

EFFLUENT ANALYSIS OF MODEL PYRRONE COMPOUNDS

BY GAS CHROMATOGRAPHY

By

Philip Ross Young

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute and State University
in candidacy for the degree of

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INTRODUCTION

Certain types of aromatic-heterocyclic polymers are receiving attention as possible solutions to the increasing need for thermally stable materials.⁽¹⁻⁵⁾ The unusual thermal properties of these step-ladder and ladder polymers have been attributed in part to their aromatic structure and redundancy in chemical bonds.⁽⁶⁻⁸⁾

Considerable effort has been spent in this laboratory and elsewhere on the polyimidazopyrrolones or pyrrones. These polymers retain many of their useful properties for extended periods above 300° C.⁽⁹⁾ The chemistry of this class of thermally stable polymers has been previously described.⁽¹⁰⁻¹²⁾ These polymers are prepared by the reaction of an aromatic dianhydride with an aromatic tetraamine to yield a linear precursor polymer (equation (1) on page 37) which is then thermally cyclized, or cured, to the final double-stranded structure (equation (2) on page 37). This cyclization reaction proceeds with the elimination of volatiles. Several intermediates are possible for this process.

Although the pyrrene structure may be desirable from a materials point of view, the double-stranded chains are a disadvantage in conducting much of the basic research required of a new polymer system. Extreme intractability in the solid state and insolubility in common organic solvents⁽¹³⁻¹⁴⁾ limits their study by more common methods of analysis. In addition, several isomeric species are thought to exist at various stages of cyclization.⁽¹⁵⁾ Since, to date, these

have been impossible to fractionate or separate, the contribution of these polymeric intermediates to the total chemistry of the pyrrones can not be fully appreciated and many basic questions remain unanswered. Therefore, the decision was made to study model compounds in an effort to provide information on the analogous polymer system.

An earlier model compound study made at the National Aeronautics and Space Administration, Langley Research Center was limited since it was concerned only with half of the polymer repeat unit (equation (3) on page 37) and did not provide quantitative information on cyclization processes.⁽¹⁶⁾ However, this study established that the route to the fully cyclized pyrrone structure is highly competitive between imide and benzimidazole intermediates. It also indicated that cross-link reactions can occur. The information obtained from this study provided the background for a closer look at how pyrrones are formed. The present study is concerned with the complete polymer repeat unit. A gas chromatographic technique was developed to study these models and allows a quantitative understanding of their thermal cyclization. By correlating the structure of the model compound with the temperature at which a reaction occurs and with the nature and quantity of effluent, information has been obtained which provides a new insight into the chemistry of the pyrrones.

Description of Model Compounds

The model compounds investigated in this study are listed in table I. They represent the complete polymer repeat unit at various

reaction stages.

Compounds (I) through (V) belong to the reaction scheme outlined in figure 1. This scheme parallels that anticipated for the most common polymer and shows the isomeric arrangements which can prevail in the polymer. A tetraamine instead of a diamine is reacted with a dianhydride in preparing the polymer.

As shown in figure 1, two moles of o-phenylenediamine (OPD) are reacted with one mole of pyromellitic dianhydride (PMDA) yielding the amide-acid-amine (I). This compound can exist as meta and para isomers, depending on how the two anhydride rings open. The elimination of two moles of water by (I) can yield either isomeric meta and para benzimidazole-acids (III) or imide-amine (II) for which there are no isomers. The isomerism of the benzimidazole-acid (III) is dictated by that of the respective amide-acid-amine isomer. Loss of two moles of water by either (II) or (III) yields the cis and trans pyrrone isomers (IV) and (V). Either isomer can be formed from the imide-amine (II) but isomerism again dictates which pyrrone will be formed from the benzimidazole precursor.

Salt-like polymers, for which (VIa) and (VIb) in table I are models, have been reported.⁽¹⁷⁾ Again, numerous isomeric intermediates and products are possible during cyclization. Finally, compounds (VIIa) and (VIIb) were included to give an appreciation for isomer effects and because they were readily available as derivatives of (IV) and (V), respectively. No polymers based on these two models have been reported.

Also shown in table I are the volatiles which would be eliminated by a compound in converting to the fully cyclized pyrrone model. Thus, the completeness of a reaction should easily be determined by measuring the quantity of the effluent released during cyclization. Supposedly, these models will undergo the same reactions as the polymer. A quantitative study of the model reactive processes should therefore increase the knowledge of similar processes occurring in the polymer.

Review of GC-Thermal Methods of Analysis

One of the limitations of gas chromatography is the inability to perform separations on nonvolatile samples. Compounds must show an appreciable vapor pressure by 350° C in order to elute from gas chromatographic columns. Pyrolytic techniques have therefore been employed to extend the range of gas chromatography to these materials. Pyrolysis may be defined as the thermal fragmentation of nonvolatile materials to yield smaller molecules having greater volatility than the original material. The chromatographic analysis of these volatile molecules then yields a fingerprint of the material pyrolyzed and information on its thermal decomposition.

The research in pyrolysis-gas chromatography has been reviewed. (18, 19) Ideal conditions for successful pyrolysis-GC has also been described. (20) These conditions require the pyrolysis to be conducted at high dilution so that undesirable recombination reactions can not occur. Too high a sample temperature may produce uncharacteristic

fragments such as methane, carbon, and hydrogen. Also, it is desirable to heat the sample to the pyrolysis temperature rapidly and reproducibly to insure that the products will be characteristic of the original material. Numerous techniques have been employed in an effort to achieve these conditions.

Resistance filaments and preheated furnaces are the most commonly used methods for heating the sample. The resistance heater may either be coated or placed in direct contact with the sample. Current is then passed through the filament to achieve pyrolysis. Since the resistance of the filament will change with use, it is difficult to obtain reproducible temperatures with this technique. This deficiency can be largely overcome by thrusting the sample into a preheated furnace by placing it on a wire or in a magnetically controlled boat.⁽²¹⁾ However, it is often difficult to achieve thermal equilibrium quickly because the boat also must be heated to the pyrolysis temperature. More recently, pyrolysis based on the Curie point principle has been described.⁽²²⁾ This technique takes advantage of the ferromagnetic properties of selected alloys to achieve rapid temperature stabilization. Pyrolysis based on this principle offers possibly the most stable and reproducible sample temperatures. Numerous other methods ranging from laser pyrolysis⁽²³⁾ to heating the sample in the injection port⁽²⁴⁾ have been used to achieve sample pyrolysis.

Since complete fragmentation of the material under question is normal in pyrolysis-gas chromatography, sample temperatures between 500° C and 1,000° C are commonplace.⁽²⁵⁻²⁷⁾ Other model compound studies have been based on this principle.⁽²⁸⁻²⁹⁾ However, for this study it was felt that more information could be obtained by using gas chromatography to study model relations at temperatures which were too low to break carbon to carbon bonds. The techniques which provide complete sample pyrolysis were not applicable to the study of the cyclization reactions which generally occurred below 300° C. It was also desirable in the present study to have accurate, reproducible, and programmable sample temperatures so that meaningful correlation between the model compounds and the analogous polymer would be possible. Therefore it was necessary to construct the apparatus used in this study.

Description of Chromatographic Analysis

The use of gas chromatography as a separative tool needs no discussion. It is generally accepted that GC is accurate to 3-5 percent when applied to quantitative analysis. The use of gas chromatography is therefore a direct approach to the analysis of the effluents of the compounds given in table I. It can separate the compounds evolved and provide a quantitative measure of their concentration. However, chromatographic conditions and a method for heating the model compounds and sampling their effluents had to be developed.

As shown in table I, water, methanol, and 2-propanol were the anticipated products to be analyzed. The analysis of alcohols by gas chromatography presented no problem. However, the analysis of water can be complicated by the lack of detector response and by excessive tailing of the water peak due to adsorption. The thermal conductivity detector was used in this research because it is sensitive to water, whereas the other available detector, flame ionization, was not.⁽³⁰⁾ The column was patterned after one previously reported to give excellent quantitative data on mixtures of water and alcohol.⁽³¹⁾ It consisted of a powdered Teflon solid support coated with a 6 percent Carbowax 20M liquid phase. Carbowax 20M is the union Carbide trade name for a polyethylene glycol having an average molecular weight of 20,000. Dual 9-foot by 1/4-inch copper columns packed with this material yielded symmetrical peaks suitable for quantitative treatment.

The equipment used in this study is shown in figure 2. It consisted of a small furnace with the appropriate plumbing, a temperature programmer, heaters, and various temperature and voltage readouts. Figure 3 shows a close-up of the furnace assembly. The device was mounted in the GC carrier gas flow system between the flow meter and the injection port. Figure 4 shows the furnace and disassembled plumbing. The model compound to be analyzed was placed in a sample tube as described later. The tube was inserted in the furnace, and connected between two three-way ball valves. These manually operated

valves allowed for both isolation and purge of the sample tube. With the tube isolated, carrier gas flowed in the by-pass line around the furnace and into the chromatograph. This was essential to maintain a continuous carrier gas flow through the thermal conductivity detector.

The sample tube was purged when the valves were turned to the sweep position. The carrier gas now carried all volatile products into the chromatographic column. The effluents were thus "injected" into the chromatograph, separated, and a response proportional to the quantity of effluent displayed on a recorder. Calibration of this response then yielded quantitative data. The furnace could be programmed at several rates or run isothermally with periodic purges of the sample tube. After a purge was made, the valves were returned to the by-pass position to isolate the sample for further heating. Correlation of the sample temperature with the quantitative data on the effluents yielded information on the thermal cyclization processes occurring in the model compounds.

EXPERIMENTAL

Gas Chromatography

Apparatus. All work was performed on an F & M Series 810 Research Gas Chromatography equipped with a Honeywell-0.2 to +1.0 mv recorder. The chromatographic conditions for both the calibration and model compound effluent analysis are summarized in table III.

Furnace Assembly. The furnace apparatus shown in figure 2 was constructed at NASA, Langley Research Center. The furnace was made from 8 cm x 3 cm brass rod wrapped with 15 turns of 24 gauge nicrome wire and sprayed with a 2 mm layer of aluminum oxide. The nicrome wire was connected to a terminal mounted on one of two 6.5 x 6.5 x 0.7 cm asbestos end plates. Three 0.7 cm diameter holes were drilled about the center and ran the length of the furnace. These holes allowed for the insertion of the sample tube, the reference thermocouple, and for preheating the carrier gas. The furnace was heated to 400° approximately 50 times with no apparent ill effects.

Two three-way brass ball valves (Whitey Research Tool Co., Cat. No. 43XS4) were connected into the system as shown in figure 4. Depending on the position of these valves, the carrier gas could either pass through the sample tube or be diverted around the furnace in a 0.25 in. o.d. copper by-pass line. It was necessary to heat these valves to 80° with heater tape to prevent condensation of sample effluents. This temperature was monitored by two chromel

alumel thermocouples attached to the valves. Two variacs supplied current to the tapes.

Programmer Assembly. A block diagram of the program circuit is given in figure 5. An F & M Model 240 Power Proportional Temperature Programmer was used to program the furnace. Since this programmer was designed for use with larger furnaces, a step-down transformer was employed to protect the small furnace being used here. A voltmeter across the secondary monitored the voltage being applied to the furnace. Observation of the voltage required in programming from 25° to 400° indicated proper temperature control without large voltage fluctuations.

Two thermocouples were inserted in the furnace block at the sample position. One of these provided the required temperature information for the programmer. A second continuous chromel alumel thermocouple was connected directly to a strip-chart recorder for a permanent record of the furnace temperature. This temperature was constantly compared with the programmer digital temperature readout and any discrepancies greater than $\pm 1^\circ$ were manually corrected by adjusting a potentiometer in the program calibration circuit. Thus the furnace temperature was both automatically and manually controlled.

Model Compound Sampling. Approximately 50 mg of the model compound to be analyzed was weighed to the nearest 0.1 mg on a Mettler Balance and mixed with an equal weight of 60/80 mesh Firebrick (Chromosorb P) on glassine weighing paper. Since some of the model

compounds melted, it was necessary to mix them with Firebrick to prevent the Pyrex sample tube from becoming plugged. The mixture was carefully transferred to the center of the sample tube and sandwiched with Firebrick and glass wool as shown in figure 6.

Silicone rubber O-rings around the tube were used as seals to connect the tube to the valves. The system was checked for leaks at the start and completion of each analytical experiment and was pressure tight to 40 psi at room temperature and also at 400°.

Since it was not known in advance how the model compounds would react, it was necessary to run each sample at least two times. A survey experiment was made to determine the attenuation required to keep a peak on scale at a given temperature. An analytical experiment was then made based on the survey run. It was also decided to run every model compound at the same heating rate and purge conditions regardless of how or when they reacted. A 5° C/min programmed heating rate from 25° to 400° C was employed and purges of 20 second duration were made every 5 minutes. Since the compounds sublimed at slightly over 400°, this temperature was chosen as an upper limit. A portion of a typical chromatograph is given in figure 7.

A reproducibility check was made on the system by running the para-benzimidazole-acid model (IIIb) three times. Two runs were made on 50 mg samples and one run on a 100 mg sample. The percent conversion for these three runs was calculated to be 74.96, 76.65, and 76.42, respectively.

Absolute Calibration. An absolute calibration for water, methanol, and 2-propanol was made using a 5 μ l Hamilton Syringe. Since the delivery of syringes is very precise, but not necessarily accurate, this syringe was gravimetrically calibrated at the 1 μ l and 3 μ l marks. Twenty-five discharges of water were weighed at each mark and it was determined that 0.9 mg and 3.0 mg of water were delivered at these two settings.

Various weight percent solutions of water, methanol, and 2-propanol were prepared by weighing each component to the nearest 0.1 mg. Approximately 3 ml of each standard solution was prepared in a 4 ml bottle fitted with a rubber septum. It was found that evaporation could be minimized by placing this bottle in a larger bottle partially filled with the same concentration of solution.

Five 1 μ l injections of each sample were made and a planimeter was used to determine peak areas. Only planimeter counts agreeing within 3 percent for each sample were used. The weight of each component injected was then calculated based on the volume injected, the density of water, methanol, and 2-propanol, and their respective weight percent in each standard. The calibration curve was obtained by making a log/log plot of mg standard vs. respective planimeter counts.

Initially, 1 μ l injections were made on fourteen standard solutions and the resultant data was used to construct the calibration curve. However, due to the large quantities of effluents released

by the model compounds, it was necessary to extend the calibration curve. Therefore the procedure was repeated with 3 μ l injections of new standard solutions. The weight of effluent released at each temperature by a model compound was then determined from peak area and this calibration curve.

Model Compounds

General. Melting points were determined on the DuPont 900 Differential Thermal Analyzer using a 10° C/min temperature program. Infrared spectra were obtained on potassium bromide pellets and recorded on the Perkin-Elmer Models 137 and 421 Spectrophotometers. Nuclear magnetic resonance spectra were obtained on a Varian A-60A Spectrometer and were run in deuterated dimethyl sulfoxide.

Elemental Analysis. Huffman Laboratories, Inc., Wheatridge, Colorado, performed the elemental analyses. The results are summarized in table IV for each model compound.

Materials. All starting materials were obtained from commercial sources and were recrystallized or sublimed several times before use. Solvents were used as received from the supplier.

Preparation of Model Compounds. N,N'-Bis(o-Aminophenyl)-2,5-Dicarboxyterephthalamide (I).- A solution of 6.54g (0.03 mol.) of pyromellitic dianhydride (PMDA) in 65 ml of dimethylacetamide (DMAC) was added to a stirred solution of 6.48g (0.06 mol.) of o-phenylenediamine (OPD) in 65 ml of DMAC. The solution was stirred for 30 minutes at room temperature and 700 ml of benzene was added. After

24 hours, 4.69g (45 percent) of white crystals were recovered by filtration. The mother liquid was refiltered after 192 hours and 3.80g additional crystalline amide-acid-amine was obtained. No attempt was made to recover further product and efforts to obtain meta and para isomer separation were unsuccessful.

The recovered products were highly complexed with DMAC. Soxhlet extraction on the first crop of crystals for 10 hours with benzene yielded the purified white, crystalline product, which did not melt.

N,N'-Bis(O-Aminophenyl)-Pyromellitimide (II).- Amide-acid-amine (I), 2.0g, was slurried in 50 ml of ethanol and 5 ml of concentrated HCl was added. The resultant red solution was boiled for 1 hour, filtered hot, and a white residue was obtained. The infrared spectrum indicated this to be the imide-amine hydrochloride. This residue, when washed with water, yielded 0.4g (22 percent) of crude imide, which was purified by crystallization from acetone. The red-brown product did not melt.

4,6-Bis(2-Benzimidazolyl)-1,3-Benzenedicarboxylic Acid (IIIa) and 3,6-Bis(2-Benzimidazolyl)-1,4-Benzenedicarboxylic Acid (IIIb).- A solution of 21.8g (0.1 mol.) of PMDA in 220 ml of dimethylformamide (DMF) was added to a solution of 21.6g (0.2 mol.) of OPD in 216 ml of DMF and stirred for 1 hour at room temperature. The resultant amide-acid-amine solution was boiled for 1 hour, during which time the para-benzimidazole-acid (IIIb) precipitated. This product was recovered by filtration from the cooled solution and washed with benzene. A nonmelting yellow powder, 10.85g, was obtained.

The original DMF filtrate was concentrated on a flash evaporator and precipitated into benzene in a Waring Blender. This precipitate was recovered (25.73g), washed with 6.9g of Na_2CO_3 , and filtered. The filtrate was acidified ($\text{pH}\approx 4$) with concentrated HCl and 12.00g of crude meta-benzimidazole-acid was obtained. The fraction remaining insoluble to base was not identified. Pure meta isomer was obtained by recrystallizing two times from pyridine followed by 2 hours at 100° to remove traces of DMF and pyridine. The white, crystalline compound did not melt.

13H,15H-Bis-Benzimidazo[1,2-a:1',2'-a] Benzo[1,2-c:4,5-c']

Dipyrrole-13,15-Dione (VI).- A slurry of 3.00g (0.0075 mol.) of meta-benzimidazole-acid (IIIa) in 30 ml of acetic anhydride was boiled for 2 hours. The mixture was filtered hot and the residue washed with benzene. A golden colored powder, 2.01g (74 percent), was obtained. Vacuum sublimation at 260° yielded the purified isomer, mp. 410° .

7H,15H-Bis-Benzimidazo[1,2-a:1',2'-a] Benzo[1,2-c:4,5-c']

Dipyrrole-7,15-Dione (V).- The acetic anhydride reaction was repeated on 3.00g of para-benzimidazole-acid (IIIb) and 2.50g (92 percent) of orange powder was obtained. Vacuum sublimation at 260° yielded the purified isomer, mp. 440° .

Salt of o-Phenylenediamine and 1,4-Discarboisopropoxy

Terephthalic Acid (VIb).- A solution of 33.83g (0.1 mol) of 1,4-discarboisopropoxy terephthalate⁽¹⁷⁾ in 3.38 ml of DMAC was added to a stirred solution of 21.6g (0.2 mol) of o-phenylenediamine in 220 ml

of DMAC. The solution was stirred for 1 hour at room temperature and the solvent removed on a flash evaporator. The resultant residue was crystallized from water with charcoal. Tan needle-like crystals, 46g (78 percent), were recovered as the dihydrate. Water of crystallization was removed by recrystallizing from tetrahydrofuran/heptane, mp. 157°.

Salt of O-Phenylenediamine and 4,6-Dicarboisopropoxy Isophthalic Acid (VIa).- The reaction for the preparation of the para-salt isomer was repeated with the meta-diester-acid isomer. However, tan crystals and a green oil, which eventually solidified, were obtained upon crystallization from water. Repeated recrystallizations of just the tan crystals eventually yielded pure, leaf-like, hydrated crystals. Water of crystallization was again removed by recrystallizing from tetrahydrofuran/heptane, mp. 110°.

Dimethyl 4,6-Bis(2-Benzimidazolyl)-1,3-Benzenedicarboxylate (VIIa).- Cis-Pyrrone (IV), 2.0g (0.00552 mol), was slurried in 35 ml of methanol and 0.60g (>0.01104 mol) of solid sodium methoxide was added. The mixture was boiled for 1 hour and poured into 100 ml of water. The crude meta-isomer, 1.85g (79 percent), was recovered by filtration and recrystallized from methanol, yielding the purified product as the alcoholate. Methanol was removed by heating at 110°/vac. White crystals, which exhibited an endotherm at 210° but did not melt, were obtained.

Dimethyl 3,6-Bis(2-Benzimidazolyl)-1,4-Benzenedicarboxylate

(VIIb).- The reaction for the preparation of the meta-isomer was repeated with 2.0g of trans-Pyrrone. This time, 2.13g (91 percent) of crude para-isomer was recovered and purified by recrystallization from chloroform. Pale yellow crystals, which exhibited an endotherm at 220° but did not melt, were obtained.

ANALYSIS

Characterization of Model Compounds

In addition to the elemental analyses summarized in table IV, these model compounds were also characterized by IR and NMR. The infrared spectra are given in figures 8-17. It was impossible to determine the NMR spectra of compounds IIIb, IV, and V, due to their extreme insolubility. Also, the NMR spectrum of compound II could not be determined due to the limited availability of pure compound. However, the NMR spectra of compounds VIIa and VIIb, which indirectly prove the isomeric structures of IIIa, IIIb, IV and V, are given in figure 18. The appearance of the two anhydride protons denotes the isomerism of these two models. Since they are equivalent for the para isomer and nonequivalent for the meta isomer, they appear as 1 and 2 peaks, respectively. Similar splitting of the aromatic protons were observed in the NMR spectra of the meta and para salt isomers (VIa and VIb). Also, the NMR spectrum indicated that the amide-acid-amine model used in the GC study was the para isomer. ⁽³²⁾

Calibration

An absolute calibration for water, methanol, and 2-propanol was performed by injecting known amounts of these compounds and determining the respective peak areas as a function of concentration. A planimeter was used to determine these areas. It was possible to obtain peak areas agreeing within 3 percent by utilizing a consistent

technique for loading and injecting the standards. The average peak area from five such injections was used in determining a data point for the calibration curve.

A plot of this data is given in figure 19. Due to the wide range of concentrations injected and the resultant range of areas, it was convenient to make a log/log plot of the data. The curves obtained for the three standards are essentially linear over four orders of magnitude. This characteristic of the thermal conductivity detector has been reported earlier.⁽³⁰⁾ This plot also confirms the linearity of the detector used in this research as well as the reproducibility of the injection and integration techniques.

It should be noted in figure 19 that the curve for water dips below that for methanol and 2-propanol for small amounts injected and eventually crosses both curves as the amount injected increases. This would suggest that some irreversible adsorption of water has occurred at low concentrations. While this adsorption probably occurred at all concentrations, it is more apparent at low concentrations. This could have been a source of error in this experiment if the model compounds had cyclized very slowly and considerable data had to be taken on small amounts of water. Fortunately the models reacted rapidly and evolved large quantities of water.

Time limitations did not permit continuous model compound effluent analysis immediately after obtaining the absolute calibration curves. However, periodic injections of various standards during the

model compound experiment agreed with these curves to within 5 percent.

Correction for Background Water

As the research progressed, it became apparent that there was residual or background water in this system. This background was observed even though steps had been taken to remove water from the carrier gas and from materials used in preparing the sample tubes. Therefore blank runs were made so that this background could be determined and subtracted from the model compound runs. All conditions were the same as those employed while analyzing the model compounds except that no sample was present. It was determined that the residual water was approximately 1 mg and was reproducible.

Figures 20 and 21 give plots of mg of water detected vs. temperature for the average of three blank runs and for each of the model compounds. Thus, at any one temperature, the average background water from the blank runs could be subtracted from the total water evolved during an experiment to give a reliable value for the water of cyclization.

Two possible sources of this residual water are: (1) the helium carrier gas and (2) moisture adsorbed on the materials used in preparing the sample tubes. The GC scrubber column of 5 angstrom molecular sieve was regenerated at 300° for 2 hours under a helium purge before starting this investigation. However, on one occasion, a blank run was made to 300° and about 1 mg of water was detected.

After 24 hours, the sample tube was reheated to 300° and 0.23 mg of water was detected even though the apparatus remained assembled but under a slow helium purge. Therefore some water must remain in the carrier gas even after passing through the molecular sieve column.

Glass wool and Firebrick were used in packing the sample tubes to hold the model compounds in place during heating and purging. A sketch of a tube is given in figure 6. These materials were vacuum dried periodically at 110° but were exposed to the atmosphere during preparation of the sample tubes. On the average, 0.15g of glass wool and 0.45g of Firebrick were used for each tube. Thermal gravimetric analysis showed that Firebrick will pick up approximately 2 percent in weight when exposed to 100 percent humidity for 16 hours at room temperature. The water pick-up and thermal gravimetric measurements which were made on Firebrick are summarized in figures 22 and 23. While a 2 percent weight increase under these conditions is not severe, it alone could account for the 1 mg of background water since there was a potential for 9 mg of water from just the Firebrick. Similar measurements were not made on the glass wool but it probably also contributed to the background.

Data Reduction

The amount of effluent at each temperature was calculated using the calibration curves in figure 19 and was corrected for background water. The total effluent evolved during an experiment was then determined by summing the amounts at the 25° temperature intervals.

The theoretical amount of effluent released during a quantitative cyclization was calculated based on the millimoles of model compound analyzed. The percent conversion for each compound was then calculated from the theoretical and observed quantities of effluents. This data is summarized in table II. An index of conversion for each model was obtained by dividing the sum of the effluent at a given temperature by the total effluent observed. Plots of this data for a given series of model compounds are given in figures 24, 25, and 26.

DISCUSSION

Initially, quantitative conversion to the pyrrone structure was anticipated for each of the model compounds. However, as shown in table II, only the amide-acid-amine (I) and the meta-benzimidazole-acid (IIIa) yielded what could be considered as 100 percent ring closure under the conditions of this experiment. It should also be noted in table II that the meta and para benzimidazole-esters (VIIa and VIIb) eliminated some water when, theoretically, there was none to eliminate. The following explanation of these results is offered:

During the course of these experiments, very large pressure peaks were observed in the chromatograms of certain models at elevated temperatures while the blank runs exhibited no such peaks. These peaks resulted each time a purge of the sample tube was made as shown in figure 7 and were analogous to the air peak observed when injecting liquid samples. The pressure peaks for the survey and analytical runs on each model correlated surprisingly well at each temperature. Plots of pressure peak height vs. temperature are given in figure 27. Significantly, those models which had large pressure peaks also exhibited poor theoretical yields.

Since a pressure peak is probably associated with the evolution of a gas or mixture of gases, and since pyrrone polymers have been reported to decarboxylate at elevated temperature^(11, 33), some qualitative tests were made for CO₂. A three gram sample of

para-benzimidazole-acid (IIIb), which showed a 74 percent conversion, was programmed from room temperature to 350° at 5° C/min under a nitrogen purge. The purge gas was passed through a dry ice/acetone cold trap and bubbled through a barium hydroxide solution. A precipitate began forming at about 270°. This spot test for CO₂ was repeated on the meta-benzimidazole-ester (VIIa), which exhibited one of the largest pressure peaks and poorest theoretical conversions. Again, a precipitate formed, this time starting at about 260°.

The positive tests for CO₂ probably explain the poor conversions of these two compounds. For compound IIIb, every mole of CO₂ lost through decarboxylation accounts for one mole of water which can not be eliminated during cyclization. Therefore the theoretical evolution of water is not achieved and cyclization can not be quantitative. The same is true for the ester model (VIIa) since each mole of CO₂ accounts for a mole of methyl alcohol. It is not understood how compound VIIa decarboxylates, but the fact that it did may help explain the small amounts of water observed.

Similar tests for CO₂ were not made on the other model compounds due to the limited availability of pure material. It is thought, however, that some decarboxylation also occurred in those models which exhibited large pressure peaks and poor theoretical yields.

Gas chromatography could have been used to monitor this evolution of CO₂ had the problem been anticipated when the experiment was designed. The GC system employed in this study could not be used

to confirm the presence of CO_2 since the Carbowax column would not separate light fixed gases. This aspect is a subject for further investigation and should be re-examined if these studies are to be performed on the related polymers.

Index of Conversion Curves

The index of conversion curves are shown in figures 24, 25, and 26. The effluent analyses in figure 24 indicate that the cyclization reactions were completed in one step, mostly within a 25° interval. It is generally accepted that the corresponding polymeric cyclization reactions involve distinct imide and/or benzimidazole intermediates. (11, 15, 34) It was therefore anticipated that the conversion index curve for the model amide-acid-amine reaction given in figure 1 would show at least two inflections as it converted to the various intermediates and each of these in turn converted to the fully cyclized pyrrone. It was anticipated that these inflections could then be correlated with the curves from the pure intermediates. However, figure 24 indicates that all of these models cyclized by a concerted reaction.

Two step reactions were also anticipated for the salt-like models VIa and VIb, since several mechanistic routes are available for these models. Among these is the elimination of water between the salt link followed by the loss of 2-propanol to form an imide and finally the elimination of more water to form the pyrrone structure. The possibility of the two sides reacting by different mechanisms

can not be ruled out. If any of these reactions occurred at different temperatures, then breaks in the index curve would be seen. However, the smoothness of the curves in figure 25 suggests that distinct intermediates are not involved under the conditions of this experiment. Perhaps a non-selective ring closure mechanism is involved since the elimination of water and alcohol appears to occur simultaneously. Also, the fact that the 2-propanol curves for the two isomers are identical above 175° and the water curves are identical above 200° suggest that the same product is being formed. This is supported by the infrared spectra of the two compounds after heating to 295° .⁽³²⁾

The conversion curves for the benzimidazole-esters (VIIa and VIIb) in figure 26 are complicated by the presence of water as discussed earlier. However, the curves also support the idea of a concerted ring closure reaction.

The conversion curves for the amide-acid-amine (I) provide a further insight into the mechanism of ring closure. It is evident from figure 24 that this model does not cyclize through a para-benzimidazole-acid (IIIb) intermediate since it is completely cyclized at the temperature that the benzimidazole begins to react. Compounds II and IIIa cyclize in the same temperature range as compound I suggesting these as possible intermediates. However, the meta-benzimidazole-acid (IIIb) can be eliminated because NMR data indicates that the amide-acid-amine used in this study was the para isomer and therefore could not lead to meta-oriented intermediates. Therefore, the amide-acid-amine (I) must have cyclized through the imide

route. If the activation energy required to go from amide-acid-amine to imide-amine is greater than that required to go from imide-amine to pyrrone, then the reaction could occur smoothly in a concerted fashion as indicated in figure 24.

Polymers formed from meta-oriented salt intermediates have been reported as reacting at a slightly lower temperature than polymers from para intermediates.⁽¹⁷⁾ This is confirmed from this study which shows that the meta-oriented models begin reacting at a lower temperature than the corresponding para model.

Consideration for Polymer Chemistry

This study has provided a number of additional points pertinent to pyrrone polymer chemistry. Since the amide-acid-amine models cyclized readily at a fairly low temperature, cyclization of the corresponding polymer at low temperature also would be anticipated. The fact that it is necessary to cure the polymer under more severe conditions^(15, 35) indicates that the polymeric reactions may be more complex than the model reactions. The possibility that the polymer may be cross-linking or decarboxylating should be investigated. It would be desirable to cure the polymer longer at a temperature where cyclization is known to start rather than at some arbitrarily higher temperature which gives a more rapid cure. This could minimize any decarboxylation and may result in greater cyclization and increased thermal stability. If possible, it would be desirable to force the prepolymer through the imide-amine or meta-benzimidazole-acid

routes by chemically blocking other paths since these two intermediates exhibit good yields at fairly low temperature. Since meta-oriented models reacted at a lower temperature than their corresponding para isomer, polymers from meta-oriented precursors might also be expected to cyclize at lower temperatures. The information obtained from this study also shows that benzimidazole-ester intermediates definitely are not desirable as precursors to pyrrones since the model compounds exhibited very poor yields.

The gas chromatographic technique described in this investigation was developed to study model compounds. It yielded a quantitative understanding of their thermal cyclization and gave an insight into similar processes occurring in the polymer. It has also suggested ways to improve the synthesis of the polymer. However, this technique could easily be adapted to the study of similar processes occurring in the polymer. This study would supplement other methods of polymer analysis currently being used such as differential thermal analysis, thermal gravimetric analysis, and torsional braid analysis. The polymer could be shaped as films, foams, moldings, and laminates. The evolution of solvent and cyclization products has always been a problem in processing these materials. The technique would allow volatile products to be monitored as the prepolymer was cured and would indicate the mildest conditions that could be used to effect such a cure.

CONCLUSIONS

A gas chromatographic study was made on the effluents produced during the thermal cyclization of several pyrrone model compounds.

From this study it is concluded that:

1. The cyclization reactions occurring in these model compounds are concerted according to gas chromatographic data.

2. An analysis of the effluents indicated that only two of the model compounds achieved quantitative cyclization. These were the amide-acid-amine and meta-benzimidazole-acid.

3. Decarboxylation was observed for the para-benzimidazole-acid and the meta-benzimidazole-ester.

4. Polymers should form at lower temperatures from meta-oriented intermediates than from the respective para-oriented intermediate.

5. This technique could be used to study polymeric cyclization processes and to predict the performance of similar new polymer systems by studying their model compounds.

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TABLE I.-DESCRIPTION OF MODEL COMPOUNDS

No.	Structure	Code name	Cyclization Volatiles
I		Amide-Acid-Amine	4 moles of water
II		Imide-Amine	2 moles of water
IIIa		<u>Meta</u> -Benzimidazole-Acid	2 moles of water
IIIb		<u>Para</u> -Benzimidazole-Acid	2 moles of water
IV		<u>Cis</u> -Pyrnone	None
V		<u>Trans</u> -Pyrnone	None
VIa		<u>Meta</u> -Ester-Amine Salt	2 moles of 2-propanol 4 moles of water
VIb		<u>Para</u> -Ester-Amine Salt	2 moles of 2-propanol 4 moles of water
VIIa		<u>Meta</u> -Benzimidazole-Ester	2 moles of methanol
VIIb		<u>Para</u> -Benzimidazole-Ester	2 moles of methanol

TABLE II.- RESULTS OF EFFLUENT ANALYSES

<u>No.</u>	<u>Model Compound</u>	<u>Sample Size</u>	<u>Calculated Effluent</u>	<u>Observed Effluent</u>	<u>% Conversion</u>
I	Amide-Acid-Amine	50.0 mg	8.29 mg H ₂ O	7.94 mg H ₂ O	96
II	Imide-Amine	50.0 mg	4.52 mg H ₂ O	3.79 mg H ₂ O	84
IIIa	<u>Meta</u> -Benzimidazole-Acid	50.1 mg	4.53 mg H ₂ O	4.60 mg H ₂ O	101
IIIb	<u>Para</u> -Benzimidazole-Acid	49.9 mg	4.50 mg H ₂ O	3.38 mg H ₂ O	75
Via	<u>Meta</u> -Ester-Amine Salt	50.0 mg	6.50 mg H ₂ O 10.84 mg 2-PrOH	5.34 mg H ₂ O 8.73 mg 2-PrOH	82 81
VIb	<u>Para</u> -Ester-Amine Salt	50.0 mg	6.50 mg H ₂ O 10.84 mg 2-PrOH	4.64 mg H ₂ O 9.55 mg 2-PrOH	71 88
VIIa	<u>Meta</u> -Benzimidazole-Ester	50.3 mg	7.56 mg MeOH	3.10 mg MeOH 0.66 mg H ₂ O	41
VIIb	<u>Para</u> -Benzimidazole-Ester	50.0 mg	7.52 mg MeOH	4.32 mg MeOH 0.48 mg H ₂ O	57

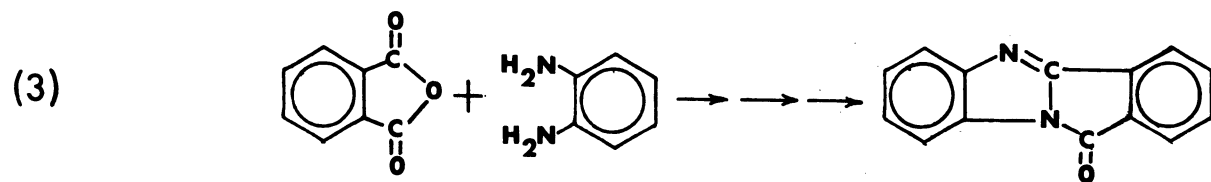
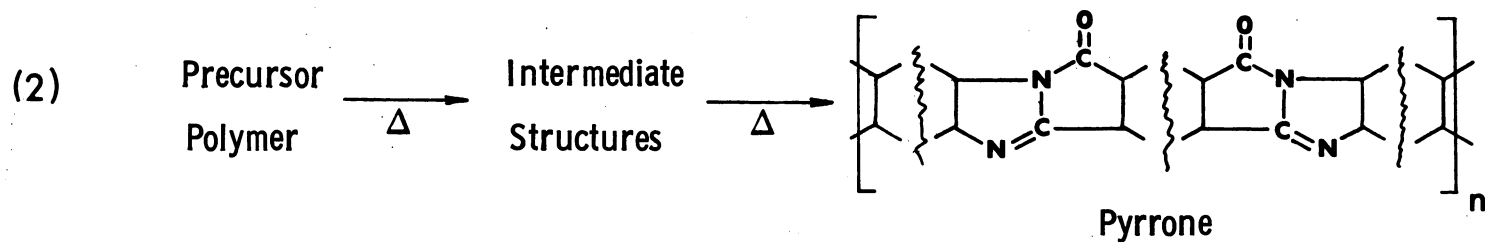
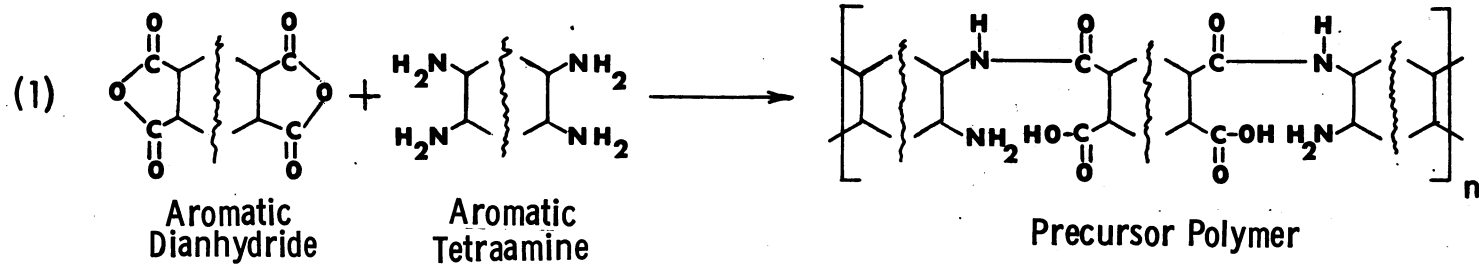
TABLE III. -GAS CHROMATOGRAPHIC CONDITIONS

Column packing:	6% Carbowax 20M on Fluoropak 80
Column tubing:	9' x 1/4" copper
Oven temperature:	120°
Injection port temperature:	170°
Detector:	Thermal conductivity
Filament type:	W-2
Detector temperature:	210°
Detector current:	150 ma
Carrier gas:	Helium
Flow rates:	40 cc/min at 40 psi
Chart speed:	1 in/min
Attenuation:	As required

TABLE IV.- ELEMENTAL ANALYSIS OF MODEL COMPOUNDS

Compound	%C		%H		%N		%O	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
Amide-Acid-Amine (I)	60.45	60.83	4.41	4.17	12.54	12.90	22.18	22.10
Imide-Amine (II)	66.05	66.33	3.79	3.54	13.37	14.06	16.14	16.07
<u>Meta</u> -Benzimidazole-Acid (IIIa)	65.62	66.33	3.84	3.54	13.67	14.06	14.62	16.07
<u>Para</u> -Benzimidazole-Acid (IIIb)	65.95	66.33	3.69	3.54	14.33	14.06	16.06	16.07
<u>Cis</u> -Pyrroline (IV)	73.10	72.93	3.11	2.78	15.62	15.46	9.21	8.83
<u>Trans</u> -Pyrroline (V)	73.13	72.93	3.01	2.78	15.61	15.46	9.24	8.83
<u>Meta</u> -Ester-Amine Salt (VIa)	59.82	60.64	6.33	6.18	9.82	10.10	23.44	23.08
<u>Para</u> -Ester-Amine Salt (VIb)	60.75	60.64	6.20	6.18	10.10	10.10	23.07	23.08
<u>Meta</u> -Benzimidazole-Ester (VIIa)	67.34	67.60	4.41	4.25	13.04	13.14	15.30	15.01
<u>Para</u> -Benzimidazole-Ester (VIIb)	67.32	67.60	4.14	4.25	12.68	13.14	15.39	15.01

Equations



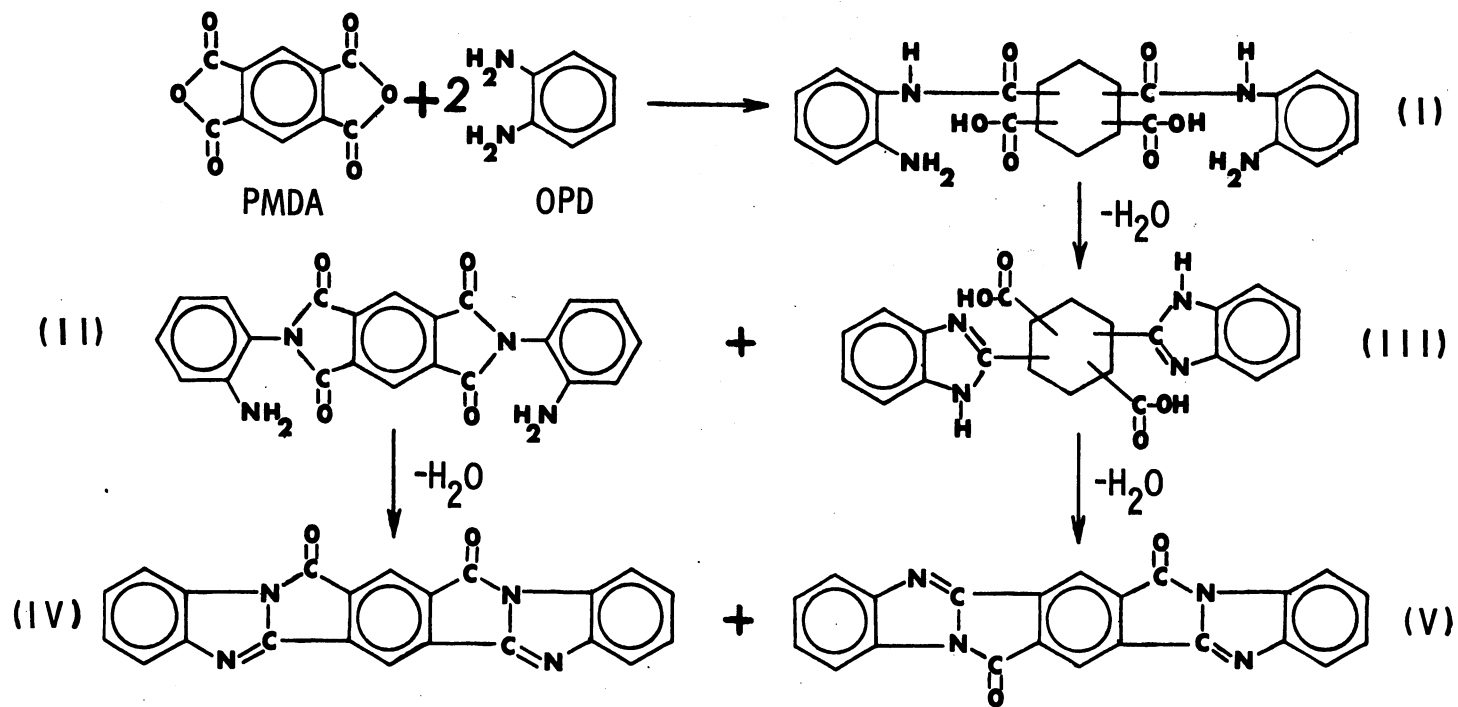


Figure 1.- Reaction scheme for pyrrone model compound study.

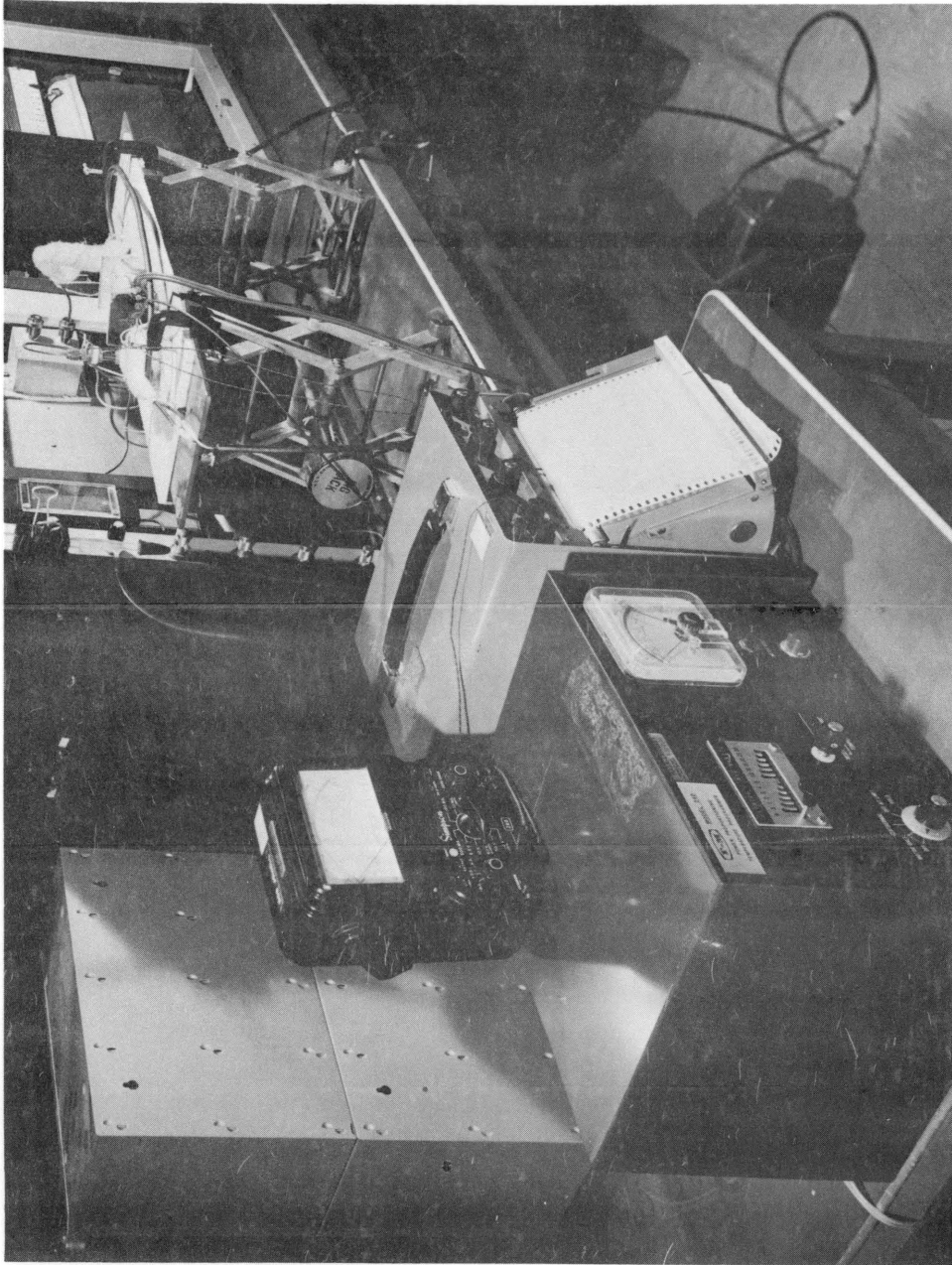


Figure 2.- View of research equipment.

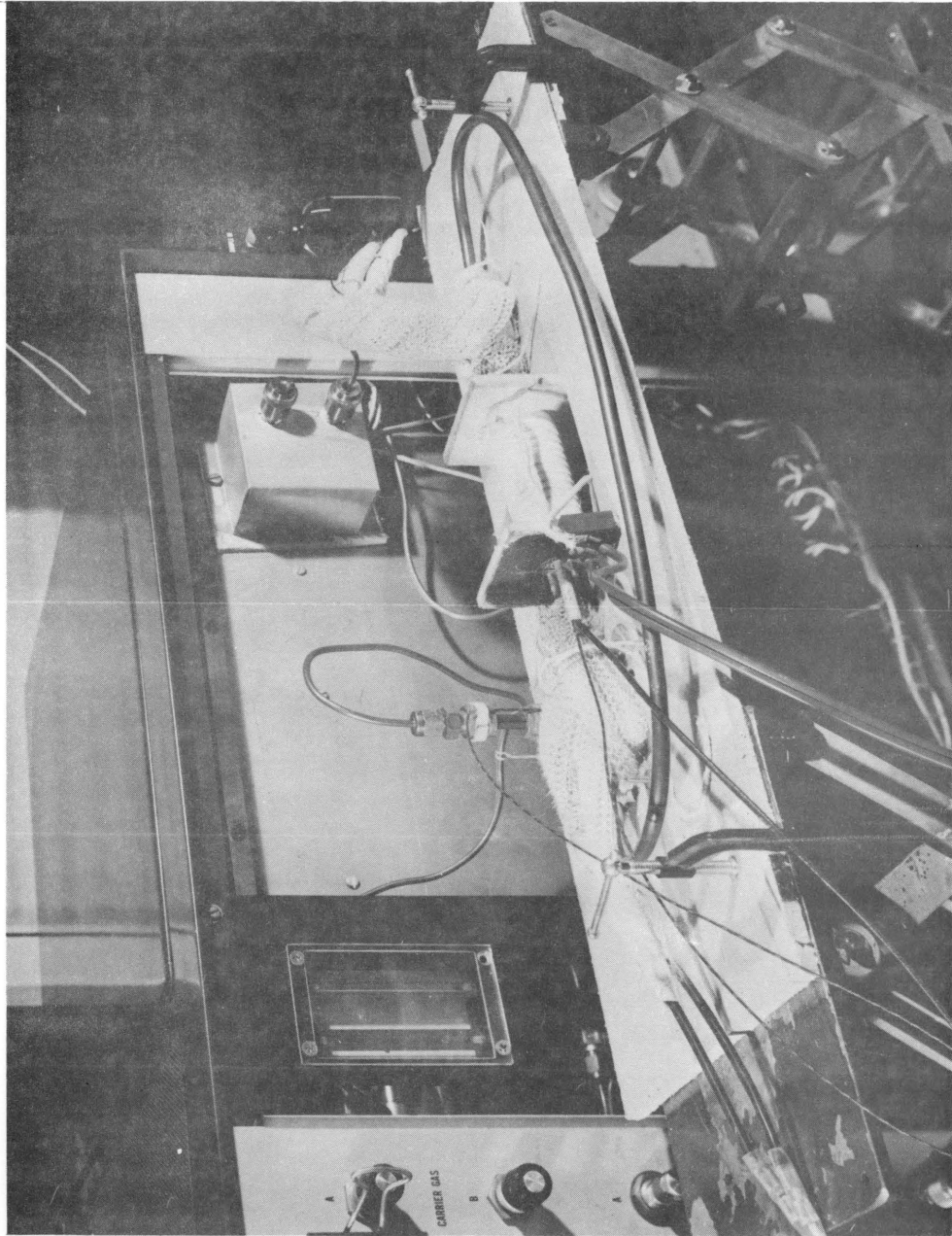


Figure 3.- View of furnace assembly.

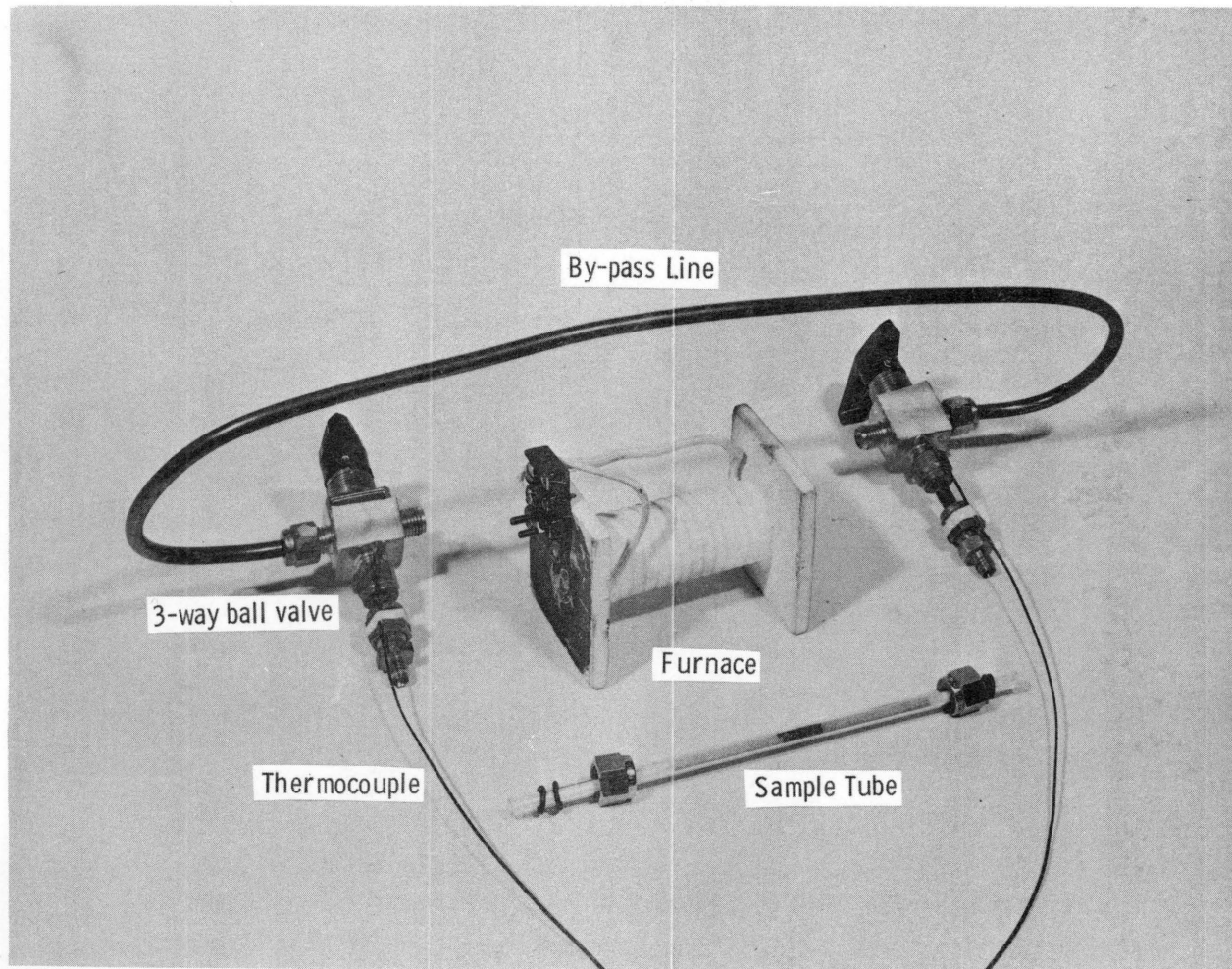


Figure 4.- Disassembled furnace, sample tube, and plumbing.

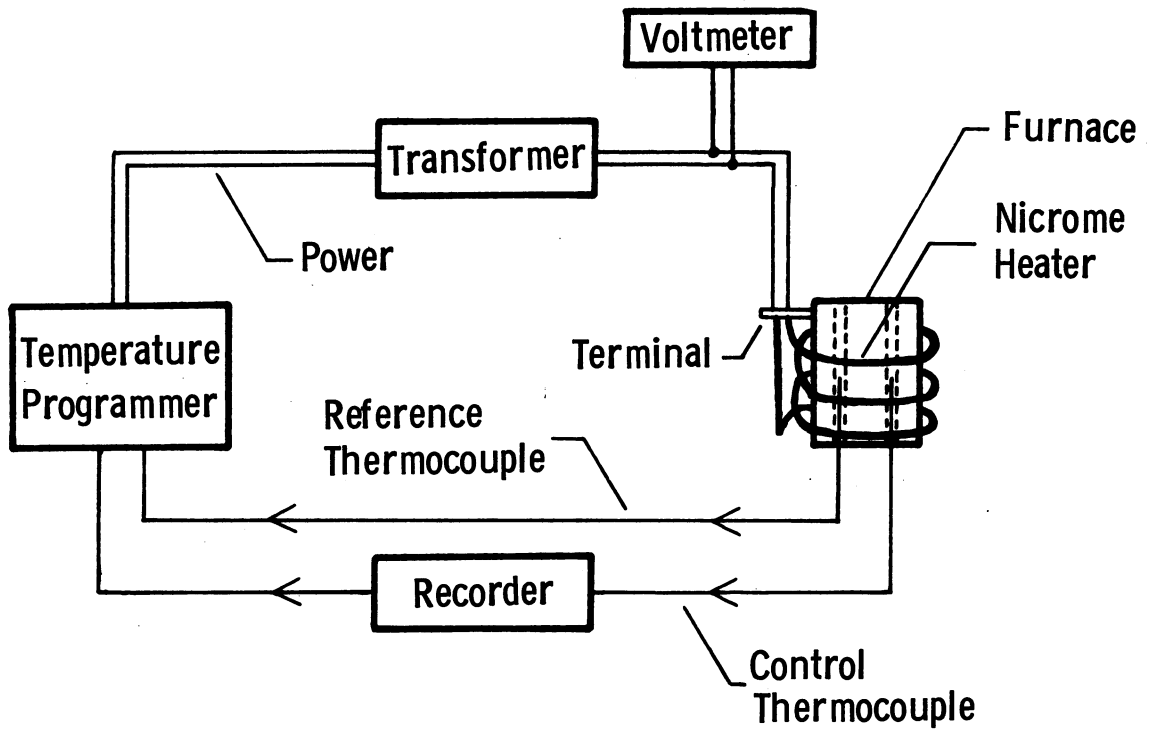


Figure 5.- Block diagram of program circuit.

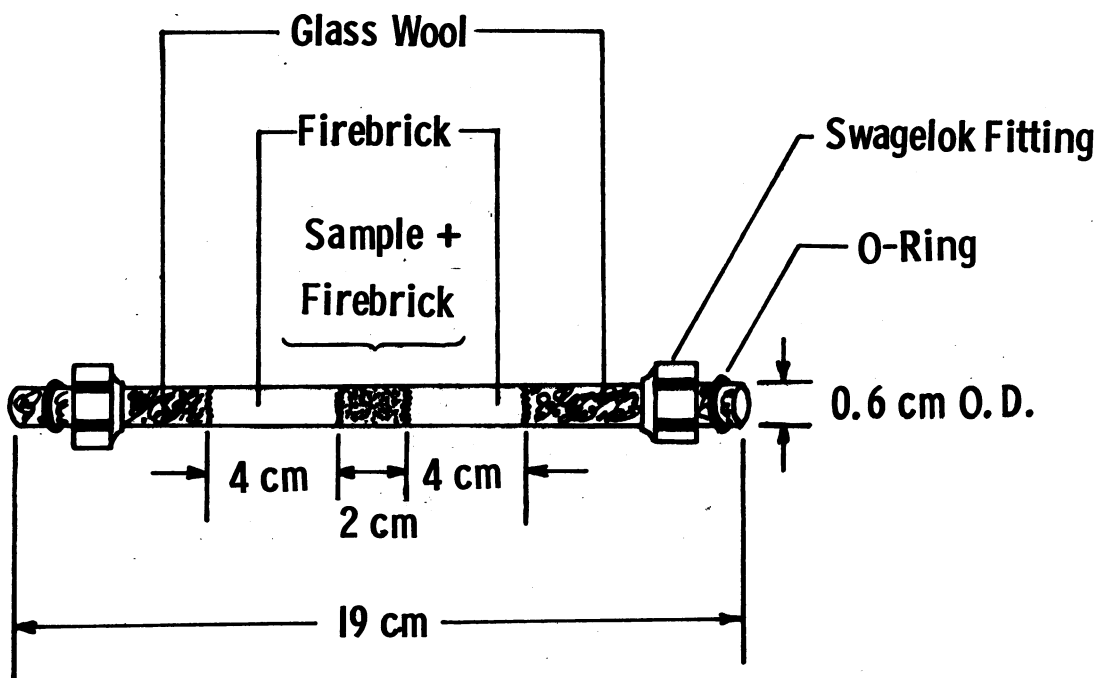


Figure 6.- Sketch of sample tube.

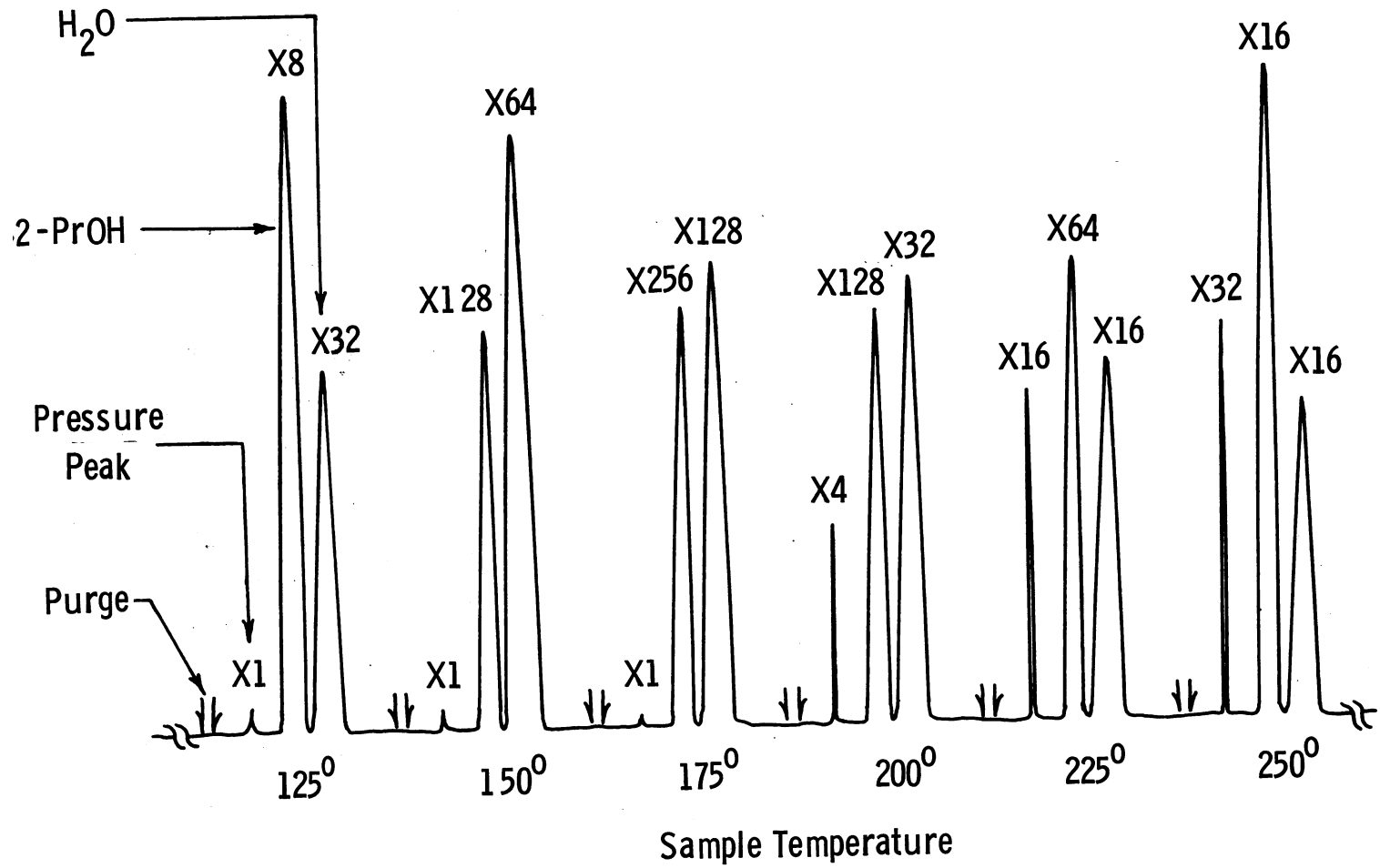


Figure 7.- Portion of typical chromatograph.

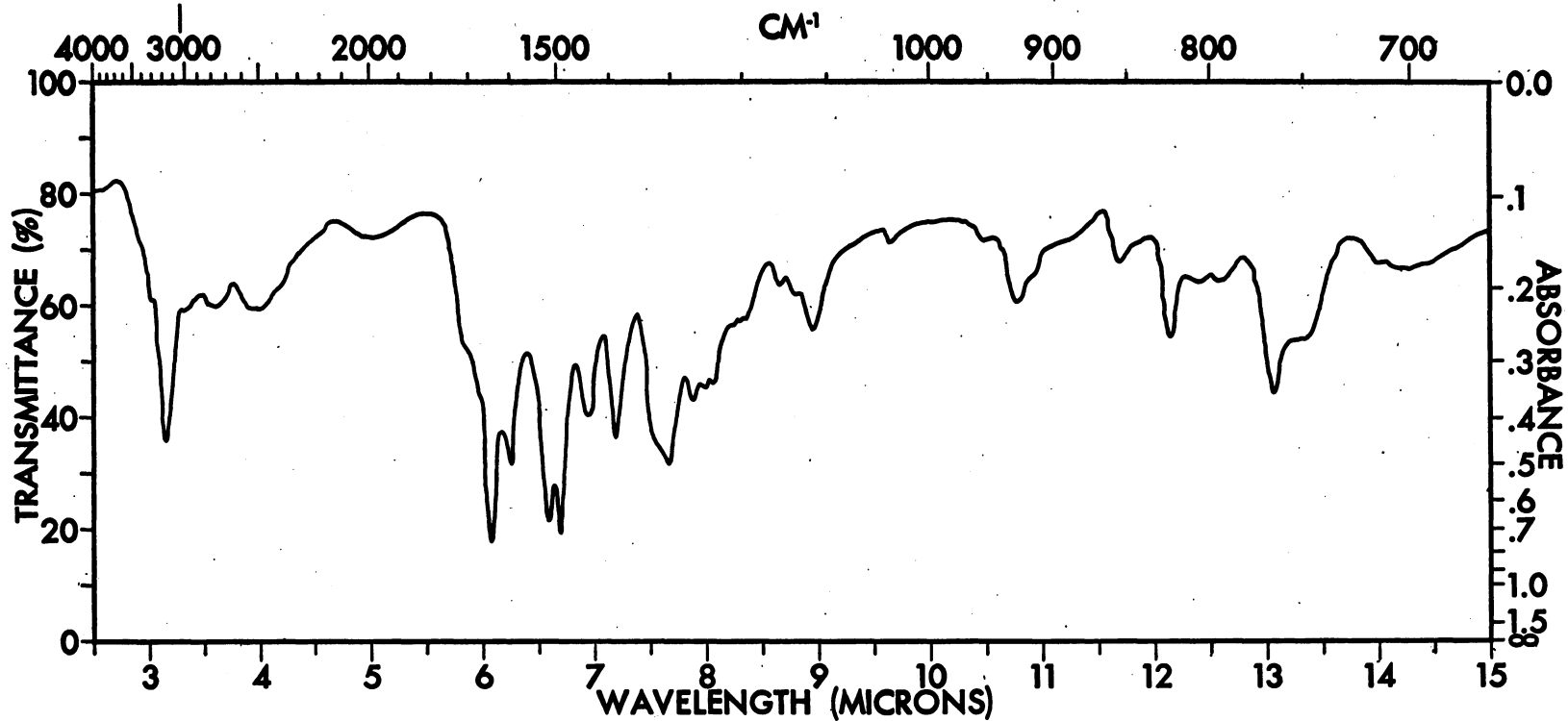


Figure 8.- Infrared spectrum of amide-acid-amine (I).

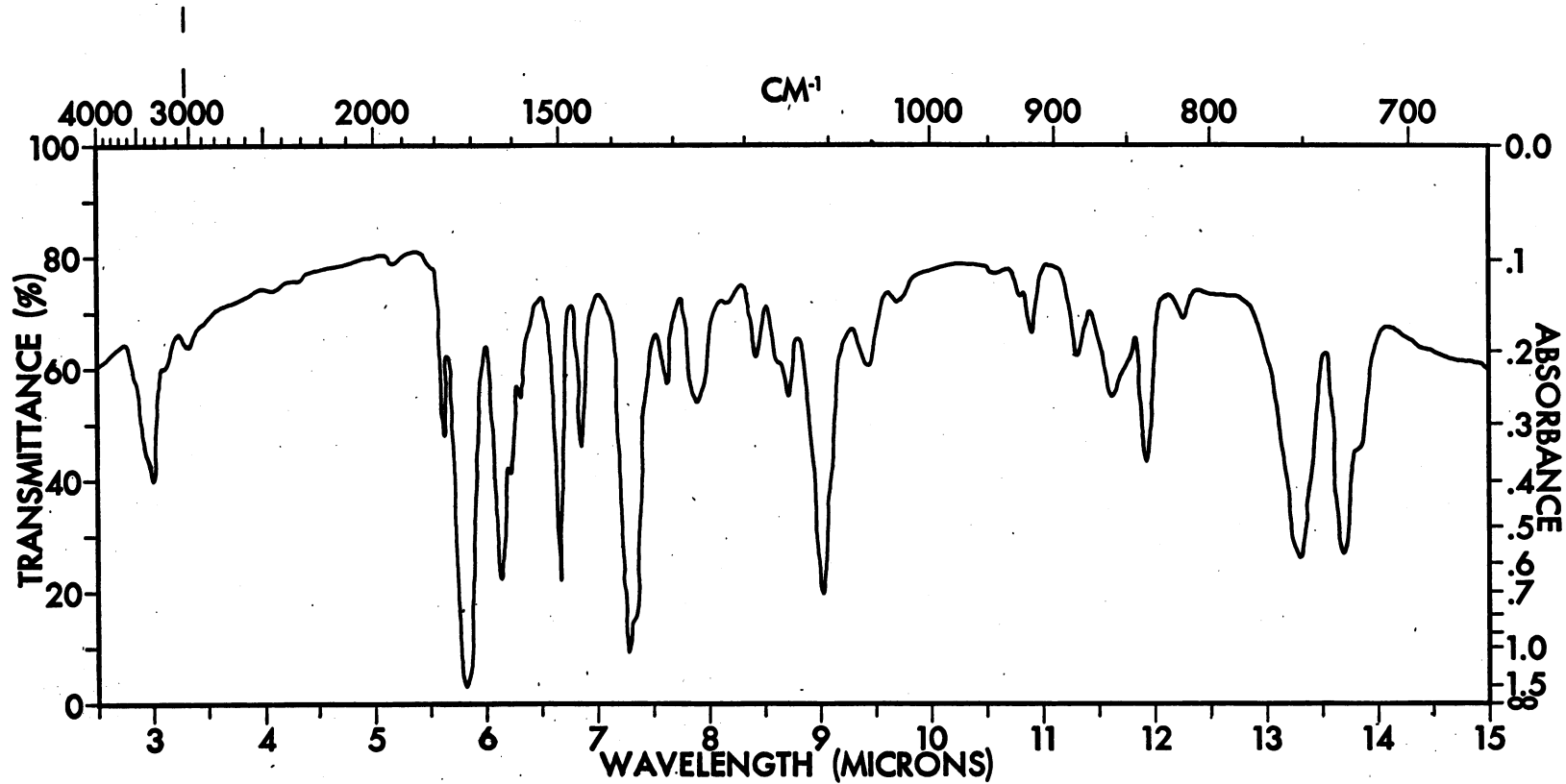
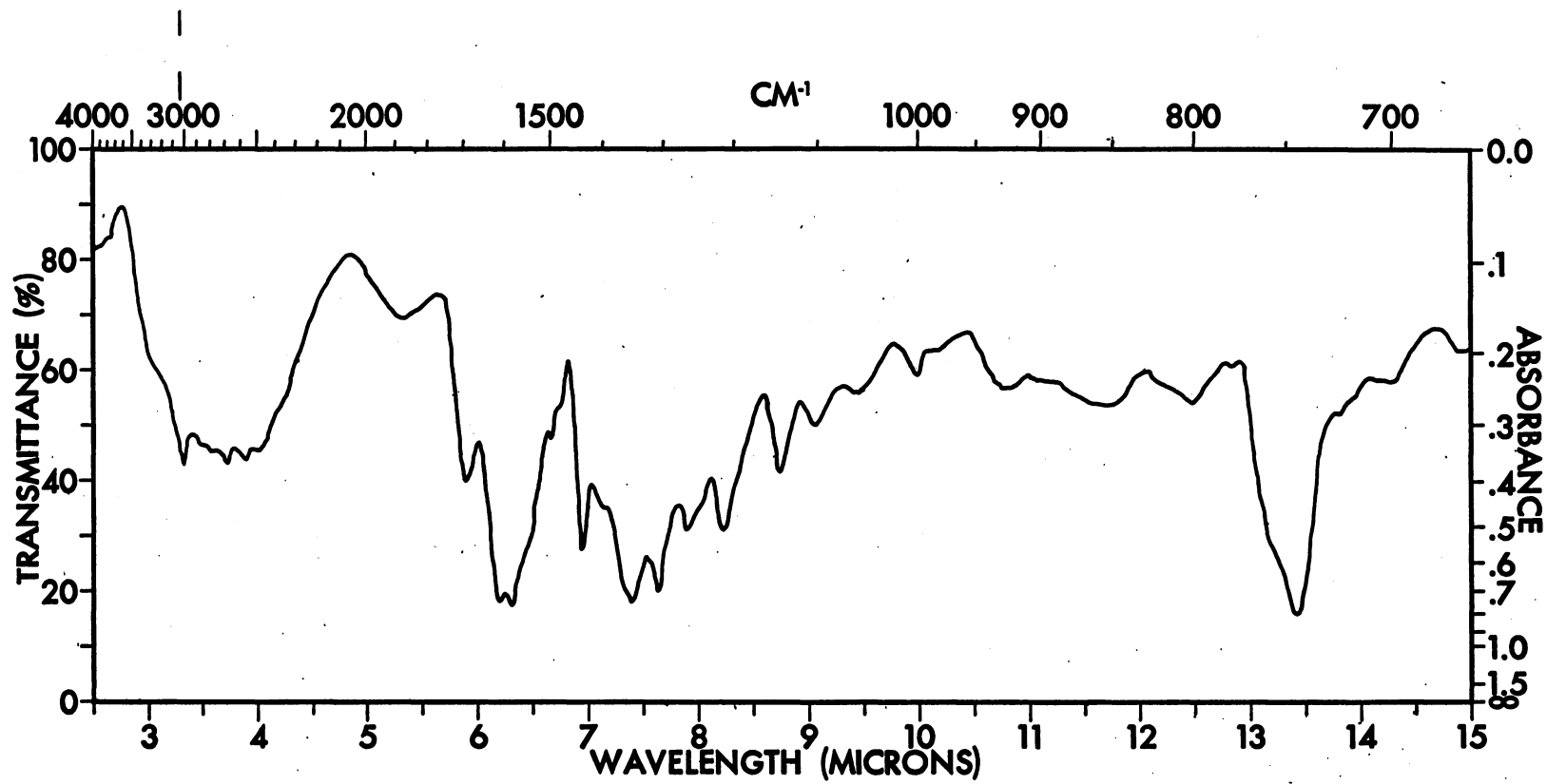


Figure 9.- Infrared spectrum of imide-amine (II).



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Figure 10.- Infrared spectrum of meta-benzimidazole-acid (IIIa).

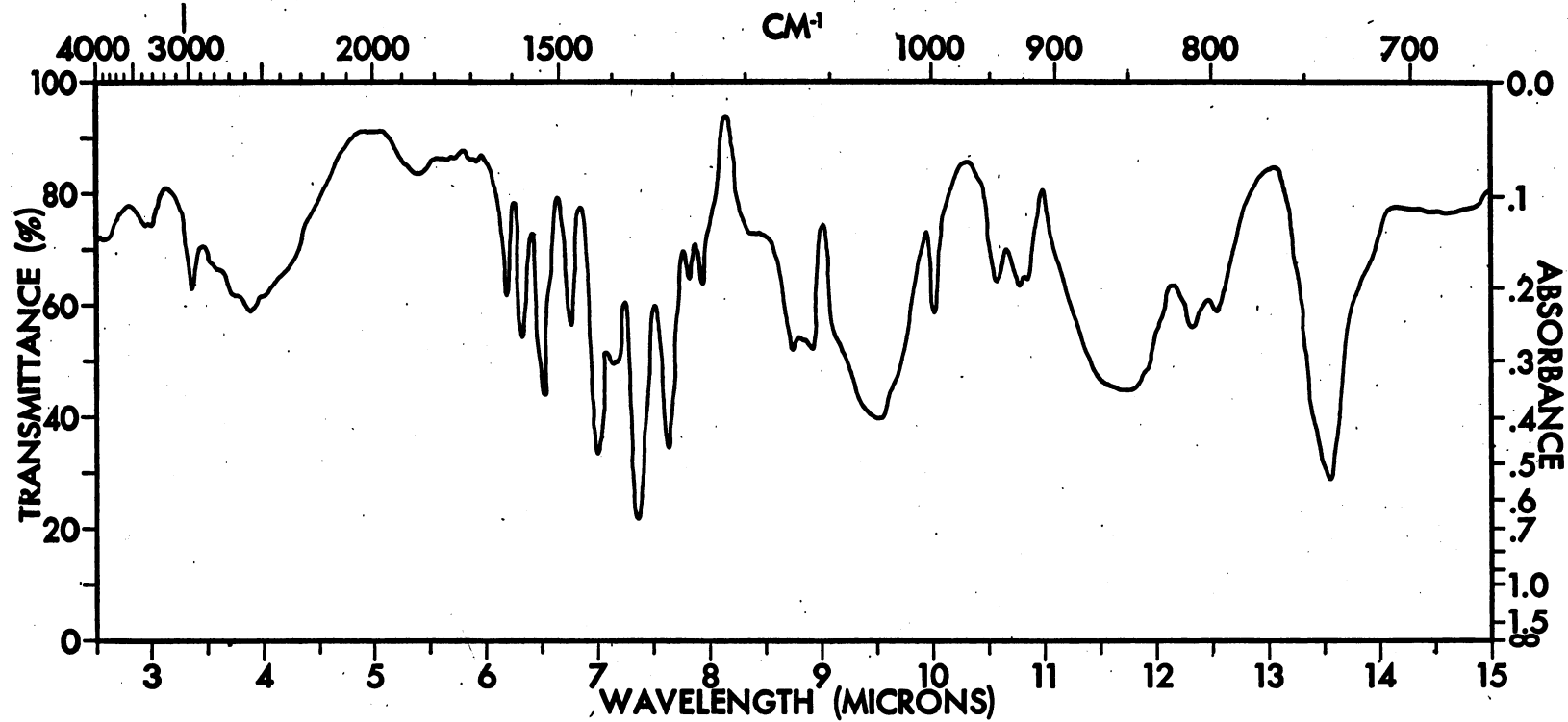
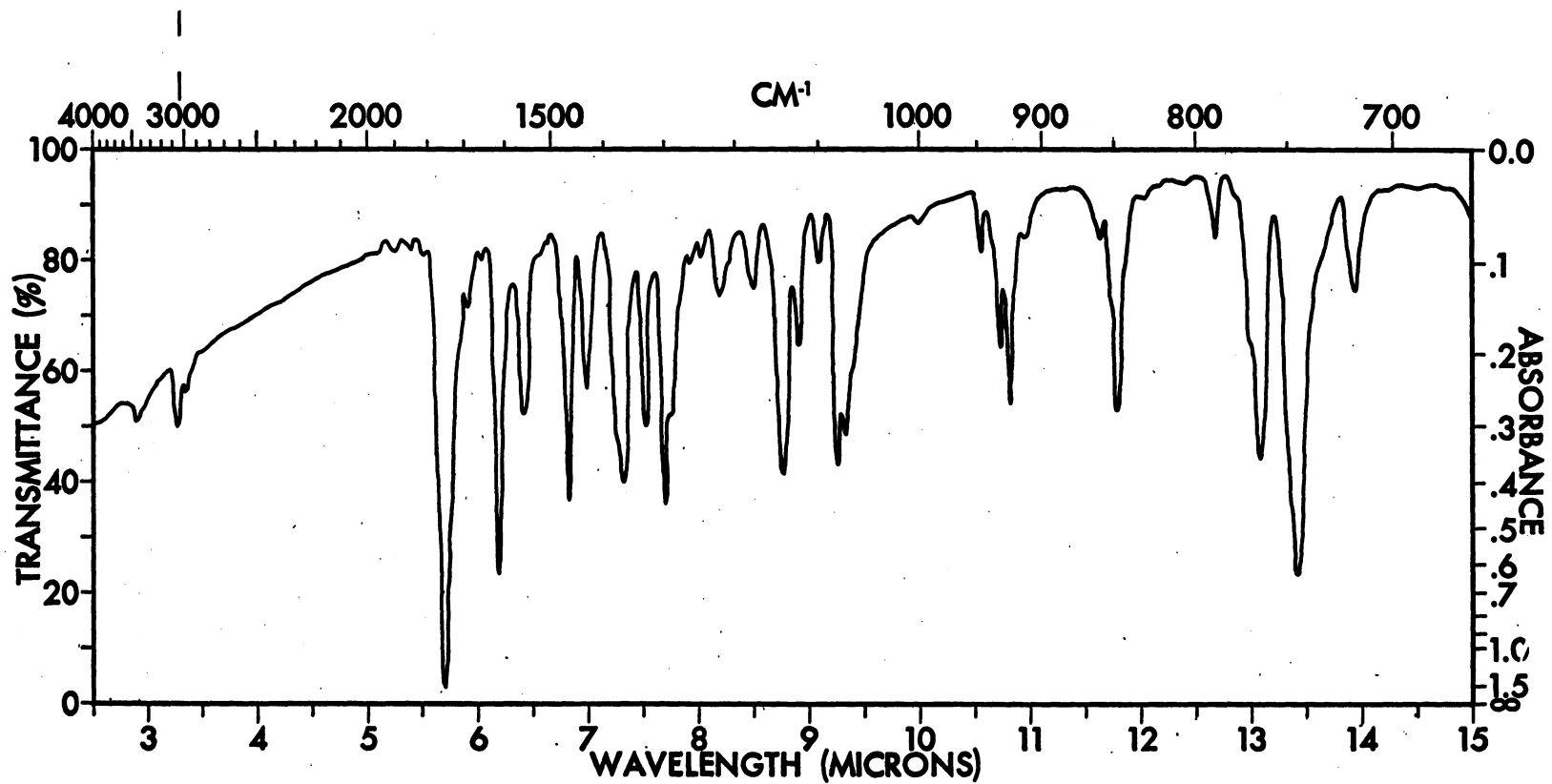


Figure 11.- Infrared spectrum of para-benzimidazole-acid (IIIb).



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Figure 12.- Infrared spectrum of cis-pyrrone (IV).

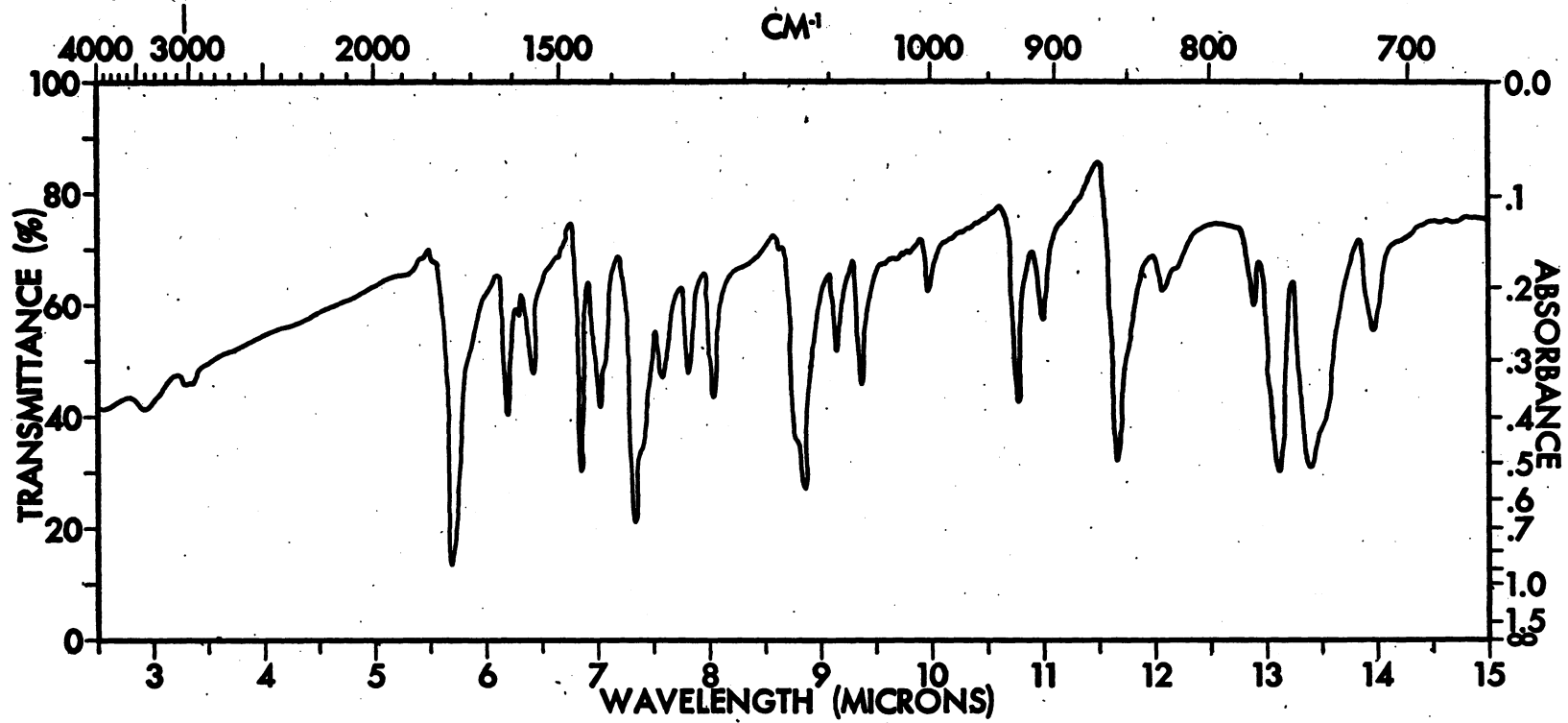


Figure 13.- Infrared spectrum of trans-pyrrone (V).

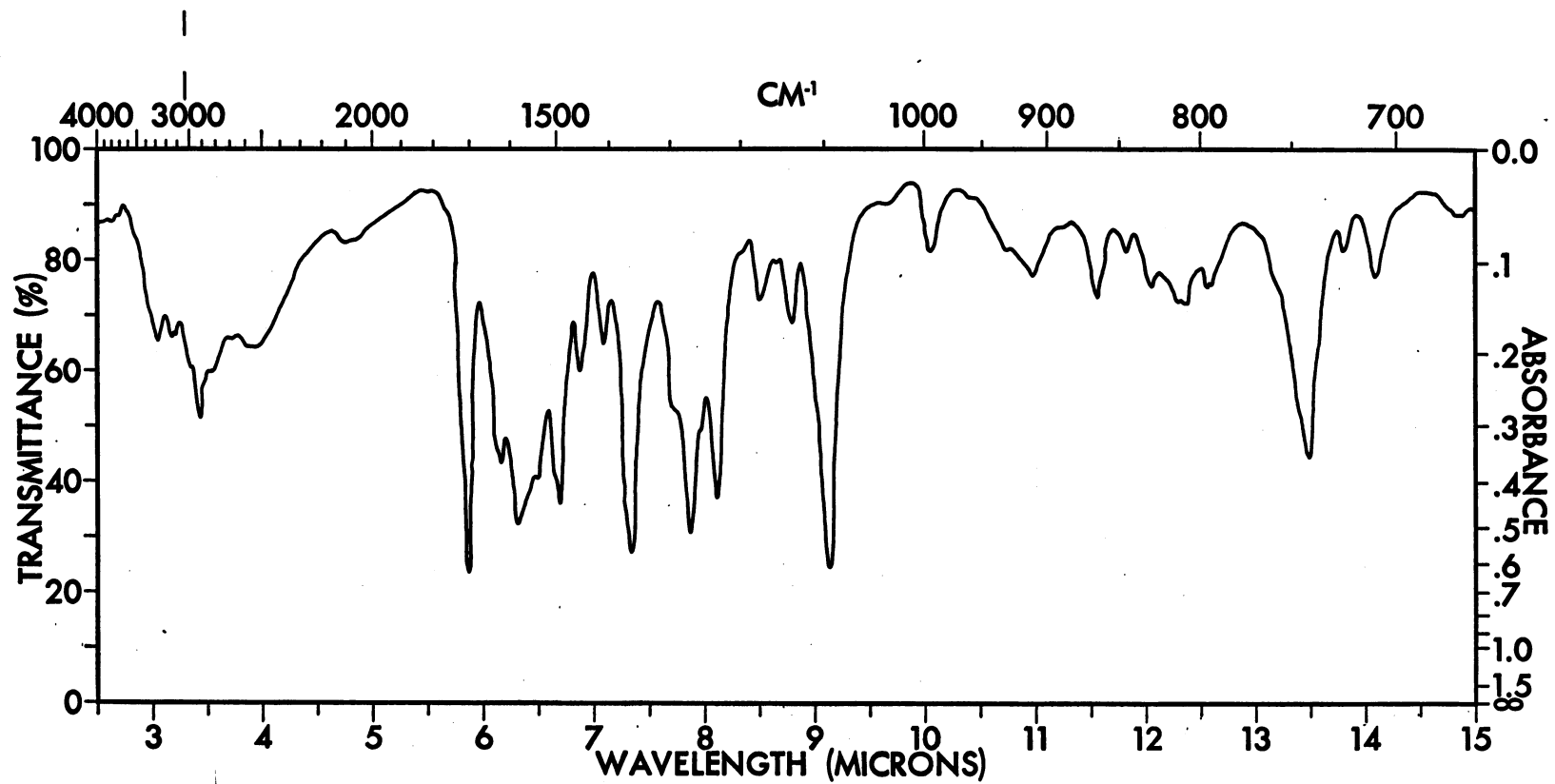


Figure 14.- Infrared spectrum of meta-ester-amine-salt (VIa).

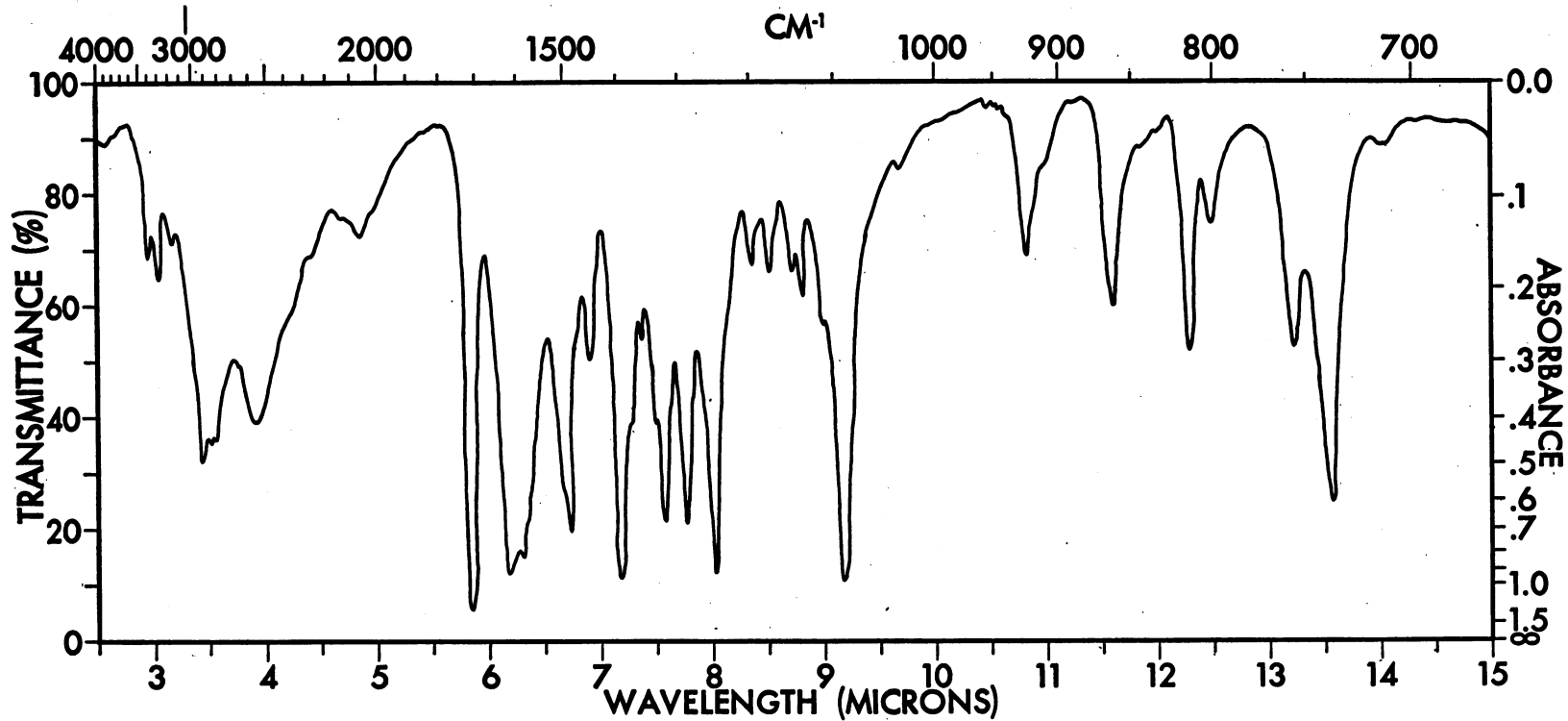


Figure 15.- Infrared spectrum of para-ester-amine-salt (VIb).

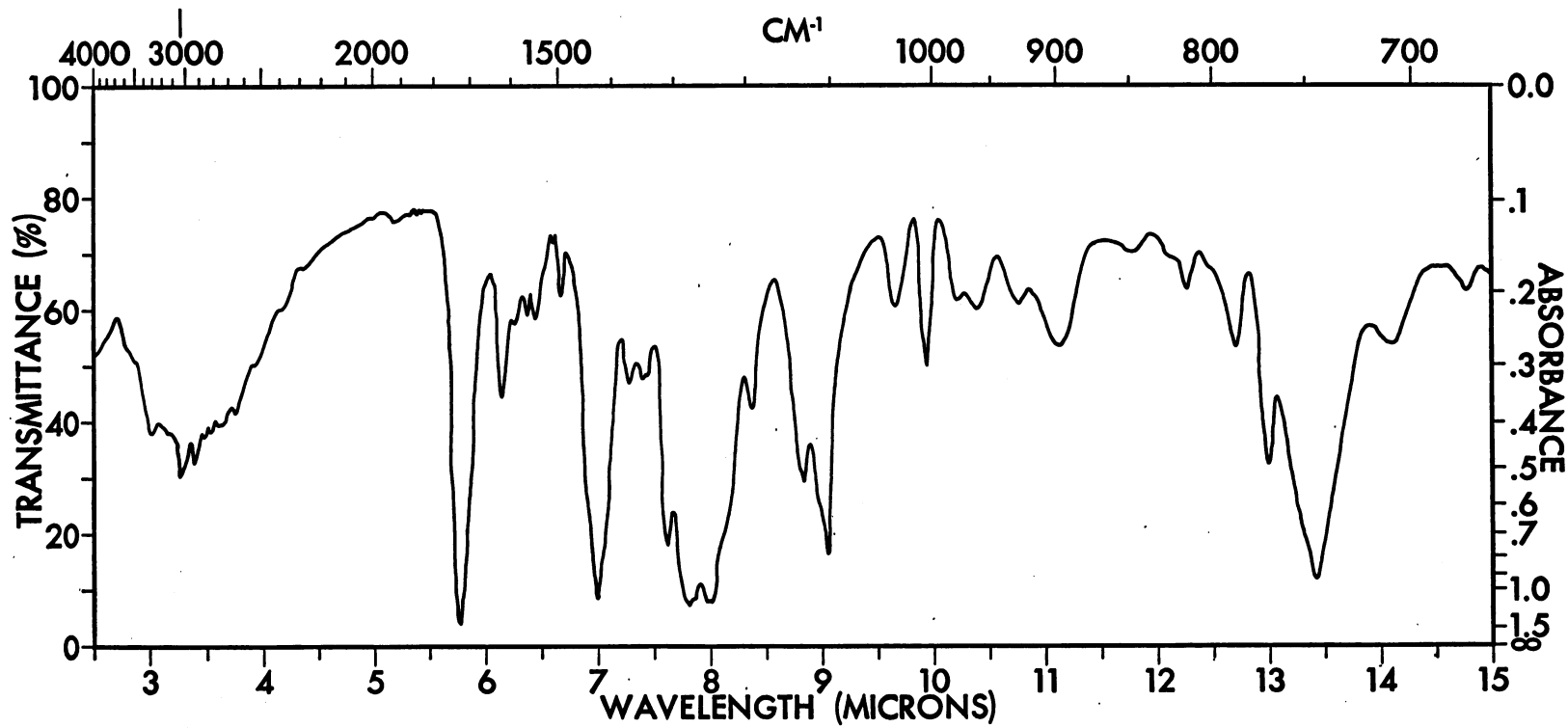


Figure 16.- Infrared spectrum of *meta*-benzimidazole-ester (VIIa).

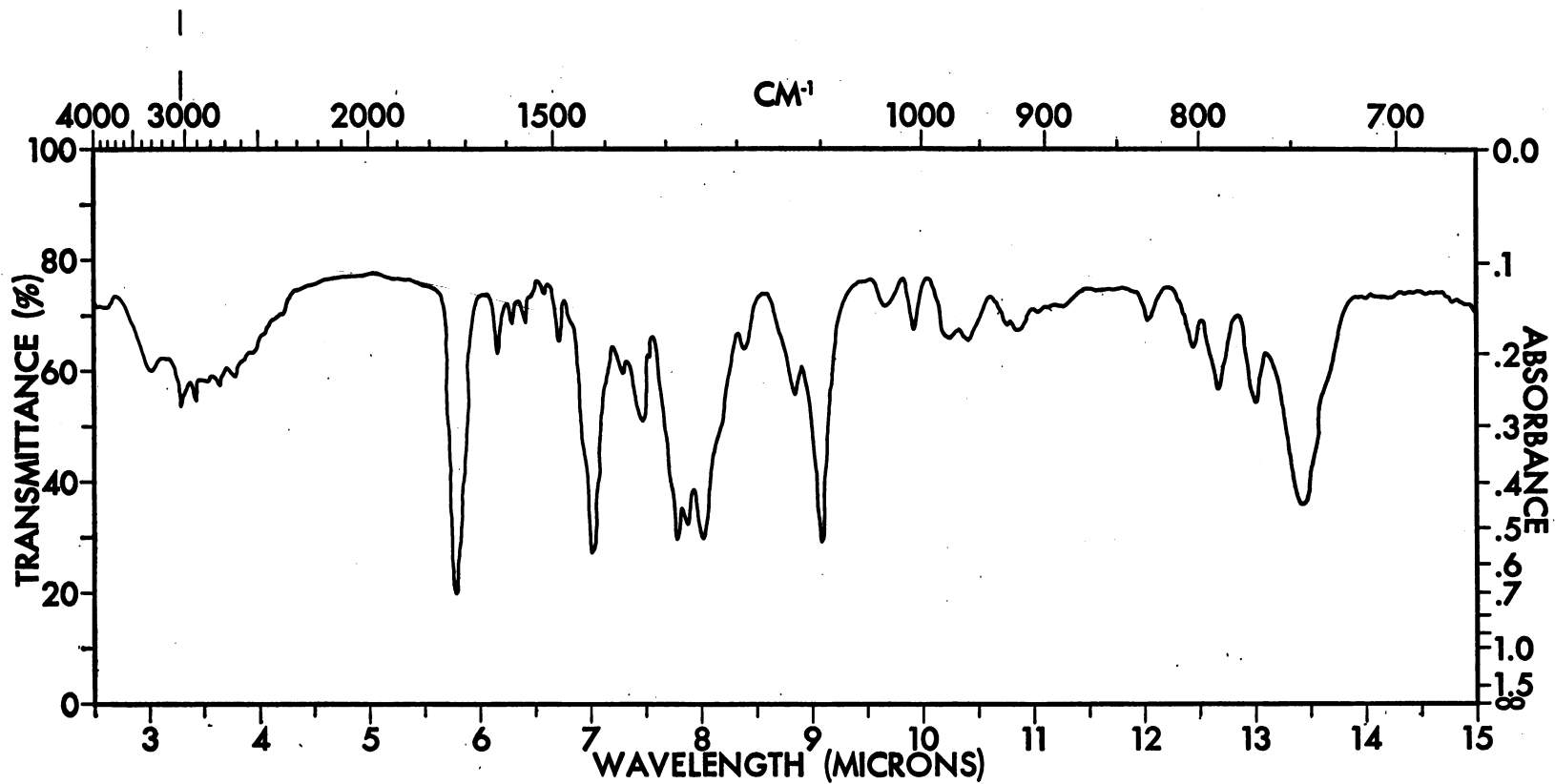


Figure 17.- Infrared spectrum of para-benzimidazole-ester (VIIb).

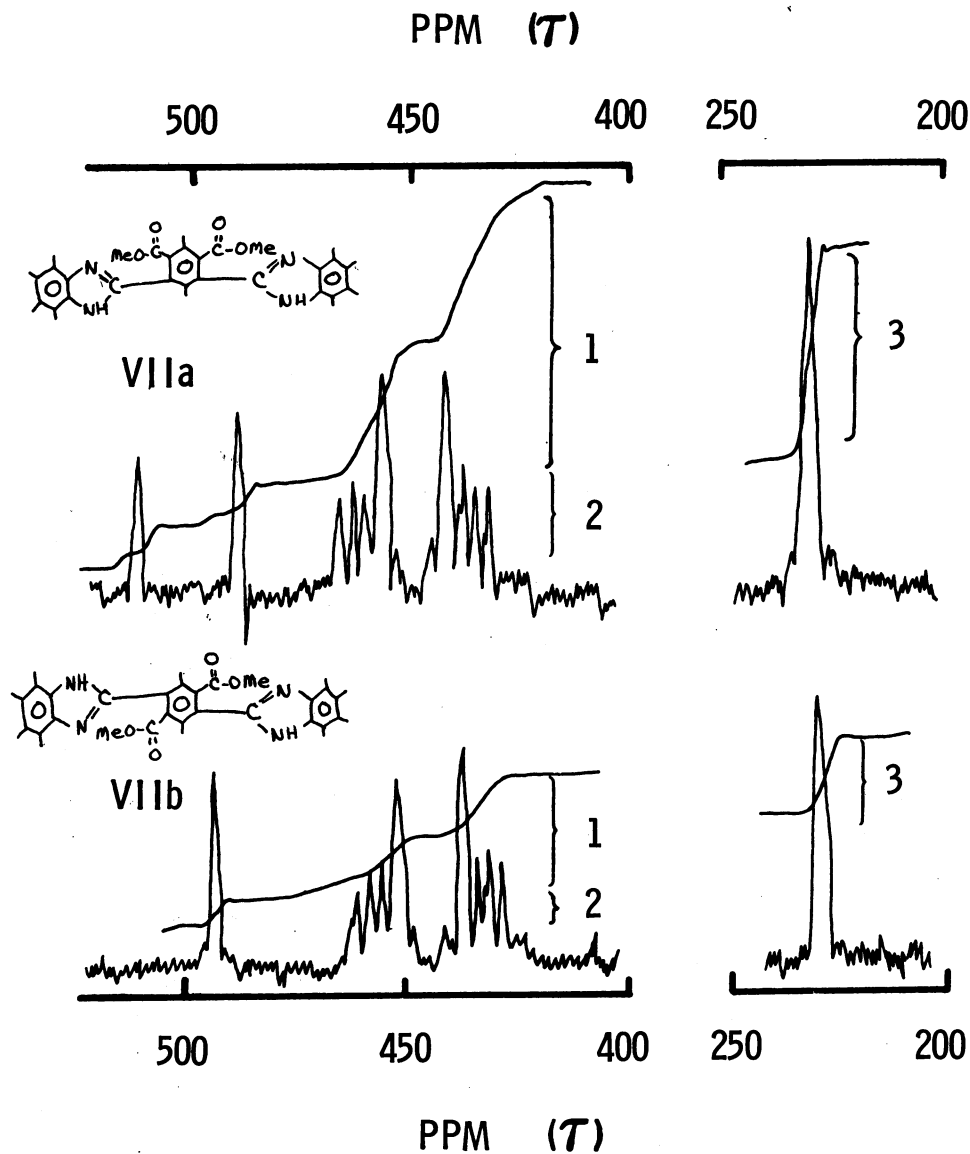


Figure 18.- NMR spectra of meta- and para-benzimidazole-ester model compounds (VIIa and VIIb).

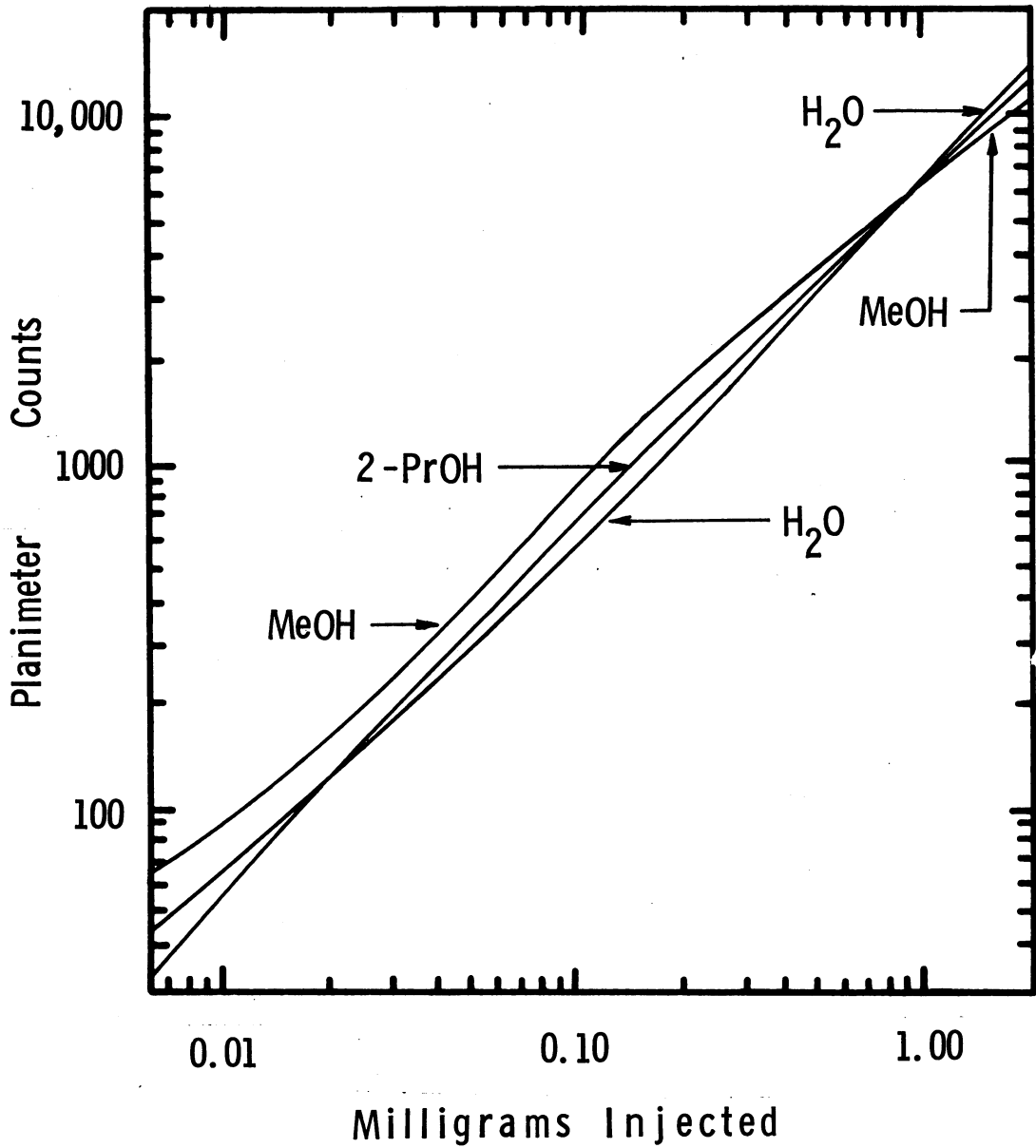


Figure 19.- Absolute calibration curves for water, methanol, and 2-propanol.

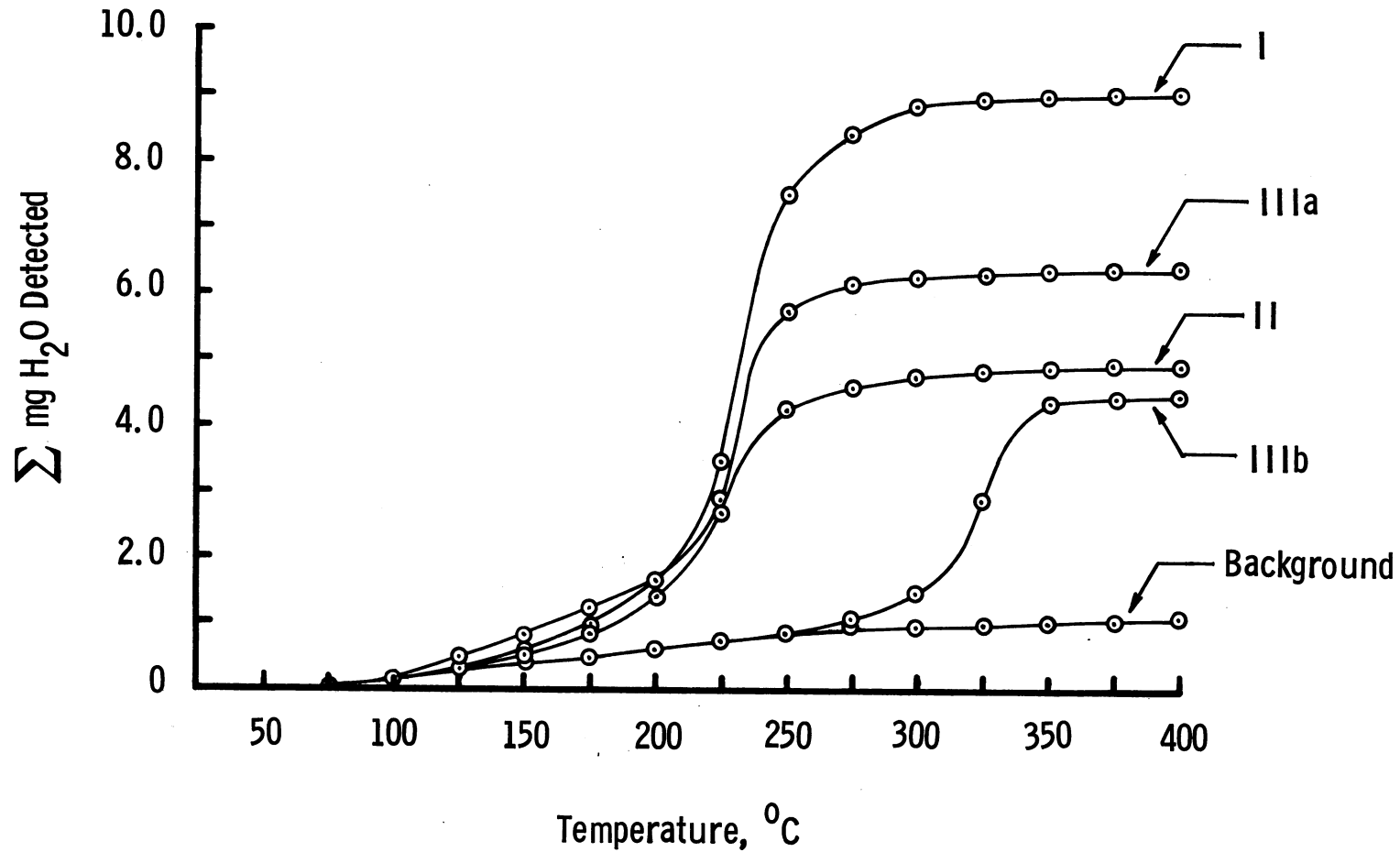


Figure 20.- Total milligrams of water detected for amide-acid-amine (I), imide-amine (II), meta- and para-benzimidazole-acids (IIIa and IIIb) and the average background.

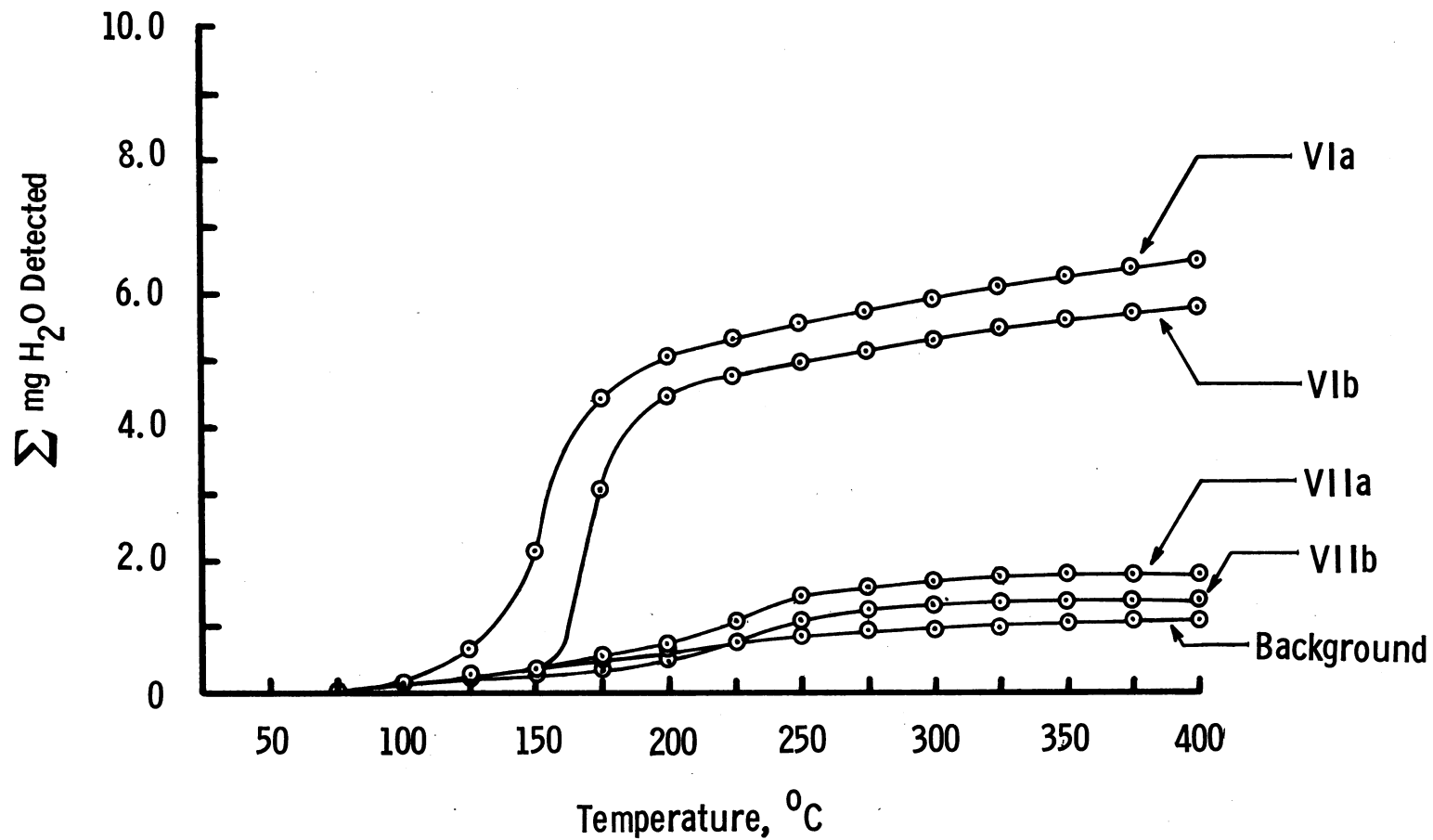


Figure 21.- Total milligrams of water detected for meta- and para-ester-amine-salts (VIa and VIb), meta- and para-benzimidazole-esters (VIIa and VIIb) and the average background.

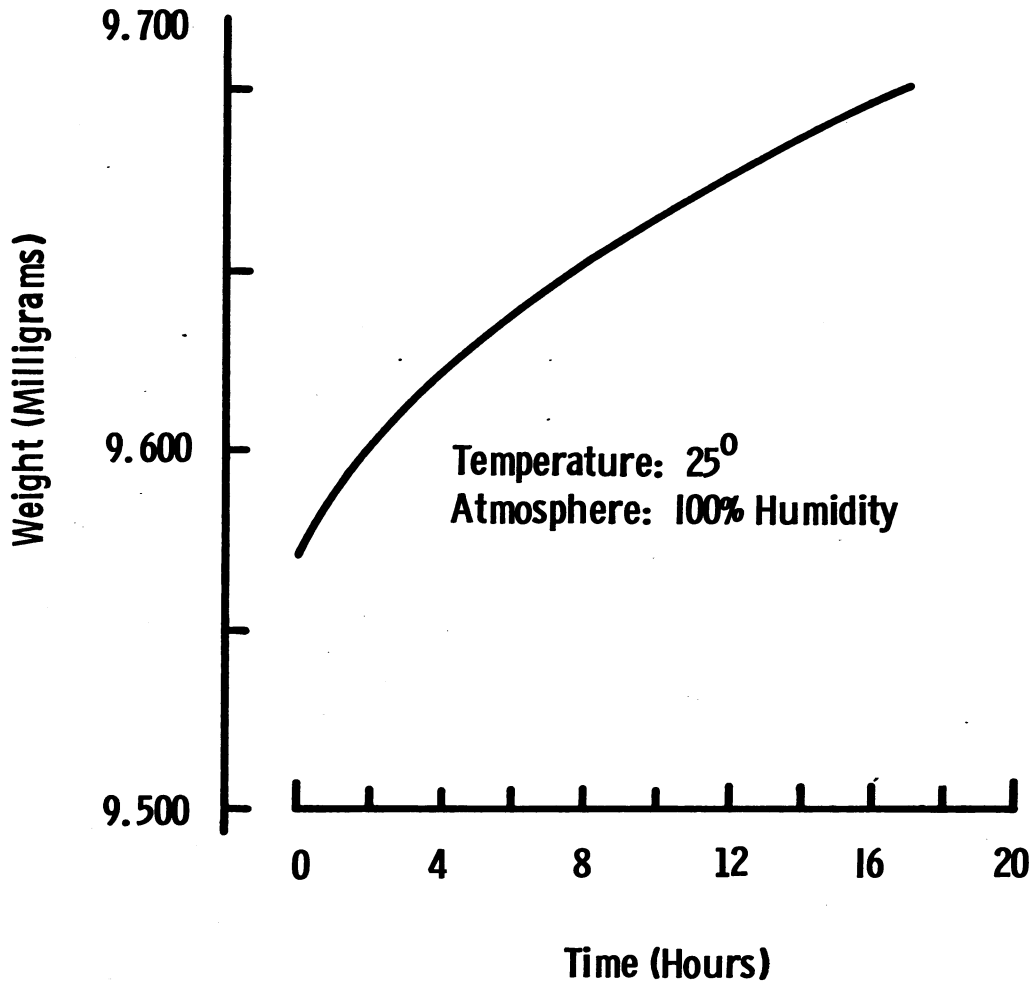


Figure 22.- Water pickup of firebrick (chromosorb P).

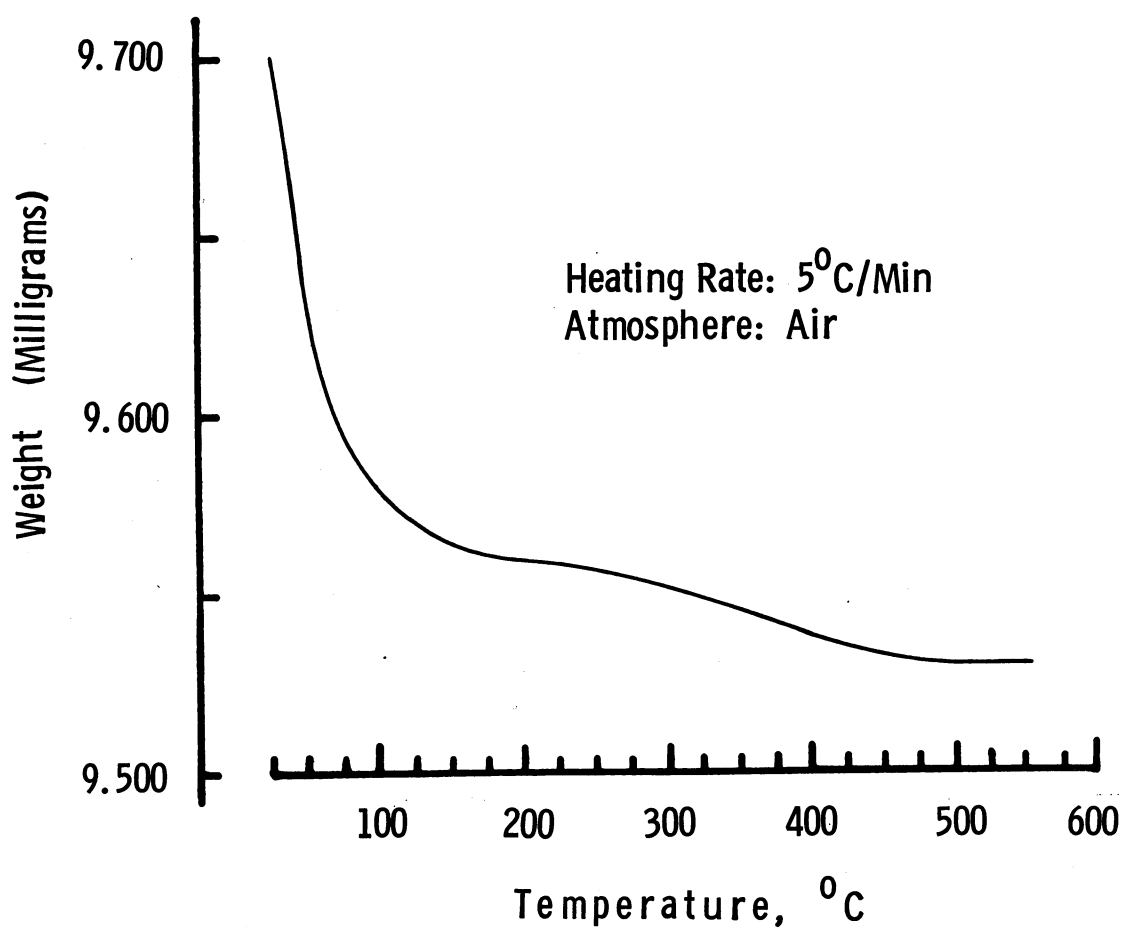


Figure 23.- TGA weight loss of firebrick (chromosorb P).

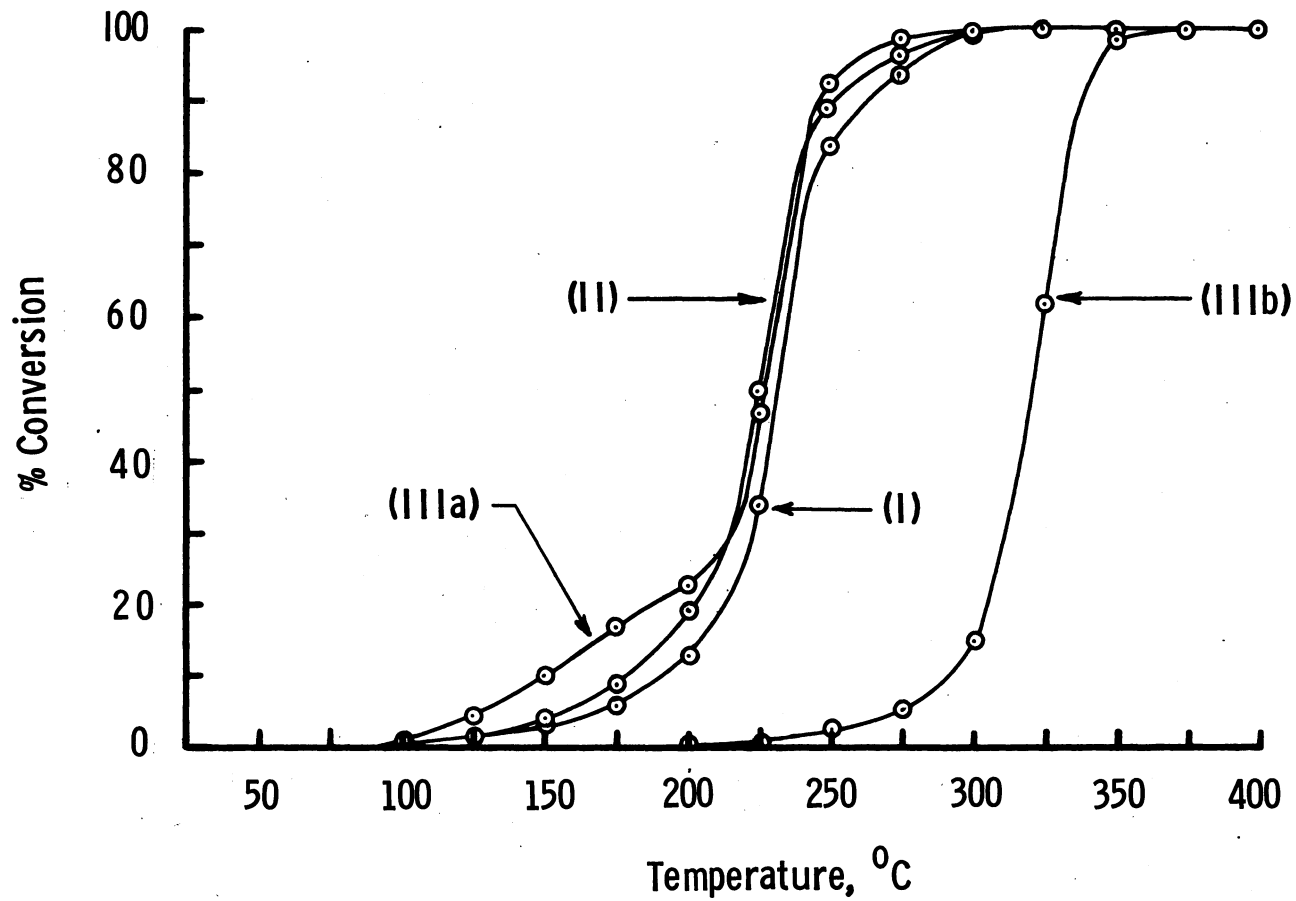


Figure 24.- Index of conversion curves for amide-acid-amine (I), imide-amine (II), meta-benzimidazole-acid (IIIa), and para-benzimidazole-acid (IIIg).

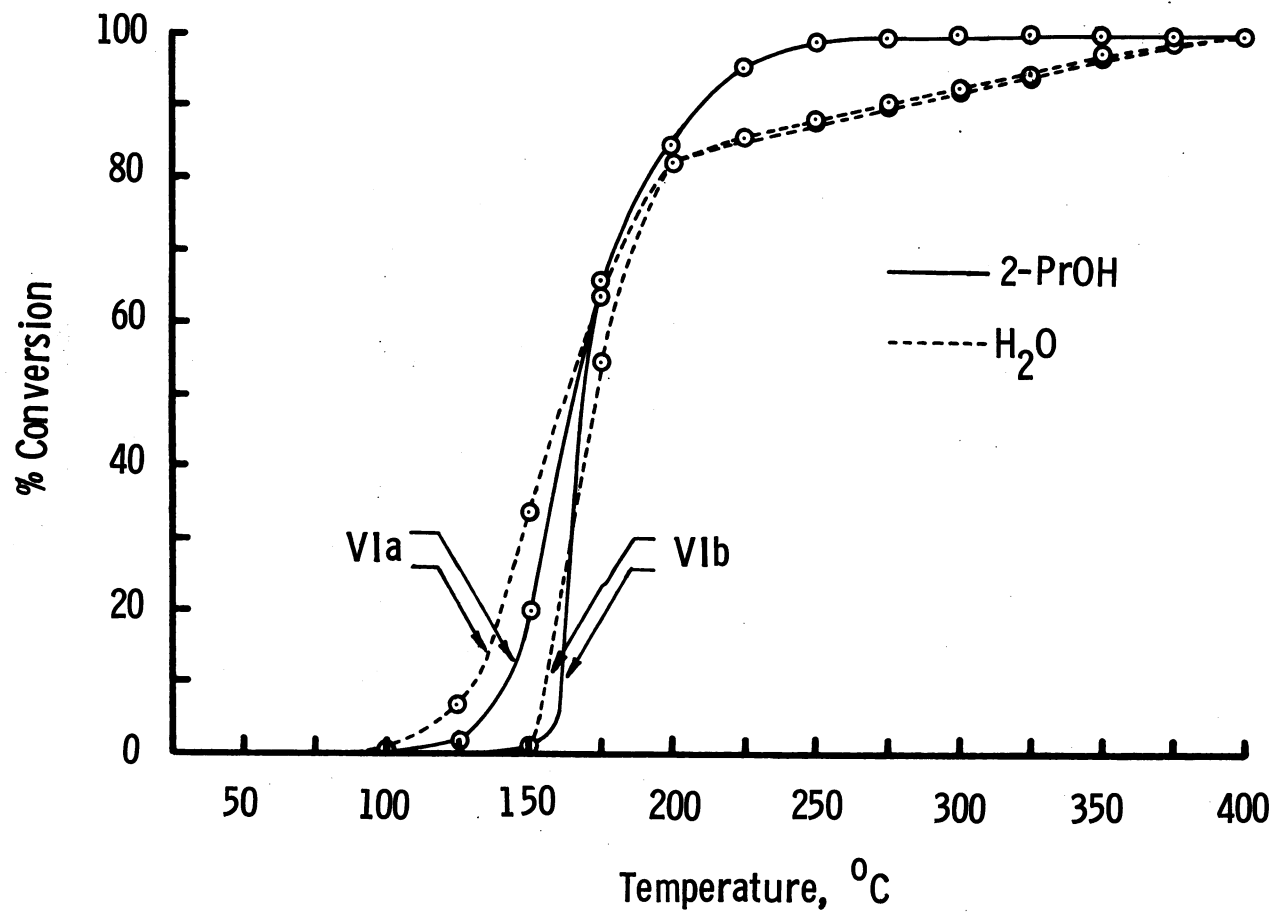


Figure 25.- Index of conversion curves for meta-ester-amine-salt (VIa) and para-ester-amine-salt (VIb).

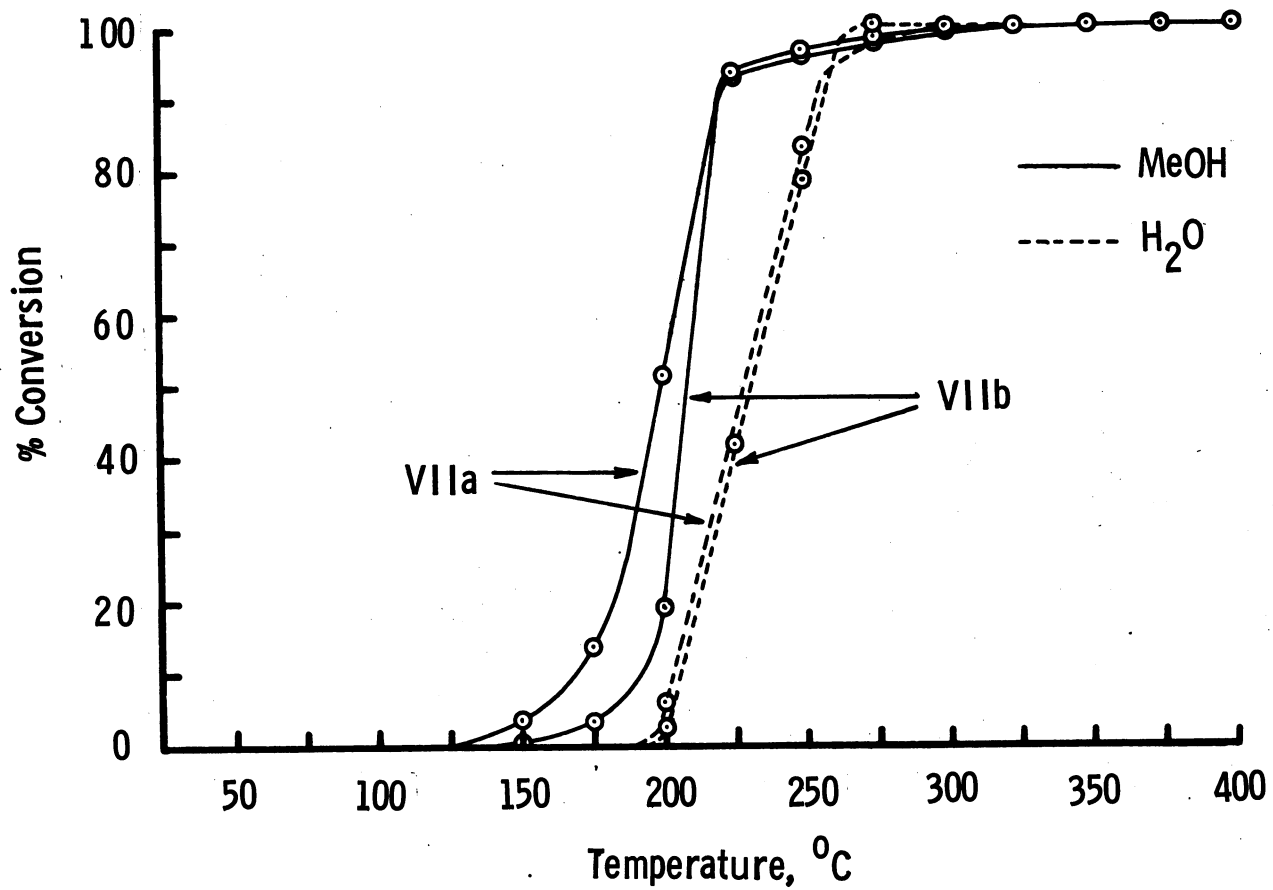


Figure 26.- Index of conversion curves for meta-benzimidazole-ester (VIIa) and para-benzimidazole-ester (VIIb).

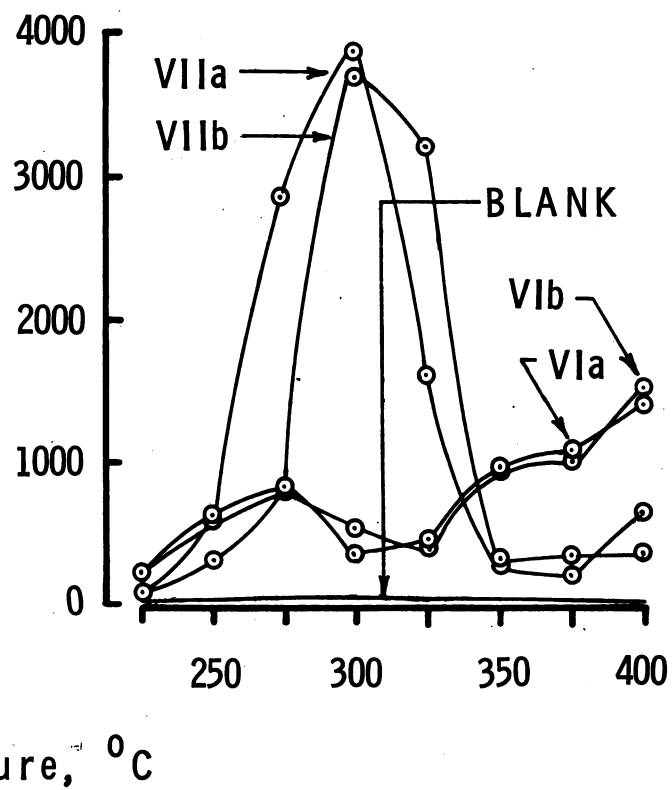
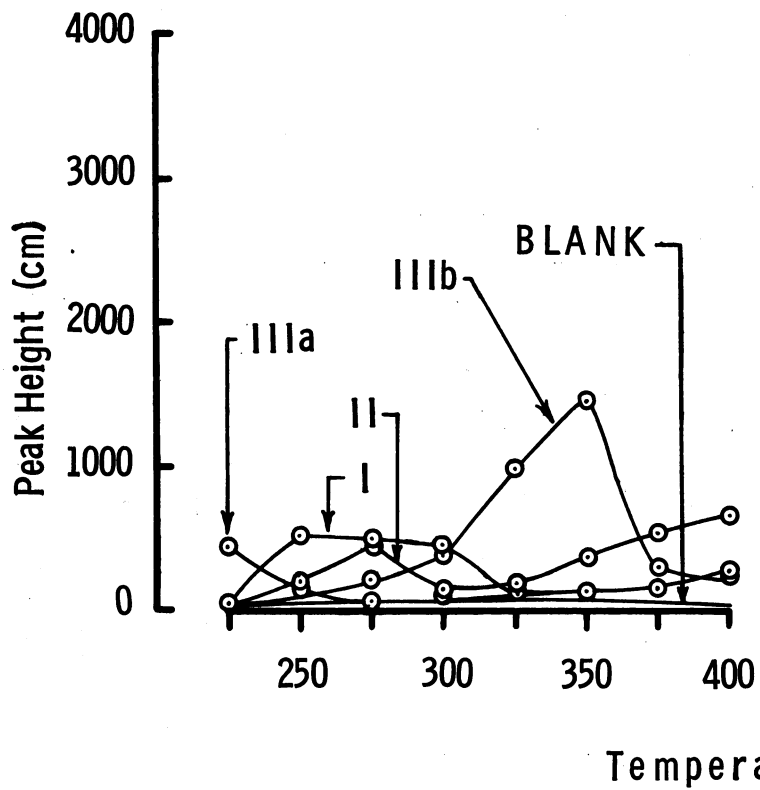


Figure 27.- Plot of pressure peak height versus temperature for each model compound.

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EFFLUENT ANALYSIS OF MODEL PYRRONE COMPOUNDS

BY GAS CHROMATOGRAPHY

By

Philip Ross Young

ABSTRACT

A gas chromatographic study was made to quantitatively analyze the effluents produced during the thermal cyclization of several polyimidazopyrrolone (pyrrone) model compounds. The study yielded information on analogous polymeric reactions. The model compounds were programmed at 5° C/min from 25° to 400° C and volatile species were purged into a gas chromatograph at 25° intervals. An analysis of the effluents revealed that the cyclization reactions are concerted and generally occur below 250° C. The percent of conversion of the model compounds is readily determined by quantitating those reaction products amenable to gas chromatographic analysis. Only the amide-acid-amine and meta-benzimidazole-acid model compounds exhibited complete conversion to the pyrrone structure. Evidence that decarboxylation has occurred in the other compounds is presented.