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R. A. Gaudiana^a; R. T. Conley^a

^a Department of Chemistry, Wright State University, Dayton, Ohio

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Weak-Link Versus Active Carbon Degradation Routes in the Oxidation of Aromatic Heterocyclic Systems. III

R. A. GAUDIANA and R. T. CONLEY*

*Department of Chemistry
Wright State University
Dayton, Ohio 45431*

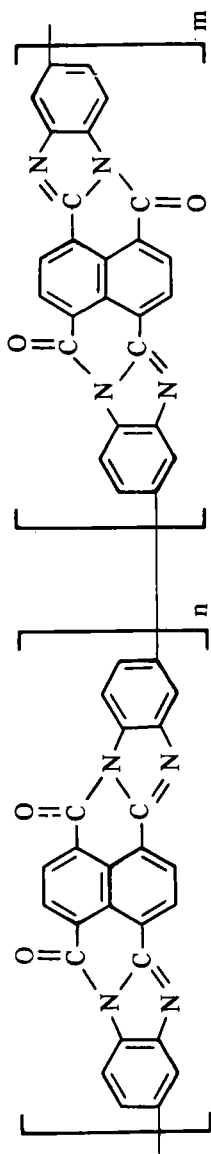
SUMMARY

A polybenzimidazolone prepared by the condensation of 1,4,5,8-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine and several model compounds were thermally degraded (300-500°C) under inert and oxidative conditions. In every case only small fragments, i.e., carbon oxides, cyanogen (trace), and water, were detected by spectroscopic and chromatographic analysis of all phases of the pyrolysis products. The significance of these results is discussed in light of the mechanism by which this aromatic heterocyclic system undergoes oxidative degradation.

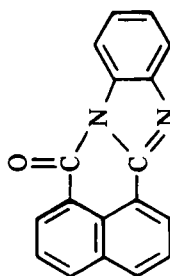
INTRODUCTION

In a series of previous papers [1] a mechanism for the thermooxidative degradation of polybenzimidazolone, polybenzimidazole, and structurally related model compounds was described as being one of preferential oxygenation of the amino-benzenoid linkage as opposed to an active carbon or a unit-by-unit destructive process. We now wish to report in detail the results which were obtained when poly(6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j] benzo[1mn] [2,8] phenanthroline-2,13-diyl) and model

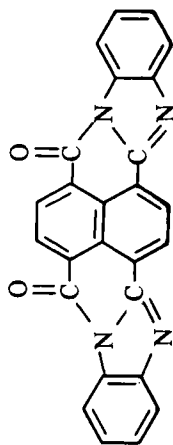
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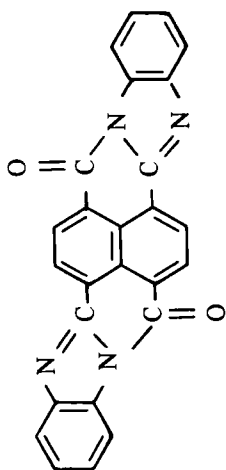
polybenzimidazolone



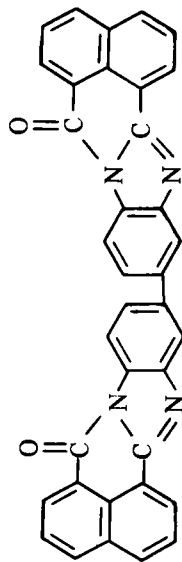
I



III



II



IV

compounds (I-IV) related to its repeat units were subjected to degradative conditions identical to those used for the benzimidazole and benzimide systems [1b]. A mechanistic interpretation is discussed in light of these results and in conjunction with those obtained from the latter materials.

RESULTS AND DISCUSSION

Synthesis

The procedure utilized in the synthesis of the model compounds closely paralleled the method employed in the preparation of the parent polymer, i.e., condensation in polyphosphoric acid [2]. It was thought desirable to use identical synthetic procedures for both the polymer and the model compounds because impurities and spurious functional groups which could have been detected in the latter might affect the mode of degradation of the system [3]. Since vivid color changes were observed, often leading to rather erroneous conclusions regarding the extent of reaction, and since it was subsequently found that continued heating of the reaction mixtures after approximately 90% reaction produced intractable tars, it was found most expeditious to follow the progress of the reactions by spectrophotometric means. The procedure involved removal of aliquots of the mixtures at various time and temperature intervals; after hydrolysis, filtration, and drying in vacuo, infrared spectra of the solids (as Nujol mulls) were examined and compared to spectra obtained from mixtures of the reactants. Generally, the total reaction time was found to be 3 to 5 hr. Between 170 and 210°C the reaction mixtures were homogeneous and translucent, and crude yields of the desired products were always in excess of 80% although yields of purified materials* were considerably lower.

Model compound I was synthesized mainly as an aid in spectral characterization since it was anticipated that its vapor pressure would be too high to allow it to be of great utility in the degradation study itself. Model compounds II and III (the trans-cis isomers, respectively) were not synthesized individually and were separated as their potassium salts [4, 5].

Degradation Studies

The pyrolysis apparatus was identical to that described in the preceding paper, Part II of this series [1b].

*Purified denoting samples resulting in 0.3% of the calculated values for carbon, hydrogen, and nitrogen on combustion analysis.

The polymer and model compounds (I-IV) were subjected to numerous oxidative degradations under a variety of time and temperature conditions. In every case they produced one condensable and three gas phase degradation products. The gaseous products were collected in 10 cm gas cells equipped with sodium chloride optics and were identified by a comparison of their infrared spectra with spectra found in the literature [6, 7] as well as standard samples. The major fraction of these gases consisted of carbon dioxide and carbon monoxide. The third gaseous component, which was found in minute quantities, was identified as cyanogen on the basis of the following observations. The infrared spectra of the gases revealed a weak band between 2100 and 2200 cm^{-1} ; however, due to its low intensity and the fact that carbon monoxide absorbs strongly in this region, a precise band assignment was difficult. In the 700 to 750 cm^{-1} region cyanogen has two highly intense bands and these were discernable in the spectra of the pyrolysis gases. Hydrogen cyanide exhibits intense infrared bands in the 1390 to 1400 cm^{-1} region; these bands did not appear in any of the spectra. Furthermore, when the effluent gases were bubbled through an aqueous silver nitrate solution an off-white solid precipitated. Examination of the precipitate by infrared spectroscopy revealed the presence of a 2165 cm^{-1} band assigned to a nitrile moiety [8-11].

Separation and examination of the gaseous degradation products by gas chromatography was accomplished by the following procedure. A 25.3-ml gas sample loop which was connected to the effluent end of the pyrolysis apparatus permitted the sampling of the gases at any point in the degradation. The separation was carried out by passing the gases from the sample loop into a 6-ft Silica Gel column cooled in a Dry Ice-acetone bath. After the elution of oxygen (retention time: 6 min) and carbon monoxide (retention time: 15 min), the Dry Ice-acetone bath was removed and the column was heated to room temperature. Approximately 7 min after the column reached room temperature carbon dioxide eluted. The retention times were identical to those of standard samples of the gases treated in an identical manner. Since this procedure was known to be useful in the separation of several gases [12], i.e., oxygen, nitrogen, carbon monoxide, carbon dioxide, nitrous oxide, nitric oxide, and methane, it was concluded that no materials other than the carbon oxides were present in the gas phase degradation products.

The only condensable material which was isolated from the degradation products was water. It was identified by a comparison of its retention time in the gas chromatograph as well as its infrared spectrum [12] with a standard sample. When recrystallized samples of model compound IV were

pyrolyzed, *o*-dichlorobenzene, the recrystallization solvent, was detected in the trapping system in minor amounts.

In an attempt to be absolutely certain that no condensable degradation products were formed, several different solvents were used in the trap system, i.e., ether, methylene chloride, chloroform, acetone, and ethanol. All solvents were closely examined by thin-layer chromatography using a number of developers, vapor-phase chromatography with four functionally different columns under a variety of operating conditions, ultraviolet and visible spectroscopy using a large path length cells (10 cm), and infrared spectroscopy of the residual material remaining in the traps after evaporation of the solvent. This latter material was identified as water and the respective model compound. Examination of the boat residue from each degradation by infrared spectroscopy did not reveal an ingrowth or subtraction of any single band or intensity inversion of any group of absorption bands, but instead it merely showed a gradual proportional broadening and weakening of every band in the spectrum as degradation progressed until approximately 35% weight loss was observed. Thereafter band changes are noticeable but interpretation of the changes are not meaningful because of the complex nature of the residual char (see Fig. 1). These observations, coupled with elemental analysis of the boat residues obtained from the initial stages of the degradations [1a], led to the conclusion that the material was a highly cross-linked oxygenated nitrogenous-carbon char. Spectrophotometric and chromatographic examination of the solutions obtained by continuous extraction of the boat residues were shown to contain only the respective undegraded model compounds. An identical result was obtained upon examination of the pyrolysis tube sublimate.

Several thermal degradations were also performed in an attempt to determine whether or not a condensable fraction was produced in the absence of oxygen. However, regardless of the conditions of the experiment, none of the degradations yielded condensable materials. Similar results were obtained when the polymer [13] and a closely related polybenzimidazolone [14] were thermally degraded under inert conditions. It was shown by mass spectral analysis of the effluent gases that carbon monoxide and trace quantities of carbon dioxide and water were produced in the initial stages of degradation. As the degradation progressed, hydrogen, hydrogen cyanide, and cyanide ions were detected along with a mass 40 peak tentatively assigned to the NCN moiety. It can, therefore, be concluded that in the temperature range from 300-500°C under either oxidizing or thermal conditions, polybenzimidazolone and its model compounds degrade essentially into small fragments rather than benzenoid moieties typical of most aromatic polymers, and that an overwhelming percentage of these fragments did not contain nitrogen.

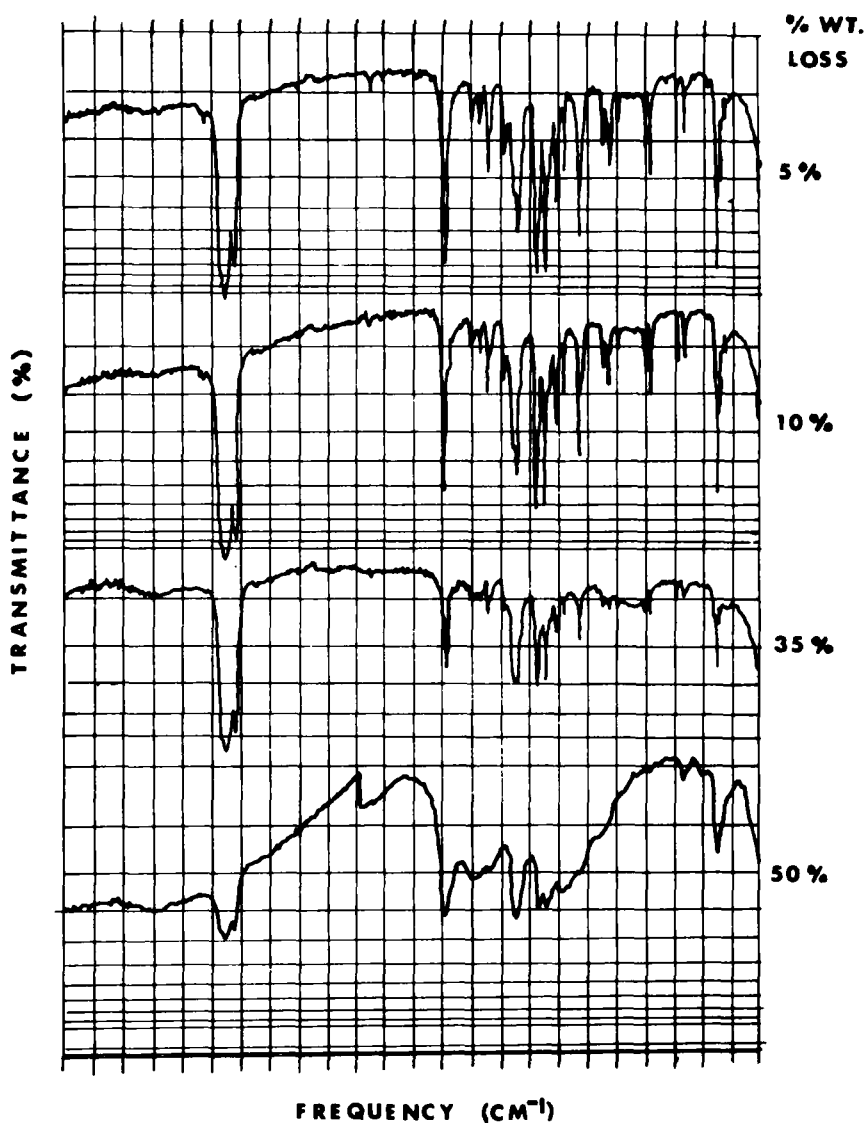


Fig. 1. Typical infrared spectra of boat residues from various stages of degradation (Nujol).

Mechanistic Conclusions

Product analysis of the degradation reactions of polybenzimidazole and its model compounds made two characteristics outstandingly evident. The first is the absence of nitrogen and its oxides in the gaseous degradation products; this behavior is analogous to that exhibited by related imidazole and imide species subjected to identical reaction conditions [1b]. It is proposed that this behavior is mainly due to the involvement of nitrogen in coupling and cross-linking reactions frequently undergone by nitrogen-containing materials during oxidation [15]. The second outstanding and rather unique feature of the degradation reactions of this system is the absence of condensable pyrolysis products (excluding water); this result was not specific to oxidative degradation, but it was noted under inert conditions as well [13, 14]. These observations, coupled with the results obtained from the imidazole and imide materials, aided in the formulation of a plausible mechanism for the oxidative degradation of the imidazolone system.

In the mechanisms postulated for the imidazoles and imides [1b], it was proposed that oxygen preferentially attacked the amine portions of the molecules (i.e., weak-link degradation) as opposed to a unit-by-unit destructive process [16] (i.e., active-carbon degradation) in the initial stages of reaction. The latter stages of reaction probably involve a non-selective oxygenation of the nitrogenous carbon char which is enhanced by its radical nature [17]. During the initial stages of reaction the imidazolone moiety undergoes two simultaneous reactions (Fig. 2). The first is oxygen addition to the nitrogen heterocyclic and adjacent benzoid ring, producing an oxygenated complex (V) closely analogous to that proposed for the imidazole system (Ref. 1b, Fig. 3, structure VI). The second reaction is homolytic cleavage of the carbonyl moiety, producing a nonoxygenated diradical (XI) which is also very similar to the radical species of the imidazole series (Ref. 1b, Fig. 3, structure XII). Parallel reaction pathways were invoked in the imide mechanism as well (Ref. 1b, Fig. 4, structures XIV and XVIII). Direct decomposition of the oxygenated imidazolone intermediate (V) may also result in the formation of species XI. This latter moiety may react with oxygen to form intermediate XII. However, either XI or XII on decomposition can produce the carbon oxides, water, char, and a cyanonaphthenoid radical (X). An analogous pathway was described for the imidazole system; in that case, however, a stable benzenoid molecule was produced which, if it survived subsequent thermal degradation, can escape the reaction zone. The radical nature of the

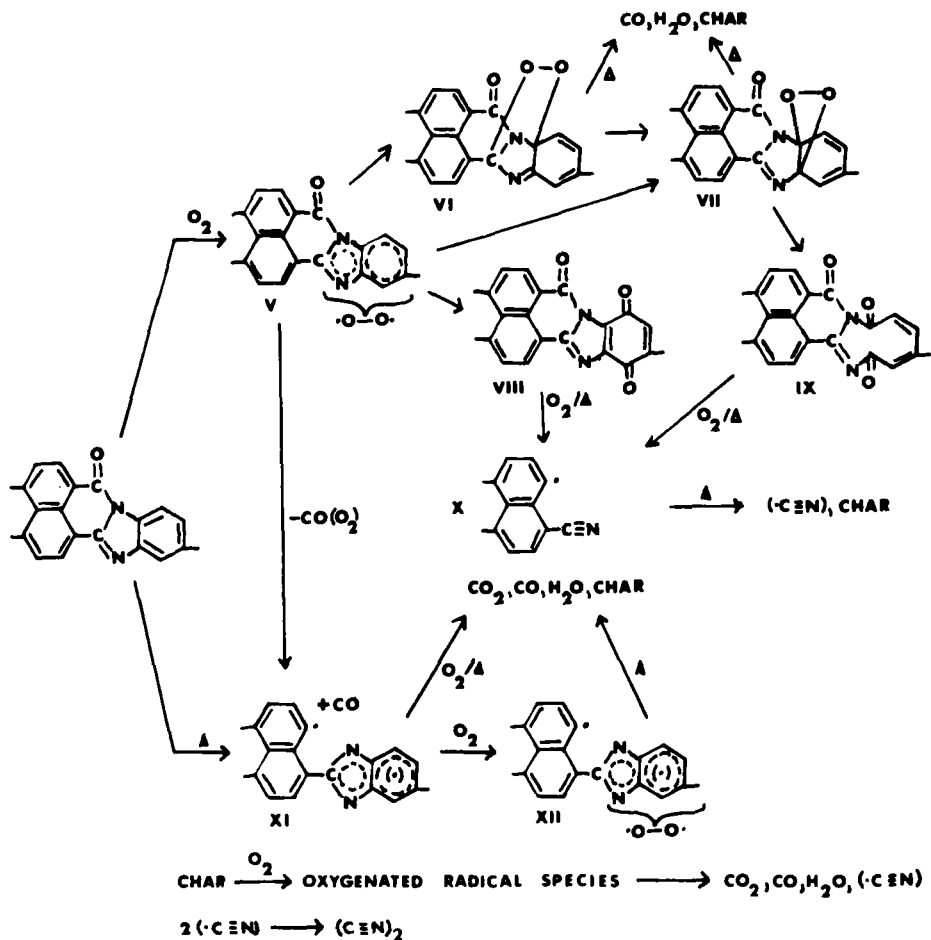


Fig. 2. Proposed mechanism for the thermooxidative degradation of poly-benzimidazolone.

cyanonaphthanoid species (X) must therefore account for the absence of α -cyanonaphthalene in the degradation products of the imidazolone. For example, it can be seen that in order for this formation to occur X must abstract a hydrogen atom from a neighboring species and escape the reaction zone. In the experimental temperature range being investigated, this is a very unlikely process even under inert conditions; when the radical must compete with oxygen for a hydrogen atom, the process becomes

even less favorable. This postulate is verified by the fact that hydrogen appears in the products only as water; hence none of the radical species produced in these reactions effectively abstracts hydrogen when compared to the oxygen reactions taking place. An identical argument was proposed to explain the absence of nitrilo-moieties in the degradation of the imide system [1b], and the same cyanonaphthenoid species was invoked in both mechanisms.

Since the imidazolone moiety contains the imidazole ring system as a basic building block, then transannular (VI) and endo-peroxides (VII) [18-20] as well as quinoid-imidazolone (VIII) and diene-dione (IX) [21-23] structures can be drawn in this system in analogy to those drawn for the imidazoles (Ref. 1b, Fig. 3, structures VII-X). The fact that none of these species was isolated or detected spectroscopically lends support to the view that their existence is extremely short-lived or, in other words, once they are formed they instantaneously decompose at the degradation temperature (ca. 500°C).

EXPERIMENTAL

Synthetic Studies

Polybenzimidazolone. A purified sample of the polymer was supplied by the Materials Laboratory, Wright-Patterson Air Force Base. It was synthesized by condensing 1,4,5,8-naphthalene tetracarboxylic acid and 3,3'-diaminobenzidine in 115% polyphosphoric acid [2].

Synthesis of 1-Benzimidazo(2,1-a)benz(de)isoquinolin-7-one. A 250-g portion of 115% polyphosphoric acid was heated to 120°C in a nitrogen atmosphere for 1/2 hr. After cooling the reaction vessel to 25°C, a mixture of 15 g (0.139 mole) of *o*-phenylenediamine and 27.5 g (0.139 mole) of 1,8-naphthalic anhydride was added under a continuous blanket of dry nitrogen. The stirred polyphosphoric acid mixture was slowly heated. At about 120°C, the solution turned yellow. On reaching a maximum temperature of 190°C, the viscous liquid had turned dark brown. In addition, small white solid particles could be seen suspended in the liquid phase. A small aliquot was removed from the reaction vessel and examined by infrared spectrophotometric techniques. The infrared spectrum obtained from the yellow solid resulting from hydrolysis and isolation of the reaction products indicated the presence of approximately 50% unreacted anhydride. The

progress of the reaction was followed by removing aliquots at 30 min intervals. After 1-1/2 hr at 190°C the anhydride content of the reaction mixture was below 10%. Little further change was noted on continued heating. On cooling to 60°C, the reaction mixture was poured over ice and the resultant ice-acid mixture rapidly agitated. A yellow solid was obtained by filtration of the mixture. The solid was washed with water until the washings were neutral. It was then placed in a high-speed blender with 160 ml of 20% aqueous sodium hydroxide. The mixture was heated at its boiling point for 3 hr, refiltered, and washed with water until the washings were neutral. After drying in vacuo for 12 hr at 100°C, the infrared spectrum of the product indicated the absence of anhydride. Several recrystallizations from methylene chloride-ether yielded 11.8 g (31.5%) of a bright yellow dye, mp 201°C.

Sublimation of the product at 125-130°C at 0.04 mm yielded 5.0 g (13.3%) of a fluorescent, light yellow solid (1) which melted at 206°C.

Analysis calculated for $C_{18}H_{10}ON_2$: C, 79.99%; H, 3.73%; N, 10.36%. Found: C, 80.11%; H, 3.91%; N, 10.50%.

Synthesis of II and III. To previously heated (under a nitrogen blanket) polyphosphoric acid (250 g), a mixture of 16 g (0.148 mole) of *o*-phenylenediamine and 20.9 g (0.0686 mole) of 1,4,5,8-naphthalene tetracarboxylic acid was added slowly with stirring and under a protective dry atmosphere. The temperature was slowly raised to 80°C. The reaction became strongly exothermic and the temperature rose sharply to 120°C at which time the solution turned to a dark red color. The reaction mixture was heated to 160°C and took on a translucent dark red color with white suspended particles in the reaction mass. An aliquot withdrawn from the reaction was hydrolyzed and the product mixture isolated. Infrared examination of the product mixture clearly indicated the presence of anhydride. The temperature was increased to 210°C and maintained at that point until the white particles disappeared (total reaction time including the slow heating period, 5 hr). The reaction mixture was rapidly cooled to 60°C and then poured over ice to hydrolyze the gummy mass. Filtration of this solution yielded a red solid. The solid was washed with water until the washings were neutral and then treated with a 10% solution to sodium hydroxide. After boiling for 2 hr, the alkaline solution was cooled and the red solid recovered by filtration. The solid was washed with water until the washings were neutral and then treated with a 10% solution to sodium hydroxide. After boiling for 2 hr, the alkaline solution was cooled and the red solid recovered by filtration. The solid was washed with water until the washings were neutral, washed with acetone, and dried in vacuo at 100°C for 12 hr. The resulting mixture, 26.0 g (90.7%), mp 410°C, was examined by infrared spectroscopy for anhydride contamination. None was detected. This

mixture of II and III was used without further purification for separation of the isomeric compounds.

Separation of II from III. To a solution of 212 g of 95% ethanol, 14 g of water, and 42 g of potassium hydroxide, 25 g of the mixture of II and III, prepared as described previously, was added. The mixture was heated at reflux for 1 hr, cooled to 10°C, and the potassium salt of the trans isomer (II) which had precipitated was removed by filtration. The isolated material was treated in a similar manner with 45 g of 25% ethanol, 7 g of water, and 12 g of potassium hydroxide. The potassium salt of II was again isolated by filtration. The potassium salt was treated with p-toluenesulfonic acid to destroy the salt and II was isolated. The red-orange solid was recrystallized four times from methylene chloride (large volume)-carbon tetrachloride mixture to yield 3.1 g (12.3%) of the trans isomer II.

The material was sublimed at 280° and 0.01 mm to further purify the product, mp 510°C.

Analysis calculated for $C_{26}H_{12}O_2N_4$: C, 75.66%; H, 2.91%; N, 13.58%. Found: C, 75.60%; H, 2.81%; N, 13.34%.

Isolation of III. The filtrates from the initial isolation of the potassium salt of II were combined and the ethanol removed by distillation. After cooling this mixture to 40°C an equal volume of water was added. The solution was decolorized with activated charcoal and 860 g of 50% aqueous p-toluenesulfonic acid were slowly added. The temperature of the mixture was raised to 55°C for 1/2 hr and then to 90°C for an equal time. The cis isomer was removed by filtering the hot solution and water washed free of alkali and salt. After four recrystallizations from methylene chloride-carbon tetrachloride mixture, 3.05 g (12.3%) of a bright red dye (III) were obtained.

The product was sublimed at 310°C and 0.03 mm pressure, mp 490°C.

Analysis calculated for $C_{26}H_{12}O_2N_4$: C, 75.66%; H, 2.91%; N, 13.58%. Found: C, 75.79%; H, 2.90%; N, 13.43%.

Synthesis of IV. As described previously, pretreated polyphosphoric acid (115%, 500 g) was used to condense 55.6 g (0.278 mole) of 1,8-naphthalic anhydride and 32.0 g (0.149 mole) of 3,3'-diaminobenzidine. Within 1 hr the temperature was raised to 190°C at which point an exothermic reaction was noted. The solution temperature was maintained at 205°C for 3 hr. The reaction was monitored for anhydride at 1/2 hr intervals, and it was noted that after 3 hr the reaction had proceeded to 95% completion. The mixture was cooled to 60°C and isolated, washed, treated with base

and rewashed as previously described. The resulting product was dissolved in concentrated sulfuric acid, treated with activated charcoal, filtered, and reprecipitated by the addition of water. The product was acetone washed and dried in vacuo at 110°C for 12 hr. After three recrystallizations from *o*-dichlorobenzene, 14.6 g (18.1% yield) of IV were obtained, mp 310°C. The crude material was sublimed at 310°C and 0.05 mm to give a purified crystalline product, IV, mp 430°C.

Analysis calculated for $C_{36}H_{18}O_2N_4$: C, 80.29%; H, 3.31%; N, 10.40%. Found: C, 80.36%; H, 3.35%; N, 10.25%.

Degradation Studies

The pyrolysis apparatus used in this study was identical to that described in Part II of this series [1b].

Pyrolytic Degradation of I in Oxygen at 500°C. A sublimed sample of compound I (250 mg) was placed in a ceramic boat and covered with a layer of graphite. The boat was then inserted into the furnace which was maintained at 500°C in an oxygen flow stream. Although sublimation began immediately, enough of the material had decomposed so that a gas sample was obtained and analyzed by infrared spectrophotometry.

By this technique the gas was shown to contain carbon monoxide, carbon dioxide (major component), and a nitrile-containing moiety. When the gas was bubbled through an aqueous silver nitrate solution an off-white solid precipitated; the solid was identified as silver cyanide. Ultraviolet spectrophotometric analysis of the ether solution from the cold traps was identical to compound I. The residue obtained by evaporation of the ether from the cold traps, the pyrolysis tube sublimate, and the boat residue exhibited spectra identical to the starting material; no other condensable material could be detected by the techniques used.

Pyrolytic Degradation of II (trans) in Oxygen at 500°C. A sample of compound II (500 mg) was placed in a ceramic boat and inserted into the furnace maintained at 500°C in an oxygen flow stream. Sporadic flashing and glowing of the sample was noted. Infrared analysis of samples of the gaseous effluent taken at 5 min intervals revealed the presence of carbon dioxide, carbon monoxide, and a nitrile-containing material. When the effluent was bubbled through an aqueous silver nitrate solution an off-white solid precipitated; analysis of the solid using infrared techniques identified it as silver cyanide. Ultraviolet spectral analysis of the ether traps using 50 mm silica cells revealed the presence of the starting material. After

evaporation of the ether from the traps, infrared spectral analysis of the residue showed that it contained the starting material and water. The boat residue and the tube sublimate were also identified as the starting material by infrared analysis of Nujol mulls of these substances; in the case of the former a large amount of carbon char was present as evidenced by scattering in its spectrum.

In other experiments samples (250 mg) of the material were pyrolyzed for 30 min intervals between 250 and 600°C in either an oxygen or helium flow stream. Infrared spectral analysis of the boat residues and tube sublimates as Nujol mulls and KBr pellets clearly illustrated that no changes in band intensities had occurred under oxidative conditions at the lower temperatures. However, as weight loss became greater and sporadic flashing was observed, the spectra showed some over-all band broadening, lack of distinctiveness of the bands, and some background scattering presumably due to char formation as the molecules degraded.

The spectral data from the pyrolysis in inert atmosphere was identical to that obtained from the oxidation experiment except that scattering was not as great at the higher temperatures since the extent of degradation was not as severe.

Pyrolytic Degradation of III (cis) in Oxygen at 500°C. Compound III was pyrolyzed at 500°C in a manner identical to that described for compound II. The behavior of the sample, the gaseous products, and the nature of the residue were found to be identical to II. Experiments on 250 mg samples in oxygen and helium between 250 and 600°C indicated markedly similar thermal and thermooxidative degradation for these two isomeric compounds.

Pyrolytic Degradation of Model Compound IV in Oxygen at 400°C. A sample of recrystallized IV (521.1 mg) was heated in a stream of dry oxygen for a total time of 5 hr and 15 min. For 2 hr and 15 min the temperature was maintained at 300°C to saturate the system with oxygen. For the final 3 hr the temperature was maintained at 400°C. Sample flashing was observed at the 400°C temperature. This phenomenon could be minimized at the earlier stages (the first hour) of oxidation by eliminating the 300°C oxygen exposure.

Gas chromatographic analysis of the ether traps using a silica gel column (40-60 mesh) at both isothermal (50 and 175°C) and program temperature (30-150° at 5°C/min) modes of operation resulted in the detection of only two components, water and o-dichlorobenzene (recrystallization solvent). A second experiment was run using the same pyrolysis conditions. Similarly,

no volatiles other than water and *o*-dichlorobenzene could be detected using Ucon, Carbowax, Silicone, or Silicone-gum nitrile columns and a wide range of isothermal and programmed temperature conditions. It was noted that when the traps were first opened, there was a strong pungent odor present. This odor rapidly disappeared on standing at room temperature. When a trap was raised slowly to room temperature under a helium flow and bubbled through a silver nitrate solution, a white precipitate was formed. The solid produced from the solution was identified as silver cyanide by infrared analysis. The spectrum of the gaseous material was not identical to hydrogen cyanide (1400 cm^{-1} band was absent) and was presumed to be $(\text{CN})_2$, cyanogen.

Pyrolytic Degradation of IV in Oxygen at 450°C . Recrystallized samples of compound IV ranging in weight from 200 to 500 mg were pyrolyzed in oxygen for 30 min; the boat residue consisted of a black char and a reddish crystalline substance. The ether traps were shown to contain water and *o*-dichlorobenzene by vapor-phase chromatographic and infrared analysis. The second and third samples were exposed to oxygen at 450°C for 120 and 180 min, respectively; at various time periods both samples underwent sporadic, localized flashing. The black charred boat residues were continuously extracted with *o*-dichlorobenzene for 24 hr. The solid extracts were identified by infrared spectroscopy as starting material. The gases escaping from the trap system were reactive toward silver ion, yielding a precipitate which was identified by its infrared spectrum as silver cyanide.

Pyrolytic Degradation of IV in Nitrogen at 450°C . A sublimed sample of IV (257.1 mg) was heated at an oven temperature of 450°C under dry nitrogen for 30 min. Approximately 8 min after insertion of the sample into the hot zone, a yellow sublimate was detected in the cold region of the tube prior to the trapping system. On cooling of the sample, the residue was found to be a dark charlike material (242.9 mg, 94.5% weight retention). The infrared spectrum was weakly characteristic of the starting material (no new bands were present and no intensity inversions of bands were noticeable). The sublimate in the tube was removed and compared spectrally with the starting material to confirm its identity. The trap contained only a single component, water. No other condensable materials could be detected.

Oxidation of Compound IV at 250, 300, 350, and 400°C in Oxygen for Extended Exposure Time. Using procedures identical to those previously described, degradations were carried out on recrystallized samples of compound IV at temperatures between 250 and 400°C for exposure time upwards of 18 hr. Residues, trapped components, and gaseous effluents were investigated using infrared and ultraviolet spectroscopy and vapor-phase chromatography. Using these techniques, compound IV, water, carbon dioxide, carbon monoxide, cyanogen, and *o*-dichlorobenzene (the recrystallization solvent) were the only materials detected from the degradation.

Pyrolytic Degradation of Compound IV in Air at Temperatures Between 250 and 450°C for Extended Exposure Time. Using the procedures previously described, degradations were performed in dry air. The results were virtually identical in all respects with those obtained in oxygen. Spectral studies, vapor-phase chromatography, and weight loss studies all yielded essentially identical data to that already described in oxygen.

Pyrolytic Degradation of Compound IV in Oxygen at 500°C. A sublimed sample (250 mg) of compound IV was pyrolyzed at 500°C in an oxygen flow stream. After approximately 8 min the sample began to glow. The gaseous effluent was monitored at 10 min intervals by infrared techniques; the spectra revealed the presence of carbon dioxide, carbon monoxide, and lesser quantities of nitrile-containing material. Ultra-violet spectral analysis of the ether solutions from the traps revealed the presence of compound IV only. Infrared analysis of the boat residue and tube sublimate proved that they contained carbon char and compound IV, respectively.

In other experiments eight individual 250 mg samples of compounds IV were pyrolyzed in oxygen for 30 min at 50° temperature intervals between 250 and 600°C. Infrared spectral analysis of the boat residues and tube sublimates clearly illustrated that no changes in band intensities had occurred; the spectra were, in fact, identical to the starting material when small weight losses had occurred, and they were similar to, although much more diffuse than, the starting material for samples which had undergone extensive degradation.

Six 250 mg samples of compound IV were pyrolyzed in a helium atmosphere in a temperature range of 350-600°C for 30 min each. Infrared spectral analysis of the boat residues were identical to those mentioned above.

Pyrolytic Degradations of Polybenzimidazolone at 500°C in Oxygen. A finely ground 250 mg sample of polybenzimidazolone was thermooxidatively degraded at 500°C. Infrared monitoring of the effluent gases at 10 min

intervals revealed the presence of carbon dioxide, carbon monoxide, and a nitrile-containing material. The effluent gases were bubbled through an aqueous silver nitrate solution; the resulting off-white precipitate was identified as silver cyanide.

Analysis of the traps by ultraviolet spectroscopy exhibited no interpretable results. The boat residue which was analyzed by infrared spectroscopy contained starting material and carbon char, and in the extensive stages of degradation a sulfate salt. This latter material was assumed to be occluded solvent (H_2SO_4). The clear liquid which had condensed in the delivery tube was identified as water. As expected, no sublimate was found in the experiment.

Instruments

Infrared spectra were taken on either a Beckman IR-10 or a Perkin-Elmer Model 621 spectrometer.

Ultraviolet spectra were recorded on a Carey 14 Recording spectrometer.

Gas chromatographic analyses were obtained by use of either an F&M Model 720 or an Aerograph 1525-B chromatograph.

Pyrolyses were performed by means of a Lindberg Heavi-Duty tube furnace and control console.

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