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

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

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SUMMARY

A series of benzimidazole and benzimide model compounds were oxidatively degraded at high temperatures (350-600°C). All of the compounds degraded to small fragments, i.e., carbon oxides, cyanogen (trace), and water, as well as condensable materials such as nitriles and anhydrides. The most outstanding feature of the degradation was the origin of these latter pyrolysis products; in each case they originated from the acid portion of the molecule. Nitrogen was noticeably absent in both the gas phase and the condensable degradation products except as nitrilo-moieties. Poly-2,2′(m-phenylene)5,5′-bibenzimidazole produced similar products. The proposed mechanism invokes a preferential attack by oxygen at the aminobenzenoid rings.

INTRODUCTION

In a previous paper [1a] the oxidative degradation of poly-(6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1′,2′-j]benzo[1mn] [2,8] phenanthroline-2,13-diyl) and model compounds related to its various repeat units as well as structurally related benzimidazole and benzimide models and

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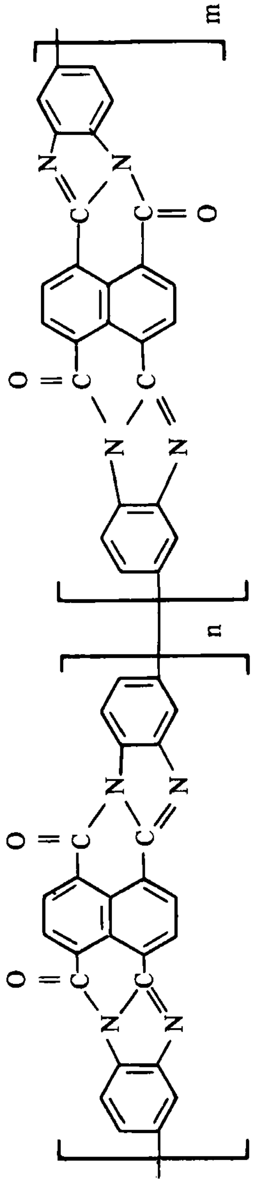
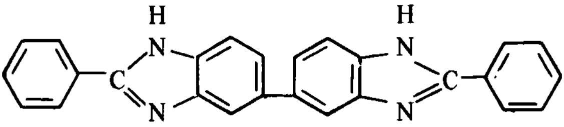
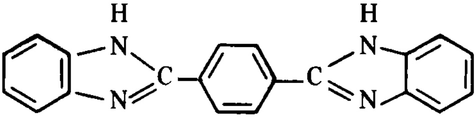


Polybenzimidazolone

poly-2,2′(m-phenylene(5,5′(6,6′)benzimidazole was described in a general fashion. The degradation was reported to proceed via oxygenation of the amine-containing benzenoid ring. It is the purpose of this article to give a detailed account and a proposed interpretation of the results obtained when polybenzimidazole, benzimidazole model compounds (I and II), and benzimide model compounds (III-V) were subjected to high temperatures (350-600°) in oxygen atmospheres.



I



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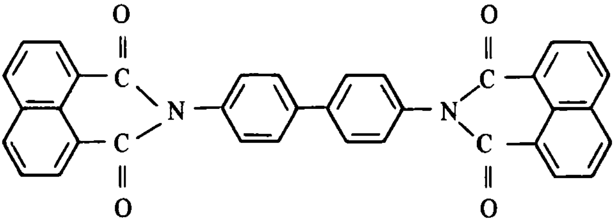

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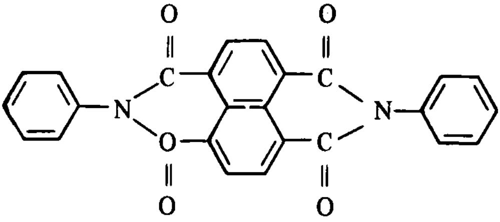
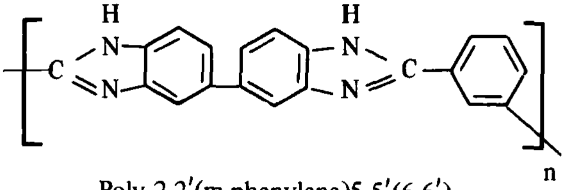
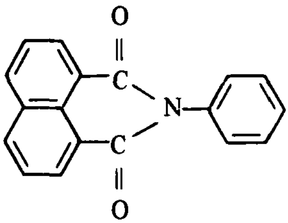


IV

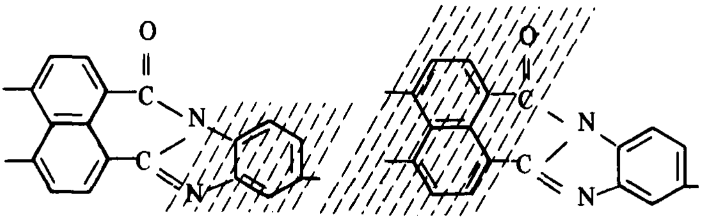


Poly-2,2′(m-phenylene)5,5′(6,6′)-
bibenzimidazole



V

Although primary interest centered on the delineation of the degradation mechanism of polybenzimidazolone, the benzimidazole and benzimide heterocyclic systems were also chosen for the study because the imidazolone can be viewed as a hybrid of the imide (A) and imidazole (B) heterocyclics.



(A) (B)

RESULTS AND DISCUSSION

Synthesis

The procedures employed in the synthesis of the imidazole and imide model compounds were identical to those used in the preparation of polybenzimidazolone, i.e., condensation of the appropriate amines and acids in polyphosphoric acid [2]. A detailed discussion of the synthetic procedure can be found in the accompanying paper, Part III of this series [lb].

Model compound V was prepared mainly as an aid in the spectral characterization of the other imide models; it was not used for pyrolysis because its high vapor pressure caused it to sublime out of the hot zone of the tube furnace before it degraded. A similar imidazole model was not prepared because synthesis and spectral characterization pertaining to this class of compounds is well documented [3-8].

Degradation Studies

After several extensive preliminary investigations concerning the instrumentation design most suitable for the study, a rather classical pyrolysis apparatus was adapted (Fig. 1). It was designed so that all phases of the degradation products under thermal or oxidative conditions could have been investigated by any one of several techniques.

When model compounds I through IV and polybenzimidazole were subjected to oxidizing atmospheres in the temperature range of 350-600°C, three gaseous degradation products were produced. These gases were collected in 10 cm gas cells equipped with NaCl optics and examined by infrared spectroscopy. The spectra were compared to those obtained from the imidazolone system [1] as well as standard samples and literature data [9, 10]; they were identified as carbon monoxide, carbon dioxide, and a nitrile-containing material. When the gases were bubbled through a solution of aqueous silver nitrate, an off-white precipitate formed; the solid was identified as silver cyanide by infrared analysis [11-14]. Since the infrared spectrum of the mixture of the gases exhibited no 1400 cm^{-1} absorption band (assigned to the H–CN bending vibration in hydrogen cyanide), it was concluded that the nitrile-containing gas was cyanogen. Separation and examination of the gaseous mixture by gas chromatographic techniques was accomplished using a procedure previously reported [15]. Carbon dioxide and carbon monoxide were identified by a comparison of their retention times with those of standard samples. Excluding cyanogen, no nitrogen-containing gases, i.e., nitrogen and nitrogen oxides, or other gaseous compounds, i.e., acetylene, ethylene, methane, etc., were detected.

In addition to the gaseous products, these compounds produced water and aromatic condensable materials. For example, when model compound I was oxidatively degraded, water together with the undegraded model and benzonitrile were identified on examination of the ethereal solution obtained from the trap system. This latter compound was identified by a comparison of its ultraviolet and infrared spectra as well as its vapor-phase

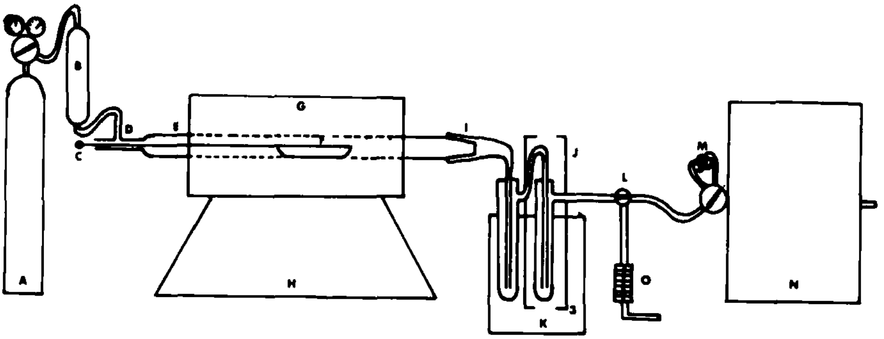
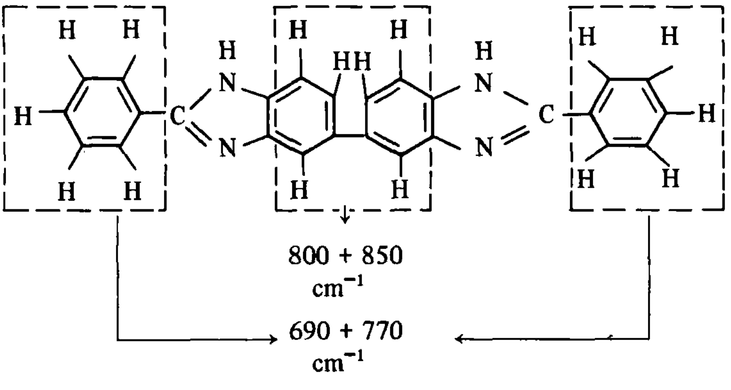


Fig. 1. Pyrolysis apparatus. (A) Gas source: O_2, N_2, helium, or air; (B) purification and drying system; (C) sample control rod; (D) gas inlet system; (E) quartz pyrolysis chamber; (F) sample and boat; (G) oven (Lindberg, 54031); (H) control console (Lindberg, 59344); (I) exit system; (J) trapping system; (K) Dewar flask; (L) 3-way valve; (M) sampling valve and loop; (N) vapor-phase chromatograph; (O) flow metering system.

chromatographic retention time with both the literature [9] and a standard sample. Infrared analysis of the pyrolysis tube sublimate showed that it contained only compound I. However, examination of the boat residues from several stages of the degradation by infrared spectroscopy revealed intensity inversions of the absorption bands assigned to the out-of-plane bending vibrations of the benzenoid hydrogen atoms on the 1,2,4-trisubstituted benzene rings (800 and 850 cm^{-1}) relative to hydrogen atoms on the mono-substituted benzene rings (690 and 770 cm^{-1}).



The hydrogen atom absorption bands from the nitrogen-containing benzene rings gradually decreased in the initial stages of degradation while the absorption bands from the carbon-containing benzene rings increased (Fig. 2). This result was interpreted as being due to the rupture of one of the bonds of the nitrogen-containing benzene rings. This change in the infrared spectrum could have been brought about by oxygen addition or, since a similar observation has been reported for the thermally induced degradation of the parent polymer [16], it could have occurred primarily through homolytic cleavage [17] of the 1,2,4-trisubstituted rings.

The thermoooxidative degradation of poly-2,2′(m-phenylene)5,5′(6,6′) bibenzimidazole gave results which were analogous to the pyrolyses of the model compounds. The gas phase degradation products were carbon dioxide, carbon monoxide, and trace quantities of cyanogen. The condensable phase degradation products were water and 1,3-dicyanobenzene. Both 1,3- and 1,4-dicyanobenzene were obtained when the corresponding polymers were thermally degraded [18]. The boat residues from several stages of the degradations were examined by infrared spectroscopy. However, definite interpretation regarding band intensity inversions was not performed because of the diffuse nature of the spectra.

The thermooxidative degradation of model compound III, a diimide, gave strikingly similar results to those obtained from the previously mentioned materials. The gas phase degradation products obtained from several stages of degradation were carbon dioxide, carbon monoxide, and cyanogen. Examination of the trap system from various stages of degradation by spectroscopic and vapor-phase chromatographic techniques revealed the presence of water, compound III, and 1,8-napthalic anhydride. The anhydride was also found in the pyrolysis tube sublimate along with compound III. Unfortuantely, examination of the boat residues from several stages of the degradation failed to show any evidence of band intensity inversions as was the case for compound I.

At this point one facet of the degradation was outstandingly clear. In no instance was there to be found any nitrogen-containing benzenoid moiety from the amine-ring linkage in either the solid or liquid phases of the degradation products, and furthermore, the gas phase products contained only trace quantities of a nitrogen-containing gas, i.e., cyanogen. It was reasoned that perhaps this unusual phenomenon was due to the fact that the aromatic condensable fragments (i.e., benzonitrile from compound I and 1,8-naphthalic anhydride from compound III), in each case, were derived from those sections of the molecules which were located at their ends. It was, therefore, decided to synthesize an imidazole model (II) and an imide model (IV) in which the nitrogen-containing benzenoid portions were located at the ends of the molecule and then to search carefully for aromatic amines and related oxygenated compounds in the degradation products.

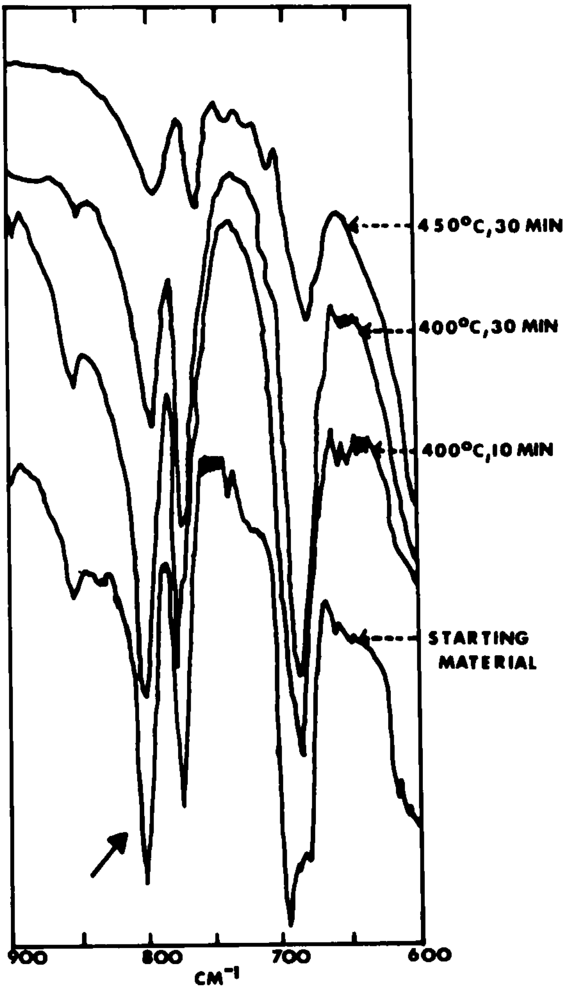
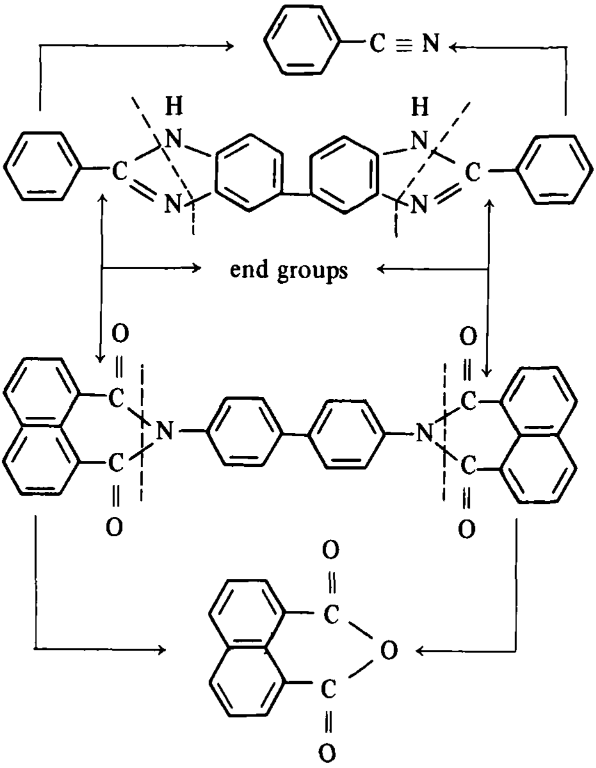


Fig. 2. Infrared spectrum of compound I at various stages of degradation in oxygen. Arrow denotes absorption band corresponding to 1,2,4-trisubstituted benzene rings.

The procedure utilized in the thermooxidative degradation of compound II was identical to that used in all previous pyrolyses. The gas phase degradation products were identified as carbon dioxide, carbon monoxide, and cyanogen by a comparison with standard samples. No other nitrogen-containing gases were found. Examination of the trapping system revealed the presence of water, compound II, and a nitrile-containing compound which was identified as 1,4-dicyanobenzene. The tube sublimate consisted of compound II and terephthalic acid; the latter substance was identified by a comparison of its infrared spectrum with that of a standard sample and a mixed melting point (both the mixture and the individual samples did not melt but sublimed at 300°C). Infrared analysis of the boat residues obtained from various stages of the degradation were shown to contain carbon char and minute amounts of compound II.

In an attempt to isolate o-phenylenediamine or a related nitrogen-containing aromatic material, the effluent was passed through a trap con-



taining concentrated hydrochloric acid. The acid was neutralized and extracted with ether; the ethereal extracts were examined by visible and ultraviolet spectroscopy and were shown to be void of any organic material. Infrared analysis of the residue revealed the presence of a very weak absorption band at 2250 cm^{-1} which was assigned to a C≡N stretching vibration. It was concluded from these results that a nitrogen-containing aromatic material related to the amine ring moiety of compound II was not produced.

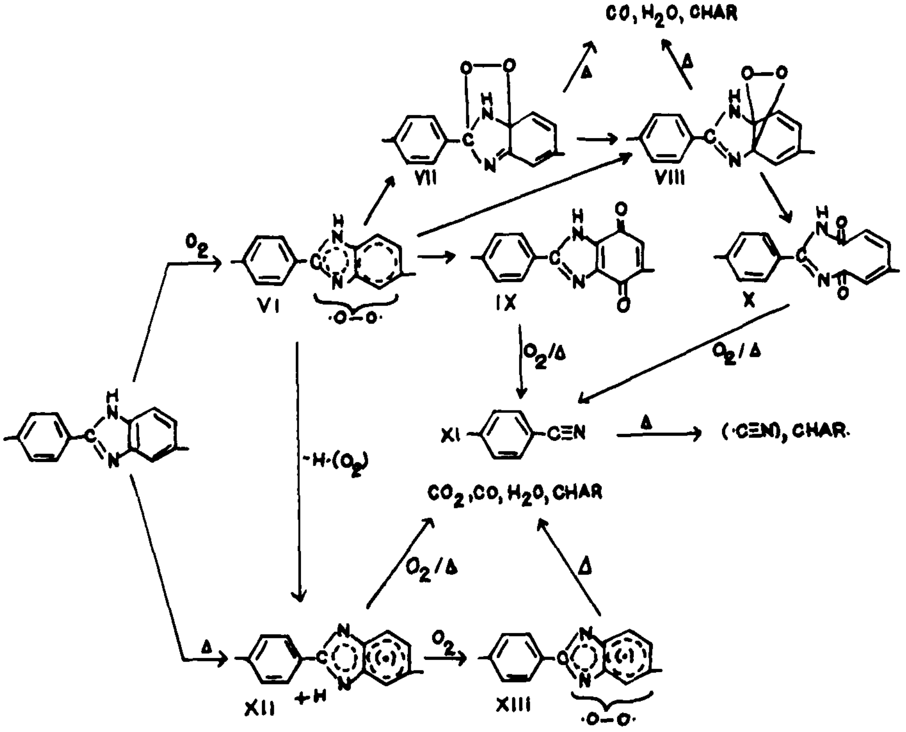
The thermooxidative degradation of compound IV resulted in gas phase degradation products consisting of the carbon oxides and cyanogen. Analysis of the products from the trapping system revealed the presence of water, compound IV, and a material which was tentatively identified as 1,4,5,8-naphthalenedianhydride. The tube sublimate was analyzed by infrared spectroscopy; it contained compound IV and the dianhydride. However, because so little of the latter material was recovered, the resulting spectrum was very weak, making definite interpretation impossible. The boat residues from several stages of degradation were analyzed by infrared spectroscopy, but the spectra merely exhibited a gradual proportional decrease of all band intensities.

The effluent from the pyrolysis was passed through concentrated hydrochloric acid in an attempt to isolate any aromatic amine fragment which might have escaped from the ether filled traps. The acid was neutralized and extracted with ether. The ethereal extracts were examined by visible and ultraviolet spectroscopy using 10 cm cells; the spectrum was void of any absorptions. The ether solution was evaporated to yield water. Hence, it was concluded that the thermooxidative degradation of the imide model compounds did not produce nitrogen-containing benzenoid moieties of any kind.

These observations led to the conclusion that, regardless of its position in the model compound, the amine portion of the molecule in all these systems underwent complete degradation followed by the formation of a crosslinked nitrogenous-carbon char (see Ref. 1a for elemental analyses of the carbon chars).

Mechanistic Conclusions

Several reactions must be proposed for the thermooxidation of the benzimidazoles (Fig. 3) since the nature of the products obtained from both thermal and oxidative degradation revealed very close similarities. For



$$\text{CHAR} \xrightarrow{O_2} \text{OXYGENATED RADICAL SPECIES} \longrightarrow CO_2, CO, H_2O, (\cdot C{\equiv}N)$$

$$2(\cdot C{\equiv}N) \longrightarrow (C{\equiv}N)_2$$

Fig. 3. Proposed mechanism for the thermooxidative degradation of polybenzimidazole.

example, degradation of the polymer in vacuo yielded hydrogen, hydrogen cyanide, and nitrilo-moieties [17, 18]; under oxidative conditions water, cyanogen, and analogous nitrile compounds (XI) were detected along with large amounts of carbon dioxide and carbon monoxide. These observations, coupled with the fact that replacement of the imidazole hydrogen atom with a phenyl group markedly increased the stability of the resulting polymer under isothermal conditions in air [19], led to the conclusion that the most labile site for either oxygenation or thermal scission was the imidazole hydrogen-nitrogen bond. Furthermore, because of their aromatic nature, the imidazole ring [20] and the adjacent benzenoid ring have a great potential for resonance stabilization, thus making radical formation very facile. Hence, either hydrogen abstraction by oxygen or homolytic cleavage of the imidazole hydrogen-nitrogen bond resulted in the formation of the same radical species (XII).

Since product analysis indicates that the nitrogen-containing heterocyclic and benzenoid rings are the weak-link in the oxidation of the benzimidazole system and yet the exact nature and position of the atom(s) undergoing initial oxidation was not delineated, species VI is the only oxygenated structure that can be drawn with any certainty. The subsequent formation and decomposition of either a transannular peroxide [21-23] (VII), an endoperoxide (VIII), or a quinoid-imidazole [24-26] (IX) can account for the observed products; rearrangement of the transannular peroxide (VII) to the endoperoxide (VIII) followed by the formation and decomposition of a diene-dione (X) will give the same results. However, the fact that none of these oxygenated species were isolabile nor spectroscopically observable under experimental conditions, i.e., temperatures in excess of 400°C, suggests that their formation was instaneously followed by catastrophic decomposition.

The similarity between structures XIII, formed by either thermal or oxidative scission of the imidazole hydrogen–nitrogen bond, and VI formed by oxidative means alone, helps emphasize the competitive and complex nature of the reactions being studied.

The oxidative degradation of the imide system (Fig. 4) most probably follows reaction pathways analogous to those of the imidazole system on the basis of product similarity. For example, the oxygenated species XIV (analogous to VI, Fig. 3) can be written as XV or XVI (analogous to structures VII-X) since the oxidation of either may yield an anydride, the carbon oxides, char, and water. These intermediates can also be used to explain the relative amounts of completely labeled and partially labeled carbon dioxide that were produced when a polyimide was subjected to high temperatures (ca. 300°C) in an oxygen-18 enriched atmosphere [27].

A nonoxygen induced degradation occurring simultaneously with oxidative degradation is a likely possibility, particularly since the radicals (XVIII) formed by this reaction can account for product formation (with the exception of the anhydrides). A rather interesting and perhaps significant thermal reaction is the rearrangement of the imide to the isoimide [28] (XX). Thermal degradation of the latter species may produce carbon

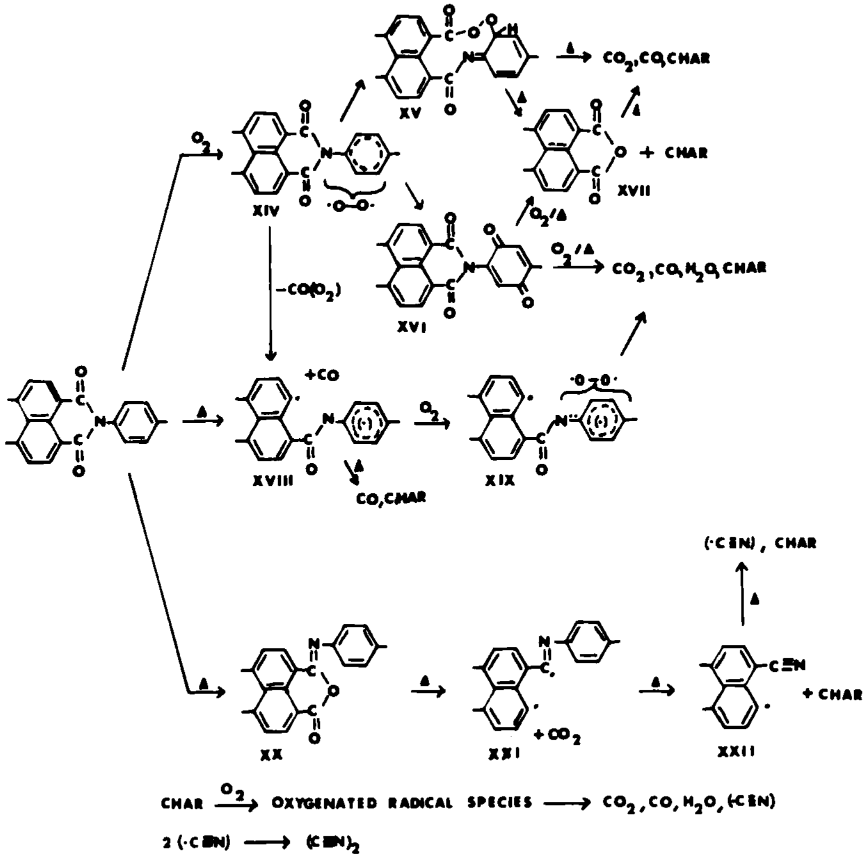


Fig. 4. Proposed mechanism for the thermooxidative degradation of polyimides

dioxide and eventually the nitrilo-naphthanoid radical (XXII). It is the radical nature of this nitrilo-moiety, as opposed to the stable cyanobenzenoids (XI) produced by the imidazole system, that may account for the absence of cyanonaphthalene and related products.

The absence of nitrogen in the gas phase products as either nitrogen or nitrogen oxides and in the condensable phase products except as nitrilo-moieties may be rationalized by invoking the well-documented coupling reactions observed in amine oxidations [29]. Hence, the large quantities of char produced in these experiments are highly crosslinked, as evidenced by infrared analysis of the pyrolysis residues, and probably free radical in nature [17]. It is the radical nature of these chars that enhances their susceptibility toward oxygenation, and undoubtedly this accounts for the pronounced differences in weight retention of the polymeric materials when degraded in air as opposed to inert conditions [30].

EXPERIMENTAL

Synthetic Studies

Polybenzimidazole. A purified sample of the polymer was supplied by the Materials Laboratory, Wright-Patterson Air Force Base. It was synthesized by melt condensation of diphenyl isophthalate and 3,3′-diaminobenzidine.

Synthesis of I (2,2′-diphenyl-5,5′-bibenzimidazole). A mixture of 16.00 g (0.075 mole) of 3,3′-diaminobenzidine and 18.18 g (0.149 mole) of benzoic acid was slowly heated to 220°C. After 1 hr, an examination of a sample obtained from an aliquot by infrared spectroscopy indicated no carbonyl group from the acid remained. The reaction mixture was cooled to 65°C, hydrolyzed, and the product isolated and washed until neutral. The resulting solid was recrystallized twice from N,N-dimethylacetamide and water. After drying at 110°C for 3 hr in vacuo, the product I, mp 337°, was sublimed at 300° and 0.05 mm (mp 409°).

Analysis calculated for $C_{26}H_{18}N_4$: C, 80.81%; H, 4.69%; N, 14.50%. Found: C, 80.60%; H, 4.78%; N, 14.39%.

Synthesis of II. To a pretreated 250 g portion of 115% polyphosphoric acid, a mixture containing 18.0 g (0.1610 mole) of o-phenylenediamine and 13.4 g (0.0805 mole) of terephthalic acid was added with rapid stirring in an inert atmosphere. The temperature was raised to 195°C where it was held for 30 min. After this unusually short reaction time, an examination of a sample obtained from an aliquot by the usual techniques indicated no carbonyl group from the acid remained. The reaction mixture was cooled to 65°C, hydrolyzed, and the white flocculent product isolated and washed with water. After grinding it in the blender with saturated sodium bicarbonate, it was filtered, washed several times with water, and dried in a vacuum oven for 12 hr. The crude yield was 19.1 g (76.5%).

After one recrystallization from a large volume of N,N-dimethylformamide and water, the off-white granular solid, mp (decomp) 472°C, was sublimed at 250°C and 10^{-5} mm. The pure white sublimate melted at 482°C.

Analysis calculated for $C_{20}H_{14}N_4$: C, 77.40%; H, 4.55%; N, 18.05%. Found: C, 77.27%; H, 4.49%; N, 18.00%.

Synthesis of III. A 250 g portion of 115% polyphosphoric acid was heated to 175°C in a helium atmosphere. When the acid cooled to 75°C a mixture containing 11.8 g (0.0642 mole) of benzidine and 25.32 g (0.128 mole) of 1,8-napthalic anhydride was added. The reaction mixture was heated to 240°C over a 2-hr period; no exothermic reaction was noted. The temperature was held at 200°C for 3 hr at which time the anhydride bands, by infrared analysis, ceased to decrease. The reaction mixture was cooled to 60°C and poured over ice in order to hydrolyze the acid. The yellow-green solid was filtered, washed several times with water, and then, after grinding in the blender in 10% sodium hydroxide solution, it was boiled in this solution for 12 hr. The solid was filtered, washed with water until neutral, and dried in vacuo for 36 hr. The crude yield was 28.8 g (82.5%).

After two recrystallizations with concentrated sulfuric acid and water followed by two recrystallizations from N,N-dimethylforamide and water, the solid had lost its yellow-green color, mp 505°C.

Analysis calculated for $C_{36}H_{20}O_4N_2$: C, 79.40%; H, 3.70%; N, 5.14%. Found: C, 79.16%; H, 3.75%; N, 5.30%.

Synthesis of IV (N,N′-diphenyl-1,4,5,8-naphthalene diimide). A 250-g portion of 115% polyphosphoric acid was heated to 125°C in a helium atmosphere. When the acid cooled to 65°C, a mixture containing 11.91 g (0.1436 mole) of aniline and 21.9 g (0.0718 mole) of 1,4,5,8-naphthalene tetracarboxylic acid was added. The reaction mixture was heated to 240°C over a period of 5-1/2 hr; no exothermic reaction was noted. The temperature was held at 240°C for 2 hr at which time the acid bands, by infrared analysis, ceased to decrease. The reaction mixture was cooled to 60°C and poured over ice to hydrolyze the acid. The dark green solid was filtered, washed several times with water, and then, after grinding in the blender in 10% sodium hydroxide solution, it was boiled in this solution for 2 hr. The solid was filtered, washed with water until neutral, and dried in a vacuum oven for 12 hr. The crude yield was 25.0 g (83.2%).

After four recrystallizations with N,N-dimethylformamide and water, the pink needlelike crystals, mp 472-3°C, were sublimed at 290°C and 0.31 mm. The light pink sublimate melted at 475°C.

Analysis calculated for $C_{26}H_{14}O_4N_2$: C, 74.64%; H, 3.37%; N, 6.70%. Found: C, 74.64%; H, 3.35%; N, 6.60%.

Synthesis of V (N-phenyl-1,8-naphthalimide). Polyphosphoric acid (115%, 250 g) was heated to 120°C in a nitrogen atmosphere for 1/2 hr. After cooling the acid to 25°C, a mixture of 10.93 g (0.139 mole) of aniline and 27.5 g (0.139 mole) of 1,8-naphthalic anhydride was added under a protective blanket of dry nitrogen.

The temperature was slowly increased to 200°C. At 210°C the solution turned dark yellow and became homogeneous. The reaction mixture was examined by removal by an aliquot, hydrolysis and isolation of the products; the infrared spectrum indicated an imide concentration of approximately 20%. This procedure was repeated every 1/2 hr. After 2-1/2 hr (the anhydride content was less than 5%) the reaction mixture was cooled to 65°C. The solution was hydrolyzed and worked up as previously described for compounds I to IV. The solid was collected by filtration, washed with water until neutral, and dried in vacuo at 110°C for 12 hr. Several recrystallizations from acetone-water produced 9.0 g (23.6%) of a white crystalline V, mp 200°C. V was sublimed at 120°C and 0.05 mm; after sublimation, the melting point was unchanged.

Analysis calculated for $C_{18}H_{11}O_2N$: C, 79.11%; H, 4.06%; N, 5.13%. Found: C, 79.01%; H, 4.09%; N, 5.09%.

Degradation Studies

Typical Operation of the Pyrolysis Apparatus. The sample to be oxidized and its ceramic boat (F, Fig. 1) were weighed and placed into the cool zone of the pyrolysis chamber for 15 min while a flow of the particular carrier gas was maintained over the sample. The sample was moved into and out of the hot zone using the Nichrome wire rod (C). Samples for gas phase analysis were passed directly from the pyrolysis unit (H) into the sample coil loop (M) of the gas chromatographic unit (N) or an infrared gas sampling cell (not shown) through valve (L). When gas analyses were not carried out, the effluents were vented into the hood. At the termination of each run, the boat and residue were cooled at the end of the pyrolysis chamber and desiccated prior to reweighing for weight loss data.

All apparatus in the flow system were thoroughly cleaned with chromic acid solution, water rinsed, baked overnight at 120°C, and then desiccated prior to use. This procedure was repeated between runs.

Pyrolytic Degradation of Compound I in Oxygen at 500°C. Ceramic boats charged with 250 mg of compound I were inserted into the pyrolysis tube maintained at 500°C in an oxygen flow stream. The gas phase of the degradation products was analyzed by infrared spectroscopy. The spectra revealed the presence of carbon dioxide, carbon monoxide, and a nitrile-containing material. When the effluent gas was bubbled through an aqueous silver nitrate solution a white precipitate formed; the infrared spectrum of this solid was identical to that of silver cyanide.

The effluent was bubbled through an acetone-Dry Ice cooled ether trap; the ultraviolet spectrum of the resulting solution using 10 mm silica cells indicated the presence of benzonitrile. This material was identified by comparing its spectrum to that of an authentic sample of benzonitrile and to the published spectrum (A.P.I. Index).

Gas chromatographic analysis indicated the presence of only one material, the retention time of which was identical to an authentic sample of benzonitrile. When the latter was added to the trap solution one enhanced peak was obtained on the chromatogram; the operating conditions were as follows:

bridge current	100 mA
detector temperature	250°C
injection temperature	235°C
column temperature	120°C (isothermal)
column	SE 30 (5%) on chromasorb W
flow rate	60 ml/min
attenuation	1 X

Infrared analysis of the white sublimate in the pyrolysis tube showed it to be the starting material. The clear liquid in the delivery tube was identified as water. The boat residue, a black charred solid, was identified as the starting material mixed with large amounts of carbon char. In additional experiments samples of compound I (approximately 100 mg each) were heated in oxygen for 30 min each in the 250 to 550°C range at 50° intervals. At temperatures above 400°C similar results to those described above were obtained.

Pyrolytic Degradation of Compound II in Oxygen at 500°C. An unweighed quantity of model compound II was placed in the pyrolysis tube at 500°C in an oxygen atmosphere. Samples of the gaseous effluent were analyzed by infrared spectroscopy; the gases proved to be identical to all previous examples - carbon dioxide (major component), carbon monoxide, and a nitrile-containing material. The boat residues were also examied by infrared; the soft gray solid contained a very small amount of starting material. The tube sublimate was identified as terephthalic acid by infrared analysis and by running a mixed melting point determination with a stock sample. In this case the mixture did not melt but sublimed at 300°C.

Ultraviolet spectral analysis of the ether traps after filtration and drying were found to contain starting material. Infrared analysis of the ether trap solution and residue showed the presence of a weak nitrile band along with starting material.

The traps were filled with concentrated hydrochloric acid and the effluent was bubbled through them. The acidic solution was neutralized, extracted several times with ether, dried, filtered, and evaporated; spectral examination of the ether extracts failed to give any evidence of the presence of aniline, an aromatic amine moiety, or any oxidized aromatic nitrogen-containing materials. Using the same technique, samples of II (100 mg each) were introduced into the pyrolysis chamber at several temperatures ranging from 300-600°C in an oxygen atmosphere for 30 min. Infrared spectral analysis of the boat residues showed a gradual decrease in band intensities accompanied by broadening and scattering.

Pyrolytic Degradation of Polybenzimidazole at 400 and 500°C in Oxygen. An unweighed quantity of polybenzimidazole, the polymer formed by condensation of phenyl isophthalate and 3,3′-diaminobenzidine, was placed in the pyrolysis chamber at 500°C in an oxygen flow stream. Infrared spectral analysis of the gaseous effluent using a 10-cm gas cell gave results which were identical to all previous examples, i.e., carbon dioxide (major component), carbon monoxide, and a nitrile-containing material. Infrared analysis of the boat residue resembled starting material, although the degree of scattering made definite interpretation impossible. Due to the sample size a very weak infrared spectrum was obtained on the pyrolysis tube sublimate; however, infrared spectra coupled with ultraviolet spectral analysis of an ether solution of the white solid revealed the presence of nitrile-containing material which was tentatively identified as 1,3-dicyanobenzene.

Ultraviolet analysis of the ether traps from the pyrolysis using 10 cm cells failed to yield any interpretable results. Examination of the concentrated hydrochloric acid traps followed by the usual work-up procedure failed to detect any amine-containing material by ultraviolet analysis. Samples of the polymer were introduced into the furnace at several temperatures (250-550°C) in an oxygen atmosphere for 30 min each. Identical results were obtained at 400°C although the rate of degradation was noticeably slower. Infrared spectral analysis of the boat residues showed an over-all decrease in all band intensities along with broadening and scattering as the degradation progressed.

Pyrolytic Degradation of Compound III in Oxygen at 500°C. A 250-mg quantity of compound III was placed in the pyrolysis furnace at 500°C in an oxygen flow stream. The effluent gases were analyzed by infrared spectroscopy at various time intervals during degradation; the total contact time was 15 min.

The boat residue after this time period was a black char, an infrared spectrum of which looked similar to that of the starting material, although the degree of scattering made definite interpretation impossible. The liquid which condensed in the trap was water, and the sublimed solid which had collected was 1,8-naphthalic anhydride and a small amount starting material. An infrared spectrum of the gaseous material, collected by means of a 10-cm gas cell, was identified as carbon dioxide and monoxide; a weak C≡N stretching vibration was also observed. The white precipitate which formed when the gases were passed through an aqueous silver nitrate solution was identified as a silver cyanide. The ether trap solutions were filtered and ultraviolet spectral analysis revealed the presence of 1,8-naphthalic anhydride. The ether was stripped off; an infrared spectrum of the residue, although weak, was identified as anhydride and water.

Pyrolytic Degradation of Compound III in Oxygen at Several Temperatures. Samples of compound III (100 mg) were pyrolyzed in oxygen for 30 min each in a temperature range of 250-550°C. Above 400°C identical results were obtained as those described above for III.

Pyrolytic Degradation of Compound IV in Oxygen at 500°C. An unweighed quantity of compound IV was placed in the furnace at 500°C in an oxygen atmosphere. The gases were analyzed by infrared spectroscopy at various time intervals during the degradation; the gases proved to be exactly the same as in all previous pyrolyses, i.e., carbon dioxide, carbon monoxide, and a nitrile-containing material. Infrared analysis of the boat residue which was a black char was very similar to that of the starting material, although the degree of scattering made definite interpretation impossible. The liquid which condensed in the trap was water and the solid which had collected was the starting material. The ethereal solutions were filtered, and the ultraviolet spectrum determined. An infrared spectrum of the trap residue after removing the solvent showed an ingrowth of a 1730 cm^{-1} band as well as the starting material. Spectral identification of the oxidation products by these two techniques indicated the presence of 1,4,5,8-naphthalene dianhydride.

The traps were filled with concentrated hydrochloric acid and the effluent bubbled through them. After pyrolysis was complete the acidic solution was neutralized and extracted several times with ether; the ether was dried, filtered, and evaporated. Examination of the ether extracts failed to give any evidence of the presence of aniline or any oxygenated products.

Seven samples of compound IV (100 mg each) were pyrolyzed in oxygen for 30 min at 50° intervals in the 250-550°C range. Upon lowering the pyrolysis temperature to 425°C, the material sublimed prior to undergoing oxidation which made identification of condensable pyrolysis products impossible. This is quite different from the 500°C experiment wherein extensive reaction occurred prior to volatilization of the sample. The boat residues and pyrolysis tube sublimates were analyzed by infrared spectroscopy as KBr pellets and Nujol mulls. The tube sublimate consisted of the starting material and a small amount of 1,4,5,8-naphthalene dianhydride. The boat residue was shown to contain only the starting material and char.

Pyrolytic Degradation of Compound V in Oxygen at 500°C. The pyrolysis was attempted in the usual manner; however, after 1 min at this temperature most of the material sublimed. A gas analysis was attempted but no results were obtained. After 3 min contact time there remained a very small amount of boat residue which, by infrared analysis, consisted of the starting material and carbon char. A liquid had collected in the exit end of the pyrolysis apparatus. Upon cooling, the liquid solidified; an infrared spectrum of the material was identical to that of the starting material.

Instruments

Infrared spectra were taken on either a Beckmann 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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