hydrogen levels by measuring C-H absorption in perfluorocarbons synthesized by fluorination of polyalkyl ethers.[4.23] However, no direct applications employing perfluorocarbon media as solvent to study chemical reactions at elevated temperatures and pressures using infrared spectrometric techniques were found in the literature.

The perfluorocarbon solvent chosen for the initial portion of this work was a product of Air Products and Chemicals trade named APF-240™. APF-240™ is perfluoro-diisopropyldecalin. The boiling point of APF-240™ is 240 °C. Allowing a 10 °C margin of safety, the upper temperature limit for this work was taken as 230 °C.

Solubilities of Hydrocarbons in Perfluorocarbons

Hydrocarbons (C_nH_{2n+2}) and perfluorocarbons (C_nF_{2n+2}) are mutually immiscible at room temperature, but form clear homogeneous mixtures at high temperatures.[4.24] The compounds used in this study likewise showed very low solubilities in APF-240™, less than 1 g/l at room temperature. However, the solubilities proved to be a strong function of temperature, increasing markedly when the mixtures were heated to 65 °C. Accordingly, 65 °C was taken as the lower temperature limit for this portion of the work.

Solubilities of Gases In Perfluorocarbons

In contrast to hydrocarbons, gases such as oxygen, nitrogen, carbon dioxide, hydrogen and helium show good solubilities in perfluorocarbons. In fact, perflouorodecalin, because of its ability to carry oxygen and carbon dioxide, has been used as a blood substitute. Riess and Le Blanc present the following data for the solubilities of gases in perfluorocarbons.[4.25] Nitrogen is soluble in perfluorodecalin to the extent of 0.34 g/l (0.012 M) at 25 °C and one bar (15 psia) pressure. Although no direct data were found in the literature for the solubility of hydrogen, as a general rule, gases show about a twenty times greater solubility in perfluorocarbons than they show in water. Using the literature value[4.26] of the solubility of hydrogen in water of 1.6×10^{-3} grams per liter at 25 °C, the solubility of hydrogen in perfluorodecalin at 25 °C and one bar (15 psia) was calculated to be 0.032 grams per liter (0.016 M). Nitrogen and hydrogen have similar solubilities in perfluorodecalin when expressed in molarity. Increasing the pressure increases the solubility of gases in perfluorocarbons, in accord with Henry's law. Increasing the temperature decreases the solubility of nitrogen in perfluorocarbons, as would be expected, but interestingly, the solubility of hydrogen increases with increasing temperature. The author did not state the temperature range over which this increase was observed, but his interest in the solubility of gases in perfluorocarbons was primarily for biomedical applications. The highest temperature for which data were presented was 37 °C.

Solvent Shift Effect

One effect of changing the solvent is the potential for changing the location of the absorbance peaks. Figure 4-14 presents the spectrum of benzene in carbon tetrachloride along with the spectrum of benzene in APF-240™. In the case of replacing carbon tetrachloride with APF-240™, a shift to higher wavenumber of five to six cm^{-1} was observed for the aromatic peaks in benzene. Aliphatic peaks showed an even larger shift to higher wavenumber. Figure 4-15 presents the spectrum of tetralin in carbon tetrachloride along with the spectrum of tetralin in APF-240™. As in the case of benzene, the aromatic peaks are shifted to higher wavenumber by five to six cm^{-1}, whereas the aliphatic peaks are shifted to higher wavenumber by eight to eleven cm^{-1}.

These shifts to higher wavenumber caused no problems in data analysis because they were consistent for all the peaks. They should be borne in mind, however, if comparisons are to be made to literature spectra. It should also be noted that the solvent shift effect changed only the location of the peaks, and not the peak heights. In other words, absorbance peak height was not a function of solvent employed.

The Temperature Dependence of the Absorptivity

Rearranging Equation 4.1 to the form

$$\mathbf{A/bc = a,} \qquad \text{Eq. 4-2}$$

the absorbance is proportional to the absorptivity so long as the pathlength and concentration remain constant, and subject to the restriction that the work is conducted

Figure 4-14

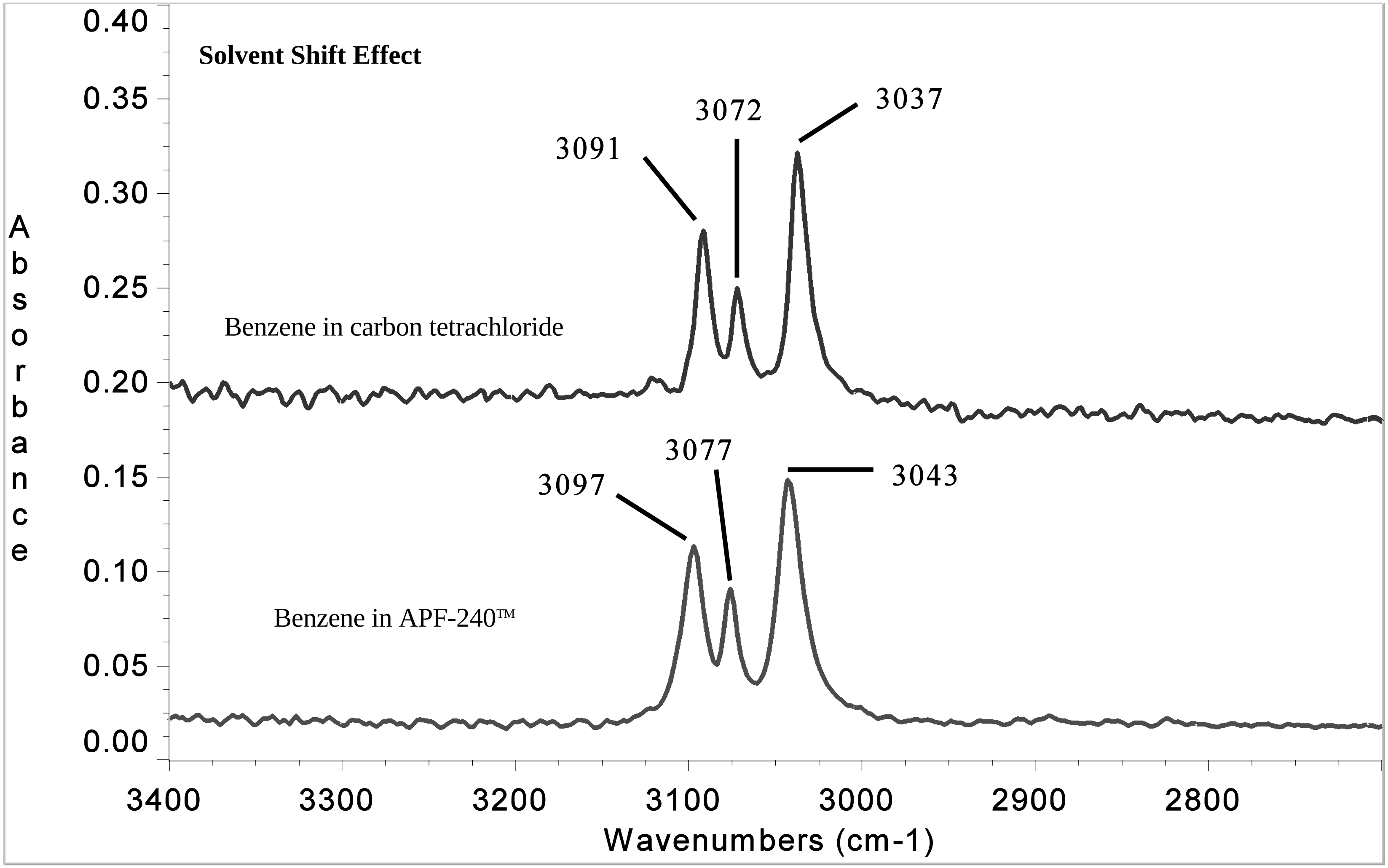
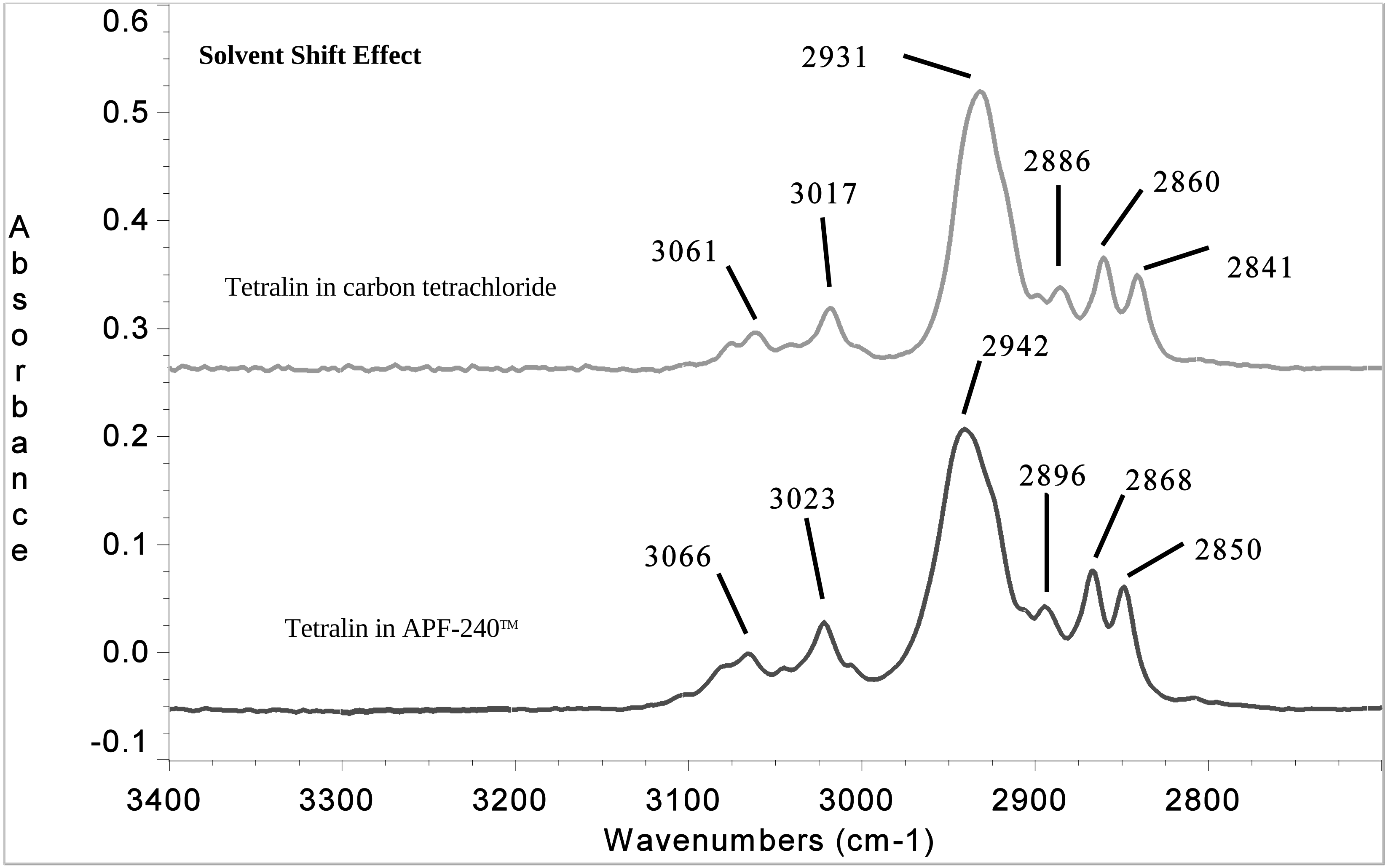

Solvent Shift Effect
Benzene in carbon tetrachloride
3091
3072
3037
Benzene in APF-240™
3097
3077
3043
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-15



Solvent Shift Effect
Tetralin in carbon tetrachloride
Tetralin in APF-240™
2931
3061
3017
2886
2860
2841
2942
3066
3023
2896
2868
2850
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

in the linear region of the absorbance versus concentration curve. To determine whether the absorptivity varies with temperature over the range from 65 to 230 ^{o}C, a solution containing 1 g/l of decalin in APF-240™ was scanned at 65 ^{o}C and then scanned again 40 minutes later at 230 ^{o}C. Figure 4-16 presents these two spectra. The absorbance peak heights at 65 ^{o}C are virtually identical to those at 230 ^{o}C, and the constancy of the absorptivity over this temperature interval was confirmed. The same result was obtained with solutions of naphthalene and tetralin.

Figure 4-16 also presents a good example of the noise which plagued early operations in this study. A considerable portion of the work in developing this method went into reducing this noise level.

One effect that elevated temperature did have on the shape of the spectra appeared in the case of naphthalene. Figure 4-17 presents the spectra of naphthalene at 65 ^{o}C, along with the spectra of naphthalene at 230 ^{o}C. Two spectral features are worthy of note in the high temperature spectra. One is the near disappearance of the shoulder at 3096 cm^{-1}, and the other is the merging of the two peaks at 3072 cm^{-1} and 3058 cm^{-1} into one peak at 3058 cm^{-1}. However, the height of the most prominent peak, at 3058 cm^{-1}, remained the same. It is this peak height that was used for quantitation purposes. It should also be mentioned that this was a temperature effect and not a reaction, because the spectrum at 230 ^{o}C returned to the shape of the spectrum at 65 ^{o}C when the solution was allowed to cool to 65 ℃. Interestingly, the near disappearance of the shoulder and the merging of the two peaks into one is also characteristic of the vapor phase spectrum of naphthalene.[4.27]

Figure 4-16

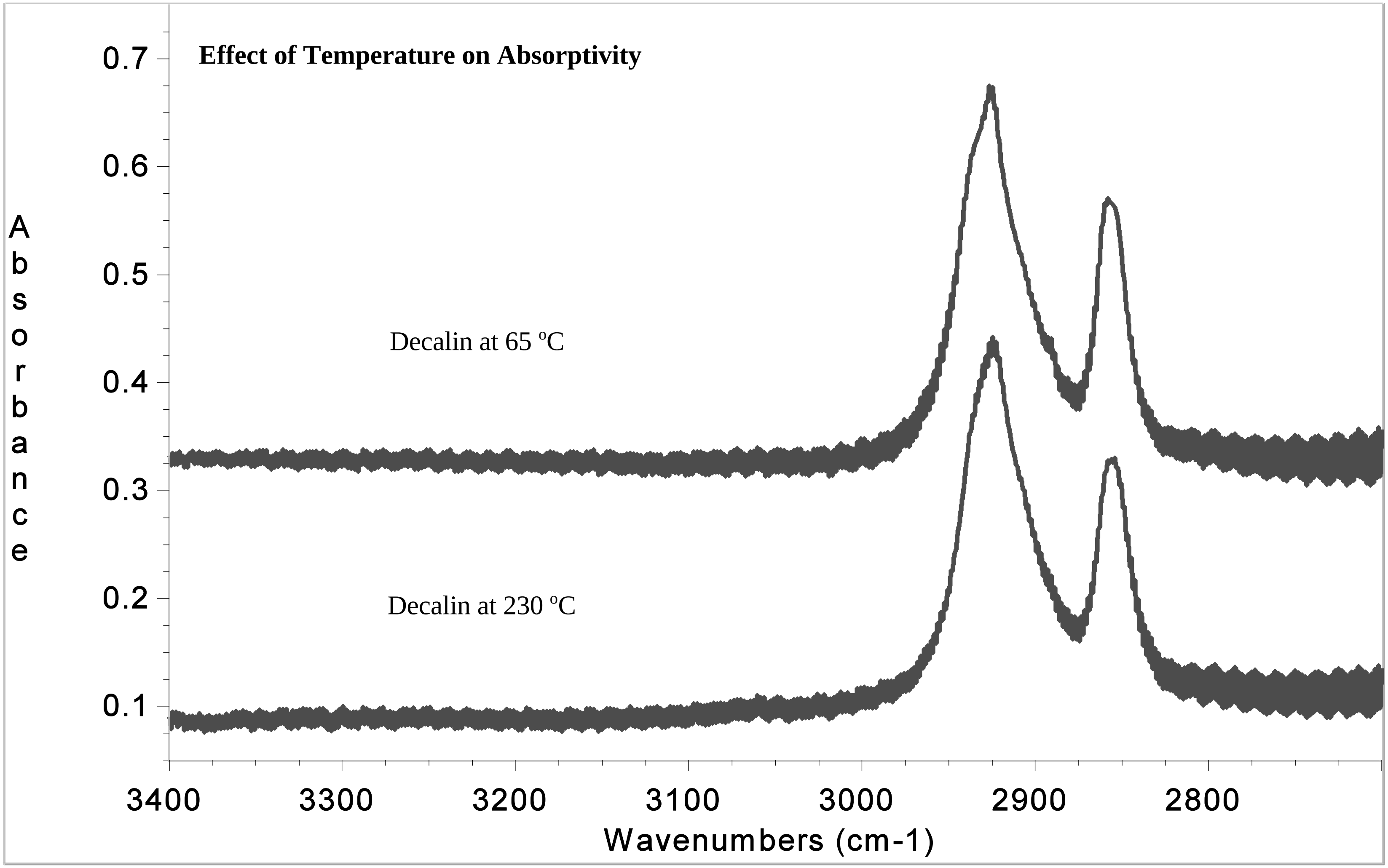
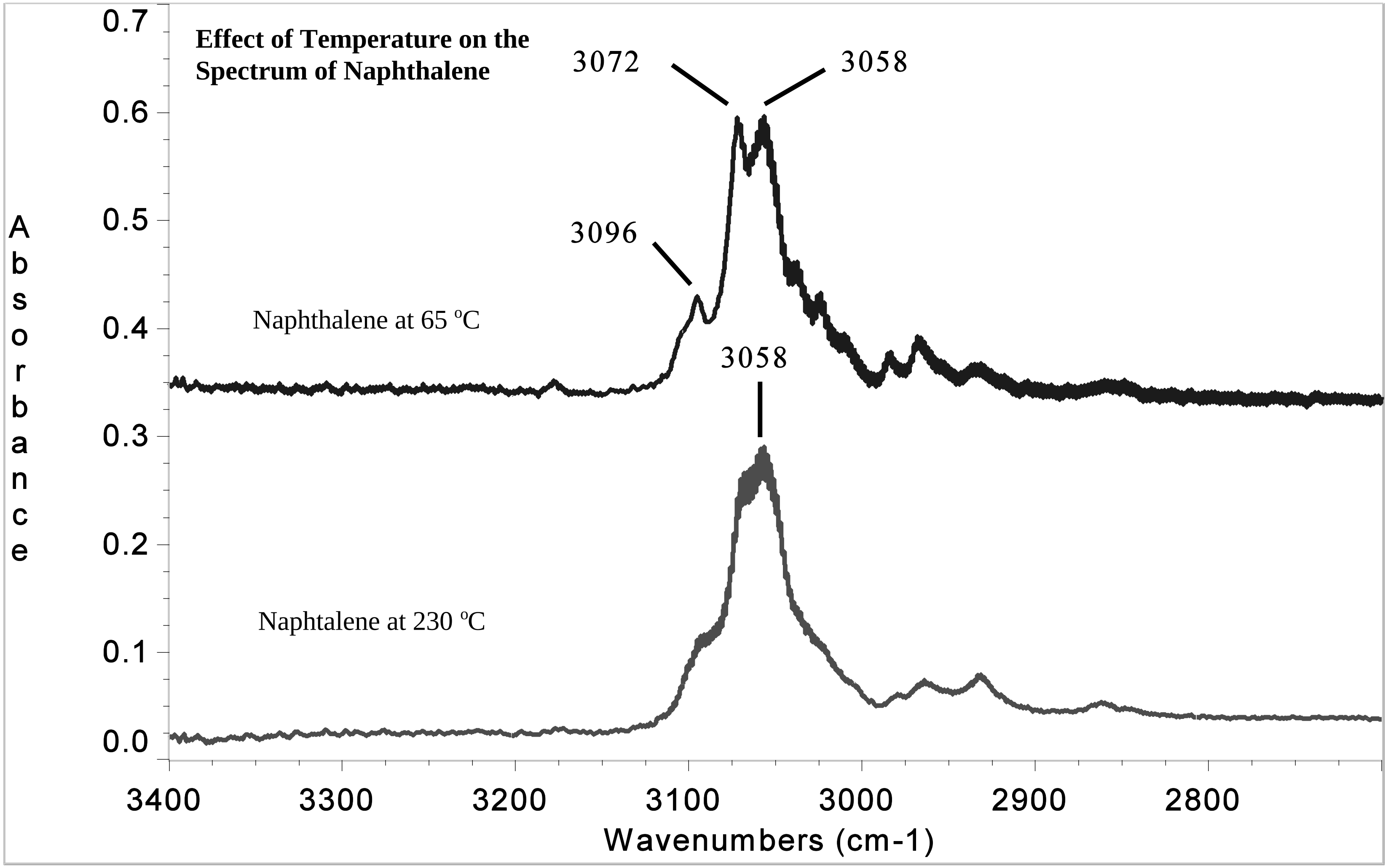

Effect of Temperature on Absorptivity
Decalin at 65 ºC
Decalin at 230 ºC
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 4-17


Effect of Temperature on the Spectrum of Naphthalene
3072
3058
3096
Naphthalene at 65 ºC
3058
Naphtalene at 230 ºC
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Effect of Pressure on Absorptivity

As noted in Chapter II, pressures up to 8000 bars had no effect on the spectra of hydrocarbons in the liquid phase. It was considered unlikely that pressures of 35 bars would affect the spectra of hydrocarbons in solution in this study.

Stability Studies, 65 °C to 230 °C

With the establishment of the accuracy, reproducibility, and linearity of the test equipment, and the demonstration that solvent, temperature and pressure effects were minimal, it was possible to proceed with the high temperature testing. Appendix B provides a detailed description of the procedure employed for obtaining high temperature spectra. A routine was developed in order to study the stability of the compounds at elevated temperatures. This stability test consisted of stepping the samples from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding at the initial temperature and each intermediate temperature 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.

The compounds were subjected to the stability study under three different conditions. The first was in a liquid filled, sealed cell with no atmosphere present. The second was under a 35 bars nitrogen blanket with a vapor space above the reactor of about 20 ml. The third was with a 35 bars hydrogen blanket with a vapor space above the reactor of about 5 ml.

GC Analysis of Reactants and Products

About half-way through the sealed cell stability studies, the method was amended to include the saving of the reactor products for future gas chromatographic analysis. The reactants were also subjected to GC analysis to determine their purity. The details of the chromatographic procedure are presented in Chapter III. As the development of the GC method was also an ongoing process, some of the amendments to the procedure are noted in Chapter V.

The Extension to 350 °C

Two major modifications to the procedure were required to extend the testing to 350 °C. The first involved modification of the materials used in the operation of the cell. The cylindrical wall of the sample cavity was formed by a polytetrafluoroethylene (PTFE) flat washer, known in infrared spectroscopic terminology as the spacer. The seal between the sample cavity and the gas pressurization chamber was formed by a Viton™ o-ring. Neither of these materials is suitable for use at temperatures much above 250 °C. The PTFE spacer was replaced with a Grafoil™ spacer while the Viton™ o-ring was replaced with a Kalrez™ o-ring. The second modification was the replacement of APF-240™ with a higher boiling solvent. While perfluorocarbons with boiling points as high as 400 °C have been prepared[4.28], none were available commercially at the time this work was conducted. Air Products[4.28] suggested the use of a perfluoropolyalkyl ether, available from DuPont. The perfluoropolyalkyl ethers, owing to their thermal stability, find use as high temperature lubricants. DuPont markets a line of these lubricants under the trade name Krytox™. The solvent chosen to extend this work to 350 °C was

Krytox™ GPL-107, hereinafter referred to simply as Krytox™. The boiling point of Krytox™ is over 450 °C. The chemical formula of Krytox™ is

$$\mathrm{F-(\underset{\displaystyle CF_3}{\underset{|}{CF}}-CF_2-O)_n-CF_2-CF_3}$$

where n = 10 to 60. The average molecular weight of Krytox™, as determined by NMR[4.29], is about 8250 daltons, so the average value of n is a little less than 50.

Because many modifications were made to the procedure as the results of the 230 °C testing were obtained, a discussion of the details of the 350 °C experimental procedure is deferred until Chapter V.

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CHAPTER V

RESULTS AND DISCUSSION

The goal of this research is to develop an FTIR spectroscopic method for studying the release of hydrogen from cyclic olefins at elevated temperatures and pressures. This is an ongoing process, and while tremendous progress has been made, a good deal of future work remains before this process will be developed into a routine procedure. As data were gathered and analyzed, refinements were made to the method. Many difficulties had to be overcome in order to extend routine FTIR spectroscopic measurements at room temperature and ambient pressure to the conditions of low severity coal liquefaction. This chapter traces the development of the method from the initial conditions of room temperature and ambient pressure to the final conditions of 350 °C and 35 bars (500 psig) hydrogen.

In order to extend solution spectroscopy to conditions of elevated temperatures and pressures, it was necessary to find a suitable solvent or solvents. Solvents which show good transparency in the mid-infrared region and good solubility of hydrocarbons, *e.g.*, carbon disulfide and carbon tetrachloride, are typically low boiling and cannot be used at high temperatures without the application of pressure. Even with applied pressure, these types of solvents could be in the two phase region or supercritical region at the temperatures and pressures involved in this work. Since this would not have been acceptable for the current work, a high boiling solvent with good transparency in the mid-infrared region had to be found.

The search for a high boiling solvent which was transparent in the mid-infrared region led eventually to perfluorocarbon media. The first perfluorocarbon obtained was perfluorodiisopropyldecalin. Air Products and Chemicals markets perfluorodiisopropyldecalin under the trade name Multifluor APF-240™. APF-240™ contains less than one part per million residual hydrogen, and so should not exhibit hydrocarbon stretches which might interfere with FTIR data. Because of the low solubility of hydrocarbons in APF-240™, it was necessary to heat the mixtures to 65 °C in order to achieve dissolution of the solutes at the one gram per liter level. Consequently, the lower temperature limit of this work was taken as 65 °C. Since the boiling point of APF-240™ is 240 °C, the upper temperature limit for this work was taken to be 230 °C, allowing a 10 °C margin of safety.

This work was divided into two parts. The work between 65 °C and 230 °C constitutes the initial portion of this study. For the extension to 350 °C, an even higher boiling solvent had to be found. Furthermore, the o-ring which forms the seal between the sample cavity and the gas pressurization chamber was composed of Viton™ rubber, which is not suitable for use above 250 °C. Neither was the polytetrafluoroethylene (PTFE) spacer which forms the cylindrical wall of the sample cavity. Modifications to the cell had to be made for the extension of this work to 350 °C, as described later in this chapter.

The work in the temperature interval from 230 °C to 350 °C constitutes the second portion of this work. An even higher boiling perfluorocarbon, a perfluoropolyalkylether obtained from DuPont and trade named Krytox™ GPL-107 (CAS # 60164-51-4), was employed for this portion of the work.

The initial portion of this work was intentionally qualitative in nature, its exploratory purpose being to discover what difficulties would be encountered in extending the temperature to 230 °C, and perhaps to anticipate difficulties that might be encountered in the extension to even higher temperatures. The second portion of this work was likewise qualitative in nature. For both portions, some quantitation of analytical data was attempted, but the results are considered somewhat less than statistically reliable. The purpose here was to determine the necessary modifications to the procedure, to make the proper adjustments, and to fine tune the technique to the point where reliable measurements of the relative concentrations of reactants and products, and perhaps even intermediates, could be measured during the course of a reaction. These qualitative measurements were sufficient to propose reaction pathways, whereas quantitative data will be necessary to determine kinetics mechanisms.

Results of the Stability Studies, 230 °C

The compounds of interest to this study are isotetralin (ISO) and its potential products under conditions of hydrogenation or dehydrogenation. These are naphthalene (NAP), 1,2-dihydronaphthalene (1,2-DHN), 1,4-dihydronaphthalene (1,4-DHN) and decalin (DEC). Tetralin (TET) is also of interest, because of the potential for isomerization of isotetralin to tetralin while maintaining the fused ring structure.

Figure 5-1 presents a proposed reaction pathway for isotetralin, which was developed by Bedell.[5-1] Hexahydronaphthalene (HHN) and octahydronaphthalene (OHN) are possible intermediates, but were not present at sufficient concentrations to be detected by FTIR or GC under the experimental conditions employed in this testing.

The stability studies consisted of analyzing each compound by FTIR and taking the samples through a temperature program from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding at the initial and each intermediate temperature for thirty minutes. FTIR 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. Appendix B provides a detailed description of the procedure employed for obtaining high temperature spectra.

The compounds were subjected to the 230 °C stability study under three different test conditions. The first was in a liquid filled, sealed cell with no atmosphere present. The second was under a 35 bars (500 psig) nitrogen blanket with a vapor space above the reactor of about 20 ml. The third was under a 35 bars hydrogen blanket with a vapor space above the reactor of about 5 ml. The reactivities of the various compounds were determined by comparing the spectra of the reactants with that of the corresponding product mixture. Major absorbance peak locations were assigned to each of the reactants and to the product mixtures. For ease of identification of the products, Table 5.1 provides a compilation of the major absorbance peak locations associated with each of the compounds in this study. Some of the peak locations are unique to individual molecules, but many of them are common to the group. Because some of the peaks are

Figure 5-1

FIGURE 1: REACTION PATHWAY FOR ISOTETRALIN.

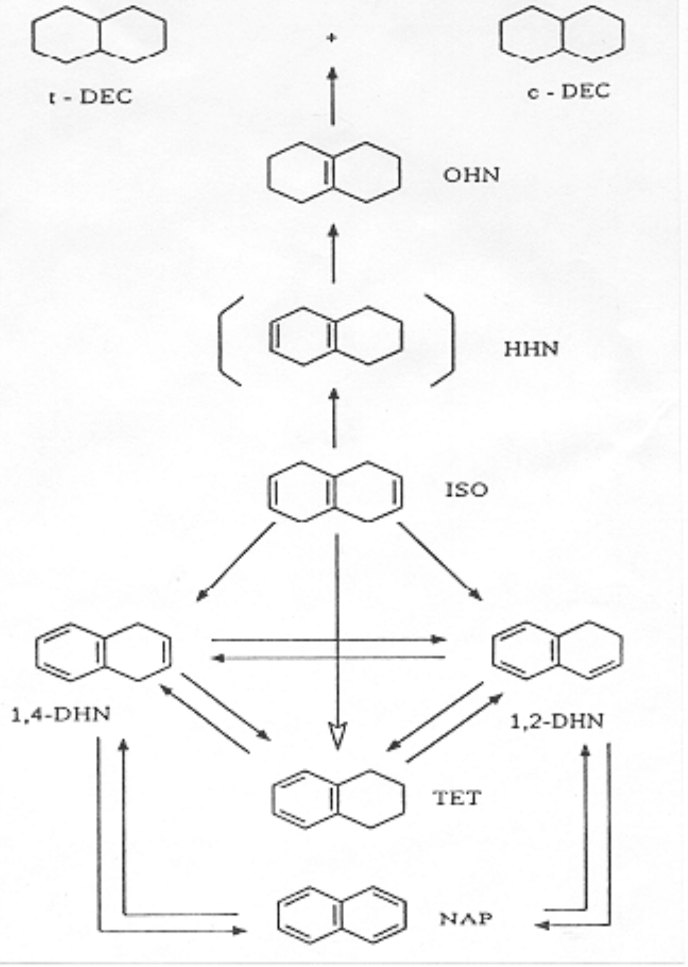


Table 5.1

Characteristic Absorbances for Compounds of Interest to this Study (cm^{-1})

2826	2841	2851	2858	2865-2867	2885	2895-2896	2932-2936	2942	2981-2982	3024-3026	3036-3038	3041-3043	3058-3060	3064-3066	3071-3075
													NAP		**NAP**
				DEC			**DEC**								
		TET		TET		TET weak		**TET**		TET				TET	
ISO			ISO		ISO strong				ISO		ISO strong				
	1,2-DHN strong					1,2-DHN		**1,2-DHN**				1,2-DHN		1,2-DHN	1,2-DHN
1,4-DHN strong						1,4-DHN strong broad	1,4-DHN					**1,4-DHN**			1,4-DHN

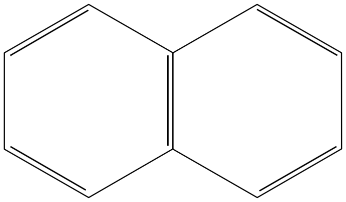
Boldface type indicates the most prominent peak for that compound.

rather broad, a good deal of overlap occurs, particularly in the aromatic/olefinic stretching region. Nevertheless, because of the differences in the structures of the molecules, it was possible to assign certain stretches to definite functional groups within these molecules.

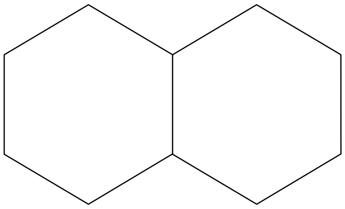
The data gathered in the stability tests were used to assign characteristic absorbance peak locations to the individual molecules. Figure 5-2 presents the structures of the molecules of interest to this study. The uniqueness of the functional groups in some of the molecules allows for assignment of certain stretches to definite functional groups. Starting with naphthalene, two aromatic CH environments exist which give rise to two broad peaks centered around 3072 cm^{-1} and 3058 cm^{-1}. Decalin gives rise to two methylenic (CH_2) stretches around 2865 cm^{-1} and 2932 cm^{-1}. The absorption at 2865 cm^{-1} is associated with a symmetrical CH_2 stretch, whereas the absorption at 2932 cm^{-1} is associated with an asymmetrical CH_2 stretch.[5.2] Absorption by the two tertiary C-H groups in decalin, which occurs near 2890 cm^{-1}, was not detected as a separate peak. Absorption resulting from this C-H stretch is very weak and is usually lost in other aliphatic C-H absorption.[5.3] In the case of isotetralin, the four olefinic CH groups all exist in the same environment, and there is no aromaticity. Since the only stretch in the olefinic/aromatic portion of the spectrum of isotetralin centers around 3036 cm^{-1}, the peak at this location was assigned to the olefinic functional groups in isotetralin. This is in excellent agreement with literature values. The Coblentz [5.4] value for the olefinic stretch in 1,4-cyclohexadiene is 3040 cm^{-1} and a literature value[5.5] found for isotetralin places the olefinic stretch at 3028 cm^{-1}. Allowance for the solvent shift effect associated

Figure 5-2

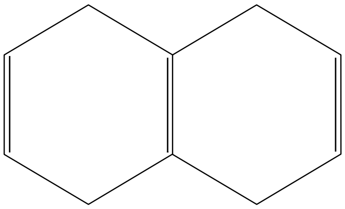
Structures of Compounds of Interest to this Study



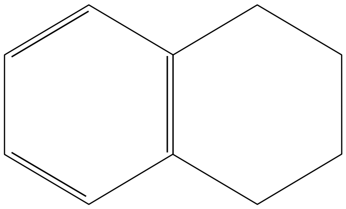
Naphthalene (NAP)



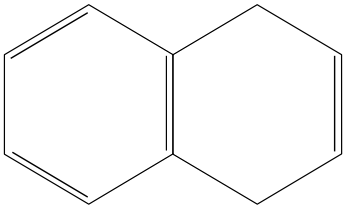
Decahydronaphthalene
Decalin (DEC)



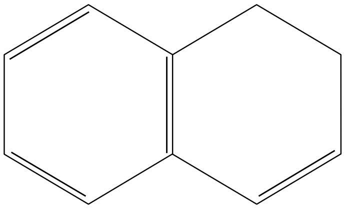
1,4,5,8- Tetrahydronaphthalene
Isotetralin (ISO)



1,2,3,4- Tetrahydronaphthalene
Tetralin (TET)



1,4- Dihydronaphthalene
(1,4- DHN)



1,2- Dihydronaphthalene
(1,2- DHN)

with APF-240™ would place this stretch near 3036 cm^{-1}, as found. Similarly, as shown in Figure 5-1, only one methylenic (CH_2) environment exists in isotetralin, and the aliphatic stretches at 2826 cm^{-1}, 2858 cm^{-1} and 2885 cm^{-1} were assigned accordingly. For 1,4-dihydronaphthalene, the most prominent peak is centered around 3042 cm^{-1}, about 6 cm^{-1} from the olefinic stretch in isotetralin. This stretch was assigned to the olefinic group in 1,4-dihydronaphthalene, but there is considerable overlap with the aromatic groups, which absorb broadly over the range from 3000 cm^{-1} to 3100 cm^{-1}, with local maxima at 3042 cm^{-1} and 3070 cm^{-1}. The stretches at 2833 cm^{-1} and 2895 cm^{-1} were assigned to the methylenic environments.

1,2-Dihydronaphthalene also exhibits a peak around 3042 cm^{-1}, and this peak was likewise assigned to the olefinic group in 1,2-dihydronaphthalene. This peak merges with the aromatic absorbances in the region from 3000 cm^{-1} to 3100 cm^{-1}, with local maxima at 3024 cm^{-1}, 3064 cm^{-1} and 3073 cm^{-1}. The peaks at 2841 cm^{-1}, 2896 cm^{-1} and 2942 cm^{-1} were assigned to methylenic stretches. The peak at 2942 cm^{-1}, which happens to be the most prominent peak in 1,2-dihydronaphthalene, is also the most prominent peak in tetralin. Furthermore, this peak is only present in 1,2-dihydronaphthalene and tetralin. The absence of this peak from 1,4-dihydronaphthalene indicates that this stretching arises from a CH_2 group with at least one CH_2 group for a neighbor. This is the predominant environment in decalin, and accordingly, the most prominent peak in the spectra of decalin is centered at 2932 cm^{-1}. Two such CH_2 groups with at least one CH_2 group for a neighbor exist in 1,2-dihydronaphthalene. Four such groups exist in tetralin, in two distinct environments, and tetralin shows a stronger absorbance in this region than does 1,2-dihydronaphthalene. The stretches at 2851 cm^{-1}, 2866 cm^{-1}, 2895 cm^{-1} and 2942 cm^{-1} were assigned jointly to the two distinct methylenic environments in tetralin. Tetralin also absorbs widely in the aromatics range, with local maxima at 3024 cm^{-1} and 3064 cm^{-1}.

Ambient Pressure Naphthalene Stability Study, 230 ºC

Naphthalene proved to be stable at temperatures up to 230 ºC under ambient pressure. Figure 5-3 presents the spectrum of naphthalene at 65 ºC and atmospheric pressure, along with the initial scan of naphthalene at 230 ºC and atmospheric pressure. The two distinct peaks at 3058 cm^{-1} and 3072 cm^{-1} in the 65 ºC spectrum merged into one peak at about 3058 cm^{-1} in the 230 ºC spectrum, but the peak height at 3058 cm^{-1}, which was used for quantitation, remained constant. Also presented in Figure 5-3 is the spectrum of naphthalene after having been held at 230 ºC and atmospheric pressure for four hours. The height of the absorbance peak at 3058 cm^{-1} in the initial scan at 230 ºC is the same as the height of the peak at 3058 cm^{-1} in the final scan at 230 ºC, indicating that no reaction took place upon extended time at elevated temperatures. On cooling to 65 ºC, the shape of the spectrum returned to the shape of the original spectrum, indicating that the merging of the two peaks is a temperature effect and not the result of a reaction.

Ambient Pressure Decalin Stability Study

Decalin proved to be stable at temperatures up to 230 ºC under ambient pressure. Figure 5-4 presents the scan of decalin at 65 ºC, along with the initial scan at 230 ºC and

Figure 5-3

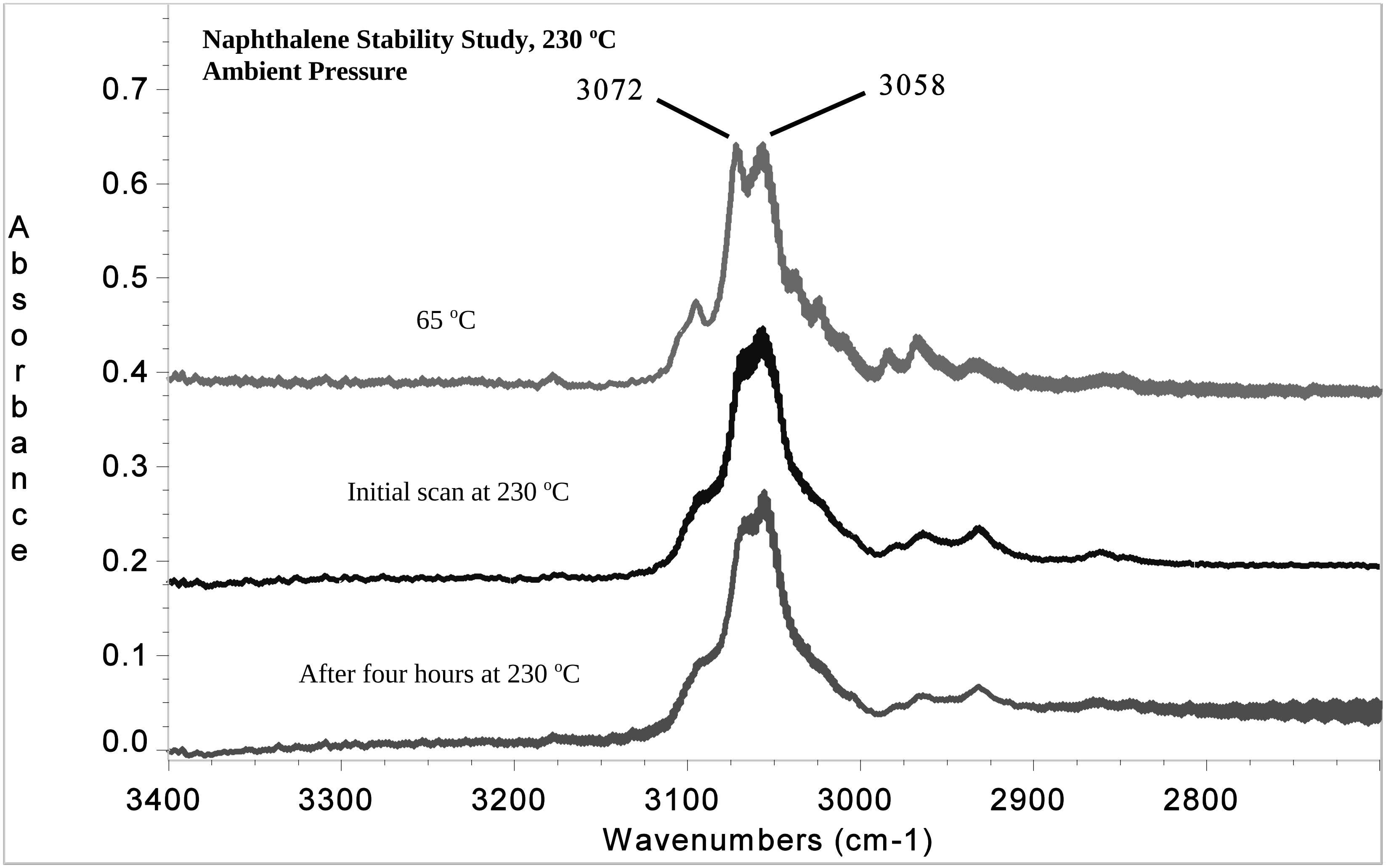
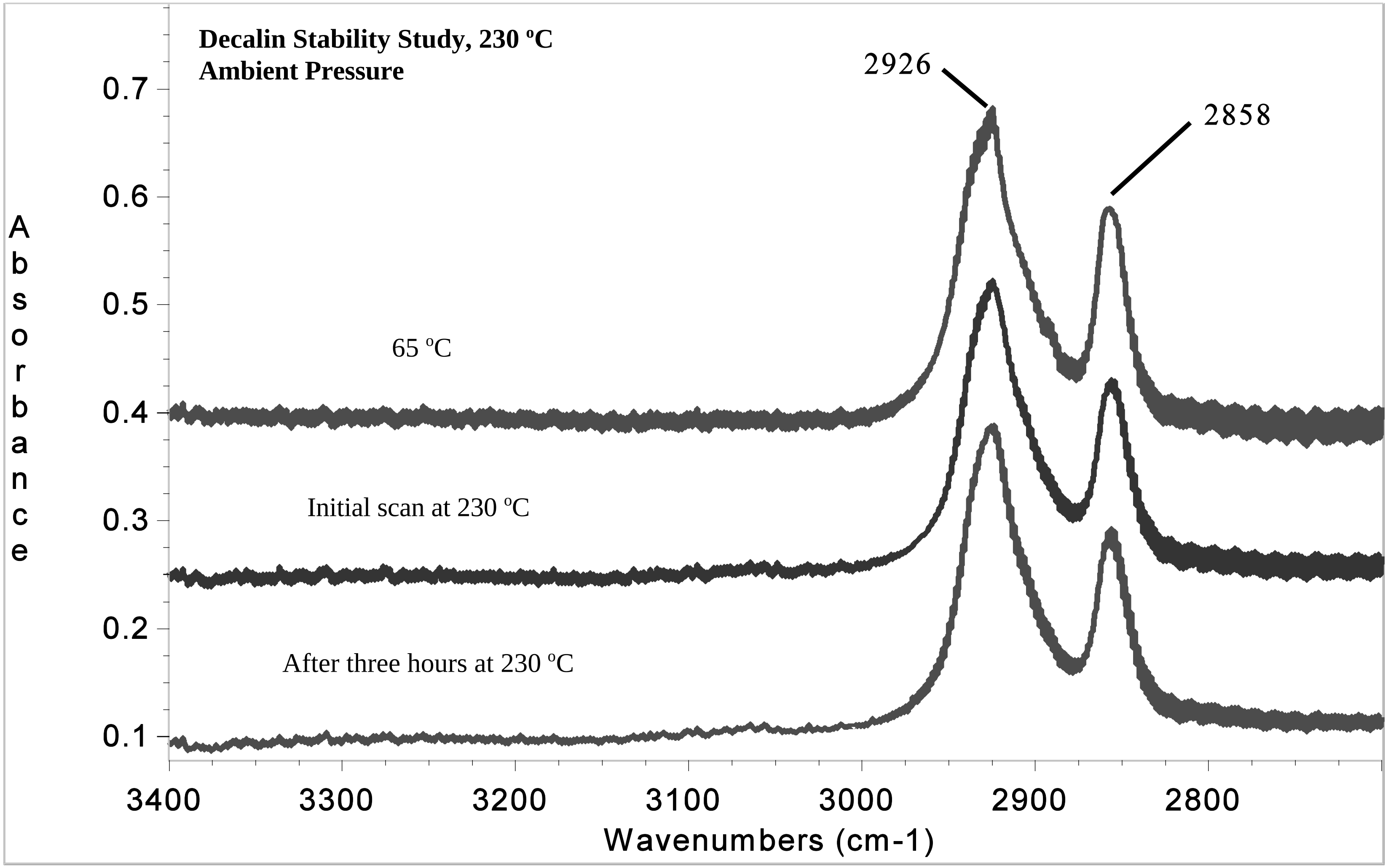

Naphthalene Stability Study, 230 ºC
Ambient Pressure
3072
3058
65 ºC
Initial scan at 230 ºC
After four hours at 230 ºC
Absorbance
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-4


Decalin Stability Study, 230 ºC
Ambient Pressure
2926
2858
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

the scan after three hours at 230 ºC. The ratio of the peak heights in the 230 ºC scans are the same, indicating that no reaction had taken place.

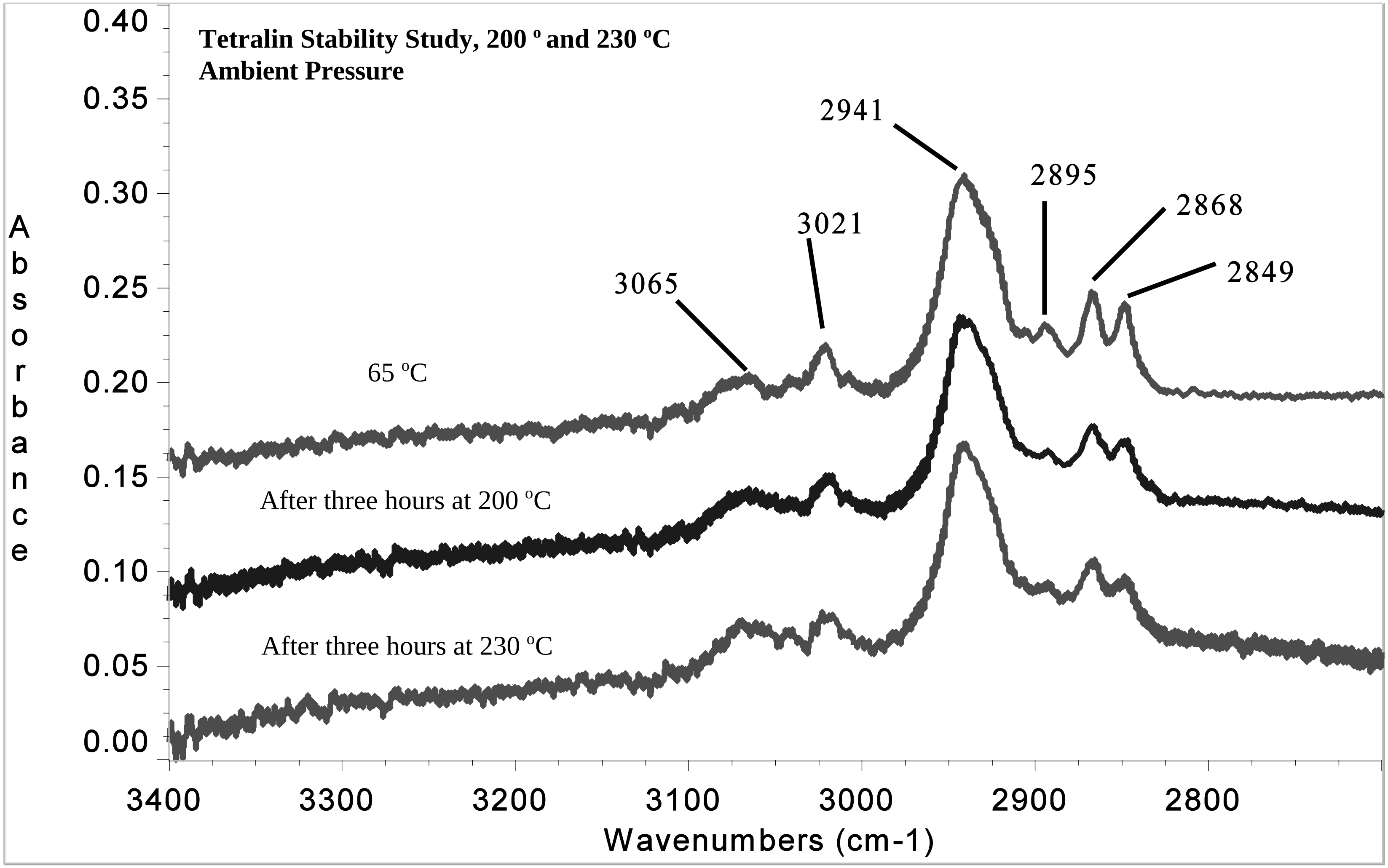
Ambient Pressure Tetralin Stability Study, 200 ºC and 230 ºC

Tetralin proved to be stable at temperatures up to 230 ºC under ambient pressure. Figure 5-5 presents the scan of tetralin at 65 ºC, along with the scan of tetralin after three hours at 200 ºC. The testing at 200 ºC was followed immediately by a three hour test at 230 ºC. The scan after the three hours at 230 ºC is also presented in Figure 5-5. The high temperature scans are almost identical, indicating that no reaction had taken place.

Ambient Pressure Isotetralin Stability Study, 230 ºC

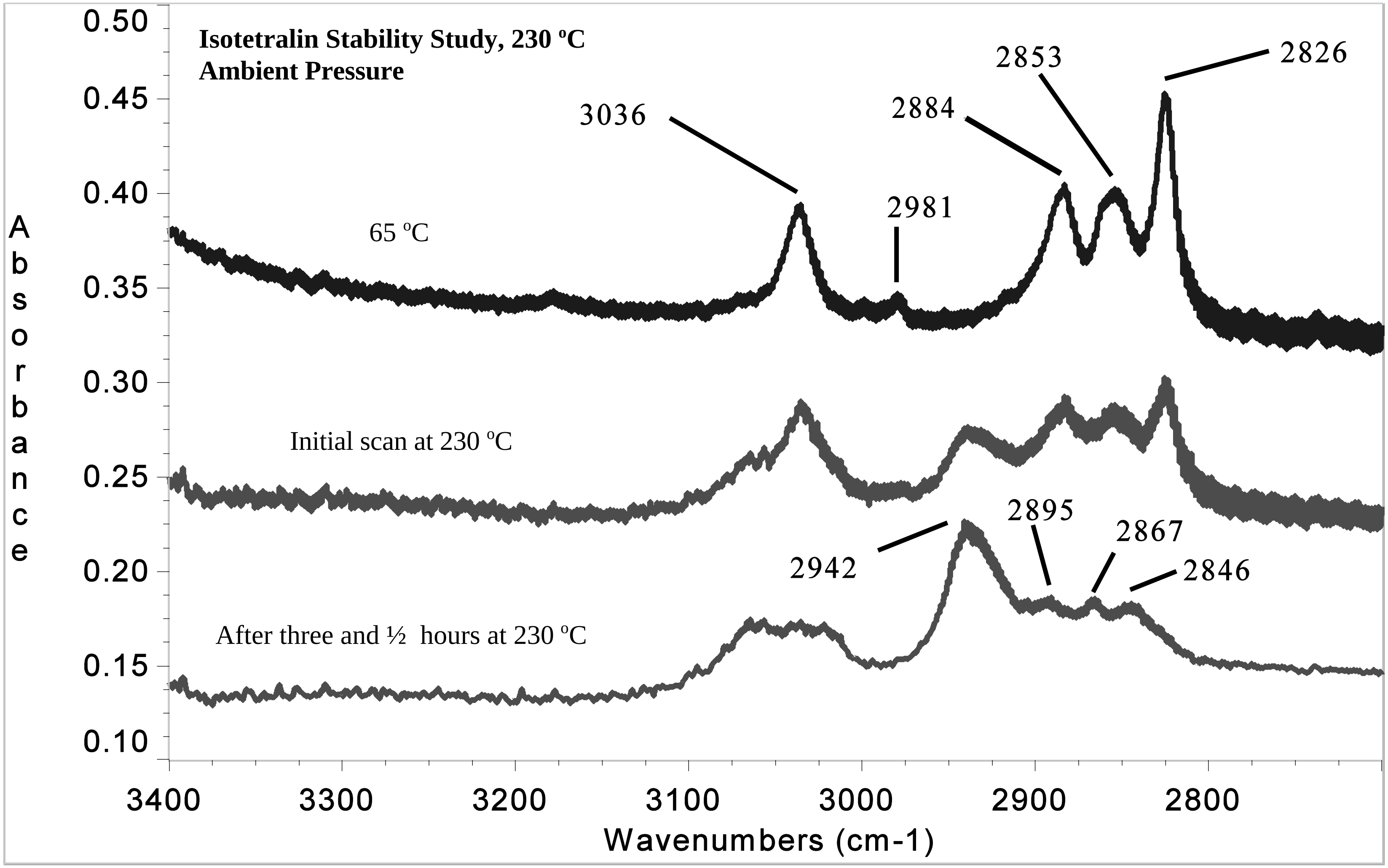
Isotetralin proved to be highly reactive at 230 ºC under ambient pressure. Figure 5-6 presents the spectrum of isotetralin at 65 ºC, along with the initial scan at 230 ºC and the scan after three and one-half hours at 230 ºC. The initial scan at 230 ºC shows that isotetralin had already begun to react. The most prominent peak in the reactant scan, at 2826 cm^{-1}, which is unique to isotetralin, was not observed in the product scan, indicating the complete reaction of isotetralin. The peak at 2884 cm^{-1} , also unique to isotetralin, was likewise not observed in the product scan, confirming the complete reaction of isotetralin. Although weak, the peak which arose in the product spectrum around 2867 cm^{-1} is unique to tetralin, indicating that an isomerization to tetralin had occurred. The most prominent peak in the product scan, around 2942 cm^{-1}, is also the most prominent peak in the scan of tetralin. The broad increase in aromaticity could have been explained by isomerization to tetralin except that the spectrum of tetralin

Figure 5-5



Tetralin Stability Study, 200 º and 230 ºC
Ambient Pressure
2941
2895
2868
3021
2849
3065
65 ºC
After three hours at 200 ºC
After three hours at 230 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-6


Isotetralin Stability Study, 230 ºC
Ambient Pressure
3036
2981
2884
2853
2826
65 ºC
Initial scan at 230 ºC
2942
2895
2867
2846
After three and ½ hours at 230 ºC
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

contains a definite valley at 3048 cm^{-1} which was not seen in the product from this stability test. It was postulated that the increase in aromaticity could also have been contributed to by dehydrogenation of isotetralin to naphthalene. To support this postulate, it was decided to subject the reaction product mixture to gas chromatographic analysis. GC analysis of product mixtures became a standard part of the method thereafter. Table 5.2 presents the results of these analyses where available. The product mixtures had to be stored at 65 °C to prevent the dissolution of the solutes from APF-240™. The vapor pressure of the solutes at this temperature is appreciable, and it appeared that the products from this reaction had vaporized out of solution by the time the GC method was developed.

Because of the high reactivity of isotetralin at 230 °C, it was decided to subject isotetralin to the stability test at the reduced temperatures of 200 °C, 150 °C and 100 °C. The results of the 200 °C stability test were qualitatively the same as those of the 230 °C test, with the rate of formation of products reduced somewhat, as would be expected. The four hours at 200 °C were followed immediately by three hours at 230 °C. The final product scan at 230 °C matched exactly with the final product scan from the previous 230 °C stability test, and since the last three or four scans were identical, it was thought that the reaction had stopped. GC results were not available for the product from this test because the solutes had volatilized out of solution before the GC method was developed.

Isotetralin reacted even more slowly at 150 °C. Figure 5-7 presents the scan of isotetralin at 65 °C, along with the initial scan at 150 °C and the scan after four and

Table 5.2

Relative Concentrations of Reactants and Products (by GC)

	NAP	DEC	TET	ISO	1,2-DHN	1,4-DHN
Reactant	Pure	Pure	Pure	92% ISO 8% 1,4-DHN	94% 1,2-DHN 6% NAP	89% 1,4-DHN 10% NAP
Products (Ambient Pressure)	NO-D	NO-D	NO-D	NO- VS	87% 1,2-DHN 13% NAP	33% 1,4-DHN 60% NAP 7% 1,2-DHN
Products (Nitrogen Blanket)	NO-VR	NO-VS	Pure	NO-VS	89% 1,2-DHN 11% NAP	NO-VR
Products (Hydrogen Blanket)	Pure	95% DEC 5% NAP	84% TET 16% DEC	73% NAP 15% 1,4-DHN 11% TET	76% 1,2-DHN 24% NAP	47% 1,4-DHN 53% NAP

NAP = Naphthalene DEC = Decalin TET = Tetralin ISO = Isotetralin

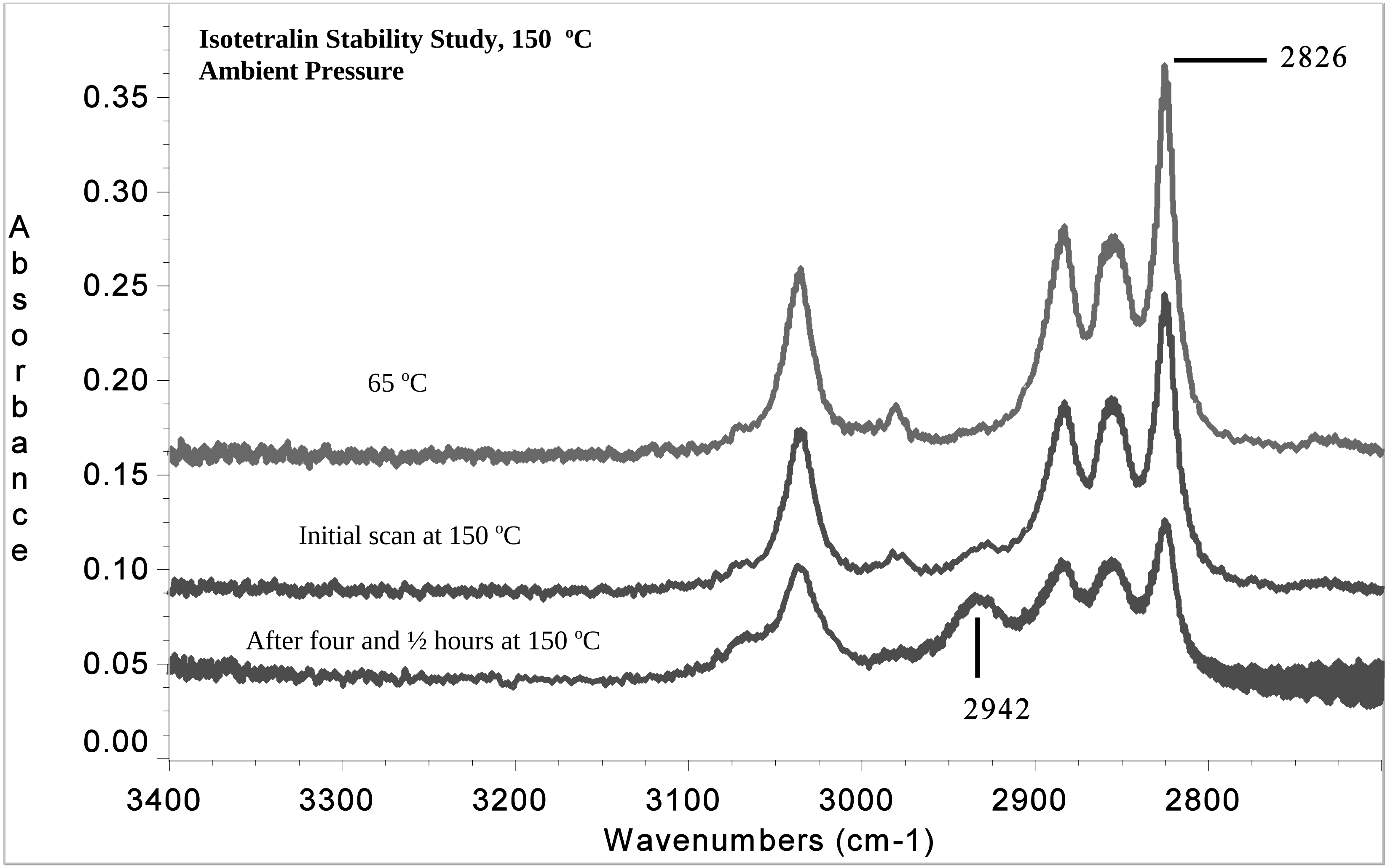
1,2-DHN = 1,2-Dihydronaphthalene 1,4-DHN = 1,4-Dihydronaphthalene

NO-D = Not Obtained - Discarded

NO-VR = Not Obtained - Volatilized out of Reactor

NO-VS = Not Obtained - Volatilized out on Storage

Figure 5-7


Isotetralin Stability Study, 150 ºC
Ambient Pressure
2826
65 ºC
Initial scan at 150 ºC
After four and ½ hours at 150 ºC
2942
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

one-half hours at 150 °C. The diminution of the characteristic isotetralin peak at 2826 cm^{-1} and the emergence of the broad peak centered at 2942 cm^{-1} clearly indicated that the isomerization to tetralin had begun. Since the product scans were changing over the thirty minute scanning interval, it was concluded that isotetralin was still reacting when the test was stopped. GC results were not available for the product from this test because the solutes had volatilized out of solution before the GC method was developed.

Isotetralin appeared to be stable at 100 °C. The scan of the product after seven hours at 100 °C was indistinguishable from the reactant scan.

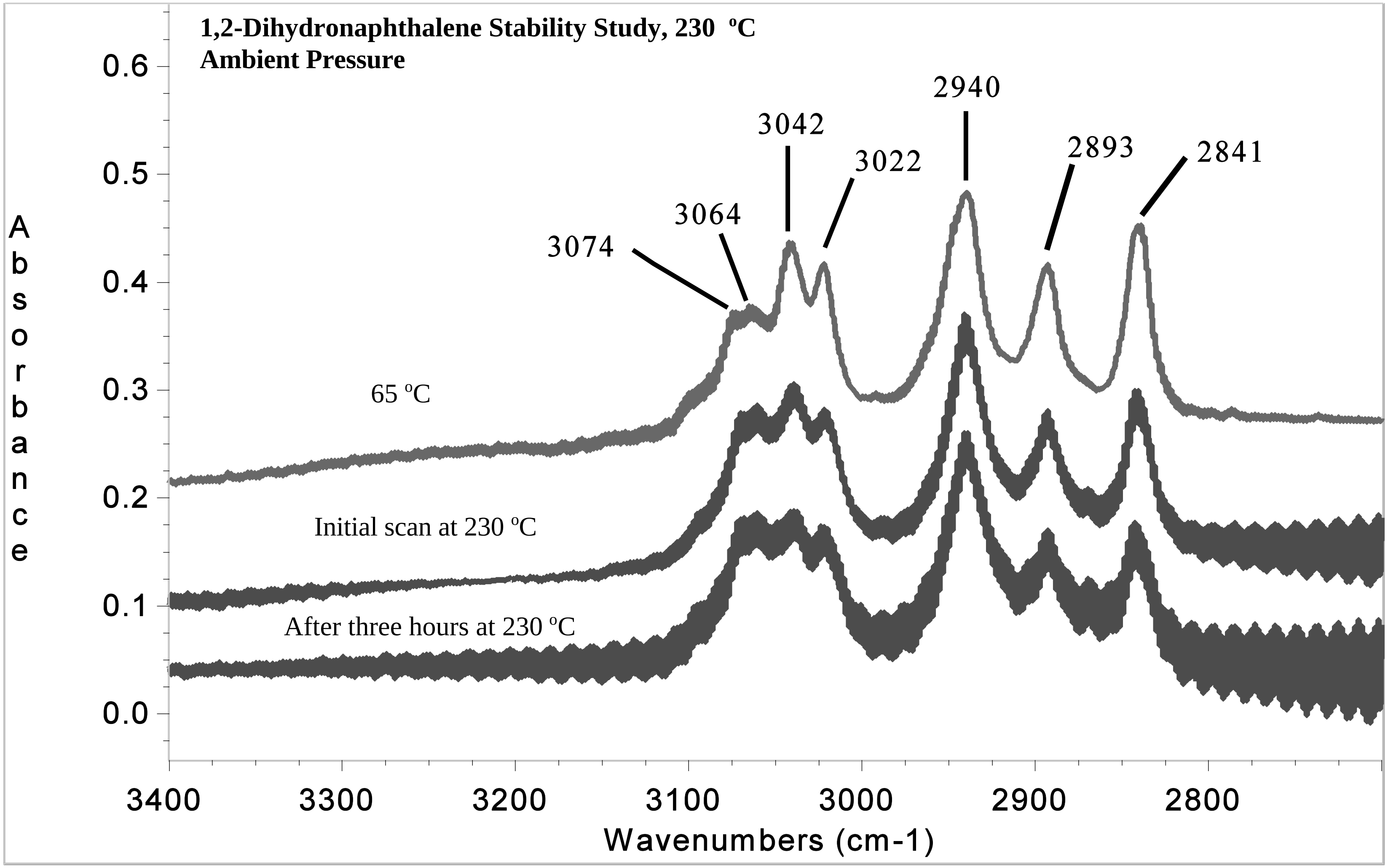
Ambient Pressure 1,2-Dihydronaphthalene Stability Study

The noise which plagued the ambient pressure stability studies was particularly noticeable in this test. Figure 5-8 presents the spectrum of 1,2-dihydronaphthalene at 65 °C, along with the initial scan at 230 °C and the scan after three hours at 230 °C. 1,2-Dihydronaphthalene appeared to be stable under these conditions. GC analysis indicated that the product was 87% 1,2-dihydronaphthalene and 13% naphthalene. Since the reactant analyzed as 94% 1,2-dihydronaphthalene and 6% naphthalene, only about 7 or 8% of the 1,2-dihydronaphthalene dehydrogenated to naphthalene. Differences this small may not be detectable by FTIR as employed in this experimentation, particularly not with the noise level as high as it was.

Ambient Pressure 1,4-Dihydronaphthalene Stability Study

The original ambient pressure 1,4-dihydronaphthalene stability study was so noisy that the test was repeated after the noise problem was addressed. The results of the repeat test are presented here.

Figure 5-8

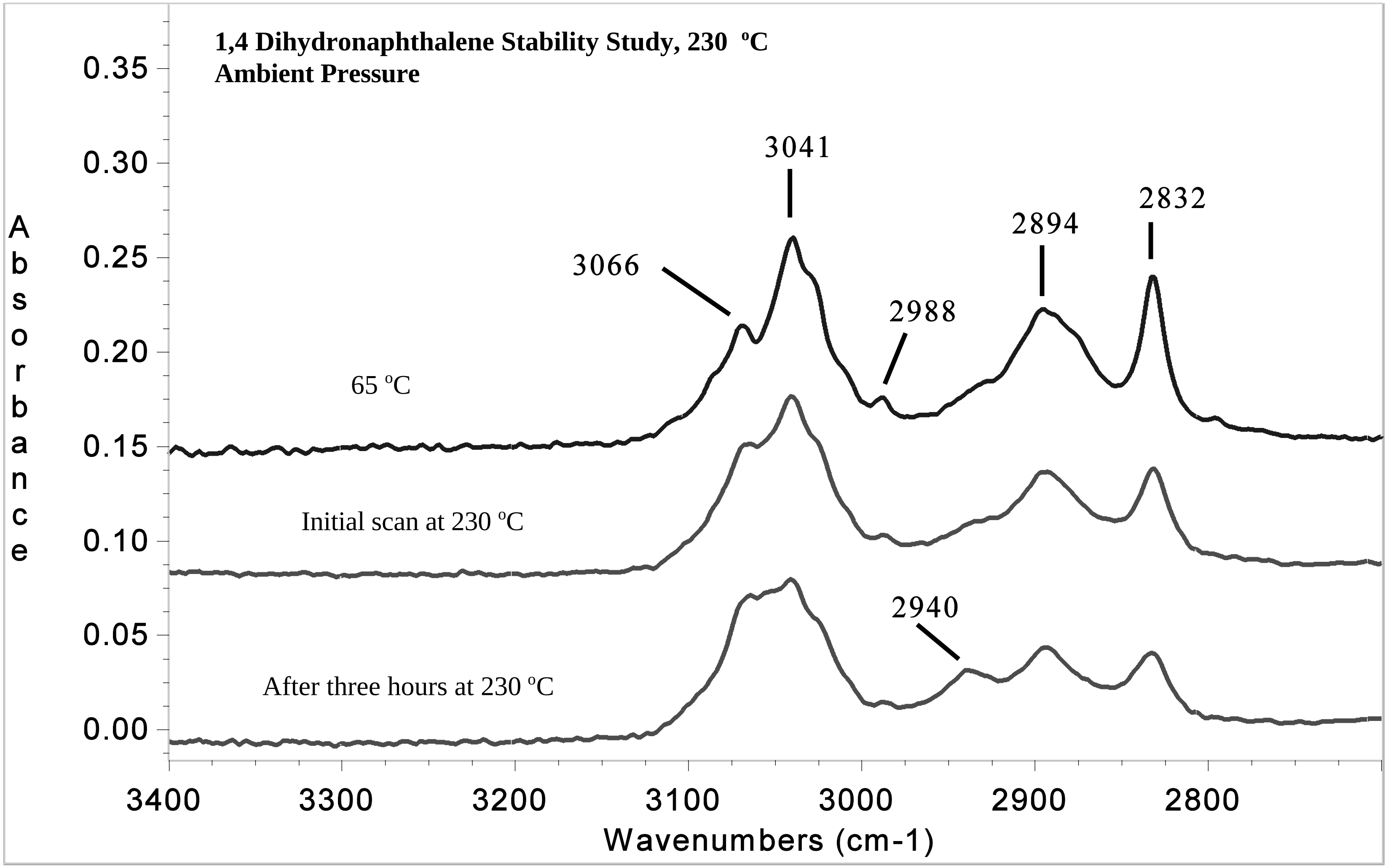

1,2-Dihydronaphthalene Stability Study, 230 ºC
Ambient Pressure
3074
3064
3042
3022
2940
2893
2841
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

1,4-Dihydronaphthalene proved to be highly reactive at 230 ºC under ambient pressure. Figure 5-9 presents the spectrum of 1,4-dihydronaphthalene at 65 ºC, along with the initial scan at 230 ºC and the scan after three hours at 230 ºC. The reduction in height of the peak at 2832 cm^{-1} by more than 50% indicated a substantial reaction had taken place. The growth of the peak at 2940 cm^{-1} was thought to be caused by isomerization to 1,2-dihydronaphthalene. The decrease in the peak height around 3041 cm^{-1} and increase in peak height around 3066 cm^{-1} was most likely caused by dehydrogenation to naphthalene. GC analysis indicated that the product mixture contained 33% unreacted 1,4-dihydronaphthalene, 60% naphthalene and 7% 1,2-dihydronaphthalene, which was considered good confirmation of the IR results.

Nitrogen Blanket Stability Studies

Using the format developed for the ambient pressure stability studies, the compounds in this study were tested under a 35 bars nitrogen blanket. The stability studies were conducted under a nitrogen blanket for two reasons. The first reason was for safety concerns. Once the response of the system to combined elevated temperatures and pressures was studied using an inert gas, and the necessary modifications made, then the transition to hydrogen could be made with a wider margin of safety. The second reason was to separate the effects of high pressure itself from the effects of high pressure hydrogen. The reactions of some of the compounds in this study are highly dependent on the environment in which the reactions take place.

Figure 5-9


1,4 Dihydronaphthalene Stability Study, 230 ºC
Ambient Pressure
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
3066
3041
2988
2894
2832
2940

Modifications to the cell to allow for high pressure operation forced a repositioning of the cell within the spectrometer box. This resulted in an unexpected but welcomed reduction in the noise level.

Nitrogen Blanket Naphthalene Stability Study

In the 35 bars nitrogen blanket naphthalene stability study, a broad peak emerged around 2952 cm^{-1}, indicative of methylene stretches. Since naphthalene had been shown to be stable in the ambient pressure stability test, and since hydrogenation to aliphatics in a nitrogen atmosphere was considered unlikely, contamination was suspected. Since the contaminant was not detected at the start of the run, it was suspected that it came from the cell and mixed with the reactor contents during the run. To confirm this suspicion, the cell was rinsed thoroughly, filled with neat APF-240™, and subjected to the standard stability test with no solute present. No peak was detected around 2952 cm^{-1} on this run, so the naphthalene stability test was repeated. This time no peak emerged around 2952 cm^{-1}, and the presence of a contaminant, perhaps tetralin or 1,2-dihydronaphthalene from a previous run, was confirmed. The implication here to the development of this method was that because of the design of the cell, thorough cleaning between runs, which is absolutely necessary, is difficult to achieve by flushing the reactor. Complete disassembly of the cell, cleaning, and reassembly between each run was considered impractical. Performing a stability test with neat APF-240™ and watching for the emergence of stray hydrocarbon peaks between each run would have been too time consuming. It was decided to flush the reactor with 100 times its volume, or 30 ml, of carbon tetrachloride between runs.

In the repeat test, naphthalene proved to be stable at temperatures up to 230 °C under a 35 bars nitrogen blanket. Figure 5-10 presents the spectrum of naphthalene at 65 °C, along with the initial scan at 230 °C and the scan after two and one-half hours at 230 °C. The ratio of the peak heights in the 230 °C scans remained constant, indicating that no reaction had taken place. However, the high temperature peak heights were somewhat less than the reactant peak heights, more than could be accounted for just by temperature effects. This loss in the peak heights could have been caused by several things, the most likely of which was a loss in the interferometer signal strength.

Considerable effort was expended in attempting to determine the cause of the loss of interferometer signal strength, the details of which are beyond the scope of this document. All of the tests performed kept indicating that the cell itself was the cause of the problem. At length, the cell manufacturer was contacted. The cell manufacturer indicated that his experience had been that decomposition products from samples at high temperatures tend to deposit on the sample cavity window over a period of time, obscuring the radiation path and thus accounting for the loss of signal strength. The cell was disassembled and a brown residue was observed on the sample cavity window. The window was cleaned and the cell was reassembled. A substantial rebound in the interferometer signal strength was observed.

Nitrogen Blanket Tetralin Stability Study

Tetralin proved to be stable at temperatures up to 230 °C under a 35 bars nitrogen blanket. Figure 5-11 presents the spectrum of tetralin at 65 °C under a 35 bars nitrogen blanket, along with the initial scan at 230 °C and the scan after three hours at

Figure 5-10

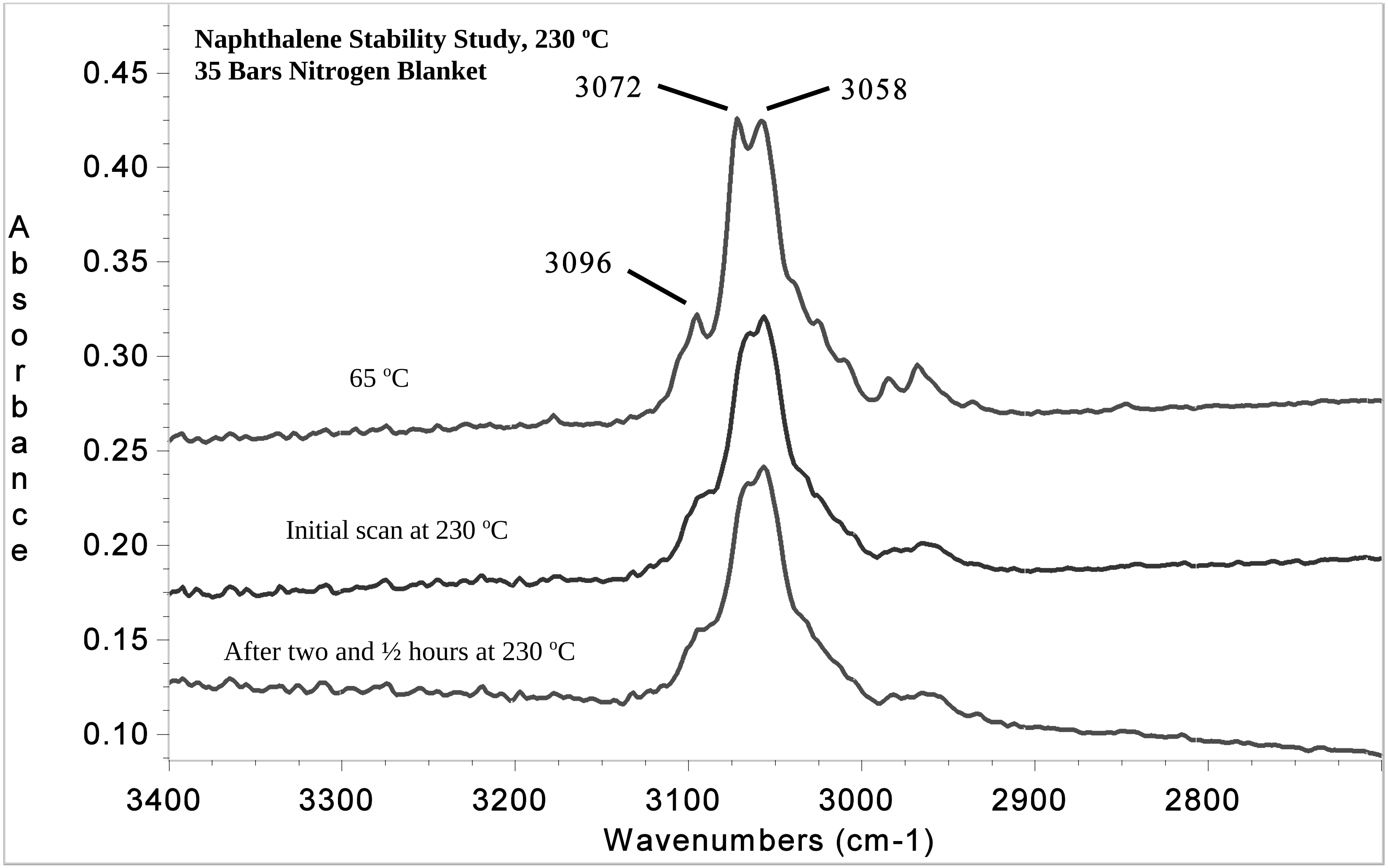
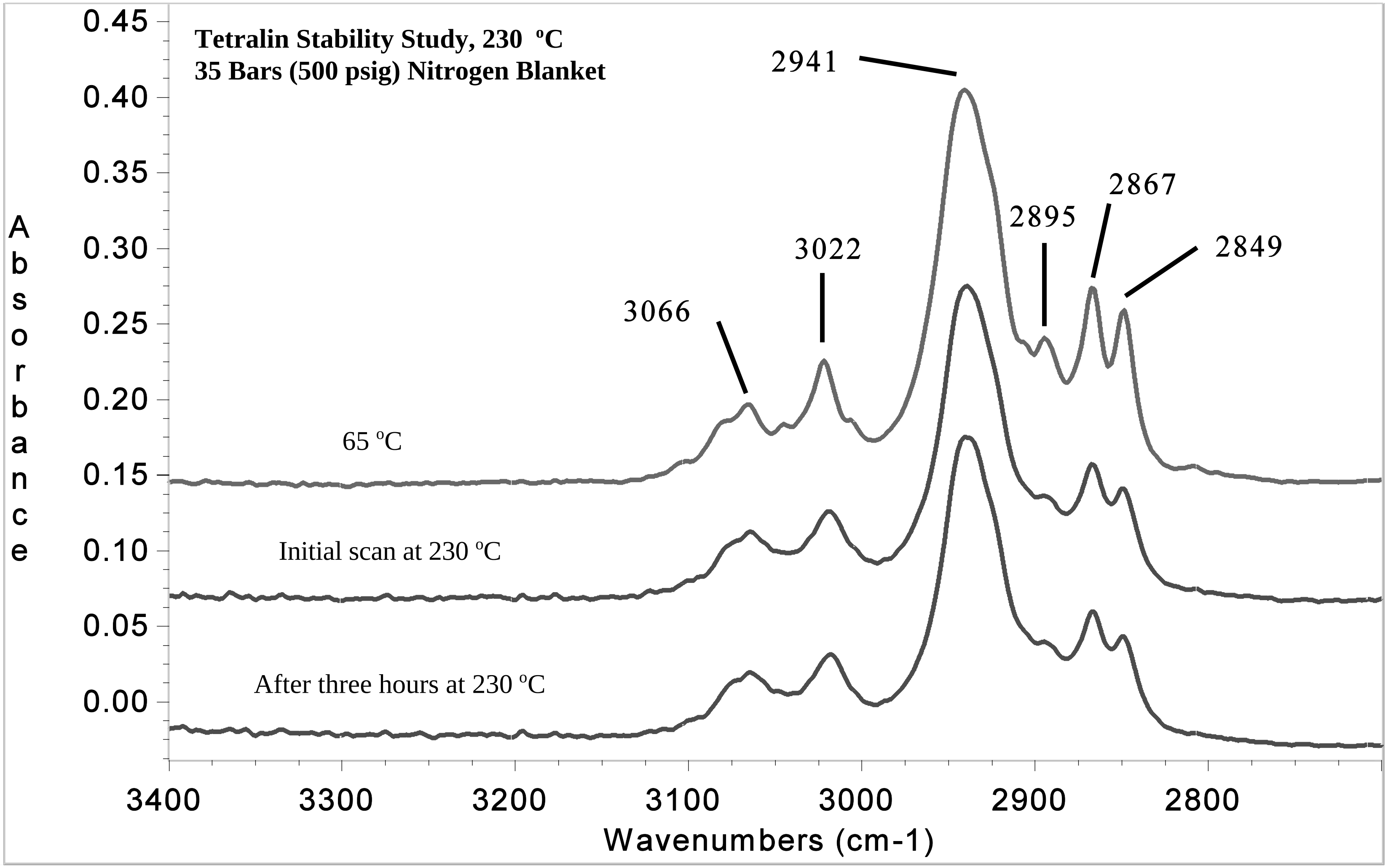

Naphthalene Stability Study, 230 ºC
35 Bars Nitrogen Blanket
3072
3058
3096
65 ºC
Initial scan at 230 ºC
After two and ½ hours at 230 ºC
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-11


Tetralin Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
2941
2867
2895
2849
3022
3066
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

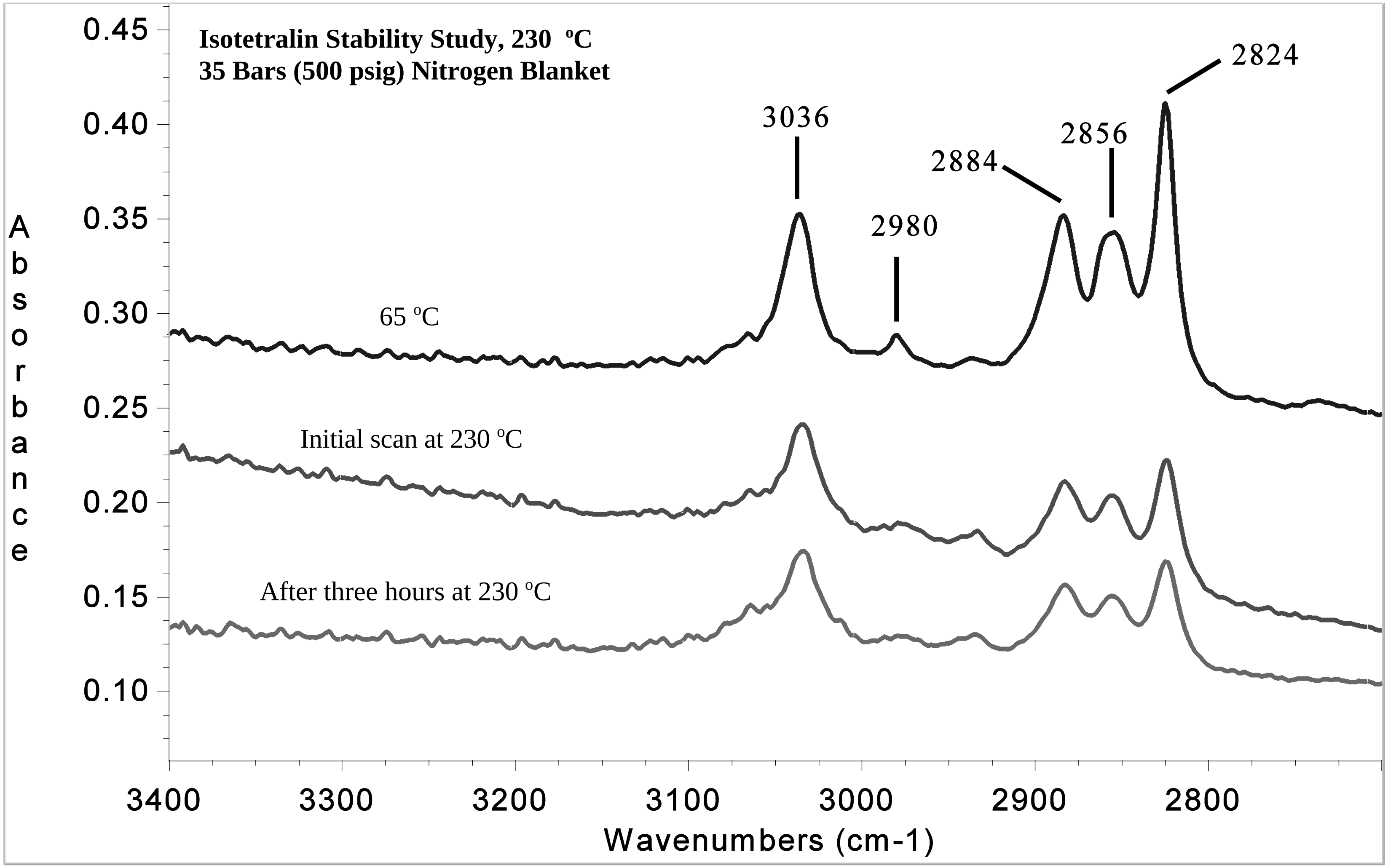
230 °C. The ratio of the peak heights in the reactant scan and product scans remained the same. However, a ten per cent overall reduction in peak heights from reactant to product was observed. Since the cell window had been cleaned recently, this loss in peak heights was thought to be caused by volatilization of tetralin into the vapor space above the reactor, rather than loss in the interferometer signal strength.

Nitrogen Blanket Isotetralin Stability Study

Unlike the ambient pressure isotetralin stability study, in which isotetralin reacted completely, isotetralin reacted only slightly at 230 °C under a 35 bars nitrogen blanket. Figure 5-12 presents the spectrum of isotetralin at 65 °C, along with the initial scan at 230 °C and the scan after three hours at 230 °C. The emergence of the peak at 2942 cm^{-1} was indicative of a slight isomerization to tetralin, while the loss in the peak heights of the aliphatic peaks and gain in the aromatic peak heights was probably caused by dehydrogenation of isotetralin to naphthalene. GC analysis was not available because the hydrocarbons volatilized out of the reaction mixture during storage.

By this point in the development of this method, the spectra generated were being subjected to detailed scrutiny. Temperature effects which had previously been thought to be negligible were found to be noticeable upon closer inspection. Of particular concern was the difference due to temperature between the spectra of reactants at 65 °C and the spectra of products at 230 °C. The procedure was amended to include the scanning of the products after they had been allowed to cool to 65 °C.

Figure 5-12


Isotetralin Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
3036
2980
2884
2856
2824
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Nitrogen Blanket Decalin Stability Study

Decalin proved to be stable at temperatures up to 230 ºC under a 35 bars nitrogen blanket. Figure 5-13 presents the scan of decalin at 65 ºC, along with the initial scan at 230 ºC and the scan after three hours at 230 ºC. The sample was left in the cell at 65 ºC and ambient pressure overnight. By morning the interferometer signal had decayed to one tenth of the value observed at the start of the test. Since the sample cell window had been cleaned recently, some other source of signal loss was suspected. The cell was disassembled and a clear odorless liquid, probably water, was observed on the stainless steel bevel faces which deflect the radiation into the sample cavity and deflect the radiation returning from the sample to the detector. Since water is a strong absorber of infrared radiation, it was suspected that moisture from the industrial grade nitrogen which had been used to pressurize the external gas pressurization chamber had condensed on the surfaces inside the cell. The method was amended and thereafter ultra-high purity nitrogen, containing less than one part per million water, was used to pressurize the external gas pressurization chamber.

Nitrogen Blanket 1,2-Dihydronaphthalene Stability Study, 230 ºC

The results of the 230 ºC nitrogen blanket 1,2-dihydronaphthalene stability study were almost identical to those of the ambient pressure study. Figure 5-14 presents the spectra of 1,2-dihydronaphthalene at 65 ºC along with the initial scan at 230 ºC. Figure 5-15 presents the scan of 1,2-dihydronaphthalene after three hours at 230 ºC and the scan after the reaction product had been allowed to cool to 65 ºC. The interferometer signal strength was carefully monitored during this test, and no loss in signal strength

Figure 5-13

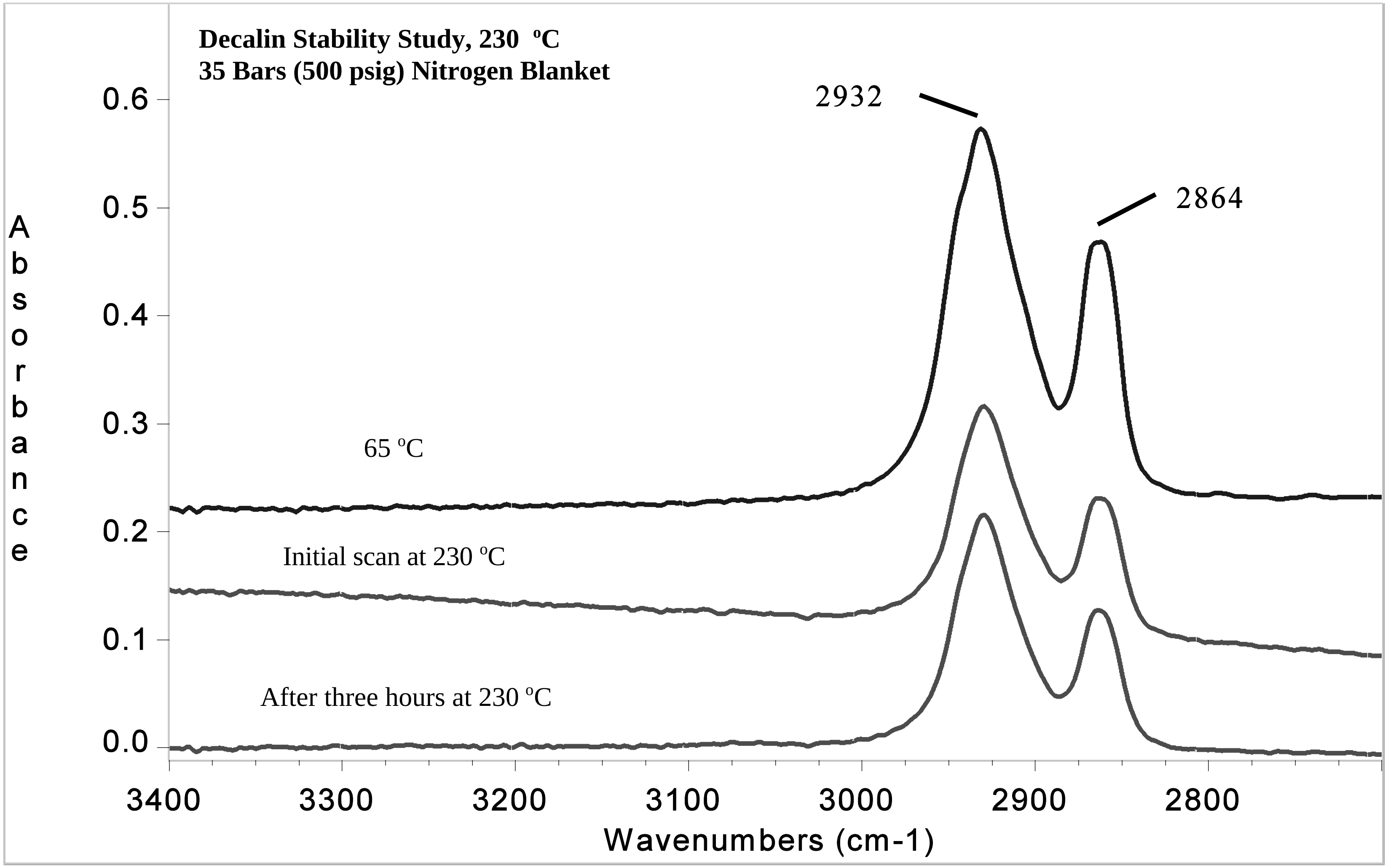

Decalin Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
2932
2864
65 ºC
Initial scan at 230 ºC
After three hours at 230 ºC
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-14

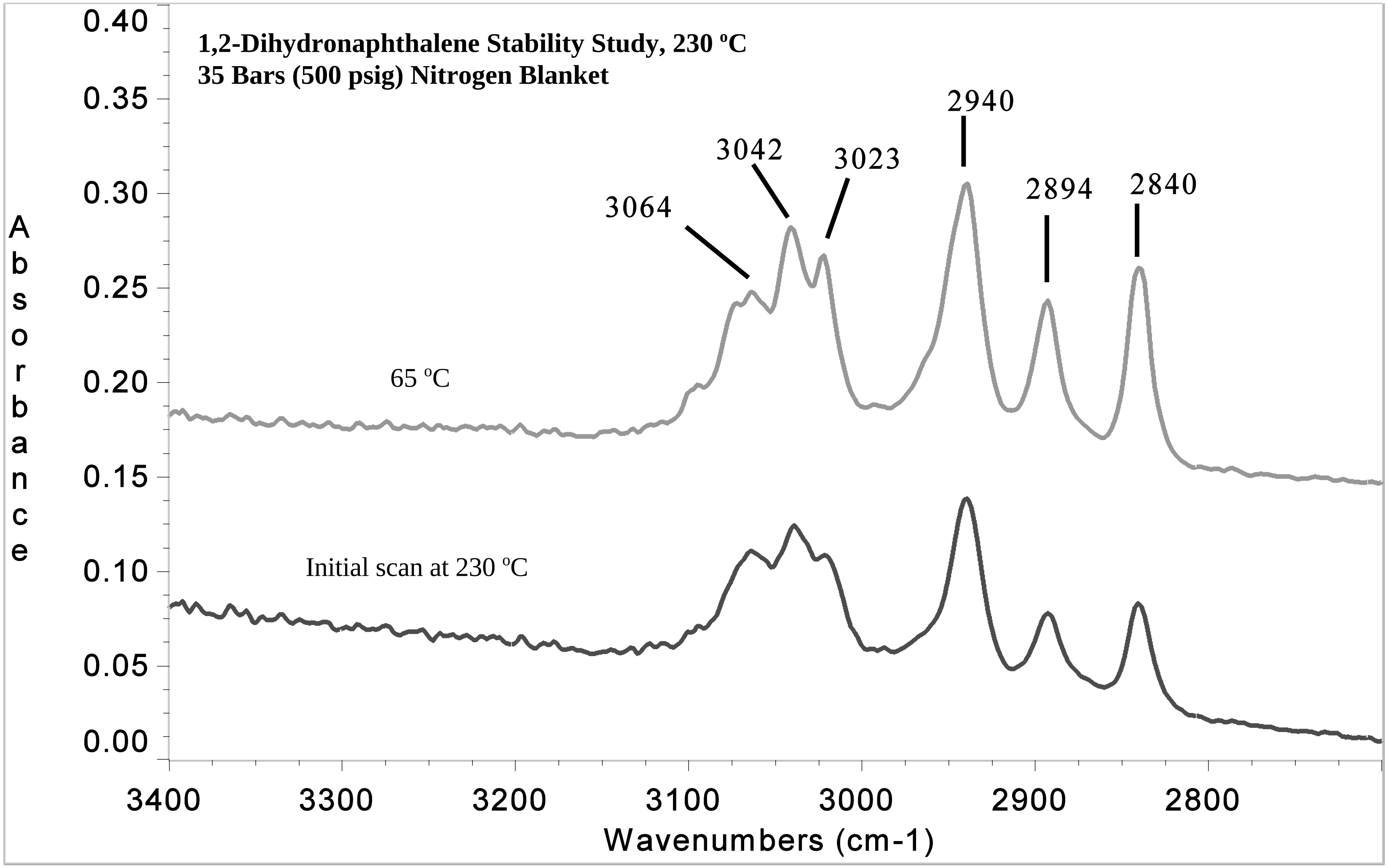
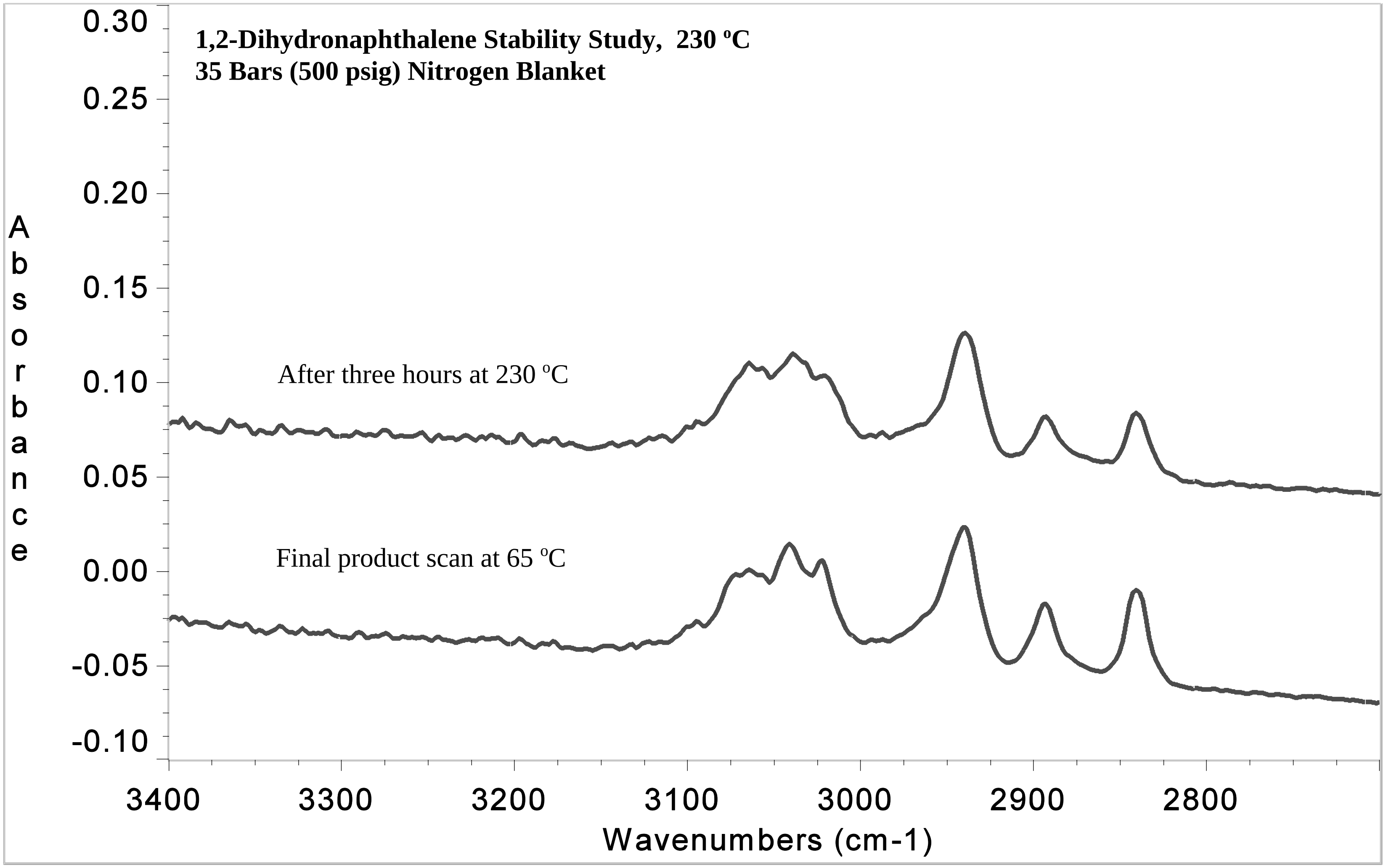

1,2-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
3064
3042
3023
2940
2894
2840
65 ºC
Initial scan at 230 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-15


1,2-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
After three hours at 230 ºC
Final product scan at 65 ºC
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

was observed. As in the ambient pressure test, 1,2-dihydronaphthalene was observed to react only slightly at 230 °C. GC analysis indicated that the product was 89% 1,2-dihydronaphthalene and 10% naphthalene. This was in close agreement with the results of the ambient pressure study for this reaction, which were 87% 1,2-dihydronaphthalene and 13% naphthalene. A loss of about 8% in the aliphatic stretches could have been accounted for by the reaction, but the actual loss of about 20% in the aliphatic peak heights indicated that some of the products may have volatilized into the vapor space above the reactor.

Nitrogen Blanket 1,4-Dihydronaphthalene Stability Study, 230 ºC

The presence of a nitrogen blanket appeared to stabilize 1,4-dihydronaphthalene, preventing dehydrogenation to naphthalene in much the same way that it prevented isotetralin from isomerizing to tetralin. Figure 5-16 presents the spectrum of 1,4-dihydronaphthalene at 65 ºC under a 35 bars nitrogen blanket, along with the initial scan at 230 ºC. Figure 5-17 presents the scan after three hours at 230 ºC and the scan after cooling to 65 ºC. The peak height ratios in the reactant and the product are almost the same. The reduction in all the peak heights was thought to be caused by volatilization into the vapor space above the reactor. Unlike the ambient pressure study, in which a 60% conversion to naphthalene occurred, 1,4-dihydronaphthalene exhibited very little reactivity in this test. No confirming GC analysis was obtained because the solutes volatilized out of the reaction mixture on storage.

Figure 5-16

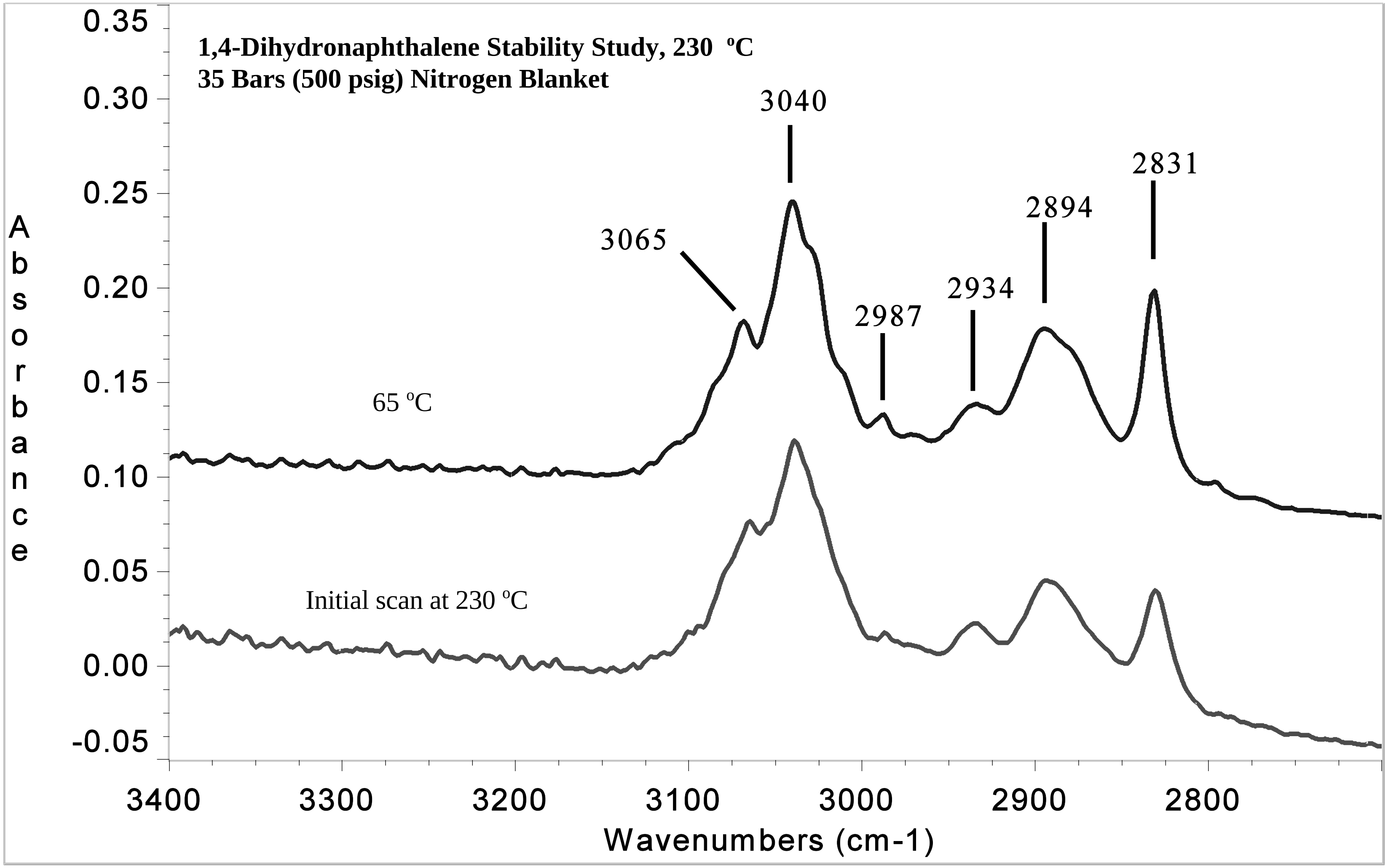
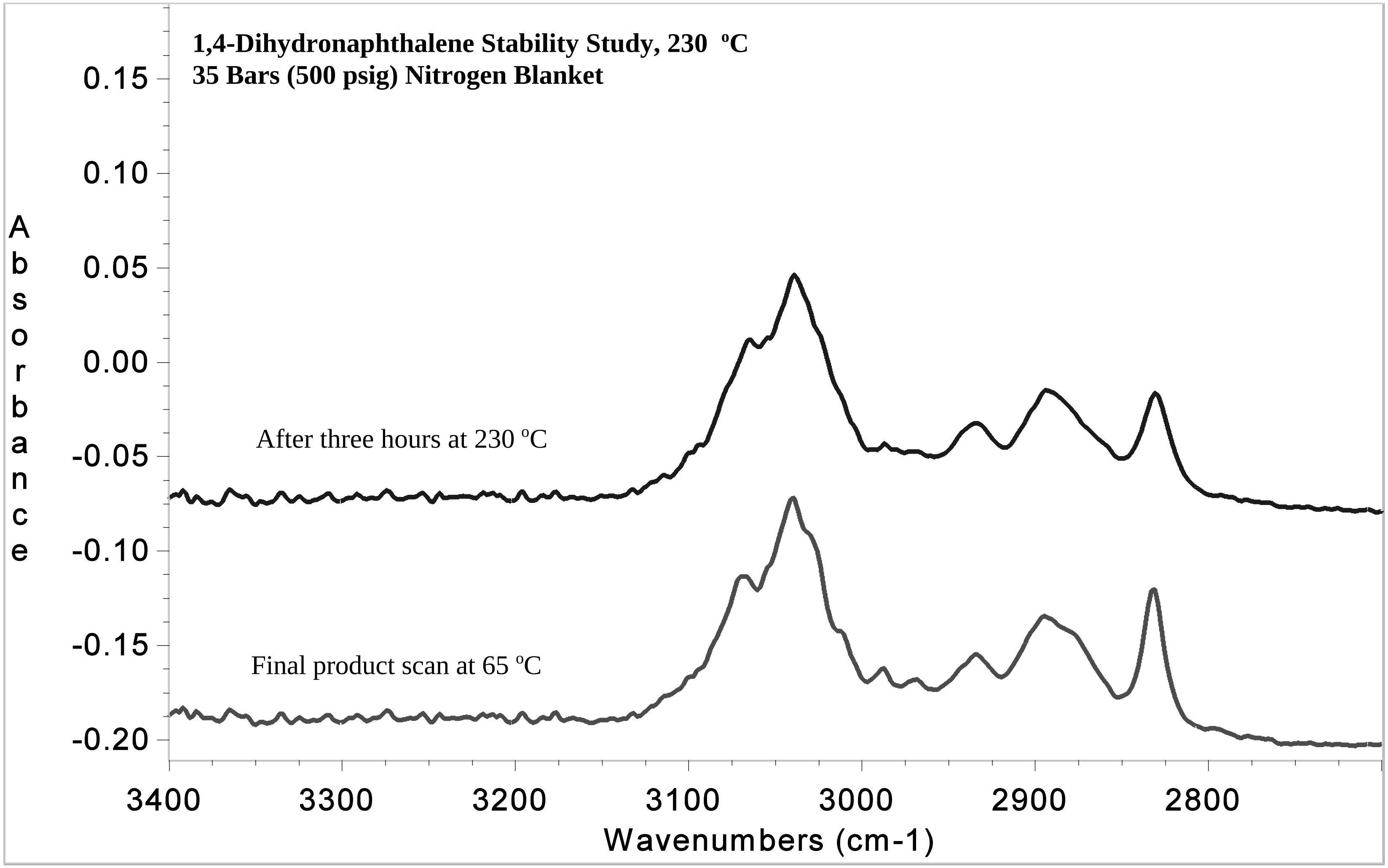

1,4-Dihydronaphthalene Stability Study, 230 °C
35 Bars (500 psig) Nitrogen Blanket
3040
3065
2987
2934
2894
2831
65 °C
Initial scan at 230 °C
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-17


1,4-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Nitrogen Blanket
After three hours at 230 ºC
Final product scan at 65 ºC
Absorbance
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Hydrogen Blanket Stability Studies, 230 ºC

With the demonstration of the safe operation of the FTIR cell at 230 ºC under a 35 bars (500 psig) nitrogen blanket, it was now possible to extend the testing to 35 bars hydrogen.

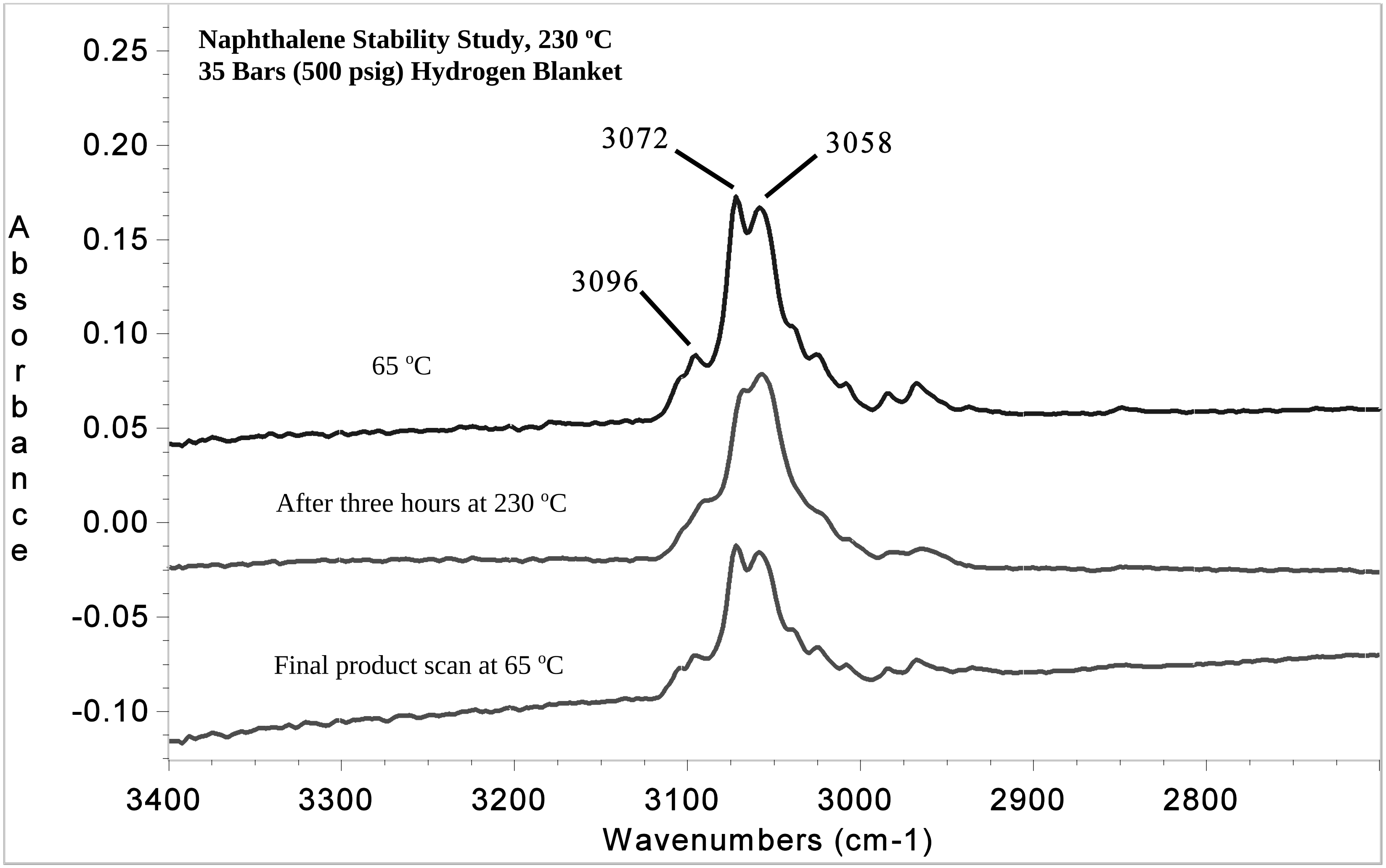
Hydrogen Blanket Naphthalene Stability Study, 230 ºC

Naphthalene proved to be stable at temperatures up to 230 ºC under a 35 bars hydrogen blanket. Figure 5-18 presents the spectrum of naphthalene at 65 ºC, along with the scan after three hours at 230 ºC and the scan after cooling to 65 ºC. The peak height ratios were the same after the reaction as they were before the reaction, indicating that no reaction occurred. The reduction in the peak heights was thought to be due to volatilization of the naphthalene into the vapor space above the reactor and possible condensation in the high pressure tubing upon cooling. The evaporative loss was quite significant, close to 15%. GC analysis showed that the reaction product was pure naphthalene.

Hydrogen Blanket Decalin Stability Study, 230 ºC

Decalin proved to be stable at temperatures up to 230 ºC under a 35 bars hydrogen blanket. Overall losses in peak heights amounted to only about 7 or 8%, and were thought to be due to volatilization into the vapor space above the reactor. GC analysis indicated that the reaction product was 95% decalin and 5% naphthalene. Closer inspection of the product spectra did reveal a slight increase in aromaticity. At concentrations this low, however, it was not clear if naphthalene was formed or if the naphthalene was residual from the naphthalene stability study conducted in the cell

Figure 5-18



Naphthalene Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
3072
3058
3096
65 ºC
After three hours at 230 ºC
Final product scan at 65 ºC
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

immediately prior to this test. It was thought unlikely that decalin would dehydrogenate to naphthalene under the conditions employed in this study. Therefore, contamination was the most likely source of naphthalene.

Hydrogen Blanket Tetralin Stability Study, 230 °C

Tetralin appeared to be stable or only slightly reactive at 230 °C under a 35 bars hydrogen blanket. Figure 5-19 presents the spectrum of tetralin at 65 °C, along with the scan after three hours at 230 °C and the scan after cooling to 65 °C. The overall reduction in the peak heights was thought to be caused by volatilization into the vapor space above the reactor. However, the relative reduction in the aromatic peak heights was greater than the reduction in the aliphatic peak heights, which may have indicated a slight hydrogenation to decalin. GC analysis indicated the product was 84% tetralin and 16% decalin, providing confirmation that some decalin was present in the product.

Hydrogen Blanket Isotetralin Stability Test, 230 °C

Isotetralin proved to be highly reactive at 230 °C under a 35 bars hydrogen blanket. The course that this reaction followed will be presented here in some detail. Figure 5-20 presents the spectrum of isotetralin at 65 °C, along with the initial scan at 230 °C. Figure 5-21 presents the scans after one-half hour, after one hour, and after two hours at 230 °C. Figure 5-22 presents the scan after three hours at 230 °C, along with the scan after cooling to 65 °C. Isotetralin began to react at temperatures well below 230 °C. This was also observed in the ambient pressure stability tests. As in the ambient pressure isotetralin stability test, the absence of the characteristic isotetralin peaks at 2825 cm^{-1}, 2855 cm^{-1}, and 2884 cm^{-1} in the product scan indicated the complete reaction

Figure 5-19

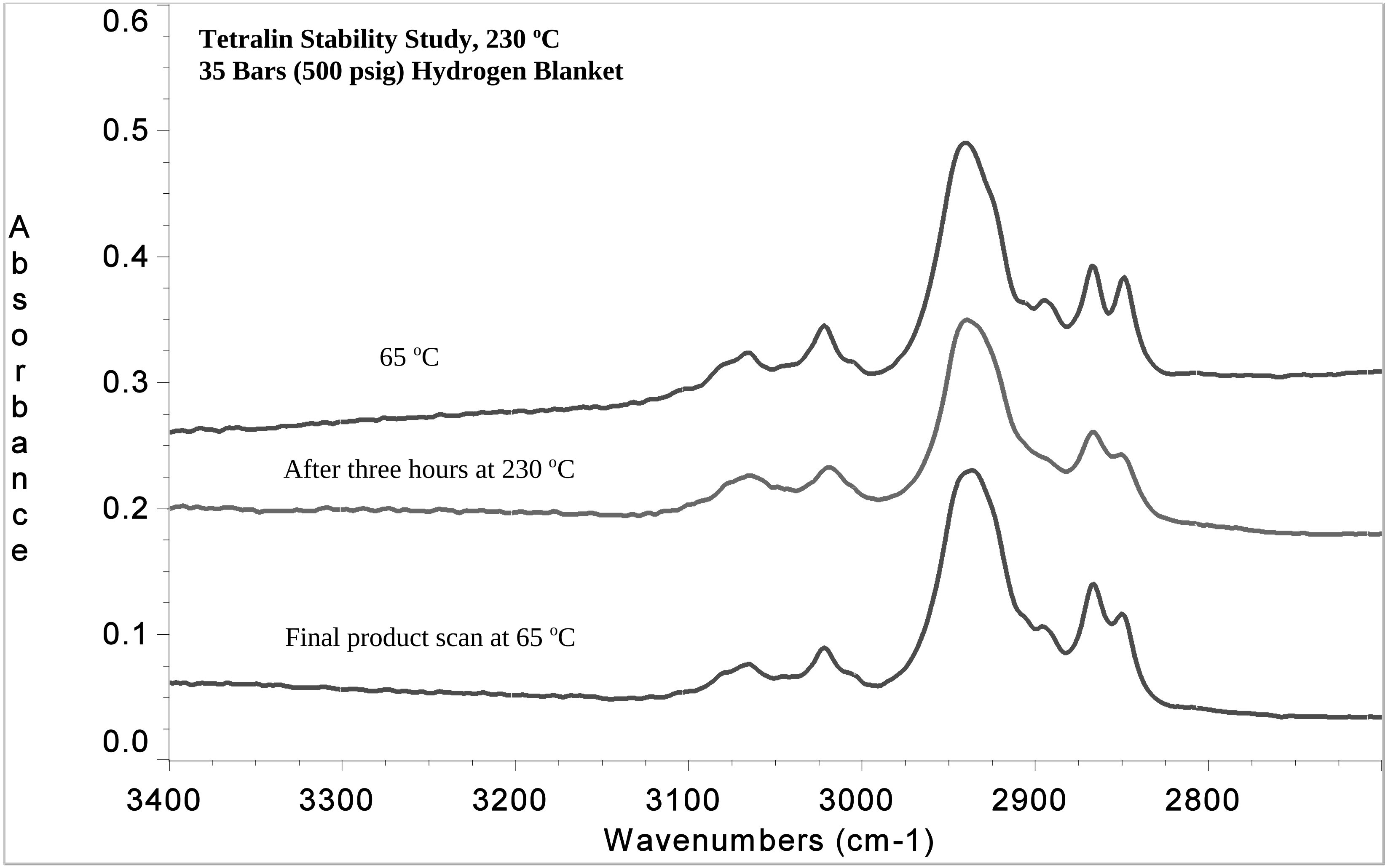

Tetralin Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
65 ºC
After three hours at 230 ºC
Final product scan at 65 ºC
Absorbance
0.6
0.5
0.4
0.3
0.2
0.1
0.0
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-20

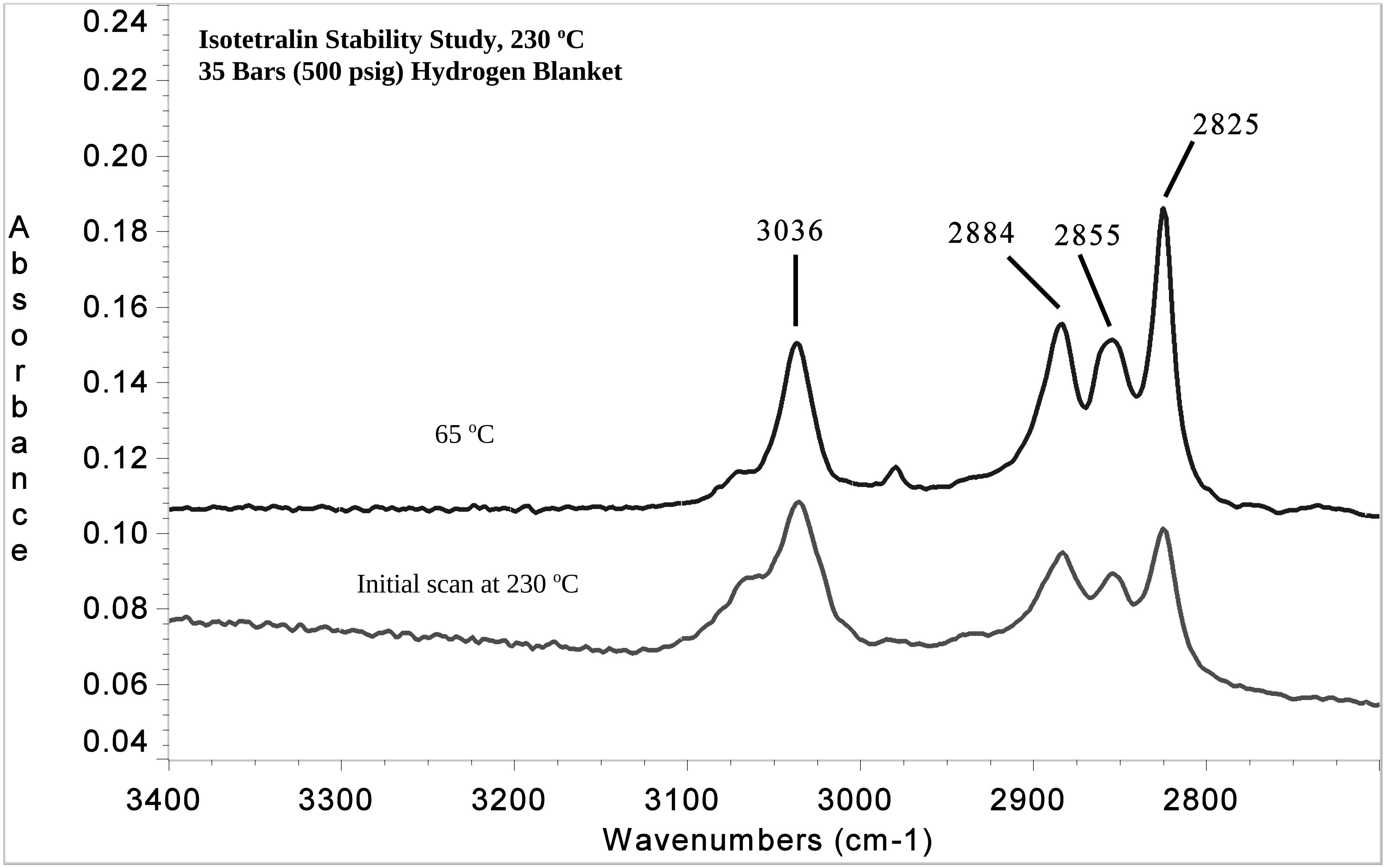

Isotetralin Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
3036
2884
2855
2825
65 ºC
Initial scan at 230 ºC
Absorbance
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-21

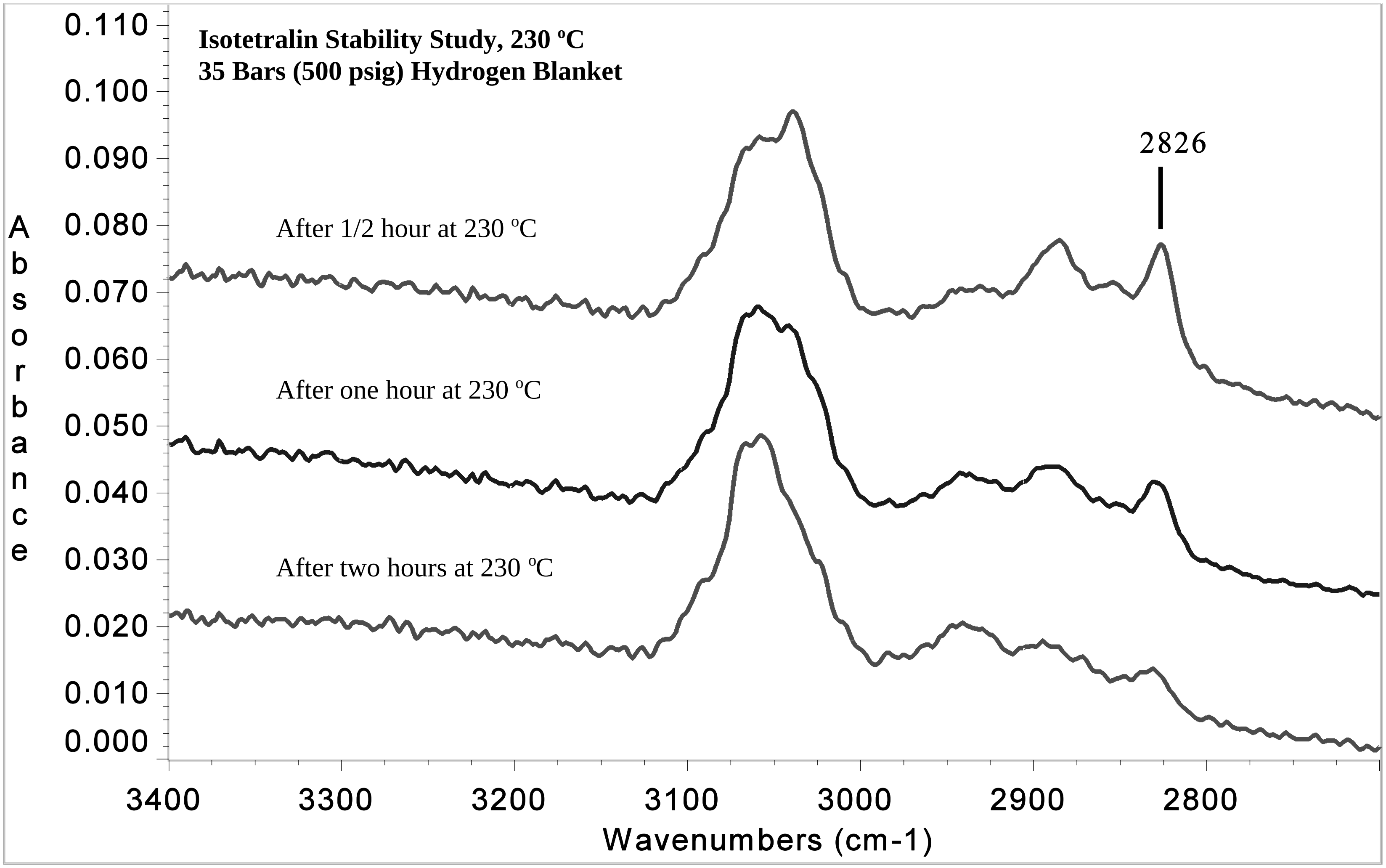
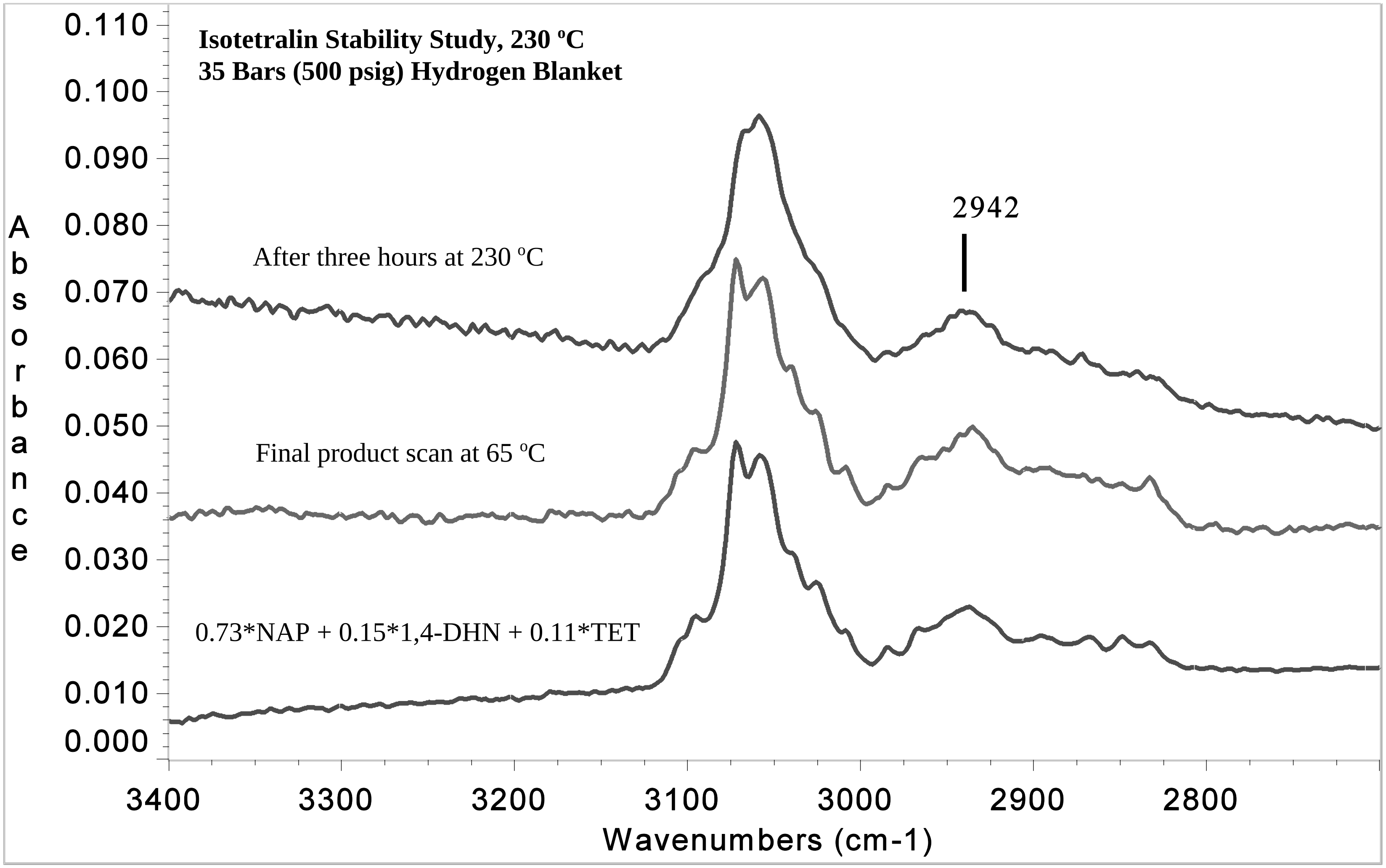

Isotetralin Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
2826
After 1/2 hour at 230 ºC
After one hour at 230 ºC
After two hours at 230 ºC
Absorbance
0.110
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-22


Isotetralin Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
2942
After three hours at 230 ºC
Final product scan at 65 ºC
0.73*NAP + 0.15*1,4-DHN + 0.11*TET
Absorbance
0.110
0.100
0.090
0.080
0.070
0.060
0.050
0.040
0.030
0.020
0.010
0.000
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

of isotetralin. The emergence of the peak at 2942 cm^{-1} is characteristic of the isomerization product, tetralin, and of the dihydronaphthalenes. The dehydrogenation to naphthalene is clearly evidenced by the growth and broadening of the peak in the aromatic region. The scans at half hour intervals showed the steady diminution of the characteristic isotetralin peaks and the steady growth of the product peaks. After one half hour at 230 ^{o}C, the characteristic isotetralin peak at 2825 cm^{-1} had decreased to about half of its initial height at 230 ^{o}C. The next half hour saw an additional 50% decrease in the height of this peak. After two hours at 230 ^{o}C, the peak at 2825 cm^{-1} was reduced to about 15% of the initial height at 230 ℃. It remained at this value thereafter, since one of the products, 1,4-dihydronaphthalene, absorbs at 2833 cm^{-1}, and some overlap of absorbance peaks was observed. The last two scans at 230 ^{o}C were virtually identical, and it was concluded that the reaction had slowed significantly or stopped.

Also included in Figure 5-22 is a synthetic FTIR scan for the final product generated using the OMNIC™ software and the product compositions as determined by GC analysis. GC analysis indicated that the product contained 73% naphthalene, 15% 1,4-dihydronaphthalene and 11% tetralin. The absence of isotetralin confirmed that the reaction was complete. The synthetic scan was generated by multiplying 0.73 times the neat naphthalene scan, 0.15 times the neat 1,4-dihydronaphthalene scan, and 0.11 times the neat tetralin scan, and summing the scans using the spectral addition routine. The comparison with the final product scan was considered very good.

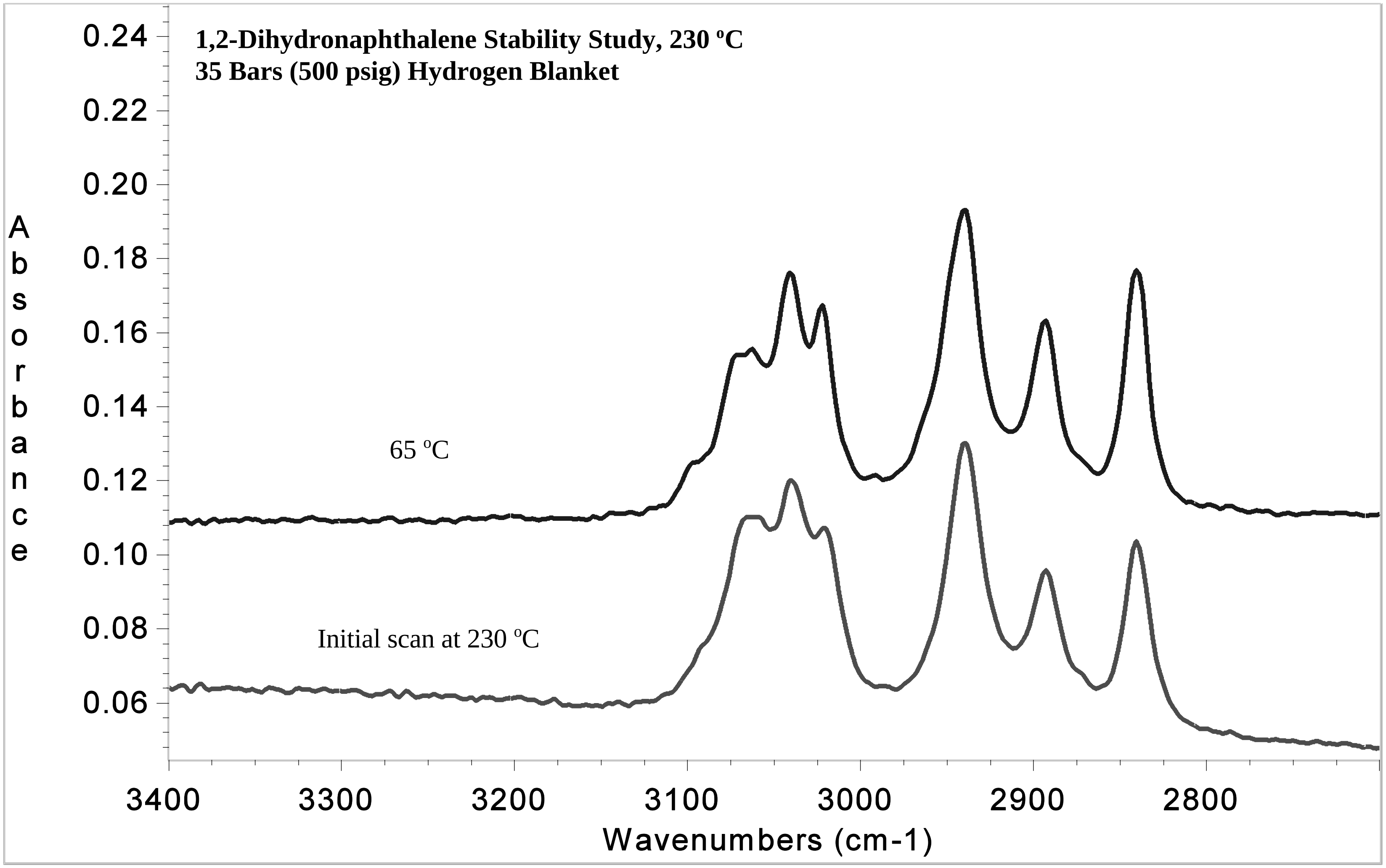
Dehydrogenation of isotetralin to 1,4-dihydronaphthalene and naphthalene appeared to be favored over isomerization to tetralin by a factor of about eight to one, based on the final product composition. Isomerization to tetralin was considered to be a competing reaction because tetralin, once formed, was considered to be stable under these reaction conditions. Tetralin did not appear to dehydrogenate in the hydrogen blanket stability test using neat tetralin as starting material.

This particular study provided convincing evidence of the ability of this technique to follow the course of the reaction of cyclic olefins *in situ* at high temperatures and pressures. The generation of synthetic FTIR scans using the final product compositions as determined by GC analysis for comparison to the actual final product scans was incorporated into the method at this time.

Hydrogen Blanket 1,2-Dihydronaphthalene Stability Study, 230 ºC

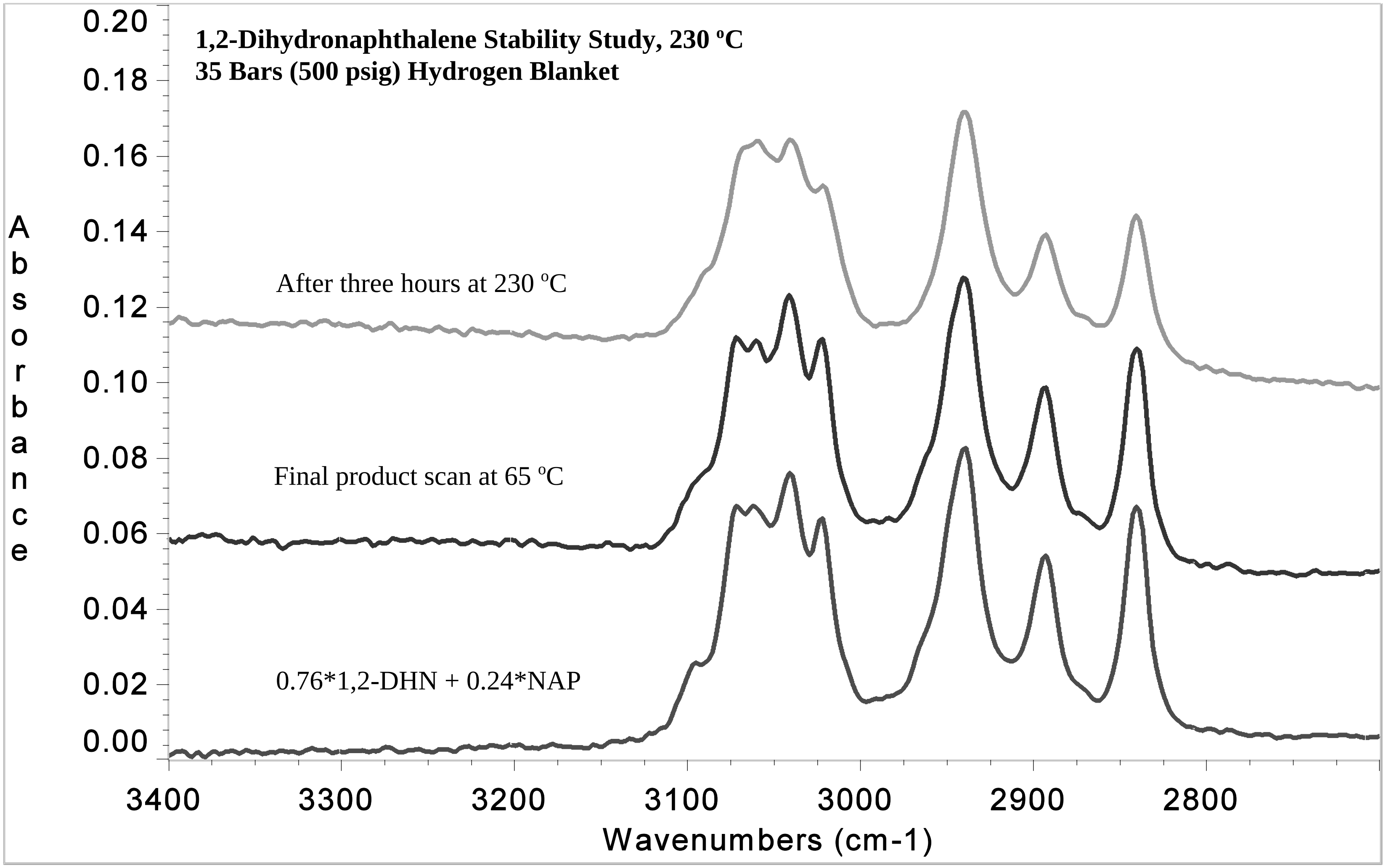
The ambient pressure and nitrogen blanket stability studies both indicated that 1,2-dihydronaphthalene was somewhat reactive at 230 °C, dehydrogenating to naphthalene with conversions of less than 10%. 1,2-Dihydronaphthalene proved even more reactive under a hydrogen blanket, with a conversion to naphthalene of more than 20%. Figure 5-23 presents the spectrum of 1,2-dihydronaphthalene at 65 ºC along with the initial scan at 230 °C. A slight reaction had taken place by the time 230 °C was reached. Figure 5-24 presents the scan after three hours at 230 ºC, and the scan after cooling to 65 ºC. The decrease in the aliphatic peak heights and the accompanying slight increase in aromaticity was indicative of a dehydrogenation to naphthalene. GC analysis indicated that the reaction product contained 76% unreacted 1,2-dihydronaphthalene and

Figure 5-23



1,2-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket

Figure 5-24


1,2-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
After three hours at 230 ºC
Final product scan at 65 ºC
0.76*1,2-DHN + 0.24*NAP
Absorbance
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

24% naphthalene. The synthetic FTIR scan generated using these compositions is also presented in Figure 5-24. Agreement between the synthetic scan and the final product scan was very good.

Hydrogen Blanket 1,4-Dihydronaphthalene Stability Study, 230 °C

1,4-Dihydronaphthalene proved to be highly reactive at 230 °C under a 35 bars hydrogen blanket, dehydrogenating to naphthalene with a conversion of about 50%. Figure 5-25 presents the scan of 1,4-dihydronaphthalene at 65 °C, along with the initial scan at 230 °C. A noticeable reaction had taken place by the time 230 °C was reached. Figure 5-26 presents the scan after three hours at 230 °C, and the scan after cooling to 65 °C. GC analysis indicated that the final product mixture contained 47% unreacted 1,4-dihydronaphthalene and 53% naphthalene. Figure 5-26 also presents the synthetic FTIR scan generated using these compositions. Agreement with the final product scan was very good.

Extension of Operating Conditions to 350 °C and 35 Bars

With the demonstration of safe operation and the method of acquiring FTIR data at 230 °C and 35 bars well established, the useful operating range of the AABSPEC cell was now extended to 350 °C and 35 bars. Several modifications to the cell were made to accomplish this extension. The existing 240 volt plug and socket failed and was replaced with a more heat resistant model. The polytetrafluoroethylene (PTFE) sample cavity pathlength spacer was replaced with a Grafoil™ spacer supplied by the cell manufacturer. The Viton™ o-ring which provided the seal between the sample window and the gas pressurization chamber was not recommended for use above 250 °C. At the

Figure 5-25

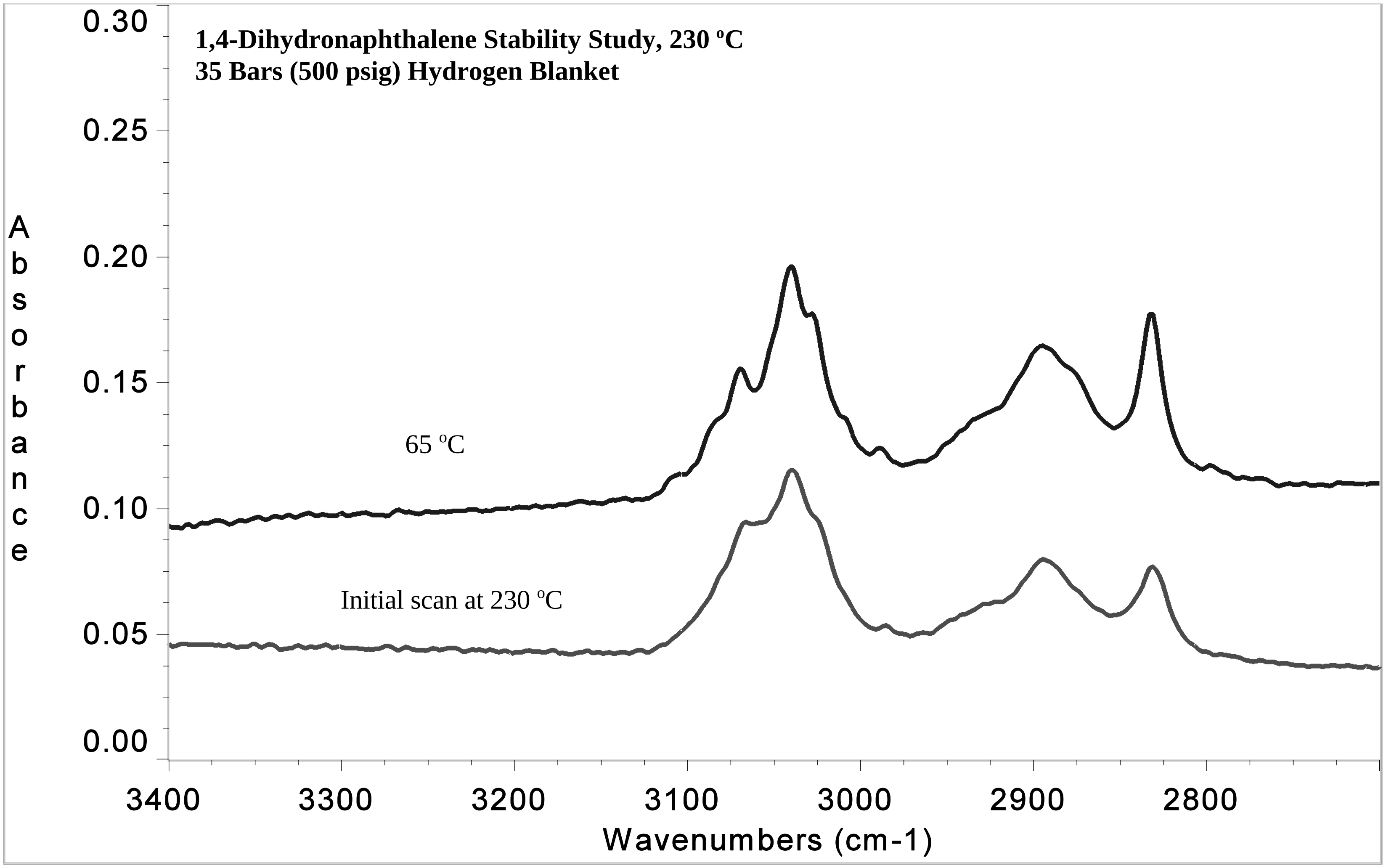
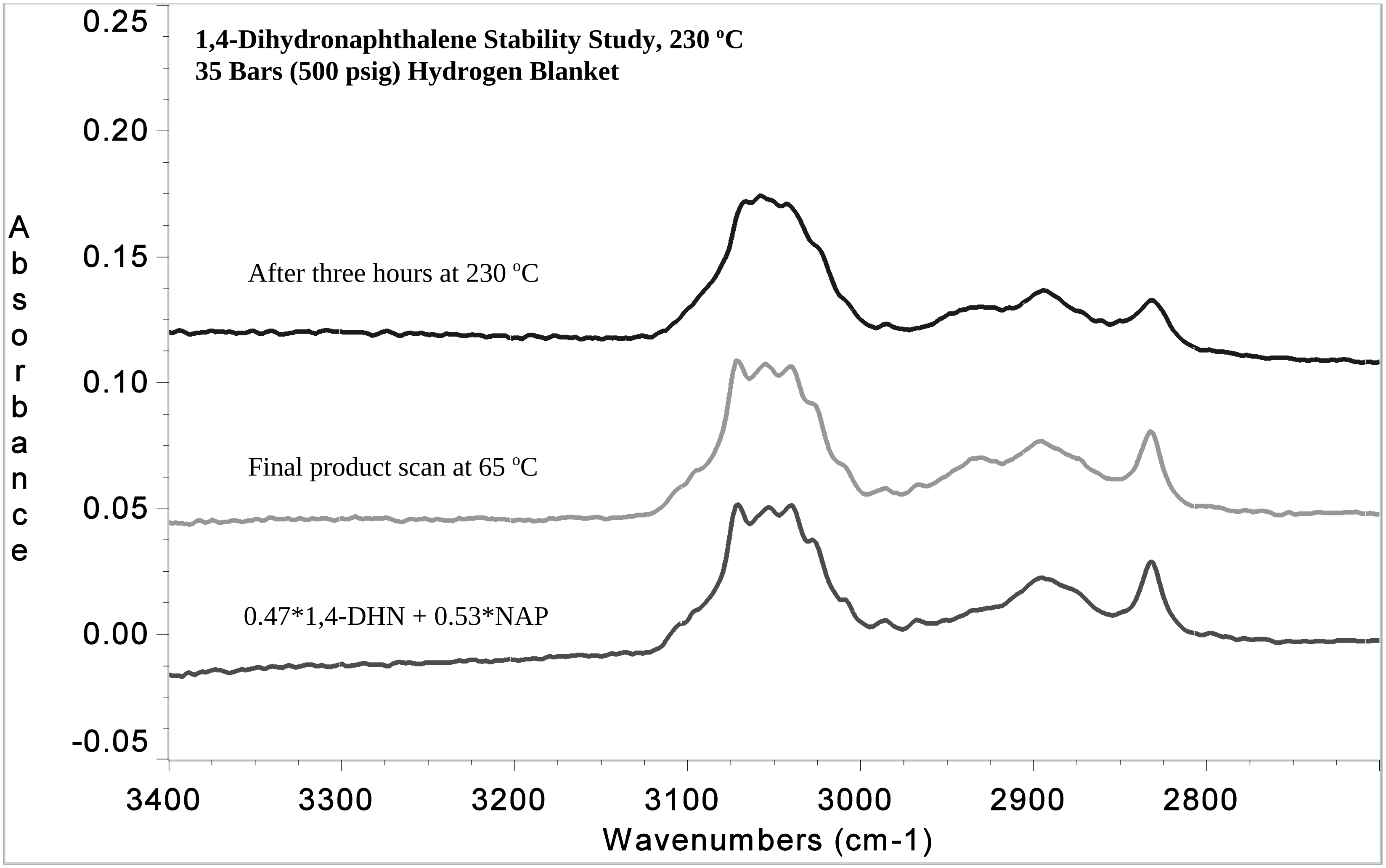

1,4-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
65 ºC
Initial scan at 230 ºC
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-26


1,4-Dihydronaphthalene Stability Study, 230 ºC
35 Bars (500 psig) Hydrogen Blanket
After three hours at 230 ºC
Final product scan at 65 ºC
0.47*1,4-DHN + 0.53*NAP
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

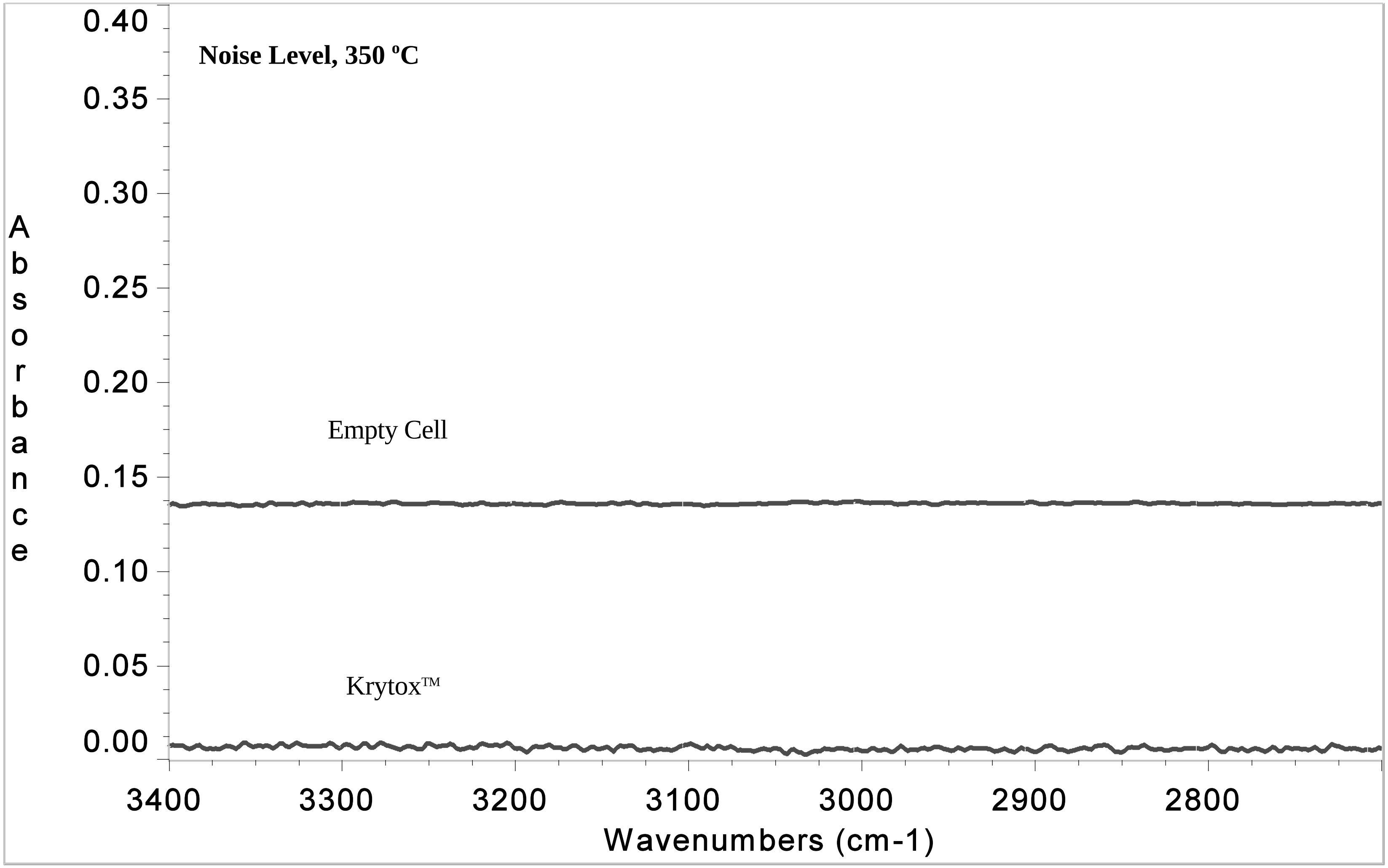
cell manufacturer's instruction, the Viton™ o-ring was replaced with a layered construction of two Grafoil™ spacers (which were flat washers) and a stainless steel flat washer. The design of the spacer/o-ring assembly for the pressurization chamber windows was not modified as these parts were provided with cooling by circulating liquid which prevented their exposure to the high temperatures in the sample cavity. The layered construction allowed for temperature extension to 350 °C and provided a seal between the sample chamber and the atmosphere. However, the sample space was not sealed away from the gas pressurization chamber. When liquid samples were introduced, they leaked across the sample chamber seal into the gas pressurization chamber.

The layered construction did allow for the collection of spectra using the empty cell at 350 °C and 35 bars. There was some concern that background infrared radiation might interfere with the signal at such a high temperature. Scanning the empty cell as both background and sample should have generated a straight line, with any aberration being indicative of the noise level. Figure 5-27 presents the noise level at 350 °C under a 35 bars blanket. The noise level was no worse than in previously acquired spectra, and concerns over interference from background radiation were allayed.

Solubility of Hydrocarbons in Krytox™

In order to extend the stability studies to 350 °C, it was necessary to replace APF-240™ (b.p. 240 °C) with a higher boiling solvent. The solvent chosen was a DuPont proprietary product, trade named Krytox™. Krytox™ is a line of general purpose lubricants, with varying degrees of heat resistance. The product chosen for this study was Krytox™ GPL-107. Krytox™ is a perfluoropolyalkylether. It has a boiling point of

Figure 5-27


Noise Level, 350 °C
Empty Cell
Krytox™
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

over 450 °C, is quite stable at 350 °C, and is sufficiently transparent to infrared radiation in the range of interest to this study. On the other hand, it is a very viscous liquid and proved difficult to work with.

The compounds of interest to this study are even less soluble in Krytox™ than they are in APF-240™. The solubility of naphthalene in Krytox™ is quite low, less than 1 gram per liter 65 °C. It was necessary to heat the mixture to 130 °C to achieve dissolution at the one gram per liter level. This made sample handling quite difficult, and it was anticipated that special sample handling techniques would need to be developed.

Krytox™ is not soluble in conventional organic solvents, or in halogenated organics, which made reactor clean up difficult. Historically, DuPont had recommended Freon-113™ as a solvent for Krytox™, but due to environmental concerns now recommends perfluorohexane or methylnonafluorobutyl ether (HFE). Initial efforts to locate a supplier of perfluorohexane failed, but a gallon of HFE (b.p. 60 °C) was obtained. HFE proved to be an excellent solvent for Krytox™, one part Krytox™ being soluble in about two parts HFE at room temperature. A gallon of perfluorohexane was eventually obtained. Perfluorohexane also proved to be an excellent solvent for Krytox™, and replaced HFE as the solvent of choice for reactor clean up. Perfluorohexane was the preferred solvent because it contains no C-H bonds which might have interfered with C-H stretches in the samples under study if any of the clean up solvent was residual in the reactor during the stability tests.

One further point about Krytox™ and its high boiling point was worth noting. DuPont cautioned strongly against injecting Krytox™ on a GC column. Because the boiling point of Krytox™ is greater the temperature of the column, build up of residue on the column could be expected. This build up of residue could interfere with analytical results in future tests. DuPont suggested using an extraction technique to remove the reaction products from the Krytox™ before injecting on the GC.

Testing of the High Temperature Kalrez™ O-ring

A high temperature Kalrez™ o-ring was obtained from the cell manufacturer and tested at 360 °C in a muffle furnace. The o-ring did not deform, so it was then tested as the seal between the sample cavity and the gas pressurization chamber. The initial test consisted of pressurizing the empty cell (no sample present) with 35 bars hydrogen in the sample cavity and 35 bars nitrogen in the gas pressurization chamber. The cell was heated gradually to 350 °C and maintained there for one hour. Upon disassembly of the cell, the Kalrez™ o-ring appeared to be intact.

Background scans, 250 °C, 300 °C and 350 °C

The cell was filled with neat Krytox™ and background scans were obtained at 250 °C, 300 °C and 350 °C, all under a 35 bars hydrogen blanket. The noise level at 350 °C with Krytox™ as sample was only slightly greater than the noise level obtained for the empty cell. Figure 5-27 (p. 119) also presents the noise level for the AABSPEC cell when filled with neat Krytox™ at 350 °C.

Troubleshooting of the Cooling Unit

During normal operation, the combination of the flowrate to the cell and low temperature of the coolant is sufficient to cause condensation of atmospheric moisture on the coolant lines at the discharge of the chiller. During the collection of the background scans at 350 ^{o}C, it was observed that this condensation had stopped. Also, the return coolant line had become hot. Both of these observations indicated that the coolant flow was inadequate. Measurements indicated that the flowrate through the cell was only 34 milliliters per minute. The manufacturer's specifications call for a minimum flowrate of 70 milliliters per minute for sustained high temperature operation.

During the 230 ^{o}C testing, quick-connects were installed in the plumbing lines on an interior panel of the spectrometer to facilitate installation and removal of the cell. Since the cooling coils within the cell are plumbed with 1/8 inch copper tubing, 1/8 inch copper tubing was likewise used from the cell to the quick connects and from the quick connects to the suction and discharge ports of the chiller. To decrease the resistance to flow, the 1/8 inch line form the chiller discharge to the quick-connect panel and from the quick-connect panel back to the chiller suction were replaced with 1/4 inch copper tubing. The flowrate improved substantially.

Modification of the Pathlength

As noted earlier in this document, the PTFE pathlength spacer used in operations up to 230 ^{o}C was not suitable for use at temperatures above 250 ^{o}C. The Grafoil™ spacer which replaced the 0.5 mm PTFE spacer was 0.4 mm thick. Furthermore, Grafoil™ compresses to about 60% of its original thickness when subjected to a sufficient mechanical load. Since the Grafoil™ spacer bears the same load that the Kalrez™ o-ring bears in forming the seal between the sample cavity and the gas pressurization chamber, compression of the spacer was expected. Since, according to Beer's Law, absorbance peak height is directly proportional to pathlength, a reduction in absorbance peak height of 80% times 60%, or roughly one-half, can be expected. Testing at 130 ºC using naphthalene and tetralin confirmed this expectation. Because of the decrease in pathlength, it was necessary to use more concentrated solutions in order to achieve absorbance peak heights similar to those obtained in the 230 ºC portion of this work. Also, more concentrated solutions could be employed while maintaining operation in the linear region of the Beer's Law Curve.

Amendments to the Procedure for the Stability Studies

The procedure for the stability studies was amended to include the handling of samples at 130 ºC. Also, the holding of samples at intermediate temperatures for one-half hour was eliminated. Since the reactive compounds begin to react at temperatures significantly below 250 º C, holding at temperatures less than 250 ºC could alter the final product slate. For this reason, the samples were heated to the temperature of the study as quickly as possible, but not to exceed the cell manufacturer's criterion of 50 ºC in 10 minutes. For the reactive molecules, the sampling interval was shortened to 15 minutes and in some cases 10 minutes, in order to follow more closely the course of the reaction.

Naphthalene Stability Studies, 250 ºC, 300 ºC and 350 ºC

Naphthalene was subjected to the amended stability study as follows:

(1) Heated from 130 ºC to 250 ºC at a rate of 5 ºC per minute,

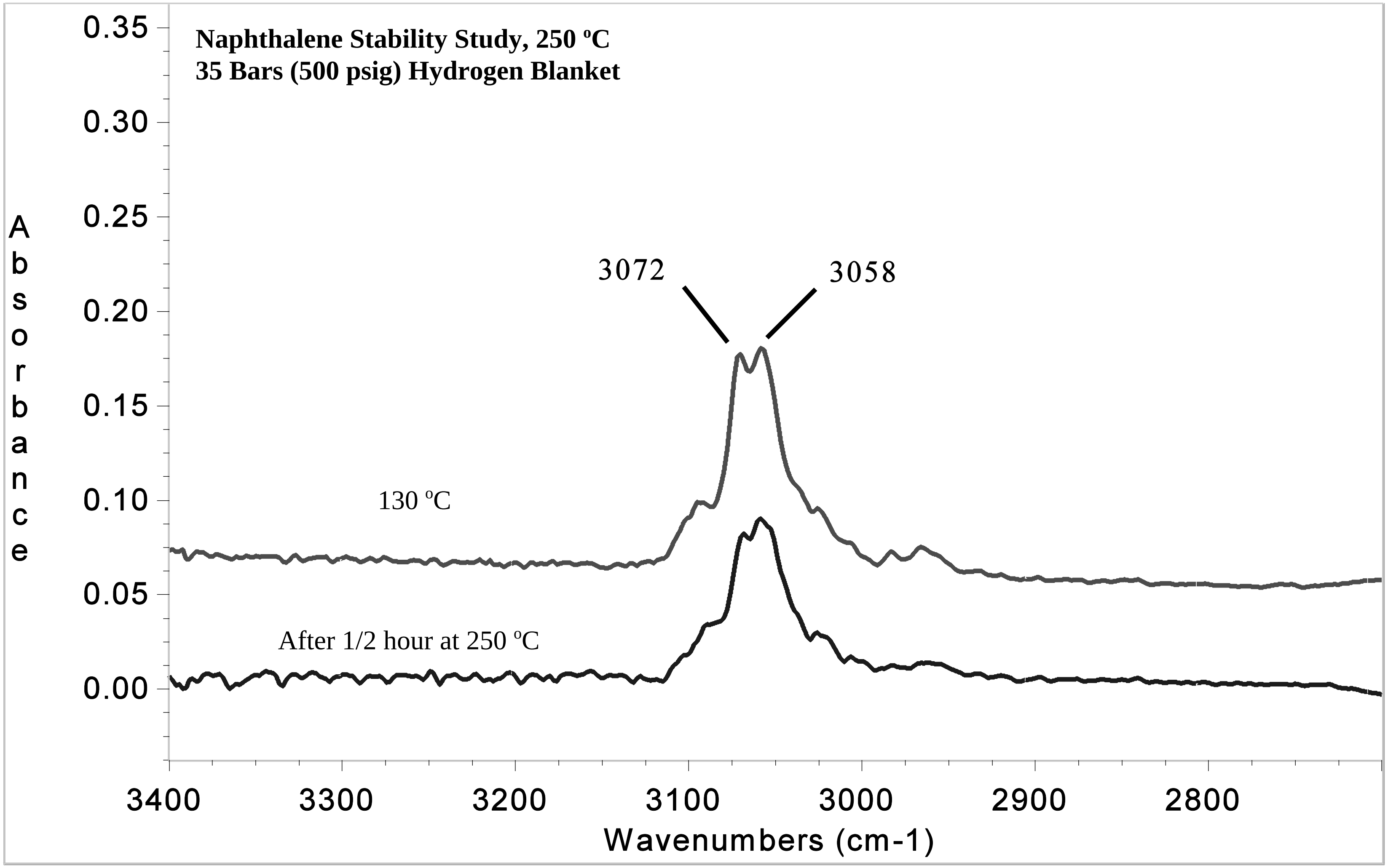
(2) held at 250 ºC for one half hour,

(3) held at 300 ºC for one half hour and

(4) held at 350 ºC for one hour.

Figure 5-28 presents the spectrum of naphthalene at 130 ºC, along with the spectrum of

Figure 5-28


Naphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
3072
3058
130 ºC
After 1/2 hour at 250 ºC
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

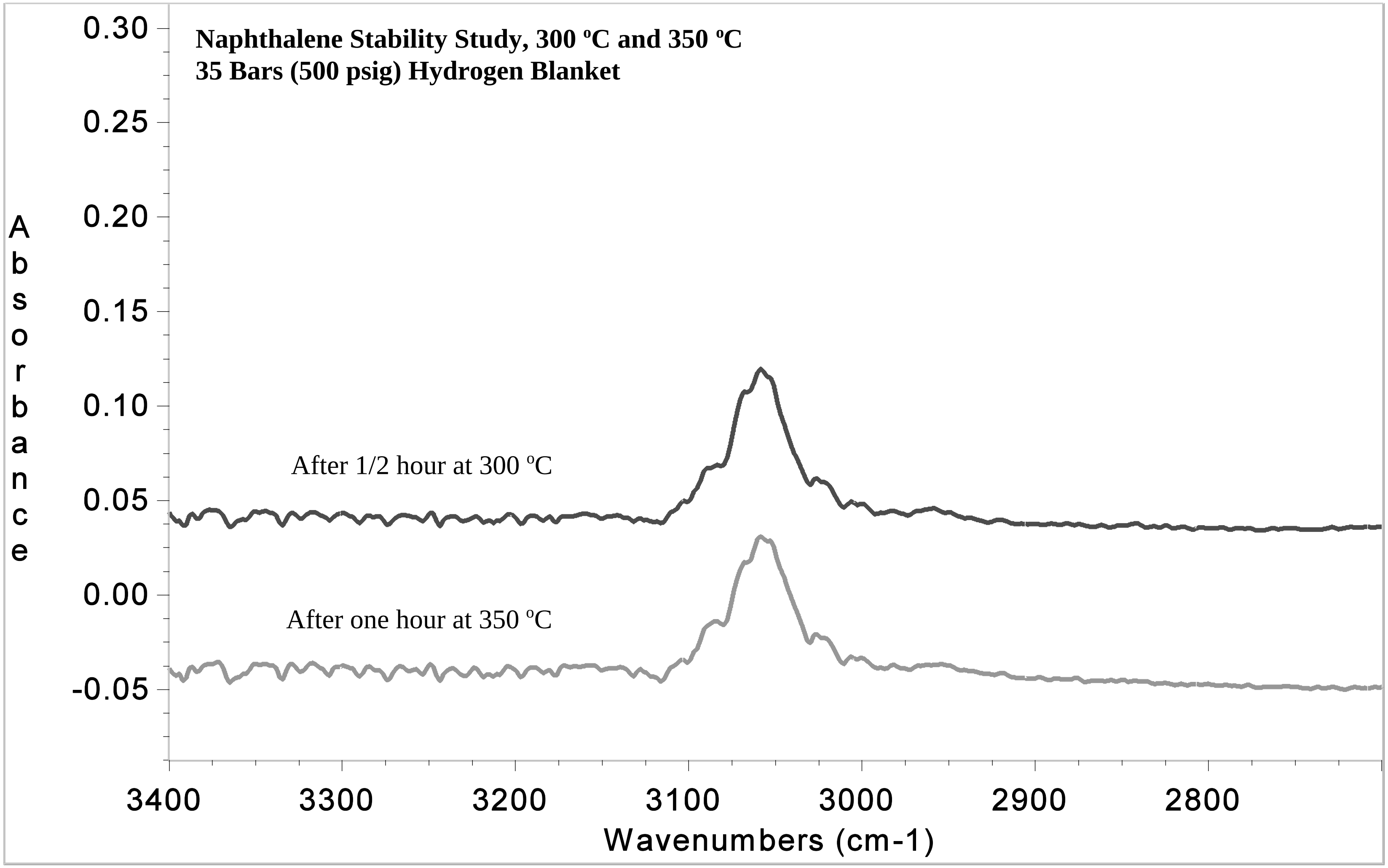
naphthalene after step (2) above. Figure 5-29 presents the spectra of naphthalene after steps (3) and (4) above. After one hour at 350 °C, the coolant flow again proved inadequate. The test was aborted. GC analysis, using a toluene extraction procedure described in Appendix C, indicated that the product was pure naphthalene.

Two items are worthy of note in the high temperature spectra. The first is that although the peaks at 3058 cm^{-1} and 3072 cm^{-1} are beginning to merge, the merging is not as complete as it was in the previously reported 230 °C stability studies. Evidently, some time is required for this phenomenon to take place. This merging of the peaks has been shown to be a temperature effect; as the sample cools, the two distinct peaks become apparent again.

The second item of interest is the loss of absorbance peak height at 250 °C and higher as compared to the 130 °C scan. Vaporization of naphthalene into the vapor space above the reactor was suspected, and possibly loss of interferometer signal strength due to deposition of char on the sample window, as had been observed in previous studies. Both of these possibilities were subsequently addressed.

Upon disassembling the cell for cleaning, a brown tar-like residue was noticed on the sample window and the stainless steel reflecting surface which is in contact with the sample during operation. Char formation seems unavoidable at these high temperatures, and since any buildup of char can obscure the optical path, complete disassembly and cleaning of the reactor after every run was indicated. The procedure was amended accordingly. Furthermore, the interferometer signal strength, both voltage and gain, is to be recorded from the initial scan of the reactant to the final scan of the cooled products,

Figure 5-29


Naphthalene Stability Study, 300 ºC and 350 ºC
35 Bars (500 psig) Hydrogen Blanket
After 1/2 hour at 300 ºC
After one hour at 350 ºC
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

in order to monitor any decay therein.

Minimization of the Vapor Space above the Reactor

During operation of the cell at 230 ºC, the compounds in this study were only slightly above their normal boiling points, and therefore, their vapor pressures were only slightly above one atmosphere. This was substantially lower than the total pressure of 35 bars used in this work. Little volatilization of solute into the vapor space above the reactor was expected under these conditions. However, at the higher temperatures employed in this portion of the work, the vapor pressures become significant compared to 35 bars. At 350 ºC, the vapor pressures of naphthalene, tetralin and cis-decalin are 10, 11 and 13 bars, respectivley. It was, therefore, desirable to reduce the volume of the vapor space above the reactor to minimize volatilization of the solutes. The limiting factor for reducing this volume was the length of tubing required to connect the reactor to the hydrogen supply. About 20 cm of tubing was required. Since it is necessary to monitor the pressure during the reactions, this volume must also include a pressure indicating device. This was accomplished by connecting an inverted Bourdon Tube pressure gauge filled with oil between the hydrogen supply and the reactor. Because of the small internal diameter of 1/8 inch tubing, the 20 centimeter run of tubing provided a volume of about one milliliter. A valve was installed so that the reactor/pressure gauge assembly could be isolated from the hydrogen supply after the reactor was pressured up.

Further Cooling System Modifications

The cooling system in the AABSPEC cell consists of two coils of 1/8 inch copper tubing. The coils are in a parallel arrangement with a single source and a single discharge. The coolant flow is divided among the two coils. To increase the flow of coolant through the coils, an auxiliary pump was installed and each coil was provided with its own pump. Furthermore, the 1/8 inch quick-connects were replaced with 1/4 inch quick-connects and all the 1/8 tubing outside the cell, other than the minimum required to make connections, was replaced with 1/4 inch tubing.

Decalin Stability Studies, 250 °C, 300 °C and 350 °C

Decalin proved to be stable at temperatures up to 350 °C under a 35 bars hydrogen blanket. Figure 5-30 presents the spectrum of decalin at 130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 250 °C, and after one hour at 250 °C. The spectra at 250 °C show a significant loss in the absorbance peak heights when compared to the spectrum at 130 °C. This loss is discussed in the next paragraph. Figure 5-31 presents the scan after one-half hour at 300 °C, the scan after three hours at 350 °C, and the scan after cooling to 130 °C. The ratio of the absorbance peak heights did not change, indicating that no reaction had taken place. GC analysis confirmed that the product was pure decalin.

The loss of absorbance peak heights mentioned in the previous paragraph will now be addressed. The record of the interferometer signal strength showed only a slight decline in signal strength, not enough to account for such a substantial loss in peak heights. Since the volume of the vapor space above the reactor was only one milliliter, volatilization of solute into the vapor space was not suspected. Upon disassembly of the cell for routine cleaning, sample was found in the gas pressurization chamber. The inlet and exit windows were wet with sample solution, thus accounting for the loss in

Figure 5-30

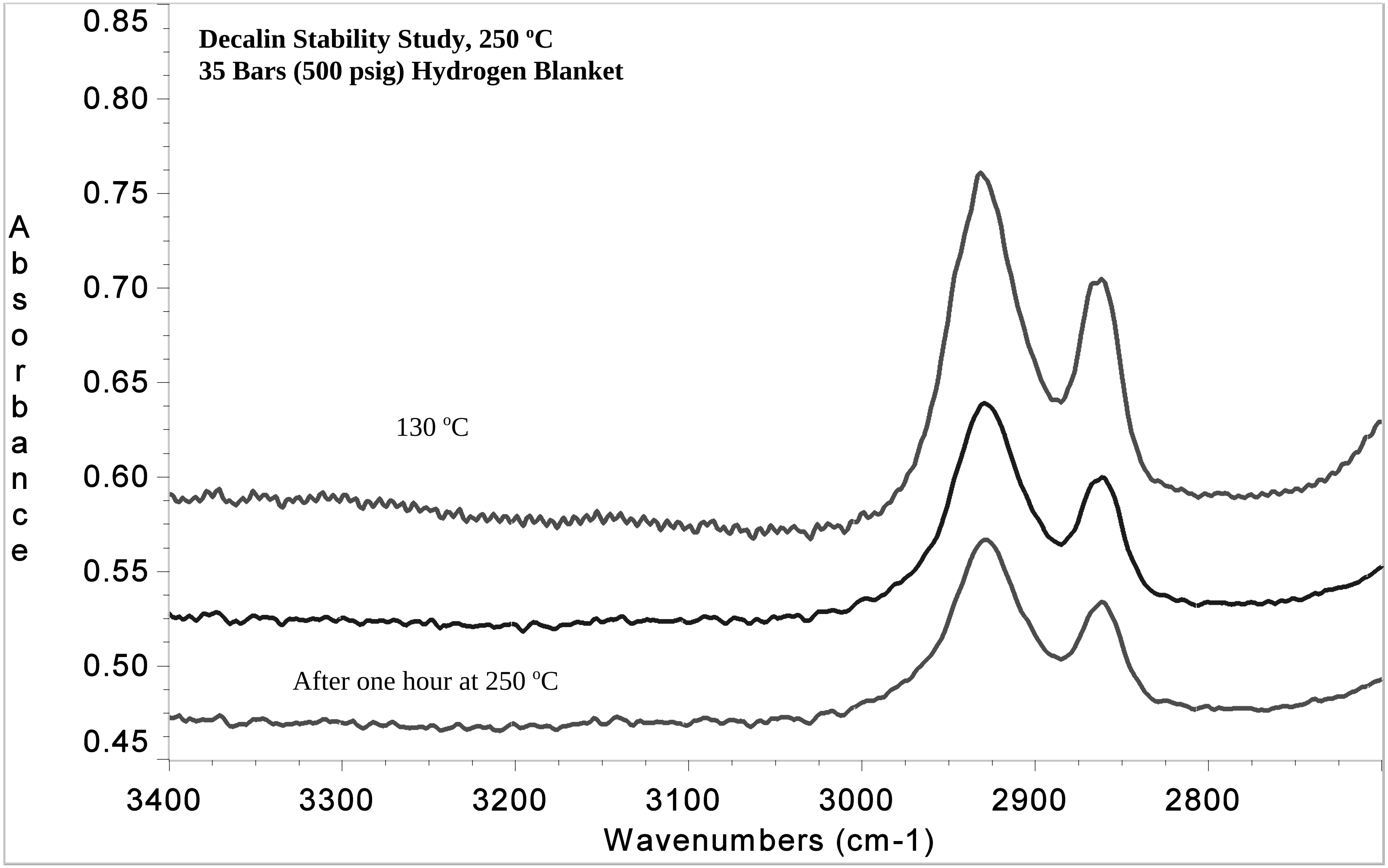
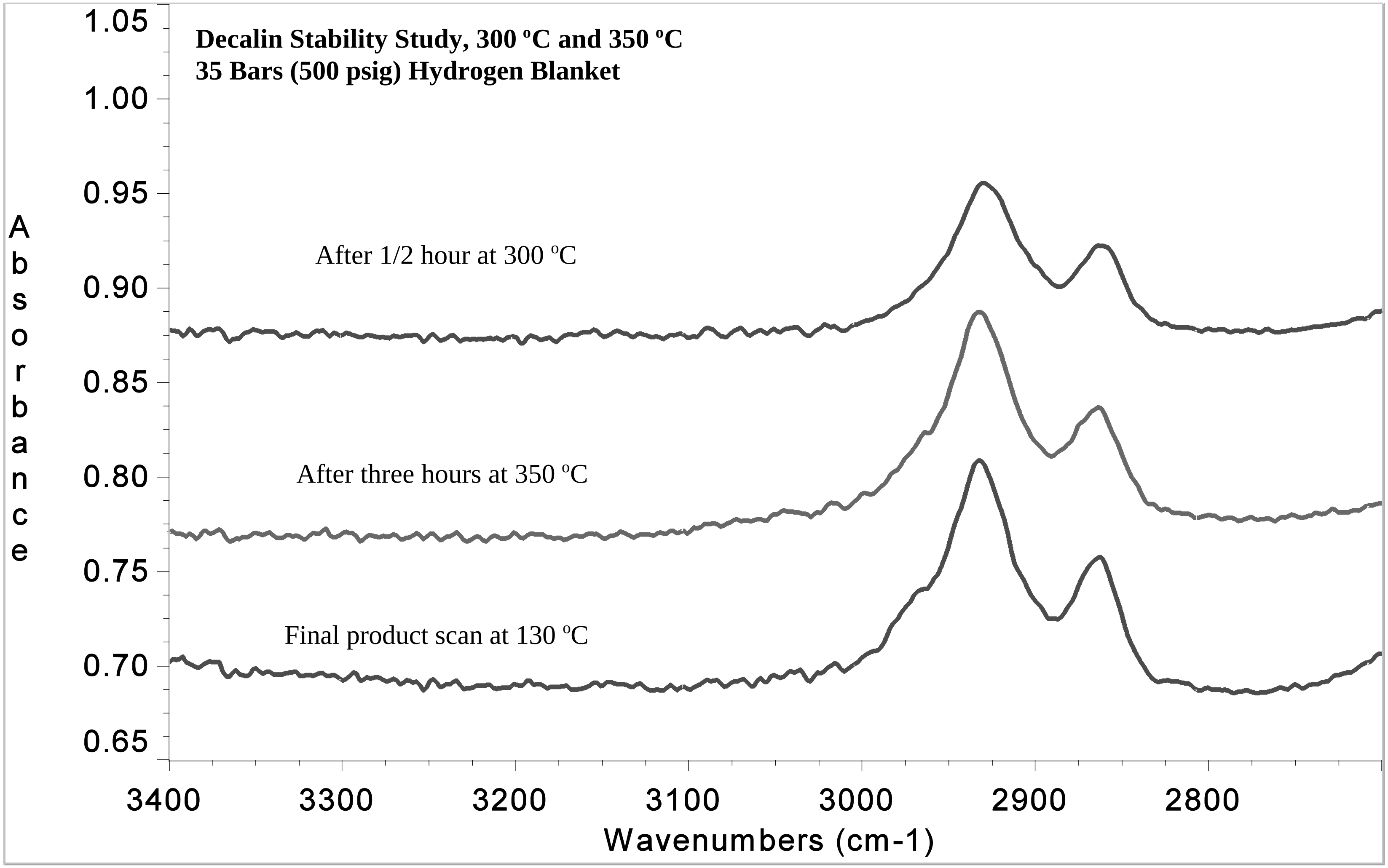

Decalin Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
After one hour at 250 ºC
Absorbance
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-31


Decalin Stability Study, 300 ºC and 350 ºC
35 Bars (500 psig) Hydrogen Blanket
After 1/2 hour at 300 ºC
After three hours at 350 ºC
Final product scan at 130 ºC
Absorbance
1.05
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

absorbance peak height. The Kalrez™ o-ring had failed and allowed the sample solution to enter the gas pressurization chamber. It was noticed that the heating of the reactor had caused the pressure in the sample cavity to rise above the pressure in the gas pressurization chamber, and this may have caused the o-ring to split. The procedure was amended to provide for a slight pressure differential across the sample window. It was thought that maintaining the gas pressurization chamber at about one bar higher pressure than the sample cavity might prevent the rupture of the Kalrez™ o-ring in future tests.

Tetralin Stability Study, 250 °C, 300 °C and 350 °C

Tetralin proved to be stable at temperatures up to 350 °C under a 35 bars hydrogen blanket. Figure 5-32 presents the spectrum of tetralin at 130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 250 °C, and after three hours at 250 °C. Figure 5-33 presents the initial scan at 300 °C and the scan after two hours at 300 °C. Figure 5-34 presents the initial scan at 350 °C, the scan after three hours at 350 °C, and the scan after cooling to 130 °C. Comparison of the 130 °C scans before and after testing revealed a slight increase in the absorbance peak heights, although it was not clear why. It was clear, however, that losses due to volatilization had been minimized and that the integrity of the Kalrez™ o-ring was maintained.

GC analysis confirmed that the product was pure tetralin. This is in contrast to the results of the 230 °C hydrogen blanket stability study, in which the product analyzed as 84% tetralin and 16 % cis-decalin. The latter result was suspect at the time, because it was not thought likely that tetralin would hydrogenate to decalin under the conditions of the stability test. Further scrutiny of previous GC results revealed a systematic error

Figure 5-32

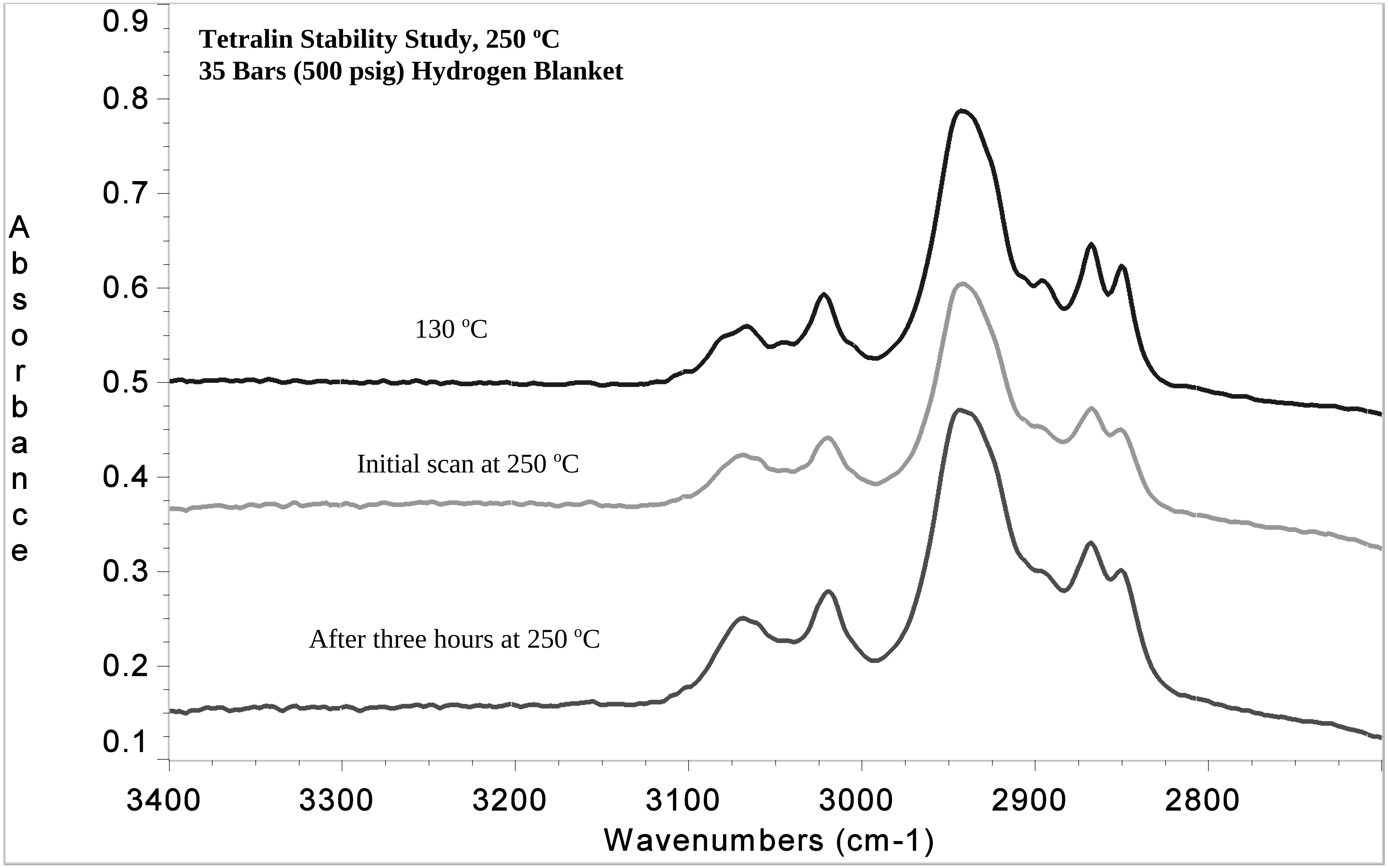
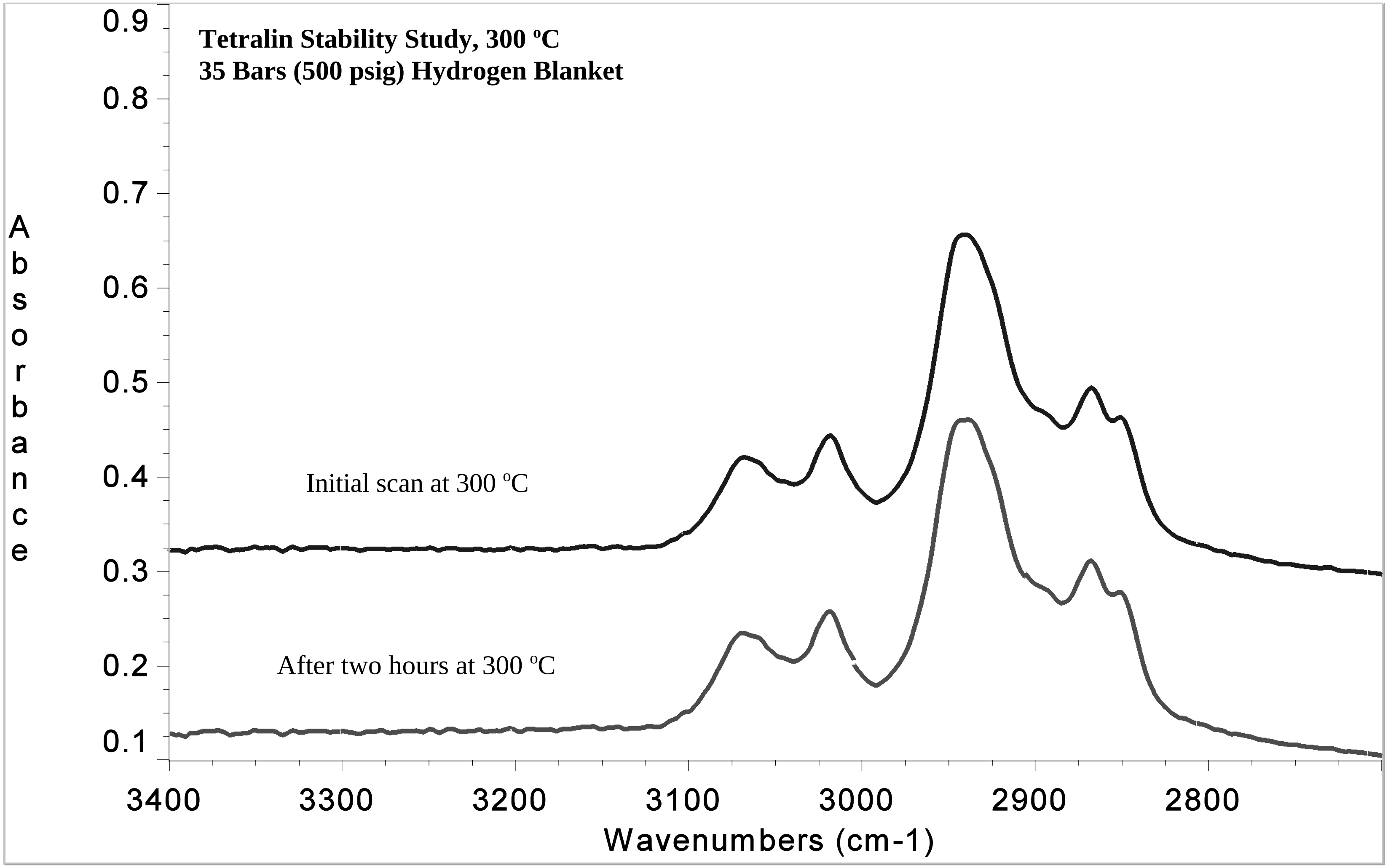
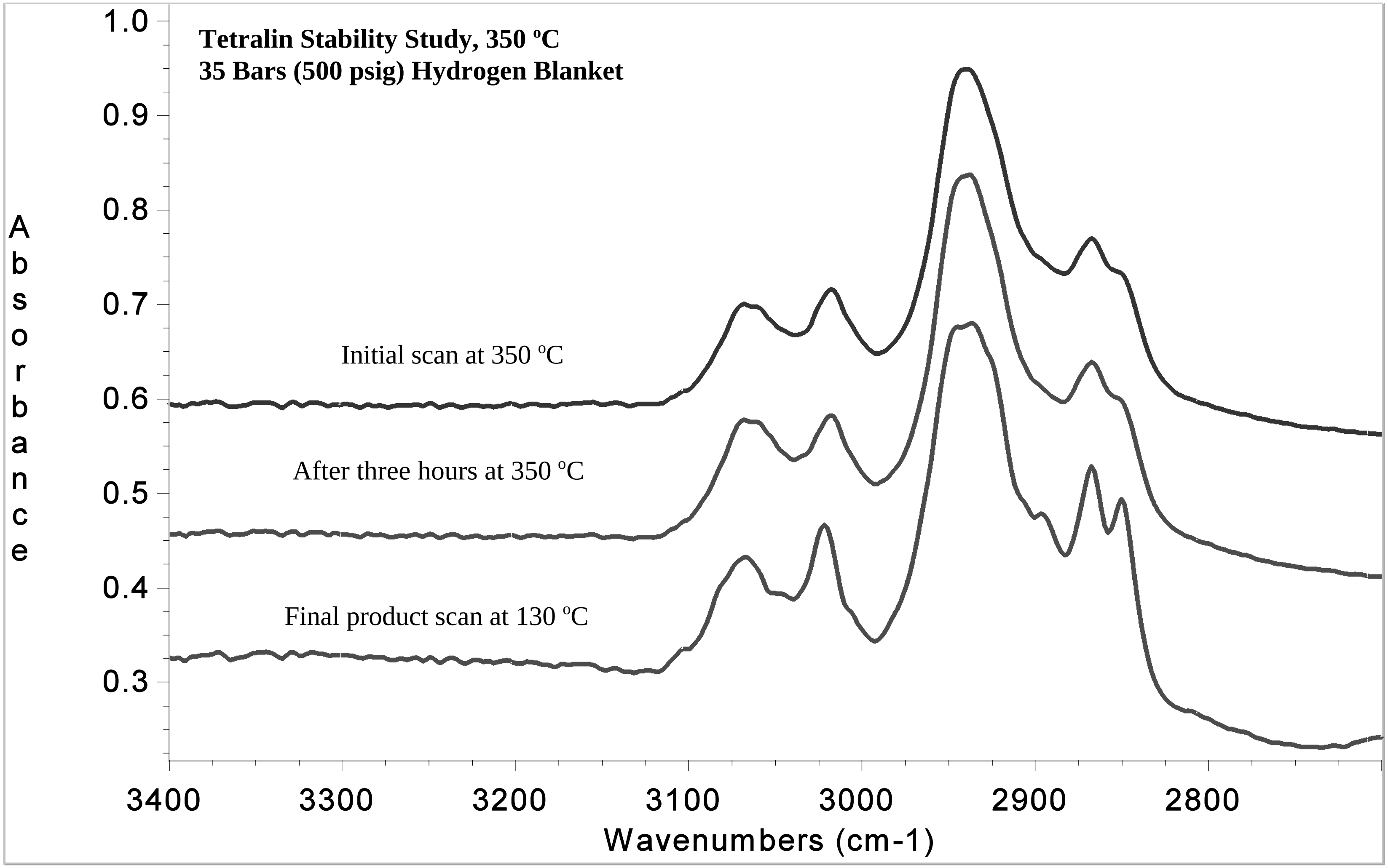

Tetralin Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 250 ºC
After three hours at 250 ºC
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-33



Tetralin Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
Initial scan at 300 ºC
After two hours at 300 ºC
Absorbance
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-34


Tetralin Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
Initial scan at 350 ºC
After three hours at 350 ºC
Final product scan at 130 ºC
Absorbance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

in that a number of products from the 230 ºC stability tests contained products from the immediately previous test. A number of previous GC results are now suspect, particularly the result of the 230 ºC hydrogen blanket cis-decalin stability test. GC analysis of the product from this stability study indicated that the product contained 5% naphthalene, whereas subsequent testing has clearly demonstrated the stability of cis-decalin. It was reasoned that products from previous stability studies were residual in the cell, and that copious flushing had not removed them from the cell. Since complete disassembly and cleaning of the cell between runs had already been necessitated by deposition of char on the sample window and reflecting surface, no amendment to the procedure was necessary at this time.

Isotetralin Stability Study, 250 ºC

As expected, isotetralin proved to be highly reactive at 250 ºC under a 35 bars hydrogen blanket. Figure 5-35 presents the spectrum of isotetralin at 130 ºC, along with the spectrum after heating at a rate of 5 ºC per minute to 250 ºC. A substantial reaction had taken place by the time 250 ºC was reached. Figure 5-36 presents the spectrum of isotetralin after 30 minutes, after one hour, and after two hours at 250 ºC. Figure 5-37 presents the spectrum after three hours at 250 ºC and after cooling to 130 ºC. The reduction in the peak heights which are characteristic of isotetralin, at 2826 cm^{-1}, 2854 cm^{-1}, 2884 cm^{-1} and 3036 cm^{-1}, along with the increase in aromaticity and the increase in peak height at 2936 cm^{-1} clearly indicated that a reaction had taken place. GC analysis indicated that isotetralin reacted completely to give 46% naphthalene, 34 % tetralin and 20% 1,4-dihydronaphthalene. A trace of 1,2-dihydronaphthalene was also detected.

Figure 5-35

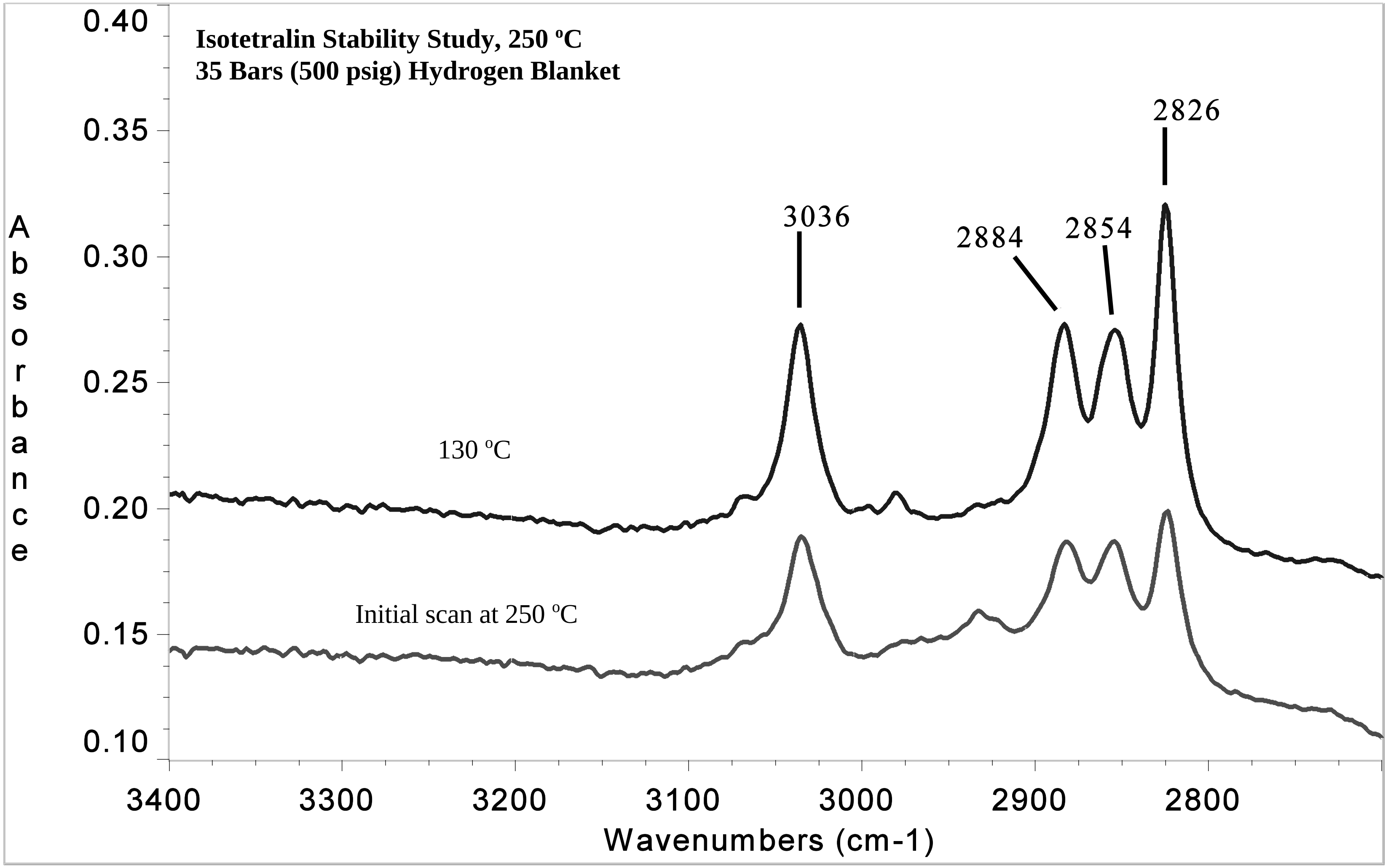

Isotetralin Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
2826
3036
2884
2854
130 ºC
Initial scan at 250 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-36

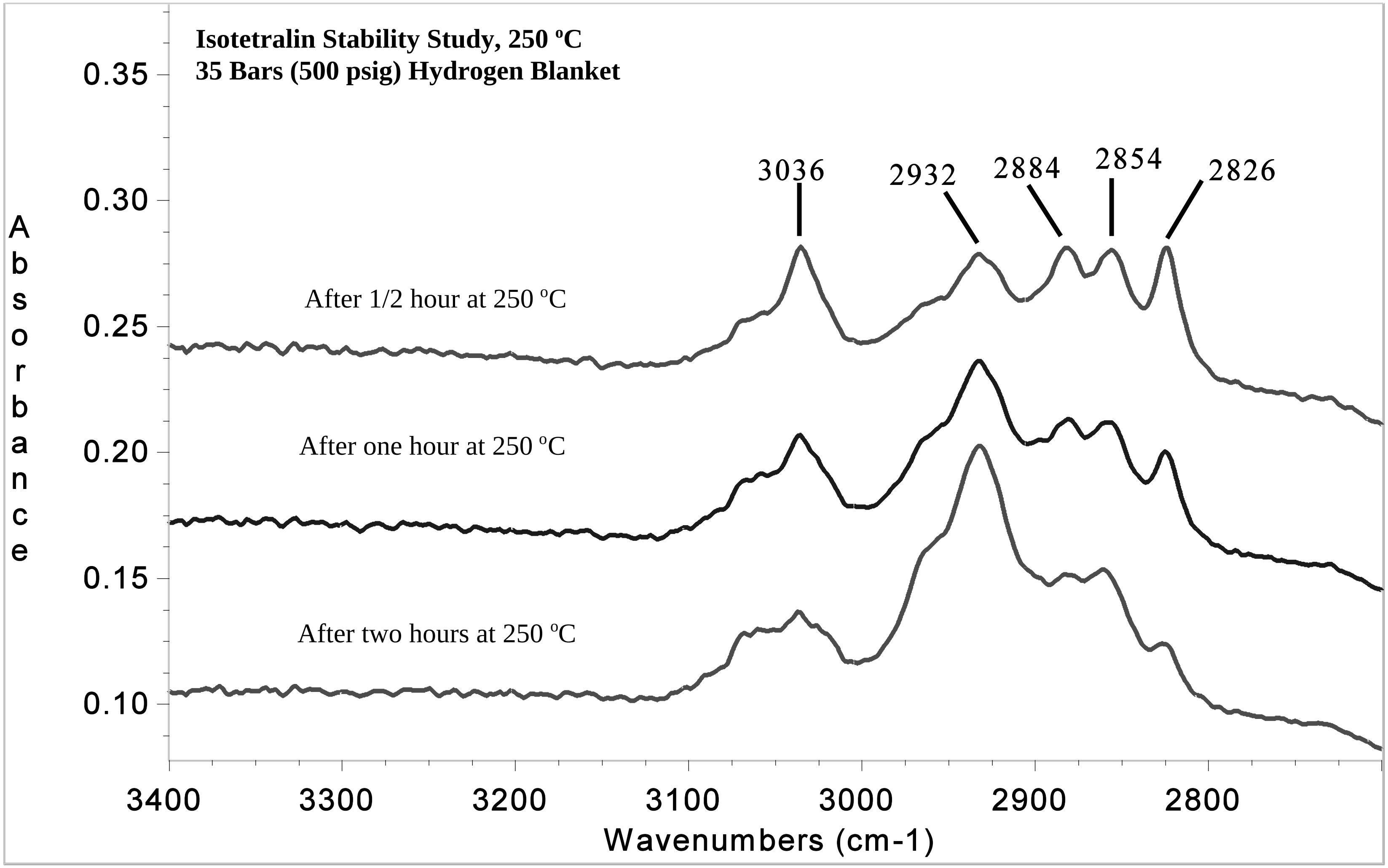

Isotetralin Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
3036
2932
2884
2854
2826
After 1/2 hour at 250 ºC
After one hour at 250 ºC
After two hours at 250 ºC
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-37

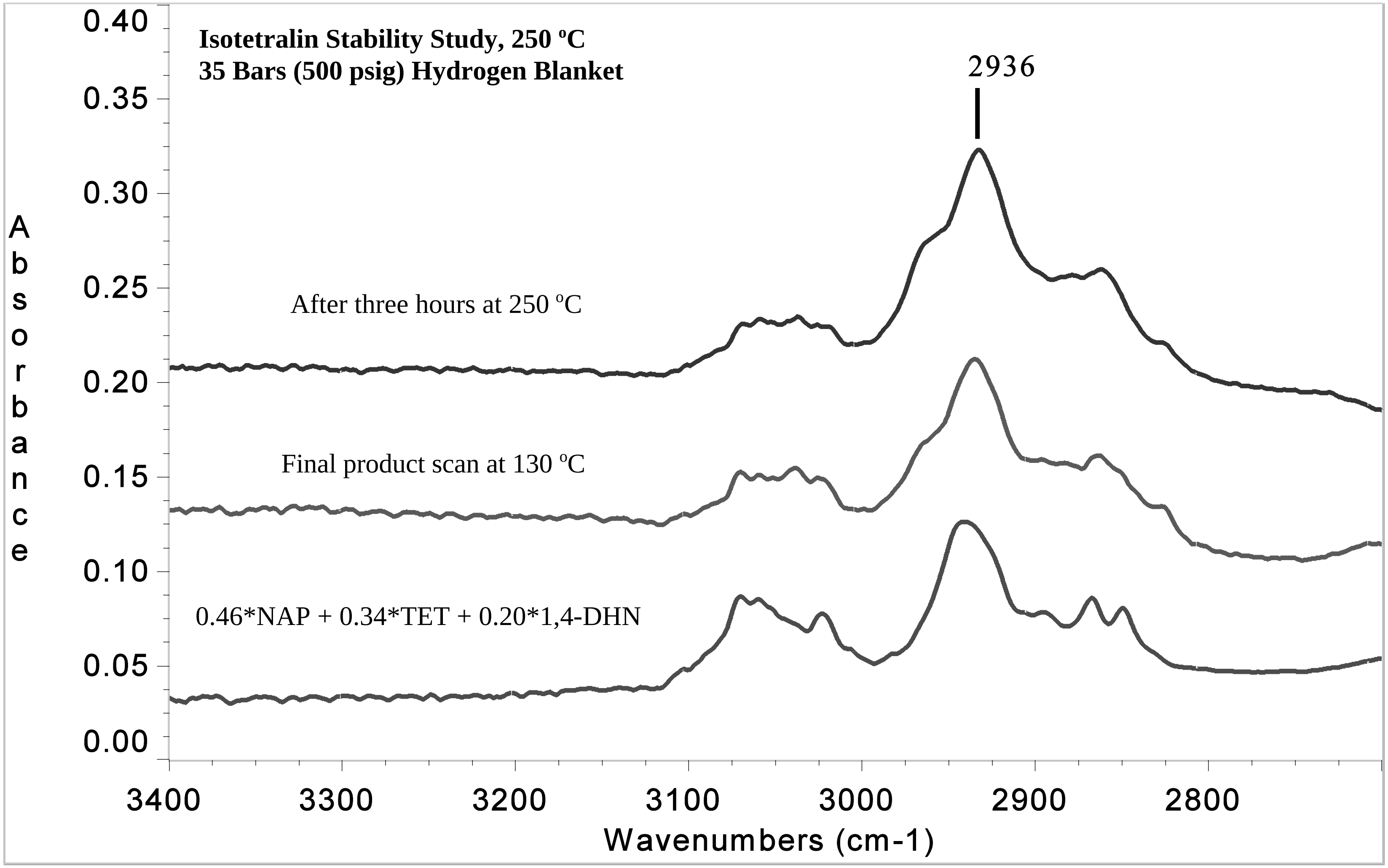

Isotetralin Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
2936
After three hours at 250 ºC
Final product scan at 130 ºC
0.46*NAP + 0.34*TET + 0.20*1,4-DHN
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

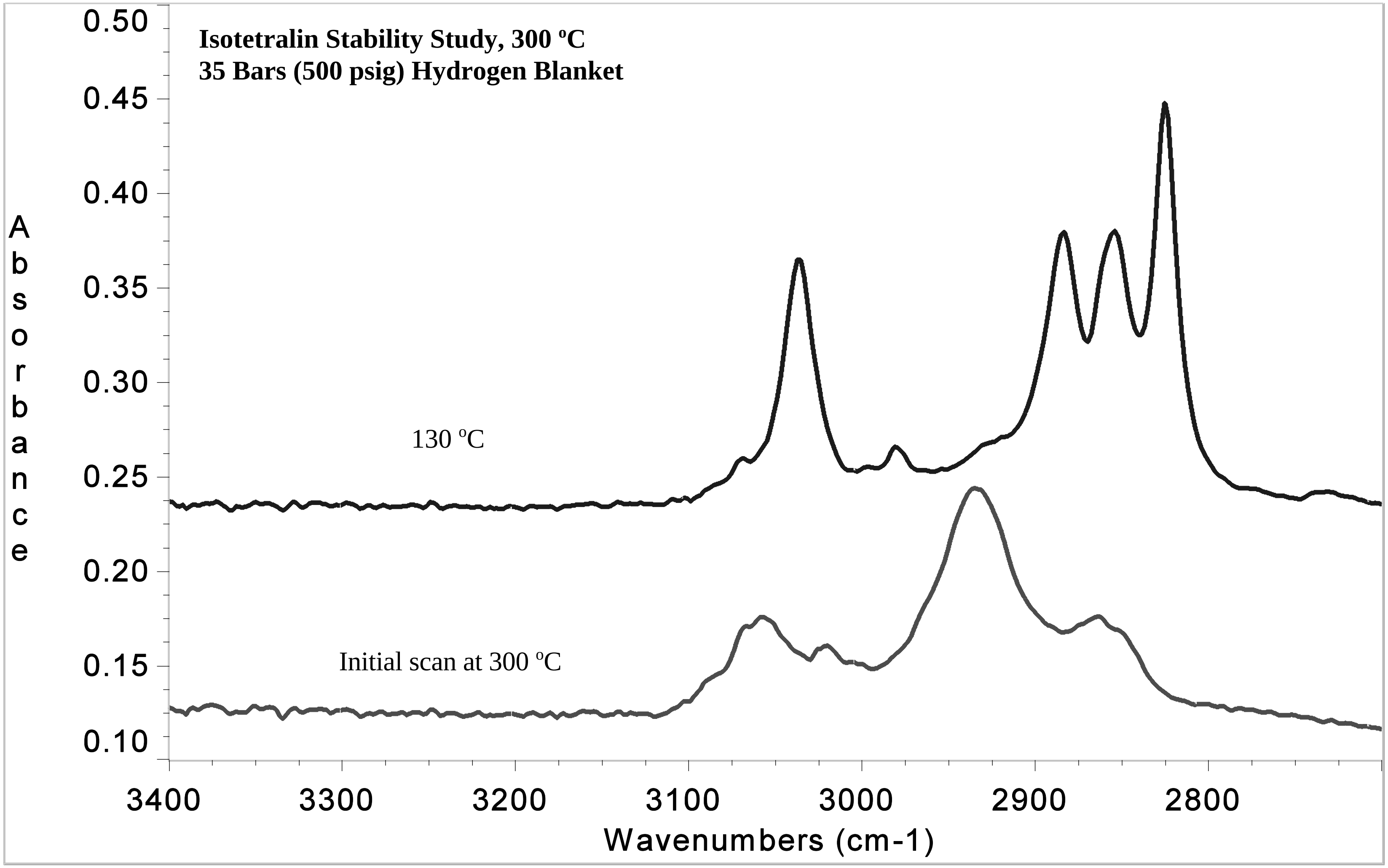
Figure 5-37 also presents the synthetic scan generated using these results. Agreement with the final product scan was considered fair.

Isotetralin Stability Study, 300 °C

The initial scan of isotetralin at 130° C using the stock solution prepared for the 250 °C stability study just one day earlier resulted in considerably weakened absorbances. It was suspected that storage of the solution in the oven at 130 °C to prevent precipitation of solute resulted in vaporization of solute out of the solution. The procedure was amended to include preparation of the reactant solution immediately before the reaction is conducted.

Isotetralin proved to be highly reactive at 300 °C under a 35 bars hydrogen blanket. Figure 5-38 presents the spectrum of isotetralin at 130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 300 °C. A substantial reaction had taken place by the time 300° C was reached. Figure 5-39 presents the spectra of isotetralin after 15 minutes, after 30 minutes, and after 45 minutes at 300 °C. The reaction was stopped after 45 minutes in the hope of catching a reaction intermediate. The disappearance of the characteristic isotetralin peaks and the growth of the aromatic peaks and the peak at 2934 cm^{-1} indicated that a reaction had taken place. GC analysis indicated that isotetralin reacted completely to give 63% naphthalene, 32 % tetralin, and 5% 1,2-dihydronaphthalene. Figure 5-40 presents the synthetic scan generated using these results. For the purpose of comparison, the reaction product scan, after cooling to 130 °C, is also presented in this figure. Agreement between the synthetic scan and the final product scan was considered good, except that the synthetic scan showed a bias in

Figure 5-38



Isotetralin Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 300 ºC
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-39

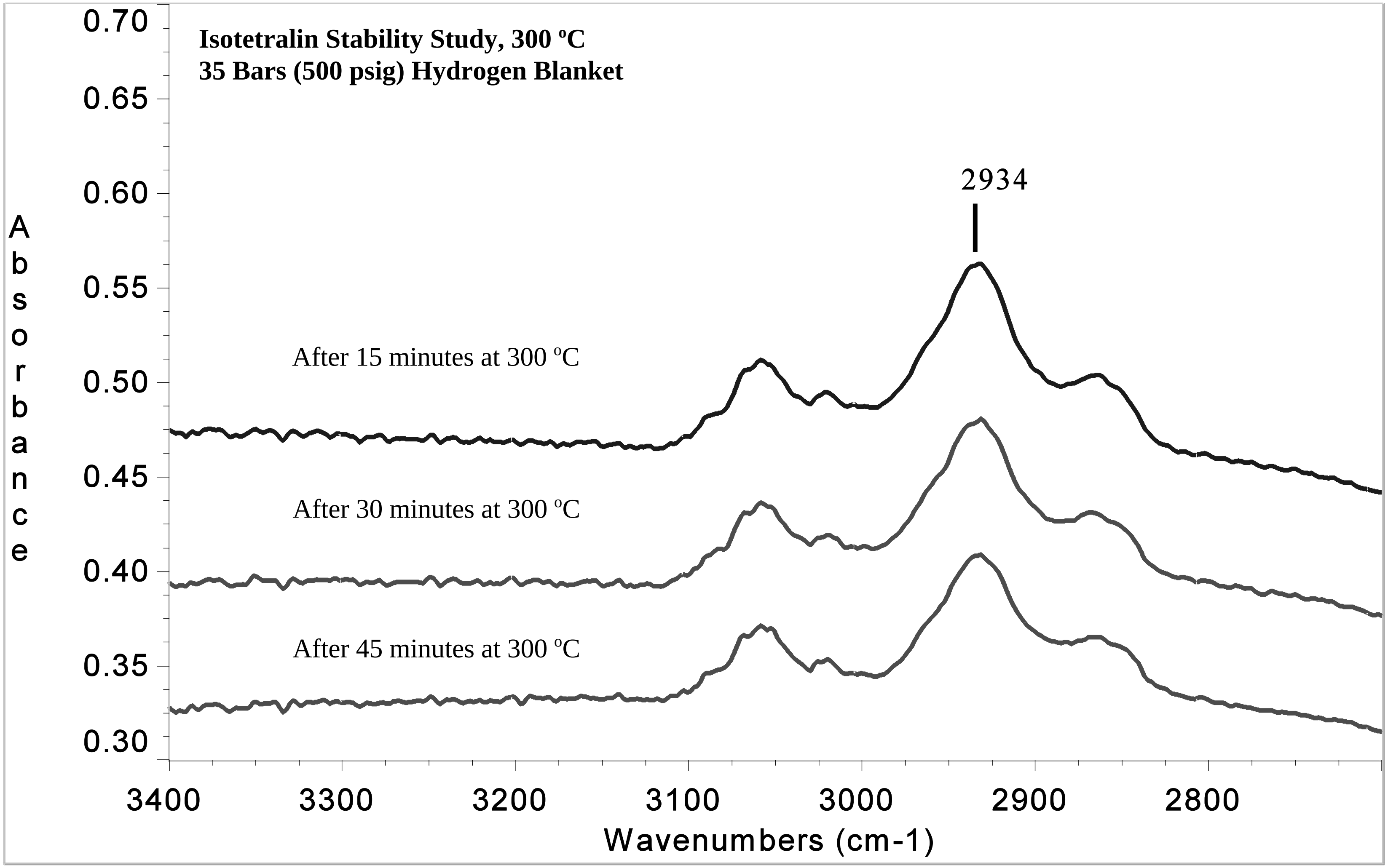
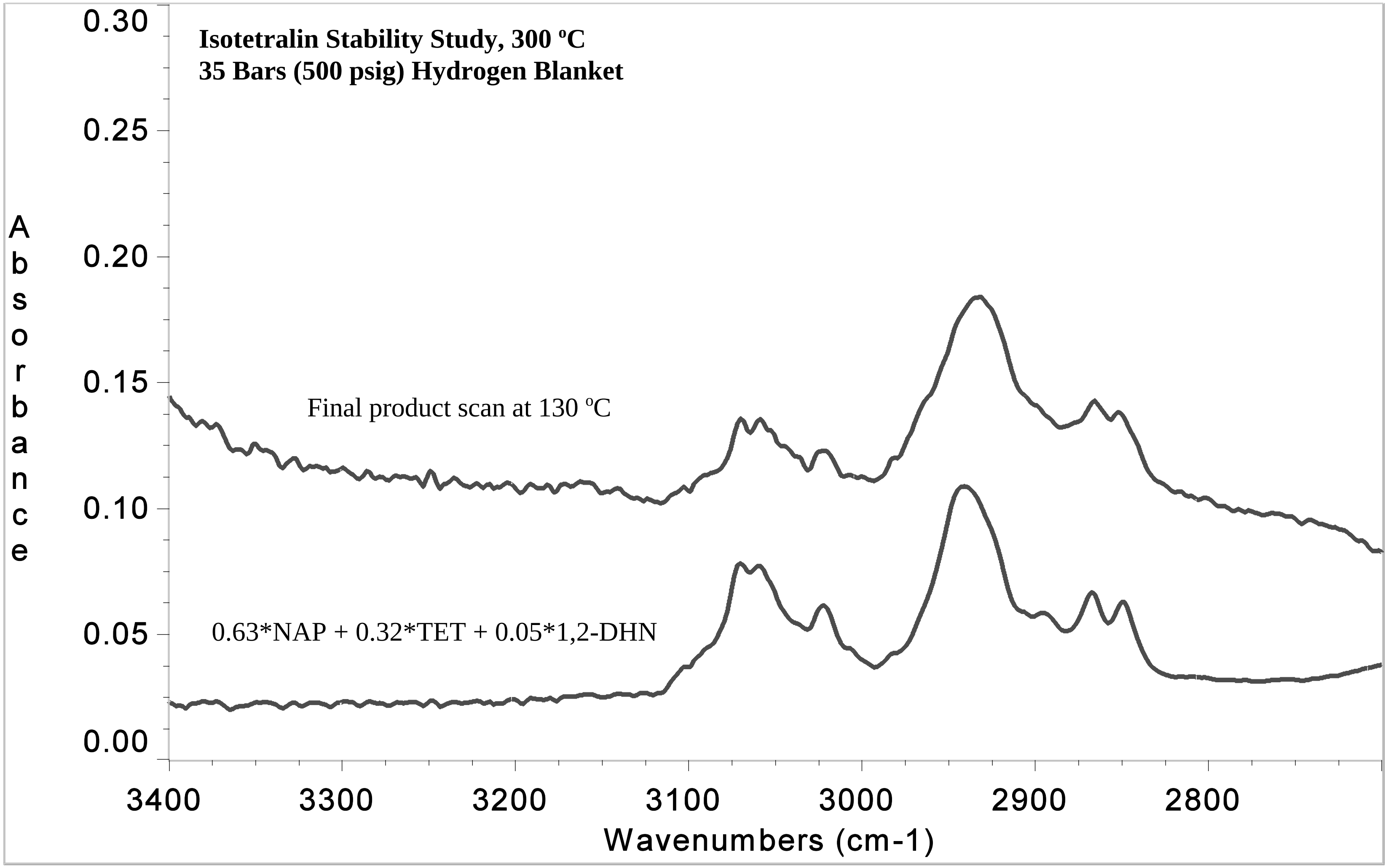

Isotetralin Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
2934
After 15 minutes at 300 ºC
After 30 minutes at 300 ºC
After 45 minutes at 300 ºC
Absorbance
0.70
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-40


Isotetralin Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
Final product scan at 130 ºC
0.63*NAP + 0.32*TET + 0.05*1,2-DHN
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

favor of the aromatic peaks which are characteristic of naphthalene.

Isotetralin Stability Study, 350 ºC

Isotetralin proved to be highly reactive at 350 ºC under a 35 bars hydrogen blanket. Figure 5-41 presents the spectrum of isotetralin at 130 ºC, along with the spectrum after heating at a rate of 5 ºC per minute to 350 ºC. A substantial reaction had taken place by the time 350 ºC was reached. Figure 5-42 presents the spectrum of isotetralin after 10 minutes, 20 minutes, and after one hour at 350 ºC. Figure 5-43 presents the scan after two hours at 350 ºC. The spectrum obtained after cooling to 130 ºC appears to have been lost in the computer. The disappearance of the characteristic isotetralin peaks and the growth of the aromatic peaks and the peak at 2936 cm^{-1} indicated that a reaction had taken place. GC analysis indicated that isotetralin reacted completely to give 66% naphthalene and 34 % tetralin. Fortunately, both of these products are stable and scans of them at 350 ºC were available. Figure 5-43 also presents the synthetic scan generated using the GC results with the neat scans of naphthalene and tetralin at 350 ºC. Agreement between the synthetic scan and the scan after two hours at 350 ºC was quite good. Comparison of the starting material with the end product, both at 130 ºC, was not available because the file containing the final product spectrum was lost.

There appeared to be two competitive mechanisms operating here, one of isomerization to tetralin, and the other dehydrogenation to naphthalene. Both tetralin and naphthalene have been shown to be stable once formed. A discussion of the competition between these two mechanisms is deferred until the results of the

Figure 5-41

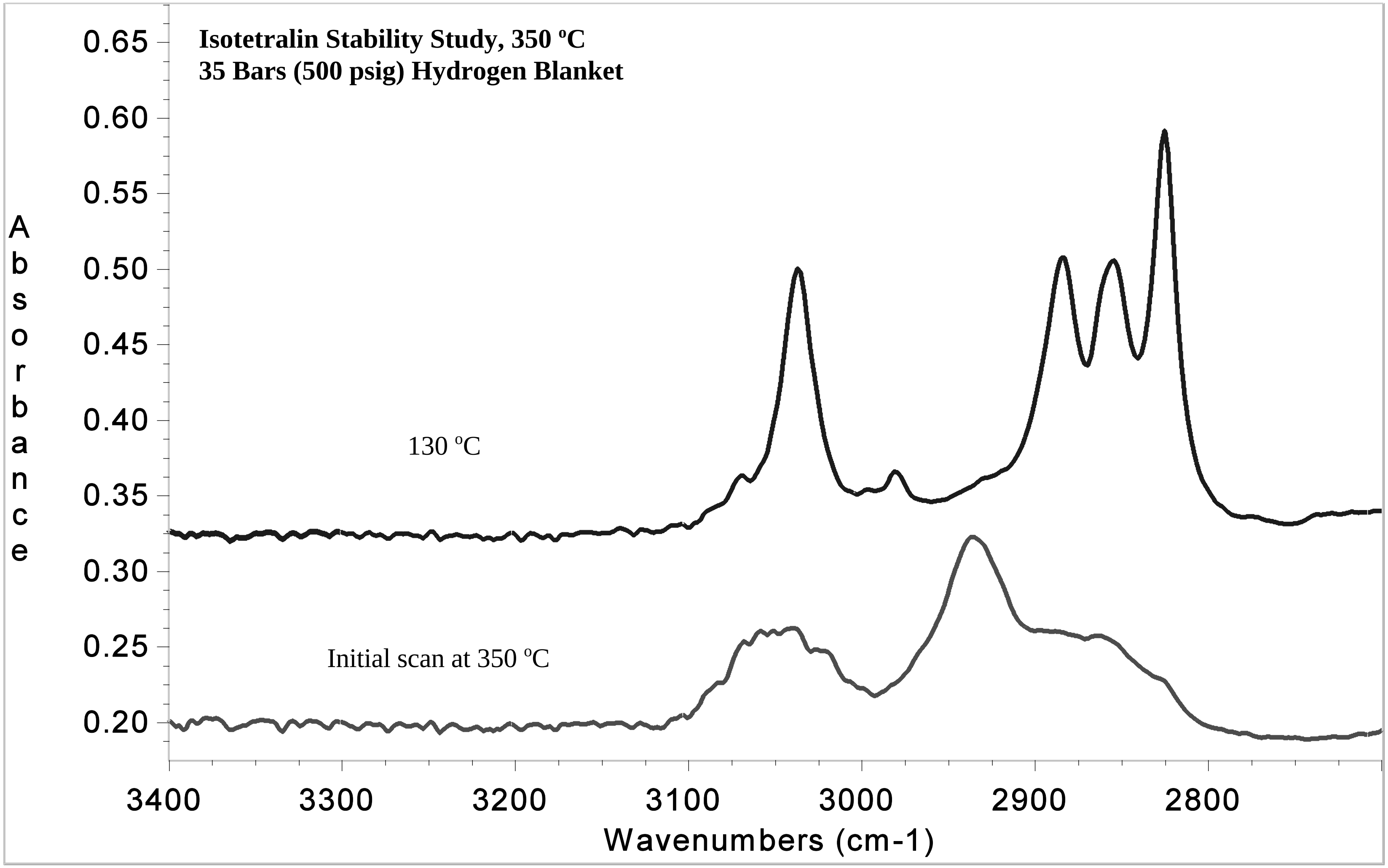

Isotetralin Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 350 ºC
Absorbance
0.65
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-42

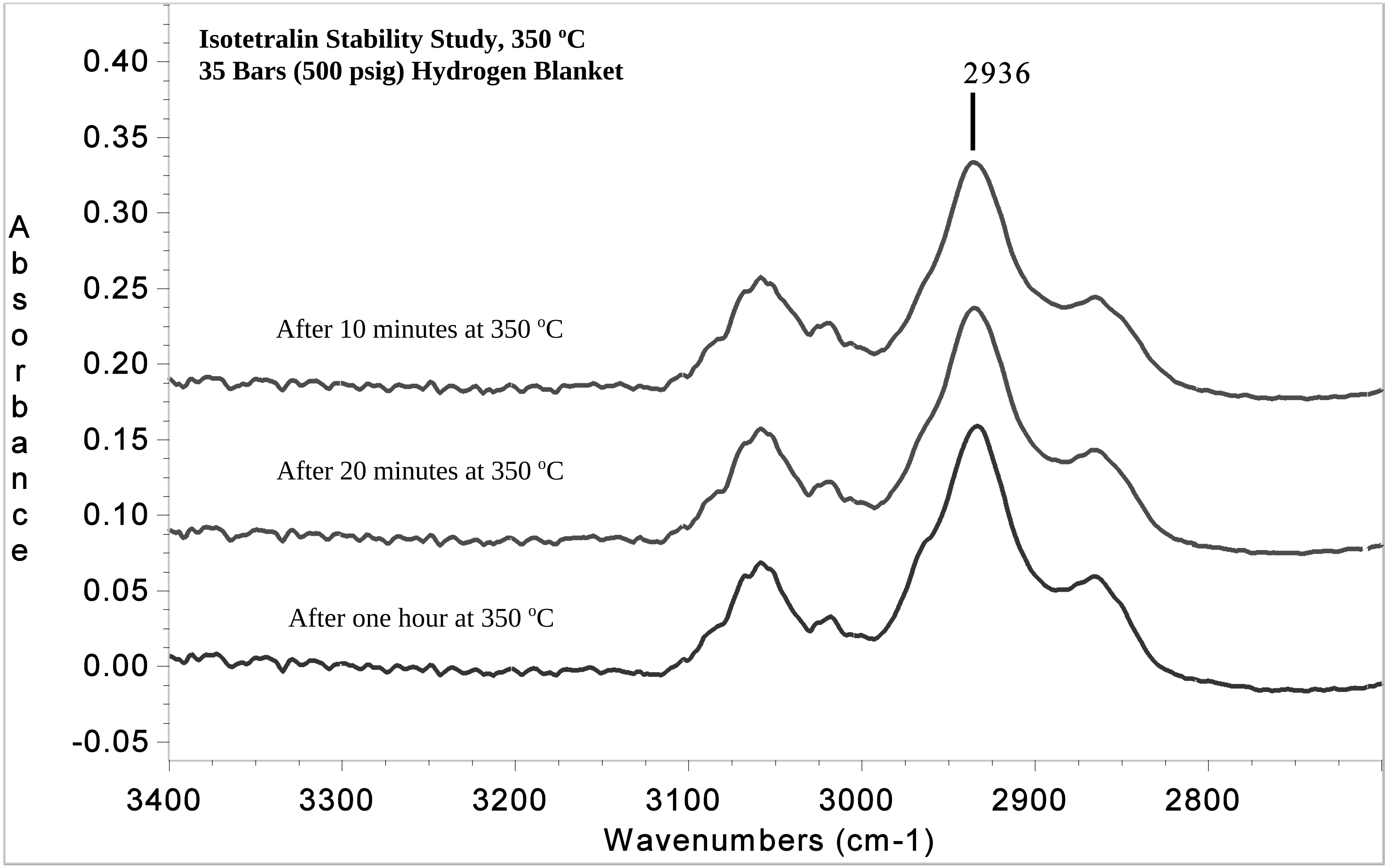
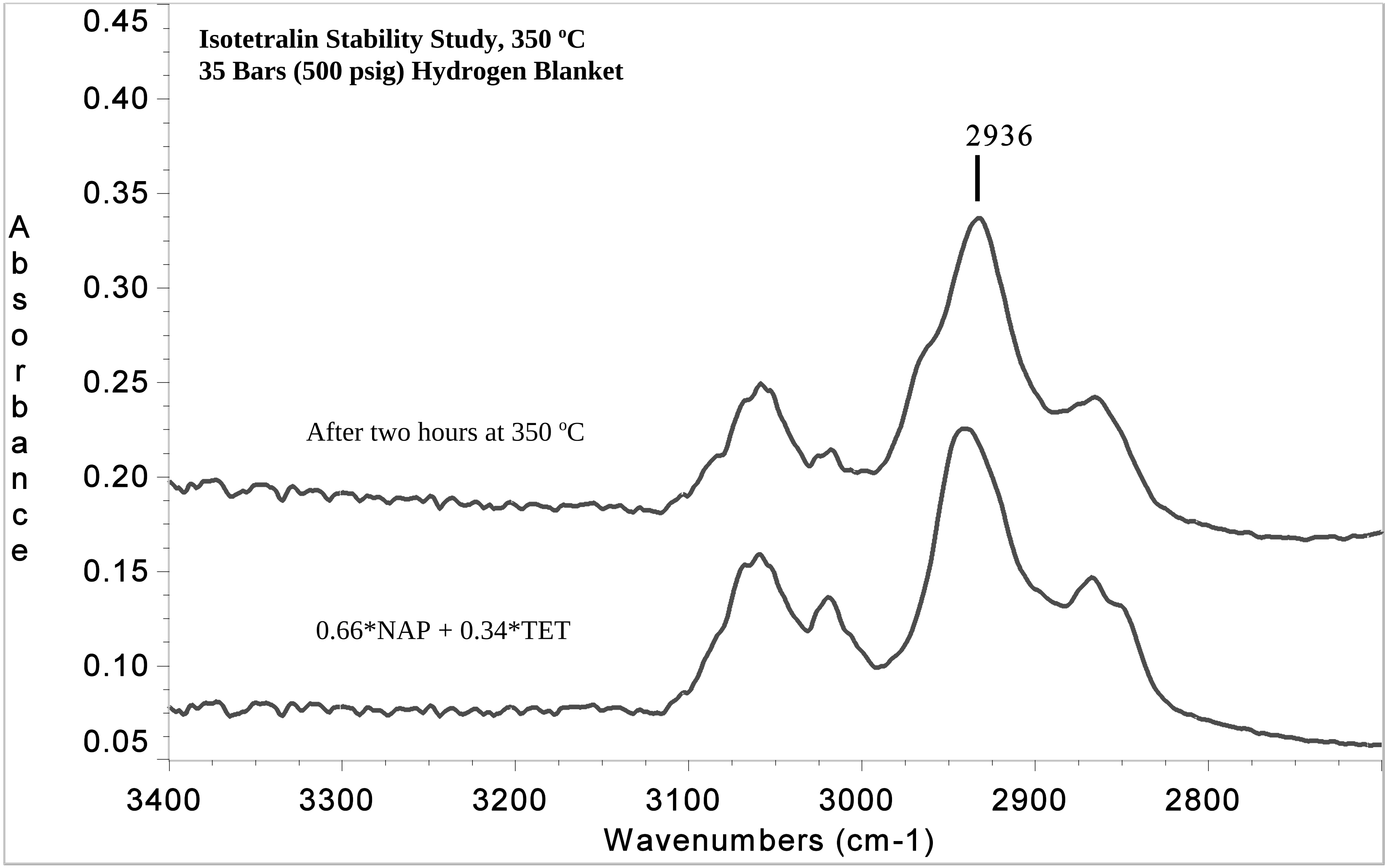

Isotetralin Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
2936
After 10 minutes at 350 ºC
After 20 minutes at 350 ºC
After one hour at 350 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
-0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-43


Isotetralin Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
2936
After two hours at 350 ºC
0.66*NAP + 0.34*TET
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

1,4-dihydronaphthalene and 1,2-dihydronaphthalene stability studies are presented, since one or both of these compounds may be intermediates in the dehydrogenation mechanism and maybe even in the isomerization mechanism.

1,4-Dihydronaphthalene Stability Study, 250 ºC

1,4-Dihydronaphthalene proved to be reactive at 250 ºC under a 35 bars hydrogen blanket. Figure 5-44 presents the spectrum of 1,4-dihydronaphthalene at 130 ºC, along with the spectrum after heating at a rate of 5 ºC per minute to 250 ºC. A slight reaction had taken place by the time 250 ºC was reached. Figure 5-45 presents the spectrum of 1,4-dihydronaphthalene after one, two, and three hours at 250 ºC. The reduction in the peak heights which are characteristic of 1,4-dihydronaphthalene, at 2832 cm^{-1}, 2896 cm^{-1}, and 3041 cm^{-1}, along with the increase in the peak height at 2936 cm^{-1}, clearly indicated that a reaction had taken place. GC analysis indicated that the reaction product was 68% naphthalene, 16% unreacted 1,4-dihydronaphthalene, 13% 1,2-dihydronaphthalene and 3% tetralin. Figure 5-46 presents the synthetic scan generated using the GC results, along with the scan of the final product after having cooled to 130 ºC. Agreement between the two scans was fair, and once again a bias in favor of naphthalene was observed in the synthetic scan.

1,4-Dihydronaphthalene Stability Study, 300 ºC

1,4-Dihydronaphthalene proved to be highly reactive at 300 ºC under a 35 bars hydrogen blanket. Figure 5-47 presents the spectrum of 1,4-dihydronaphthalene at 130 ºC, along with the spectrum after heating at a rate of 5 ºC per minute to 300 ºC. A substantial reaction had taken place by the time 300 ºC was reached. Figure 5-48

Figure 5-44

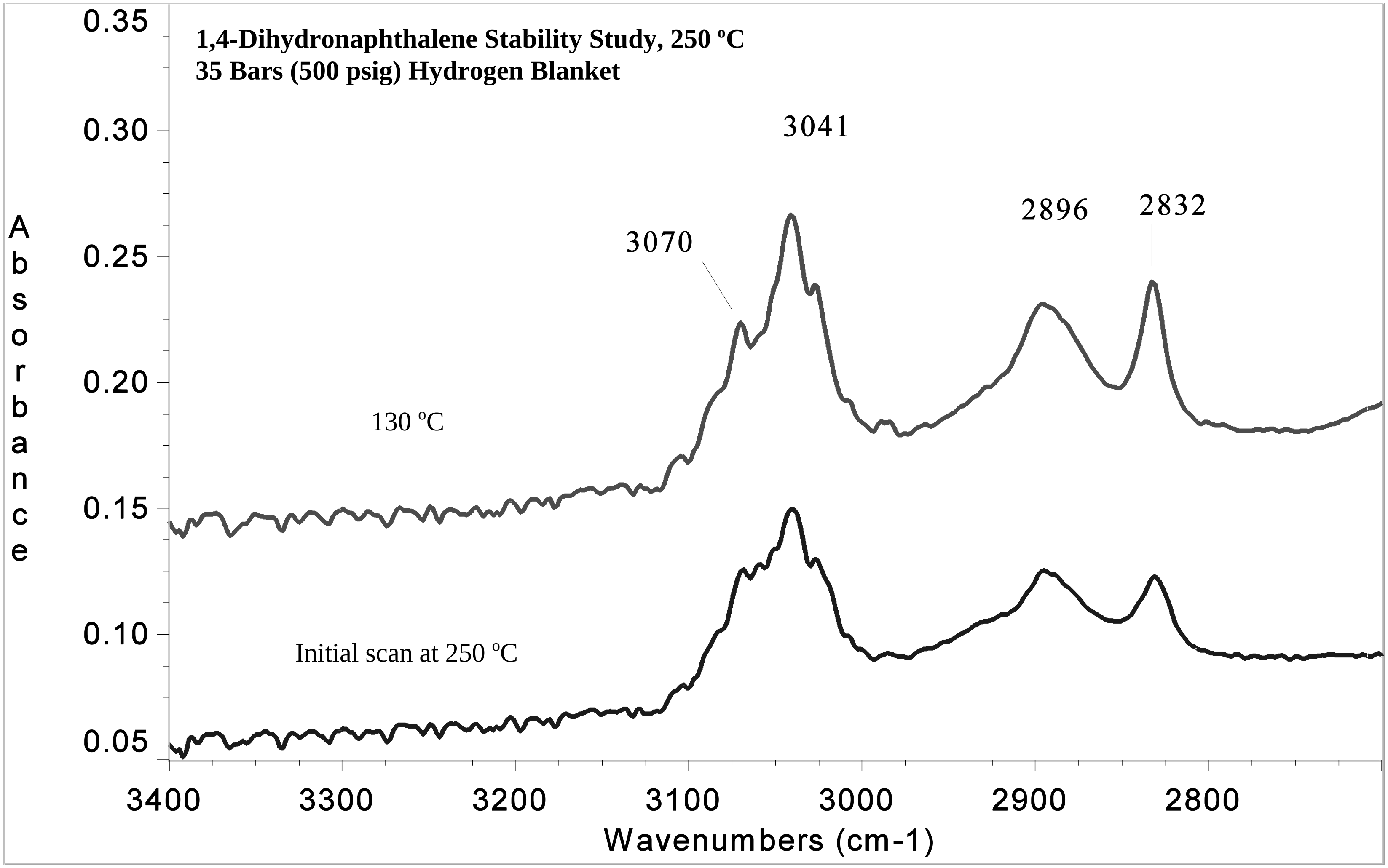

1,4-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
3041
3070
2896
2832
130 ºC
Initial scan at 250 ºC
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-45

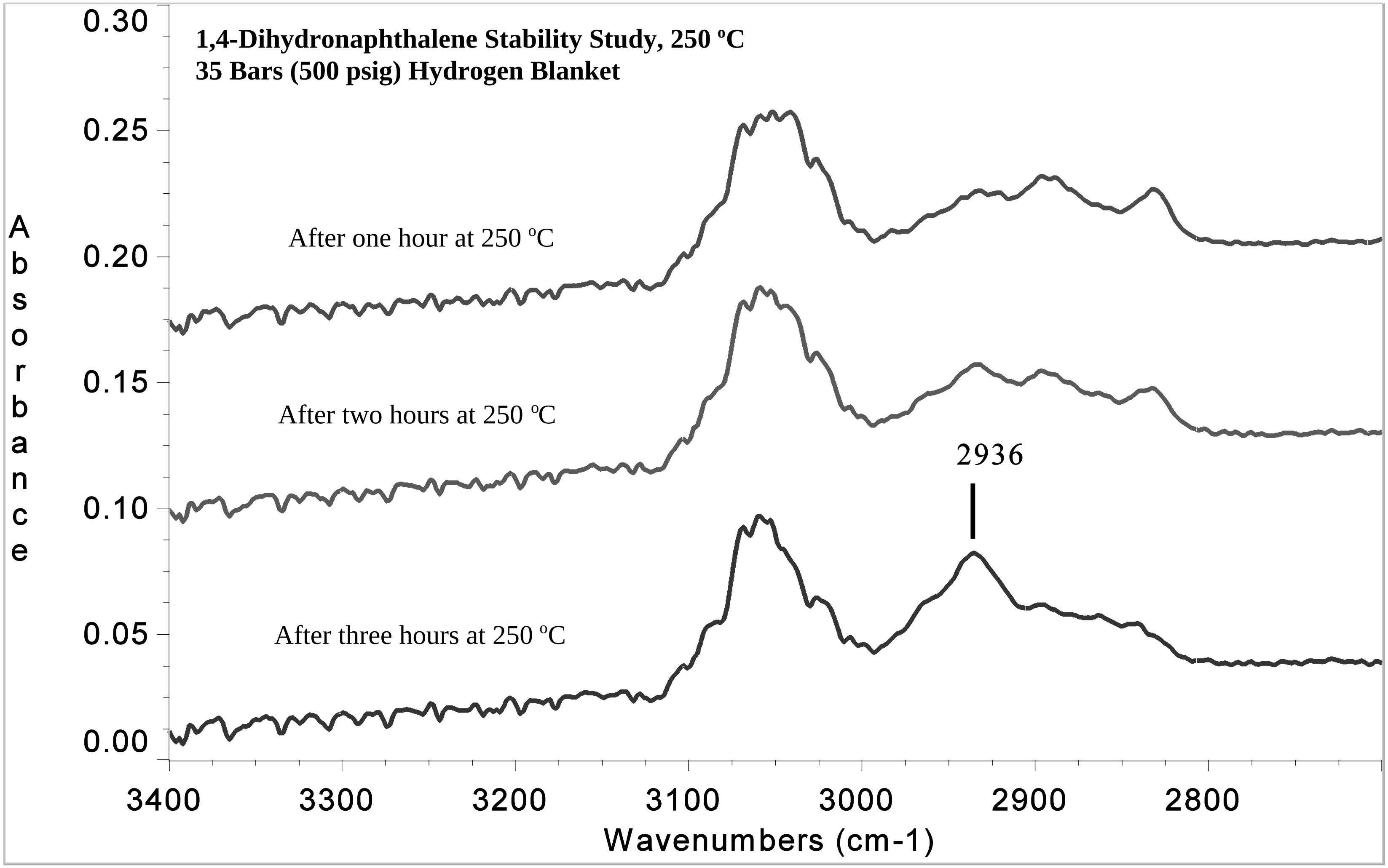
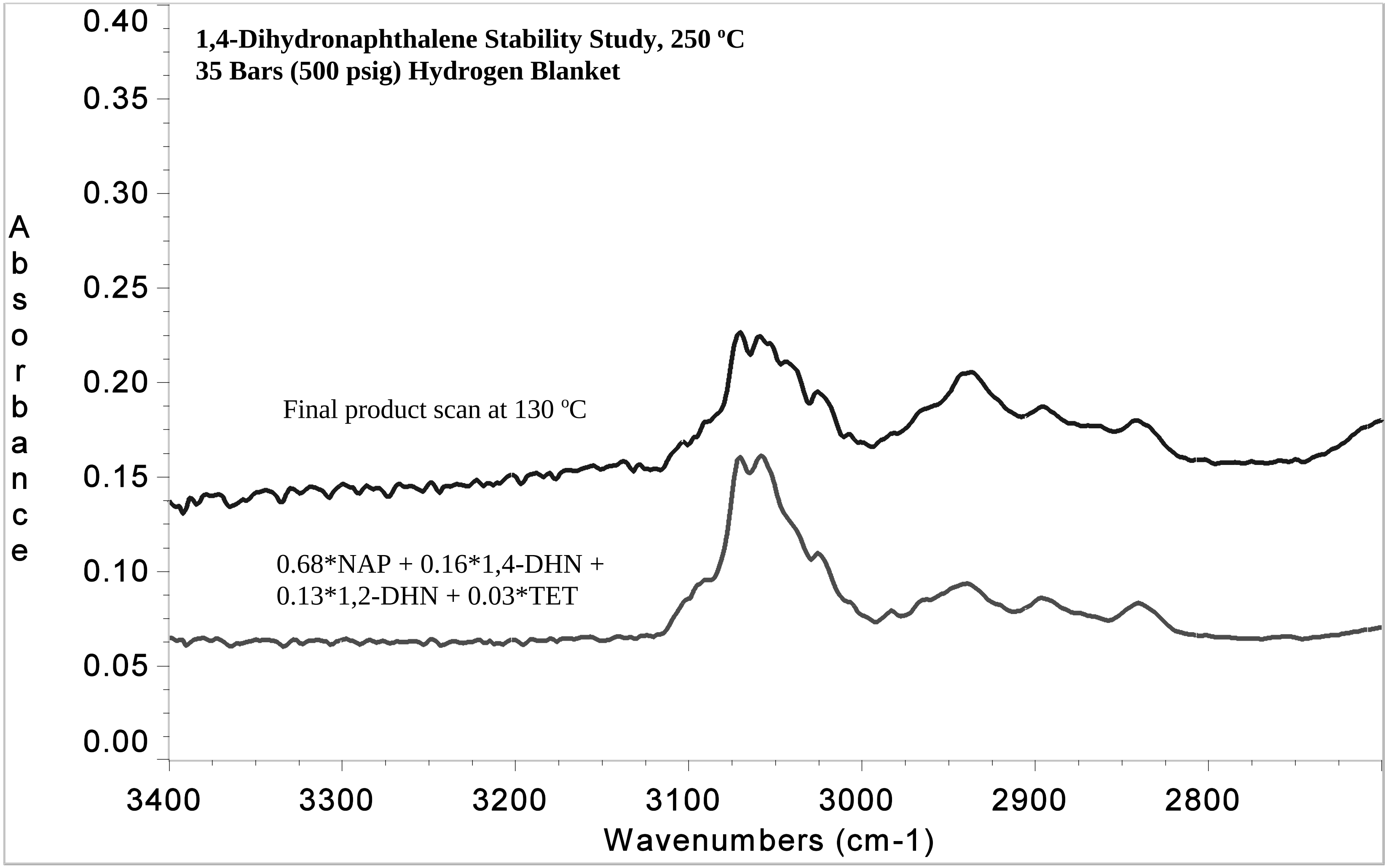
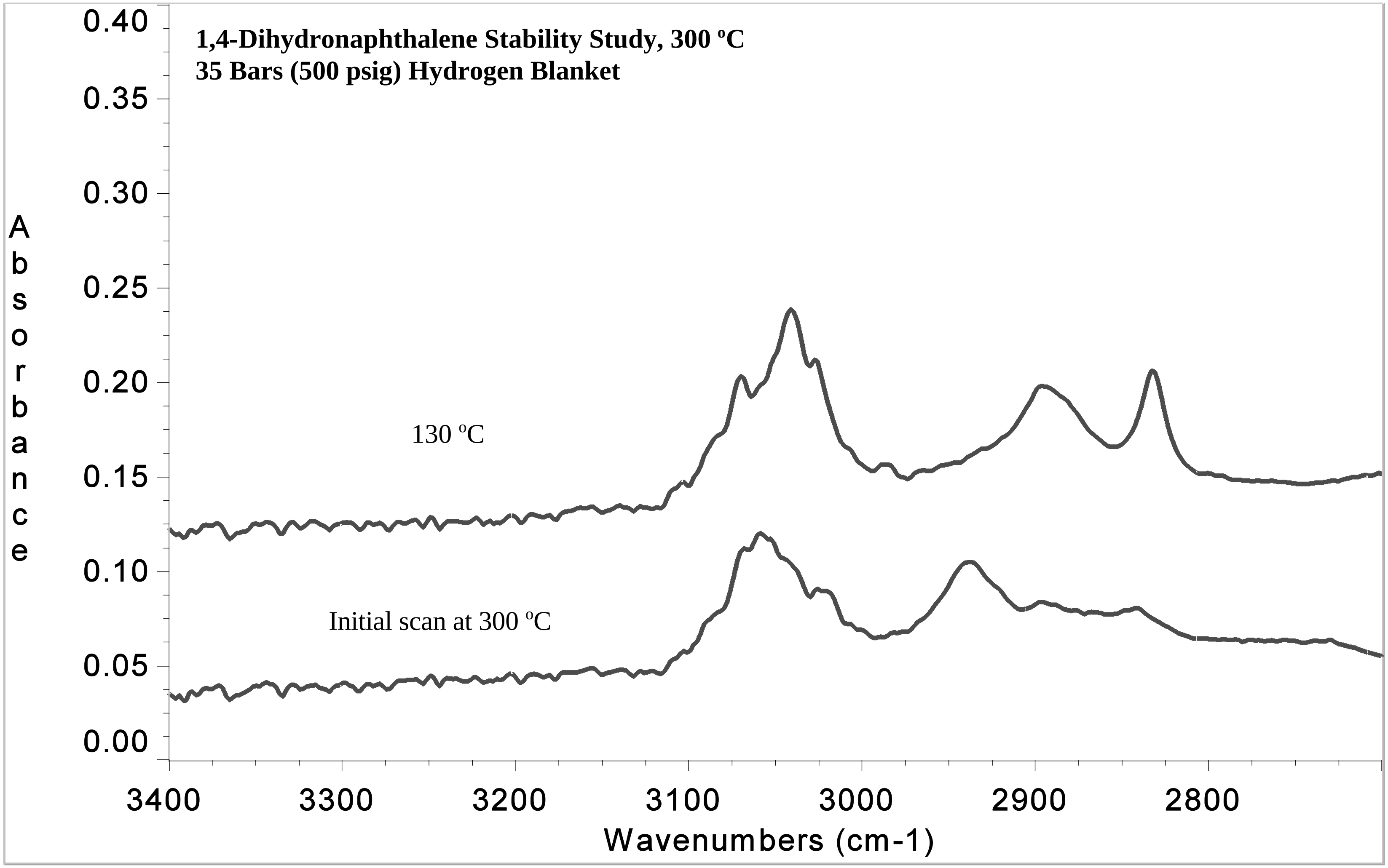

1,4-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
After one hour at 250 ºC
After two hours at 250 ºC
After three hours at 250 ºC
2936
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-46



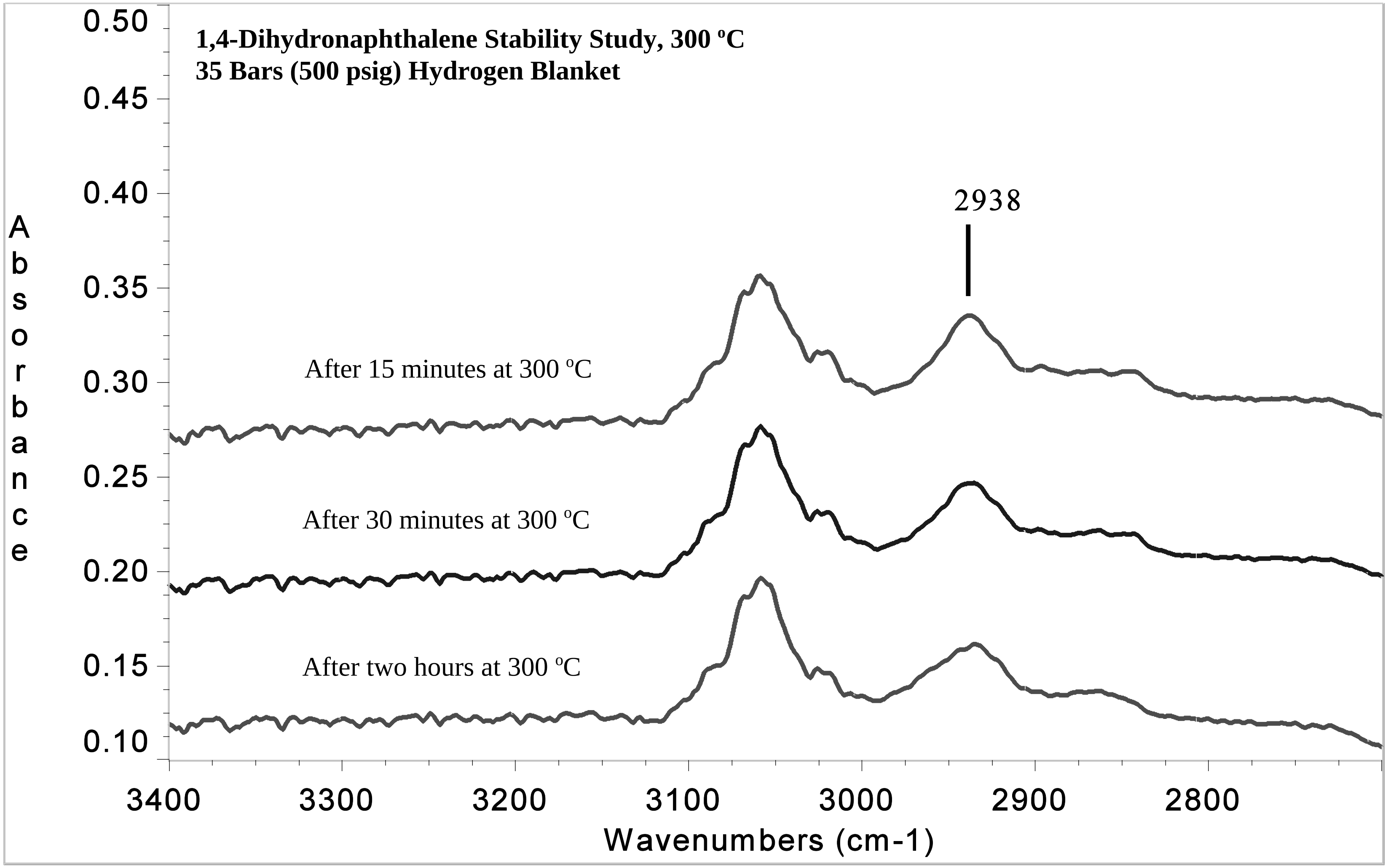
1,4-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
Final product scan at 130 ºC
0.68*NAP + 0.16*1,4-DHN +
0.13*1,2-DHN + 0.03*TET
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-47



1,4-Dihydronaphthalene Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 300 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-48


1,4-Dihydronaphthalene Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
2938
After 15 minutes at 300 ºC
After 30 minutes at 300 ºC
After two hours at 300 ºC
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

presents the spectrum of 1,4-dihydronaphthalene after 15 minutes, 30 minutes, and two hours at 300 ºC. The reduction in the heights of the characteristic 1,4-dihydronaphthalene peaks and the emergence of a peak around 2938 cm^{-1} indicated that a reaction had taken place. GC analysis indicated that 1,4- dihydronaphthalene reacted completely to yield 92% naphthalene and 8% tetralin. Figure 5-49 presents the synthetic scan generated using the GC results, along with the scan of the reaction product after having cooled to 130 ºC. Agreement between the scans was good, but a strong bias in favor of naphthalene was seen. The aliphatic peaks, although qualitatively the same, were reduced accordingly.

1,4-Dihydronaphthalene Stability Study, 350 ºC

1,4-Dihydronaphthalene proved to be highly reactive at 350 ºC under a 35 bars hydrogen blanket. Figure 5-50 presents the spectrum of 1,4-dihydronaphthalene at 130 ºC, along with the spectrum after heating at a rate of 5 ºC per minute to 350 ºC. A substantial reaction had taken place by the time 350 ºC was reached. Also shown in Figure 5-50 is the spectrum of 1,4-dihydronaphthalene after 20 minutes at 350 ºC. Figure 5-51 presents the spectrum of 1,4-dihydronaphthalene after 45 minutes at 350 ºC, after two hours at 350 ºC, and after cooling to 130 ºC. As with the lower temperature tests, 1,4-dihydronaphthalene is again seen to be quite reactive. No peaks appeared in the GC analysis of the reaction product from this mixture. It was suspected that something went wrong with the extraction procedure.

Figure 5-49

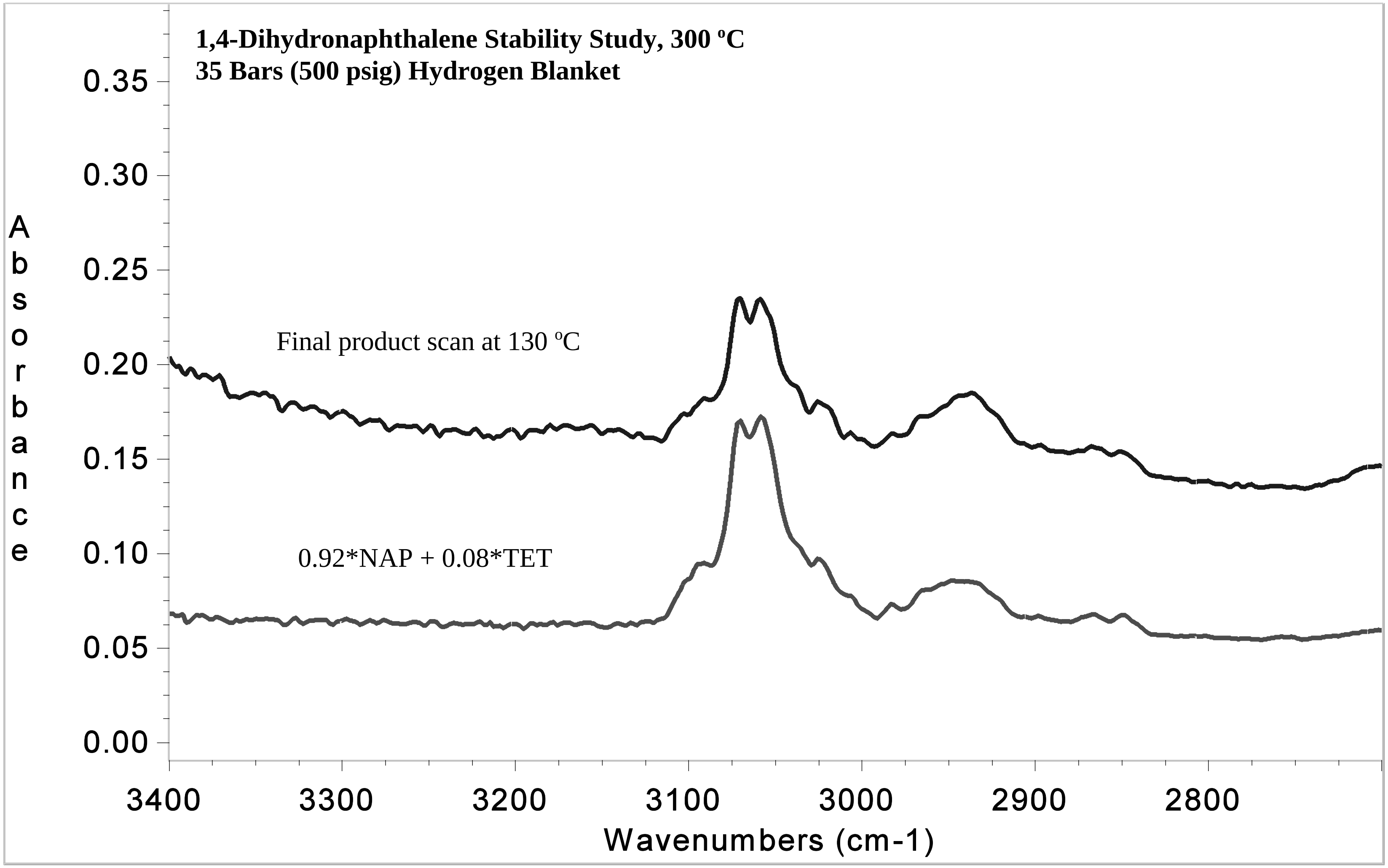

1,4-Dihydronaphthalene Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
Final product scan at 130 ºC
0.92*NAP + 0.08*TET
Absorbance
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-50

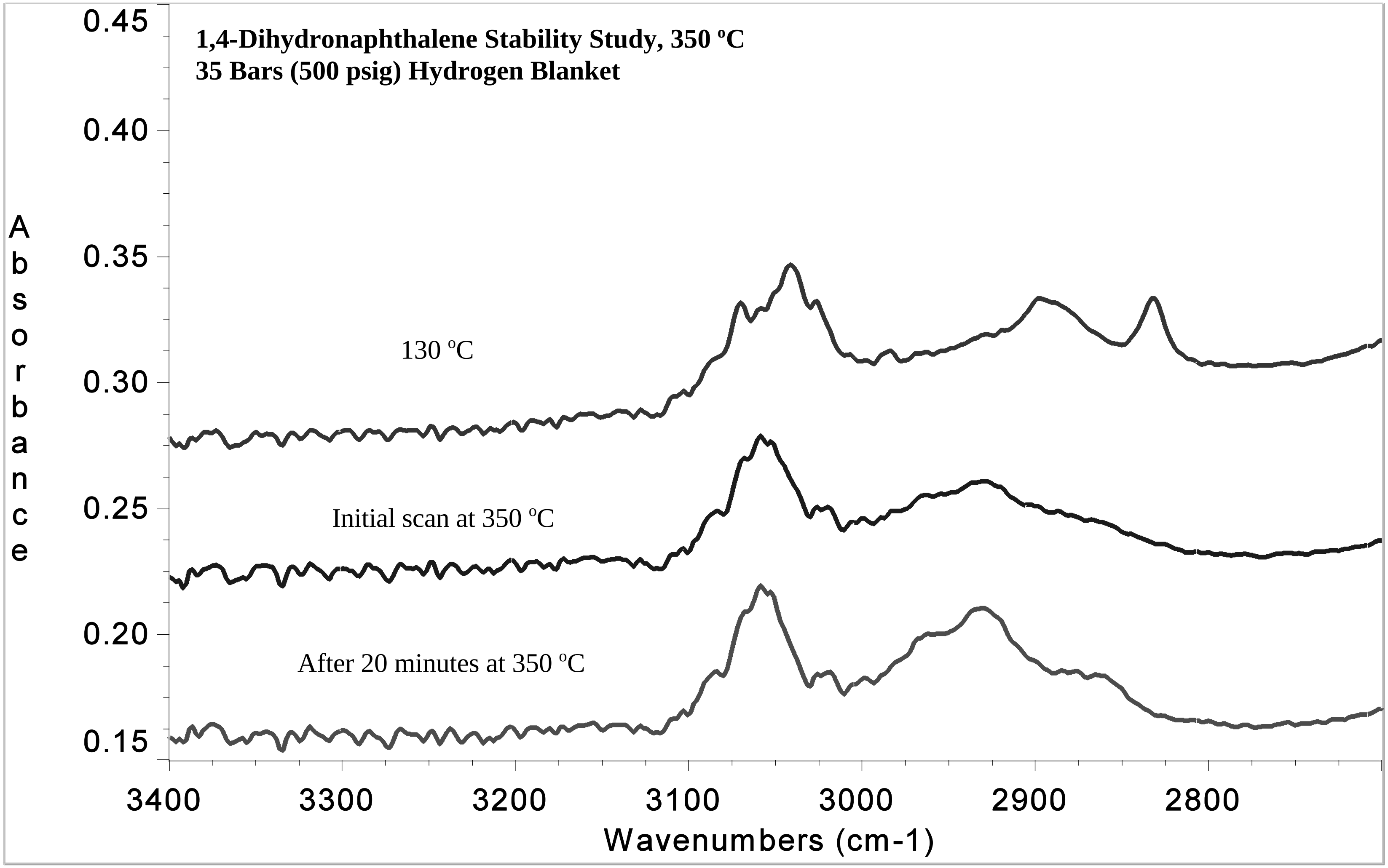
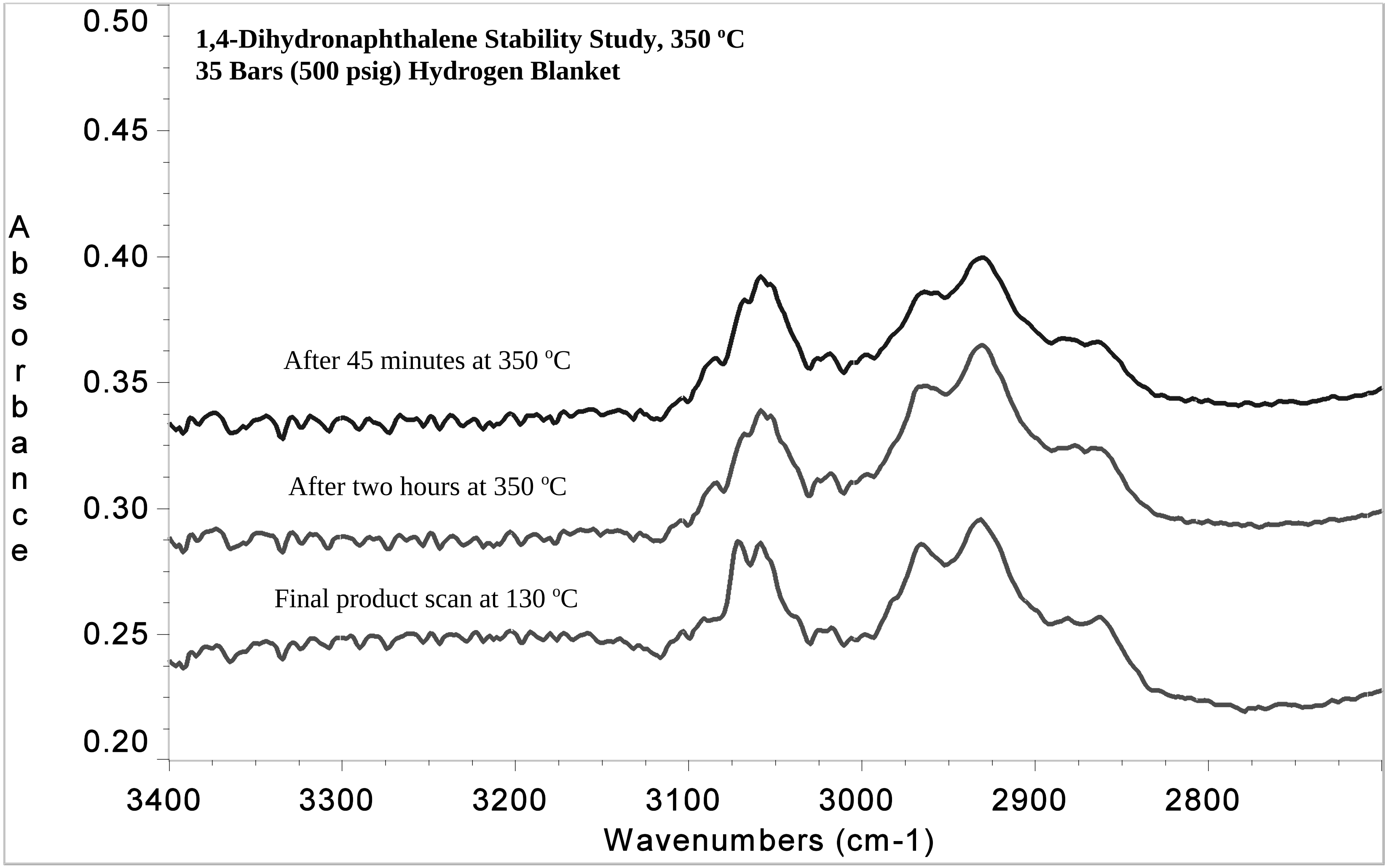

1,4-Dihydronaphthalene Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 350 ºC
After 20 minutes at 350 ºC
Absorbance
0.45
0.40
0.35
0.30
0.25
0.20
0.15
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-51


1,4-Dihydronaphthalene Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
After 45 minutes at 350 ºC
After two hours at 350 ºC
Final product scan at 130 ºC
Absorbance
0.50
0.45
0.40
0.35
0.30
0.25
0.20
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

1,2-Dihydronaphthalene Stability Study, 250 °C

1,2-Dihydronaphthalene proved to be reactive at 250 °C under a 35 bars hydrogen blanket. Figure 5-52 presents the spectrum of 1,2-dihydronaphthalene at 130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 250 °C. A slight reaction had taken place by the time 250 °C was reached. Figure 5-53 presents the spectrum of 1,2-dihydronaphthalene after one, two, and three hours at 250 °C. The reduction in the peak heights which are characteristic of 1,2-dihydronaphthalene, at 2842 cm^{-1}, 3022 cm^{-1}, and 3041 cm^{-1}, clearly indicated that a reaction had taken place. GC analysis indicated that the reaction product was 62% naphthalene and 38% unreacted 1,2-dihydronaphthalene. Figure 5-54 presents the synthetic scan generated using the GC results, along with the scan of the final product after having cooled to 130 °C. Agreement between the synthetic scan and the final product scan was considered poor. The bias to naphthalene is observed, but moreover, GC analysis indicated that the only aliphatic species present was 1,2-dihydronaphthalene. If this had been the case, then the stretches in the aliphatic region in the final product scan would match precisely with the scan of 1,2-dihydronaphthalene. This is not the case, and the broad stretches in the aliphatic region suggest the presence of some other compound. These stretches and the strong absorbance at 2942 cm^{-1} suggest the presence of tetralin, since both tetralin and 1,2-dihydronaphthalene absorb near this wavelength.

1,2-Dihydronaphthalene Stability Study, 300 °C

1,2-Dihydronaphthalene proved to be highly reactive at 300 °C under a 35 bars hydrogen blanket. Figure 5-55 presents the spectrum of 1,2-dihydronaphthalene at

Figure 5-52

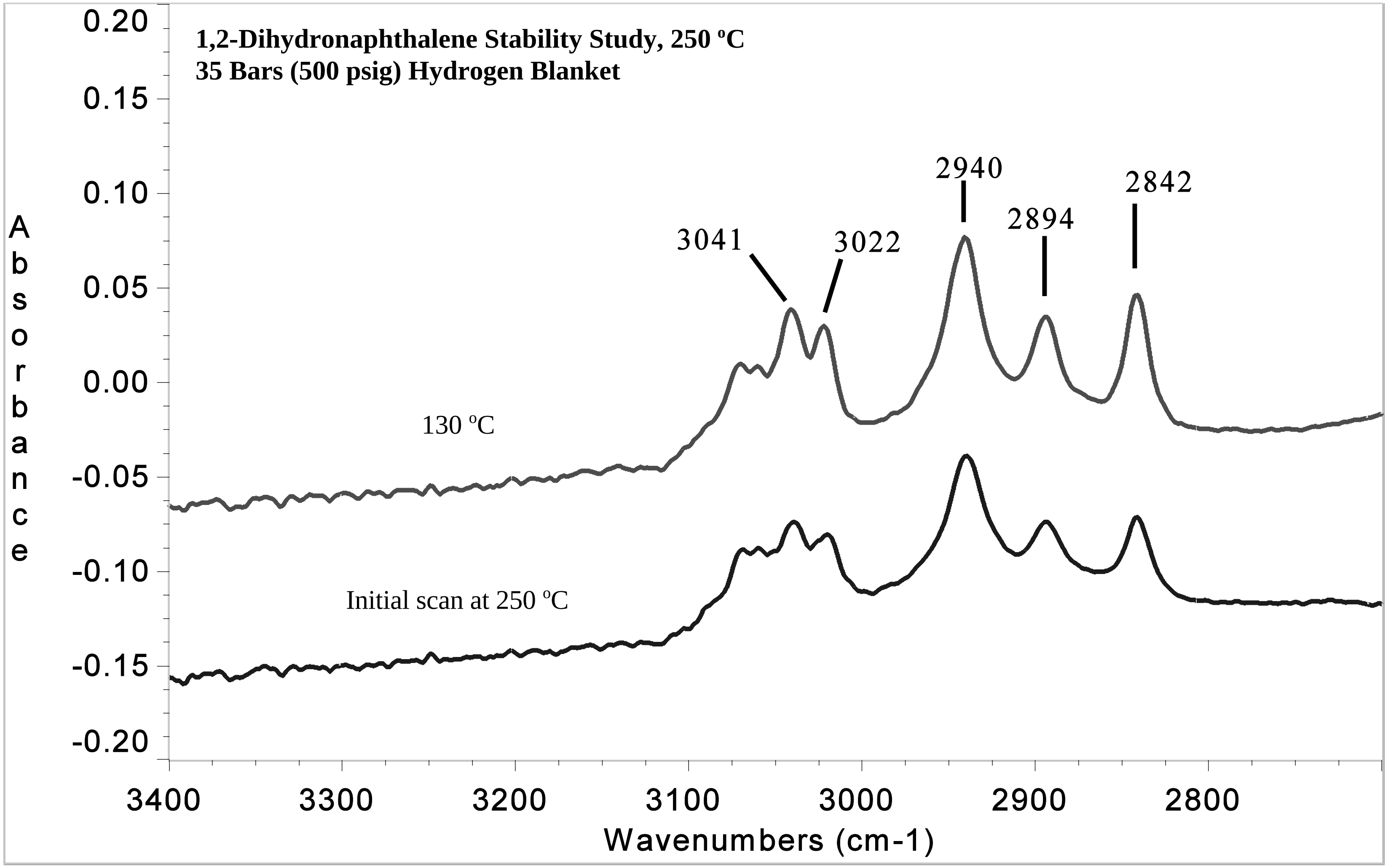
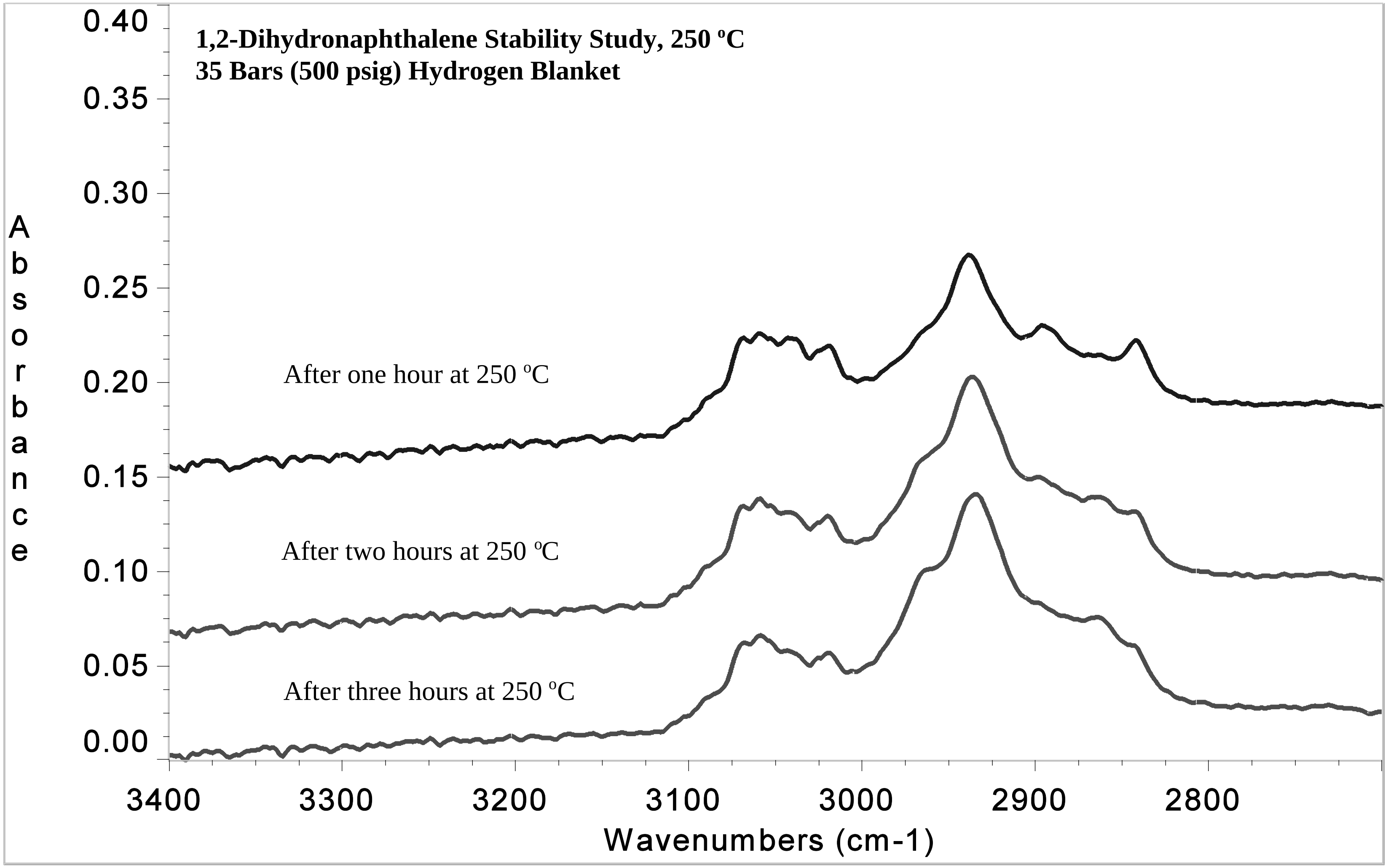

1,2-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
3041
3022
2940
2894
2842
130 ºC
Initial scan at 250 ºC
Absorbance
0.20
0.15
0.10
0.05
0.00
-0.05
-0.10
-0.15
-0.20
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-53



1,2-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
After one hour at 250 ºC
After two hours at 250 ºC
After three hours at 250 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-54

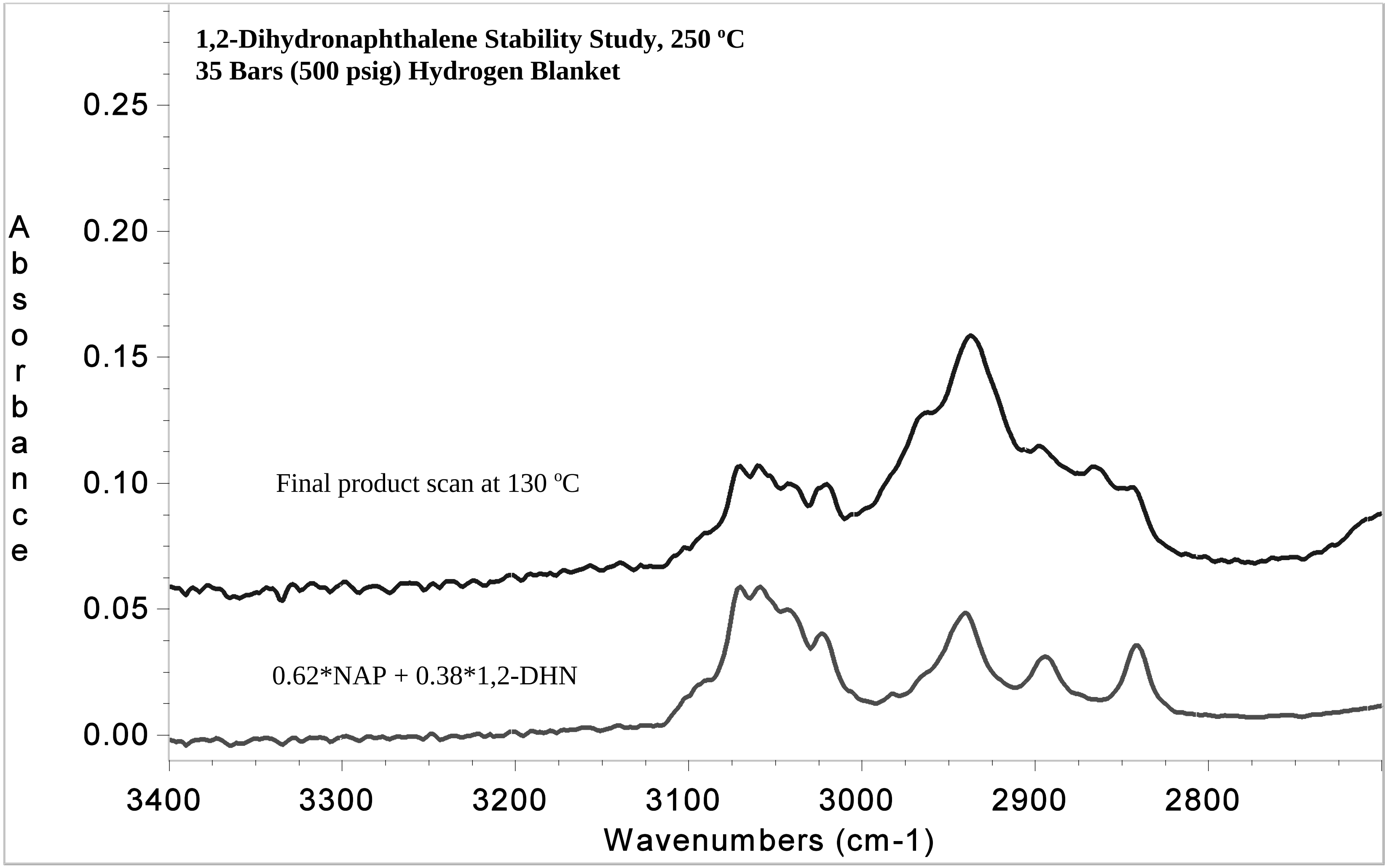
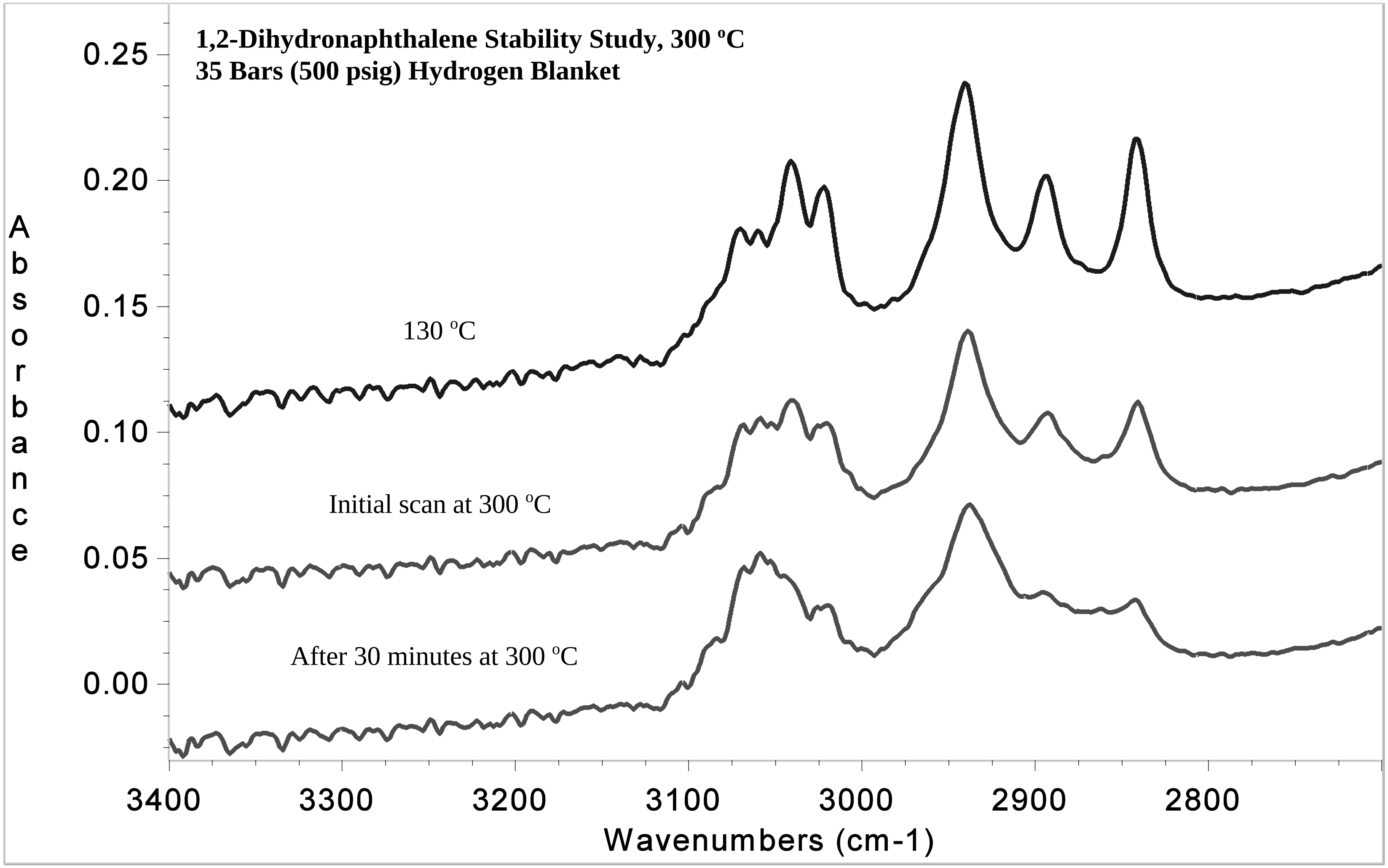

1,2-Dihydronaphthalene Stability Study, 250 ºC
35 Bars (500 psig) Hydrogen Blanket
Final product scan at 130 ºC
0.62*NAP + 0.38*1,2-DHN
Absorbance
0.00
0.05
0.10
0.15
0.20
0.25
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-55


1,2-Dihydronaphthalene Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 300 ºC
After 30 minutes at 300 ºC
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 300 °C. A substantial reaction had taken place by the time 300 °C was reached. Figure 5-55 also presents the spectrum of 1,2-dihydronaphthalene after 30 minutes at 300 °C. Figure 5-56 presents the spectrum of 1,2-dihydronaphthalene after one hour at 300 °C, after two hours and 30 minutes at 300 °C, and after cooling to 130 °C. The reduction in the heights of the characteristic 1,2-dihydronaphthalene peaks and the growth of the peak at 3060 cm^{-1} indicated that a reaction had taken place. No peaks appeared in the GC analysis of the reaction product. It was now suspected that something could be wrong with the GC rather than the extraction procedure.

1,2-Dihydronaphthalene Stability Study, 350 °C

1,2-Dihydronaphthalene proved to be highly reactive at 350 °C under a 35 bars hydrogen blanket. Figure 5-57 presents the spectrum of 1,2-dihydronaphthalene at 130 °C, along with the spectrum after heating at a rate of 5 °C per minute to 350 °C. A substantial reaction had taken place by the time 350 °C was reached. Figure 5-57 also presents the spectrum of 1,2-dihydronaphthalene after 15 minutes at 350 °C. Figure 5-58 presents the spectrum of 1,2-dihydronaphthalene after 30 minutes at 350 °C, after two hours at 350 °C, and after cooling to 130 °C. As with the lower temperature tests, 1,2-dihydronaphthalene is again seen to be quite reactive. GC analysis indicated that the product was almost pure naphthalene, with a trace of unreacted 1,2-dihydronaphthalene or tetralin. Since the FTIR scan clearly indicates the presence of aliphatic stretches, it was concluded that the GC results were grossly in error.

Figure 5-56

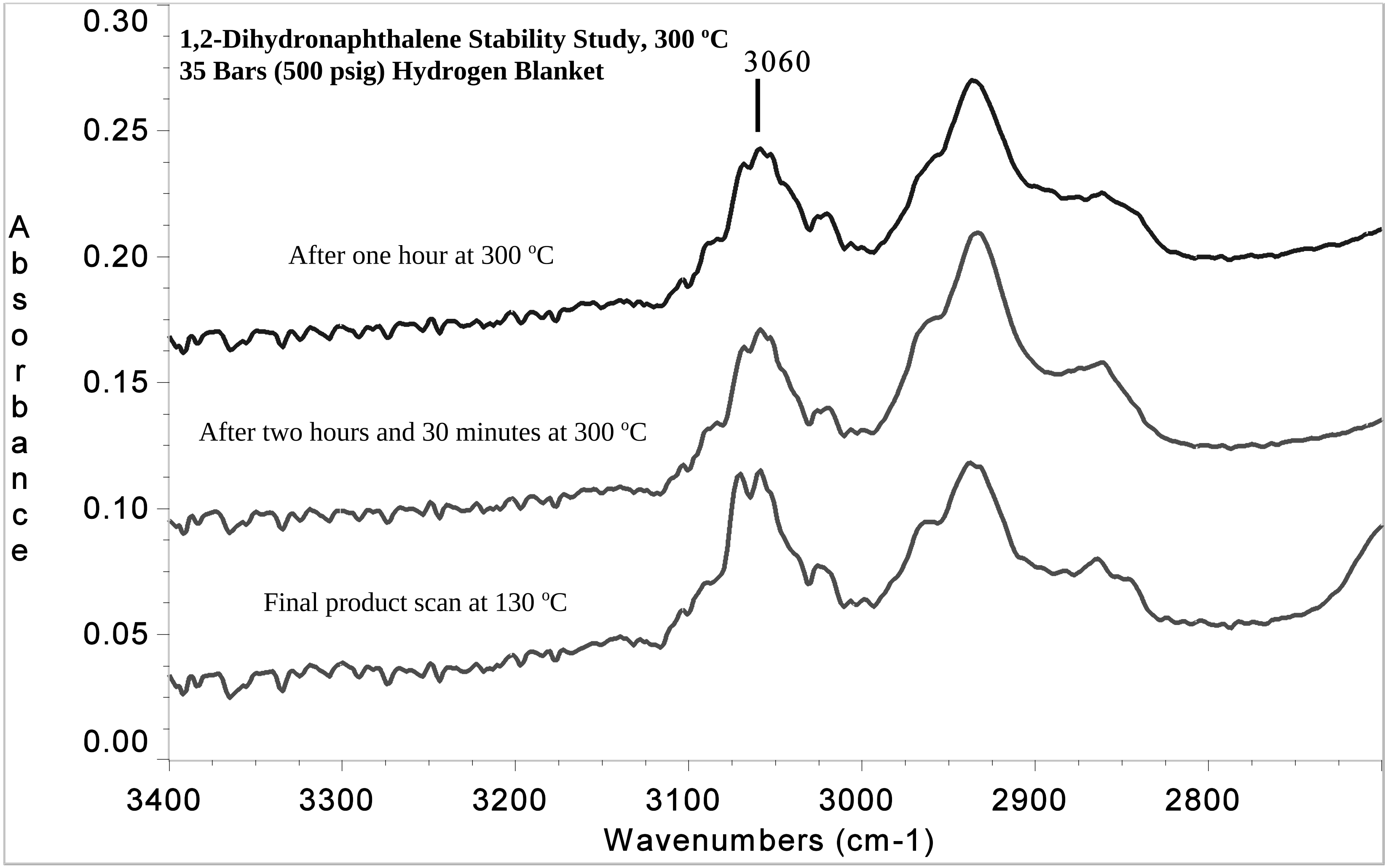

1,2-Dihydronaphthalene Stability Study, 300 ºC
35 Bars (500 psig) Hydrogen Blanket
3060
After one hour at 300 ºC
After two hours and 30 minutes at 300 ºC
Final product scan at 130 ºC
Absorbance
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-57

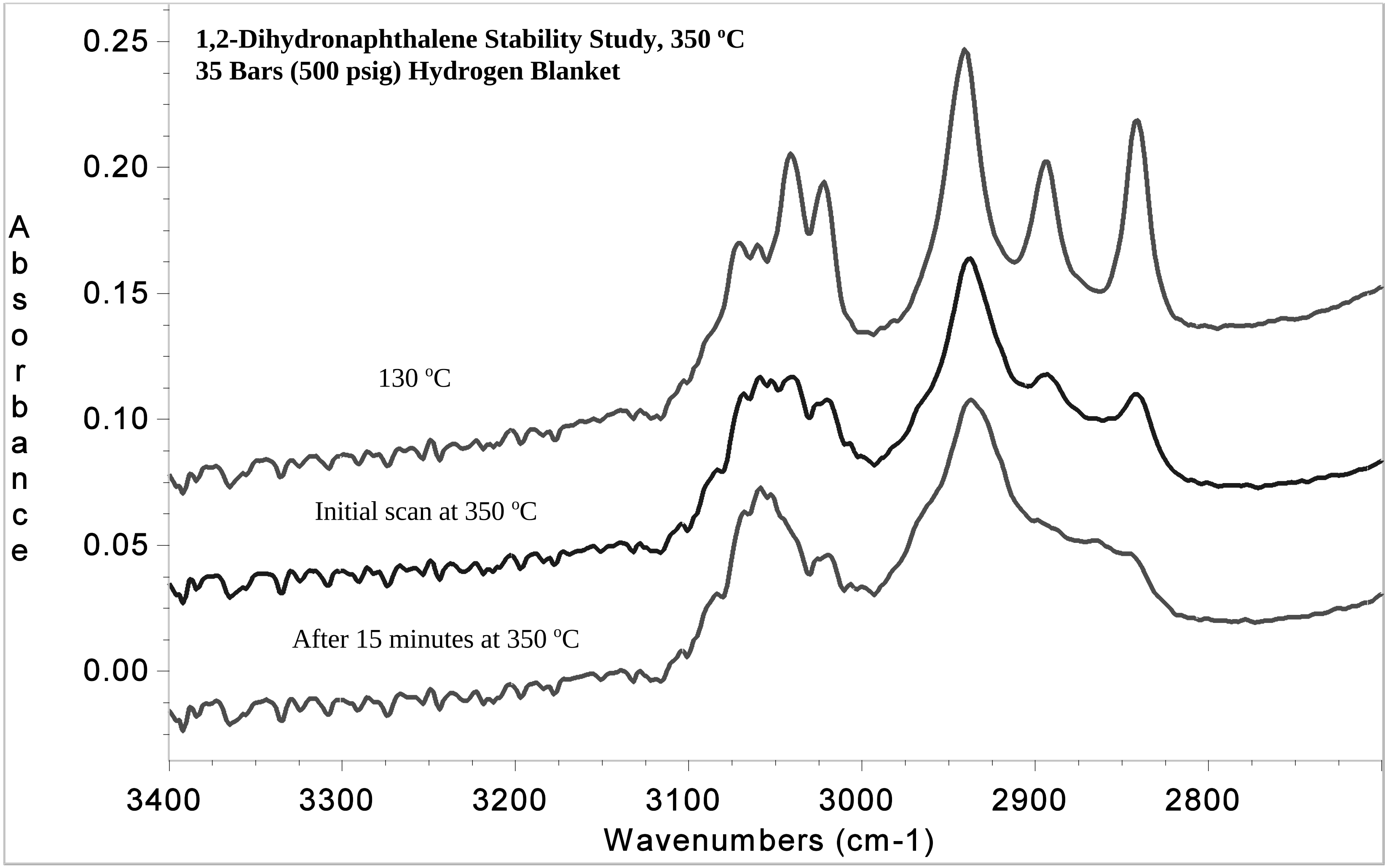
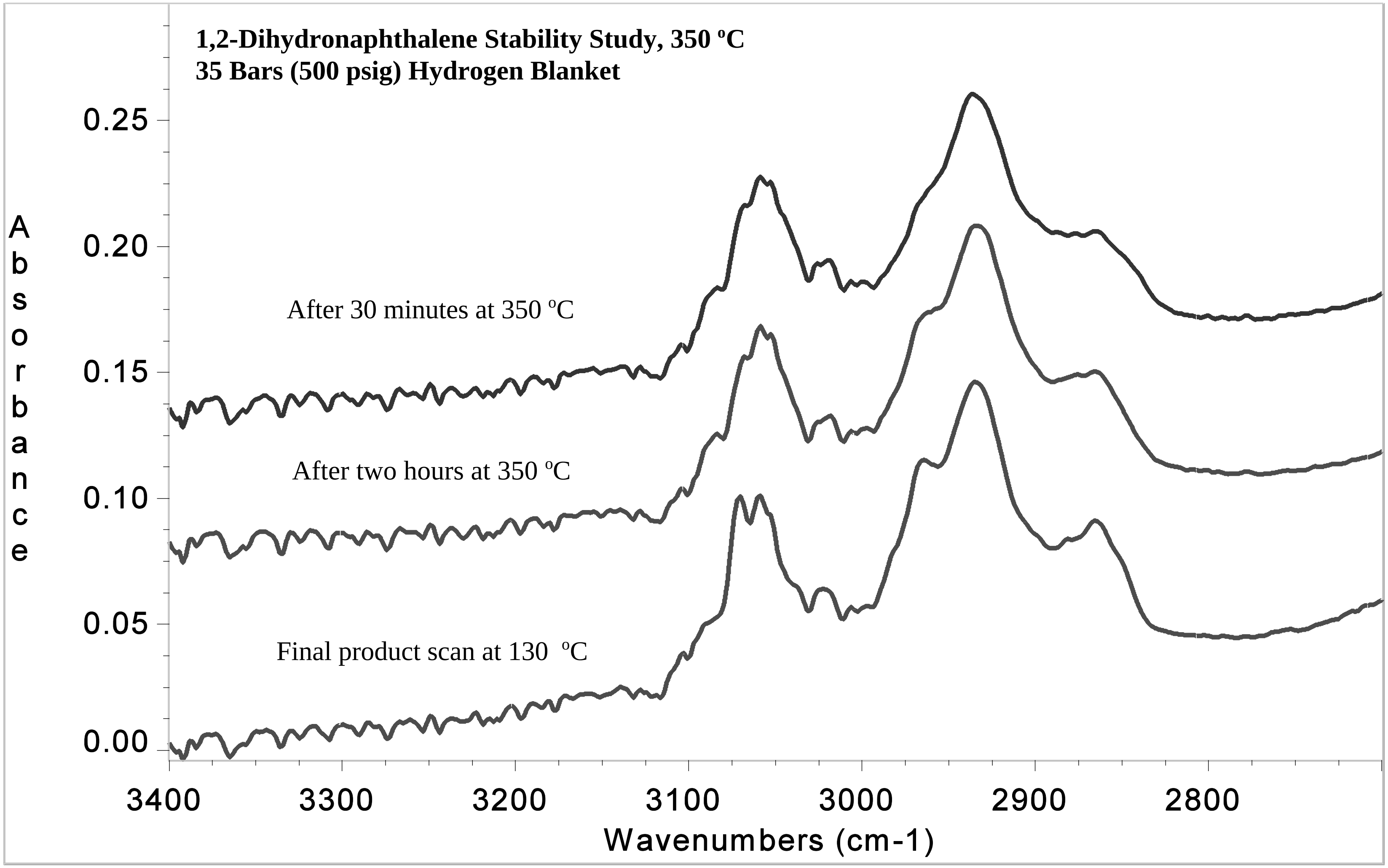

1,2-Dihydronaphthalene Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
130 ºC
Initial scan at 350 ºC
After 15 minutes at 350 ºC
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

Figure 5-58


1,2-Dihydronaphthalene Stability Study, 350 ºC
35 Bars (500 psig) Hydrogen Blanket
After 30 minutes at 350 ºC
After two hours at 350 ºC
Final product scan at 130 ºC
Absorbance
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

The Effect of Temperature on the Final Product Distribution

This section provides a comparison of the results from the hydrogen blanket stability studies for the reactive compounds in this study, viz., 1,2-dihydronaphthalene, 1,4-dihydronaphthalene and isotetralin.

Certain trends became evident upon analyzing the data from the hydrogen blanket stability studies. Table 5.3 presents the results from the GC analyses for the 250 ºC, 300 ºC and 350 ºC hydrogen blanket stability studies. The GC results from the 230 ºC hydrogen blanket stability study are also presented in Table 5.3 for ready comparison.

The Effect of Temperature on the Final Product Distribution for 1,2-Dihydronaphthalene

Of the reactive compounds in this study, 1,2-dihydronaphthalene proved the least reactive at elevated temperatures under a 35 bars hydrogen blanket. Figure 5-59 presents the spectra of the final products from the stability studies. The agreement between the synthetic scan generated using the GC results and the final product scan was very good for the 230 ºC test, but was poor for the 250 ºC test. No comparison was available for the 300 ºC and 350 ºC tests because no peaks were detected by GC analysis for these products.

Both the GC results and the FTIR scan indicated the presence of unreacted 1,2-dihydronaphthalene in the 230 ºC product. The GC result of 24% dehydrogenation to naphthalene was considered reliable. In the case of the 250 ºC test, the GC results were not considered reliable. However, the presence of the peaks at 3042 cm^{-1} and 2895 cm^{-1} in the FTIR scan indicated the presence of one of the dihydronaphthalenes. The

Table 5.3

Relative Concentrations of the Final Products (by GC)

Hydrogen Blanket Stability Studies

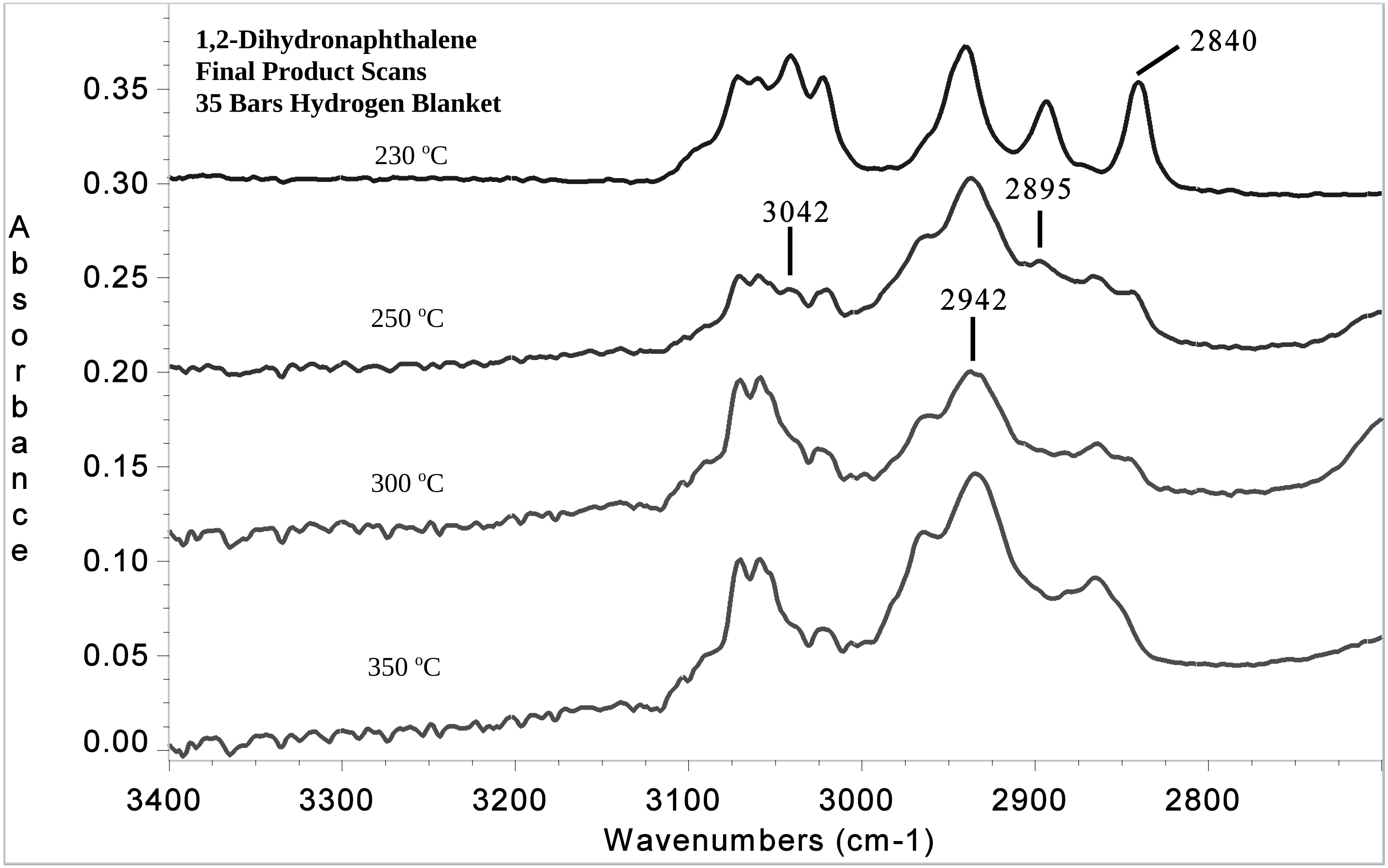
Reactant	1,2 -DHN	1,4-DHN	ISO
230 ºC	76 % 1,2-DHN 24% NAP	53% NAP 47% 1,4-DHN	73% NAP 15% 1,4-DHN 11% TET
250 ºC	62% NAP ? 38% 1,2-DHN	68 % NAP ? 16% 1,4-DHN 13% 1,2-DHN 3% TET	46% NAP 34% TET 20% 1,4-DHN
300 ºC	No peaks	92% NAP ? 8% TET	63% NAP 32% TET 5% 1,2-DHN
350 ºC	?	No peaks	66% NAP 34% TET

NAP = Naphthalene TET = Tetralin ISO = Isotetralin

1,2-DHN = 1,2-Dihydronaphthalene 1,4-DHN = 1,4-Dihydronaphthalene

? = Of dubious validity

Figure 5-59


1,2-Dihydronaphthalene
Final Product Scans
35 Bars Hydrogen Blanket
230 ºC
250 ºC
300 ºC
350 ºC
2840
3042
2895
2942
Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

possibility of 1,4-dihydronaphthalene being present as the result of an isomerization was ruled out because 1,4-dihydronaphthalene shows a sharp absorbance at 2831 cm^{-1}, which was not observed in the final product scan for the 250 °C test.

In the 300 °C product scan, the distinct peaks of naphthalene became apparent in the aromatics stretching region. The reduction in the peak heights at 3042 cm^{-1} and 2840 cm^{-1} by over 50% from the starting material peak heights clearly indicated that 1,2-dihydronaphthalene had reacted. Since the peak at 2942 cm^{-1} was not diminished by 50%, but actually increased by about 20%, it was clear that one of the products absorbed at 2942 cm^{-1}. 1,4-dihydronaphthalene was eliminated as a potential product because the strongest absorbance for 1,4-dihydronaphthalene is at 3040 cm^{-1}, and an isomerization of to 1,4-dihydronaphthalene would have resulted in a sharp increase in this peak, rather than the decrease that was observed. Furthermore, as mentioned earlier, the presence of 1,4-dihydronaphthalene would have produced a peak at 2831 cm^{-1}, which was not observed. It was concluded that the product which was responsible for the absorption at 2942 cm^{-1} was tetralin, although some unreacted 1,2-dihydronaphthalene may have been present.

At 350 °C, the ratio of the aliphatic peak heights to the aromatic peak heights is greater than the ratio of the aliphatic peak heights to the aromatic peak heights in the 300 °C scan, indicating that the higher temperature favors the hydrogenation of 1,2-dihydronaphthalene to tetralin over the dehydrogenation to naphthalene. The presence of unreacted 1,2-dihydronaphthalene could not be ruled out solely on the basis of FTIR data.

One further item of interest is the emergence of a peak around 2965 cm^{-1} in the 250 ^{o}C and higher scans. The presence of a peak at this wavenumber is not consistent with any of the suspected products from this testing. The only hydrocarbon functionality which shows appreciable absorbance at this wavenumber is the methyl group, CH_3. A ring opening mechanism and the formation of an alkyl chain with a methyl group was therefore postulated. In previous research, Kim [5.6] found traces of n-butylbenzene in the products from the hydrogenation of naphthalene at 380 ^{o}C in the presence of a molybdenum naphthenate catalyst. Tetralin was detected as an intermediate in this reaction. However, naphthalene and tetralin have proven to be stable under the conditions employed in the current testing. No peak emerged at 2965 cm^{-1} when naphthalene and tetralin were subjected to the identical testing which caused the emergence of said peak when 1,2-dihydronaphthalene and 1,4-dihydronaphthalene were employed, and some other explanation seemed more plausible. A second possibility would be the formation of methylindene or methylindan. Methylindene could be formed by the isomerization of a dihydronaphthalene, subsequent hydrogenation could lead to methylindan. The peak at 2965 cm^{-1} is most pronounced in the high temperature spectra for the dihydronaphthalenes, and much less so in the high temperature spectra of isotetralin, where the dihydronaphthalenes are thought to be present only as intermediates. The identity of the compound giving rise to the peak at 2965 cm^{-1} could be verified by a complementary analytical technique such as GC-MS.

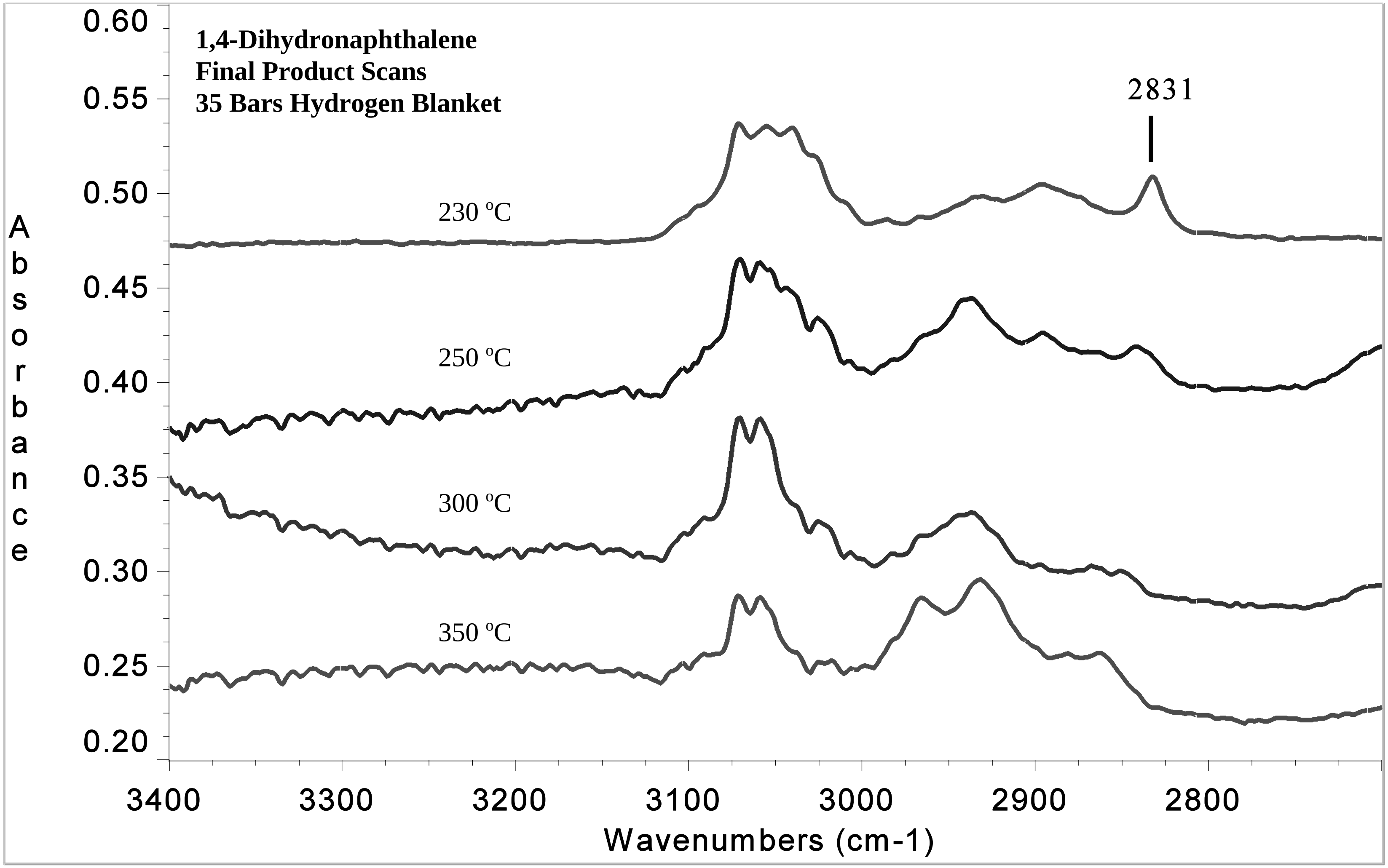
The Effect of Temperature on the Final Product Distribution for 1,4-Dihydronaphthalene

The next most reactive compound in this study was 1,4-dihydronaphthalene. Figure 5-60 presents the final product scans for the 1,4-dihydronaphthalene hydrogen blanket stability studies. In the case of 1,4-dihydronaphthalene, agreement between the synthetic scan and the final product scan from the 230 °C test was very good. For the higher temperature studies, the agreement between the synthetic scans generated from the GC data and the final product scans was either poor, absurd, or there was no GC data.

The products from both the 230 °C and 250 °C tests contained unreacted 1,4-dihydronaphthalene, as determined by GC. The GC data for the 230 °C test were considered reliable. The relative concentrations of the products, as determined from the GC data for the 250 °C test, were not considered accurate. However, the GC results did indicate a substantial conversion for 1,4-dihydronaphthalene, over 80%. The reduction in the peak height at 2831 cm^{-1} by about 75% confirmed this reactivity.

As expected, 1,4-dihydronaphthalene reacted even more completely at higher temperatures, as can be seen by the virtual absence of the peak at 2831 cm^{-1} in the 300 °C and 350 °C final product scans. The distinct peaks of naphthalene can also be observed in these scans. It seemed likely that the products were naphthalene and tetralin, although 1,2-dihydronaphthalene could also be present at a low concentration. The ratio of the aliphatic peak heights to the aromatic peak heights in the 350 °C scan is greater than the ratio of the aliphatic peak heights to the aromatic peak heights in the 300 °C

Figure 5-60



1,4-Dihydronaphthalene
Final Product Scans
35 Bars Hydrogen Blanket
2831
230 ºC
250 ºC
300 ºC
350 ºC
Absorbance
0.60
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

scan, indicating that hydrogenation of 1,4-dihydronaphthalene to tetralin (and possibly some isomerization to 1,2-dihydronaphthalene) was favored over the dehydrogenation to naphthalene as the temperature was increased.

The emergence of a peak around 2965 cm^{-1} was also observed in the high temperature scans for 1,4-dihydronaphthalene. Again, the formation of a compound containing a methyl group was suspected.

The Effect of Temperature on the Final Product Distribution for Isotetralin

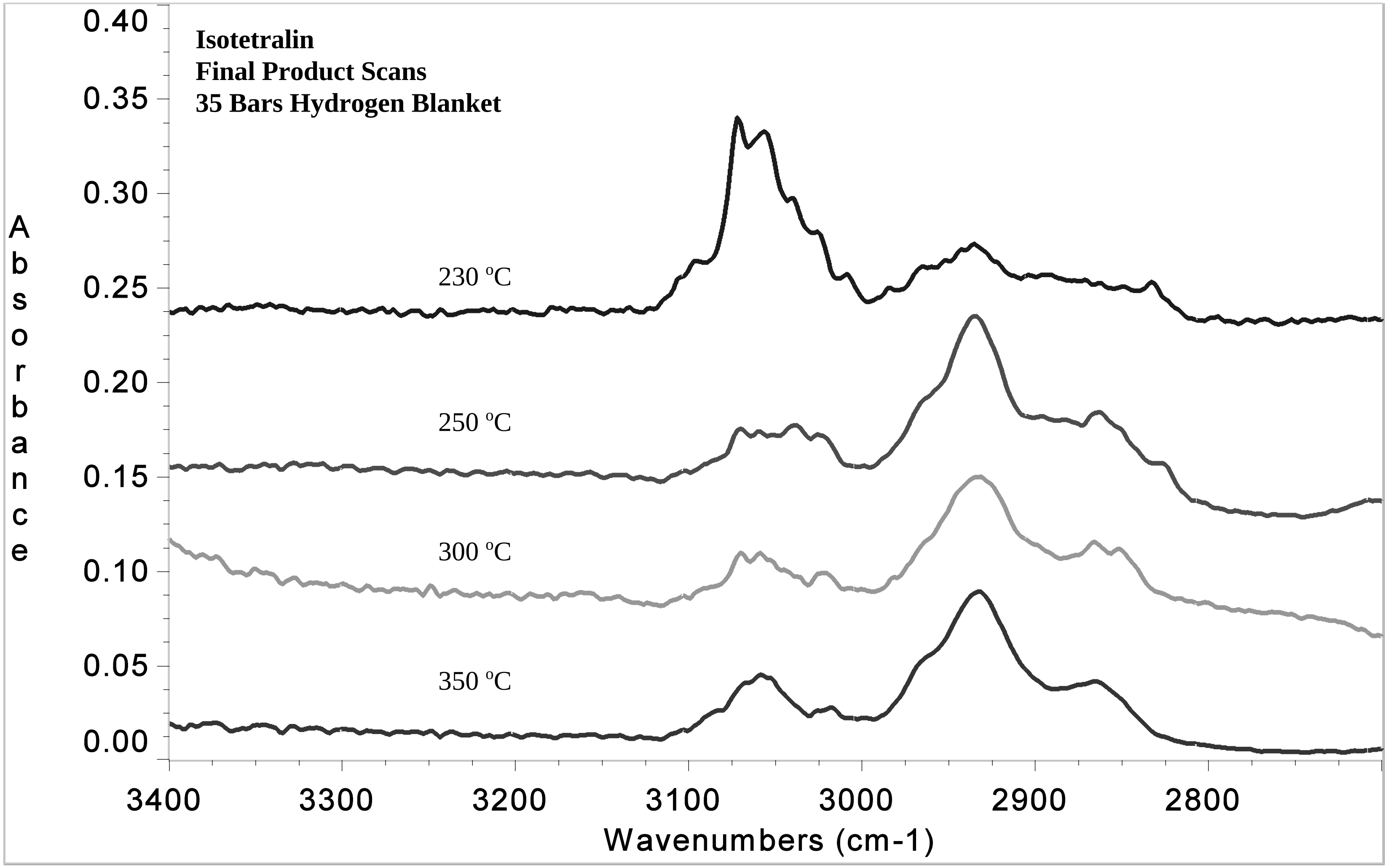
Of primary interest to this study is the reactivity of the cyclic olefin isotetralin. Isotetralin proved to be the most reactive of the compounds in this study. Fortunately, the agreement between the synthetic scans generated from GC results and the final product scans was fair to very good. Figure 5-61 presents the final product scans from the isotetralin hydrogen blanket stability studies.

At the temperatures employed in these studies, dehydrogenation products (naphthalene and the dihydronaphthalenes) were favored by a two to one or greater ratio over the isomerization product (tetralin). This was particularly true in the 230 °C study, where the dehydrogenation products were favored by an eight to one ratio. At 250 °C and above, this ratio was consistently about two to one.

Isotetralin also showed some stretching near 2965 cm^{-1} for the high temperature products, and the formation of traces of a compound containing a methyl group was suspected.

In closing, it should be noted that, with the exception of possible traces of a compound containing a methyl (CH_3) group, no hydrogenation products which were

Figure 5-61


Isotetralin
Final Product Scans
35 Bars Hydrogen Blanket
230 ºC
250 ºC
300 ºC
350 ºC
Absorbance
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
3400
3300
3200
3100
3000
2900
2800
Wavenumbers (cm-1)

more than tetrahydro- substituted (i.e., hexahydro-, octahydro- or decahydronaphthalene) were detected in any of the products from any of the studies performed in this research.

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Chapter VI

Conclusions

The goal of this research, to develop an FTIR spectroscopic method for studying the release of hydrogen from cyclic olefins at elevated temperatures and pressures, has been attained. As with any analytical method, there is ample room available for future refinements. The work presented here establishes the foundation for future development. Appendix D provides a detailed description of the state of the art for this method at the time of the publication of this document. This chapter provides a summary of the results of the current research, and the conclusions that can be drawn therefrom.

Naphthalene, decalin and tetralin were found to be stable at temperatures up to 230 °C under ambient pressure with no atmosphere present, and under a 35 bars nitrogen blanket. Naphthalene, decalin and tetralin were also found to be stable at temperatures up to 350 °C under a 35 bars hydrogen blanket.

For the reactive molecules, i.e., 1,2-dihydronaphthalene, 1,4-dihydronaphthalene and isotetralin, there appeared to be a temperature dependent competition between the mechanisms of hydrogenation and dehydrogenation. 1,2-Dihydronaphthalene proved to be slightly reactive at 230 °C under ambient pressure and under a 35 bars nitrogen blanket. A dehydrogenation to naphthalene of less than 10% was observed in both cases. The presence of a 35 bars hydrogen blanket increased the conversion to naphthalene at 230 °C to about 20%. At 250 °C under a hydrogen blanket, the conversion increased to about 40%, and some tetralin appeared to be present in the product scan. Even greater conversions were obtained in the 300 °C and 350 °C hydrogen blanket tests, the higher temperature tending to favor the hydrogenation of 1,2-dihydronaphthalene to tetralin over the dehydrogenation to naphthalene.

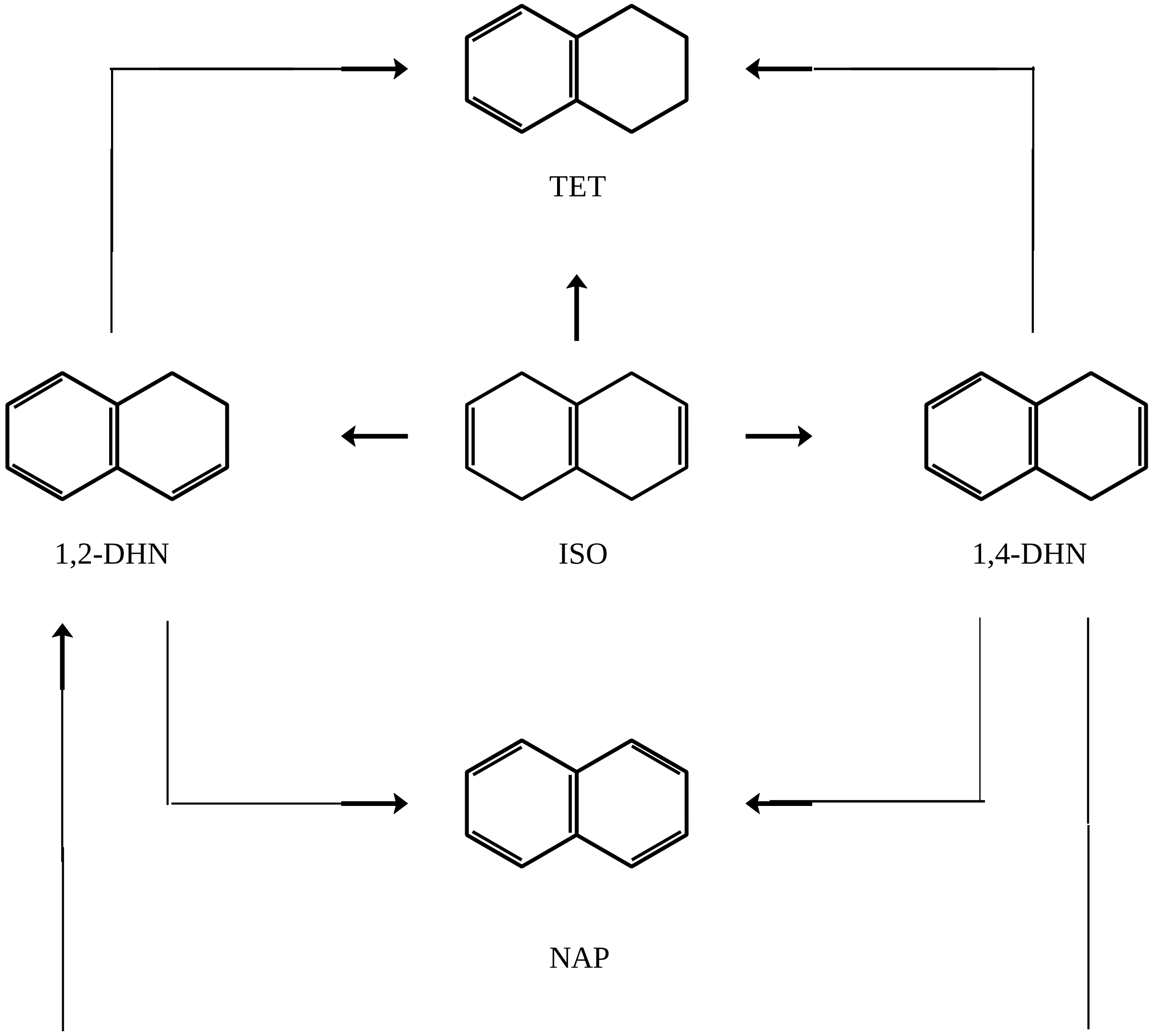
1,4-Dihydronaphthalene proved to be quite reactive at 230 °C under ambient pressure and under a 35 bars hydrogen blanket. A dehydrogenation to naphthalene of over 50% was observed in both cases. The presence of a 35 bars nitrogen blanket suppressed the reaction of 1,4-dihydronaphthalene significantly, the conversion to naphthalene being reduced to about 10%. At 250 °C under a 35 bars hydrogen blanket, the conversion increased to about 75%. The product was mostly naphthalene, but a significant amount of 1,2-dihydronaphthalene and a small amount of tetralin were also formed. Even greater conversions were obtained in the 300 °C and 350 °C hydrogen blanket tests, the higher temperature tending to favor the hydrogenation of 1,4-dihydronaphthalene to tetralin over the dehydrogenation to naphthalene.

Isotetralin proved to be highly reactive at temperatures from 150 °C to 230 °C under ambient pressure, reacting to form tetralin as the major product and naphthalene as a minor product. The presence of a 35 bars nitrogen blanket stifled the reaction of isotetralin at 230 °C. While some tetralin and naphthalene were formed, the extent of reaction was reduced significantly as compared to the ambient pressure test. At 230 °C under a 35 bars hydrogen blanket, isotetralin reacted completely to form naphthalene as the major product and 1,4-dihydronaphthalene and tetralin as minor products. The dehydrogenation to naphthalene and 1,4-dihydronaphthalene was favored over the isomerization to tetralin by a factor of about eight to one. In the temperature interval from 250 ºC to 350 ºC, the production of hydrogenation products (naphthalene and the dihydronaphthalenes) was favored over the production of the isomerization product (tetralin) by a consistent factor of about two to one. 1,4-dihydronaphthalene was detected in the 230 ºC and 250 ºC product mixtures, and 1,2 dihydronaphthalene was detected in the 300 ºC product mixture. Both are thought to be reaction intermediates.

Figure 6-1 provides a proposed reaction pathway for the thermal (non-catalytic) reactions of isotetralin based on the results of the current work. Certain items in this figure should be pointed out. Naphthalene and tetralin both proved to be stable. With the possible exception of the production of traces of a compound containing a methyl group, no hydrogenation products beyond tetra- substituted (i.e., hexa-, octa- or decahydronaphthalene) were formed. 1,2-Dihydronaphthalene dehydrogenated to produce naphthalene and also hydrogenated to produce tetralin, with the higher temperatures favoring the latter process. There was no evidence of isomerization to 1,4-dihydronaphthalene. 1,4-Dihydronaphthalene reacted in a similar fashion, but there was isomerization to 1,2-dihydronaphthalene accompanying the hydrogenation and dehydrogenation. Isotetralin dehydrogenated to produce naphthalene and also isomerized to produce tetralin. Again, the higher temperatures were seen to favor the production of tetralin.

Figure 6-1

Proposed Reaction Pathway for Isotetralin



The question which naturally arises is this: Is the conversion of isotetralin to tetralin a single step isomerization, or is there a two step mechanism wherein isotetralin is dehydrogenated to a dihydronaphthalene and the dihydronaphthalene is subsequently hydrogenated to tetralin? It may even be possible that isotetralin could be hydrogenated to 1,4-dihydronaphthalene, the resulting 1,4-dihydronaphthalene isomerized to 1,2-dihydronaphthalene, and the 1,2-dihydronaphthalene subsequently hydrogenated to tetralin in a three step mechanism. In addition, what role do the intermediates play in the competition between dehydrogenation to naphthalene and isomerization to tetralin, and how does temperature affect their formation and subsequent reactions? This and some of the many other areas which have been opened to research by the current work are discussed in Chapter VII.

Chapter VII

Future Work

The current work has established the foundation for a myriad of future investigations. The procedure for acquiring FTIR data at combined elevated temperatures and pressures is not limited to studying the release of hydrogen from cyclic olefins, but has far reaching implications for FTIR solution spectroscopy in general. Future applications of the method in the study of coal liquefaction will be presented first, followed by more general applications to FTIR solution spectroscopy.

Applications to Coal Liquefaction Studies

A number of problems which arose during the high temperature/high pressure studies need to be addressed before reliable quantitative measurements of the concentrations of reactants, intermediates and products, which are necessary to determine kinetics mechanisms, can be obtained.

The linear region of the absorbance versus concentration curves for the compounds in this study was quite narrow. It may be possible to extend the linear region of the absorbance versus concentration curves by adjusting the optical characteristics of the system.

Maintaining the samples at a sufficiently high temperature to prevent dissolution of the solutes on transferring from the oven to the reactor proved quite challenging. Owing to their small volume, the sample bottles cooled quite rapidly on exposure to ambient air. A better sample handling technique could be developed, or a flow system with a preheater might be employed.

The effect of temperature on the shape of spectra and, particularly, the dependence of peak height (and therefore concentration) on temperature should be examined in some detail. Also, high temperatures cause volatilization of solutes into the vapor space above the reactor. The vapor space above the reactor needs to be minimized, or, at least, it should be insulated and heated to minimize condensation of solutes in the cool tubing leading to the pressure gauge. Alternatively, the tubing and pressure gauge could be replaced with a very low volume pressure transducer.

The Kalrez™ o-rings were not recommended for use over 288 ℃, and had to be replaced after each of the 300 ℃ and 350 ℃ stability studies. The manufacturer supplies gold o-rings, and these may be required, particularly if extension to even higher temperatures is desired. The cell manufacturer has also made available windows constructed from sapphire or diamond. These may be advantageous if extension to higher temperatures and pressures is desired.

The identification of the peak which emerged around 2965 cm^{-1} in the higher temperature stability studies for the reactive compounds also remains for future work. The use of a hyphenated analytical technique such as GC-MS may help identify this compound.

The toluene extraction procedure developed for GC analysis of hydrocarbons in Krytox™ is still in the very early stages of development. Considerable future work will be required to develop this method to the point where reliable data can be obtained on a routine basis. Also, the development of an internal standard technique will be necessary to acquire quantitative measurements of the concentrations of reaction products.

Because of the very strong interactions between hydrocarbons and perfluorocarbons in solution, it could be argued that the release of hydrogen from cyclic olefins in perfluorocarbon media does not provide an accurate model of hydrogen donation under actual coal liquefaction conditions. If another class of suitable solvents could be found, then a direct comparison of kinetics mechanisms could be performed to determine how appreciable solvent effects are.

The presence of a hydrogen acceptor is known to influence the release of hydrogen from the donor. Studies with model acceptors should be performed. Benzophenone is particularly well suited to this type of study because of the highly intense carbonyl absorbance around 1700 cm^{-1}, whereas the hydrogenated form, diphenylmethane, does not absorb near this wavenumber. For purposes of comparing hydrogen donor ability, not only cyclic olefins, but also conventional donors, should be tested. It may be desirable to operate the system in flow-through mode and pump the donor/acceptor solution through the cell for these studies.

Applications to FTIR Spectroscopy in General

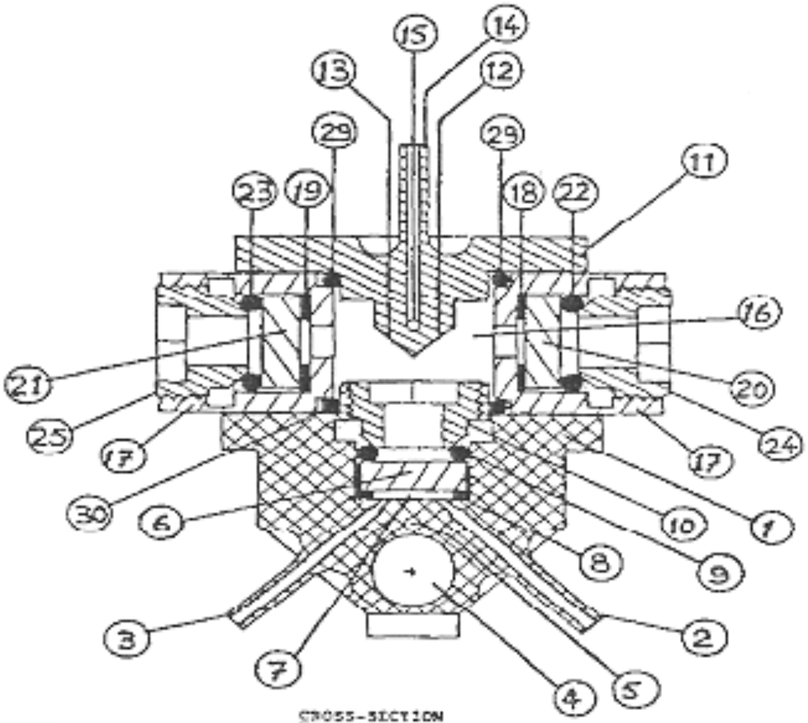
The current research also has implications for the future of high temperature/high pressure FTIR spectroscopy in general. The method could be used to study reaction kinetics in general, in solution in a batch system, or with some modifications, in a flow system. Non-catalytic and catalytic studies could be performed. Homogeneous catalysis could be studied in either batch or flow-through mode. A catalyst disc could be employed with either a batch or a flow system to study heterogenous catalysis. For the flow system, the catalyst could also be slurried into the cell (heterogeneous catalysis).

Gases could be dissolved in the solution by the application of a suitable gas blanket. The gas pressure could be maintained by a regulator as the gas dissolves and reacts. If gases are generated by a reaction, then a gas flow system could be employed.

The operating range of the cell could be extended to its temperature and pressure limits of 425 ^{o}C and 140 bars using Krytox™ as solvent. The use of gold o-rings will be required. Diamond or sapphire windows may be advantageous in this application. It may also be possible to find other suitable solvents or employ supercritical fluids in future testing.

APPENDIX A

CELL SCHEMATIC



CROSS-SECTION

LEGEND:

1. CELL BODY
2. CELL INLET/OUTLET PIPE
3. CELL INLET/OUTLET PIPE
4. HEATER CAVITY
5. THERMOCOUPLE CAVITY
6. CELL WINDOW
7. SAMPLE CAVITY
8. PATHLENGTH SPACER
9. WINDOW SEAL (O-RING)
10. HOLLOW SCREW
11. OPTICS UNIT
12. REFLECTING FACE
13. REFLECTING FACE
14. GAS INLET/OUTLET PIPE
15. INLET/OUTLET CROSS-HOLE
16. GAS PRESSURIZATION CHAMBER
17. SPACER UNIT
18. WINDOW CUSHION (OPTIONAL)
19. WINDOW CUSHION (OPTIONAL)
20. SECONDARY WINDOW
21. SECONDARY WINDOW
22. SECONDARY WINDOW SEAL (O-RING)
23. SECONDARY WINDOW SEAL (O-RING)
24. HOLLOW SCREW
25. HOLLOW SCREW
26. ASSEMBLY SCREW
27. ASSEMBLY SCREW
28. ASSEMBLY SCREW
29. ASSEMBLY SEAL (O-RING)
30. ASSEMBLY SEAL (O-RING)
31. CASTELLATED EDGE (CELL BODY)
32. CASTELLATED EDGE (CELL BODY)
33. CASTELLATED EDGE (CELL BODY)
34. CASTELLATED EDGE (CELL BODY)

APPENDIX B

A Procedure for Obtaining High Temperature Spectra

1. Check IR source coolant and nitrogen purge flows.
2. Scan empty spectrometer as background.
3. Scan empty spectrometer as sample. This should give a straight line.
4. Mount cell and attach coolant lines, power cord and thermocouple.
5. Scan empty cell as sample. This provides a check for residual hydrocarbons.
6. Scan empty cell as background.
7. Scan empty cell as sample. This should give a straight line.
8. Fill cell with neat solvent (APF-240™) and remount as in Step 4.
9. Scan neat solvent as sample. This is a check for impurities.
10. Scan neat solvent as background.
11. Scan neat solvent as sample. This should give a straight line.
12. Place cell in oven at 65°C.
13. Place a glass pipette in the oven at 65°C.
14. Sample preparation
    a. Solid sample handling (naphthalene, isotetralin)
        i. Weigh the appropriate amount of solid to give a one gram per liter solution. The volume of the reactor is about 0.3 milliliters. One to two milligrams of solute mixed with one to two milliliters of solvent should provide much more solution than is

required to fill the reactor.

- ii. Pipette the appropriate amount of solvent, one milliliter of solvent per milligram of solute.
- iii. Reweigh to determine the mass of solvent used.
- iv. Store in the oven at 65°C until ready to use.
- v. Shaking may be necessary to achieve dissolution.

b. Liquid sample handling (decalin, tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene)

- i. Pipette the appropriate amount of solute to give a one gram per liter solution. The specific gravities of these liquids are close to unity, so one microliter of liquid should weigh about one milligram. One to two milligrams of solute in one to two milliliters of solvent should suffice.
- ii. Weigh the solute.
- iii. Pipette the appropriate amount of solvent, one milliliter of solvent per milligram of solute.
- iv. Reweigh to determine the mass of solvent used.
- v. Keep in the oven at 65°C until ready to use.
- vi. Shaking may be necessary to achieve dissolution.

15. Mount cell as in Step 4 and preheat to 65 °C.
16. Fill the cell with sample solution using a hot pipette.

17. Scan sample using neat solvent as background.
18. The sample can now be subjected to the stability test. The stability test consists of stepping the samples from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding at the initial temperature and each intermediate temperature for thirty minutes. Scans are obtained before and after each step, and a scan is taken every thirty minutes at the final temperature for a period of three to four hours.

Appendix C

Development of a GC Method using Toluene Extraction

As noted earlier in this paper, a toluene extraction procedure was developed in order to carry out GC analysis of the product mixtures. This was necessary because of the high boiling point of Krytox™, over 450 °C. DuPont cautioned strongly against injecting Krytox™ onto a GC column. Since, in this application, the injection port temperature is 300 °C, a build-up of residue on the injection port could be expected. However, the solutes could be extracted from the reaction product mixtures using a suitable solvent and the resulting extract injected onto the column. While these solutes have very low solubilities in Krytox™, they are readily soluble in toluene, and a small amount of toluene should suffice to extract virtually all of the solutes into the toluene phase.

The procedure developed was as follows:

1) While maintaining the reactor at 130 °C to prevent precipitation of solutes, pour the reaction product into a preweighed bottle. A milky suspension forms on cooling.
2) Weigh the bottle to determine the mass of the reaction product recovered. This was generally around 0.15 grams, or about 1/3 of the charge to the reactor. Because of the high viscosity of Krytox™, even at 130 °C, only a portion of the product could be removed by pouring out the contents of the reactor.

3) The density of Krytox™ is about 1.7 g/ml. The amount of product recovered is usually about 0.1 ml. Three to four times this volume of toluene should easily extract all the solutes from the Krytox™. Pipette the appropriate volume of toluene into the bottle containing the product mixture.

4) Weigh the bottle to determine the amount of toluene used for the extraction.

5) Pipette one microliter of a 100 ppm solution of diphenylmethane in toluene into the bottle for use as an internal standard.

6) Shake at 65 °C for 10 to 15 minutes to insure extraction of solutes into the toluene phase. The sample is now ready for injection onto the GC column. Because of the low concentration of solutes in the toluene, adjustments to the sensitivity of the detector may be necessary to achieve peak area counts sufficient for quantitation.

APPENDIX D

A Procedure for Obtaining High Temperature Spectra

(The State of the Art as of March 18, 1998)

1. Check IR source coolant and nitrogen purge flows.
2. Scan empty spectrometer as background.
3. Scan empty spectrometer as sample. This should give a straight line.
4. Mount cell and attach coolant lines, power cord and thermocouple.
5. Scan empty cell as sample. This provides a check for residual hydrocarbons.
6. Scan empty cell as background.
7. Scan empty cell as sample. This should give a straight line.
8. Fill cell with neat solvent (APF-240™) and remount as in Step 4.
9. Scan neat solvent as sample. This is a check for impurities.
10. Scan neat solvent as background.
11. Scan neat solvent as sample. This should give a straight line.
12. Place cell in oven at 65°C.
13. Place a glass pipette in the oven at 65°C.
14. Sample preparation
    a. Solid sample handling (naphthalene, isotetralin)
        i. Weigh the appropriate amount of solid to give a one gram per liter solution. The volume of the reactor is about 0.3 milliliters. One to two milligrams of solute mixed with one to two

milliliters of solvent should provide much more solution than is required to fill the reactor.

- ii. Pipette the appropriate amount of solvent, one milliliter of solvent per milligram of solute.
- iii. Reweigh to determine the mass of solvent used.
- iv. Store in the oven at 65°C until ready to use.
- v. Shaking may be necessary to achieve dissolution.

b. Liquid sample handling (decalin, tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene)

  - i. Pipette the appropriate amount of solute to give a one gram per liter solution. The specific gravities of these liquids are close to unity, so one microliter of liquid should weigh about one milligram. One to two milligrams of solute in one to two milliliters of solvent should suffice.
  - ii. Weigh the solute.
  - iii. Pipette the appropriate amount of solvent, one milliliter of solvent per milligram of solute.
  - iv. Reweigh to determine the mass of solvent used.
  - v. Keep in the oven at 65°C until ready to use.
  - vi. Shaking may be necessary to achieve dissolution.

15. Mount cell as in Step 4 and preheat to 65 °C. Apply desired gas blanket and pressurize the gas pressurization chamber with ultra-high purity nitrogen.
16. Fill the cell with sample solution using a hot pipette.
17. Scan sample using neat solvent as background.
18. The sample can now be subjected to the stability test. The stability test consists of stepping the samples from 65 °C to 100 °C, 150 °C, 200 °C, and finally to 230 °C, while holding at the initial temperature and each intermediate temperature for thirty minutes. Scans are obtained before and after each step, and a scan is taken every thirty minutes at the final temperature for a period of three to four hours.
19. For operation above 230 °C, APF-240™ is replaced with Krytox™ and the temperature in steps 12, 13, 14.a.iv and 14.b.iv is increased to 130 °C. The sample is heated as rapidly as possible (but not to exceed the cell manufacturer's criterion of 50 °C in ten minutes) to the temperature of the study. Rapid heating is necessary to minimize the formation of products at temperatures below 250 °C, which can alter the product ratios in the higher temperature tests. For the reactive compounds, the scanning interval is shortened to 15 or even 10 minutes in order to more closely follow the course of the reaction.
20. The gas pressurization chamber should be maintained at a slightly greater pressure (one to two bars differential) than the sample chamber to prevent rupture of the Kalrez™ o-ring.

21. The interferometer signal strength (both voltage and gain) should be recorded each time a scan is taken.
22. The coolant flow must be carefully monitored during high temperature operation. The discharge lines leaving the cooler should sweat. The return lines will be warm but should not feel hot to the touch.
23. The final product scan should be taken when the reaction products have cooled to the initial temperature of the study, i.e., 65 °C or 130 °C.
24. Because the solvents employed are highly viscous, the solutions must be removed while still hot, i.e., at 65 °C or 130 °C.
25. The solutes are quite volatile and their concentrations in solution can change significantly in a matter of days or even hours. Reactants (samples of charges to the reactor) and product mixtures should be injected onto the GC as quickly as practical.
26. APF-240™ solutions can be injected directly onto the GC. Krytox™ solutions must be handled in accord with Appendix C.
27. A synthetic scan should be made using the GC results and the OMNIC™ software for comparison to the final product scan.
28. The reactor must be disassembled and thoroughly cleaned with perfluorohexane after each run.