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LOW TEMPERATURE INFRARED CELL AND ITS APPLICATION IN ISOPRENE AND NITROGEN DIOXIDE REACTION STUDIES

BY

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INTRODUCTION

The purpose of this research was to explore the application of low temperature infrared spectroscopy to the study of several chemical problems. In particular the following items were investigated:

1. The design, manufacture, and operation of a low temperature optical cell suitable for infrared spectroscopic studies of gas-solid samples at liquid nitrogen temperature (-196°C) and above.
2. The recording and study of the infrared spectra of nitrogen dioxide and isoprene at 25°C and at lower temperatures.
3. A preliminary study of the reaction between nitrogen dioxide and isoprene at various temperatures using infrared techniques.

In recent years infrared studies have been developed and used successfully in research as well as in industry for qualitative and quantitative chemical determinations. These methods have been extended by the use of specially designed accessories to studies of chemical reactions at high and low temperatures. Low temperature studies are applied in the identification of free radicals, intermediate products, and studies of reactions which are rapid at room temperatures. It was the desire of the author to explore and use the cold temperature techniques in connection with infrared spectroscopy.

HISTORICAL

Infrared spectroscopy is not a new field. Sir William Hershel (43) in 1800 discovered infrared radiation by placing a thermometer at successive points in a glass prism dispersed spectrum of the sun and observing the temperature rise. Essentially these components are still used today: a hot source of continuous radiation, prism dispersion, and a temperature sensitive device known as a detector. Julius (17) was the first one who pointed out the analytical possibilities of a new field of science. In 1892 he demonstrated the relationship between the structure of the organic molecules and their infrared spectra. His conclusions were confirmed and extended by the monumental work of Coblenz (22). The earliest applications of infrared spectroscopic techniques to the chemical industry occurred in the 1920's. However, the greatest advances in this technique have been made in the last twenty years during which time commercially available instruments were manufactured and sold at reasonable prices (40). Infrared spectroscopy has been a valuable tool for the chemist. As any analytical technique, it can be used to identify compounds by their characteristic spectra or to determine the concentration of a material by measuring the absorption band intensity. Many molecule structural problems have been solved by the use of infrared spectroscopy. Recently, the usefulness of infrared spectroscopy has been extended to studies at low temperatures.

I. Low Temperature Studies

There are numerous problems which can be solved by low temperature infrared spectroscopy. Hornig (51) has listed a number of them:

1. The study of interaction forces between molecules at close distances of approach.
2. The determination of the structure of crystals.
3. The study of hydrogen bonding.
4. The study of molecular species which exist only in crystals or are stable only at low temperatures.
5. The study and identification of molecules.

The latter study is aided by the characteristically sharp spectra at low temperatures, which make possible the observation of many more transitions.

The changes in the absorption spectra with the change of the temperature of the sample were observed by Lorenz (67) in 1927 and Fesefeldt (34) in 1930. Avery and Ellis (5) in 1942 reported that the width of the infrared absorption bands decreased by roughly 50% on passage from room temperatures to -195°C. This important observation was confirmed by Mador and Quinn (69) who noticed the sharpening of the bands at low temperatures. They believed that this was explained, at least partly, by the phenomenon that higher rotational levels will depopulate at lower temperatures. The crystallization of a liquid gives rise to a further narrowing of the absorption bands (78).

One of the main subjects in cold temperature work is the study of free radicals and other extremely reactive species. Free radicals are defined as molecular fragments which normally have a short lifetime (of the order of milliseconds), which are highly reactive, and which are characterized generally by having an unpaired electron. The recent developments in the low temperature work have been in the direction of studies in stabilization of reactive molecules. Therefore, most of the work has been focused on free radical studies.

The production, trapping, and stabilization of free radicals at low temperatures in rigid media first were studied systematically by Lewis (63) and his students in the early 1940's. Absorbance bands were observed in the ultraviolet region which disappeared upon warming the cell. This phenomenon was observed when a solution consisting of tetraphenylhydrazine, ethyl ether, isopentane, and ethyl alcohol in a glass cell at liquid nitrogen temperature (-196°C) was irradiated with ultraviolet light. The cold temperature study of chemical compounds later also was started in the infrared region with great success.

The sample has to be trapped, cooled, and maintained at the cold temperature to enable one to perform the necessary measurements. To do this, special equipment has to be designed. The required parts of this equipment are a sample holder, a container for the coolant, and windows transparent in the spectral region of interest.

Lorenz (67) designed a cold cell in 1927 for studies in the ultraviolet region. This cell consisted of a copper container for the coolant liquid. The container had a thick base to which a copper finger was attached. This copper finger had an opening where a crystal was held in place by screws. An electric heater on an outside shell prevented the windows from fogging. Thomas (97) had a similar cell which contained a double set of quartz windows.

The first cold cell for studies in the infrared range was designed by Zunino (105) in 1936. This cell was a reflection type which utilized an aluminized mirror on which the sample was deposited. The energy beam was directed toward the mirror, reflected, and then proceeded through its normal path.

Conn and co-workers (24) continued this idea and applied the cell for low and high temperature studies. It was primarily used for examination of solid layers at liquid air temperature, but it was equally suitable for gases at low or high temperatures. This cell consisted of a Pyrex tube seven centimeters wide into one end of which a flat Pyrex plate had been sealed. This was silvered on the inside. The outer end contained the sodium chloride window. The window was held in place by a brass plate which was waxed to the Pyrex tube. Percenam paint was used to make the joint tight. There were two side limbs, one to conduct the gas under examination, the other for thermocouple leads which were hard soldered onto a piece of tungsten fused into the surface of the silvered base. The lower part of the cell was immersed in a constant temperature bath. The condensation of water on the sodium chloride window was overcome by having a small heating coil wrapped around the cell, just below the window. In order to obtain "cell out" readings for the estimation of percentage absorption, an additional plane mirror was swung into the path of the beam. The mirror reflected the radiation onto an adjustable vertical mirror which returned it to the inclined mirror and into the original path of the beam from the cell. This arrangement required only one sodium chloride window, which were expensive at that time.

Avery and co-workers (5,6) used a similar reflection type cell for their work in the temperature range of $0^{o}C$ to $-195^{o}C$.

The reflection type cell avoids the necessity of maintaining the infrared transparent window at the temperature of the sample. However, the reflected beam contains radiation reflected directly from the surface to the sample film, in addition to the radiation transmitted by the film and then reflected at the mirror surface. This effect can lead to an erroneous apparent transmission since strong absorption by the sample is generally accompanied by a high reflectivity from the sample surface as discussed in the paper by McMahon and co-workers (72).

Transmission cold cells or cryostats for infrared absorption spectroscopy are designed to eliminate the problems caused by reflection type cells and to obtain a better means for observation of temperature effects on absorption spectra and studying unstable compounds. The problem in designing a research cryostat is to make provisions for keeping the specimen in thermal contact with the primary refrigerant while observing or measuring some property at low temperatures. Two types of cryostats are widely used in cold temperature work. They can be made from either glass or metal. The choice between glass and metal construction depends on the availability of shop facilities and skilled craftsmen. Both types of cold cells must contain four essential features for gas-liquid-solid studies. They are a tank containing the refrigerant, such as liquid nitrogen, a vacuum space around this tank to decrease the rate of heat transfer to the refrigerant, a cold surface on which vapors can be condensed, and provisions for observing the material and measuring its properties.

The glass Dewars offer advantages of economy, simplicity, flexibility, and visibility. The advantages of metal cryostats are the immunity from breakage, better temperature uniformity, and the ease with which certain mechanical features may be incorporated. For some time it was believed that highly polished metal surfaces reduced heat transfer. This has been proven to be false (71).

McMahon, Hainer, and King (72) described in 1949 a transmission cold cell for infrared studies. The sample was introduced into the cell as a gas and condensed onto one side of the vacuum tight infrared window which was bathed on the inner side by cold helium gas. The helium gas removed energy absorbed by the sample and transferred it to the walls of the container which was immersed in liquid helium. The windows were made of silver chloride.

In 1950 Holden, Taylor, and Johnston (50) designed a metal cold cell. The metal Dewar was similar to that of Henry and Dolecek (47). The cryostat was made of brass Dewar. The absorption cell was supported from the bottom of the inner can. A high vacuum was maintained in the space between the cans by means of a metal diffusion pump. Thermal contact was established between the cell and the refrigerant by a "heat valve", which consisted of a thin metal wall surrounding, but not in contact with, a metal block. The wall and block were soft-soldered to the cell, but only the monel wall was soldered to the base of the refrigerant containers. Thermal contact between the refrigerant and the cell was varied by evacuating the thin space between the upper face of the block and the base of the container or by introducing helium. A metal bellows connected the refrigerant vessel to the head of the cryostat. Since the head was essentially at room temperature, an ordinary gasket permitted a vacuum tight seal to be made between it and the outer can.

The sample was introduced into the cell as a gas after the cell was cooled to a temperature at which the gas would condense. The cell was maintained at constant temperature while the infrared absorption spectrum was obtained.

Duerig and Mador (31) in 1952 designed a metal cryostat which could be adapted for a variety of operations. It was a portable unit thirty four inches tall consisting of the outer vacuum jacket including appropriate windows, liquid nitrogen container, and radiation shield, stainless steel liquid helium container, and copper crystal holder, which was in direct contact with the coolant. Alkali halides were used for optical materials between or on which the sample was deposited. To improve the thermal contact between the crystal and the copper holder, silicone grease loaded with silver dust, silver conducting paints, and soldering with indium were used to bring the temperature of the crystal to five to eight degrees Kelvin. A novel feature was the Sylphon bellows mounting of the helium vessel which permitted the whole assembly, including sample holders, to be moved up two inches. This permitted either of two samples or a blank to be aligned with the beryllium X-ray windows for irradiation or the rock-salt windows for spectral absorption measurements. The cell was used also for a study of the optical properties of the alkali halides at various temperatures. Such a study was carried on at the same time by Kaiser (53) and Dutton and Maurer (32).

Cylinders of Monel metal silver were soldered in such a way as to form a double Dewar by Becker and Pimental (10). Liquid hydrogen or helium was used in the inner reservoir as refrigerant and liquid nitrogen in the outer reservoir as a radiation shield. A silver chloride window was held in contact with a thin silver sheet and a copper block by a screw. The copper block was cooled through a copper rod protruding into the refrigerant. Temperature was measured with a copper constantan thermocouple held by Wood's metal in a gold tube embedded in the silver chloride window. With liquid hydrogen as the coolant, the window temperature was $20^{\circ}K \pm 3^{\circ}$. The sample was deposited on the window through a glass tube directed at the window. Geiger (38) designed a similar cell for cold temperature studies.

Fateley and co-workers (33) designed an easily demountable cell using three separate sections made of stainless steel. Leaks could be easily found. Ring seals were used to make each section vacuum tight.

De More and Davidson (27) performed cold temperature studies with a cell which could be used to obtain pure absorption spectra or for reflectance techniques. The cell consisted of a windowed cold finger suspended in a vacuum chamber in such a manner that gases from storage vessels could be effused onto one of the cold windows. The cell was suitable for use with liquid helium, nitrogen, or hydrogen. The coolant containers were constructed of brass, the neck from stainless steel, and the outer jacket from aluminum. Vacuum seals were made by means of O-rings. Silver soldering was used throughout except for the seal where Pyrex parts were used. Soft solder was used there. During effusion the cold finger was rotated to face the jets of gases which were deposited on the sample window. The cases where reflectance techniques were employed, the sample window was aluminized.

White (102) made his cell from #316 stainless steel. The outer jacket contained four windows, two of which were sodium chloride and in line with one another for infrared studies. The other two were positioned at 60° angles with respect to one of the infrared windows. One contained the spraying nozzle, the other was quartz or sapphire for ultraviolet studies. In cases where frosting or condensation of water appears, dry and de-oiled air can be sprayed on the outside windows (66) or small heating wires can be inserted in the windows to cancel the cooling from within the cell (37).

One of the earlier glass type cold cells for infrared spectroscopic studies of molecules was designed by Wagner and Hornig (99) in 1950. The cell could be inserted into the beam of the spectrophotometer without changing the optical path. The cell was composed of a copper cooling block, a coolant reservoir, and a glass enveloping jacket. The cooling block consisted of a piece of solid copper through which a rectangular hole had been machined in such a way that a shoulder existed in the center of the block. The rock salt plate rested against this shoulder and was held in position by means of an annular copper plug. Thin films of the sample were obtained by subliming the salt to be studied onto the polished rock salt plate. A thin layer of vacuum grease between the shoulder and the salt plate was found necessary to obtain adequate thermal contact. The temperature was measured by a thermocouple. The glass coolant reservoir was attached to the cooling block by means of a copper to glass housekeeper seal which gave an extremely satisfactory vacuum tight joint. The rock salt or silver chloride windows were sealed onto the flat ground ends of the glass jacket with clear Glyptal lacquer. A similar cell was constructed by Dows (30) but he added a radiation shield made from a copper sheet. The sample was deposited on the cooled window through a glass tube and condensed on the window.

Walsh and Willis (101) described a cell which could be used for the study of materials which are liquids or solids at room temperature. The specimen to be studied was carried on a one inch diameter rock salt plate which was inserted into a brass holder and held firmly by screwing the two halves together. A thin lead washer was between the brass holder and the plates to ensure good heat transfer. The inside surfaces of the cell were silvered. A copper rod was connected to the brass holder. The inside container was sealed into a Pyrex tube, and the space between them was evacuated. The cooling agent was poured in the inside tube. The sample was placed on the rock salt plate by sublimation techniques or by placing a drop of liquid between the salt plates and inserting them in the holder.

A glass tube with windows inserted in a styrofoam container containing liquid nitrogen was used by Nelson (75) for low temperature studies. Although this type cell had many limitations, it had an advantage in the uniformity of the temperature throughout the sample because the container was surrounded by the coolant. Fontana (36) produced a "cold well" cryostat which had the same advantage but could not be used for absorption studies.

Lord and co-workers (65) and Linevsky (64) described a glass Dewar type cold cell which contained a cold finger with a window on which the sample was deposited. About the same cell with modifications was designed by Stewart (93). The sample again was condensed as a thin film on the cold salt plate at low temperature. The cell used silver chloride lenses as beam condensers (4). The sample was introduced in the cell through a polyethylene tubing. Because of the small diameter of the lenses, it was necessary to install two movable blades on the slit holder to avoid vignetting. The cell had to be cooled thirty to sixty minutes before the sample was introduced.

A cold cell with two windows on each side was described by Nikitin (77). The vacuum jacket was made of molybdenum glass with the windows cemented to it. The copper cold finger was welded to a steel tube with a channel drilled in it which contained the refrigerant. The water and carbon dioxide present in the jacket froze on the steel tube. The windows were free of condensation when this was done. In this way the cell could be cooled to -120°C. For further cooling to -160°C the cell had to be evacuated. A heating coil was wrapped around the steel tube with which the temperature of the cell could be increased to +300°C.

A rather complex glass cryostat was designed by Schoen and co-workers (88) for studies of absorption spectroscopy of short-lived intermediates. One of the important features of this design was a movable and removable liquid helium reservoir with an infrared transparent cold surface affixed to it. Standard taper and ball-and-socket ground joints were used to achieve flexibility and interchangeability of accessories. The central helium finger was insulated by a separate vacuum jacket, which terminated in a ball section of a large ball-and-socket joint. This joint remained at room temperature and permitted rotation of the helium Dewar around a vertical axis during the experiment. The glass bellows permitted expansion and contraction during temperature changes. A stopcock was provided for periodic evacuation of the vacuum jacket to remove helium that diffused through the glass. The tip of the helium finger terminated in a Kovar metal cup. A thin-walled copper box with a one inch diameter tube through its center was soldered to the cup. The copper box was connected to the helium reservoir by several holes in the Kovar cup. The tube through the box was internally threaded and equipped with copper washers and screw rings so that disks of various window materials could be installed. The window could be turned to any point for deposition or observation.

The base of the Dewar was made from a two liter round-bottom flask with female sections of standard taper joints, set in at 90-degree intervals. This arrangement permitted the use of various plug-in windows, observation ports, wire leads, and gas carriers.

A copper shield, silver plated and highly polished, was cemented to the walls of the nitrogen reservoir. To reduce the heat leaks, the inside of the outer vacuum wall and the outside of the nitrogen container were silvered, and a copper sponge was inserted in the neck of the finger just above the surface of the liquid helium. Measurements could be continued for 45-60 minutes without refilling.

Roberts (84) described a cold cell designed for the absorbance measurements of solid samples, whose mounting allowed the sample in the cooled state to be moved out of the beam and brought back again into the same position. This movement was done by an air-tight push rod connected by a bellows-fitting to an operating lever outside the cell casing.

A cold temperature cell for studies of liquid samples and their reactions was designed by Nencini and Pauluzzi (76). The sample was circulated from the reaction vessel to the stainless steel absorption cell. The solution was pumped back to the reaction vessel. The whole unit was immersed in a constant temperature bath. The temperature range for this cell was -60° to 100°C.

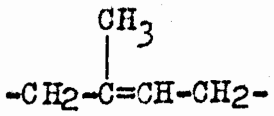
Janz and Fitzgerald (52) and Lovell and White (68) made cells from modified standard liquid cells for the study of spectral changes for liquid-solid transitions.

II. Isoprene-Nitrogen Dioxide Reaction

The olefin and nitrogen dioxide reaction is known to be of a significant importance, particularly in the study of atmospheric pollutants and effluents from automobiles, buses, trucks, various types of incinerators, and perhaps from other types of combustion devices as well (1). The reaction, which reportedly undergoes several steps, must be slowed down to negligible rates in order to examine the intermediate reaction products which are unstable at room temperature. One suitable means for this is the use of a cold temperature cell.

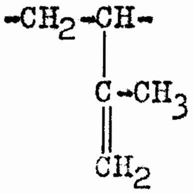
A. Isoprene

Isoprene (2-methyl-1,3-butadiene) is a colorless liquid at room temperature with the boiling point +34.1°C, and the melting point -146°C (56). Since the discovery of isoprene in the oily distillate of caoutchouc and guttapercha by Bouchardat in 1837, a large amount of work has been carried out in the polymerization of this hydrocarbon (54). Polymerization, to a small degree, occurs in the liquid isoprene at room temperature as evidenced by the appearance of a yellow color. Some investigators, who studied the subject, obtained and identified some low polymers. Komarewski (54) made isoprene polymers which were identified as mixtures of dipentene and an aliphatic dimer. D'Ianni (29) described three possible structures for isoprene polymers



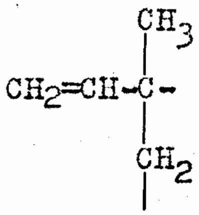
$$-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-$$

1,4 addition



$$\begin{array}{l}-CH_2-CH-\\ \qquad\quad |\\ \qquad\quad C-CH_3\\ \qquad\quad \|\\ \qquad\quad CH_2\end{array}$$

3,4 addition

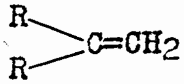


$$\begin{array}{l}\qquad\qquad\quad CH_3\\ \qquad\qquad\quad |\\ CH_2{=}CH-C-\\ \qquad\qquad\quad |\\ \qquad\qquad\quad CH_2\\ \qquad\qquad\quad |\end{array}$$

1,2 addition

Rakova and Korotkov (80) determined that when polymerized singly, isoprene was more reactive and copolymerized at a rate three times greater than butadiene.

Although several infrared spectra of isoprene have been published, a detailed study of the absorbance bands has not been made (9, 82). The isoprene infrared absorbance band assignments were made according to Bellamy (12) and will be discussed further in the experimental section.

Low temperature studies of polymerization of isoprene have not been made in connection with infrared studies. End group analysis of the large polymer molecules of isobutene was attempted by infrared methods at low temperatures. This was not successful. However, in the shorter isobutene polymer molecules with molecular weight less than 3 X 10^4 grams/mole the  $\begin{matrix}R\\R\end{matrix}{>}C{=}CH_2$ group was noted by the absorbance bands at 1780 cm^{-1}, 1642 cm^{-1}, and 895 cm^{-1} (35).

Avery and Ellis (5) stated that the separation of the maxima of P and R branches of the hydrocarbon infrared bands should be proportional to the square root of the absolute temperature of the sample. This relation holds for propane, propene, and trimethylpropane in the temperature range from +25°C to -195°C. The band positions of trimethylpropane seemed to be independent of temperature. Some of the propene bands changed in intensity as well as position. They reported narrowing of the band width with decrease in temperature. The same phenomenon was noted by Sutherland (96) and Walsh and Willis (100), who attributed it to the interaction between neighboring chains in the crystalline lattice or changes in the crystal structure.

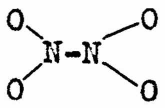
B. Nitrogen Dioxide

The red fumes of nitrogen dioxide were referred to in 1670 by Clark who called the vapors by the alchemical name "the flying dragon." A century later in 1777 the gas was prepared by Priestley, and in 1816 its empirical formula was established independently by Dulong and Gay-Lussac (42). From these beginnings nitrogen dioxide has grown in technical importance to the central position which it occupies today in the chemical industry.

The chemistry of the NO_2-N_2O_4 system is very complex. At high temperatures in the gas phase nitrogen dioxide is overwhelmingly the principal species present, whereas the liquid is almost pure dinitrogen tetroxide. Nitrogen dioxide, molecular weight 46.01 grams/mole, has a boiling point of

+21.3°C and a melting point of -9.3°C (55). At low temperatures nitrogen dioxide is a colorless solid. Between -20°C and -30°C it is pale yellow. At the melting point it becomes honey colored. The color darkens as the temperature is raised. The color of the gas phase nitrogen dioxide is brownish-red. Pure dinitrogen tetroxide liquid is stable, under atmospheric pressure, from the freezing point to the boiling point. Dissociation to nitrogen dioxide is small (the concentration of nitrogen dioxide in dinitrogen tetroxide is less than one percent).

Nitrogen dioxide has been one of the favorite molecules studied by infrared spectroscopists. The early work in 1933 by Bailey and Cassie (7, 20), Harris and co-workers (45, 46), Sutherland (94, 95), and Schaffert (85, 86) dealt with the determination of the nitrogen dioxide and dinitrogen tetroxide absorbance bands and the molecular structure of these molecules. Although there were some disagreements between these early workers, the conclusions of Harris and King (46), based on the spectra of nitrogen dioxide and dinitrogen tetroxide, have been accepted. They concluded that the nitrogen dioxide molecule is angular, and that the dinitrogen tetroxide molecule has the O_2N-NO_2 structure. The dinitrogen tetroxide structure has been discussed in detail by Gray and Yoffe (42) who stated that the



model of dinitrogen tetroxide is the accepted type.

In the last ten years a large number of spectroscopists have studied the nitrogen dioxide molecules by infrared spectrophotometry. The fundamental frequencies of gaseous and solid nitrogen dioxide were studied and assigned to the various vibrational modes by Wilson and Badger (104), De More (26), and Fateley (33). The data of the various infrared studies of nitrogen dioxide were compiled and discussed in detail by Herzberg (48) in 1945. Fateley obtained a rather pure nitrogen dioxide solid film by using dilute mixture of nitrogen dioxide in an inert gas, slow desposition rate, and a rigid matrix. The relative intensities of the absorbance bands were dependent on the procedure used in deposition process,

Perkins and Wilson (79) assigned eight dinitrogen tetroxide fundamental frequencies. In 1954 Gray and Yoffe (42) reported twelve possible fundamental frequencies of dinitrogen tetroxide. One of these frequencies, v_8, did not agree with Perkins and Wilson assigned frequency.

Wiener and Nixon (103) studied the infrared spectrum of dinitrogen tetroxide at -180°C. When dinitrogen tetroxide was condensed at -78°C in a vacuum system, a bluish tinge in the solid was noticed which indicated the presence of dinitrogen trioxide and hence nitric oxide. A pure sample was obtained by fractional distillation.

Snyder and Hisatsune (91) stated that at low temperatures the solid is entirely dinitrogen tetroxide and thus offers an opportunity to isolate the dinitrogen tetroxide species in a simple manner. They also studied dinitrogen tetroxide in gas and liquid states. These workers observed that the spectra of dinitrogen tetroxide in the three different physical states remained practically unaltered in going from one phase to another. The liquid dinitrogen tetroxide spectrum showed a band at 1617 cm^{-1} (strongest of nitrogen dioxide) proving that nitrogen dioxide exists in the liquid.

When the sample, dinitrogen tetroxide, was deposited slowly on a silver chloride window cooled to -180°C, the film formed was transparent and in evidence only from the interference patterns of reflected visible light. The film became cloudy, chalky white, when warmed up to -120°C remaining so until the distillation occurred at -40°C. Such behavior seems characteristic of an amorphous to crystalline state change and has been reported for other compounds similarly treated by Giauque and Kemp (39) in 1938 and Comeford and Gould (23) in 1960.

Further evidence for assuming an amorphous phase before warming was that the spectrum of the film did not exhibit the doublet splitting of absorbance bands to a large degree which is characteristic of a crystalline solid. The fact that the doublets appeared at all seemed to indicate that the prewarmed state of the sample was a mixture of both the amorphous and crystalline states. The 1964 cm^{-1}, 1680 cm^{-1}, and 1581 cm^{-1} bands disappeared or weakened upon warming, whereas other bands (1400 cm^{-1}, 1109 cm^{-1}, and 815 cm^{-1}) weak or non-existant before warming increased in intensity.

Hisatsune, Devlin, and Wada (49) and Fateley (33) also noticed the disappearance of many bands of dinitrogen tetroxide upon annealing. When the sample was recooled, the bands were still missing. Therefore, they concluded that the bands could not arise from any phase transitions in the solid but must be associated with some unstable species of dinitrogen tetroxide. Malherbe and Bernstein explained this phenomenon as being caused by unstable rotational isomers (70).

Begun and Fletcher (11) in their study of dinitrogen tetroxide in liquid and gaseous states noticed a brownish color appear in the liquid dinitrogen tetroxide at +38°C which they attributed to nitrogen dioxide. No large frequency changes between the absorbance bands of liquid and gas were observed.

C. Review of Olefin and Nitrogen Dioxide Reaction

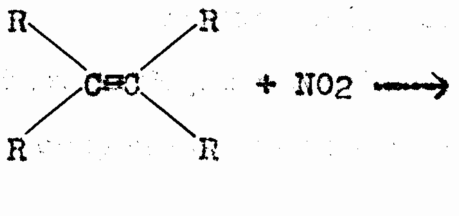
The chemistry of the nitrogen dioxide-dinitrogen tetroxide system is very complex. In analyzing a particular reaction, the first problem is to determine whether nitrogen dioxide or dinitrogen tetroxide is the reacting species. Often distinction is not difficult. Thus at high temperatures in gas phase nitrogen dioxide is overwhelmingly the principal species present, whereas the liquid at low temperatures is almost pure dinitrogen tetroxide. Therefore, liquid phase reactions at low temperatures involve dinitrogen tetroxide, and gas phase reactions at high temperatures involve nitrogen dioxide. There are exceptions to the above statement. In the reactions with unsaturated hydrocarbons in the liquid phase it is believed that the reactions are of nitrogen dioxide and not dinitrogen tetroxide type (42).

Nitrogen dioxide is an odd electron molecule and a number of its reactions belong to classes typical of free radicals, such as association with other radicals, its own dimerization, and addition to unsaturated compounds. When nitrogen dioxide is one of the radicals two distinct associations are possible:

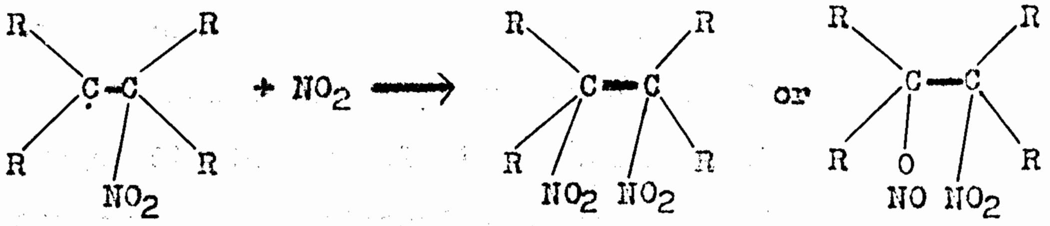
a) nitro compound formation
b) nitrite formation

In the first case the association to nitro compounds is easy and the stabilization is easy. In the second case, the association to the nitrite is easy, but the stabilization is difficult, because to prevent subsequent O-N bond fission, energy equivalent to 20K cal./mole has to be dissipated. Therefore, nitrites are not formed directly in the gas phase though they may be formed in solution (41).

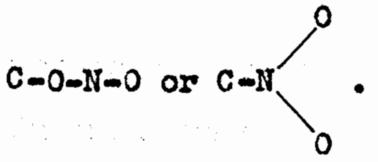
Detailed studies of the products of dinitrogen tetroxide and unsaturated hydrocarbons have been conducted in the liquid state and in the absence of any large amount of oxygen. Under these conditions addition products are formed. Levy and Rose (60) and Brown (19) in 1947 postulated that the first step in these reactions is an addition of nitrogen dioxide at the double bond to form a nitroalkyl radical



This radical then undergoes further reaction with nitrogen dioxide to form the dinitro compound or a nitro nitrite

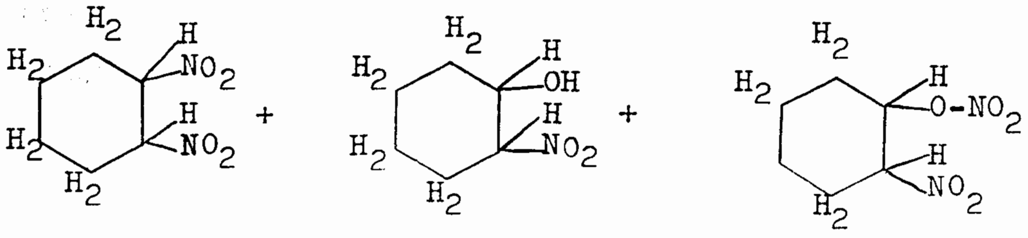


Schechter and Conrad (87) determined that the addition of first nitrogen dioxide at the terminal position of the unsaturated hydrocarbon molecule occurs exclusively by the C-N bond formation. The second nitrogen dioxide forms either



$$C-O-N-O \text{ or } C-N\begin{smallmatrix}O\\ \\O\end{smallmatrix}.$$

Levy and Scaife (61) stated that the nitro nitrite formed in the dinitrogen tetroxide and olefin reaction is unstable and with water forms a nitro alcohol. Other products found in this reaction were dinitroparaffins and nitroalkyl nitrates in good yields. Baldock, Levy, and Scaife (8) reacted cyclohexene with dinitrogen tetroxide and formed



Levy and co-workers (62) concluded that in solutions normal addition took place. The primary products formed were dinitro compounds and nitro nitrites. The secondary reactions gave nitro olefins, nitro nitrates, and nitro alcohols. Demyanov (28) reported that the products of dinitrogen tetroxide and unsaturated hydrocarbon form solids which are stable and liquids which tend to decompose, sometimes violently.

In gas phase reactions at elevated temperatures the nitrogen dioxide and olefin reactions follow an addition mechanism which is followed by complete oxidation (60). Cottrell and Graham (25) in 1953 studied the ethene and propene reactions with nitrogen dioxide. The reaction produced a high boiling oil, a dark solid, carbon dioxide, carbon monoxide, nitric oxide, and unchanged ethene or propene. These results suggest that the addition reaction forms nitro compounds and nitro nitrites which decompose to fragments which in turn are completely oxidized by more nitrogen dioxide. Because of the complexity of the reactions, the calculations of the reaction rates are difficult (57).

Schoenbrunn and Gardner (89) produced alpha-hydroxyisobutyric acid by reacting isobutylene in the presence of excess dinitrogen tetroxide. The yield was 69-74%. When ethers or esters were used as solvents, the reaction proceeded by the free radical mechanism forming a primary nitro compound. In the absence of these solvents the products were chiefly the derivatives of isobutylene nitrosonitrate which has not been isolated due to its high reactivity. The dimer, however, has been isolated, and this was taken as part of the evidence for the transitory existence of the monomer. Riebsomer (83) reported the formation of nitrosonitrate in 1945 in his studies of olefins and oxides of nitrogen.

Alshuller and Cohen (2) studied the isoprene and nitrogen dioxide reaction in gas and liquid phases. Oxidation as well as nitration was observed in the gas phase reaction. In the liquid phase reaction only nitration appeared to be the type of reaction leading to organic nitrates and nitroso compounds. The oxidation products seemed to be ketones and acids.

This conclusion was in partial agreement with Leighton (59) who stated that in the nitrogen dioxide and olefin reaction, in the majority of cases, the aldehydes and ketones corresponding to addition of an oxygen atom to one end of the olefin molecule with a split at the double bond are among the products. In some cases small amounts of aldehydes with the same number of carbons as the olefin were formed.

Alshuller and Cohen also reported that the infrared spectra of the products of isoprene and nitrogen dioxide reaction showed weak bands in the 8-9 micron region which could be the strong C-O bands of nitro alcohols. The presence of 1,2- or 2,3- dinitro compounds was not proved conclusively.

Alshuller (1) in 1958 noted a white condensation product on the walls of the olefin and nitrogen dioxide reaction vessel. An oily component was included in the white condensate which contained primary and secondary nitro compounds and alkyl nitrates. The alkyl nitrates most likely were formed by the association reaction of alkoxyl radical and nitrogen dioxide

$$RO^{\cdot} + NO_2 \longrightarrow RO\text{-}NO_2 \quad (58)$$

Alshuller (1) also observed aliphatic alcohol absorbance bands in the infrared spectra of the condensate. The reactivity of isoprene with nitrogen dioxide in the gas phase was compared with other olefins. It was determined that the diolefin, isoprene, was more reactive with nitrogen dioxide than the olefin with an internal double bond, 2-methyl-2-butene, and both of these compounds were more reactive than the externally double bonded olefin, 1-pentene. This was proved by the more rapid and complete disappearance of the olefin from the gas phase and the concurrently greater quantity of condensation product formed.

EXPERIMENTAL

I. Reagents and Apparatus

The compounds listed below were used in preparing samples for infrared spectrophotometric analysis and for obtaining data with the low temperature infrared cell procedure.

1. Isoprene (2-methyl-1,3-butadiene)
   pure grade, 99 mole % minimum,
   Special Products Division,
   Phillips Petroleum Company.
2. Nitrogen dioxide (dinitrogen
   tetroxide), 99.5 mole % minimum,
   Matheson Company, Inc.

Perkin-Elmer Corporation Model 221 Infrared Spectrophotometer equipped with scale expansion and a sodium chloride prism.

Cold cell (described in later section of this thesis).

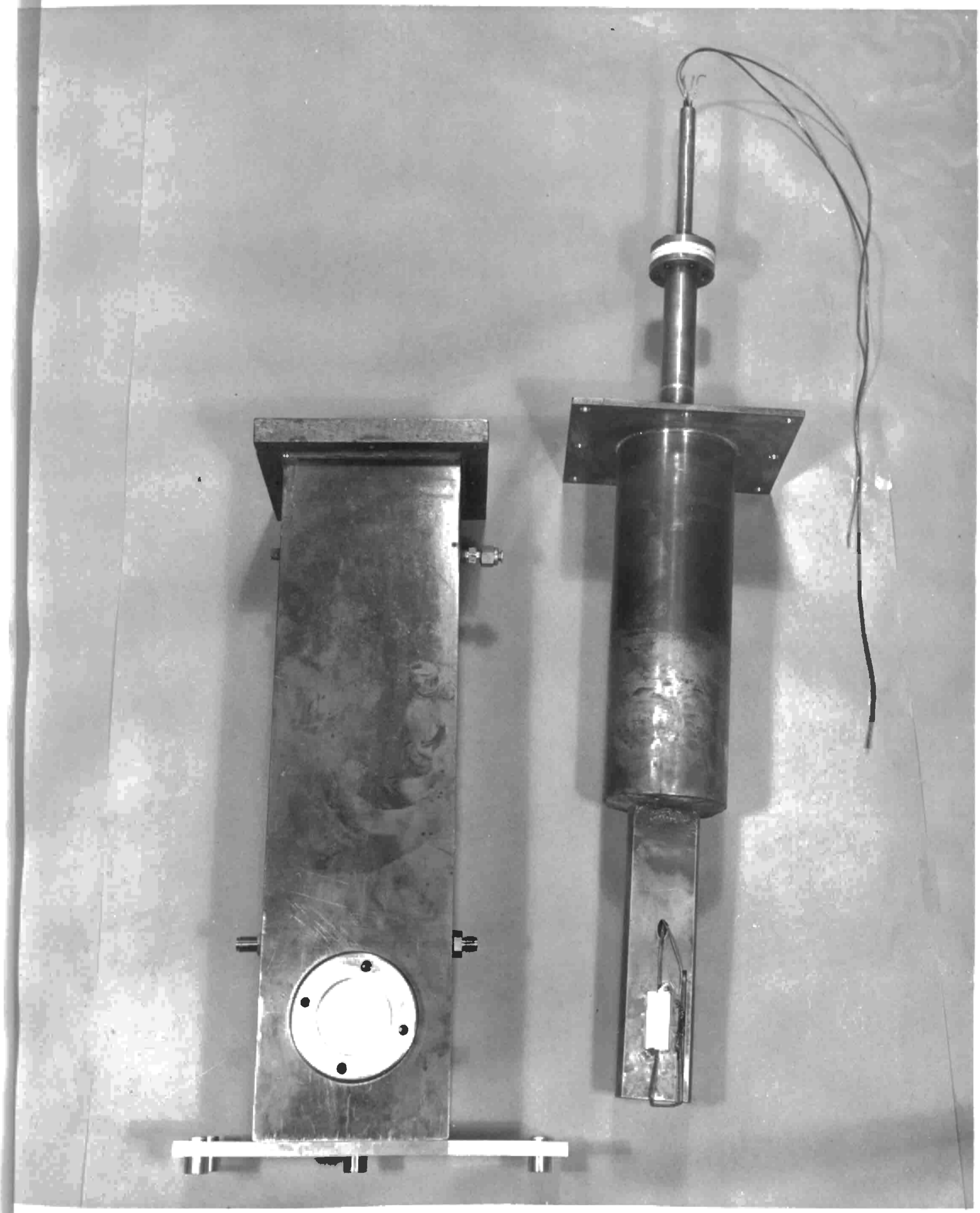
Varian Associates Model G-10 Graphic Recorder.

II. Development of the Cold Cell

The cold temperature cell for infrared spectrophotometric studies was designed in such a manner which would permit the cell to be used for trapping gas chromatography fractions, obtaining infrared spectra of samples at various temperatures, and studying chemical reactions. The cell consists of two basic sections: 1) the liquid coolant reservoir with the "cold finger" and 2) the outer jacket with appropriate windows as shown in Figure 1. The outer jacket is constructed of type #304 stainless steel which has a similar coefficient of expansion to copper and a low thermal conductivity so that the cold from the liquid nitrogen is not transferred to the windows. The walls are ¼" thick welded to withstand 40 psi. Two 3/4" thick metal plates are welded on the inside of two walls and threaded to receive the windows, the gaskets, and the lock nut. The base dimensions are 4-3/4" by 5". The outer shell is 19-5/8" high. Holes were tapped in this outer jacket to permit connections between the cold cell and the sample inlet, the vacuum pump, and the manometer. The connections are made by using glass ball and socket joints and Swagelok seals, produced by Crawford Fitting Company, Cleveland, Ohio. The top portion of the outer shell of the cold cell extends outwards 3/4" on all sides. This extended portion is designed to seal the outer jacket and the coolant reservoir. They are held in

FIGURE 1

The Outer Jacket and the Reservoir with the "Cold Finger" of the Low Temperature Infrared Cell



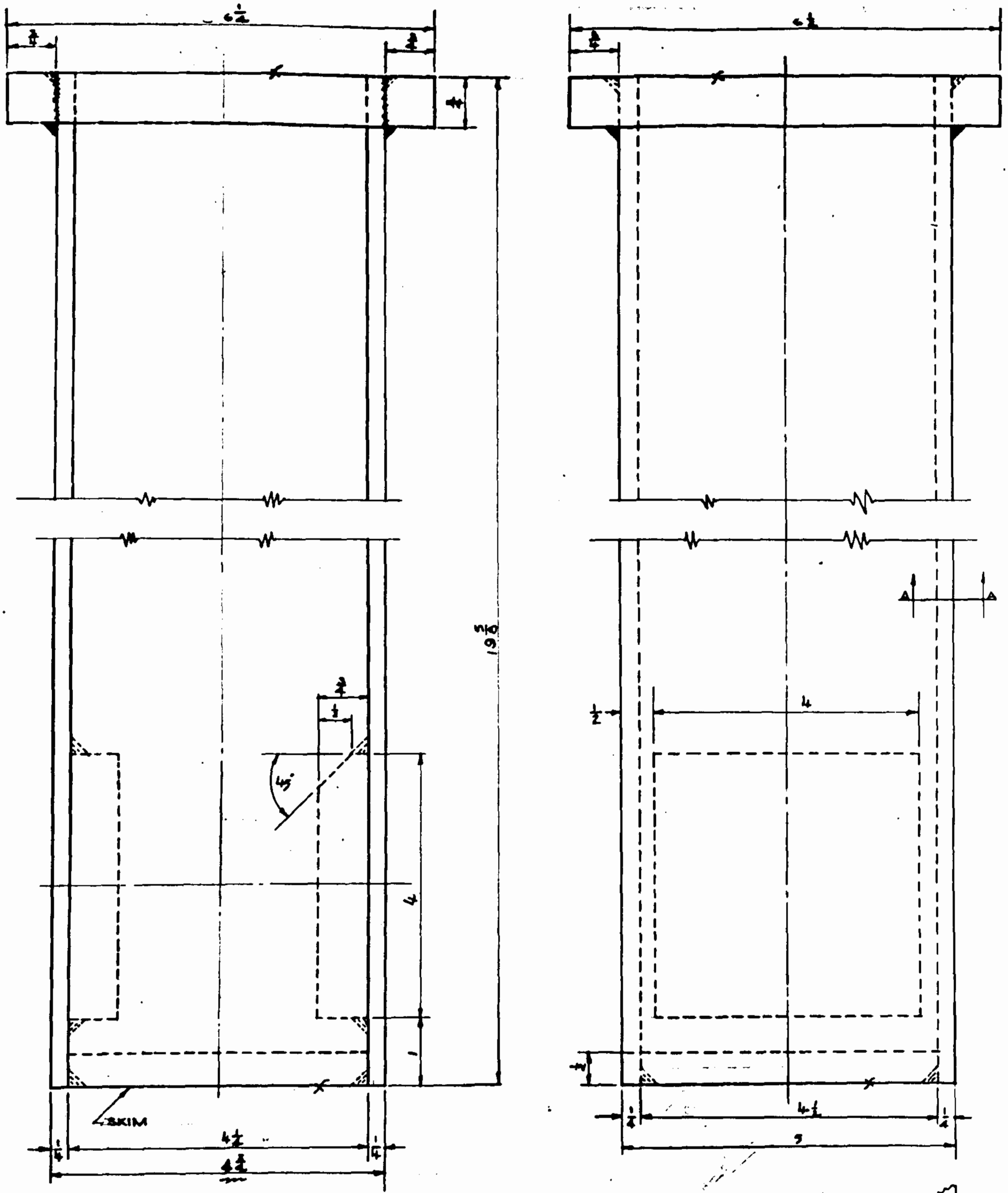
place by sixteen cap screws. Teflon and silicone rubber gaskets are used to seal the joint (92). The outer shell is illustrated in Figure 2. The stainless steel jacket was baked for 48 hours at 500°C to remove oil.

The coolant reservoir (Figure 3) is constructed of electrolytic copper 99.7% pure, quenched at 1830°F which will prevent deterioration up to -253°C. The reservoir consists of a flat plate, bolted to the outer jacket by screws, and the coolant container with a "cold finger." The coolant reservoir is made from a $3\frac{1}{2}$" O.D. copper pipe, 11" long, 3/8" thick. Because copper is easily silver soldered to produce joints that are leak free at low temperatures and has a high thermal conductivity and low emissivity, it was chosen for the assembly of the coolant reservoir. The minimum transfer of the cold is achieved by evacuating between the outer shell and the reservoir.

Because the function of the "cold finger" (Figure 4) is to bring the sample to the desired low temperature, the chosen material has to have a high thermal conductivity. Again electrolytic copper, 99.7% pure, was chosen as the material suitable for this purpose. The lower portion of the "cold finger" is made from a 2" O.D. and 8" long copper rod. An opening $1\frac{1}{2}$" X 1" through this rod provides space for the sample container and allows the energy beam to pass through. On the bottom of the "cold finger" two holes were drilled vertically in the copper rod to provide space for the Chrom-

FIGURE 2

The Outer Shell



VIEW A-A

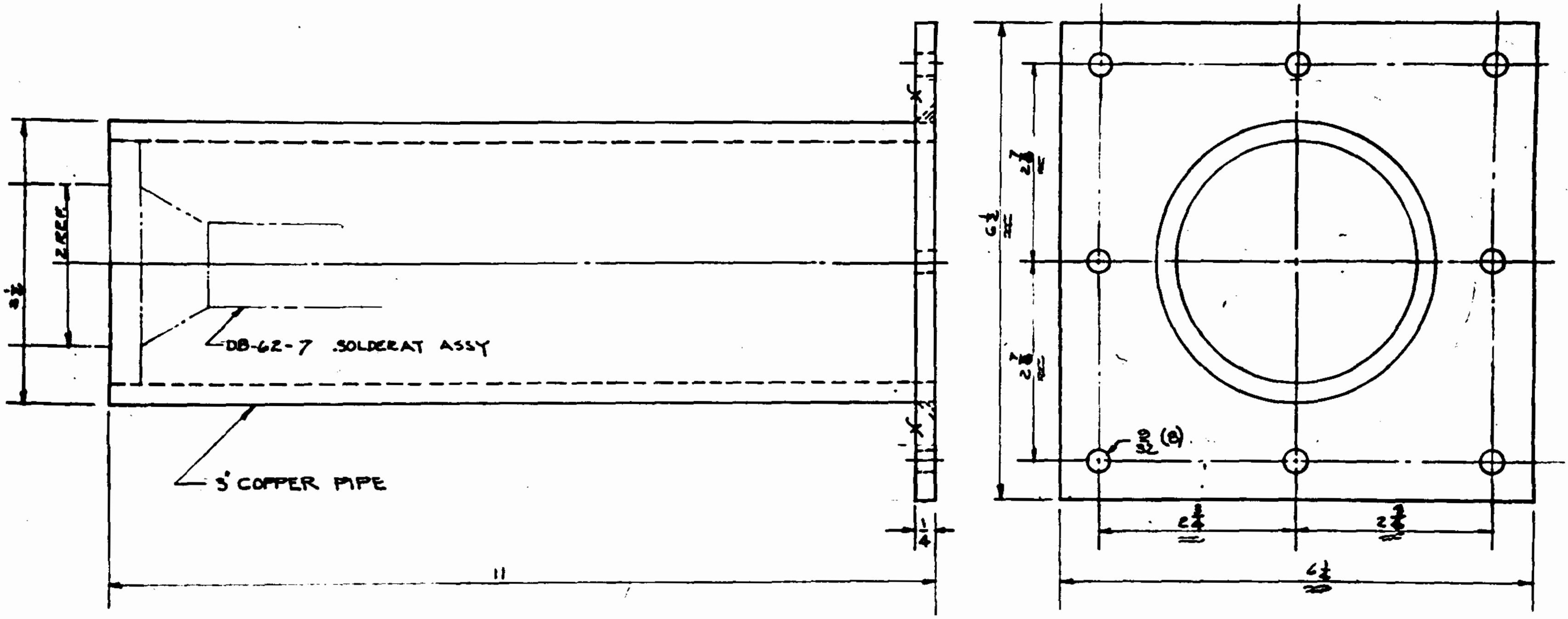
(TYPICAL CORNER WELD)

NOTES.

1. WELDED ALL OVER.
2. ALL WELDS TO WITHSTAND 60 PSI.
3. HOLD WARPAGE TO MINIMUM.
4. STAINLESS STL # 304-2B
5. 1 REQ'D
6. SCALE: 1"=1"

FIGURE 3

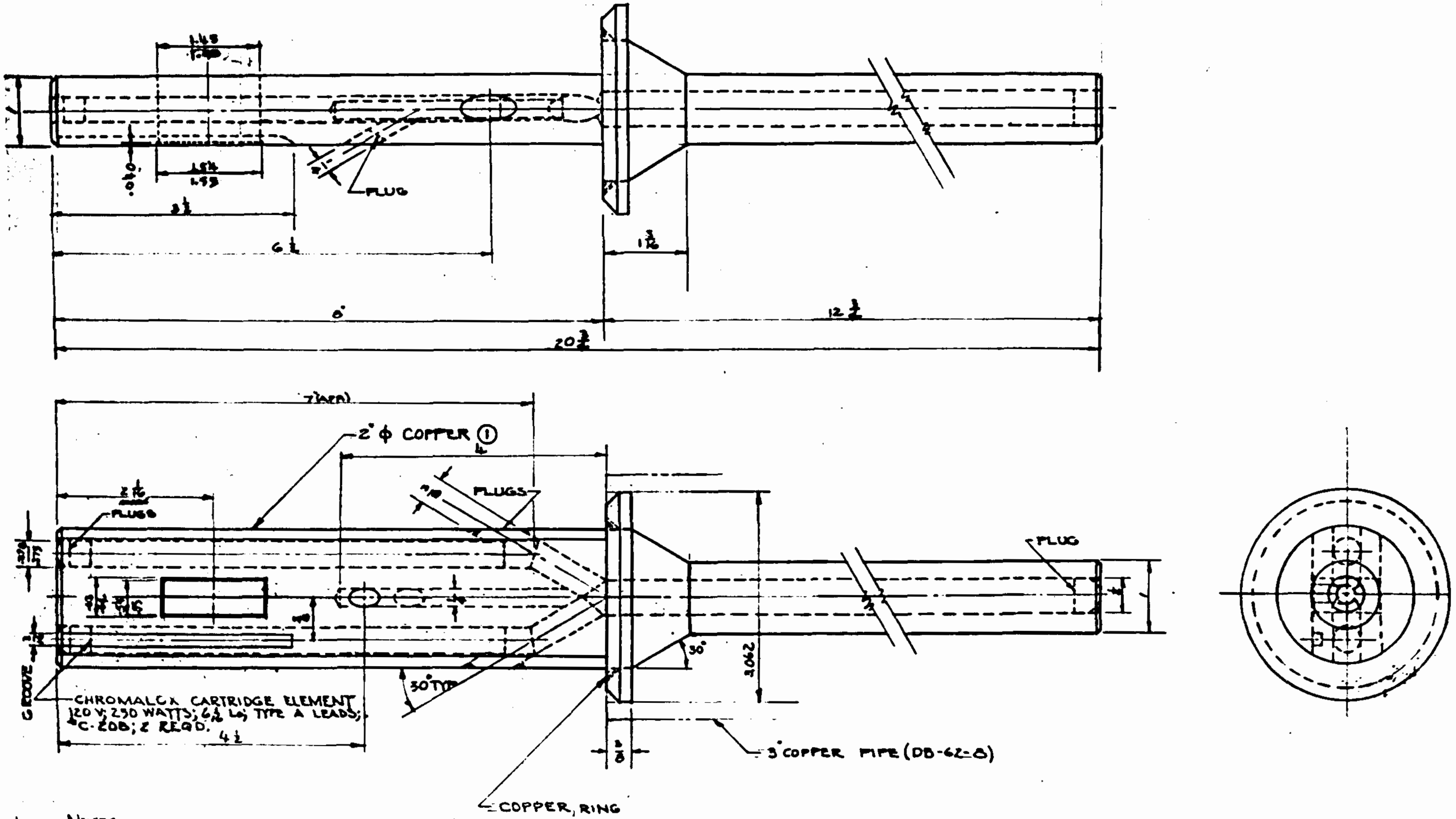
The Coolant Reservoir



MAT: COPPER
SCALE: 1"=1"
1 REQ'D.

FIGURE 4

The "Cold Finger"



NOTES

1. ALL CHAMFERS ARE 45° UNLESS DIMENSIONED
2. ALL WELDS & SOLDERS TO WITHSTAND 40 PSI
3. MOUNT SPRING CLAMPS AFTER WIRING
4. NOTCH AT ASS'Y FOR WIRING, T'COUPLES ETC.

alox cartridge elements, 120 v, 250 watts, which are used as heaters. Another small opening above the sample holder serves as the exit for the 36 gauge copper constantan thermocouple leads.

The lower portion of the "cold finger" is silver soldered to the coolant container and to the upper portion of the "cold finger" which passes through the center of the coolant reservoir. The upper portion of the "cold finger" is 1" O.D. and has ½" hole in its center through which the thermocouple leads and the electrical wires for the heaters pass. The copper rod extends 6" above the top of the coolant container at which point it is connected to the "cold finger" cap by six cap screws. This final portion of the 1" O. D. copper tubing is 6" high. The cap seal is made with two Teflon gaskets. The Teflon is used to prevent the cold from reaching the final portion of the "cold finger." The opening for the electrical wires is sealed with the Stycast #2651 epoxy resin which is rated for use between -100°F and +400°F.

The sample holder, on which the sample is condensed and frozen, is an Irtran-2 window manufactured by Eastman Kodak Company. It was selected because of its high thermal conductivity, shock resistance, non-reactivity with nitrogen dioxide, transmittance of energy in the 2-14 micron region, and insolubility in water (44). The more common optical materials used in infrared spectroscopy, such as sodium chloride and cesium bromide, react with nitrogen dioxide, producing sodium nitrate and cesium nitrate, respectively, which interfere with the analysis (3, 102). Sodium chloride also is affected by thermal shock.

The sample window is held closely in the copper mount by two microscope clamps. To obtain a good thermal contact between the sample window, the copper mount, and the coolant, Dow silicone grease coating is put on the copper mount where the Irtran-2 window comes in contact with it. The sample window is 1 mm thick, 38 mm long, and 15 mm wide.

The outside windows also are made of Irtran-2 material. The entrance window is 49.5 mm in diameter and 3 mm thick. The exit window is 25.2 mm in diameter and 2 mm thick. Both windows are hermetically molded within an encircling annular stainless steel ring. The windows are held in place by a lock nut. A silicone rubber gasket is placed between the outer jacket and the stainless steel ring. A neoprene rubber gasket is placed between the stainless steel ring and the lock nut to obtain a vacuum seal. The windows are useful in the 2-14 micron wavelength range. From 4-9 microns a $\frac{1}{4}$" thick Irtran-2 plate transmitted 72% of the energy. From 2-4 and 9-14 microns the material has a lower transmittance.

III. Study of Nitrogen Dioxide and Isoprene Reaction

A. Reaction at 25°C.

The nitrogen dioxide-isoprene reaction was studied in a

10 cm commercial gas cell with silver chloride windows. The windows were sealed to the gas cell with Fluorolube obtained from Hooker Electrical Company, Buffalo, New York. The cell could be cleaned and reassembled rapidly with this sealing agent. Also, the Fluorolube did not react with the nitrogen dioxide.

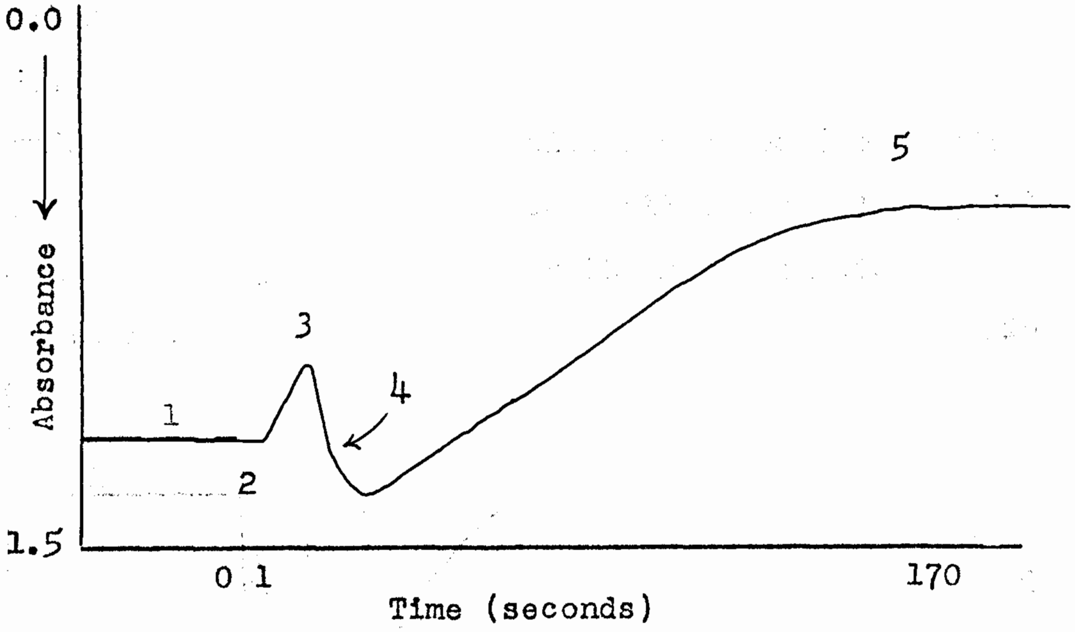
The cell was connected to a vacuum pump and to the sample container. The samples, nitrogen dioxide and isoprene, were in 500 ml round bottom flasks with stopcocks. The flasks were joined to a glass tube with a three-way stopcock which permitted the introduction of both gases through the same inlet system without coming in contact with each other before entering the cell. The cell was evacuated while in position in the infrared spectrophotometer for immediate analysis. The connection was opened between the cell and the flask with the nitrogen dioxide. A sufficient amount of nitrogen dioxide was collected in the cell to get a good infrared spectrum of the gas in the 2-15 micron region. The frequencies observed of the nitrogen dioxide gas are listed and compared with other workers' data in Table I. The same procedure was followed in obtaining the isoprene infrared spectrum (Table II). The two spectra were compared and the unique absorbance bands of each compound selected to be monitored during the reaction (Figure 8,9). The absorbance bands selected for this purpose were at 11.20 microns, the strongest unicomponent absorbance band for isoprene, and 7.95

microns, one of the strongest nitrogen dioxide bands without interference.

Nitrogen Dioxide Added to Isoprene. Isoprene Band Monitored. Isoprene was placed in the 10 cm gas cell. The pressure exerted by the sample was 100 mm Hg. The nitrogen dioxide container was connected to the cell, but the connection was kept closed. The infrared spectrophotometer was set on the 11.20 micron wavelength and the sodium chloride prism locked in a stationary position to monitor the decrease of isoprene on addition of nitrogen dioxide. The instrument controls were as follows:

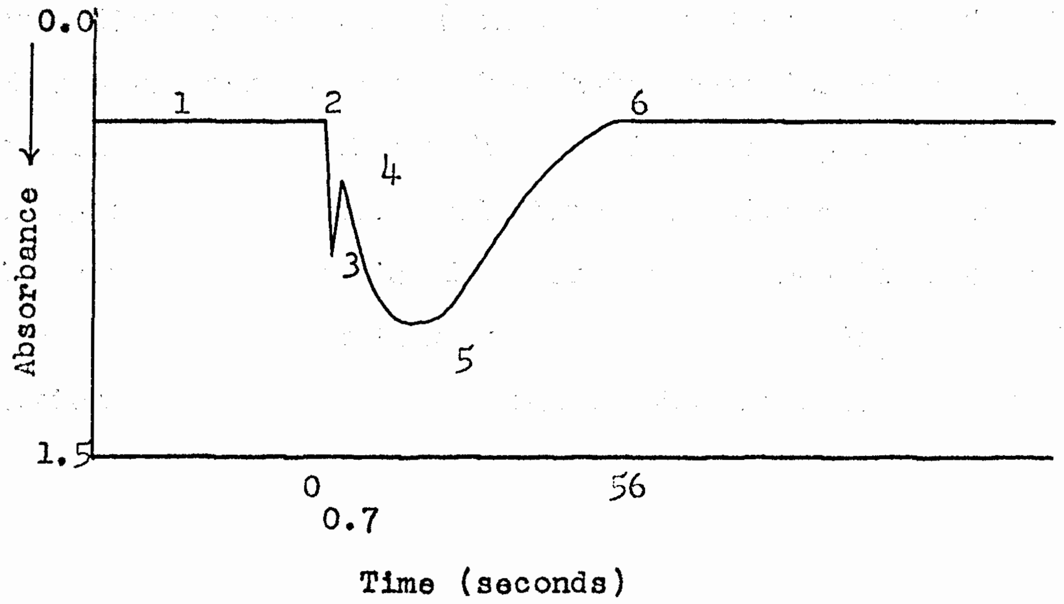
Resolution	950
Gain	Normal
Suppression	2
Drum Speed	1 cm/2 seconds

The drum was set in motion. Isoprene in the cell produced a straight base line (point 1) since the concentration remained unchanged. An excess of nitrogen dioxide was added to the isoprene at point 2. A decrease in the concentration of isoprene, caused by the reaction with nitrogen dioxide, started after one second (point 3). Part of this time was consumed by nitrogen dioxide reaching the cell from its container. A white cloud was formed inside the gas cell from the reaction. It is believed that this was the reason for the increase in absorbance (point 4). As the cloud cleared, the absorbance decreased. However, the cloud prevented the determination of the rate of reaction. No change in the absorbance took place 170 seconds after the addition of the nitrogen dioxide (point 5).



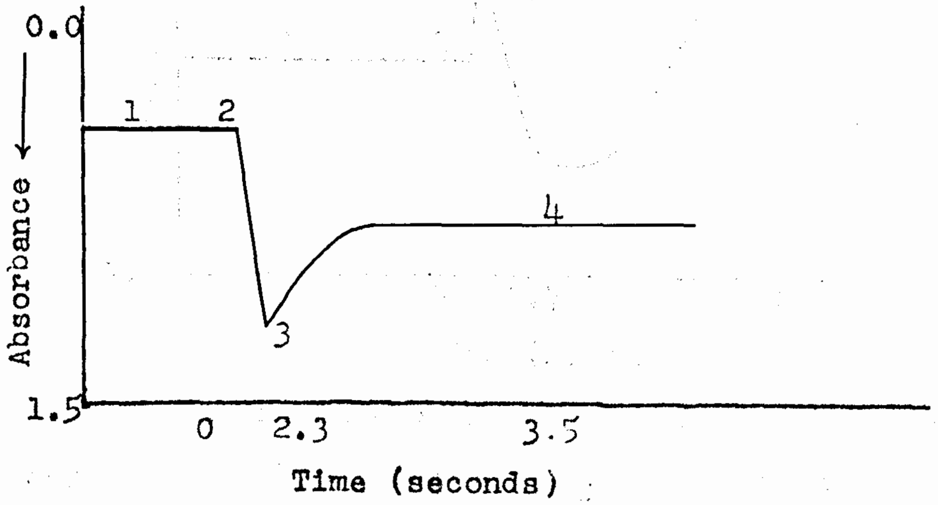
At this point the sodium chloride prism was unlocked and the 2-15 micron range scanned. No remaining isoprene was detected in the cell. However, nitrogen dioxide was detected. Therefore, it was evident that isoprene did not exist in the presence of excess nitrogen dioxide, at least not in large enough quantities to be detected by the infrared methods used.

Nitrogen Dioxide Added to Isoprene. Nitrogen Dioxide Band Monitored. The instrument settings were the same as in the previous experiment except that the wavelength was set at 7.95 microns (location of one of the strongest nitrogen dioxide absorbance bands without interference). The same amount of isoprene was in the gas cell as before,and nitrogen dioxide container was connected but closed to the cell. The drum was set in motion. No absorbance was present at 7.95 microns (point 1). Nitrogen dioxide was added, this time not in excess (point 2). There was an instantaneous increase in the absorbance caused by the presence of nitrogen dioxide (point 3). The concentration of nitrogen dioxide decreased 0.7 seconds after the nitrogen dioxide was added (point 4). The white cloud appeared again in the cell (point 5). Equilibrium was reached 56 seconds after the nitrogen dioxide was added (point 6).

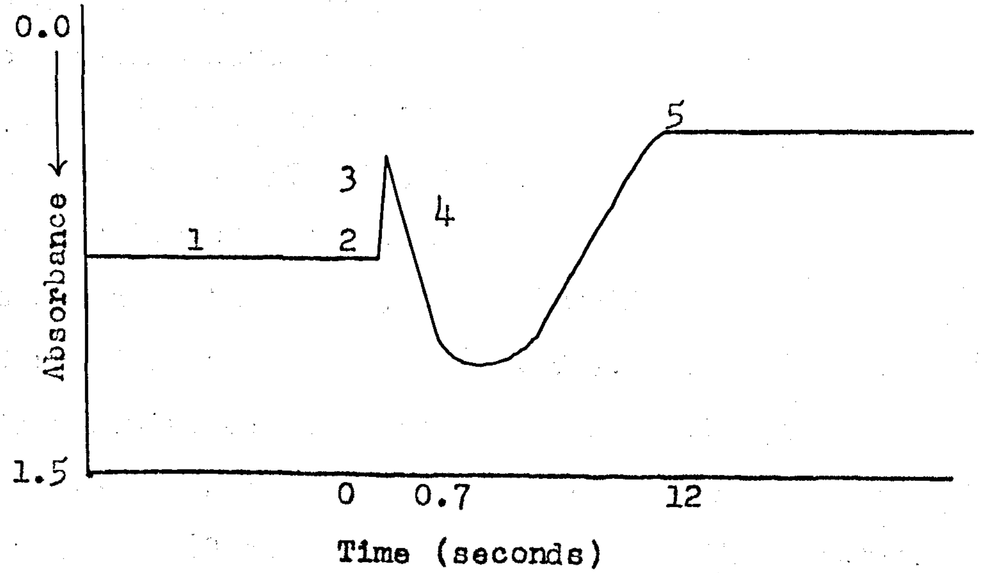


Examination of the contents of the cell after the reaction revealed that nitrogen dioxide was absent at the end of reaction. However, isoprene was present. This proved that nitrogen dioxide is not present, at least not in sufficient quantity to be detected by the infrared spectrophotometer, when isoprene is present in excess.

Nitrogen Dioxide Added to Isoprene. Reaction Product Band Monitored. Next, the formation of the reaction product was monitored. In order to do this, a spectrum of the reaction product was obtained in the 2-15 micron region and a suitable band selected for the study of the formation of the reaction product. The selected wavelength was 6.43 microns, the strongest unicomponent band of the reaction product. The drum was set in motion. The isoprene in the cell did not absorb at 6.43 microns. A straight line (point 1) was obtained since the contents of the cell remained unchanged. Nitrogen dioxide was added (point 2). An increase in the absorbance was caused by the immediate formation of the reaction product. The time which elapsed between points 2 and 3 was 2.3 seconds. During this time the white cloud was formed which contributed to the absorbance of the reaction product. No change in the absorbance was noted 35 seconds after the addition of the nitrogen dioxide to the isoprene.



Isoprene Added to Nitrogen Dioxide. The 7.95 Micron Band Monitored. The gas cell contained nitrogen dioxide, and the isoprene was in the connected container. The nitrogen dioxide 7.95 micron band was monitored by the same procedure as before. The drum was set in motion. The nitrogen dioxide absorbance gave a straight line (point 1) since no changes in the concentration of the nitrogen dioxide took place at this time. Isoprene was added (point 2). There was an immediate reaction with a decrease in the concentration of nitrogen dioxide (point 3) due to the reaction with isoprene. The increase in absorbance, which was attributed to the white cloud formation, started 0.7 seconds after the isoprene was added (point 4). Equilibrium was reached 12 seconds after the isoprene was added to the nitrogen dioxide (point 5).



The variation in the time the equilibria were reached was caused probably by the variation in the amounts of the reactants used. The gas cell was disassembled and cleaned after each experiment because the walls of the cell were covered with a yellow brown liquid, the reaction product of nitrogen dioxide and isoprene.

Isoprene and Nitrogen Dioxide Reaction Product. An infrared spectrum was obtained between 2-15 microns after the nitrogen dioxide and isoprene had reacted. The 10 cm gas cell was left intact, and the reaction product was analyzed as it had settled on the silver chloride windows of the gas cell. The excess isoprene was removed from the cell to eliminate its interference with the infrared spectrum of the product. The product was a light yellow, viscous liquid which became darker and more viscous on standing. The product eventually became a dark brown solid.

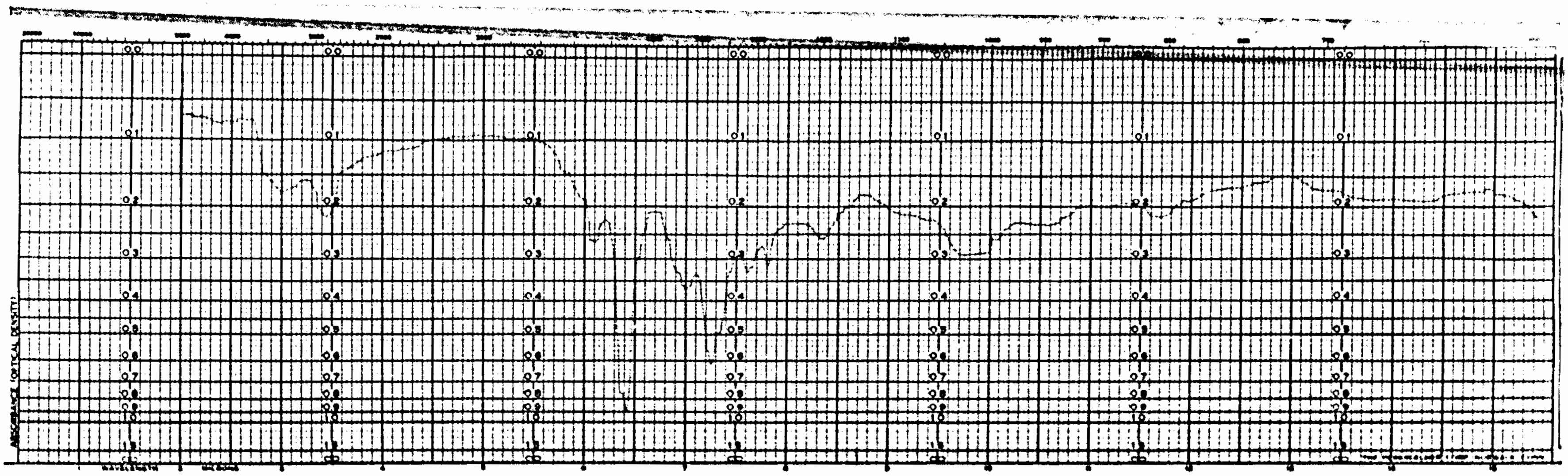
The infrared spectrum of the reaction product (Figure 5) had a strong absorbance band at 1553 cm^{-1} and 1380 cm^{-1} along with medium bands at 3400 cm^{-1}, 2900 cm^{-1}, 1650 cm^{-1}, 1460 cm^{-1}, 1320 cm^{-1}, 1280 cm^{-1}, 1200 cm^{-1}, 1020 cm^{-1}, 950 cm^{-1}, 855 cm^{-1}, 837 cm^{-1}, and 755 cm^{-1}.

The reaction product definitely contains a nitro compound as shown by the color, the solubility in sodium hydroxide, and the infrared spectrum (21, 90). In fact, the nitro compounds constituted the major portion of the product. The strong absorbance bands at 1553 cm^{-1} and 1380 cm^{-1} and the medium band at 1460 cm^{-1} showed that one of the reaction products is a primary nitro compound. Primary and secondary nitro compounds exhibit two extremely strong absorbance bands

FIGURE 5

Gaseous NO_2-Isoprene Reaction Product

Immediately after Reaction at 25°C



ABSORBANCE (OPTICAL DENSITY)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
WAVELENGTH
MICRONS

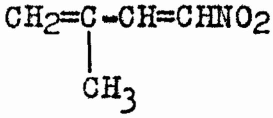
in the 1565-1545 cm^{-1} and 1383-1360 cm^{-1} regions (14, 18, 81). Primary nitro compounds also have a characteristic band at 1460 cm^{-1} which is caused by the active methylene group. This band is a valuable adjunct to the 1553 cm^{-1} band in the identification of primary nitro compounds (18).

The broadness and the shoulders on the bands suggest that other nitro compounds also are present of which some could be unsaturated. The $-NO_2$ group has little or no effect on the C=C stretching frequency. However, the band is intensified in both the alpha and beta nitro olefins. Conjugation of the nitro group by attachment to an ethylenic double bond leads to a fall in the asymmetric and symmetric $-NO_2$ stretching frequencies. The $-NO_2$ stretching frequencies of conjugated nitro alkenes are at 1550-1525 cm^{-1} and 1363-1333 cm^{-1} respectively. The symmetric stretching bands is nearly as strong as the asymmetric stretching band in the nitro alkenes, although in the nitro alkanes it is only one fourth as strong as the asymmetric stretching bands. The symmetric stretching band of $-NO_2$ in the reaction product was strong and had shoulders in the 1363-1340 cm^{-1} range, indicating the possibility of the presence of a nitro olefin.

The presence of dinitro compounds could not be verified without further separation. The symmetrical $-NO_2$ stretching band normally is split in the dinitro compounds (18).

The 1650 cm^{-1}, 1280 cm^{-1}, 855 cm^{-1}, and 755 cm^{-1} bands were assigned to an alkyl nitrate compound. The alkyl nitrate frequency range is 1639 ± 13 cm^{-1} and 1279 ± 7 cm^{-1} (18). Other compounds indicated in the mixture were primary alcohols by the 3400 cm^{-1}, 1320 cm^{-1}, and 1020 cm^{-1} bands and a small amount of a carbonyl type compound by the 1730 cm^{-1} band (13).

The mass spectrometric analysis of the yellow liquid indicated that the mixture contained a nitro compound with the molecular weight of 113 grams/mole and with the structural formula



$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CHNO_2$$

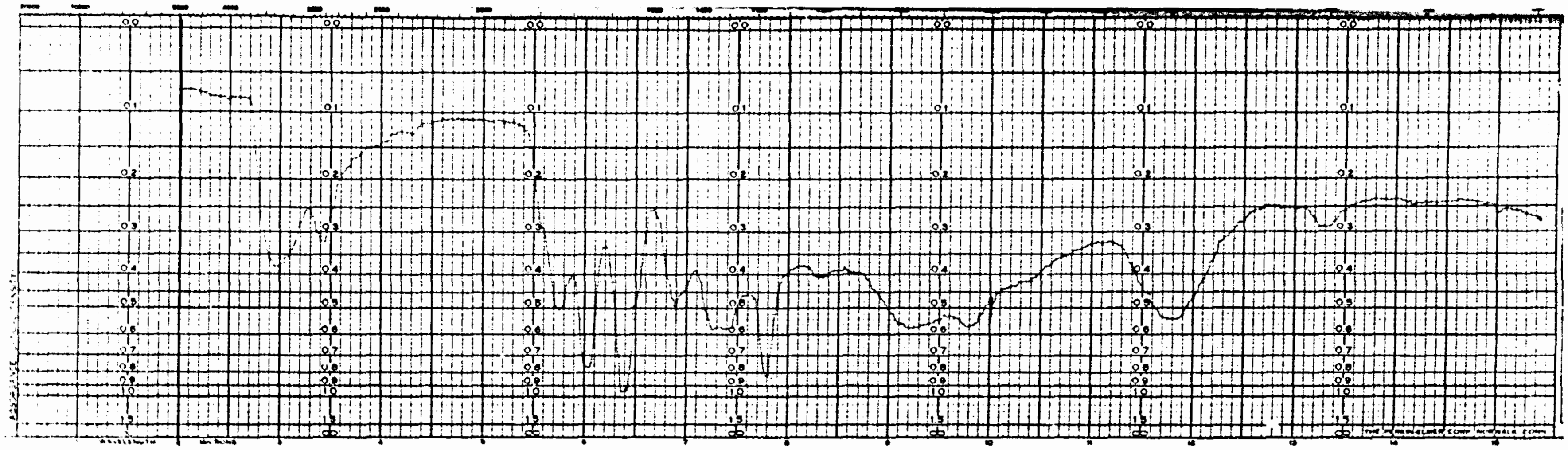
The peaks in the lower regions and the peak at m/e 30 indicated other nitro and unsaturated compounds (98). However, the conjugated unsaturation was not shown by the infrared spectra.

The reaction product of gaseous isoprene and nitrogen dioxide was allowed to stand for one hour and then re-examined. This time the infrared spectrum (Figure 6) showed that definite changes had taken place during the one hour. The -OH band at 3400 cm^{-1} and the C=O band at 1740 cm^{-1}, shifted from 1730 cm^{-1}, had more than doubled in intensity proving that the reaction product was undergoing oxidation. The broad bands at 1090 cm^{-1} and 1020 cm^{-1} indicated secondary and primary alcohols respectively. The largest increase was in the organic nitrate content as indicated by the extremely large increase in the 1650 cm^{-1}, 1280 cm^{-1}, 855 cm^{-1},

FIGURE 6

Gaseous NO_2-Isoprene Reaction Product

One Hour after Reaction at 25°C


ABSORBANCE
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.5
∞
WAVELENGTH
MICRONS
3
4
5
6
7
8
9
10
11
12
13
14
15
THE PERKIN-ELMER CORP NORWALK CONN

755 cm^{-1} bands. The 1553 cm^{-1} band did not show a noticeable decrease but the 1380 cm^{-1} and 1460 cm^{-1} bands had changed their shape, indicating the possible decrease in the primary nitro compound content.

The conclusion from the infrared data of this study is that at 25°C gaseous isoprene and nitrogen dioxide in the presence of a small amount of oxygen react rapidly and undergo nitration as well as oxidation processes, forming numerous compounds. This is in agreement with the work done previously with nitrogen dioxide and olefins (1, 2, 19, 25, 73, 74).

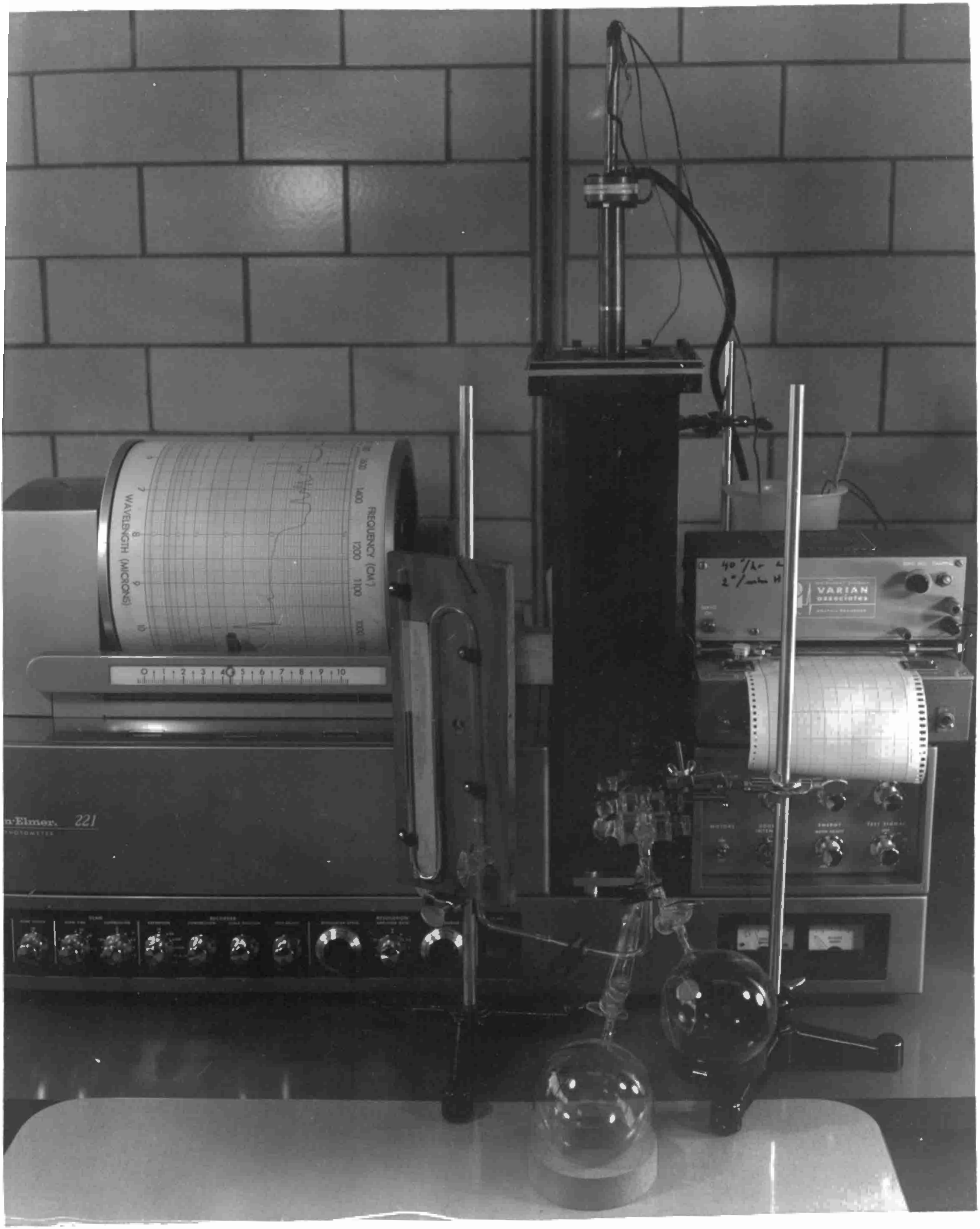
B. Isoprene in the Presence of NO_2 at Liquid Nitrogen Temperature

The reaction of isoprene and NO_2, which was rapid at 25°C, was studied at liquid nitrogen temperature. The low temperature cell (Figure 7), described in an earlier section, was used to cool the materials to the desired temperature. The cell was evacuated before the coolant, in this case liquid nitrogen, was poured in the reservoir. The temperature of the Irtran-2 window which served as the sample holder was measured by the copper-constantan thermocouple with a cold junction at 0°C. The temperature readings were taken from a Varian Associates recorder. The thermocouple was calibrated before use with liquid nitrogen, dry ice-acetone mixture, and ice water. The readings obtained using these substances matched those in the copper-constantan calibration

FIGURE 7

Low Temperature Infrared Spectrophotometric Cell

in Operation


FREQUENCY (CM.⁻¹)
1400
1200
1100
1000
WAVELENGTH (MICRONS)
7
8
9
10
0 1 2 3 4 5 6 7 8 9 10
n·Elmer. 221
PHOTOMETER
VARIAN associates
40"/hr
2"/min
MOTORS
ENERGY
TEST SIGNAL

tables. The lowest temperature obtained was -188°C. The cooling time from room temperature to -188°C was 12 minutes using liquid nitrogen.

When the temperature became steady, the sample, stored in a 500 cc flask, was introduced on the sample window through a glass nozzle with a one millimeter opening directed on the Irtran-2 window. The infrared spectra of NO_2 and isoprene were obtained in this fashion and compared with their gas and liquid phase spectra. No NO_2 was observed in the solid film deposited on the window (Figure 8). The observed frequencies of the N_2O_4 bands are recorded in Table I. The isoprene bands, when recorded immediately after depositing the sample, were broad in the 11.2 micron region. However, upon warming the sample slightly, the bands became well defined and split in many instances (Figure 9). The frequencies of many fundamental vibrations shift toward a higher frequency (Table II). No changes in the frequencies were noted upon recooling.

After the individual spectra of isoprene and N_2O_4 at -188°C were recorded, the reaction between the two compounds was investigated. Isoprene was deposited on N_2O_4 at -188°C while the infrared spectraphotometer was cycling between 5 and 8 microns at a rate of 70 seconds per cycle. In this region isoprene, N_2O_4, NO_2, $R\text{-}NO_2$ and $R\text{-}ONO_2$ bands appear. No decrease in isoprene was taking place. The infrared spectrum of N_2O_4 was superimposed on the spectrum of isoprene

FIGURE 8

A. NO_2 Gas at + 25°C

B. N_2O_4 Solid at -188°C

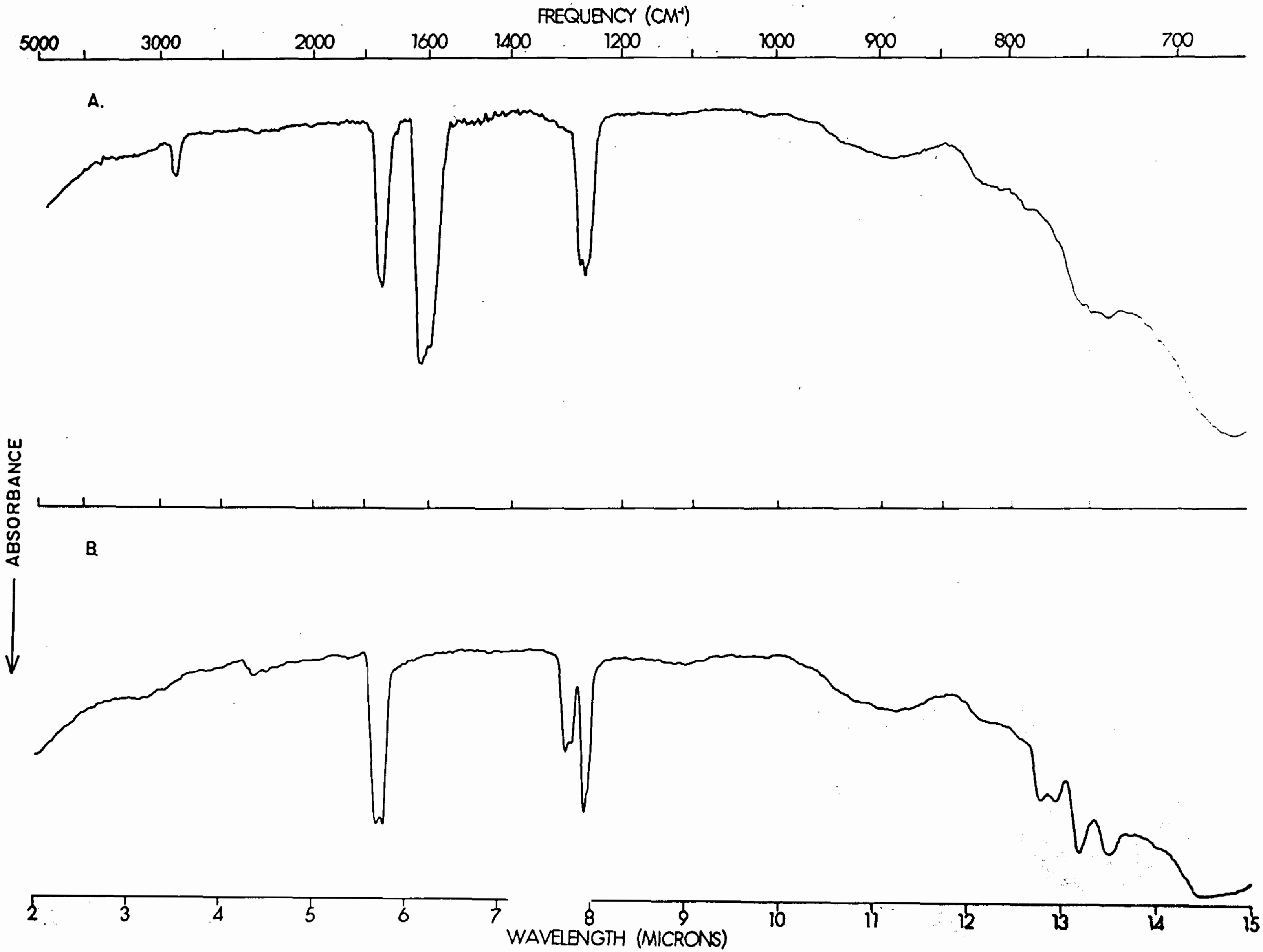

FREQUENCY (CM⁻¹)
5000
3000
2000
1600
1400
1200
1000
900
800
700
A.
B.
ABSORBANCE
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

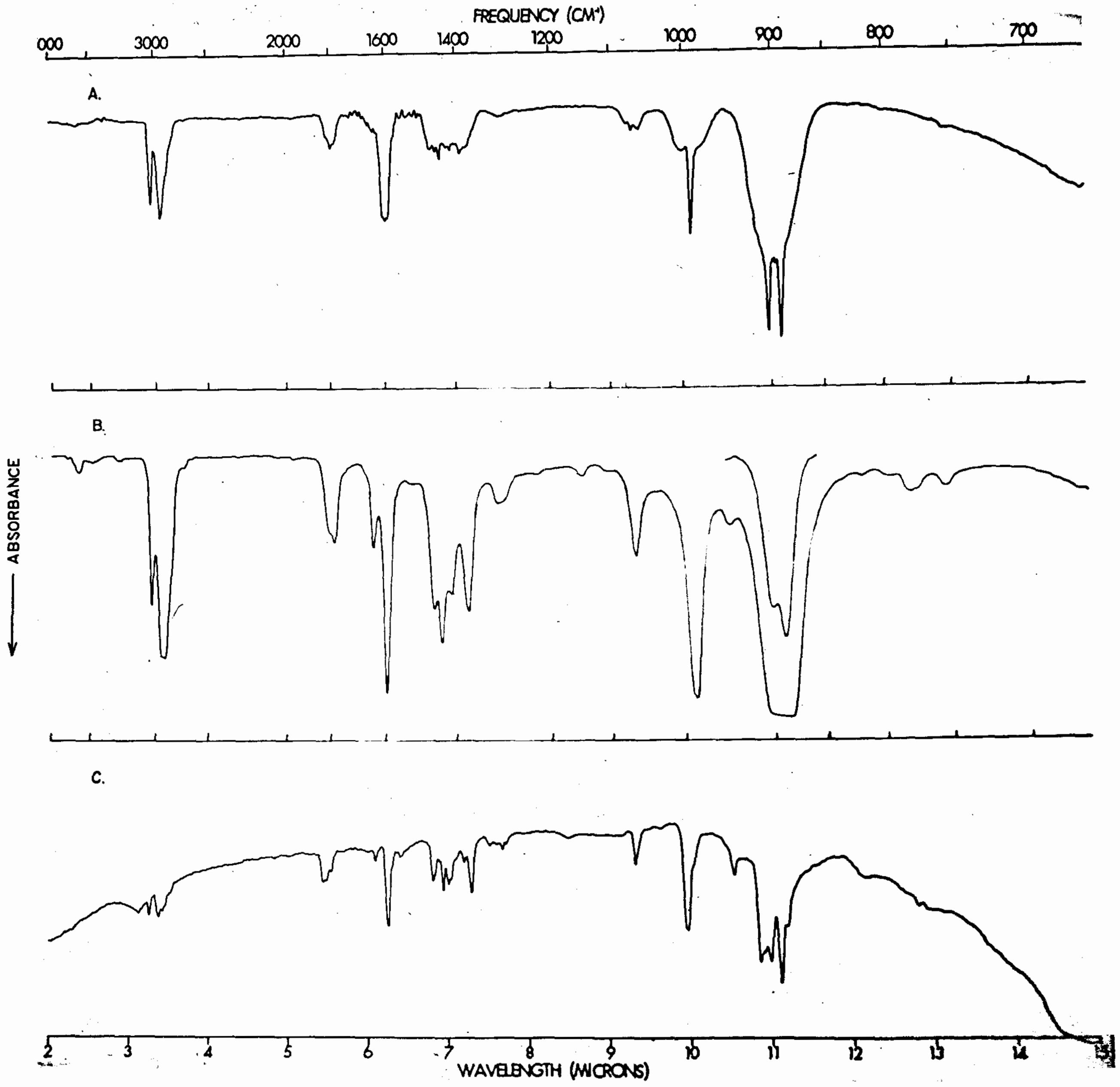
FIGURE 9

Isoprene Infrared Spectra

A. Gas at +25°C

B. Liquid at +25°C

C. Solid at -188°C


FREQUENCY (CM^{-1})
000
3000
2000
1600
1400
1200
1000
900
800
700
A.
B.
C.
ABSORBANCE
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

when the 2-15 micron region was scanned and recorded (Figure 10). No change was observed in the infrared spectrum after 30 minutes.

Therefore, it was concluded that N_2O_4 and isoprene do not react at -188°C at a rate detectable by infrared techniques.

C. Isoprene in the Presence of NO_2 at -135°C and -123°C

The sample was deposited on the Irtran-2 sample window in the same manner as in Section B. As the sample was warmed, infrared spectra of isoprene and N_2O_4 were obtained in order to record any changes taking place. At -146°C to -142°C a change in the infrared spectrum of isoprene was observed. The change was in the frequencies observed in the crystalline state to the frequencies measured in the liquid state (Figure 11). The sample was warmed to -135°C. However, no reaction was observed at this point.

Isoprene was added to N_2O_4 at -123°C. The melting point of isoprene is -146°C (56). Therefore, evaporation or migration of isoprene down the sample holder could have caused the decrease in the absorbance bands of isoprene without its reaction with N_2O_4. The gas phase isoprene infrared spectrum can be obtained using this cold cell, but, even though the volume of the cell was kept small, the vapors of the sample are distributed throughout the cell and most of the gas sample is not in the energy beam.

Because the isoprene bands decreased without actually

FIGURE 10

A. Infrared Spectrum of Solid N_2O_4 on Top of Isoprene at -188°C

B. Infrared Spectrum of the Product of the NO_2 Reaction with Isoprene at -75°C

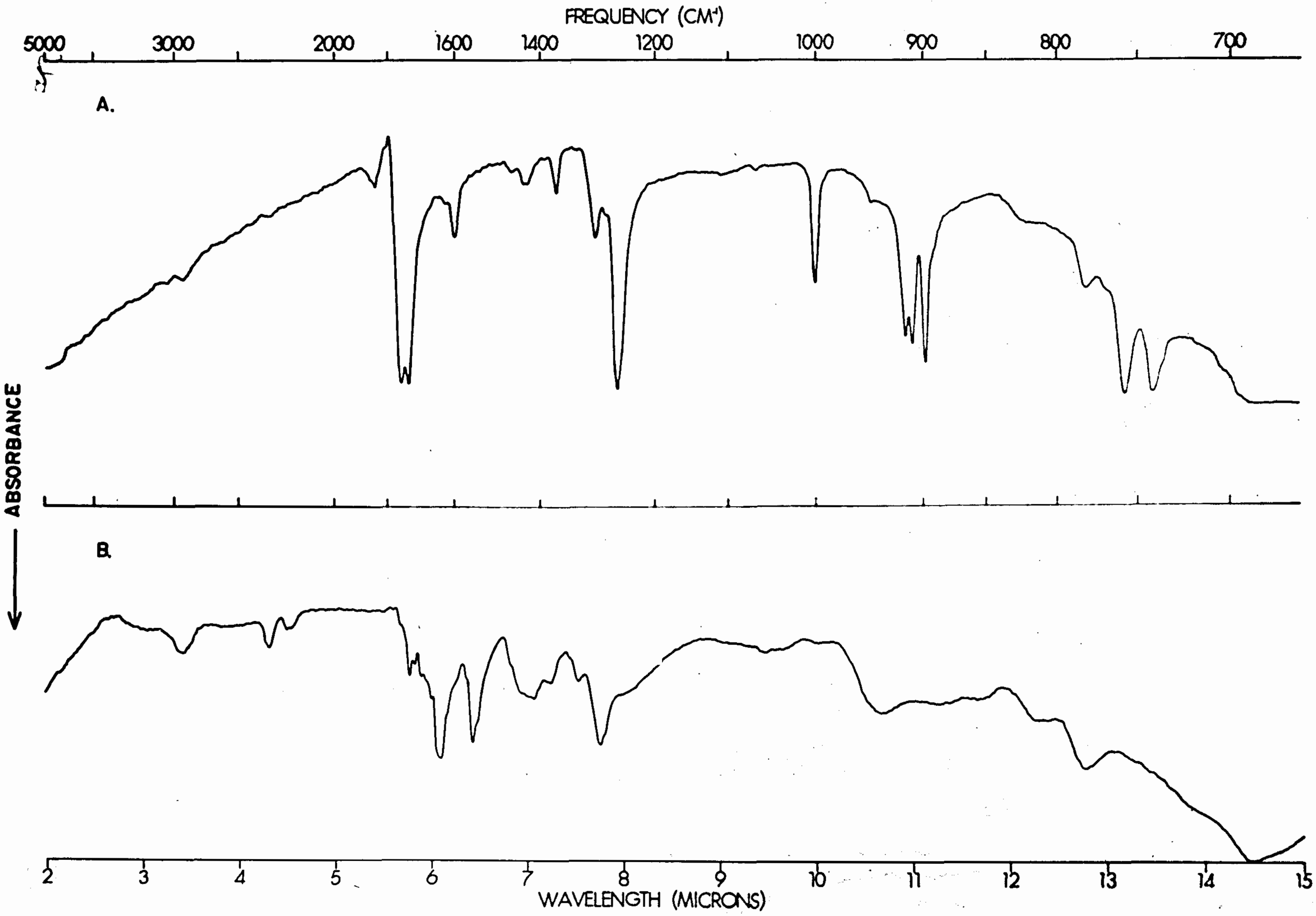
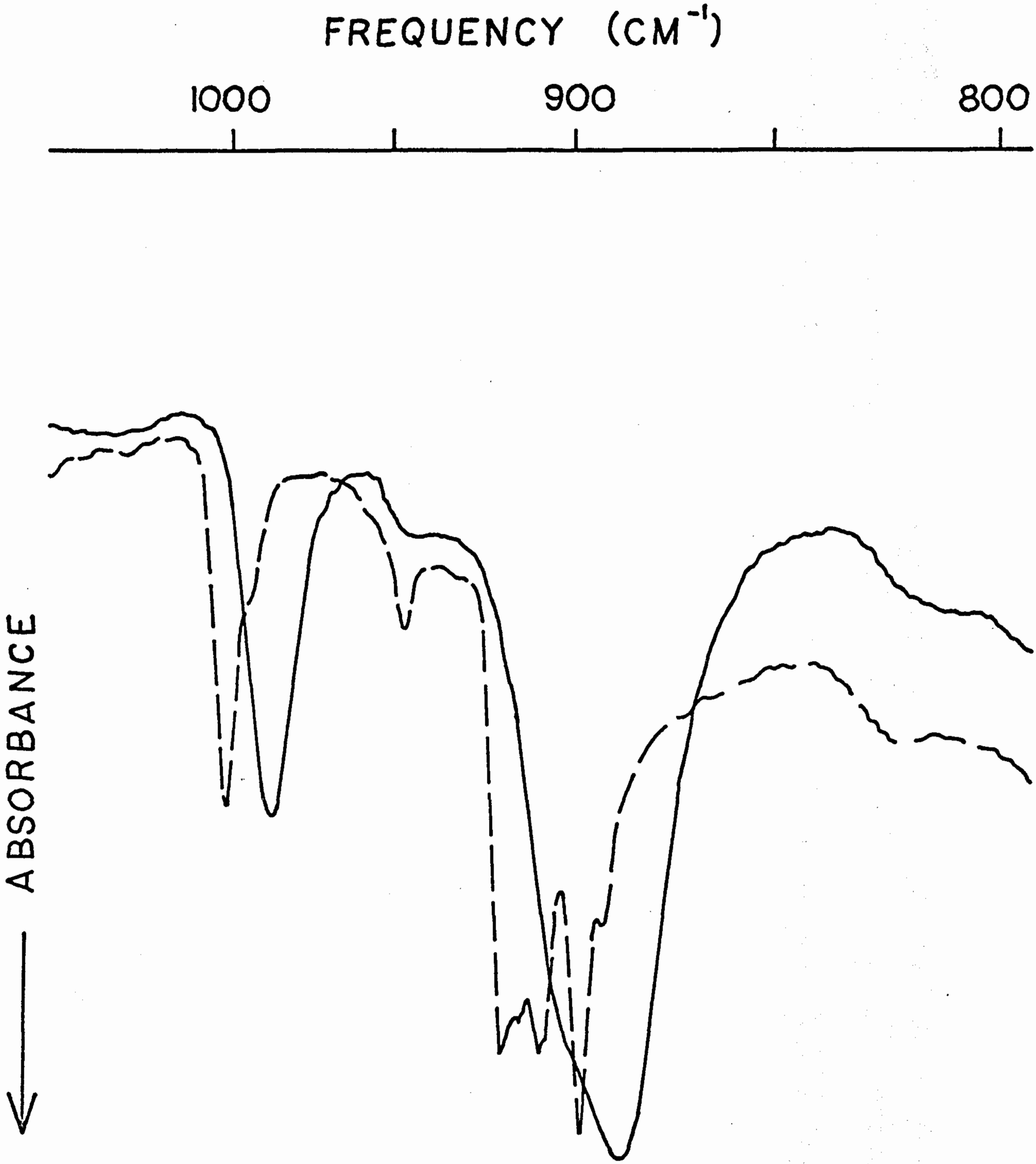

FREQUENCY (CM⁻¹)
5000
3000
2000
1600
1400
1200
1000
900
800
700
A.
B.
ABSORBANCE
2
3
4
5
6
7
8
9
10
11
12
13
14
15
WAVELENGTH (MICRONS)

FIGURE 11

-------- Isoprene at -188°C

———— Isoprene at -144°C


FREQUENCY (CM⁻¹)
1000
900
800
ABSORBANCE

undergoing a reaction, it was necessary to observe the formation of the product band. The 5-7 micron region was selected for monitoring the reaction as the decrease of the isoprene and N_2O_4 bands as well as the increase in the reaction product bands could be observed at the same time. The appearance of the product bands was taken as evidence of the reaction between isoprene and N_2O_4. The 5-7 micron region was scanned at a speed of 44 seconds per cycle. No reaction at -123°C was noticed.

The N_2O_4 and isoprene spectra obtained at -123°C were compared with the spectra obtained at lower and higher temperatures. The isoprene was a liquid at this temperature and resembled closely the spectra of the isoprene at +25°C and of the amorphous solid of isoprene at -180°C. All three spectra showed that the bands at $\sim$ 890 cm^{-1} had fused together. The crystalline isoprene from -188°C to -146°C showed three well resolved bands and two definite shoulders in the corresponding region. The spectrum of liquid isoprene at -123°C had well defined narrow bands in the 1500-1400 cm^{-1} region. At +25°C these bands appeared as shoulders.

The N2O4 spectrum at -123°C showed that the 772 cm^{-1} and 782 cm^{-1} bands present at -188°C had disappeared. A weak band appeared at 812 cm^{-1} which was not present at lower temperatures. This phenomenon also was observed by Snyder and Hisatsune (91). Otherwise no changes in the N_2O_4 frequencies were noted upon warming the solid phase sample.

The Irtran-2 spectrum did not hinder the examination of the N_2O_4 and isoprene spectra. The only possible interference was the broad, medium band between 1000-850 cm^{-1}. The absorbance of energy increased going from 1000 cm^{-1} toward a lower frequency region.

D. Reaction at -111°C

Since the reaction of isoprene and N_2O_4 had not taken place at -125°C, it was necessary to heat the sample above this temperature. It was not desirable, for obvious reasons, to warm the "cold finger" and the sample with the electric heaters from -188°C to above -125°C using liquid nitrogen as the coolant. Therefore, a new coolant, a mixture of ethyl alcohol and liquid nitrogen, was used. With this mixture the study of the reaction was continued in the -135°C to -75°C range.

The sample, N_2O_4, was deposited on the cooled sample window at -188°C as described previously. Then the coolant was changed to the ethanol-liquid nitrogen mixture. The warming of the sample was continued to -111°C. Isoprene was deposited on top of the N_2O_4 at this point. A small increase in the 1650 cm^{-1} band caused by the formation of the product and a decrease in the N_2O_4 band were noted.

This was considered the point where the isoprene-N_2O_4 reaction started at a rate measurable by infrared methods. However, the reaction was very slow and after 15 minutes about 90% of the reactants were still present.

E. Reaction at -75°C

The isoprene spectrum obtained at -75°C showed no differences from the spectrum obtained at -125°C. The N_2O_4 spectrum, however, showed the disappearance of the 1293 cm^{-1} band. This band was attributed to an impurity, possibly N_2O (102).

The reaction between isoprene and N_2O_4 became rapid at -75 C. The reaction was monitored as follows: The N_2O_4 sample was frozen on the Irtran-2 window as before. The sample was warmed to -75°C and isoprene deposited on top of the N_2O_4 layer. The 5-7 micron region was scanned using the cycling procedure with a speed of 44 seconds per cycle.

The combination spectrum of isoprene and N_2O_4 and the spectral evidence of the reaction is presented in Figure 12. The N_2O_4 band is at 1725 cm^{-1} and the isoprene band at 1588 cm^{-1}. The decrease in the isoprene and the N_2O_4 bands with the appearance and increase in the 1708 cm^{-1}, 1640 cm^{-1}, and 1550 cm^{-1} bands due to the reaction product illustrate the reaction. The reaction can be presented as a concentration, shown by the absorbance, versus time of reaction plot. The concentration of N_2O_4 (point 1) starts to decrease when isoprene is added (point 2). At first the reaction is rapid and then levels out until it reaches completion (point 3) 308 seconds after isoprene addition to N_2O_4.

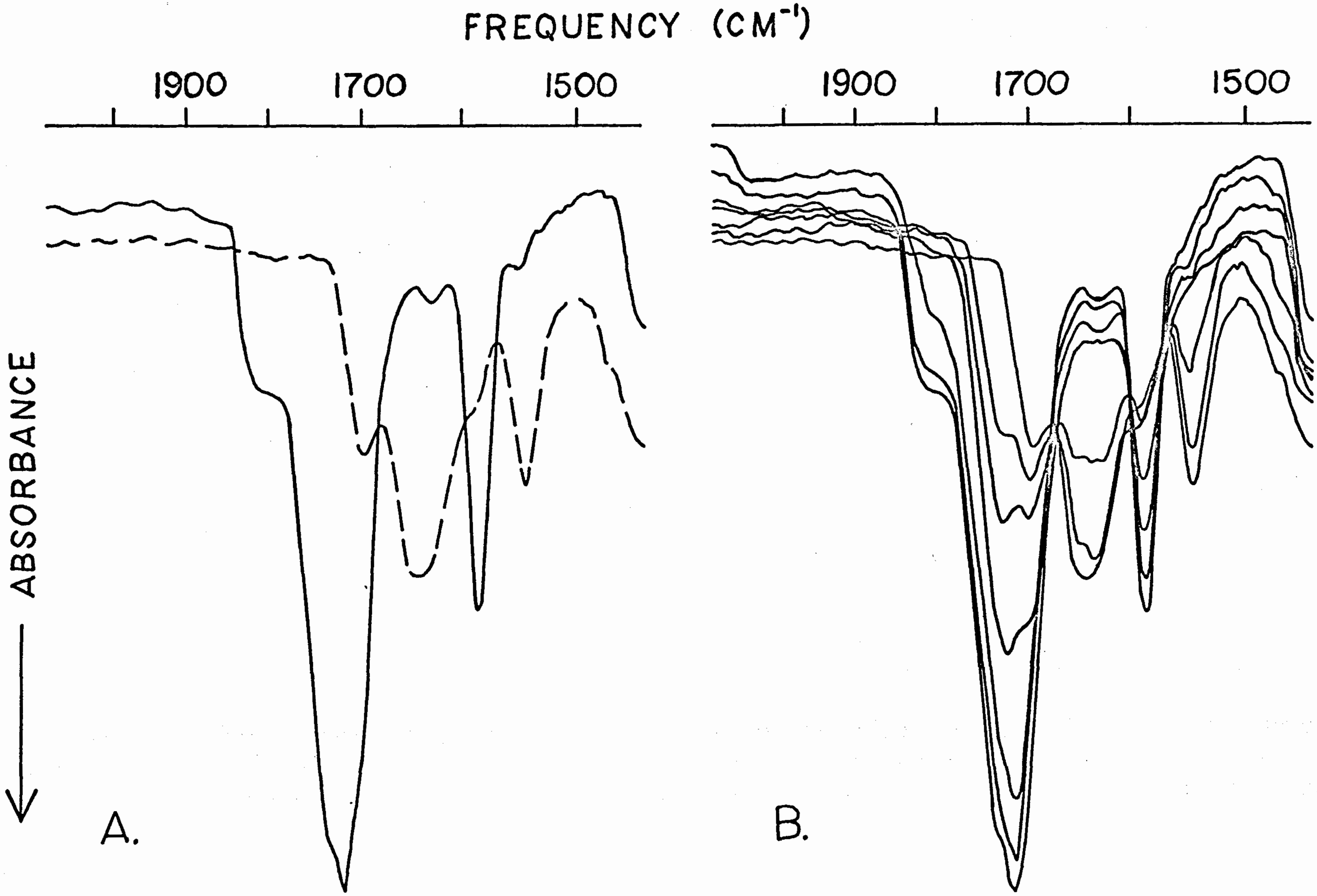
FIGURE 12

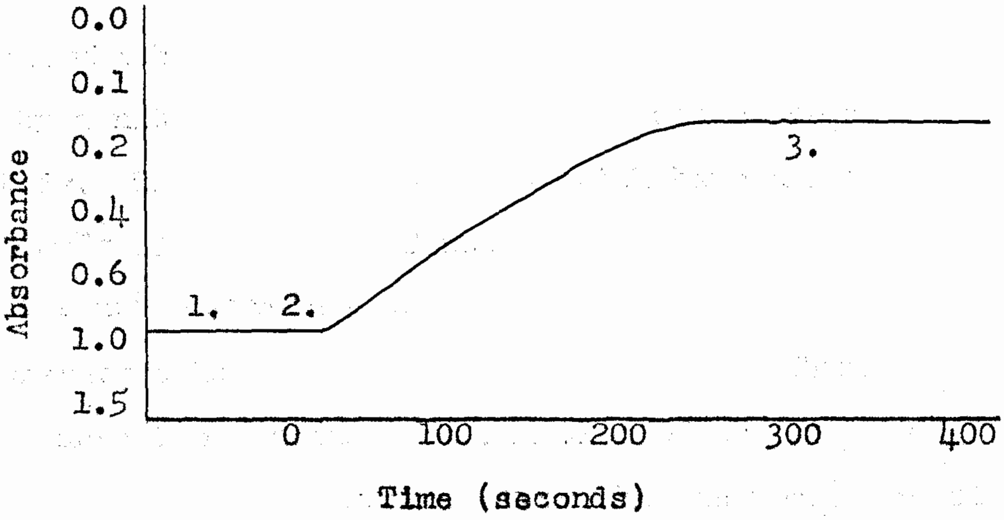
Reaction Study Curves at -75°C

A. ——————— Infrared Spectrum of Isoprene on Top of N_2O_4 at the Beginning of the Reaction

\- - - - - - - - - - - Infrared Spectrum at the End of the Reaction

B. The Changes in the Infrared Spectra from the Beginning to the End of the Reaction


FREQUENCY (CM^{-1})
1900
1700
1500
1900
1700
1500
ABSORBANCE
A.
B.



The infrared spectrum of the product was obtained in the 2-15 micron region. It showed that isoprene was still present but N_2O_4 was absent. A nitrate and a nitro compound were shown by the 1644 cm^{-1}, 1285 cm^{-1} and 1552 cm^{-1}, 1380 cm^{-1} bands respectively. The mixture of reaction products was not stable as the band ratios changed upon standing and upon warming of the sample. The 1708 cm^{-1} band could be caused by a ketone. Ketones have been identified in the gas phase reactions of NO_2 and olefins (2, 57). This band did not appear in all cases of the low temperature reactions of N_2O_4 and isoprene. The frequency is higher by about 30 cm^{-1} than the one observed in nitrites.

Nitrites have been reported to be products of N_2O_4 and olefin reactions (19, 60, 61). The nitrites have the N=0 frequency at 1681-1653 cm^{-1} and 1625-1613 cm^{-1}. Both bands are almost always double due to the co-existence of cis- and trans- forms (15). The nitrites are unstable and in the presence of water form nitro alcohols (61). The weak 1660 cm^{-1} band which decreased in intensity could have been caused by a nitrite, but positive proof cannot be made from this study. The nitroso compounds which have a single band at 1600 cm^{-1} also were not found at this time (16).

The reaction product of isoprene and N_2O_4 obtained at a low temperature had one outstanding difference from the product of these two compounds on reaction of the gases at room temperature. The products from the gas phase reaction showed an extremely strong $-NO_2$ symmetric stretching band which was of medium intensity in the low temperature reaction. The nitro compounds were the predominant products in the gas phase reaction, whereas a nitrate seemed to be the major product in the reaction at -75°C. The broad, not well defined, band at 1430 cm^{-1} in the low temperature product suggested that a large mixture of compounds was present. The products, when left overnight in the closed low temperature cell at room temperature,produced carbon dioxide and nitrous oxide as evidenced by the absorbance bands at 2330 cm^{-1} and 2225 cm^{-1}. The rest of the infrared spectrum resembled that of the product analyzed right after reaction but lacked definition. This could be caused by the formation of many products, polymerization, or the formation of solids which would cause light scattering. The products, viscous liquids and solids, were removed from the Irtran-2 window by placing the window in a dilute NaOH solution. Most of the product was removed from the window by this treatment. The remainder was scraped off gently.

SUMMARY

A low temperature cell was designed for infrared spectrophotometric studies. The cold cell consists of a stainless steel outer shell and a copper coolant reservoir with a copper "cold finger." An Irtran-2 plate, used as the sample holder, can be cooled by the "cold finger" to -188°C using liquid nitrogen as the coolant. Electric heaters are incorporated in this cell which permit an increase in temperature during the sample study. The outside windows also are of Irtran-2 material which does not react with the compounds studied and which is extremely well suited for cold temperature work. This cell can be easily disassembled for cleaning. The cold cell can be used for gas-liquid-solid transition studies, reaction studies at low temperatures, and collection and examination of gas chromatographic fractions.

The low temperature cell was applied to the study of isoprene and nitrogen dioxide infrared spectra in the +25°C

to -188°C temperature range. It was observed that the absorbance bands narrowed upon decrease in temperature. In the case of the crystalline isoprene, a change was noted in the CH and CH_2 out-of-plane deformation frequencies of CH_2= CR_1R_2 and CH =CHR_1. The change was toward a higher frequency. In numerous cases the crystalline samples exhibited split absorbance bands. The infrared spectra of the amorphous solid samples resembled those of the liquid samples. No changes in frequencies of NO_2 and N_2O_4 were observed upon changing the temperature.

The low temperature cell was applied also to the preliminary study of isoprene-NO_2 reaction. The reaction between isoprene and NO_2 in the gas phase at +25°C was rapid. On addition of either reactant in excess, the other reactant was found to be absent. The reactants underwent nitration and oxidation processes with the major products being nitro, nitrate and alcohol type compounds.

No reaction between isoprene and N_2O_4 was observed between -188°C and -115°C. At -111°C the reaction was extremely slow. At -75°C the reaction was considerably faster than at -111°C. The major products included nitrates and nitro compounds. Oxidation also was noted in the products but to a smaller degree than in the gaseous reaction.

BIBLIOGRAPHY

1. Altshuller, A. P., Private Communication.
2. Altshuller, A. P., and Cohen, I. R., Ind. Eng. Chem., 51, 776 (1959).
3. Altshuller, A. P., and Cohen, I. R., Anal. Chem., 31, 628 (1959).
4. Anderson, D. H., and Miller, O. E., J. Opt. Soc. Am., 43, 777 (1953).
5. Avery, W. H., and Ellis, C. F., J. Chem. Phys., 10, 10 (1942).
6. Avery, W. H., and Morrison, J. R., J. Appl. Phy., 18, 960 (1947).
7. Bailey, C. R., and Cassie, A. B. D., Nature, 131, 239 (1933).
8. Baldock, H., Levy, N., and Scaife, C. W., J. Chem. Soc., 2627 (1949).
9. Barnes, R. B., Liddel, U., and Williams, V. Z., Anal. Chem., 15, 659 (1943).

10. Becker, E. D., and Pimentel, G. C., J. Chem. Phys., 25, 224 (1956).

11. Begun, G. M., and Fletcher, W. H., J. Mol. Spectr., 4, 388 (1960).

12. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958, p. 34.

13. Ibid., p. 95.

14. Ibid., p. 297.

15. Ibid., p. 304.

16. Ibid. p. 305.

17. Brady, L. J., "Analytical Absorption Spectroscopy," edited by Mellon, M. G., John Wiley & Sons, Inc., New York, 1950, p. 439.

18. Brown, J. F., Jr., J. Am. Chem. Soc., 77, 6341 (1955).

19. Brown, J. F., Jr., J. Am. Chem. Soc., 79, 2480 (1957).

20. Cassie, A. B. D., and Bailey, R. L., Nature, 131, 239 (1933).

21. Cheronis, N. D., "Organic Chemistry," Thomas Y. Crowell Company, New York, 1943, p. 253.

22. Coblenz, W. W., Carnegie Inst. Technol. Bull. No. 35, 1905.

23. Comeford, J. J., and Gould, J. H., J. Mol. Spectr., 5, 474 (1960).

24. Conn, G. K. T., Lee, E., and Sutherland, G. B. B. M., Proc. Roy. Soc., A 176, 484 (1940).

25. Cottrell, T. L., and Graham, T. E., J. Chem. Soc., 556 (1953).

41. Gray, P., _Trans. Faraday Soc._, _51_, 1367 (1955).

42. Gray, P., and Yoffe, A. D., _Chem. Rev._, _54_, 1069 (1954).

43. Hackforth, H. L., "Infrared Radiation," McGraw-Hill Book Co., Inc., New York, 1960, p. 8.

44. Hale, T. A., "New Infrared Transmitting Materials for Use by Spectroscopists," Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, 1961.

45. Harris, L., Benedict, W. S., and King, G. W., _Nature_, _131_,621 (1933).

46. Harris, L., and King, G. W., _J. Chem. Phys._, _2_, 51 (1934).

47. Henry, W. E., and Dolecek, R. L., _Rev. Sci. Instr._, _21_, 496 (1950).

48. Herzberg, G., "Infrared and Raman Spectra of Polyatomic Molecules," D, Van Nostrand Co., Inc., New York, 1945, p. 284.

49. Hisatsune, I. C., Devlin, J. P., and Wada, Y., _J. Chem. Phys._, _33_, 714 (1960).

50. Holden, R. B., Taylor, W. J., and Johnston, H. L., _J. Opt. Soc. Am._, _40_, 757 (1950).

51. Hornig, D. F., _Disc. of Faraday Soc._, 9, 115 (1950).

52. Janz, G. J., and Fitzgerald, W. F., _Applied Spectr._, _9_, 178 (1955).

53. Kaiser, R., _Z. Physik._, _132_, 482 (1952).

54. Komarewsky, V. I., and Shih, C. C., _J. Am. Chem. Soc._, _72_, 1562 (1950).

71. Mauer, F. A., "Formation and Trapping of Free Radicals," edited by Bass, A. M., and Broida, H. P., Academic Press, New York, 1960, p. 138.

72. McMahon, H. O., Hainer, R. M., and King, G. W., J. Opt. Soc. Am., 39, 786 (1949).

73. Michael, A., and Carlson, G. H., J. Org. Chem., 4, 167 (1939).

74. Michael, A., and Carlson, G. H., J. Org. Chem., 5, 1 (1940).

75. Nelson, L. S., Rev. Sci. Instr., 27, 655 (1956).

76. Nencini, G., and Pauluzzi, E., Applied Spectr., 14, 138 (1960).

77. Nikitin, V. N., Pribory i Tekhnika Eksperimenta, 1, 116 (1957).

78. Olsen, D. A., Dissertation Abstracts, 20, 4544 (1960).

79. Perkins, W. D., and Wilson, M. K., Phys. Rev., 85, 755 (1952).

80. Rakova, G. V., and Korotkov, A. A., Doklady Akad. Nauk S. S. S. R., 119, 982 (1958).

81. Randall, H. M., Fowler, R. B., Fuson, N., and Dangl, J.R., "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, 1950, p. 5.

82. Rasmussen, R. S., and Brattain, R. R., J. Chem. Phys., 15, 120 (1947).

83. Riebsomer, J. L., Chem. Revs., 36, 157 (1945).

84. Roberts, V., J. Sci. Instr., 32, 294 (1955).

85. Schaffert, R., Nature, 131, 911 (1933).

86. Schaffert, R., J. Chem. Phys., 1, 507 (1933).

87. Schechter, H., and Courad, F., J. Am. Chem. Soc., 75, 5610 (1953).

88. Schoen, L. J., Kuentzel, L. E., and Broida, H. P., Rev. Sci. Instr., 29, 633 (1958).

89. Schoenbrunn, E. F., and Gardner, J. H., J. Am. Chem. Soc., 82, 4905 (1960).

90. Sidgwick, N. V., "The Organic Chemistry of Nitrogen," The Clarendon Press, Oxford, 1949, p. 231.

91. Snyder, R. G., and Hisatsune, I. C., J. Mol. Spect., 1, 139 (1957).

92. Spees, A. H., Reynolds, C. A., Boxer, A., and Pearson, G., Rev. Sci. Instr., 28, 1090 (1957).

93. Stewart, J. E., Anal. Chem., 30, 2073 (1958).

94. Sutherland, G. B. B. M., Proc. Roy. Soc., A141, 342 (1933).

95. Sutherland, G. B. B. M., Proc. Roy. Soc., A141, 535 (1933).

96. Sutherland, G. B. B. M., Disc. Faraday Soc., 9, 274 (1950).

97. Thomas, H., Ann. Phys., 38, 601 (1940).

98. Varsel, C. J., and Kuhn, W. F., Private Communication.

99. Wagner, E. L., and Hornig, D. F., J. Chem. Phys., 18, 296 (1950).

100. Walsh, A., and Willis, J. B., J. Chem. Phys., 17, 838 (1949).

101. Walsh, A., and Willis, J. B., J. Chem. Phys., 18, 5526 (1950).

102. White, C. E., Ph. D. Thesis, "Low Temperature Infrared Spectroscopic Studies," University of Maryland, 1960.

103. Wiener, R. N., and Nixon, E. R., J. Chem. Phys., 26, 906 (1957).

104. Wilson, M. K., and Badger, R. M., Phys. Rev., 76, 472 (1949).

105. Zunino, J., Z. Physik., 100, 335 (1936).

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TABLE I

INFRARED SPECTRAL DATA FOR NO_2 AND N_2O_4

Dinitrogen Tetroxide (Solid)

Frequencies in cm^{-1}

Assignment	Snyder, R.G. (91)	Wiener, R.N., and Nixon, E.R. (103)	Fateley, et al (33)	This Work -188°C
v_7	440 cm^{-1} ($\pm$ 15 cm^{-1})			
v12 asym. NO_2 bend	738	738 cm^{-1} (V.S.)	739 cm^{-1}	741 s
v_{12} + R	756	756 (V.S.)	759	758 (s)
				*772 (s) *782 (s)
v_{11} NO stretch	1256	1256 (V.S.) 1280 (m)	1253	1260(s) 1283(m)
v_9 NO stretch	1728	1734 (V.S.)	1735	1737(s)
v_9 + R	1749	1760 (V.S.)	1757	1756(s)

* Bands disappeared upon warming.

Dinitrogen Tetroxide (Liquid)

Assignment	Hisatsune (49)	Begun, G.M. (11)	This Work -40°C
v_7	~438 cm^{-1}		
v_{12} deformation	743	743 cm^{-1}	
v_{11} NO stretch	1253	1257	1260 (s)
v_9 NO stretch	1737	1733 (broad)	1737 (s)

TABLE I (continued)

Dinitrogen Tetroxide (Gas)

Assignment	Gray, P. (42)	Perkins, W.D. (79)	Begun, G.M. (11)	This Work 25°C
v_4	160 cm^{-1}			
v_3	265			
v_6	320			
v_{10}	430			
v_8	500			
v_1	684	684 cm^{-1}		
v_{12} deformation	748	748	750 (V.S.)	749 m
v_2	811	811		~810 bw
v_8		1133		
v_{11} NO stretch	1240	1260	1262(s)	1260 s
v_1	1334	1342		
v_5	1722	1722		
v_9 NO stretch	1747	1747	1748(s)	1744 s

TABLE I (continued)

Nitrogen Dioxide (Gas)

Assignment (48)	Schaffert, R. (86)	Herzberg (48)	De More, W.B.(26)	This Work 25°C
v_2 (a_1)	641	648 (s)		
			755	
v_1 $(a_1)^2$ v_1 NO_2 symmetrical stretching		1320 (from U.V.)	1306	
(2 v_2 ??)	1373	1373 (w)		
v_3 (b_1) v_3 NO_2 assymetrical stretching	1628	1621(V.S.)	1621	1622 V.S.
$v_3 + v_2$ (b_1)		2220(m)		2215 m

TABLE II

INFRARED ABSORBANCE BANDS OF ISOPRENE

Frequencies in cm^{-1}

Assignment	Gas 25°C	Liquid 25°C	Solid -180°C
$CH=CH_2$(vinyl) CH stretching	3030 (s)	3040 (s)	8070 (m)
CH_3 " " "	2948 (s)	2948 (s)	2965 (m)
CH_2 " " "		2905 (s)	2925 (m)
$CH=CH_2$ (vinyl) overtone	1815 (w)	1810 (m)	1839 (m)
$CH=CH_2$ (vinyl) overtone	1798 (w)		1828 (m)
$CR_1R_2 = CH_2$ overtone	1780 (w)	1787 (m)	1800 (w)
$C=C$ stretching		1640 (m)	1640 (w)
$C=C$ conjugated stretching	1600 (s)	1600 (s)	1599 (s)
CH_3-C asymm. deformation	1462 (m)	1460 (m)	1460 (m)
	1441 (m)	1439 (m)	1440 (m)
CH_2 in plane deformation	1441 (w)	1413 (m)	1425 (m)
	1390 (m)		1388 (w)
CH_3-C symm. deformation	1370 (w)	1372 (m)	1370 (m)
			1329 (w)
			1315 (w)
CH in plane deformation	1300 (bw)	1308 (bw)	1305 (w)
			1298 (w)
		1148 (bw)	1177 (bw)
	1073 (w)		
	1070 (w)	1067 (m)	1070 (m)
	1057 (w)		
			1037 (w)