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# Mechanism of Thermal Oxidation of the Benzimidazole System

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Ohio

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# MECHANISM OF THERMAL OXIDATION OF THE BENZIMIDAZOLE SYSTEM

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## FOREWORD

This report was prepared by Wright State University, Dayton, Ohio, under Department of the Air Force Contract F33615-68-C-1277. The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. G.F.L. Ehlers (AFML/LNP) as Project Scientist.

This report covers work from February 1, 1970 to January 31, 1971.

This technical report has been reviewed and is approved.

R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

In this report experimental evidence is reported in support of the suggestion that pyrolytic oxidation of polybenzimidazole at high temperatures initiates at the carbocyclic aromatic ring adjacent to the imidazole nucleus.

Solution oxidation of benzimidazole model compounds yielded corresponding 2-arylimidazole-4,5-dicarboxylic acid oxidation products demonstrating that the 2-arylimidazole nucleus is more resistant to oxidation than the adjacent benzenoid nucleus. Subsequent oxidative pyrolysis of solution oxidation intermediates at 300°C provided the same products (oxides of carbon, aromatic nitriles and cyanogen) obtained when the parent model compound is oxidatively pyrolyzed, demonstrating that similarly oxygenated intermediates are probable transitory intermediates in pyrolytic oxidation of polybenzimidazole.

Oxidative pyrolysis of carbon-13 labelled benzimidazole model compounds and subsequent mass analysis of carbon dioxide and cyanogen gaseous products demonstrate conclusively that: initial oxygenation occurs preferentially at the aromatic carboxyclic nucleus adjacent to the imidazole heterocyclic and that only ten percent of the cyanogen product originates from the 2(2') carbon thus accounting for the fate of both nitrogens in the imidazole nucleus.

These data were found to be consistent with the mechanism previously proposed for thermooxidative degradation of polybenzimidazole.

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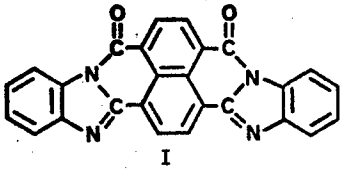
# INTRODUCTION

## A. Historical

Continued interest in the thermal oxidative behavior of high temperature polymers prompted us to initiate an exploratory program to uncover experimental techniques aimed at testing the validity of the proposed[1] mechanism for thermal oxidative degradation of polybenzimidazolone, polybenzimide and polybenzimidazole systems. The mechanistic scheme was based on work previously reported[1] from our laboratories based on a study of the mechanism by which poly(6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j]benzo[lmn][3,8]phenanthroline-2,13-diyl) (abbreviated polybenzimidazolone or BBB) degrades in oxidizing atmospheres at high temperature. The approach used involved the use of model compounds exemplifying the structural units of the parent polymer (I-IV). In addition, structurally related benzimidazole and benzimide models (V-IX) were also prepared for comparison of their thermal and oxidative stabization with those of the benzimidazolone system.



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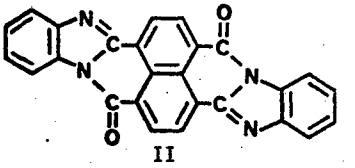

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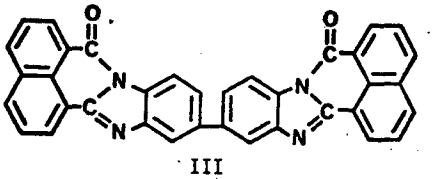

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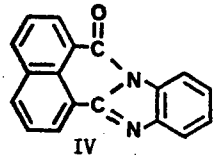

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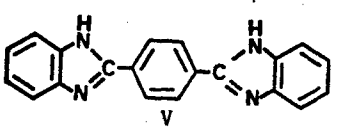

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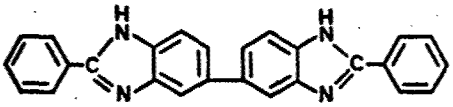

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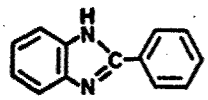

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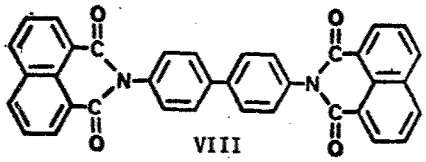

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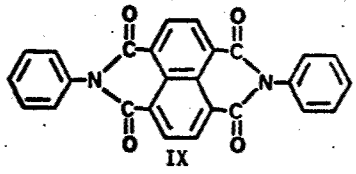


IX

The oxidative pyrolysis products (in a temperature range of 250-600°C) obtained from polybenzimidazolone and its model compounds (I-III) were carbon dioxide, carbon monoxide, water and trace quantities of cyanogen (Figure 1). The most outstanding feature of these results was the absence of condensable degradation products (solid or liquid, excluding water).

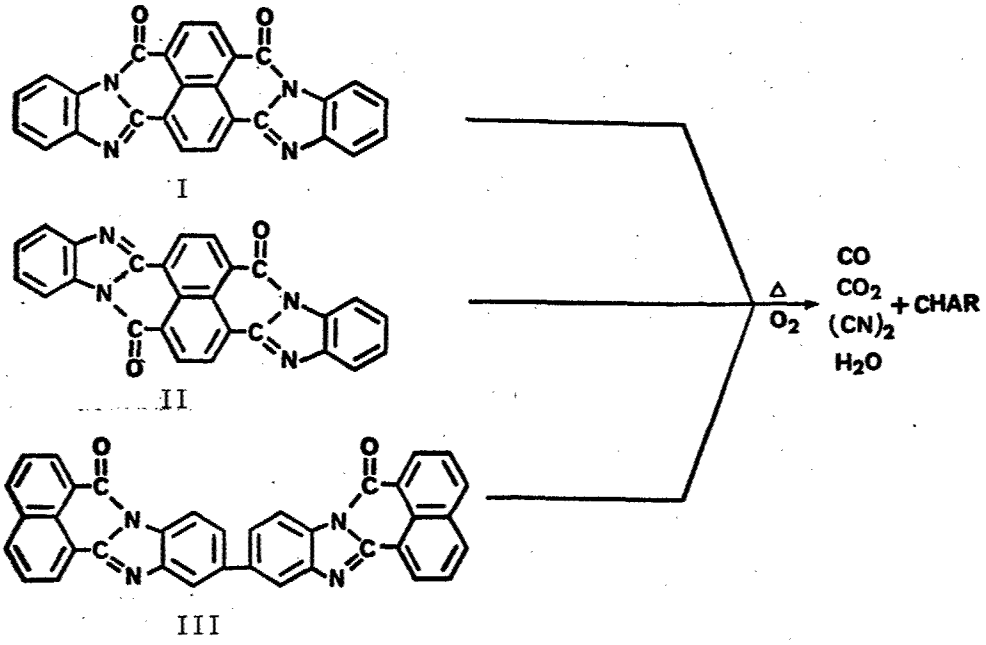
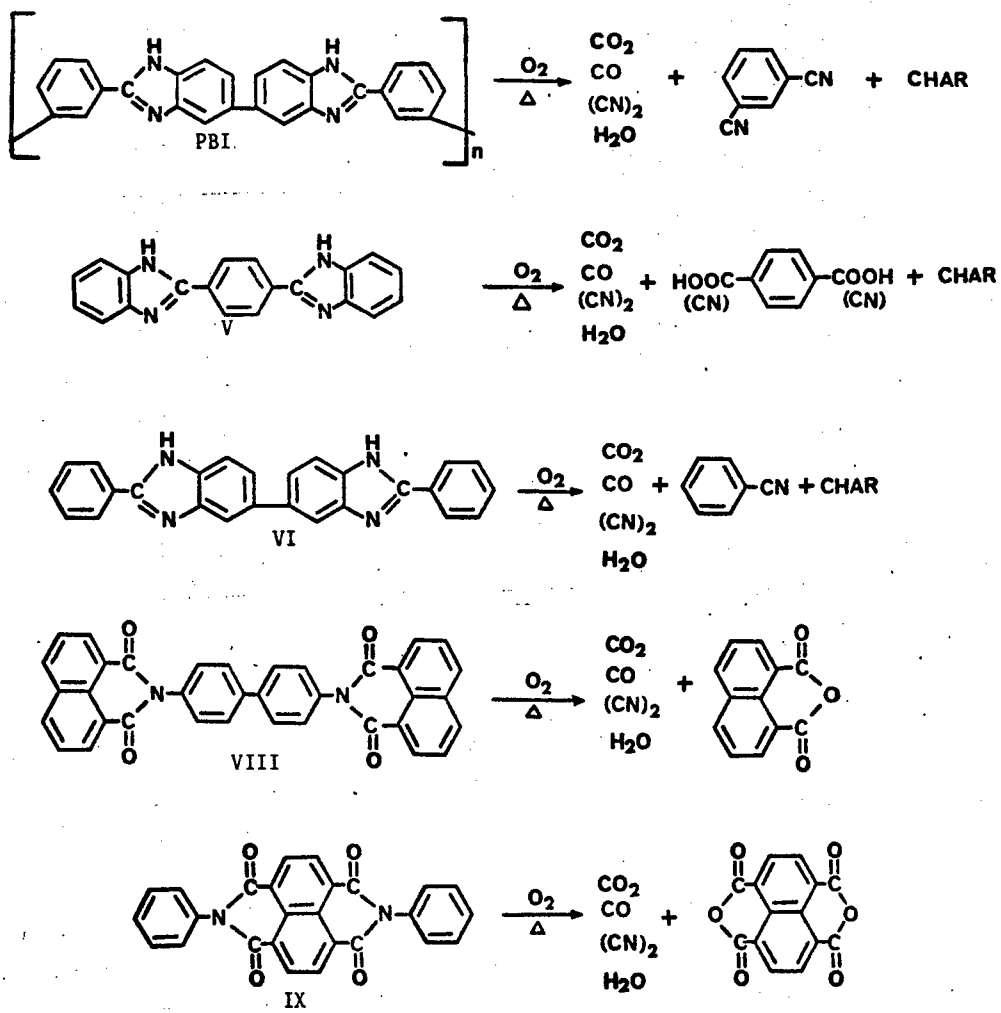



Figure 1. Products of the oxidative pyrolysis of compounds I through III in the 250 to 600°C temperature range

The degradation products obtained from model compounds V, VI, VIII and IX the benzimidazole and benzimide model compounds were identical to those obtained from polybenzimidazolone and model compounds (Figure 1), i.e., the carbon oxides, water and cyanogen. In addition, model V yielded terephthalic acids and its nitrilo analogues, model VI yielded benzonitrile, model VIII yielded 1,8-naphthalic anhydride and model IX yielded 1,4,5,8-naphthalene dianhydride. Furthermore poly-2,2'(m-phenylene)5,5'-bibenzimidazole produced small but significant amounts of isophthalic acid and its nitrilo analogues. In every case only the acid derived portions of the molecules were isolated as degradation products and all attempts to detect condensation products originating from the amine derived portions of the molecules failed.



The failure to obtain nitrogen-containing fragments from the amine residues of the model compounds and the polymers regardless of their position in the molecule offers compelling evidence that oxidative attack preferentially occurs at the benzenoid rings bearing the nitrogen function.

Several reactions were proposed for the thermal oxidation of the benzimidazoles (Figure 2) since the nature of the products obtained from both thermal and oxidative degradation revealed very close similarities. For example, degradation of the polymer in vacuo yielded hydrogen, hydrogen cyanide and nitrilo moieties[2,3]. Under oxidative conditions water, cyanogen, and analogous nitrile compounds (XV) were detected along with large amounts of carbon dioxide and monoxide. These observations and the fact that substitution of the imidazole hydrogen with a phenyl group markedly increased the stability of the resulting polymer under isothermal conditions in air[4] support the conclusion that the nitrogen-hydrogen bond is the most labile site for either oxygenation or thermal scission. Furthermore the great potential for resonance stabilization afforded by the benzimidazole system[5] was expected to make radical formation rather facile. Hence either hydrogen abstraction by oxygen or homolytic cleavage of the nitrogen-hydrogen bond resulted in the formation of the same radical species (XVI).

Species (X) is the only oxygenated structure which could be drawn with any certainty since product analysis indicated that the nitrogen containing heterocyclic and benzenoid rings were the weak-link in oxidation and yet the precise nature and position of the atoms undergoing initial oxidation was not delineated. Subsequent formation and decomposition by either transannular peroxide[6-8] (XI), an endo-peroxide (XII), or a quinone-imidazole[9-10] (XIII) can account for the observed products. Rearrangement of

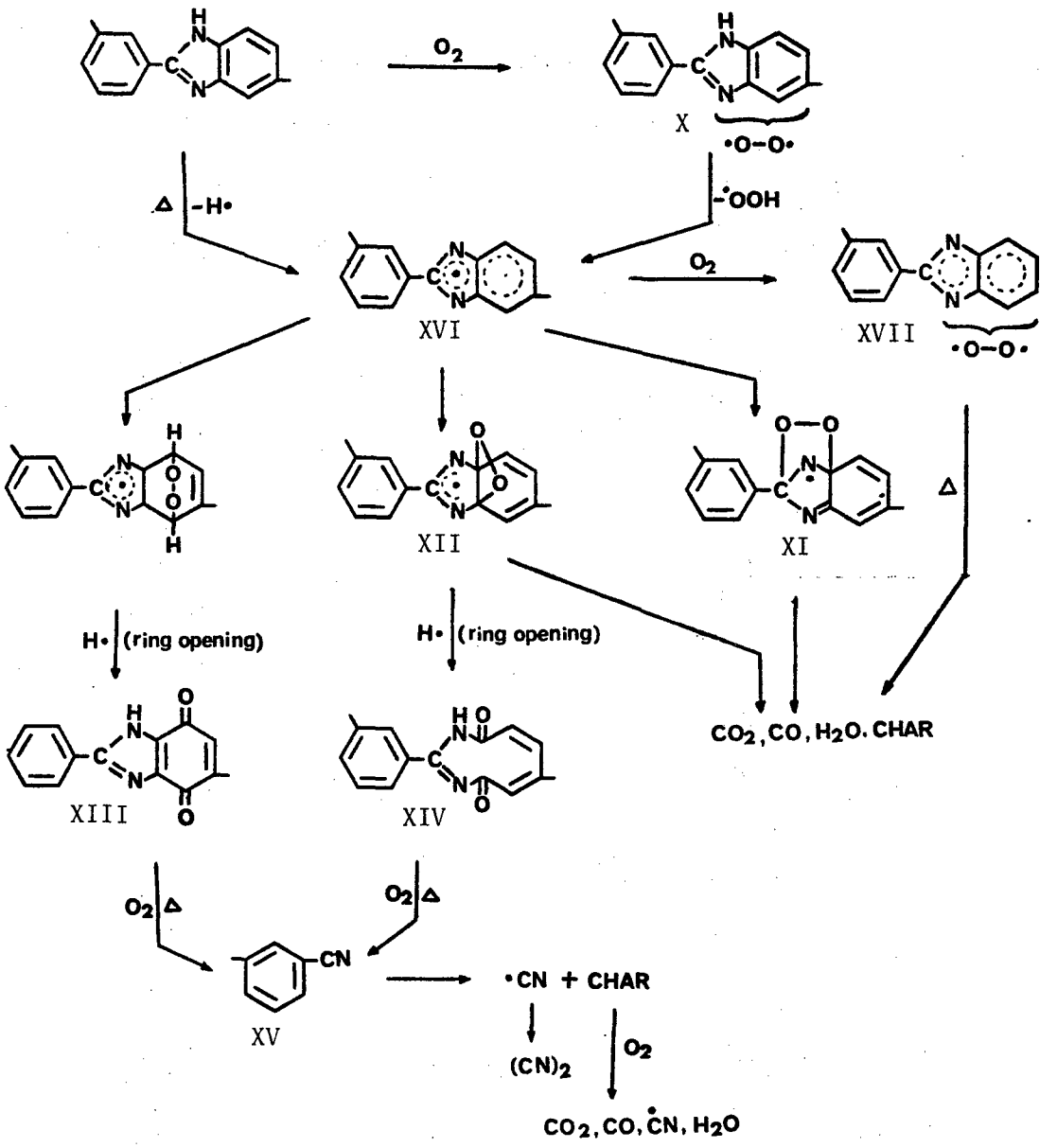
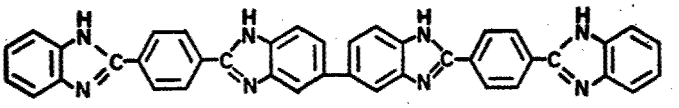



Figure 2. Proposed mechanism for thermooxidative degradation of polybenzimidazole

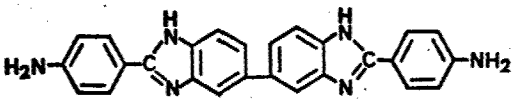
the transannular peroxide (XI) to the endo-peroxide (XII) followed by the formation and decomposition of a diene-dione (XIV) gives the same results. However, the fact that none of these oxygenated species were isoable nor spectroscopically observable under experimental conditions; i.e., temperatures in excess of 400°C for degradation of bulk polymer samples suggested

that their formation was instantaneously followed by catastropic decomposition to gaseous products and nitrile containing condensibles. This suggestion was further verified by the observation that low temperature oxidation (300°C) of polybenzimidazole film afforded no spectroscopic evidence for oxygenated intermediates. However the latter study did provide spectroscopic evidence for initial destruction of the benzimidazole biphenyl system and the development of a nitrile function on the polymer chain (XV).

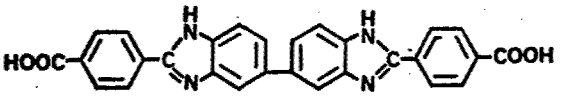
The initial stages of oxidative degradation of polybenzimidazole is catalyzed by amine and carboxylic acid functional groups at the polymer chain ends. This has been demonstrated by incorporation of the high molecular weight model compounds XVIII, V and VI into the film matrix to simulate a decrease in concentration of functional end groups. The results (Table 1) revealed a decrease in rate of degradation of polymer film at



XVIII



XIX



XX

300°C as determined by the rate of increase of nitrile absorption in the infrared[12]. Unfortunately, the introduction of model compounds XIX and XX which simulates an increase in functional end group concentration did not reveal the expected increase in rate of thermal oxidative degradation (Table

I) a result which was interpreted as due to the lack of sensitivity in the analytical technique employed. The effect of uncyclized linkages in the polymer chain, resulting in amide and free amine functions is also thought to catalyze polymer degradation in oxygen at high temperatures. The data in Table I could be interpreted as showing verification of the importance of both uncyclized linkages and free functional end groups. Thus, incorporation of model compounds XVIII, V, and VI into the polymer simulates

TABLE I

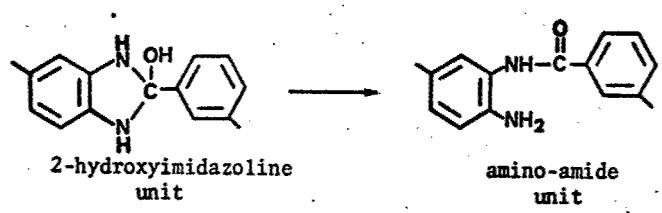
Thermooxidative Degradation of PBI Film Containing Model Compounds. Effect of Functional End Groups.

| Film Composition (Percent-by Weight) | Nitrile Absorbance (2236 $cm^{-1}$) | Percent Absorbance Reduction |
|---|---|---|
| 100 PBI | 0.099 | Reference |
| 80 PBI/20 XVIII | 0.078 | 21 |
| 80 PBI/20 XIX ($-NH_2$) | 0.098 | 1 |
| 80 PBI/20 XX ($-CO_2H$) | 0.098 | 1 |
| 100 PBI | 0.085 | Reference |
| 80 PBI/20 V | 0.068 | 21 |
| 80 PBI/20 VI | 0.068 | 21 |

a decrease in concentration of uncyclized linkages and functional end group resulting in a considerable decrease in degradation rate. Model compounds XIX and XX when included in the polymer film matrix simulate a decrease in uncyclized linkage concentration and an increase in end group concentration resulting in no apparent net change in degradation rate.

The effect of 2-hydroxyimidazoline functions on thermooxidative deg-

radation of polybenzimidazole has also been considered[13]. Such functions were thought to serve as precursors to amino-amide (uncyclized linkages) in the degradation mechanism:




The presence of hydroxyimidazoline functions was proposed to account for carbon dioxide, carbon monoxide and the large quantities of water observed in the mass thermal analysis of polybenzimidazole[2,3]. The suggestion gained support from the report[14] that melt condensation of phenylbenzoate and 3,3'-diaminobenzidine yields 2,2'-diphenyl-2-hydroxy-3-hydro-5,5'-bibenzimidazole whicih did not undergo dehydration to the bisbenzimidazole (model compound VI) below 300°C. Subsequently, however, the compound reported to have the hydroxy-imidazoline function was shown in our laboratories to be a higher melting polymorph of model VI.[23] This finding casts serious doubt on the suggestion that hydroxyimidazoline functions are present in the polymer chain to any significant extent. The present authors believe that carboxylic acid and amine end groups along with uncyclized amino amide segments better account for the appearance of water in the MTA of polybenzimidazole through cyclization and polymerization during the thermal analysis. This interpretation also agrees with the reported effect of polymer functional end groups on the initial stages of polybenzimidazole thermal oxidative degradation.

The oxidative degradation of the benzimide system (Figure 3) was assumed to follow pathways analogous to those of the benzimidazole system

because of product similarities. Thus the oxygenated species XXI (analogous to X, Figure 2) was described as XXII or XXIII (analogous to structures XI-XIV, Figure 2) since further oxidation of either yielded an anhydride, the carbon oxides, char and water. Structures XXII and XXIII also provide a reasonable explanation for the report[15] that H-film when pyrolyzed at 300 degrees in an atmosphere of 90 percent oxygen eighteen isotope evolved carbon dioxide composed of both doubly and singly labelled carbon dioxide[10].

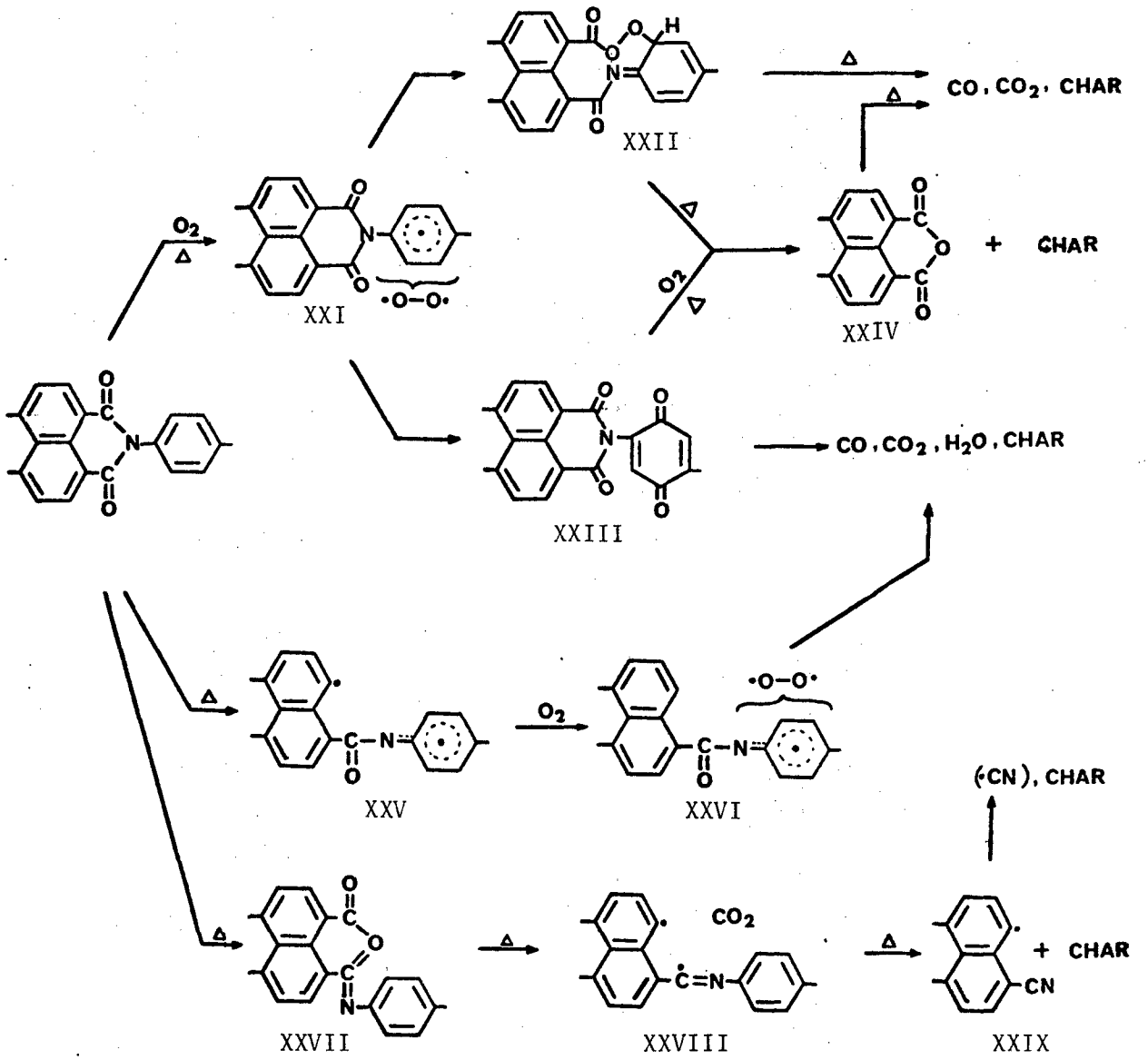



Figure 3. Proposed mechanism for thermooxidative degradation of polybenzimides

A thermally induced degradation occurring simultaneously with oxidative degradation was considered a likely possibility since the radicals XXV formed by such a process would account for product formation with the exception of anhydrides. An interesting and perhaps significant thermal reaction is the rearrangement of imide to isomide[16] XXVII. Thermal degradation of the isomide would then produce carbon dioxide and eventually the nitrilo-naphthanoid radical XXIX. It is, in fact, the radical nature of this nitrilo-moiety, as contrasted to the stable cyanobenzenoids XXIII produced by the benzimidazole system which could account for the absence of cyano-naphthalene and related products.

During the early stages of oxidative degradation the benzimidazolone system was thought to undergo two simultaneous reactions (Figure 4). The first is oxygen addition to the nitrogen heterocyclic and adjacent benz-enoid ring producing the oxygenated complex XXX which is analogous to X (Figure 2) proposed for the benzimidazole system. The second reaction is homolytic cleavage of the carbonyl producing a non-oxygenated diradical XXXVI which is similar to XVI (Figure 2). Parellel reaction paths were also proposed for the benzimide system (XXI and XXV, Figure 3). Direct decomposition of the oxygenated benzimidazolone intermediate XXX is an alternative path to XXXVI which on oxygenation gives XXXVII. Both XXXVI and XXXVII are reasonable precursors to the carbon oxides, water, char and the cyanonaphthenoid radical XXXV. As in the case of the benzimide (XXIX, Figure 3) the radical nature of the cyanonaphthanoid (XXXV) would account for the absence of 2-cyanonaphthalene in the degradation products.

Since the benzimidazolone system includes the benzimidazole ring system, then transannular (XXXI) and endo-peroxides (XXXII)[6-8] as well as

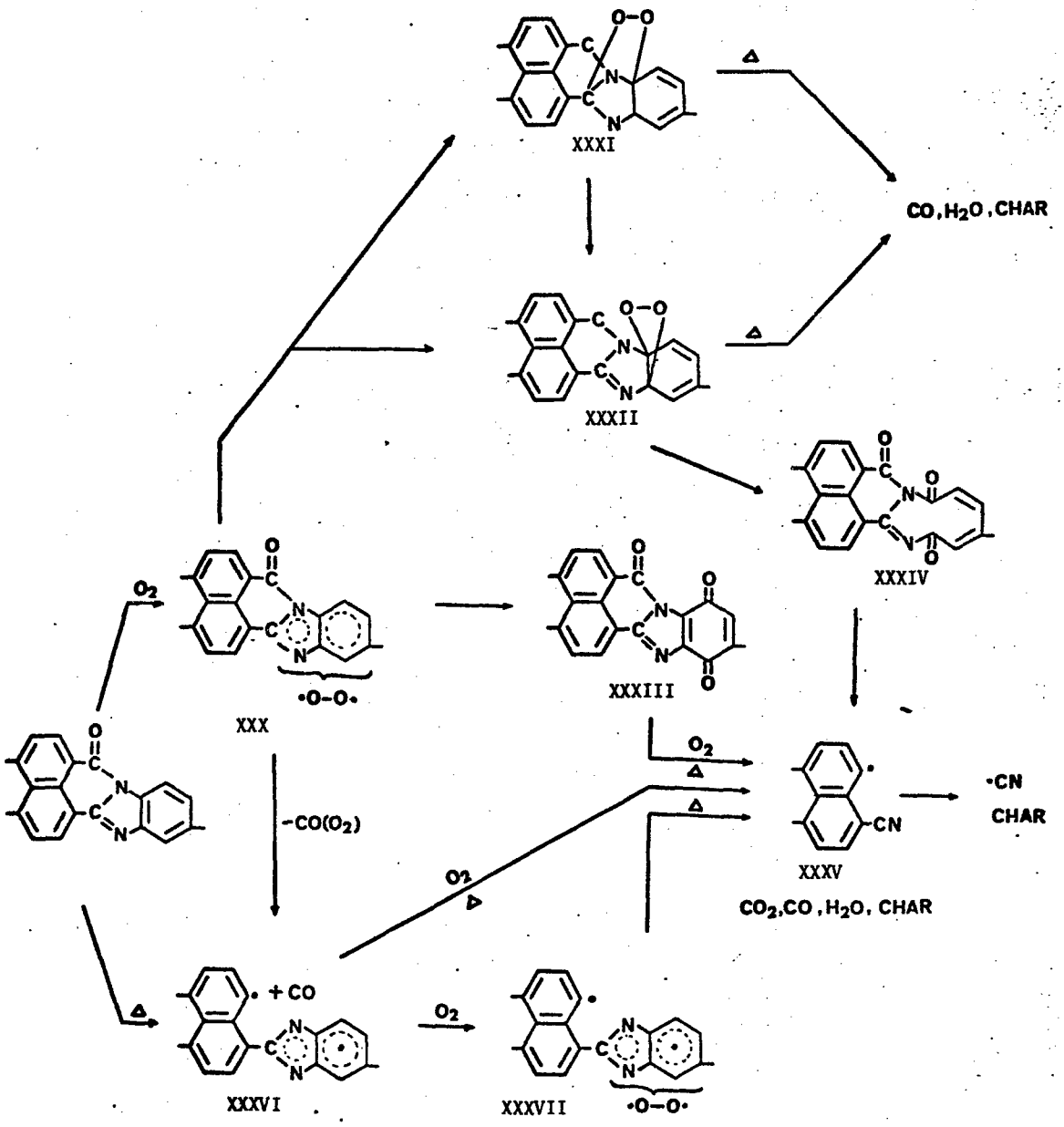



Figure 4. Proposed mechanism for thermooxidative degradation of polybenzimidazolone

quinoid imidazolone XXXIII and diene-dione (XXXIV)[9-11] were included in this system in analogy with those for the benzimidazole (Figure 2, CV-CVIII). The lack of spectral evidence of these species in degradation residues lends support to the suggestion that their existance is extremely short lived at the degradation temperature (ca. 500°C).

In summary, the experimental results indicate that in the initial stages oxidative attack occurs at the electron-rich benzenoid rings of

the polymers and model compounds. Subsequent degradation of these oxygenated species led to small molecular fragments and char. The absence of nitrogen in the gas phase as either nitrogen or nitrogen oxides and in the condensable phase products except as nitrilo compounds is probably due to the involvement of nitrogen in coupling and crosslinking reactions frequently undergone by nitrogen containing materials during oxidation[16]. Hence the large quantities of char in the oxidative degradation experiments are highly crosslinked as evidenced by the infrared analyses of pyrolysis residues and the fact that polybenzimidazole is rendered completely insoluble after short periods in oxygen at 300°C. In addition, the probable radical nature[2] of the char residues (at reaction temperatures) enhances their susceptibility toward oxygenation and thus probably accounts for the pronounced differences in weight retention in air as opposed to inert conditions[17,18]. Since the benzimidazole and benzimide systems give rise to aromatic fragments all of which originate from the acid derived portion of these molecules, the weak link in these systems must therefore be the nitrogen-containing heterocyclic and adjacent benzenoid rings.

The vigorous oxidative conditions employed in all of the above studies, including the attempted controlled oxidation of polybenzimidazole film at 300°C, were obviously not conducive to isolation of the relatively unstable intermediates proposed in the various mechanisms (Figures 2, 3, and 4). Thus a study of the solution oxidation of certain of the model compounds of the benzimidazole and benzimidazolone systems was initiated. Our purpose is that investigation was to study more controlled oxidation reactions of these systems and attempt to isolate intermediate oxidation products. These products would then be subjected to the pyrolytic oxidative conditions employed in the thermo-oxidative studies to determine whether the

mode of degradation ($CO/CO_2$ ratios, etc.) parellels that of model compounds. Positive results from such a study would permit the inclusion of these intermediates into the mechanistic scheme of high temperature degradation with a reasonable degree of confidence.

The initial results of solution oxidation of a selection of benzimidazole and benzimidazolone model compounds with a variety of oxidizing agents are summarized in Table II. In general it was quite clear that the heterocyclics are extremely inert to oxidation in solution. Their behavior under those conditions parelleled that seen in the pyrolytic oxidative studies where the model compounds resist oxidation until rather high temperatures are employed. This parellel was seen most dramatically in the benzimidazolone series where the solution oxidations resulted in either no reaction or total degradation to produce carbon dioxide as the only identifiable product when potassium dichromate in sulfuric is employed at elevated temperatures. The benzimidazole model compounds yielded similar results except that potassium dichromate in sulfuric acid did yield a solid product. Indications were that the products were salts of the benzimidazole model compound with an oxide of chromium.

TABLE II

Summary of Solution Oxidation Studies of Heterocyclic Model Compounds.

| Model Compound | Oxidizing Reagent Media, Temp. | Products |
|---|---|---|
| IV | 30% $H_2O_2$,$OH^-$ | Starting material |
| IV | 30% $H_2O_2$, $OH^-$, $O_2$ | starting material |
| IV | $MnO_4^-$ ($H_2O$,$H^+$,$OH^-$) | starting material |
| IV | $CrO_3$,ACOH | starting material |

Table II Cont.

| Model Compound | Oxidizing Reagent Media, Temp. | Products |
|---|---|---|
| IV | $K_2Cr_2O_7, H_2SO_4, 25°$ | starting material |
| IV | $K_2Cr_2O_7, H_2SO_4, 80°$ | $CO_2$ |
| I, II | $K_2Cr_2O_7, H_2SO_4, 25°$ | starting material |
| III | $K_2Cr_2O_7, H_2SO_4, 80°$ | starting material |
| III | $CrO_3, H_2SO_4, 80°$ | starting material |
| VII | 30% $H_2O_2$, ACOH | starting material |
| VII | $K_2Cr_2O_7, H_2SO_4, 25°$ | chromium compound +$CO_2$ |
| VI | $K_2Cr_2O_7, H_2SO_4, 80°$ | chromium compound +$CO_2$ |
| VI | $K_2Cr_2O_7, H_2SO_4, 25°$ | chromium compound |
| VI | $CrO_3$, ACOH | starting material |
| V | $K_2Cr_2O_7, H_2SO_4, 100°$ | chromium compound |
| V | $MuO_4^-, H_2O$ | no product |

B. Present Investigation

The present report discloses the results of our continued efforts in solution oxidation chemistry of the heterocyclic model compounds. The benzimidazole model compound solution oxidation intermediates were indeed isolated and subjected to pyrolytic oxidative conditions. The results of these investigations are also reported and discussed in the succeeding sections.

As discussed in previous paragraphs the oxidative degradation studies carried out thus far in our laboratories indicates that the decomposition most likely initiates at some weak link (the electron rich amine portion as described earlier) in the polymer or model compound. Their initial

attack produces initial decomposition products and is followed by breakdown of the remainder of the repeating unit (in the case of polymer) or model compound.

None of the present information provides unequivocal support for this mode of polymer decomposition since there is no way of using the available experimental evidence to identify the position from which the products originate at the onset of decomposition.

In order to provide some conclusive support for this mechanism, a study of the high temperature oxidation of model compounds with carbon thirteen isotope incorporated into specific positions has been initiated. In a very general way the role of carbon thirteen species is visualized as follows: a high initial rate of formation of labeled products will indicate that the labeled position is part of or close to the site of initiation of decompsotion, a constant rate of carbon thirteen containing product would indicate that decomposition is initiated in a random fashion while an increase in their rate of formation would indicate that the labeled position is quite removed from the point of decomposition.

The synthesis of two carbon-thirteen labeled isomers of benzimidazole model compound VI and their subsequent oxidative degradation and mass analysis of product gases is disclosed and discussed in the present report. In addition, one of the carbon thirteen isomers of compound VI was employed to determine the source of cyanogen in oxidative degradation. The results of this study are also discussed.

## SECTION II

## RESULTS AND DISCUSSION

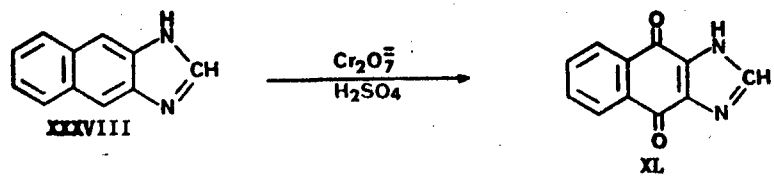
### A. Solution Oxidations

As described in the previous section, the probability of isolating or spectrally observing oxygenated intermediates in the pyrolytic oxidation of film or bulk samples of heterocyclic polymers seemed minimal. Having exhausted the available isolation and analytical techniques, it seemed reasonable to pursue the synthetic approach by independently synthesizing structurally related oxidation intermediates, and subsequently subject them to pyrolytic oxidation and product analysis. The production of similar products and product ratios to those obtained by pyrolytic oxidation of the related model compound or parent polymer system would support the suggestion that they are indeed intermediates and provide verification of the proposed mechanism for thermooxidative degradation. Of the synthetic alternatives available for this project, the most promising appeared to be oxidation reactions carried out directly on the model compound in question under conditions considerably less vigorous than it generally encounters in pyrolytic oxidation. Such reactions, if successful, would provide insight into alternative oxidation reactions of the benzimidazolone and benzimidazole systems and provide oxidation intermediates for future studies. Thus, an investigation of the dilute solution oxidation with inorganic oxidizing agents was initiated in order to determine the reactivities and behavior of the model compounds related to BBB and PBI parent polymer systems[1].

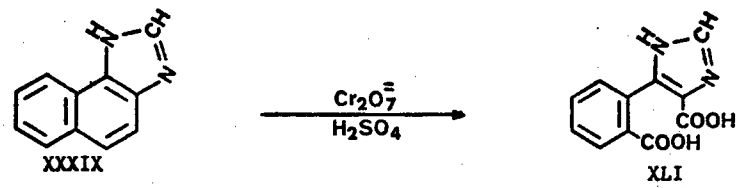
As previously reported[1] of the oxidizing agents which were tried, the

only one which showed promise was sodium dichromate in sulfuric acid. With this reagent, the benzimidazolone model compounds I, II, and III were totally inert while compound IV oxidized completely to produce carbon dioxide. The benzimidazole model compounds were more responsive to oxidation by dichromate in acid. Thus model compounds V, VI, and VII all produced carbon dioxide and an unidentified product suspected of being a compound of benzimidazole and chromate as suggested by the appearance of typical benzimidazole infrared absorptions and a broad absorption at 900-950 $cm^{-1}$ which was assigned to chromate.

Because of the apparent inertness of the benzimidazolone compounds, subsequent efforts were directed at refinement of the solution oxidation techniques for the benzimidazole systems. This system appeared to be the most promising for study, because unlike the benzimidazolones, they yielded isolatable products (chromate compounds) other than carbon dioxide on dichromate oxidation. In addition, previous workers[19,9,11] reported the isolation of oxidation products from the structurally related 2,3-naphthimidazole (XXXVIII), 1,2-naphthlimidazole (XXXIX) as shown below (Reactions 1-2).




XXXVIII XL (1)



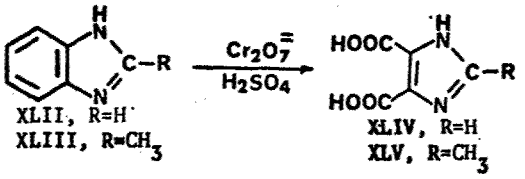

XXXIX XLI (2)

1. Oxidation of 2-Phenylbenzimidazole-Chromate Compound

As previously reported[1], the oxidation of 2-phenyl-benzimidazole (VII) with dichromate in dilute sulfuric acid at room temperature yielded an unidentified yellow solid (XLVI). This compound when digested with five percent aqueous potassium hydroxide regenerated VII. The infrared spectrum of XLVI showed the familiar benzimidazole absorptions and a broad peak at 900-950 $cm^{-1}$ which is assigned to chromate. The structure of this compound has not yet been determined. However, it was of interest to determine whether or not it represents a solution oxidation intermediate. When XLVI was treated with aqueous potassium permanganate at 80°C., a highly exothermic reaction ensued within two minutes which produced carbon dioxide. The parent 2-phenylbenzimidazole (VII) under identical conditions was inert. Thus it appears that the chromate complex XLVI is indeed an oxidation intermediate. Further attempts to investigate the nature and behavior of the proposed chromate complex have been suspended and efforts were instead directed toward controlling the dichromate oxidation of the benzimidazole model compounds to yield oxygenated heterocyclic intermediates as described in the following paragraphs.

2. Dichromate Oxidation of Benzimidazole Model Compounds

Preparation and subsequent dichromate oxidation of benzimidazole (XLII) and 2-methylbenzimidazole (XLIII) were repeated and after certain modifications of the oxidation reactions, the products, imidazole-4,5-dicarboxylic acid (XLIV) and 2-methylimidazole-4,5-dicarboxylic acid (XLV) were isolated (Reaction 3). In each of these and the subsequent oxidations of benzimi-

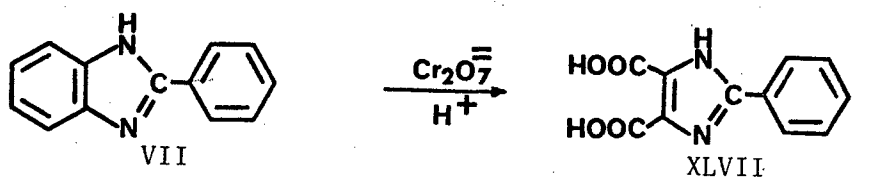



(3)

azole compounds, it was observed that the required concentration of sulfuric acid was critical and different for each compound. This effect is probably related to solubilization of the benzimidazole derivative. All of the oxidations were exothermic and it was also found that temperature control was critical for each experiment.

a. Oxidation of 2-Phenylbenzimidazole (VII)

Compound VII, 2-phenylbenzimidazole on oxidation with acid dichromate yielded 2-phenylimidazole-4,5-dicarboxylic acid (XLVII) in four percent yield (Reaction 4). The structure of the dicarboxylic was confirmed by independent synthesis through a modification of the method of Maquenue[20] by treatment of dinitrotartaric acid with benzaldehyde and ammonium hydroxide (Reaction 5). Maquenne has demonstrated that diketo-

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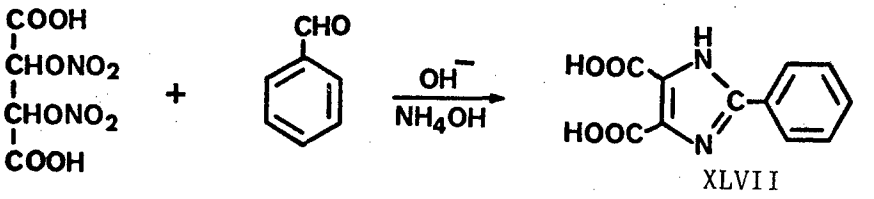


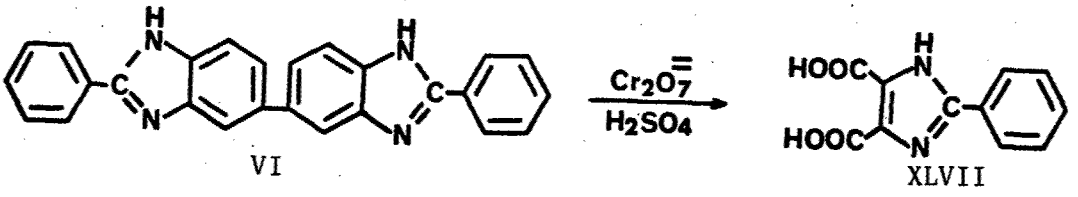

(5)

succinic acid is an intermediate in this synthesis indicating that it is a modification of the well known Debus[21] imidazole synthesis. The product of this reaction proved to be identical with the solution oxidation product of 2-phenylbenzimidazole.

b. Oxidation of 2,2'-Diphenyl-5,5'-bibenzimidazole (VI)

Appropriate modifications of the sulfuric acid potassium dichromate oxidation for compound VI which essentially amounted to effecient control

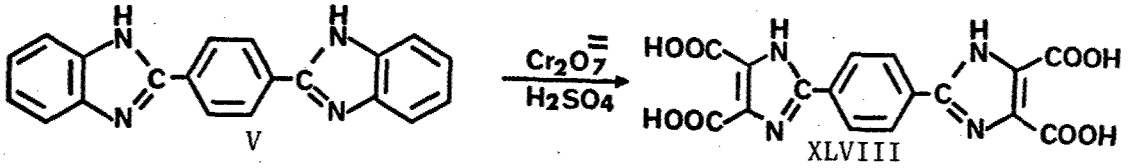
of the highly exothermic reaction resulted in the formation of 2-phenyl-imidazole-4,5-dicarboxylic (XLVII) acid in 0.7% yield (Reaction 6). The product was identical to the dicarboxylic acid obtained by similar oxidation of Compound VII.



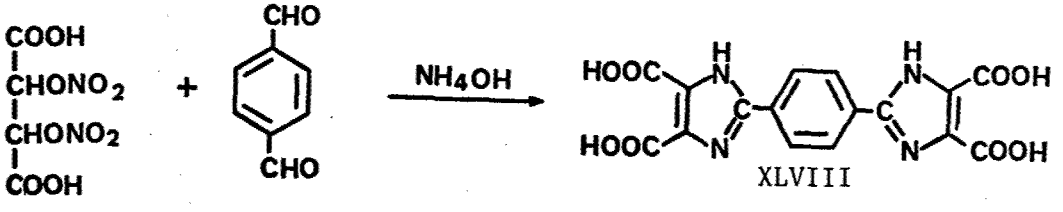

VI XLVII (6)

c. Oxidation of p-Di(2-benzimidazolyl)benzene V

As in the case of model compound VI, acid dichromate oxidation of p-di(2-benzimidazolyl)benzene V, under modified conditions yielded a product resulting from oxidation of the carbocyclic ring of the benzimidazole system (Reaction 7). The tetracarboxylic acid was identified as p-di[2-(4,5-dicarboxylic acid)imidazolyl]benzene (XLVIII) by independent synthesis with dinitrotartaric acid, terephthaldehyde and ammonium hydroxide (Reaction 8).




V XLVIII (7)

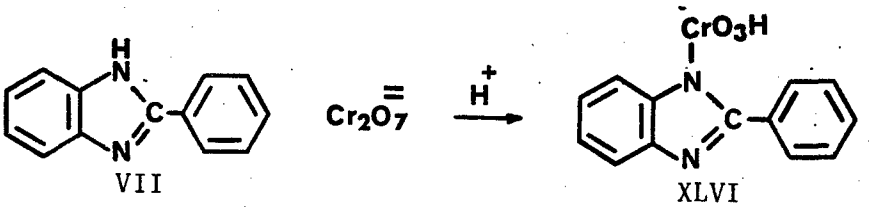



XLVIII (8)

3. Discussion of Solution Oxidations - Mechanistic Speculations

The fact that the benzimidazoles are the only heterocyclic model compounds which have to date yielded chromate compounds suggests that the

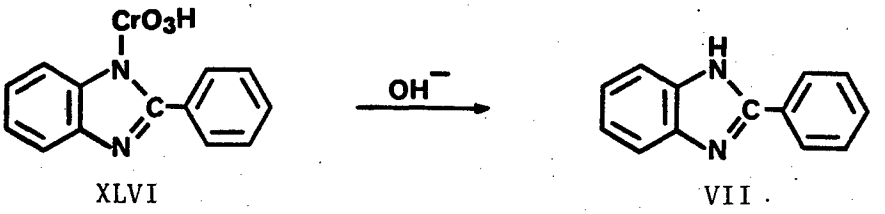
nitrogen-hydrogen bond is a prerequisite for their formation. This idea is further supported by the report[10] that 1-methylbenzimidazole (in which the N-H is replaced by N-$CH_3$) does not, on dichromate-acid oxidation, yield the corresponding 1-methylimidazole-4,5-dicarboxylic acid. It is further suggested that the chromium compound results from formation of a bond between nitrogen and chromium as shown below. (Structure XLVI, Reaction 9). The structure of XLVI might very well be dimeric. However,




(9)

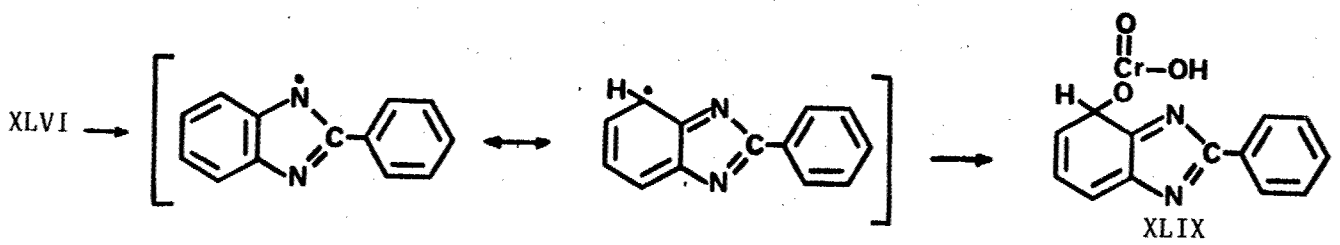
all of the mechanistic proposals which follow would apply with simple modifications if XLVI were a dimer.

It has been demonstrated that XLVI on treatment with base regenerates 2-phenylbenzimidazole as described in Reaction 10.



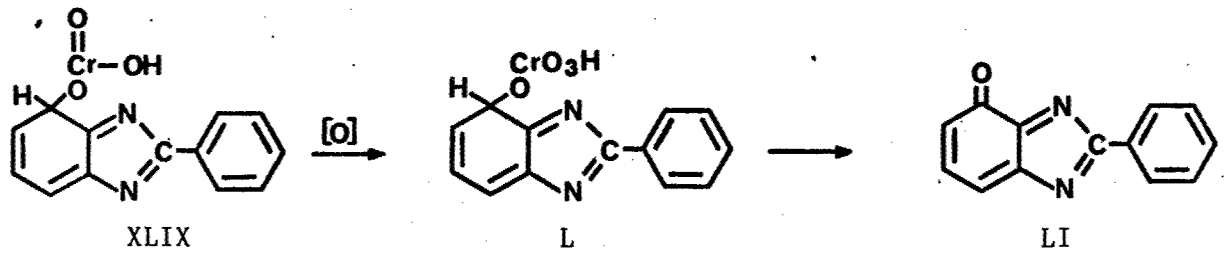

(10)

In the absence of base the chromate compound might rearrange through homolytic cleavage of the nitrogen-chromium bond and re-formation of an isomeric chromium compound such as XLIX, Reaction 11. The formation of the chromous acid ester XLIX is the key to oxygenation of the carbocylic. Further oxidation of XLIX would be expected to yield the chromate ester L,



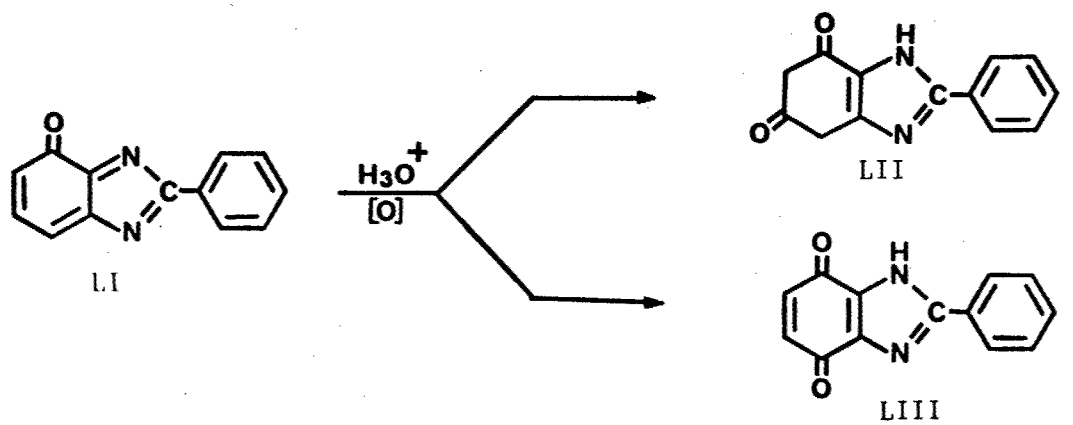

(11)

a familiar intermediate for chromic acid oxidation of alcohols to carbonyl compounds[22] such as LI, Reaction 12. This suggestion is supported by the relative ease of oxidation of XLVI by aqueous permanganate.




(12)

Subsequent acid catalyzed addition of water to LI followed by oxidation would be expected to yield quinones such as LII and LIII (Reaction 13) resulting in reformation of the imidazole system and an adjoining carbocyclic which is predicted to be readily susceptable to further oxidation to the corresponding dicarboxylic acid as observed in the solution oxidation of model compounds V, VI, and VII.

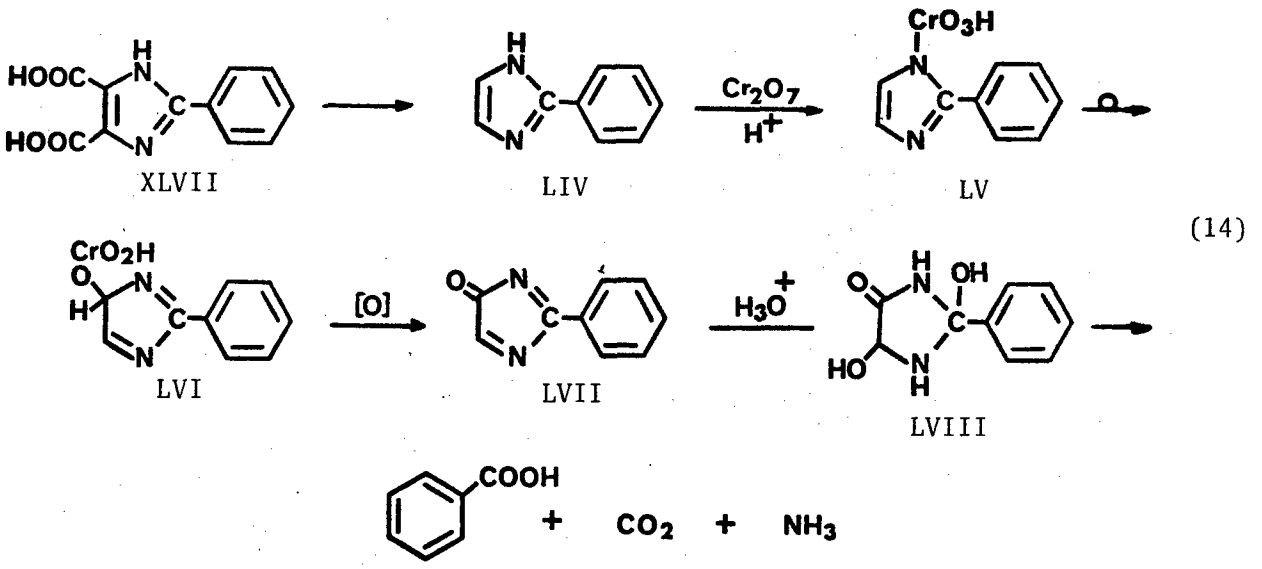



(13)

As discussed previously[1], continued solution oxidation of model compounds V, VI, and VII yields carbon dioxide as the only identifiable product. This would involve the further oxidation of the corresponding imi-

dazole-4,5-dicarboxylic acid to carbon dioxide.

Several mechanistic speculations are possible for the remaining oxidation steps. However, the following series is proposed because of its consistency with the previous oxidation steps. Imidazole-4,5-dicarboxylic acids are known to readily decarboxylate to yield the corresponding imidazole (LIV) as shown below for 2-phenylimidazole-4,5-dicarboxylic acid (XLVII). Subsequent reaction of LIV with chromate to give LV, rearrangement to the chromous acid ester LVI, oxidation to LVII which after acid catalyzed hydrolysis would be expected to yield benzoic acid, ammonia and carbon dioxide as shown (Reaction 14).




(14)

The failure to detect any benzoic acid from the solution oxidation of compounds VI and VII suggested an experiment to determine its behavior under the reaction conditions. Surprisingly, it was found that benzoic acid, when refluxed in a solution of acidic dichromate yields carbon dioxide. It has not yet been determined whether this reaction represents an oxidative decarboxylation of benzoic acid to form benzene and carbon dioxide or total oxidation of the aromatic nucleus. However, attempts to isolate benzene from the reaction mixture have met with failure. Efforts to de-

tect ammonia or other nitrogenous products from the exhaustive solution oxidation of compounds V, VI, and VII have also met with failure.

B. Pyrolytic Oxidation of Solution Oxidation Intermediates

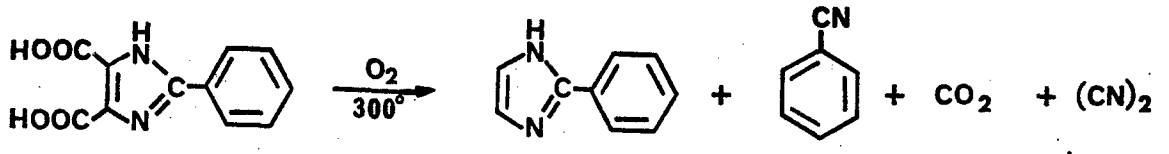
The results of solution oxidation of the benzimidazole model compounds indicate quite clearly that oxygenation of the carbocyclic ring adjacent to the imidazole nucleus is the first step and preferred route of oxygenation in solution oxidation. The carbocyclic ring has also been proposed[13] as the site of initiation of oxygenation in the pyrolytic oxidation of PBI and the related model compounds. Thus it seems reasonable to propose that the imidazole-4,5-dicarboxylic acids isolated from the solution oxidation of model compounds are structurally related to transitory oxidation intermediates in their high temperature oxidation. It has been reported previously[13] that the gaseous products of pyrolytic oxidation of PBI and the corresponding model compounds are carbon dioxide, carbon monoxide, and traces of cyanogen. Condensible products include water and isophthalonitrile from PBI, benzonitrile from compounds VII and V and terephthalonitrile from compound VI.

The suggestion that the imidazole-4,5-dicarboxylic acids isolated from solution oxidation of compounds V and VI are structurally related to pyrolytic oxidation intermediates has been tested by subjecting them to high temperature oxidation and subsequent product analysis.

1. Oxidative Pyrolytis of 2-Phenyl-4,5-dicarboxylic Acid

2-Phenylimidazole-4,5-dicarboxylic (XLVII) acid, the solution oxidation product of 2-phenylbenzimidazole (VII) and 2,2'-diphenyl-5,5'-bibenzimidazole (VI) was heated at 300° in oxygen to effect pyrolytic oxidation. (Reaction 15) Quantitative collection of evolved carbon dioxide by precipitation of the barium salt yielded two moles of carbon dioxide per

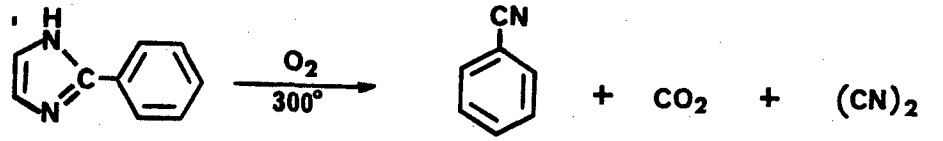
mole of starting material. Cyanogen gas was also observed by infrared analysis of the evolved gases and precipitation of the silver complex $Ag^{+}[Ag(CN)^{-}_{2}]$. Condensible products which collected on the walls of the pyrolysis tube were benzonitrile (verified by infrared spectrum) and 2-phenylimidazole (LIV) (verified by mixed melting point with an authentic sample).




XLVII LIV (15)

a. Oxidative Pyrolytis of 2-Phenylimidazole

2-Phenylimidazole (LIV), one of the products of oxidative pyrolysis of 2-phenylimidazole-4,5-dicarboxylic acid as described above, is probably the intermediate resulting from di-decarboxylation of the dicarboxylic acid. Subsequent oxidation would then convert it to benzonitrile, cyanogen, and carbon dioxide. The production of 2-phenylimidazole in this pyrolysis probably results from its sublimation and entrainment from the pyrolysis chamber before it undergoes further oxidation. To test this hypothesis, 2-phenylimidazole was subjected to the same conditions (300°C, oxygen atmosphere) and yielded unreacted starting material, carbon dioxide, cyanogen and benzonitrile (Reaction 16).

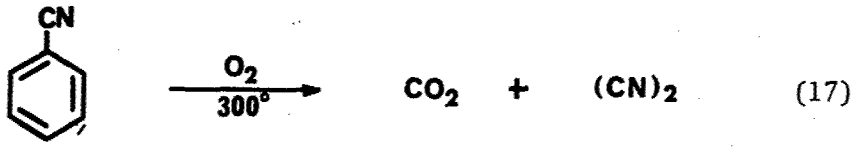



LIV (16)

b. Oxidative Pyrolysis of Benzonitrile

Benzonitrile, one of the products of oxidative pyrolysis of 2,2'-diphenyl-5,5'-bibenzimidazole, 2-phenylimidazole-4,5-dicarboxylic acid, and 2-phenylimidazole is proposed as an intermediate oxidation product of all

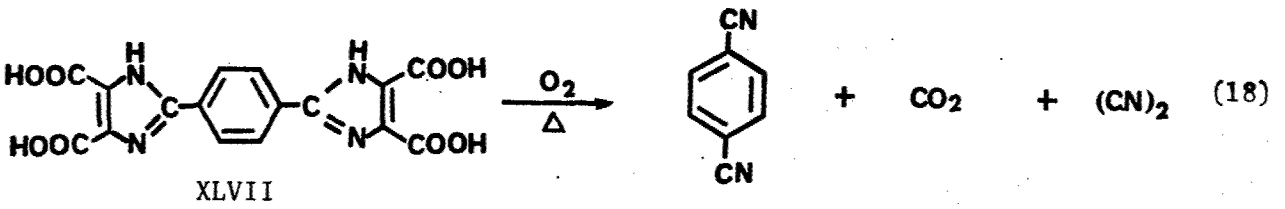
the above starting materials. Furthermore it is proposed as the probable precursor of all or some of the cyanogen resulting from the oxidative pyrolyses. The isolation of benzonitrile from the pyrolyses like that of 2-phenylimidazole is probably due to its rapid escape from the hot pyrolysis chamber before undergoing further oxidation. In order to test this suggestion, benzonitrile (on charcoal) was subjected to an oxygen atmosphere at 300°C. Cyanogen and carbon dioxide were evolved (Reaction 17) indicating that the aromatic ring was completely oxidized to carbon dioxide since no benzene, biphenyl or similar products were found.




(17)

2. Oxidative Pyrolysis of p-Di[2(4,5-dicarboxylic acid)imidazolyl] benzene (VIII)

Oxidative pyrolysis at 300°C of the solution oxidation product of compound V produced carbon dioxide, cyanogen, terphthalonitrile (verified by IR) and unidentified solid tentatively identified (by IR) as a mixture of p-di(2-imidazolyl)benzene and p-(2-imidazolyl)benzonitrile (Reaction 18).




XLVII

(18)

3. Discussion of Oxidative Pyrolyses

Oxidative pyrolysis of the di- and tetra-carboxylic acids, XLVII and XLVIII yields the same mixture of products as pyrolysis of the starting materials from which they were obtained through acid-dichromate solution oxidation. The scheme of pyrolytic oxidation events described in the preceeding paragraphs is shown in Figure 5 for 2-phenylimidazole-4,5-dicar-

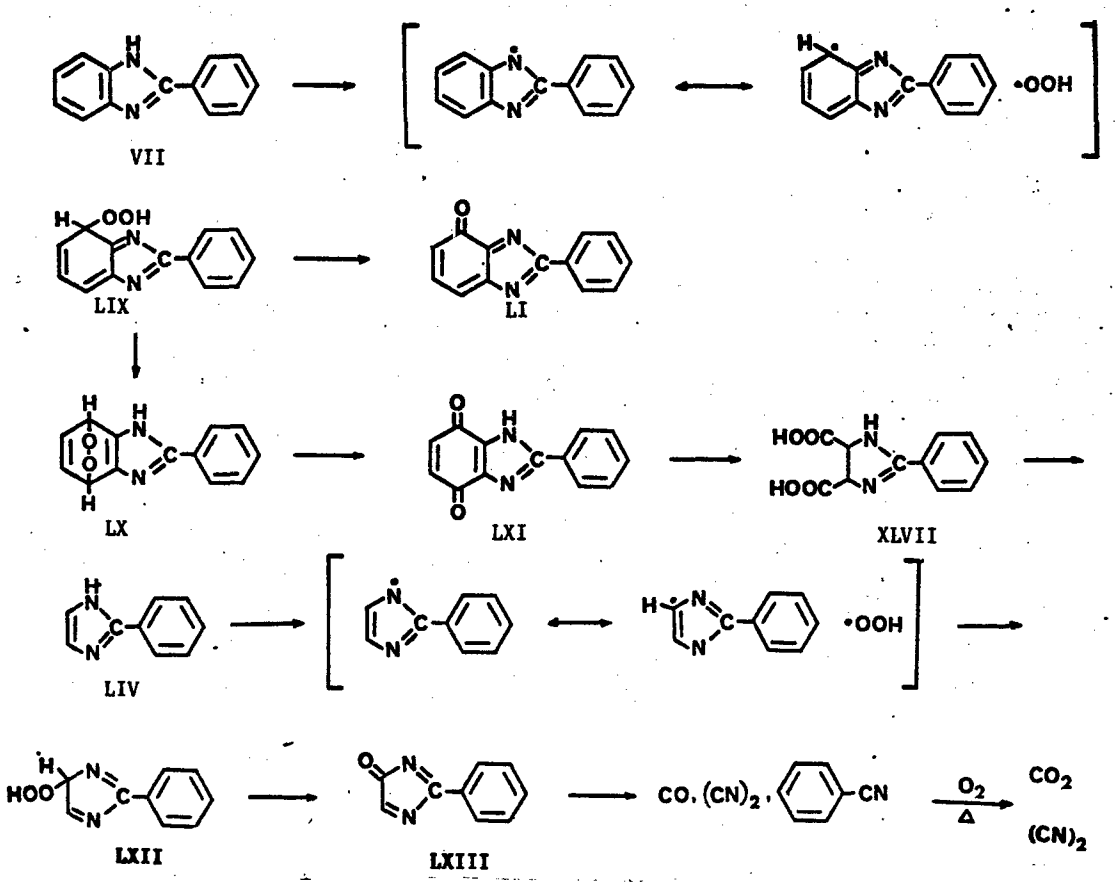



Figure 5. The proposed mechanism for the thermooxidative degradation of the benzimidazole system

boxylic acid (XLVII) and is proposed as representative for the 2-arylimidazole 4,5-dicarboxylic acid system: The interrelationships between solution and pyrolytic oxidation in the benzimidazole system are shown in Figure 6. These findings strongly suggest that the di- and tetra-carboxylic acids are identical or structurally related to transitory intermediates in the pyrolytic oxidation of PBI and benzimidazole model compounds. In addition the isolation of and subsequent oxidation of XLVII and XLVIII provide the first (although circumstantial) observation of beznimidazole pyrolytic oxidation

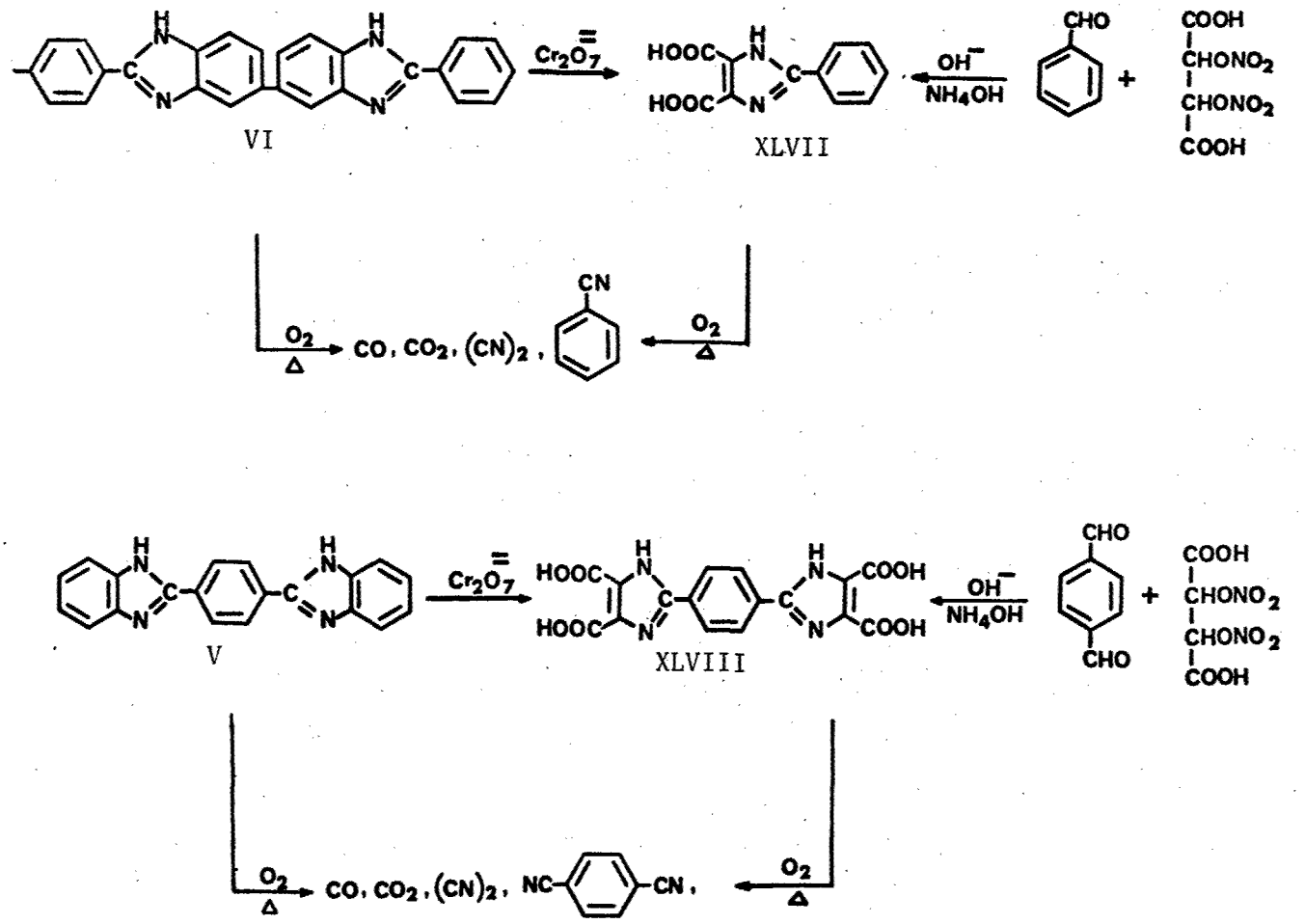


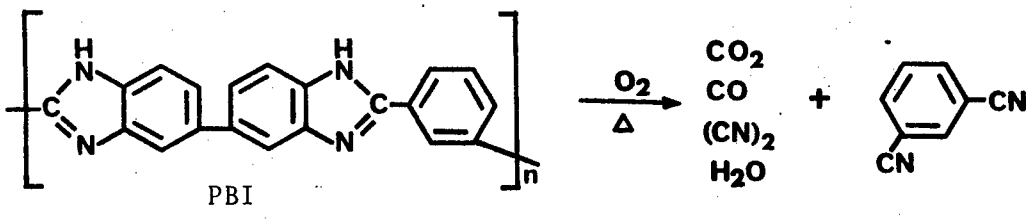

Figure 6. Interrelationships of pyrolytic and solution oxidations in the benzimidazole system

intermediary oxygenated species. It also provides confirmatory evidence that solution oxidation initiates at the carbocyclic ring adjacent to the imidazole nucleus and indirect evidence that pyrolytic oxidation initiates at the same site. Evidence supporting the proposal that oxidation initiates at the benzimidazole portion of PBI and related model compounds during oxidative pyrolysis stems from the following observations:

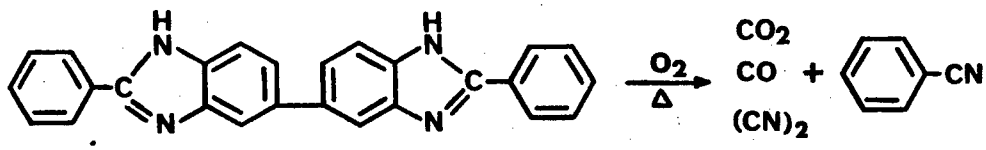
1. Isophthalonitrile in the only organic product of the oxidation of PBI[13] (Reaction 19).
2. Oxidation of model compounds V and VI yields terephthalonitrile and benzonitrile respectively[13] (Reactions 20, 21).
3. Infrared analysis of partially degraded PBI film reveals the

appearance of a nitrile function bound to the polymer chain and gradual disappearance of biphenyl absorptions[12] (Reaction 22).

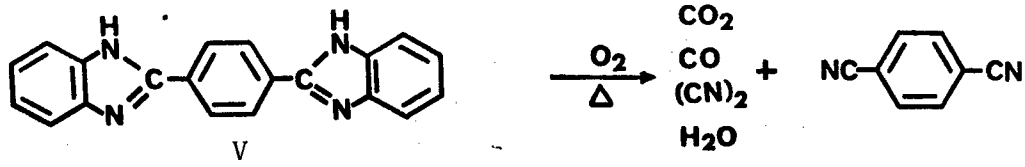
4. Solution oxidation of benzimidazole model compounds V, VI, and VII yield intermediary oxidation products resulting from initial oxidation of the carbocyclic adjacent to the imidazole ring. Subsequent oxidative pyrolysis of the solution oxidation intermediates, the tetracid XLVIII (from V) and the diacid XLVII (from VI and VII) produce the same products as oxidative pyrolysis of the corresponding model compounds.




PBI (19)




VI (20)




V (21)

Observations 1 and 3 reveal that the m-phenylene segment of PBI remains intact longer than the rest of the molecule and that by default oxidation probably initiates at the benzimidazole segment. Observation 2 indicates that the benzimidazole segment is the most reactive (to oxi-

dation) site whether it is in an internal (model compound VI) or a terminal (model compound V) position. Observation 4 by analogy and inference suggests a further refinement, namely that oxygenation initiates at the carbocyclic ring adjacent to the imidazole nucleus.

C. Comparison of Solution and Pyrolytic Oxidation of Benzimidazoles

On the strength of the observations described above certain parellels can be drawn between the proposed mechanism for solution oxidation (Figure 7) and pyrolytic oxidation (Figure 5) of the benzimidazole. The mechanisms described in Figures 5 and 7 are shown specifically for 2-phenylbenzimidazole and are intended to be generally applied to the benzimidazole system including PBI.

As in solution oxidation, homolytic cleavage of the nitrogen-hydrogen bond either thermally or oxidatively is proposed as the initial step (Figure 5) in oxidative pyrolysis of the benzimidazole system to produce an intermediate (LIX) in which the carbocyclic ring is oxygenated. Loss of the elements of water would produce LI already proposed as an intermediate in solution oxidation. Alternatively, formation of the transannular peroxide LX, subsequent peroxide cleavage and loss of hydrogen would produce the quinone LXI. Further oxidation of the quinone to the dicarboxylic acid (XLVII) which is known to be labile with respect to decarboxylation to produce the imidazole (LIV) which on further oxidation would yield the final oxidation products carbon monoxide, carbon dioxide, cyanogen and benzonitrile.

The benzimidazole pyrolytic oxidation mechanism described in Figure 5 is supported in its gross aspects by the experimental observations disclosed in the present investigation. The source of oxides of carbon pro-

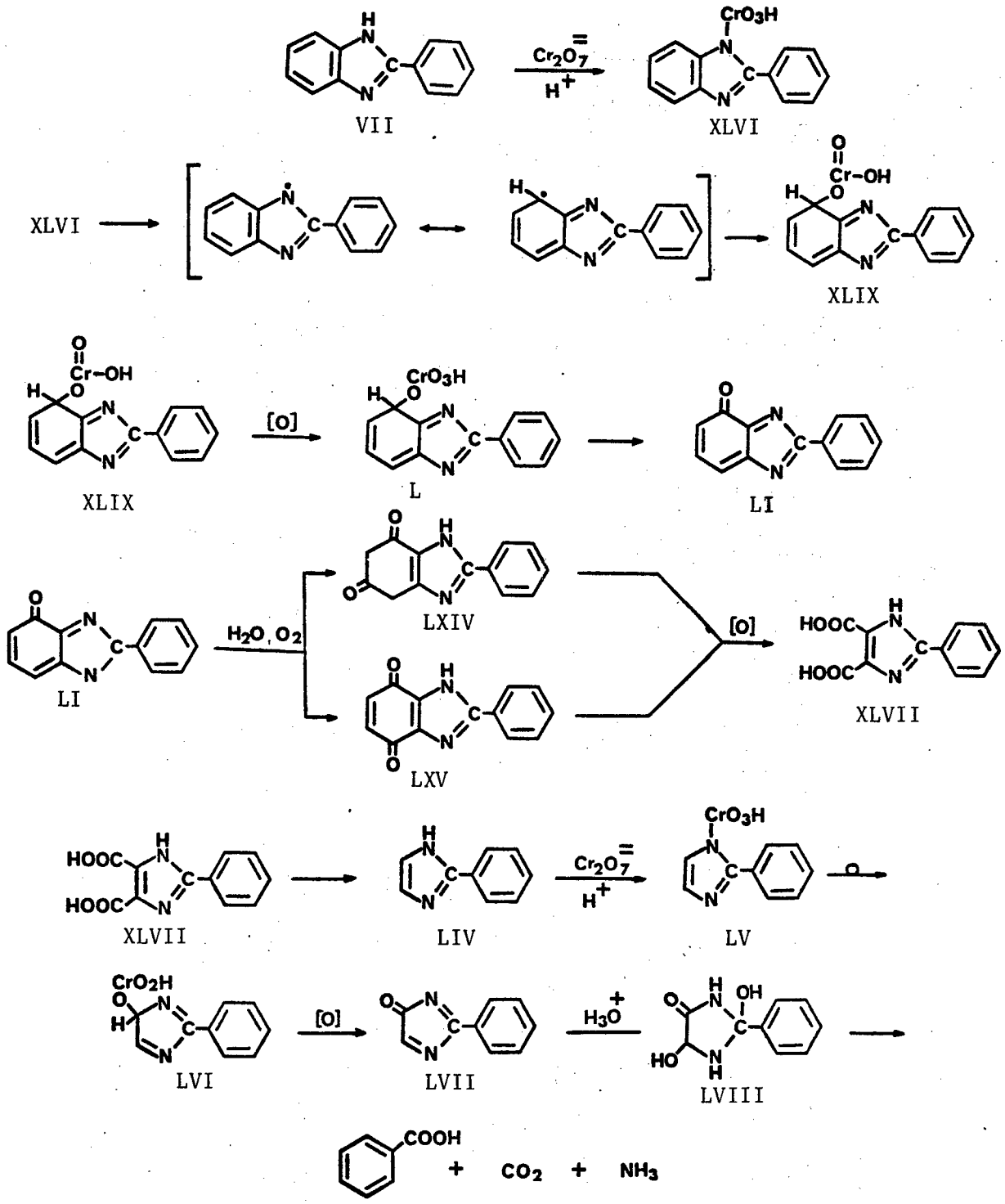
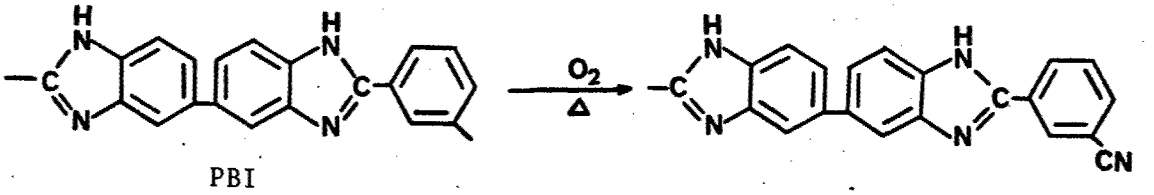



Figure 7. Proposed mechanism for the solution of the benzimidazole system

duct is assigned to the biphenyl system in the initial stages (carbons 4, 5 and 6 in the PBI system) of oxidation and to the carbons of the m-phenylene linkage in the latter states of oxidation. While there is no doubt

that the positions mentioned above are indeed the sources of carbon oxides, the sequential nature of the events proposed is still in question. There is no direct evidence that oxidation does initiate at the carbocyclic rings adjacent to the imidazole nucleus in the pyrolytic oxidation (as it clearly does in solution oxidation) of PBI or any of the model compounds studied.

Similarly the source of cyanogen (the only nitrogen containing product obtained with the possible exception of nitrogen itself) is confidently assigned to decomposition of the heterocyclic ring. Thus controlled oxidation of PBI film[12] at 300°C produces nitrile functions which are known to be bound to the polymer chain and presumed to incorporate the 2 or 2' benzimidazole carbons (Reaction 22). More vigorous pyrolytic oxidation of

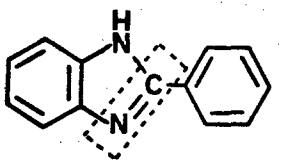



(22)

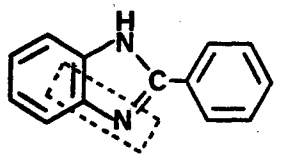
PBI, model compounds V and VI and di- and tetra-carboxylic acids XLVII and XLVIII produce trace quantities of cyanogen, isophthalonitrile (from PBI). terephthalonitrile from V and XLVIII and benzonitrile (from VI and XLVII). There can be little doubt that the source of these organic nitriles is the 2 carbon of the imidazole ring. Subsequent pyrolytic oxidation of the organic nitriles produces cyanogen relating the source of cyanogen to the 2,2'-positions of the PBI parent polymer and related positions in the model compounds and di- and tetra-acid solution oxidation intermediates. This suggestion is experimentally verified by the observation that benzonitrile, when pyrolyzed at 300° in oxygen, produces cyanogen gas.

However, implicit in the mechanism described in Figure 5 is the suggestion that cyanogen also originates from breakdown of the heterocyclic

imidazole nucleus to produce combinations of cyanogen radicals incorporating both nitrogens and the 4 and 5 carbons as well as the 2 carbon (Reactions 23 and 24). The resulting cyanogen radicals then combine to pro-




$\longrightarrow$ •CN $\longrightarrow$ $(CN)_2$ (23)




$\longrightarrow$ •CN $\longrightarrow$ $(CN)_2$ (24)

duce the cyanogen gas observed. Direct evidence for the incorporation of number 2 carbon has been presented as mentioned above. However, direct evidence for incorporation of the second nitrogen and carbons 4 and 5 into cyanogen is not provided by the pyrolysis experiments reported thus far. While it has been shown that pyrolysis of 2-phenylimidazole at 300° in oxygen does produce cyanogen, this cannot be taken as confirmatory evidence since the cyanogen found may arise from further oxidation of the benzonitrile which was also produced in this experiment.

## D. Oxidative Pyrolysis of Isotopically Labelled Model Compounds

### 1. Introduction

In order to obtain experimental evidence to provide insight to the questions raised above, model compound VI was synthesized with carbon-13 labels in specific positions. Mass Spectral analysis of the carbon dioxide oxidative pyrolysis product at various time intervals as reaction progressed would then indicate whether or not the labelled site is a position of initital oxidaton. Thus, a high initial ratio of $^{13}C/^{12}C$ and a lower final ratio

would confirm that the labelled carbon is the site of initial oxidation. It would be ideal to employ model compound VI labelled at the biphenyl carbons since these positions are the proposed site of initial oxidation. However, the synthetic problems are formidable for the preparation of ring labelled 3,3'-diaminobenzidine, a required precursor. The more accessable compounds VI-H (labelled as carbons, 2,2') and VI-T (ring labelled) at the terminal aromatic nucleus) were used for initial investigations.

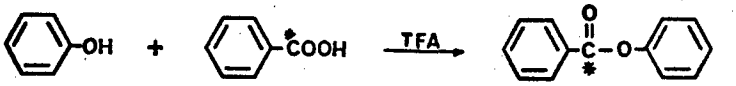
Similarly, mass spectral analysis of the cyanogen produced by oxidative pyrolysis of model compound VI-H should provide confirmatory evidence for the source of cyanogen. Thus if the product cyanogen is enriched in carbon-13 to the same degree as the 2(2') position in starting material, then cyanogen evolves only from those positions and accounts for only one ring carbon. Alternately, production of cyanogen containing a lesser degree of carbon-13 enrichment confirms that cyanogen is also evolving from another site in the heterocyclic ring and provides direct support for the proposition that both nitrogens and carbons 2,4 and 5 (of the imidazole nucleus) are sources of cyanogen.

2. Preparation of Isotopically Labelled Compounds

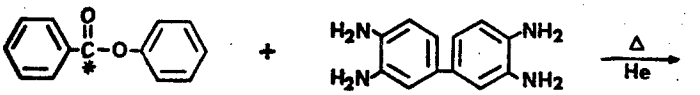
The synthesis of 2,2'-diphenyl-5,5'-bibenzimidazole (VI-H) labelled with carbon-13 at the 2,2' positions was accomplished by the melt condensation of 3,3'-diaminobenzidine and phenylbenzoate enriched with carbon-13 at the carboxylate carbon. Benzoic acid-1-C-13 was prepared by a Grignard reaction using phenylmagnesium bromide and carbon dioxide generated from carbon-13 enriched with barium carbonate. Conversion of benzoic acid to phenylbenzoate was effected by esterification of the phenol in trifluoroacetic anhydride. Finally, the labelled model compound was prepared by melt

condensation of phenylbenzoate with 3,3'-diaminobenzidine. The sequence of reactions is shown in Reactions 25-27. The final product contained 12.1 excess atom percent carbon-13 at positions 2 and 2'.


(25)




(26)

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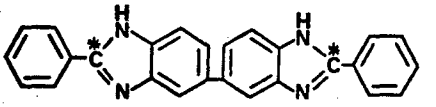
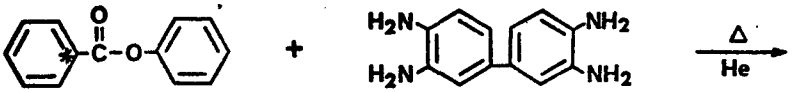
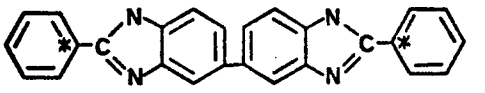



VI-H

Model compound VI labelled in the terminal aromatic nucleus, VI-T, was prepared in the same manner starting with benzoic acid-1-$C^{13}$ (approximately 4.3 atom percent C-13) as shown in reaction 28.




(28)

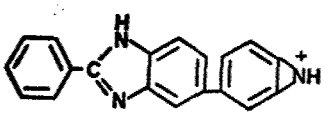



VI-T

3. Mass Spectral Analysis of 2,2'-Diphenyl-5,5'-bibenzimidazole

Carbon-13 enrichment of the labelled model compounds VI-H and VI-T were determined by mass spectroscopy (CEC-21-104) at 70 ev by comparison of intensities of the parent mass peaks, P(386) with parent mass plus one,

(P+1) peak. The mass spectra of VI was relatively simple showing the major parent peak at mass 386 and a mass/2 peak at 193. Evidence of fragmentation was seen by appearance of a major peak at mass 283 which is assigned to the benzazirinium ion (LIX) related to the characteristic fragmentation of imidazole to azirinium ion by loss of HCN.



LIX

Excess $^{13}C/^{12}C$ ratios were obtained by taking the difference in (P+1/P ratios between each labelled isomer and the unlabelled model compounds. The excess percentage of carbon-13 was then calculated for each labelled position. The values obtained are shown in Table III.

Table III

Summation of Mass Spectral Data From Analysis of

Model Compounds VI, $VIC_2$, and VIH (Mass 386)

| Compound | Mass Ratio 387/386 | Excess $^{13}C/^{12}C$ per molecule | Excess $^{13}C/^{12}C$ per labelled carbon | $^{13}C$ Excess atom % $^{13}C$ per labelled carbon |
|---|---|---|---|---|
| VI | 0.296* | - | - | - |
| VIC | 0.351 | 0.045 | 0.028 | 2.72 |
| VIH | 0.572 | 0.276 | 0.138 | 12.1 |

* Calculated Value

4. Analytical Techniques

Initial plans for mass spectral analysis of gaseous products from pyrolytic oxidations of labelled compounds involved separation of carbon mon-

oxide and carbon dioxide by gas chromatography and subsequent mass analysis of the individual gases for evaluation of $^{13}C/^{12}C$ ratios. However, several factors mitigated against this procedure. These included the long retention times on the gas chromatograph (ca. 30 minutes for each sample), the limited supply of labelled starting material and the difficulty associated with resolution of the nitrogen and carbon monoxide mass peaks in the mass spectrometer.

Table IV

Relative Mass Peak Intensities of Typical Pyrolysis Gas Sample Mixture

| M/e | I rel. | Species |
|---|---|---|
| 26 | 0.062 | $CN^+$ |
| 27 | 0.360 | $HCN^+$ |
| 28 | 20.2 | $CO^+$, $N_2^+$ |
| 29 | 0.182 | $CO^+$, $N_2^+$ |
| 30 | 0.093 | $CO^+$, $N_2^+$ |
| 32 | 100 | $O_2^+$ |
| 33 | 0.076 | $O_2^+$ |
| 34 | 0.392 | $O_2^+$ |
| 44 | 19.3 | $CO_2^+$ |
| 45 | 0.218 | $CO_2^+$ |
| 46 | 0.079 | $CO_2^+$ |
| 52 | 0.028 | $(CN)_2^+$ |

Table V

Summation of Mass Spectral Data. Analysis of Carbon Dioxide Pyrolysis Product. Oxidative Pyrolysis of Model Compound VI (Unlabelled)

| Time min. | Mass 44 | Mass 45 | Mass Ratio 45/44 |
|---|---|---|---|
| 15 | 1.86 | 0.022 | (0.0118)* |
| 30 | 8.02 | 0.088 | (0.0110)* |
| 45 | 19.3 | 0.218 | 0.0113 |

Table V Cont.

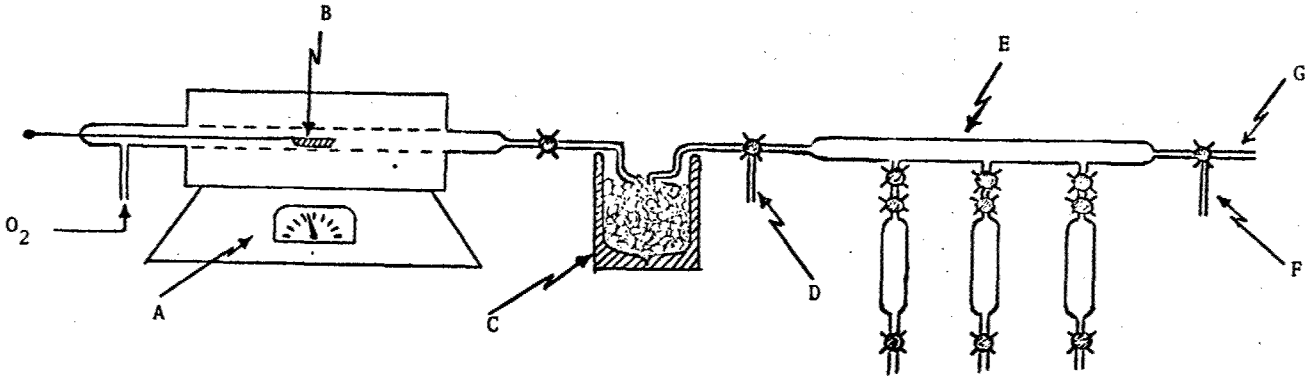
| Time min. | Mass 44 | Mass 45 | Mass Ratio |
|---|---|---|---|
| 55 | 25.9 | 0.291 | 0.0112 |
| 65 | 29.5 | 0.334 | 0.0113 |
| 75 | 32.5 | 0.370 | 0.0114 |
| 85 | 31.9 | 0.367 | 0.0115 |
| 95 | 31.4 | 0.358 | 0.0114 |
| 105 | 3.3 | 0.355 | 0.0113 |

Average Value - Man Ratio 44/45

Used as Standard in Calculations $0.0113 \pm 0.0001$

* Gas Sample Volume too Small. Value Discarded

The technique employed for collection of and mass analysis of carbon dioxide involved pyrolysis of compound VI at 445°C in an oxygen flow rate of one ml per second. The apparatus employed is described in Figure 8.




A. Tube Furnace
B. Pyrolysis Boat and Sample
C. Cooling Bath
D. Manifold Bypass
E. Gas Collection System
F. Helium Inlet
G. Vacuum Pump

Figure 8. Apparatus for pyrolysis and gas collection

Exit gases were first passed through a cooling bath to remove condensibles (benzonitrile and water) and then vented. At appropriate time intervals the exit gas flow was directed to a collection bottle attached to the mani-

fold system. The collection bottles had been previously purged and filled with helium gas. The exit gas was passed through the collection bottle long enough to allow theoretically complete filling of the bottle with the product gas mixture. Thus gas was permitted to flow through a 120 ml collection bottle for two minutes. The mixture of gases in each collection bottle ($O_2$, $N_2$, CO, $CO_2$ and $C_2N_2$) was then introduced into the mass spectrometer. Relative intensities of the more prominent peaks of a typical sample from pyrolysis of model compound VI are shown in Table IV. The mass 45/mass 44 ratio found was 0.0113 ± 0.0001 in agreement with the calculated value. This value was used as the standard in subsequent calculations. As noted above resolution of the $N_2$ and CO peaks was not possible. Mass ratio analysis of cyanogen (mass 52) present in the gas mixture was impractical due to the small quantities present in each mixture. Similarly mass analysis on the basis of the cyanide radical peak (mass 26) is impractical because of interference by the HCN (mass 27) peak. Thus the mass ratios, $^{13}C/^{12}C$ in product gas mixtures was determined solely on the basis of carbon dioxide peaks at masses 44 and 45. Determinations were made on gas mixtures resulting from oxidative pyrolysis of model compound VI (standard), VI-T and VI-H.

As noted above direct determination of $^{13}C/^{12}C$ ratios for cyanogen gas product was impractical. Fortunately, it is not necessary to determine the variation of this value as a function of time of pyrolysis, since our interest is to determine the source of total cyanogen. Thus the technique used for cyanogen collection and mass analysis differed from that described above in that the exit gases from the pyrolysis chamber, after passing through a cold trap to eliminate condensibles, was passed into an aqueous

silver nitrate solution. Silver cyanide was collected for the duration of pyrolysis of compound VI, dried to constant weight and introduced into the solids probe of the mass spectrometer. Thermolysis of the solid silver cyanide in the solids probe liberated cyanogen gas into the mass spectrometer for $^{13}C/^{12}C$ analysis, by comparison of the mass 52 and 53 peaks. The experimental value for mass 53/mass 52 ratio for cyanogen gas from thermolysis of silver cyanide obtained from oxidative pyrolysis of unlabelled model compound VI was 0.0291 in good agreement with the calculated value (0.0293). This value was used as the standard in subsequent calculations.

5. Mass Spectral Analysis of Product $CO_2$ from Oxidative Pyrolysis of Labelled Model Compounds

a. Compound VI-T

Model Compound VI-T labelled with carbon-13 in the 1-position of the terminal phenyl rings was pyrolyzed in oxygen (flow rate of 1 ml per second) at 447 $\pm$ 5°C. Gas product samples were collected after 15, 30, and 45 minutes and at 10 minute intervals thereafter up to a total reaction time of 105 minutes. The mass 45/mass 44 ratio was then determined and the excess $^{13}C/^{12}C$ ratio for each sample computed by taking the difference between the observed mass 45/mass 44 ratio and the standard ratio (0.0013) for unlabelled carbon dioxide. The results are presented in Table VI. The excess atom-percent of carbon-13 (excess over natural

Table VI

Summation of Man Spectral Data. Analysis of Carbon Dioxide Pyrolysis Product. Oxidative Pyrolysis of Model Compound VI-T

| Time (min.) | Man 45/44 Ratio | Excess $^{13}C/^{12}C$ | Excess Atom % Carbon 13 | Percent of Carbon Dioxide Product Originatin from Labelled Position* |
|---|---|---|---|---|
| 15 | 0.0125 | 0.0012 | 0.12 | 26 |

Table VI Cont.

| Time (min.) | Man 45/44 Ratio | Excess $^{13}C/^{12}C$ | Excess Atom % Carbon 13 | Percent of Carbon Dioxide Product Originating from Labelled Position* |
|---|---|---|---|---|
| 30 | 0.0126 | 0.0013 | 0.13 | 29 |
| 45 | 0.0127 | 0.0014 | 0.14 | 31 |
| 55 | 0.0128 | 0.0015 | 0.15 | 33 |
| 65 | 0.0131 | 0.0018 | 0.18 | 40 |
| 75 | 0.0134 | 0.0021 | 0.21 | 46 |
| 85 | 0.0136 | 0.0023 | 0.23 | 51 |
| 95 | 0.0134 | 0.0021 | 0.21 | 46 |
| 105 | 0.0139 | 0.0026 | 0.26 | 57 |

* Calculated from ratio: $\frac{6x \text{ Atom-fraction carbon-13 in } CO_2 \times 100}{\text{Atom-fractured carbon-13 (per labelled atom) in VIC (0.00453)}}$

abundance) for each sample of carbon dioxide was then used to calculate the percent of carbon dioxide product which originated from the labelled position by taking the ratio of the excess atom percent of carbon 13 in $CO_2$ to excess atom percent carbon 13 in VI-T. It was then assumed that all carbons in the terminal phenyl rings were equivalent sources of carbon dioxide. Thus multiplying the percent of carbon dioxide originating from the labelled position by a factor of six gave the value for percent of carbon dioxide originating from the terminal phenyl rings (Table VI). The results indicate that the percent of carbon dioxide originating from the terminal phenyl rings increases with time of pyrolysis.

b. Compound VI-H

Gas samples from the oxidative pyrolysis of Model Compound VI-H at 447±5°C were collected and analyzed for mass 45/mass 44 ratio in the same

manner described above for Model Compound VI-T. The percent of total carbon dioxide originating from the labelled positions was computed by taking the ratio of excess atom percent carbon-13 in carbon dioxide to excess atom percent carbon-13 in Model Compound VI-H. The results are presented in Table VII and indicate that the percent of carbon dioxide originating from carbons 2, 2' is reasonably constant throughout the course of oxidative pyrolysis.

Table VII

Summation of Mass Spectral Data. Analysis of Carbon Dioxide Pyrolysis Product. Oxidative Pyrolysis of Model Compound VIH

| Time (min.) | Mass $\frac{45}{44}$ Ratio | Excess $^{13}C/^{12}C$ | Excess atom % Carbon-13 | Percent of Carbon Dioxide Product Originating from labelled position* |
|---|---|---|---|---|
| 15 | 0.0196 | 0.0083 | 0.82 | 6.8 |
| 30 | 0.0196 | 0.0083 | 0.82 | 6.8 |
| 45 | 0.0202 | 0.0089 | 0.88 | 7.3 |
| 55 | 0.0195 | 0.0082 | 0.81 | 6.7 |
| 65 | 0.0202 | 0.0089 | 0.88 | 7.3 |
| 75 | 0.0192 | 0.0079 | 0.78 | 6.4 |
| 85 | 0.0203 | 0.0090 | 0.89 | 7.4 |
| 95 | 0.0204 | 0.0091 | 0.90 | 7.4 |
| 105 | 0.0202 | 0.0089 | 0.88 | 7.3 |

* Calculated from ratio: $\frac{\text{Atom-fraction carbon-13 in } CO_2}{\text{Atom-fraction carbon-13 (per labelled atom) in VIH (0.121)}}$

6. Discussion of Analytical Results (Carbon Dioxide)

The percent of total carbon dioxide originating from the terminal phenyl ring carbons and from the imidazole ring 2(2') carbons has been de-

termined for oxidative pyrolysis of model compound VI as a function of time. These values are summarized in Table VIII. The values for total carbon dioxide originating from the biphenyl carbons accounts for the remainder

Table VIII

Percent of Carbon Dioxide Product Originating from Specific Positions in Model Compound VI During Oxidative Pyrolysis at 445°C.

| Time (min.) | Carbon 2(2') | Terminal Ring Carbons | Biphenyl Carbons |
|---|---|---|---|
| 15 | 6.8 | 26 | 67 |
| 30 | 6.8 | 29 | 64 |
| 45 | 7.3 | 31 | 62 |
| 55 | 6.7 | 33 | 60 |
| 65 | 7.3 | 40 | 53 |
| 75 | 6.4 | 46 | 48 |
| 85 | 8.4 | 51 | 42 |
| 95 | 7.4 | 46 | 47 |
| 105 | 7.3 | 57 | 36 |

of the carbon dioxide. These values are also included in Table VIII for each time interval. Examination of the data in Table VIII reveals several important trends. First, the apparent constant percentage of carbon dioxide originating from positons 2 and 2' suggests a constant rate of oxidation of these positions relative to the rest of the molecule. The apparent increase in percent of carbon dioxide originating from the terminal phenyl rings and the accompanying decrease in percent carbon dioxide originating from the biphenyl carbons as reaction time increases indicates that there is a preferred site of oxidation initiation and that this site

appears to be the biphenyl positions as predicted in the mechanism proposed (Figure 5).

A critical analysis of the data obtained is not warranted until it has been demonstrated to be reproducible and some indication of its reliability is obtained. Certain operational difficulties which were encountered with the mass spectrometer suggest that while the trends observed are reliable, the specific values are of undetermined reliability. For example the fact that the percentage of carbon dioxide originating from the terminal phenyl ring carbons increases with time is accepted with confidence. However, the fact that the percentage of carbon dioxide originating from carbon atoms 2 and 2' is constant is questionable because of the high degree of scatter among the values obtained. The data also suggests a possible slight increase in these values with time. The instrument is presently undergoing a complete overhaul to correct the problems involved before repeating the determinations.

With reservations based on the foregoing statements in mind the data can be used to make several important deductions about the thermal oxidation mechanism of the 2-aryl substituted benzimidazole system. First of all, if there were no selective site for oxygenation (i.e. random oxygenation) of the molecule followed by rapid collapse to carbon dioxide, one would anticipate the percentages of carbon dioxide originating from the terminal phenyl rings, the biphenyl carbons and from the 2,2'positions to be 46.2, 46.2 and 7.7 respectively throughout the course of the reaction. The fact that the biphenyl carbons produce carbon dioxide at a considerably higher initial percentage (67%) which then decreases with time indicates that this portion of the molecule undergoes initial attack by oxygen preferentially and continues to be destroyed at a higher rate than the re-

mainder of the molecule. Similarly the terminal phenyl rings produce an initial percentage of carbon dioxide well below the calculated statistical value of 46.2 per cent and the percentage then increases with time to a higher value than the statistical value. This finding reveals that the terminal phenyl ring has an initial oxidation rate considerably lower than the biphenyl portion of the molecule. The relatively slower destruction of the phenyl rings results in their concentration being higher at any time after initiation and ultimately their apparent higher rate of reaction as the reaction proceeds.

The 2,2' carbons produce carbon dioxide at the initial percentage of about seven and changes relatively little throughout the course of the reaction. The fact that this value is constant throughout the course of reaction suggests that its rate of oxidation is between the rates for oxidation of the biphenyl and terminal phenyl carbons. Thus during the early phases of oxidation the biphenyl carbons produce the highest percentage of carbon dioxide, the 2,2' carbons produce the next highest percentage (on a per carbon basis) and the terminal phenyl carbons the lowest percentage. As the reaction progresses, and effective concentrations of each segment decreases, the apparent rate of reaction of the biphenyl and terminal phenyl carbons reverse while the rate of reaction of the 2,2' carbons would remain relatively constant. This observation is probably an artifact of the rates of oxygenation of the different segments relative to one another and one would expect, as reaction progresses even further toward completion, that the percentage of carbon dioxide originating from the 2,2' carbons would show at least a slight increase. This trend is suggested but not verified by the present data.

It is possible to evaluate a limiting value for the relative initial reactivities of each segment of the 2-arylbenzimidazole to oxygenation by plotting the ratio of percent carbon dioxide originating from one position to the percent originating from another position versus time and extrapolating to time zero. The results of such treatment are shown in Figures 9, 10 and 11 revealing a fair linear relationship in each case and demonstrating that the biphenyl position is clearly the most susceptible to attack by oxygen producing an eleven fold excess of carbon dioxide when compared to the 2,2' carbons and approximately a three-fold excess when com-

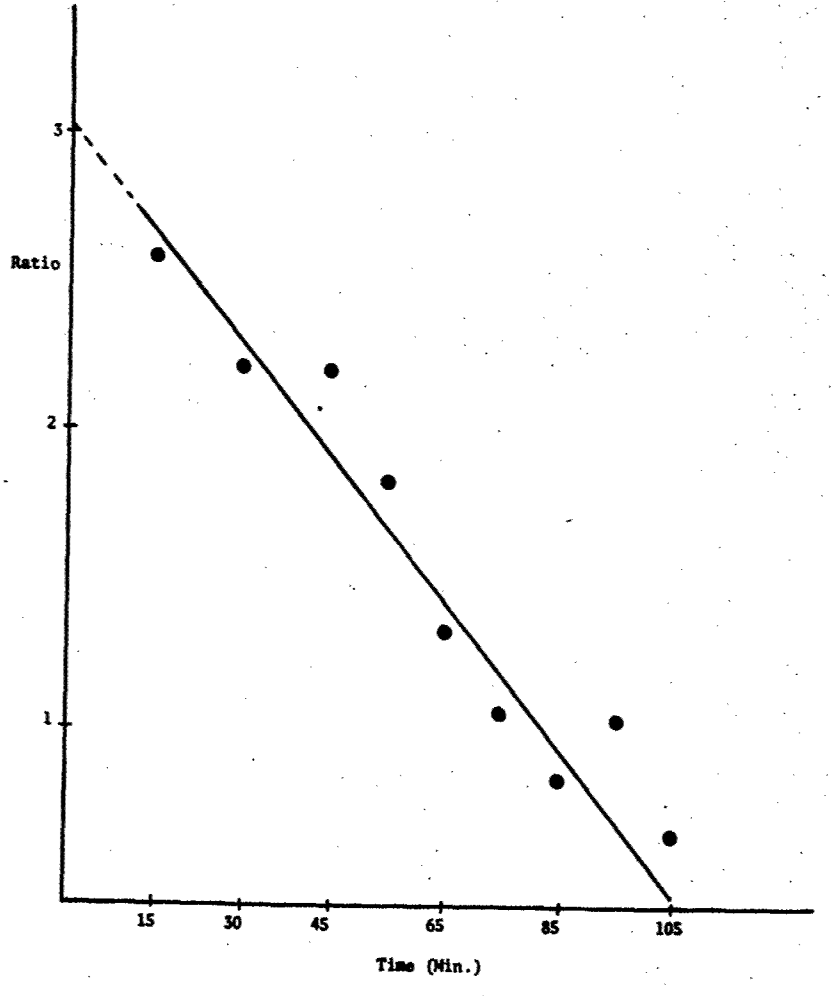



Figure 9. Ratio of percent $CO_2$ orginating from biphenyl carbons to percent originating from 2(2') carbons versus time

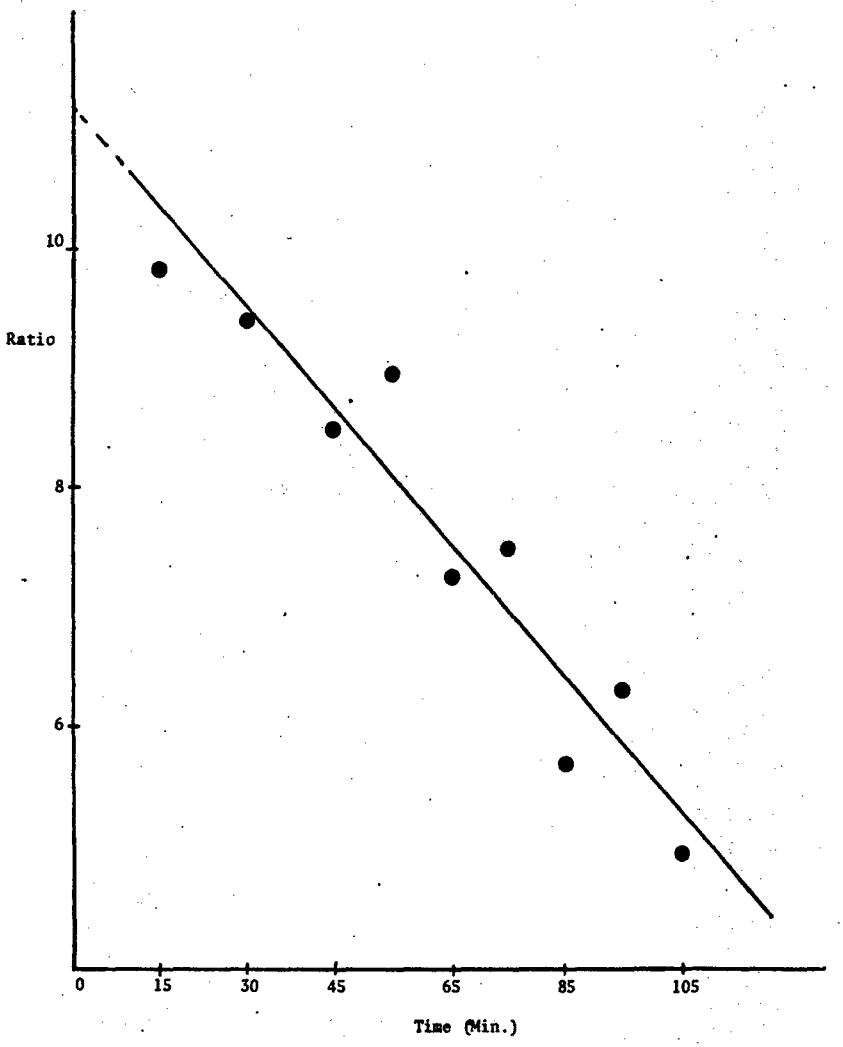



Figure 10. Ratio of percent $CO_2$ originating from biphenyl carbons to percent orginating from 2(2') carbons versus time

pared to the terminal phenyl carbons. These values indicate a surprisingly high degree of selectivity for oxygenation at elevated temperatures and are in good agreement with the postulated mechanism which proposes initial oxygenation at the biphenyl carbons. This treatment of the data suggests a mechanism which results in initial oxidation of the biphenyl ring to produce a stabilized intermediate (perhaps stablized through crosslinking) followed by oxidation of the 2,2' carbon and the terminal ring carbons in rapid sequence (Reaction 28).

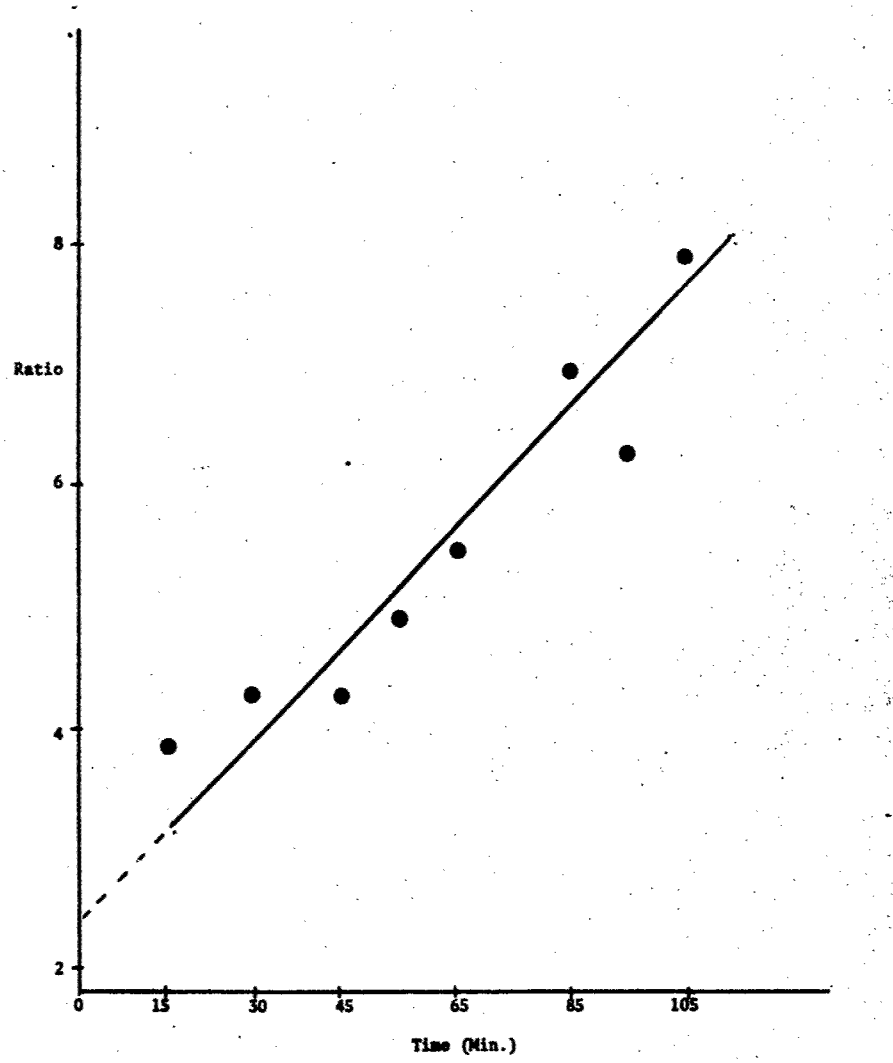
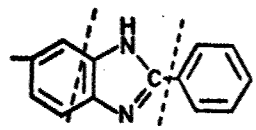



Figure 11. Ratio of Percent $CO_2$ originating from terminal phenyl carbons to percent originating from 2(2') carbons versus time

An alternative method of treating the data involves segmenting the model compound into the terminal phenyl ring, the imidazole nucleus and the remaining carbons of the biphenyl systems as shown below. Non-selective oxidation of the molecule would be expected to produce carbon dioxide from



each segment on a statistical basis or 46.2 percent from the terminal phenyl rings, 23.1 percent from the imidazole segment and 30.8 percent from the remaining biphenyl carbons.

Recalculation of the experimental data is presented in Table IX. Examination of the data reveals essentially the same trends previously discussed. The higher selectivity of the biphenyl carbons to oxygenation and lower selectivity of the remainder of the molecule is confirmed by this treatment of the data. Further analysis of the data which involves plotting the ratios of the percent carbon dioxide from the various segments of the molecule versus time and extrapolation to zero time gives an indication of limiting values for initial susceptibility to oxygenation (Figures 12, 13 and 14). The extrapolations indicate that the biphenyl carbons produce an initial 2,2-fold (3.3-fold on a per carbon basis) excess carbon dioxide when compared to the terminal phenyl rings and a 3-fold (2.2 fold on a per carbon basis) excess compared to the imidazole carbons. The imidazole carbons produce an initial 1.1-fold (2.2-fold on a per carbon basis) excess of carbon dioxide compared to the terminal phenyl carbons.

Table IX

Percent of Carbon Dioxide Product Originating From Specific Positions in Model Compounds VI During Oxidative Pyrolysis at 445°C

| Time (min.) | Imidazole Carbons | Terminal Phenyl Carbons | 4,5,6,7(4',5',6',7') Carbons |
|---|---|---|---|
| 15 | 20 | 26 | 54 |
| 30 | 20 | 29 | 51 |
| 45 | 22 | 31 | 47 |

Table IX Cont.

| Time (min.) | Imidazole Carbons | Terminal Phenyl Carbons | 4,5,6,7(4',5',6',7') Carbons |
|---|---|---|---|
| 55 | 20 | 33 | 47 |
| 65 | 22 | 40 | 38 |
| 75 | 19 | 46 | 35 |
| 85 | 22 | 51 | 27 |
| 95 | 22 | 46 | 32 |
| 105 | 22 | 57 | 21 |

The appealing feature of this method of data analysis is that it confirms in greater detail the proposed mechanism (Figure 5) which describes first oxygenation of the carbons of the carbocyclic adjacent to the imidazole nucleus still intact (but perhaps crosslinked). The subsequent steps then occur in rapid sequence and involve destruction of the imidazole nucleus and then destruction of the terminal ring carbons.

7. Mass Spectral Analysis of Cyanogen from Oxidative Pyrolysis Model Compound VI-H

Model compound VI-H labelled with 12.1 percent excess carbon-13 in the 2 and 2' positions was pyrolyzed at 447±5°C in an oxygen atmosphere (flow rate 1 ml per second). Cyanogen gas product was collected as the silver complex by precipitation from an aqueous silver nitrate solution. The silver cyanide was collected over a 105 minute period, filtered, dried to constant weight and placed in the solids probe of the mass spectrometer. The solid was then thermolyzed in the solids probe to liberate cyanogen gas which was analyzed for carbon-13 enrichment by comparison of the ratio of mass 53/mass 52 with cyanogen obtained in the same manner from labelled model compounds VIH. The results of this analysis, summarized in Table X, revealed that the cyanogen evolved from compound VI-H contained 1.22 per-

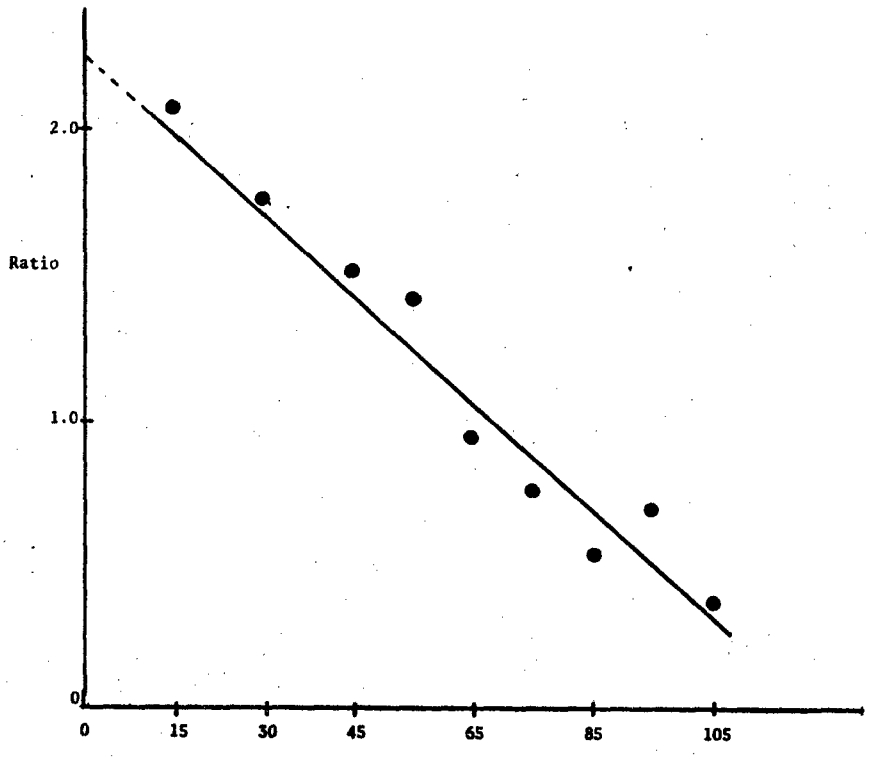



Figure 12. Ratio of percent $CO_2$ originating from 4,5,6,7 carbons to percent originating from imidazole carbons versus time

Table X

Summation of Mass Spectral Data. Analysis of Cyanogen (Mass 52) Product. Oxidative Pyrolysis of Model Compounds VI and VIH

| Origin of Cyanogen | Mass Ratio 53/52 | Excess $^{13}C/^{12}C$ per molecule | Excess $^{13}C/^{12}C$ per carbon | Excess atom % Carbon-13 per carbon |
|---|---|---|---|---|
| Model Compound VI (unlabelled) | 0.0291 | - | - | - |
| Model Compound VIH | 0.0540* | 0.0249 | 0.0124 | 1.22 |

* Average value of two determinations

Percent Cyanogen derived from labelled positions (2,2') = $100x \frac{0.0122}{0.121} = 10.1\%$

cent excess carbon-13 in each carbon. If all of the cyanogen had evolved

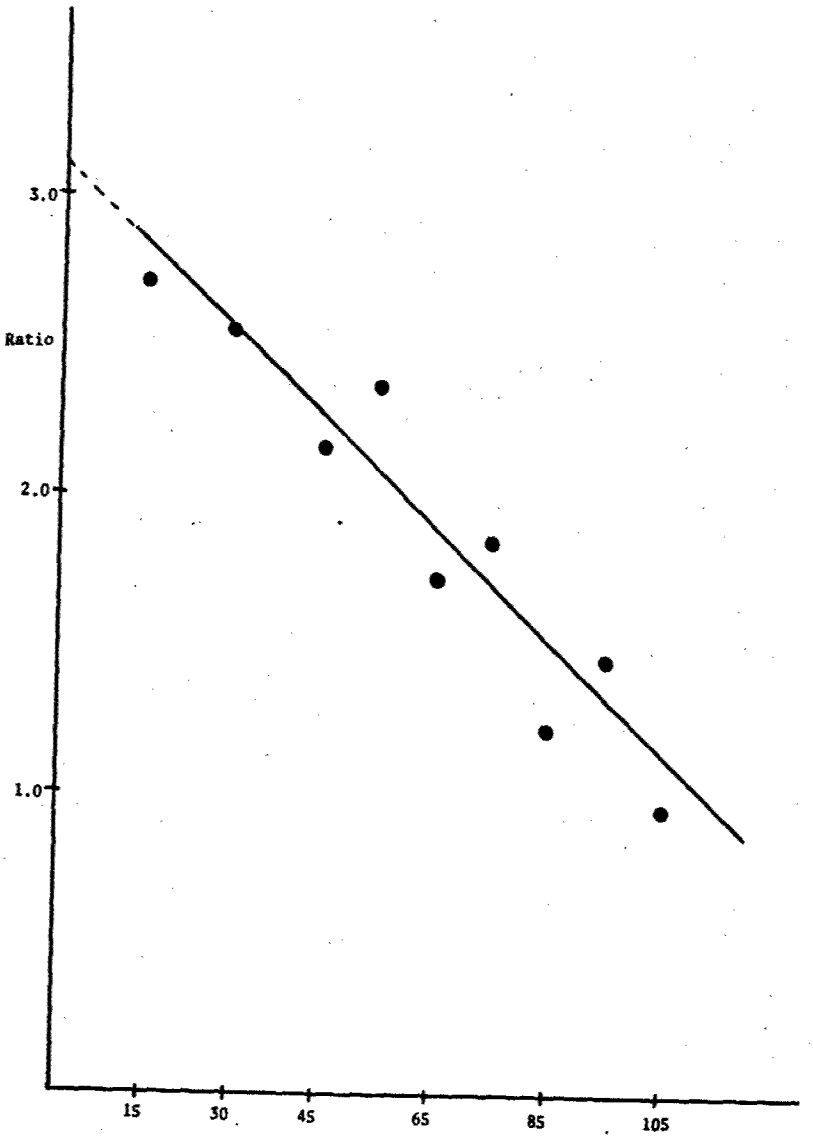



Figure 13. Ratio of percent $CO_2$ originating from 4,5,6,7 carbons to percent originating from terminal phenyl carbons versus time

from the 2 and 2' carbons, the gas would have had the same degree of enrichment as the starting material, 12.1 percent excess carbon-13 per carbon atom.

8. Discussion of Analytical Results (Cyanogen)

The experimental results reveal that 10.1 percent of the cyanogen originates from the 2 and 2' positions of compound VI. This result veri-

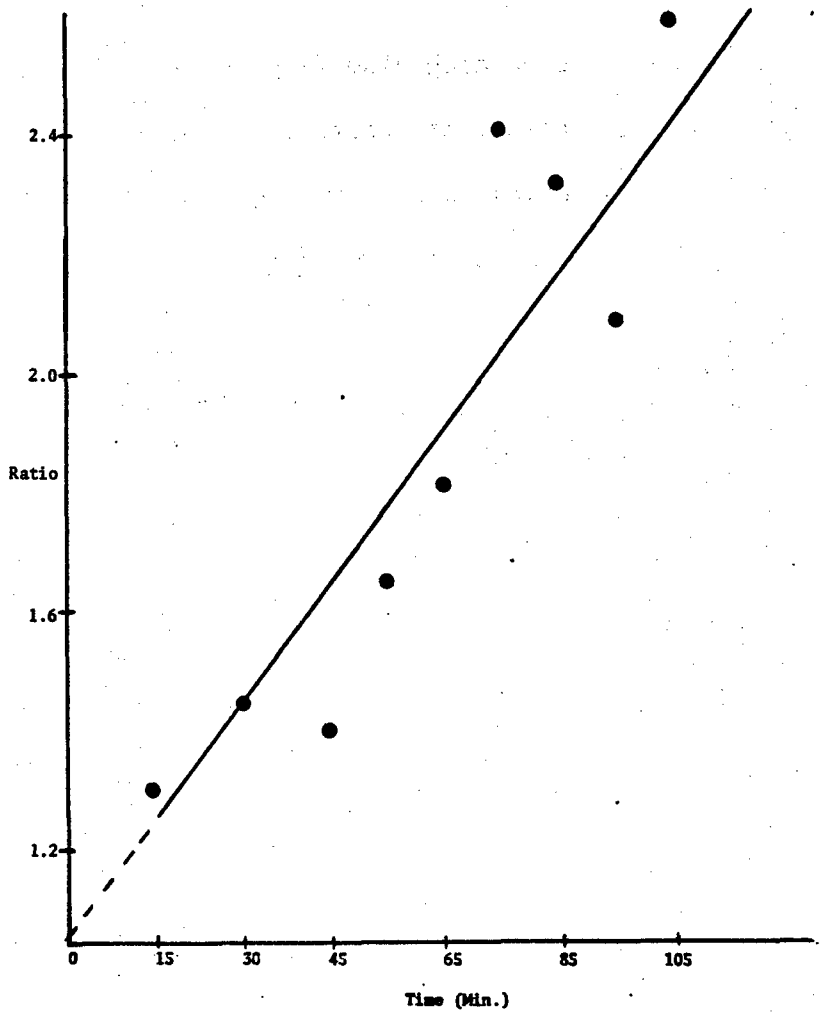



Figure 14. Ratio of percent $CO_2$ originating from terminal phenyl carbons to percent originating from imidazole carbons versus time

fies previous findings which indicate that cyanogen at least partially evolves from the 2, 2' carbons through fragmentation of benzonitrile and its subsequent fragmentation to form cyanide radical (Reaction 23), the precursor of cyanogen. Moreover, the results demonstrate that cyanogen also originates from other sites in the molecule involving both nitrogens and the 8 and 9 carbons (Reaction 24). These findings confirm conclusively

the final steps in the proposed mechanism (Figure 5) in which it was suggested that cyanogen originates from breakdown of the heterocyclic imidazole nucleus to produce combinations of cyanogen radicals incorporating both nitrogens and the 8 and 9 carbons as well as the 2 carbons.

## SECTION III

## SUMMARY AND CONCLUSIONS

Previous reports from our laboratories disclosed experimental results providing evidence supporting the suggestion that polybenzimidazole oxidizes in a stepwise manner involving initial oxygenation at a specific weak-link in the repeat unit of the polymer chain. The suggestion that during the course of thermal oxidation, the m-phenylene segment remains intact longer than the remainder of the repeat unit is supported by the observation that PBI, model compound V and model compound VI yield isophthalonitrile, terephthalonitrile and benzonitrile respectively as the only organic products[13]. Thus by default, the benzimidazole portion of the molecule was selected as the most reactive site for initial oxygenation. Additional experimental evidence for this proposal was obtained by the observation that controlled oxidation of PBI film (300°, $O_2$) resulted in the appearance and gradual increase of nitrile functions in the polymer chain and concurrent gradual disappearance of the biphenyl units[12]. This further suggested the carbocyclic ring adjacent to the imidazole heterocyclic as the likely site for initial oxygenation.

Thus oxygenation was thought to occur by reaction of molecular oxygen with the benzimidazole radical formed by homolytic cleavage of the nitrogen-hydrogen bond as shown in Figure 2.

In the present report additional experimental evidence has been presented confirming the theory that initial oxygenation occurs preferentially at the benzenoid carbocyclic adjacent to the imidazole ring. Thus the fact that model compounds V, VI and VII undergo oxidation in solution by dichromate to yield the corresponding imidazole-dicarboxylic acids XLVIII

and XLVII confirms previous reports and supports the suggestion that the aromatic heterocyclic is more resistant to oxidation than the adjacent aromatic carbocyclic.

Subsequent oxidative pyrolysis of the benzimidazole solution oxidation intermediates such as XLVII, 2-phenylimidazole-4,5-dicarboxylic acid to give products identical (oxides of carbon, cyanogen and benzonitrile) to those obtained from similar thermal oxidation of the parent model compound - confirming that identical or similar oxygenated intermediates are also transitory species in pyrolytic oxidation of the 2-aryl benzimidazole system.

Finally pyrolytic oxidation and subsequent mass analysis of product carbon dioxide of model compound VI labelled in the 2(2') (VI-H) position and in the terminal phenyl group (VI-T) confirm that the carbocyclic aromatic nucleus adjacent to the imidazole heterocyclic is the most reactive site for initial oxygenation since those carbons initially produce the greatest percentage of carbon dioxide. In the same series of experiments, it was found that the terminal phenyl carbons produce (initially) the lowest percentage of carbon dioxide proving that this position is the least reactive toward initial oxygenation.

Loss of carbon dioxide from the oxygenated carbocyclic XLVII (Figure 5) intermediate produces the 2-phenyl substituted imidazole intermediate (LIV, Figure 2) as verified by the finding that 2-phenylimidazole-4,5-dicarboxylic acid decarboxylated thermally to produce 2-phenylimidazole (Reaction 15). The next step in this major reaction path of the benzimidazole system on pyrolytic oxidation involves oxygenation of the 4 or 5 carbons of the 2-arylimidazole (identical to the 8 and 9 carbons of the benzimidazole) producing the intermediates LXII and LXIII (Figure 5) which subsequently produce oxides of carbon, benzonitrile and cyanogen. This

step is verified by the fact that 2-phenylimidazole pyrolytically oxidizes to produce carbon dioxide, cyanogen and benzonitrile (Reaction 16). The fact that cyanogen originates from all three carbons of the imidazole nucleus is confirmed first by the observation that benzonitrile, on oxidative degradation, produces cyanogen (accounting for the imidazole 2 carbon) and secondly by the fact that model compound VI-H on oxidative degradation produces cyanogen with ten percent of the enrichment of starting material. This finding accounts for the fate of all carbons and nitrogens in the imidazole nucleus by demonstrating that cyanogen also originates from its 4 and 5 carbons.

## SECTION IV

## EXPERIMENTAL

1. Dichromate Oxidation of Benzimidazole (XLII)

Potassium dichromate (37g) was added portionwise to a solution of 5g (0.042 mole) of benzimidazole in 50 ml of water and 70 ml of conc. $H_2SO_4$. After addition was complete the reaction mixture was heated at 90°C for ten minutes. The reaction mixture was then diluted with water and the resulting precipitate was filtered off, washed with acetone, dissolved in ten percent aqueous NaOH and reprecipitated with HCl. After filtering, the product was washed with water and dried to yield 2.8 g (0.018 mole, 43% yield) of imidazole-4,5-dicarboxylic acid, m.p. 273°C (lit[4] m.p. 273°).

2. Dichromate Oxidation of 2-Methylbenzimidazole (XLIII)

2-Methylimidazole-4,5-dicarboxylic acid was prepared by oxidation of 2-methylbenzimidazole according to the above procedure using 18.5g. $K_2Cr_2O_7$, 2.5g (0.019 mole) of 2-methylbenzimidazole, 25 ml of water and 25 ml of conc. sulfuric acid to yield 700 mg (41 mole, 22% yield) of 2-methylimidazole-4,5-dicarboxylic acid, m.p. 266°C.

3. Dichromate Oxidation of 2-Phenylbenzimidazole (VII)

2-Phenylimidazole-4,5-dicarboxylic acid (XLVII) was prepared by oxidation of 2-phenylbenzimidazole according to the above procedure using 45g of $K_2Cr_2O_7$, 6.0g (0.031 mole) of 2-phenylbenzimidazole, 60 ml of water and 130 ml of conc. $H_2SO_4$ to yield 300 mg (13 mole, 4.2% yield) of 2-phenylbenzimidazole-4,5-dicarboxylic acid, m.p. 264°C; nmr (TMS) δ2.52 (singlet, 1H, N-H), δ7.52 (multiplet, 2H, aromatic H), δ8.15 (multiplet, 3H, aromatic H), δ12.53 (broad singlet, 2H, carboxylic acid H).

4. Dichromate Oxidation of p-Di(2-benzimidazolyl)benzene (Model Compound V)

To a solution of 1 g of compound V in 25 ml of conc. $H_2SO_4$ was added

8 ml of water. The mixture was then cooled to 0°C and 7.2 g of potassium dichromate was added. An exothermic reaction ensued and its temperature was maintained at 75-90°C for twenty minutes. The reaction mixture was then poured into one liter of ice cold water and allowed to stand at 15°C for 30 hours. The precipitated solid was filtered and washed with water to neutrality. The solid was then dissolved in five percent aqueous NaOH, filtered and acidified with dil. HCl. The resulting solid was then filtered, washed to neutrality with water and dried, to give a solid, m.p. 270° (dec.), neut. equiv. 96.5 (calc. value 96.5). The infrared spectrum of this solid indicated it was an imidazole-carboxylic acid and it was assigned the structure p-di[2-(4,5-di-carboxylic acid)imidazolyl]benzene (XLVIII).

6. Preparation of p-Di[2-(4,5-dicarboxylic acid)imidazolyl]benzene (XLVIII)

Dinitrotartaric acid was prepared by the addition of 100 ml of concentrated $H_2SO_4$ to a mixture of 25 g (0.167 mole) of finely powdered tartaric acid dissolved in 54 ml of concentrated nitric acid and 54 ml of fuming nitric acid. The temperature was held below 38°C during the addition. The reaction mixture was cooled in an ice bath for 2.5 hours before filtering off the solid dinitrotartaric acid.

The above product was dissolved in 500 ml of ice water and the solution neutralized with cold $NH_4OH$ while the temperature was held between -5 and -12°C. To this solution, 30 ml of $NH_4OH$ was added followed by the addition of 12 g (0.09 mole) of terephthaldehyde. The reaction mixture was stirred at room temperature for 24 hours. The resulting solid was filtered, washed with water and dried to yield 3.2 g (8 mole), 10% yield, of p-di[2-(4,5-dicarboxylic acid)imidazolyl]benzene, m.p. 270°C (de-

comp.). The infrared spectra of this product was identical to that of the solution oxidation product of model compound V. The melting point of a mixture of this product and (XLVIII) was 270°C.

5. Solution Oxidation of 2,2'-Diphenyl-5,5'-bibenzimidazole (Model Compound VI)

To a mixture of 6 g (0.016 mole) of VI in 30 ml $H_2O$ was added 140 ml conc. $H_2SO_4$. The reaction mixture was then cooled in a dry-acetone bath before adding 45 g of potassium dichromate. After 10 minutes the reaction mixture was allowed to warm up to 70°C and then immediately cooled with the dry-ice acetone bath. This procedure was continued for 30 minutes after which the mixture was poured into 200 ml of ice-cold water and left at 10°C for 48 hours. The precipitated solid was filtered, washed with water to neutrality to yield 50 mg ($2.2 \times 10^{-4}$ moles, 0.7% yield) of 2-phenyl-4,5-dicarboxylic acid, m.p. 264°C.

6. Preparation of 2-Phenylimidazole-4,5-dicarboxylic Acid (XLVII)

2-Phenylimidazole-4,5-dicarboxylic acid was prepared according to the above procedure except that 19.0 g (0.18 mole) of benzaldehyde was used instead of terephthaldehyde. The product, obtained in 38 percent yield (16 g), m.p. 264°C, mixed m.p. with XLVII 264°C. The infrared spectra of 2-phenylimidazole-4,5-dicarboxylic acid was identical to that of (XLVII).

7. Oxidation of Benzoic Acid

Benzoic acid (1 g) was added to a solution of 15 ml of 1:3 dilute sulfuric acid containing 6 g of $K_2Cr_2O_7$. The reaction mixture was heated at 100°C and the off gas passed through a cold (0°C) trap and then through a solution of calcium hydroxide. Calcium carbonate precipitated as the reaction progressed and no benzene was found in the cold trap or the reaction mixture.

8. Permanganate Oxidation of Chromate-2-Phenylbenzimidazole Compounds (XLVI)

Compound XLVI (120 mg) was dissolved in a solution of 130 mg of $KMnO_4$ in 10 ml of water. The reaction mixture was heated in a steam bath under helium for five minutes while the exit gas was passed through limewater. After two minutes an exothermic reaction ensued and the limewater precipitated calcium carbonate. Attempted isolation of organic materials from the reaction mixture was unsuccessful.

9. Permanganate Oxidation of 2-Phenylbenzimidazole (VII)

Experiment 9 was repeated using 2-phenylbenzimidazole (110 mg) in place of its chromate compound. No evidence of carbon dioxide evolution was observed and the starting material was recovered in quantitative yield.

10. Oxidative Pyrolysis of 2-Phenylimidazole-4,5-dicarboxylic Acid (XLVII)

2-Phenylimidazole-4,5-dicarboxylic acid (110 mg, 0.6 mole) was heated at 300°C for thirty minutes in a tube under a stream of oxygen. The exit gases were passed through a cold trap (-5°C) and then through a solution of aqueous sodium hydroxide. After completion of reaction, excess $BaCl_2$ was added to the basic solution to precipitate $BaCO_3$ which filtered off and shown to be the equivalent 1.2 mole of carbon dioxide indicated quantitative decarboxylation of both dicarboxylic acid functions in the starting material. The cold trap was then examined and found to contain benzonitrile and a solid with m.p. 145°C. This solid, from its melting point and I.R. spectrum is assumed to be 2-phenylimidazole.

11. Pyrolytic Oxidation of p-Di[2-(4,5-dicarboxylic acid)imidazolyl]-benzene (XLVIII)

The tetracarboxylic acid (500 mg) was heated at 300°C in a hard glass test tube while oxygen was passed into it. A white sublimate collected on the side of the test tube and the exit gases, passed through an ice-salt

trap, an aqueous silver nitrate and an aqueous barium hydroxide solution produced precipitates in all the traps. The white sublimate, by infrared analysis appeared to be p-di(2-imidazolyl)benzene. The solid collected in the ice-salt trap was shown by infrared to be 1,4-dicyanobenzene and the precipitates in the silver nitrate solution and barium hydroxide solution traps were shown (by infrared) to be silver cyanide and barium carbonate respectively.

12. Oxidative Pyrolysis of 2-Phenylimidazole (LIV)

2-Phenylimidazole (500 mg) was treated in the same manner as described above for the tetraacid. Products identified were: unreacted 2-phenylimidazole, benzonitrile, silver cyanide and barium carbonate.

13. Oxidative Pyrolysis of Benzonitrile

Benzonitrile (0.5 ml) was poured on a bed of charcoal which had previously been heated under oxygen at 300°C. The mass was then treated as described above for the tetraacid. Products identified were: unreacted benzonitrile, silver cyanide and barium carbonate.

14. Preparation of Compound VI-T

A mixture of 2.0 g (0.016 mole) of benzoic-1-$^{13}C$ (ca. 14 atom % $^{13}C$) and 1.7 g of phenol (0.018 mole) were refluxed in trifluoroacetic anhydride for two hours. The resulting phenylbenzoate was precipitated by pouring the reaction mixture on ice. The aqueous phase was made alkaline by addition of 10% NaOH before filtering the solid product. The product was then washed with water until neutral and dried to yield phenylbenzoate, m.p. 66.0-67.5°C in 72% (2.05 g) yield.

The phenylbenzoate prepared above (2.05 g, 0.012 mole) and 1.16 g (0.005 mole) of 3,3'-diaminobenzidine were converted to 2,2'-diphenyl-5,5'-bibenzimidazole (VI-T) by melt condensation in a helium atmosphere. The

product was obtained in 90% yield (1.90 g). After recrystallization from DMSO - water and drying, the product was found to contain 1.28 atom % $^{13}C$ or 4.04 at % $^{13}C$ at the labelled positions.

15. Preparation of Compound VI-H

Compound VI-H was prepared in the manner described above for compound VI-T except that benzoic acid labelled with carbon-13 at the carboxylate carbon was used. The carboxylate labelled benzoic acid was prepared in the following manner.

Phenylmagnesium bromide was prepared from 6 g of magnesium turnings and 15 ml of bromobenzene in 60 ml of ethyl ether. To this cooled mixture (-10°C) was added carbon dioxide generated by acidification of 14 g (0.071 mole) $BaCO_3$ (ca. 14 atom % $^{13}C$) with hydrochloric acid. The resulting salt was liberated and worked up in the usual fashion to yield 3.3 g (0.027 mole, 38 percent yield) of benzoic acid-7 $^{13}C$.

The labelled benzoic acid was converted to model compound VI-H (2.09 atom percent carbon-13 or 14.7 atom percent carbon-13) at the 2 and 2' positions.

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13. ABSTRACT

In this report experimental evidence is reported in support of the suggestion that pyrolytic oxidation of the PBI at high temperatures initiates at the carbocyclic aromatic ring adjacent to the imidazole nucleus.

Solution oxidation of benzimidazole model compounds yielded corresponding 2-arylimidazole-4,5-dicarboxylic acid oxidation products demonstrating that the 2-arylimidazole nucleus is more resistent to oxidation than the adjacent benzenoid nucleus. Subsequent oxidative pyrolysis of solution oxidation intermediates at 300°C provided the same products (oxides of carbon, aromatic nitriles and cyanogen) obtained when the parent model compound is oxidatively pyrolyzed, demonstrating that similarly oxygenated intermediates are probable transitory intermediates in pyrolytic oxidation of PBI.

Oxidative pyrolysis of carbon-13 labelled benzimidazole model compounds and subsequent mass analysis of carbon dioxide and cyanogen gaseous products demonstrate conclusively that: initial oxygenation occurs preferentially at the aromatic carboxyclic nucleus adjacent to the imidazole heterocyclic and that only ten percent of the cyanogen product originates from the 2(2') carbon thus accounting for the fate of both nitrogen in the imidazole nucleus.

These data were found to be consistent with the mechanism previously proposed for thermooxidative degradation of PBI.

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