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Wyandotte

UNPUBLISHED PRELIMINARY DATA

INVESTIGATION OF ACTIVATED SPECIES

SUMMARY REPORT No. 2

30 April 1962 to 30 ~~March~~ April 1963

TO

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
OFFICE OF RESEARCH GRANTS AND CONTRACTS
1520 "H" STREET, N. W.
WASHINGTON 25, D. C.
CONTRACT No. NASr-24
Amendment No. 2
CONTROL No. ES-7744

L. E. KUENTZEL
R. K. SEIZINGER

April 1963

WYANDOTTE CHEMICALS CORPORATION
WYANDOTTE, MICHIGAN

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Industrial Chemicals Division
WYANDOTTE CHEMICALS CORPORATION
Wyandotte, Michigan

FOREWORD

This report was prepared by Wyandotte Chemicals Corporation, Wyandotte, Michigan, pursuant to NASA Contract No. NASr-24, Amendment No. 2. The following members of the professional research staff participated in the research and preparation of this report: Dr. Lester E. Kuentzel, Research Associate; and Mr. Reinhold K. Seizinger, Research Chemist. The work was carried out in the Organic Research Laboratories under the direction of Dr. Lester G. Lundsted, Director of Chemical Research.

Technical direction on behalf of NASA was provided by Alfred Gessow, Code RRP and Philip Pomerantz.

Approved by: Lester G. Lundsted

L. G. Lundsted, Director
Chemical Research Department

ABSTRACT

This report is the second in a series that describes efforts directed toward the preparation, stabilization and characterization of energy rich or activated species of low molecular weight. Basic techniques involve the thermal decomposition of suitable organic materials to form radicals and activated atoms, reacting these with radical trappers or active compounds and suddenly stabilizing the products at 4°K for study by infrared spectroscopy. Details of the equipment and techniques used were given in the first Summary Report dated March 1962. This report is largely concerned with the thermal decomposition of diazomethane to form carbene radicals and their reaction with the radical trapper nitric oxide in an attempt to produce dinitrosomethane. Results currently indicate that the material formed and stabilized at 4°K is a carbodiimide of the following suggested structure: HO-N=C=N-OH. This material apparently polymerizes during warmup to room temperature. Properties of the polymer are under study.

Preliminary work on the use of a microwave power generator to produce radicals and activated atoms for these studies is described. The nature of the equipment makes possible experimental attempts to produce activated helium atoms, react them with other activated atoms or groups and to stabilize any products at 4°K within microseconds of their formation. Future work proposes some investigations in this area.

INTRODUCTION

The work described by this report is a continuing investigation into the possibility of forming high energy compounds from free radicals and excited atoms generated thermally, stabilizing such compounds by sudden freezing at 4°K and characterizing them by infrared absorption spectroscopy and analysis of warm-up reaction products. The use of thermal decomposition reactions for generating the radicals and activated species and sudden chilling to cryogenic temperatures for stabilization of primary reaction products was employed because this technique appears to be the most susceptible to rapid scale-up if it should become desirable. Use of inert matrix materials for stabilization of active intermediates was generally avoided. While such matrix isolation techniques serve to simplify studies of the formation and reactions of highly active species, the presence of large amounts of inert matrix dilutes the materials under study and if such dilution is essential to stabilization, defeats the aims of this investigation. The high energy compounds sought by this work must be stable at cryogenic temperatures and in appreciable concentrations.

The "Technical Proposal for Investigation of Activated Species" by Wyandotte Chemicals Corporation, dated 21 October 1960, forms the basis of much of the investigative effort under this contract. It suggests, among a number of areas of possible interest, the formation of energy rich materials from carbene radicals and radical trappers such as nitric oxide and oxygen. Early efforts were directed toward obtaining carbene radicals from the thermal decomposition of ketene. Success in this was indicated by the formation of appreciable quantities of ethylene which results from the reaction of carbene radicals with ketene. At this point, preliminary work with the thermal decomposition of diazomethane as a source of carbene radicals appeared more promising and the investigation was directed toward these ends.

Although diazomethane is a somewhat hazardous material to make, store and handle, it does decompose thermally at a lower temperature than ketene and would be expected to yield carbene radicals and nitrogen -- the latter relatively inert and transparent to infrared radiation. An initial experiment with diazomethane produced a frozen deposit of reaction products that exhibited a high degree of chemical activity at very low temperatures as indicated by variations in the infrared absorption spectra obtained. Chief drawback was the fact that only a relatively small percentage of the diazomethane actually decomposed and attempts to increase this percentage by using higher furnace temperatures merely decomposed the diazomethane to carbon, hydrogen and nitrogen. Copper as a furnace catalyst increased the preferred type of decomposition, but only after modifications of equipment which permitted furnace pressures to be raised to the neighborhood of 1 mm. of mercury did the major portion of the diazomethane decompose in a satisfactory manner. However, reaction products deposited on the cold surface were entirely different. For the first time, a major component was ethylene which supports a postulation that carbene radicals will also attack diazomethane to give ethylene.

Investigative plans called for passing a mixture of diazomethane and nitric oxide gas through the furnace in an attempt to induce reaction between carbene radicals and NO radical trapper. Mixtures of these two gases at pressures above some 200 mm. proved to be highly explosive. Mixtures at 1 to 2 mm. pressure proved to be non-reactive and such were fed into the furnace at about 400°C. The infrared spectrum of the suddenly frozen products of this reaction was quite complex. Gases released by this deposit at various temperatures during warm-up indicated the presence of hydrogen, nitrogen, diazomethane and ethylene but nothing that would indicate a reaction product of NO and CH_2N_2. Finally, at room temperature, an amber colored film was scraped from the experimental surface. Infrared spectroscopy indicates the material to be an organic polymeric material characterized by strong absorption bands in the N-H and the C=N or C=O stretching regions of the spectrum. The apparent precursor of this polymer, stable only at low temperatures is characterized by strong absorption bands in a region indicating N=C=N or N=C=O structure.

MATERIALS

Nitric Oxide. Commercial nitric oxide (Matheson) was purified according to the procedure described by E. E. Hughs (Hughs, J. Chem. Phys., 35, 1531 (1961)). The gas was passed through two absorption traps filled with fresh silica gel and cooled to dry ice temperature. The nitric oxide was then condensed at -196°C and fractionally distilled into the gas handling system of a high vacuum line. Spectroscopic examination of the gas by infrared absorption at 720 mm. pressure showed it to be spectroscopically pure.

Diazomethane. A method described by Reimlinger, Berichte, 94, 2547 (1961), was used for the preparation of diazomethane. N,N'-dinitroso-N,N'-dimethyl-oxamid was obtained by nitrosating N,N'-dimethyl-oxamid in carbon tetrachloride with N_2O_4. A solution of 3 grams of the nitroso-oxamid in 20 ml. of anisol was added dropwise to a stirred solution of 5 grams KOH in 5 grams of water and 20 ml. of carbitol heated to 65-75°C. Diazomethane was continuously swept out of the reaction flask by a steady, slow stream of purified nitrogen or helium and carried through traps at 0°C and -20°C. It then passed through an absorption tube packed with solid KOH pellets and was finally liquified in a Dry Ice-acetone cooled isolation trap. Quantities between 0.75 and 1.0 grams were thus prepared.

In some early experiments the diazomethane was dissolved in dry octylether and kept in the isolation trap at -5°C. The compound was thus stored for prolonged periods with very little polymer formation taking place. In later experiments, the liquid diazomethane was expanded into a 200-300 ml. reservoir flask on the high vacuum line. The highly concentrated gas mixture (1:10 to 1:20 of He or N_2 to CH_2N_2) could be kept for several days at 200 to 400 mm. pressure in flasks which were covered with aluminum foil to exclude light. Polymerization to $(CH_2)_x$ and N_2 occurred in some flasks, but after scrupulous cleaning and final coating of the inside with a film of Apiezon M grease, no difficulties were encountered.

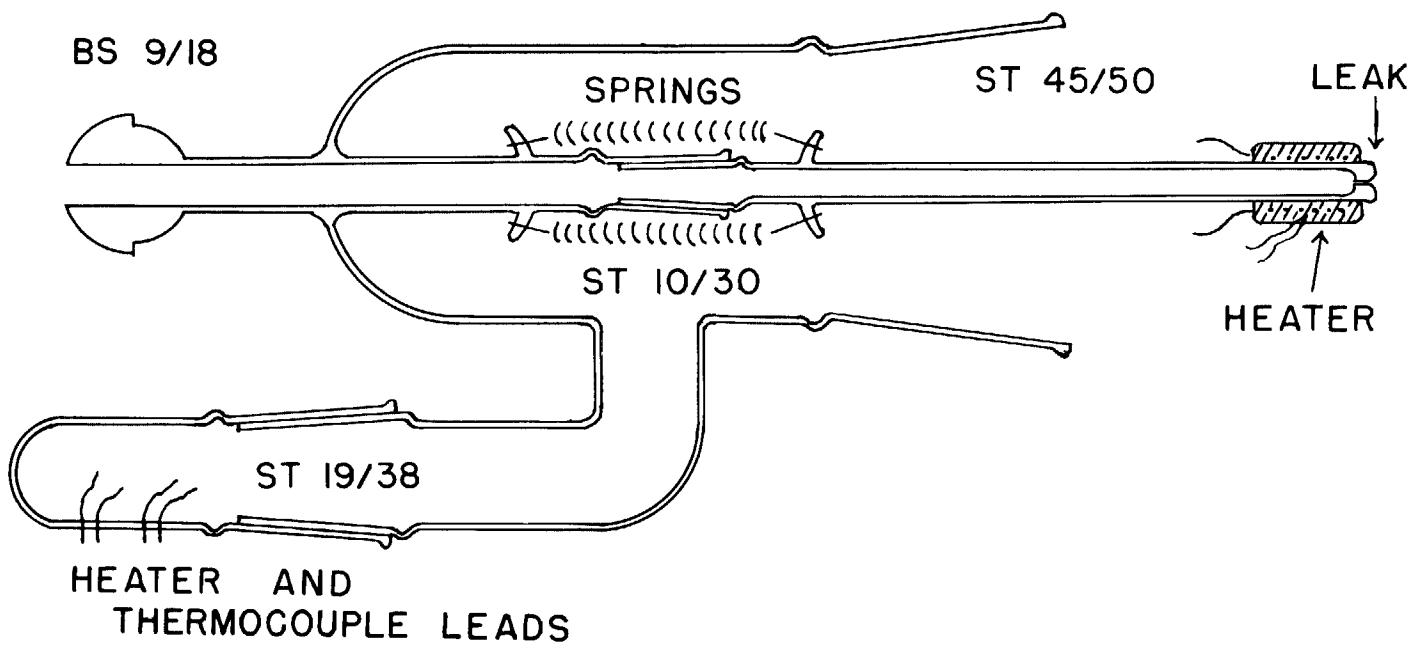
Liquid Helium. Liquid helium used to produce the cryogenic temperatures required was obtained from Gardner Cryogenics Corp. and transported in 25 liter, liquid nitrogen cooled dewars.

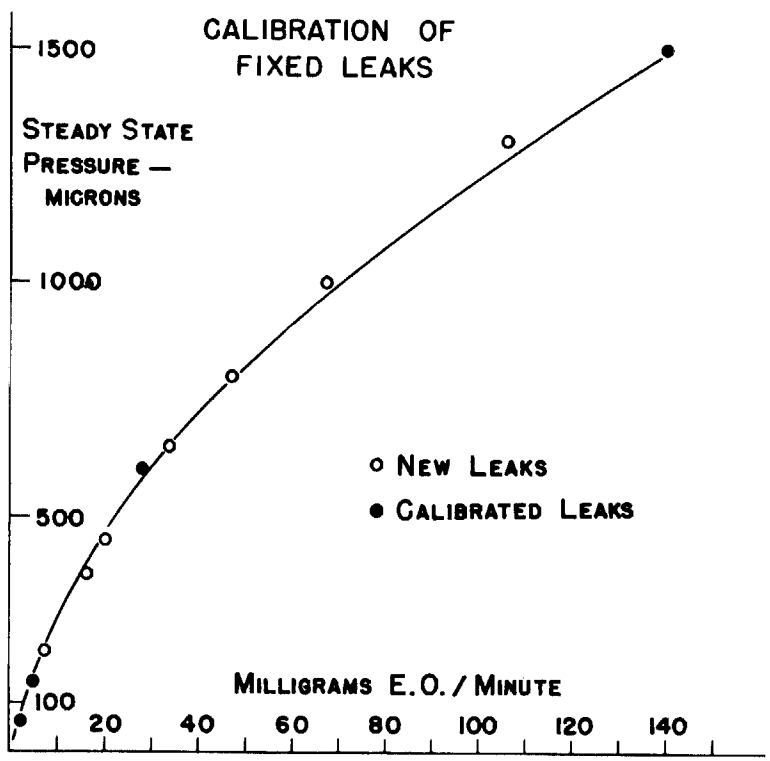
APPARATUS AND PROCEDURES

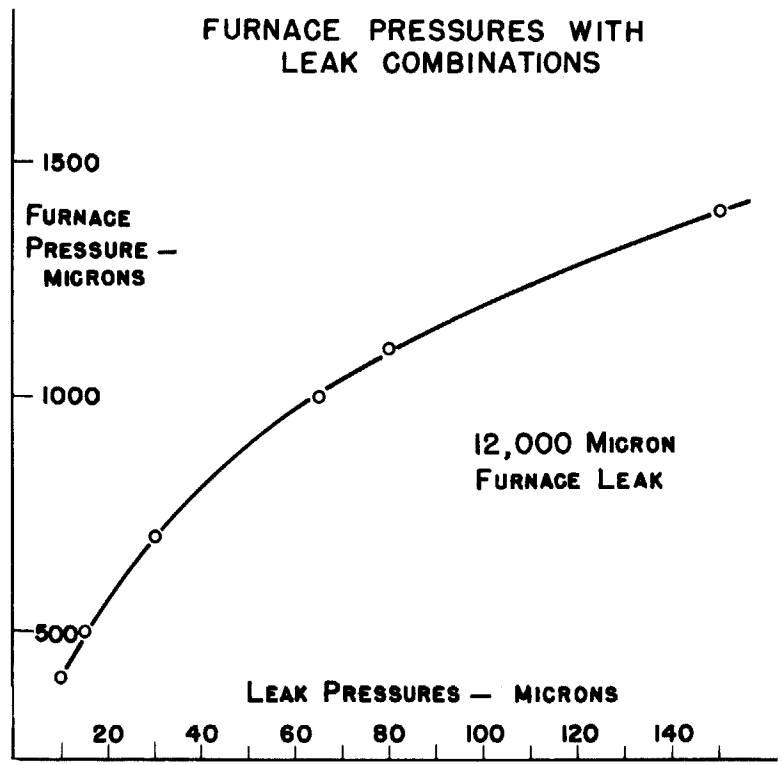
Apparatus used in this work is a modified form of the Dewar-furnace described by Schoen, Kuentzel and Broida, Review of Scientific Instruments, 29, 636 (1958). Complete details, drawing and illustrations were included in the Final Summary Report for the first year of the work under contract NASr-24 (March 1962). Basically, the apparatus consists of a vertical tube or liquid helium "finger" with a disc of cesium iodide affixed to the bottom and the whole enclosed in a Dewar system providing liquid nitrogen cooled shielding. The base of the Dewar has ports for inserting small furnaces close to the cesium iodide disc and rocksalt windows for transmitting an infrared beam through the cesium iodide disc. The liquid helium "finger" may be rotated on its vertical axis so as to position the disc first at right angles to the furnace port and then center it in the path of the infrared beam for absorption analysis of deposits on it. Furnaces consist of tubes with Nichrome wire heaters that can be positioned within a few millimeters of the cold cesium iodide disc. The latter is protected from radiant furnace heat by a system of liquid nitrogen cooled shields and shutters. Properly placed thermocouples provide furnace and disc temperatures and suitable pressure gauges supply pressure information. External liquid helium cooled traps permit trapping of gases that sublime from the cold surface during slow warm-up. It is thus possible to observe, record and correlate temperature, pressure and infrared absorption variations and to trap for independent analysis, subliming fractions of the experimental deposit during controlled warm-up. The closeness of the furnace to the disc, together with the low pressures, favors the translation of thermal reaction products to the cold surface for stabilization in microseconds of time. Experimental gases are fed through the furnaces via calibrated fixed leaks and quantities are controlled by timing the gas flow. Quantities of material suitable for infrared absorption analysis are in the neighborhood of 10 milligrams and require 8 to 15 minutes deposition time.

During later phases of the work, it became desirable to control the pressure of the experimental gas within the furnace without exposing the cold surface to excessive gas pressures. Normally, the furnace gas pressure is fixed by the size of the leak employed since the liquid helium cooled surface acts as a strong pump and there is no constriction in the exit end of the furnace. With a leak delivering some 3 milligrams per minute the steady state pressure in the furnace is of the order of 5 to 10 microns. In order to increase pressure in the furnace yet maintain the low pressure in the Dewar, the tip of the furnace was constricted to form a second, but larger, leak in the system. Two series of fixed leaks were made, one for insertion between the storage reservoir and the furnace and the other series for use as furnace tubes with an interchangeable heater. See drawing of combination furnace and leak. All leaks were compared for size by observing the steady state pressure obtained by a pumping system with each leak in turn introduced into the system. Leaks previously calibrated in an absolute manner to measure milligrams of ethylene oxide delivered per minute were also included and this information provided an approximate value in terms of milligrams per minute delivery of the other leaks when materials approximating the molecular weight of ethylene oxide were being leaked. See accompanying graphs. By a proper choice of leaks for the upstream leak and the furnace leak it was possible to obtain a steady state pressure between the leaks and in the furnace of about 1 millimeter pressure while maintaining a pressure of about 5 microns in the Dewar. This was the desired objective in an experiment described later.

COMBINATION FURNACE AND LEAK




CALIBRATION OF
FIXED LEAKS
STEADY STATE
PRESSURE —
MICRONS
1500
1000
500
100
20
40
60
80
100
120
140
MILLIGRAMS E.O. / MINUTE
NEW LEAKS
CALIBRATED LEAKS


FURNACE PRESSURES WITH
LEAK COMBINATIONS
FURNACE
PRESSURE —
MICRONS
1500
1000
500
12,000 MICRON
FURNACE LEAK
LEAK PRESSURES — MICRONS
20
40
60
80
100
120
140

A Model KV 104 Raytheon microwave power generator has been added to the accessory equipment available for experimentation. A special antenna and gas inlet system permits exposure of experimental gases to the field of the antenna within a few centimeters of the cold cesium iodide disc. Provision is made for either passing mixtures of gases through the discharge or passing one gas through the discharge and combining the effluent gas with other gases prior to stabilizing at 4°K. Pressures in the discharge are controlled by the double-leak system described above. Objectives are to decompose compounds in the discharge and immediately stabilize the products at cryogenic temperatures or to produce activated atoms and radicals in the discharge for reaction with other species just prior to stabilization.

EXPERIMENTATION AND RESULTS

During this second year of work an additional 50 low-temperature experiments involving the use of liquid helium were carried out. Much of this work was centered around a study of the thermal decomposition of diazomethane and included the development of skills and techniques for handling and storing this hazardous material as well as achieving maximum decomposition of a type useful for our investigations. Diazomethane either quietly polymerizes to polyethylene and nitrogen or explodes with very high brisance. Polymerization was minimized by storing the gas in scrupulously cleaned flasks coated with a thin film of Apiezon M grease and protecting the gas from exposure to light. Explosions appeared to be associated with solid diazomethane and were avoided, for the most part, by preventing the formation of solid during preparation, purifying or storing. Solutions of diazomethane in octyl ether proved a convenient method of storing and handling but the rate at which the diazomethane could be pumped from the solution at 0°C for experimental purposes was somewhat less than desirable. Infrared absorption spectra of the solid diazomethane at 4°K were obtained (see spectrum) and they exhibited no absorptions in the 10 to 12 micron region as had been expected from an examination of the spectrum of the gas.

The first experiment concerned with the thermal decomposition of diazomethane was carried out in the same equipment and with similar techniques as was used with experiments involving ketene and described in the March 1962 report. The furnace was an open end ceramic tube with about 15 mm. of heater and a loose plug of quartz wool in the heated zone. The diazomethane was pumped from an octyl ether solution through a fixed leak delivering about 3 milligrams per minute and passed through the furnace at about 325°C. Reaction products froze on the cold cesium iodide disc at 4°K and about 5 millimeters from the furnace. The infrared spectrum of these products is shown as the solid line in spectrum labeled "Run No. 49." The relatively weak band at 4.85 microns is the only evidence of a small amount of undecomposed diazomethane -- all other bands indicate reaction products. At about 31°K the spectrum of the deposit was again recorded during a slow warm-up. This spectrum is indicated as the dashed line on the same chart. It is observed that the strong band at 6.25 microns has disappeared and the new bands have formed at 2.8, 2.87, 2.95, 3.1 and 3.75 microns. The latter band is unusually strong and in what is normally considered a triple bond region of the spectrum. On recording the spectrum a third time and at about 65°K only two relatively weak bands remained. See dotted line on Run No. 49 chart. This is probably a small amount of ice that accumulated from a slow leak during the extended time the experiment was under way.

The interesting aspect of this experiment was the extensive chemical reaction at very low temperatures as indicated by spectrum changes. Of peculiar interest was the formation of such a strong band at 3.75 microns at so low a temperature. Unfortunately, the experiment was designed to be exploratory and no provision has been made for external trapping of subliming reaction products during the warm-up. At this point the entire apparatus set-up and accessories were dismantled, moved to another building and reassembled.

After checking out the apparatus in the new location, attempts were made to repeat the interesting result of the previously described Run No. 49. Results were very disappointing as very little of the diazomethane decomposed and,

while new bands appeared in the spectrum of the frozen products, they did not exhibit the reactivity at low temperatures. Considerable experimentation went into determining optimum conditions of temperature for decomposing the diazomethane into infrared absorbing fragments. It developed that most of the diazomethane had been decomposing to give nitrogen, hydrogen and carbon -- all infrared transparent and thus not detected. Nitrogen and hydrogen were confirmed by external trapping and mass spectroscopy. Carbon deposits were discovered upon dismantling the furnace. The use of a loose plug of copper sponge in the furnace in place of the quartz wool helped produce a decomposition of the type desired. Infrared spectra from Run No. 54 illustrate typical results. Again, a residue at 56°K appeared to be ice. There was little evidence of the formation of ethylene in these reactions so it was felt that the decomposition mechanism was not producing methylene radicals.

In a recent paper (Frey and Stevens, J. Chem. Soc., Oct. 1962, p. 3865-3867) it was pointed out that the rate of thermal decomposition of dimethyldiazirine falls off markedly below 100 mm. pressure in the reaction chamber. This is characteristic of unimolecular reactions when the rate of transformation of energized molecules approaches the rate of collisional activation. The thermal decomposition of diazomethane is believed to be such a reaction. Pressures in our furnace are of the order of a few microns. It was decided to modify the gas delivery equipment to permit the build-up of pressures in the furnace to the order of millimeters of mercury in an effort to increase the rate of thermal decomposition of diazomethane. This was achieved by a combination of two fixed leaks as described earlier in this report.

An experiment was carried out with diazomethane. The furnace temperature was about 410°C and the pressure in the furnace was about one millimeter. The reaction products were frozen at 4°K on a cold surface 5 millimeters from the furnace. An infrared absorption spectrogram of these reaction products at 4°K is labeled "Run No. 84." In this spectrogram there is ample evidence of ethylene (compare spectrogram of frozen ethylene) although the doublet at 10.5 microns was not resolved. Having established suitable conditions for the formation of carbene radicals from the thermal decomposition of diazomethane as indicated by the presence of ethylene in the reaction products, the program of experimentation called for introducing nitric oxide into the system in an effort to form reaction products and stabilize them at low temperatures.

Attempts to make mixtures of nitric oxide and diazomethane gases at pressures above 200 mm. produced violent explosions. The two gases were then admitted to the furnace via separate fixed leaks to mix at pressures of about one millimeter. Under these conditions they were not explosive and a blank run with the furnace off showed no evidence of reaction as determined by infrared analysis of the frozen gas mixture. The infrared spectrogram of Run No. 96 is typical of the results obtained by passing this gaseous mixture through the furnace at about 420°C and immediately freezing the reaction products. There is evidence of ethylene, diazomethane and nitric oxide in the frozen film. The set of four bands between four and five microns were most interesting. The band at 4.85 microns was produced only in part by diazomethane since there was no evidence of a band at 7.1 microns. These bands were scanned repeatedly during a slow warm-up and there was no change in relative or

absolute intensities until the temperature approached 70°K when the diazomethane sublimed and the band at 4.85 microns decreased in intensity somewhat. However, the band at 4.6 microns then increased in intensity to become the stronger of the set. The bands persisted in this manner until a temperature of about 135°K was reached where they slowly decreased in intensity. By room temperature they had disappeared. During this warm-up, external liquid helium traps were used to obtain fractions of the subliming gases for independent analysis by mass spectroscopy. Low-temperature fractions were hydrogen and nitrogen. Diazomethane, nitric oxide and ethylene were also trapped at appropriate temperatures. However, at temperatures when the bands between 4 and 5 microns were disappearing, nothing could be trapped. This indicates that the reaction product did not sublime or vaporize. At room temperature a film was observed on the cesium iodide disc. It was amber in color and somewhat brittle, having buckled and cracked away from the disc in places. It did not exhibit a melting point but turned dark and appeared to char at somewhat above 150°C. An infrared spectrum of the material dispersed in a KBr pellet is shown on the Run No. 96 spectrogram as a dashed curve. It exhibits the characteristics of a polymeric material with strong absorptions in the N-H (and possibly bonded O-H) and the C=N and C=O regions of the spectrum. The region of 4 to 5 microns where the apparent precursor of the polymer absorbed is characteristic of multiple bond structures such as C≡C, C≡N and N=C=N or N=C=O. It was further observed that when the original diazomethane was made by using helium gas as carrier so that there was a small amount of helium in the final material, there was a tendency for a large number of different thermal decomposition and reaction products such as illustrated by Run No. 96. However, when nitrogen was used as the carrier gas in the preparation of the diazomethane so that there was some nitrogen in the final diazomethane sample, none of these materials, including ethylene, formed in amounts sufficient to be detected by infrared. See Run No. 99. It would thus appear that the presence of a little nitrogen in the diazomethane-nitric oxide gas mixture tends to suppress reactions that form other materials than those characterized by the strong bands in the 4 to 5 micron region of the spectrum.

The objective of this series of experiments was the preparation of dinitrosomethane, $CH_2(NO)_2$. In runs using diazomethane with some nitrogen present, the only absorption bands in the spectrum of the frozen deposit of reaction products, other than relatively weak bands attributable to some undecomposed nitric oxide and diazomethane, are the four strong bands between 4 and 5 microns and a broad band around 3.2 microns (Run No. 99). These bands are not present in the spectrum of deposits obtained from the thermal decomposition of diazomethane alone. A reaction is thus indicated and it is suggested that the dinitrosomethane rearranges to form a carbo diimide, HO-N=C=N-OH. Such a structure is quite compatible with the absorption spectrum observed. On warming to room temperature the carbo diimide polymerizes. Additional properties of the polymer must await the preparation and examination of larger quantities.

Use has been made of a microwave power generator for the production of activated atoms and radicals for experimental purposes. Preliminary experiments indicate that the 2450 megacycle generator operating at about 85 watts completely decomposes diazomethane to carbon, nitrogen and hydrogen as extensive deposits of frozen discharge products are infrared transparent. Appreciable

quantities of ozone are detected by infrared absorption in the frozen deposits of oxygen exposed to the discharge. Although helium gas glows brightly in the discharge, there has been no evidence that a reaction product of any kind has been stabilized by the near-by 4°K cold surface. As a corollary to efforts to make carbene radicals by the thermal decomposition of diazomethane, an attempt was made to produce difluorocarbene radicals by passing perfluorocyclobutane through the discharge as described by Bass and Mann, J. Chem. Phys., 36, 3501 (1962). The frozen deposit exhibited but two absorption bands in the infrared at 10.05 and 7.45 microns with no evidence that any of the perfluorocyclobutane survived the action of discharge. Further studies in this area are in progress. It is anticipated that attempts to react the difluorocarbene with nitric oxide will be made with the objective of preparing $CF_2(NO)_2$.

SUMMARY AND FUTURE WORK

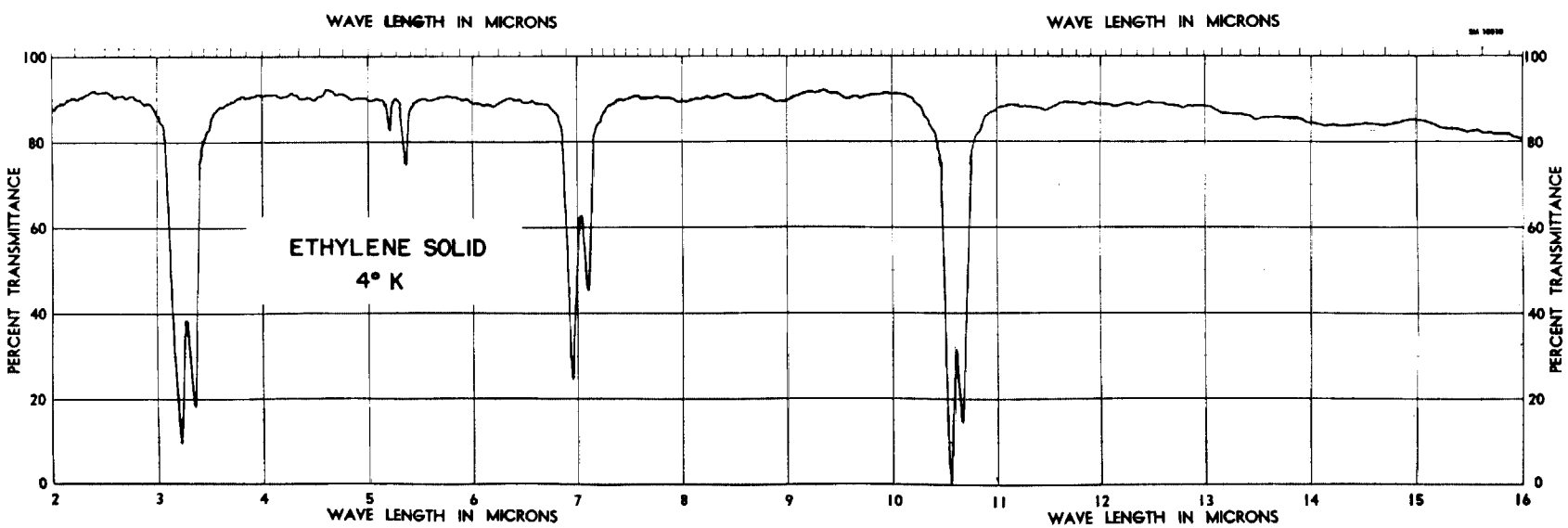
Much of the effort covered by this report was directed toward the controlled thermal decomposition of diazomethane for the production of carbene radicals as evidenced by the presence of ethylene in the frozen deposit of reaction products. This was accomplished best when the pressure in the furnace was raised to about one millimeter. Attempts were then made to introduce mixtures of diazomethane and nitric oxide into the furnace for the purpose of bringing about a reaction between the carbene radicals and the oxide to form dinitrosomethane. Mixtures of diazomethane and nitric oxide at appreciable pressures (above 200 mm.) proved highly explosive. Mixtures at one millimeter total pressure were not explosive and such were introduced into the furnace at about 420°C. Infrared spectra of the frozen deposits of the resulting products indicated the presence of a substance containing a multiple double bond structure and N-H or bonded-OH groups. It was suggested that the expected $CH_2(NO)_2$ rearranged under the experimental conditions to a form such as HO-N=C=N-OH at 4°K which polymerized at about 135°K during warm-up. Further characterization of the polymer is under way.

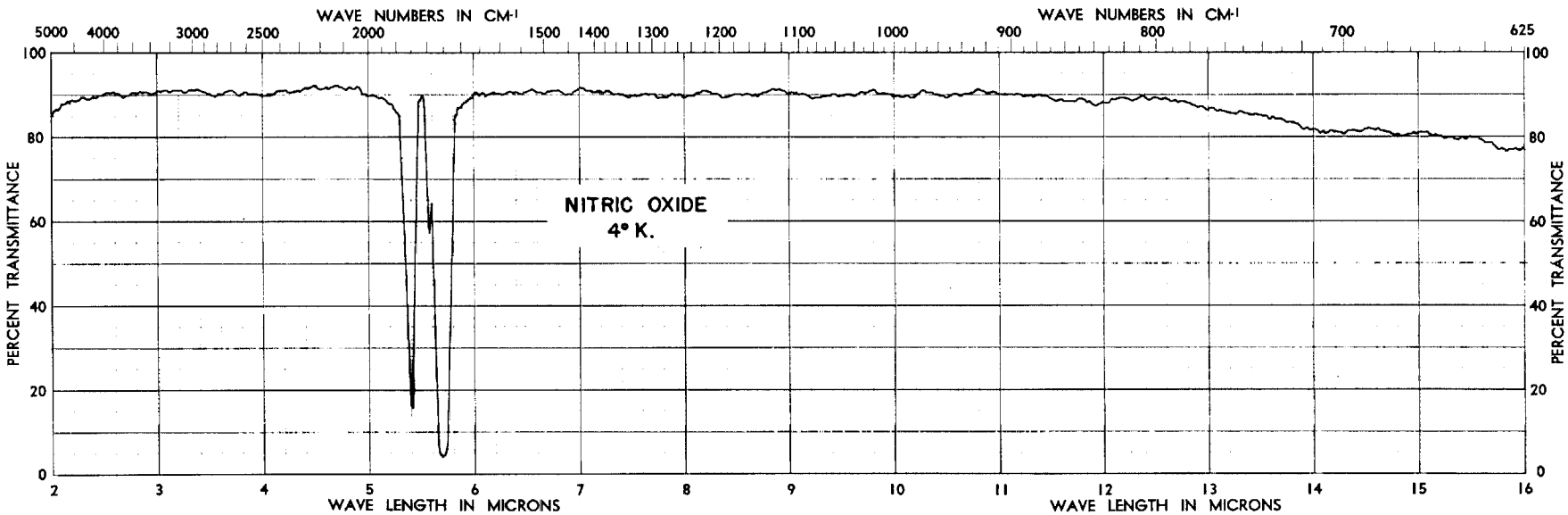
It is proposed to repeat these experiments using ketene instead of diazomethane to see if the same carbodiimide results from the reaction of nitric oxide and carbene radicals from the ketene. There is this difference between the two experiments: Pearson, Purcell and Saigh (J. Chem. Soc., 1938, 409) have shown that the lifetime of the carbene radical is much longer in the presence of ketene than in the presence of diazomethane.

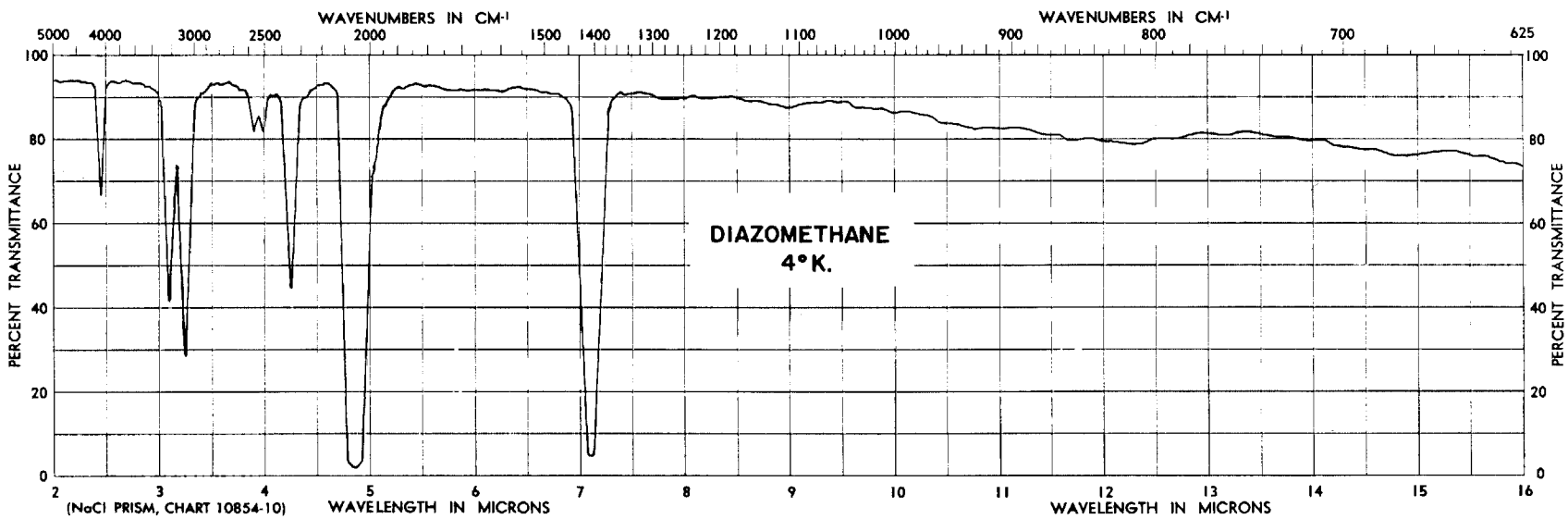
As suggested in the original technical proposal dated 21 October 1960, reactions between the carbene radical and oxygen or ammonia should produce interesting materials stabilized at low temperatures. Also reactions between the imino radical produced from ammonia in the electric discharge and oxygen or oxygen atoms might lead to energy rich materials thay could be stabilized at low temperatures for study. The mechanics for carrying out a number of these investigations in a minimum of time have now been worked out and some effort should be spent in this direction.

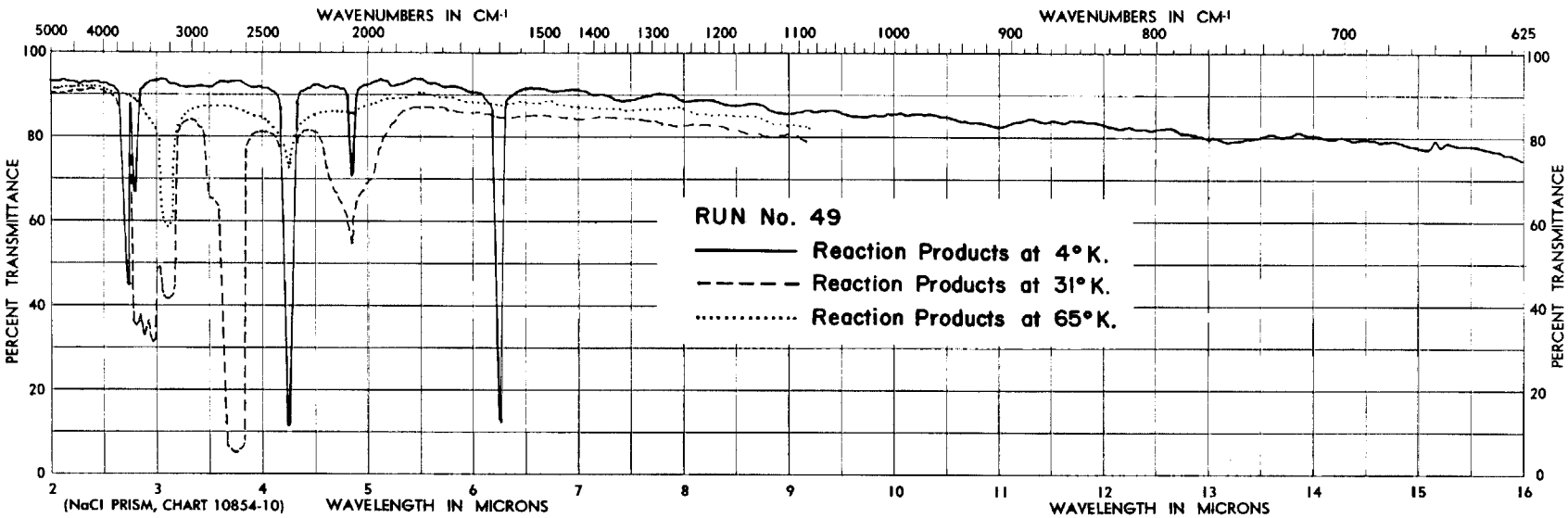
Finally, because of the tremendous gains that success in this area would provide, it is proposed to pursue investigations directed toward reacting activated helium with energetic species and immediately stabilize any products at liquid helium temperatures. Included in such experiments would be attempts to form NO-He*, CH_2-He*, H-He* and F-He*. Use of the electric discharge with its proximity to a liquid helium cooled surface for stabilizing reaction products will form the general approach. As occasion requires, mixtures of gases can be directed through the discharge or just the helium passed through the discharge. Such conditions offer a maximum probability of generating activated atoms, bringing them into contact with other activated atoms or active groups and stabilizing any resulting reaction products at low temperatures where they may be examined by infrared absorption spectroscopy. Further characterization of such products can then result from observing changes in the infrared spectrum of the deposit as it warms up, observing exothermic or endothermic reactions by abnormal temperature changes of the cesium iodide disc and trapping subliming gases for additional analysis.

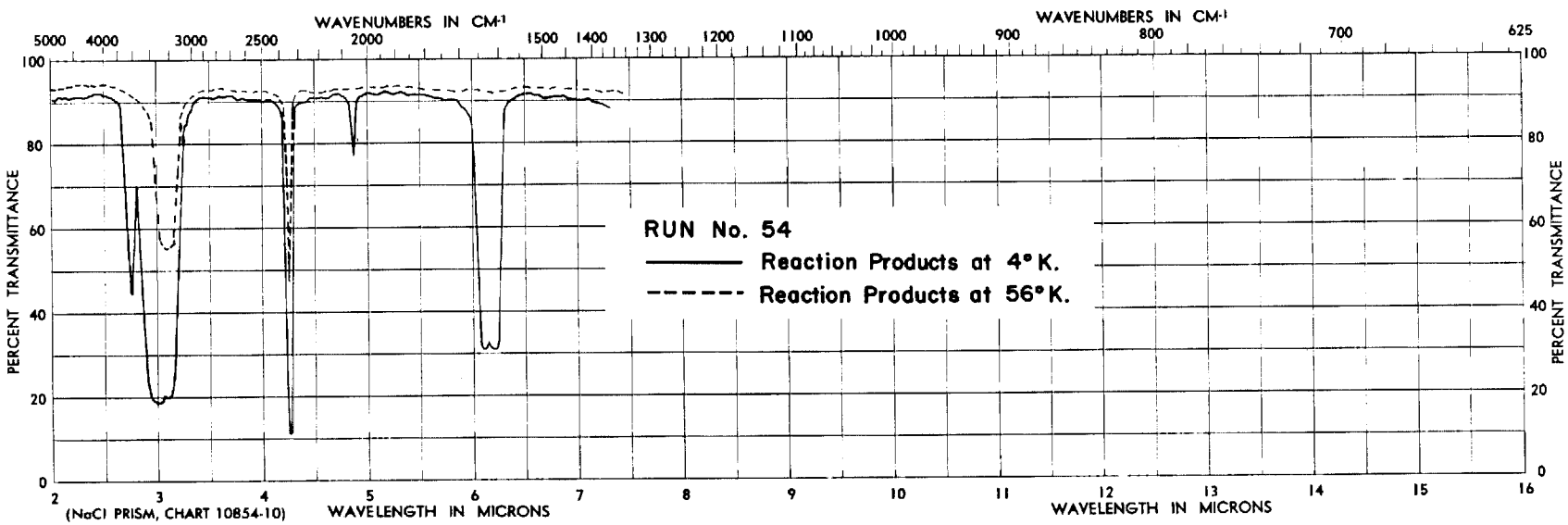
mh

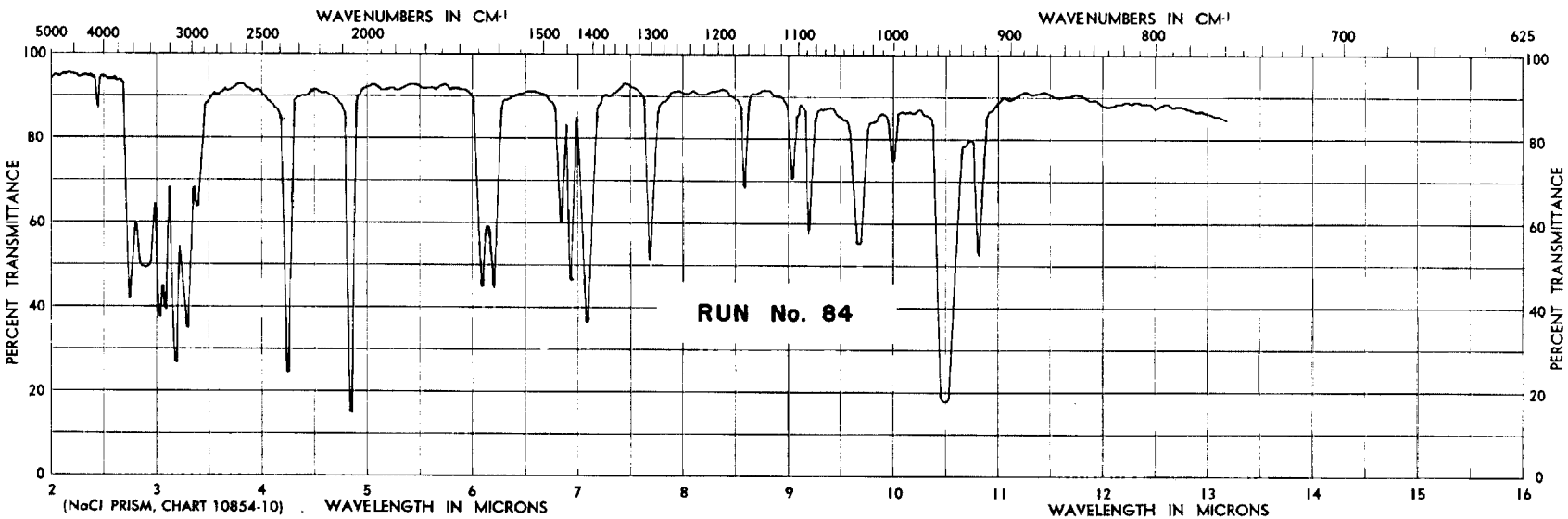

WAVE LENGTH IN MICRONS
WAVE LENGTH IN MICRONS
ETHYLENE SOLID
4° K
PERCENT TRANSMITTANCE
PERCENT TRANSMITTANCE
100
80
60
40
20
0
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
WAVE LENGTH IN MICRONS
WAVE LENGTH IN MICRONS

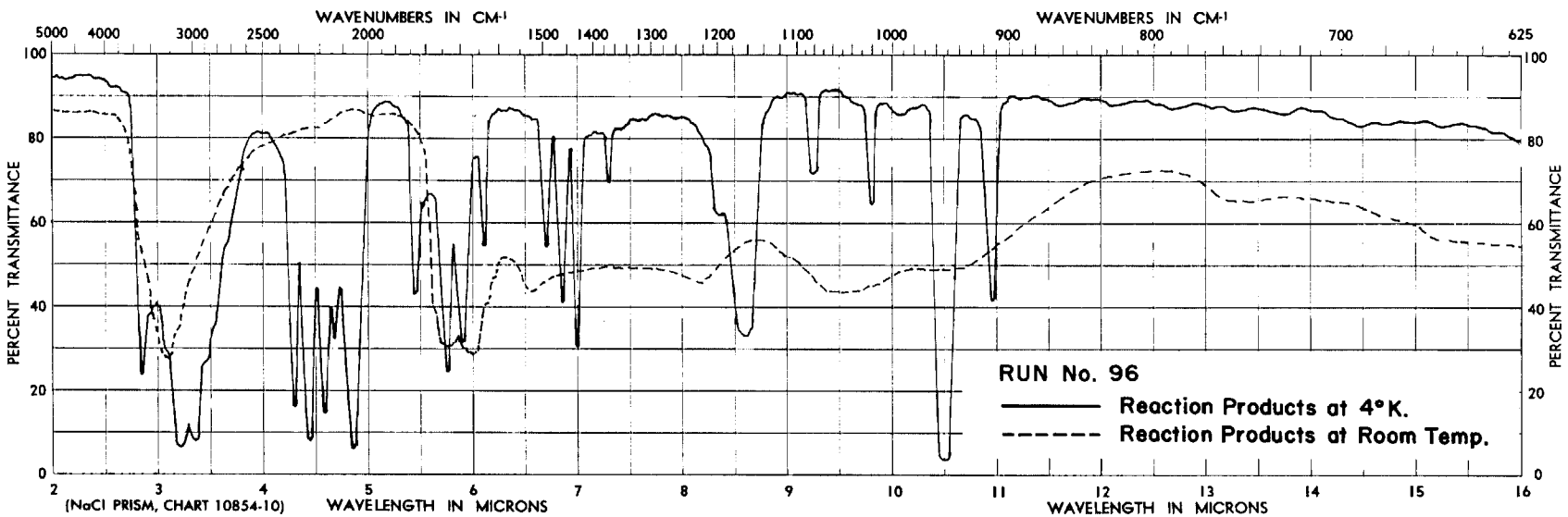

WAVE NUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVE NUMBERS IN CM-1
PERCENT TRANSMITTANCE
100 80 60 40 20 0
NITRIC OXIDE
4° K.
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
WAVE LENGTH IN MICRONS
WAVE LENGTH IN MICRONS
PERCENT TRANSMITTANCE

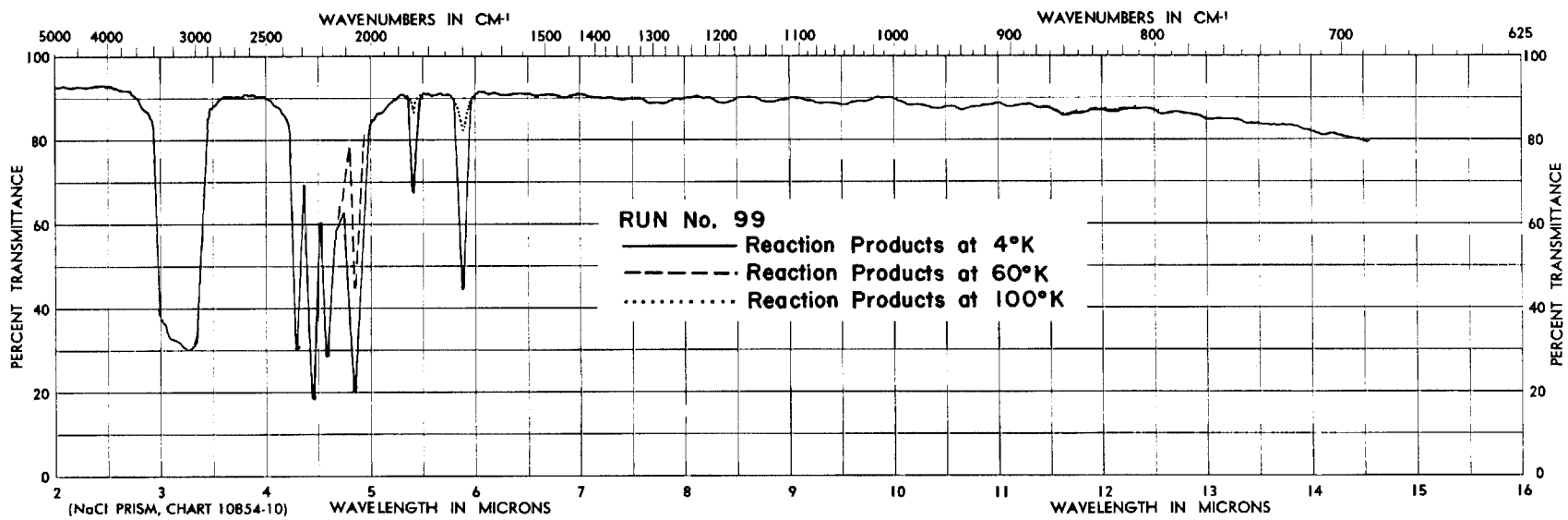

WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVENUMBERS IN CM-1
PERCENT TRANSMITTANCE
100 80 60 40 20 0
DIAZOMETHANE
4°K.
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS
WAVELENGTH IN MICRONS


WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVENUMBERS IN CM-1
PERCENT TRANSMITTANCE
100 80 60 40 20 0
RUN No. 49
Reaction Products at 4° K.
Reaction Products at 31° K.
Reaction Products at 65° K.
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS
WAVELENGTH IN MICRONS


WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
PERCENT TRANSMITTANCE
100 80 60 40 20 0
RUN No. 54
Reaction Products at 4° K.
Reaction Products at 56° K.
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS


WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVENUMBERS IN CM-1
PERCENT TRANSMITTANCE
100 80 60 40 20 0
RUN No. 84
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS
WAVELENGTH IN MICRONS


WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
PERCENT TRANSMITTANCE
100 80 60 40 20 0
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS
RUN No. 96
Reaction Products at 4°K.
Reaction Products at Room Temp.


WAVENUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
WAVENUMBERS IN CM-1
PERCENT TRANSMITTANCE
100 80 60 40 20 0
RUN No. 99
Reaction Products at 4°K
Reaction Products at 60°K
Reaction Products at 100°K
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
(NaCl PRISM, CHART 10854-10)
WAVELENGTH IN MICRONS
WAVELENGTH IN MICRONS