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

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

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### SUMMARY

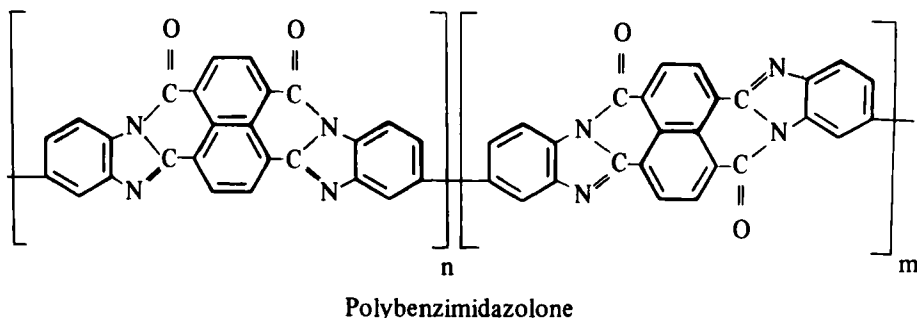
The oxidation of polybenzimidazolone and selected model compounds including compounds containing benzimidazole and benzimide ring systems has been investigated at temperatures from ambient to 700°C. Residue elemental analyses, volatile product distribution differences as a function of time and oxidation temperature, thermogravimetry, and differential thermal analysis studies are reported. The determination of the energy of activation for the over-all initial oxidation processes over the ranges of 0 to 15% weight loss and 100 to 700°C indicated a value of 35.5 kcal/mole. The elemental analyses data indicate that significant differences in residue composition exists between model compounds having amine-derived end groups and those systems bearing acid-derived end groups. Data obtained using differential thermal analyses techniques indicate little difference in the thermal behavior of the benzimidazolones in inert or oxygen atmospheres. The changes in the amounts of carbon dioxide and carbon monoxide as a function of temperature and time support a proposal for simultaneous thermal and thermooxidation processes for the degradation of these systems in oxygen atmospheres at high temperatures.

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## INTRODUCTION

In a series of previous papers [1] we reported a rather extensive investigation of the mechanism by which poly(6,9-dihydro-6,9-dioxobisbenzimidazo [2,1-b:1',2'-j]benzo[1mn] [2,8]phenanthroline-2,13-diyl) and its model compounds (I-III) as well as structurally related benzimidazole and benzimide model compounds underwent oxidative degradation at high temperature. The effect of structural variations on the nature of the pyrolysis products was noted; these results led to a proposal for a reasonable route for the attack by oxygen on these systems [1]. Figure 1 summarizes the products obtained from these studies. The most significant observation was that the benzimidazolone systems gave rise to only small molecular weight fragments.



Water is the major product, carbon dioxide next, followed by carbon monoxide. Cyanogen was found in only small quantities. No aromatic fragments could be detected from degradations carried out in the 250 to 600° temperature range.

The object of the present paper is to report supporting data including thermogravimetric analyses, differential thermal analyses, residue elemental analyses, and carbon dioxide and carbon monoxide evolution data in support of the proposed degradation route recently reported [1].

## RESULTS AND DISCUSSION

The thermogravimetric analysis of polybenzimidazolone was performed on a modified Cahn RH Electrobalance-TGA apparatus. The theory of

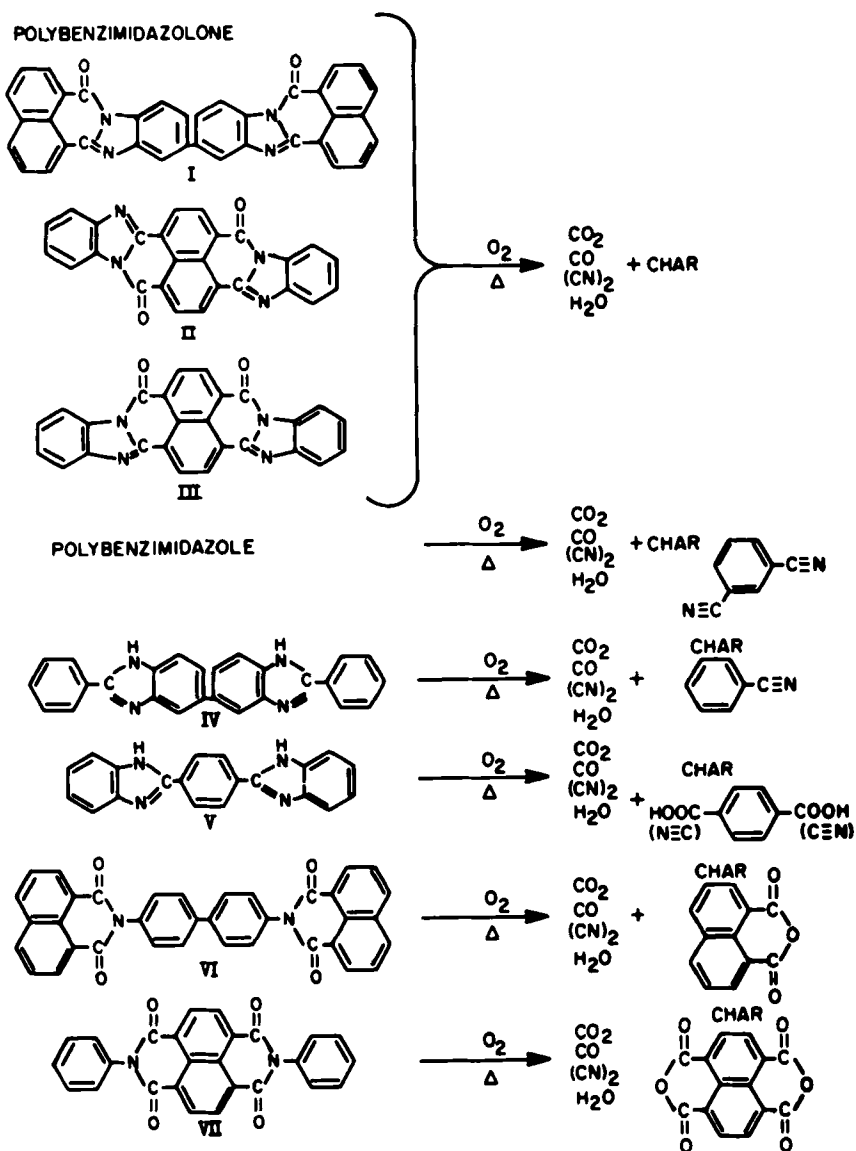


Fig. 1. Summary of the degradation products from the thermooxidative pyrolysis of the polymers and model compounds.

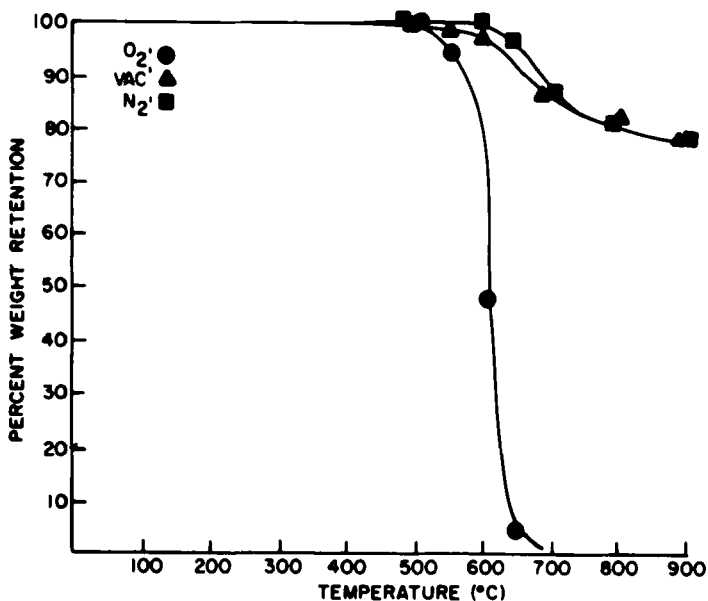


Fig. 2. Comparison of the TGA's obtained from polybenzimidazolone under various degradation conditions. Heating rate: 150°C/hr.

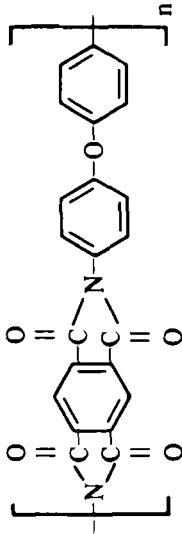
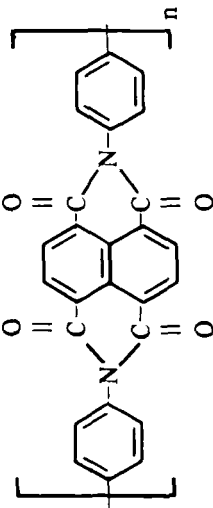
operation of the instrumentation, such as the aerodynamic forces associated with temperature and the diameter of the pyrolysis tube in a flowing gas system [2-4], and the development of suitable mathematics for data processing is well documented [5-7] and was applied as necessary in data collection and reduction. The analyses were performed at three heating rates, and the activation energy values ( $E_a$ ) were determined for the initial 15% of the reaction.

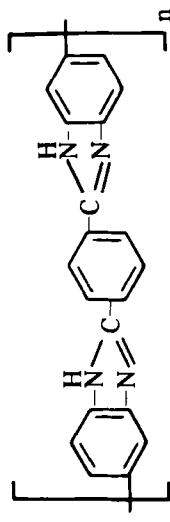
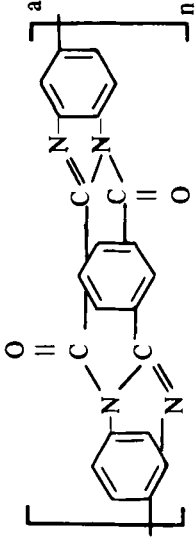
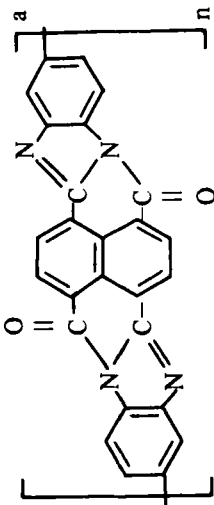
A comparison of the effect of the pyrolysis conditions, i.e., oxygen, nitrogen [8], and vacuum, on the weight retention characteristics of the polymer is illustrated in Fig. 2. As expected, oxidative conditions had the most deleterious effect on the material. It is clearly seen that the curves obtained for the degradation in vacuum and nitrogen indicated residues of approximately 76% at temperatures up to 900°C whereas the curve corresponding to the oxidative pyrolysis approached 0% weight retention at approximately 700°C. These results clearly indicate that the charred residue was susceptible to oxidation. Inert conditions, however, produced a residue which was not resistant to further degradation in the inert atmospheres.

Table 1. Rate Data for the Pyrolysis of Polybenzimidazolone in Oxygen (from TGA)

Heating rate (°C/hr)	Starting weight (mg)	% Reaction	Wt loss (mg)	Rate wt loss (mg/min)	Rate wt loss - k (%/min)	T (°C)	Log k	1/T × 10 <sup>-3</sup> (°K)
75	10.46	5	0.52	0.040	0.382	569	-1.582	1.187
		10	1.05	0.140	1.34	579	0.107	1.173
		15	1.57	0.233	2.23	583	0.348	1.167
150	11.00	5	0.55	0.069	0.631	588	-1.800	1.161
		10	1.10	0.236	2.14	600	0.330	1.145
		15	1.65	0.354	3.22	603	0.508	1.141
270	9.98	5	0.499	0.129	1.28	619	0.107	1.114
		10	0.998	0.369	3.69	632	0.567	1.104
		15	1.497	1.07	10.7	636	1.029	1.100
				% RXN	E <sub>a</sub> (kcal/mole)			
				5	32.1			
				10	27.4			
				15	47.1			
					35.5 av			

Table 2. A Comparison of the Activation Energy Data for a Series of Structurally Related Polyimides, Polybenzimidazoles, and Polybenzimidazolones

Polymer	Oxidative conditions		Inert conditions	
	T (°C)	E <sub>a</sub> (kcal/mole)	T (°C)	E <sub>a</sub> (kcal/mole)
	468-485	32 <sup>9,10</sup>	585-632	74 <sup>13,14</sup>
	375-440	9.2 <sup>11</sup>	-	-

	525-700	34 <sup>12</sup>	550-800	30-41 <sup>13</sup>
	440-600	31 <sup>14</sup>	—	—
	470-502	28.8 <sup>11</sup>	—	—
	569-636	35.5 <sup>b</sup>	500	85.3 <sup>15</sup>

<sup>a</sup> Trans link shown.

<sup>b</sup> Up to 18% reaction.



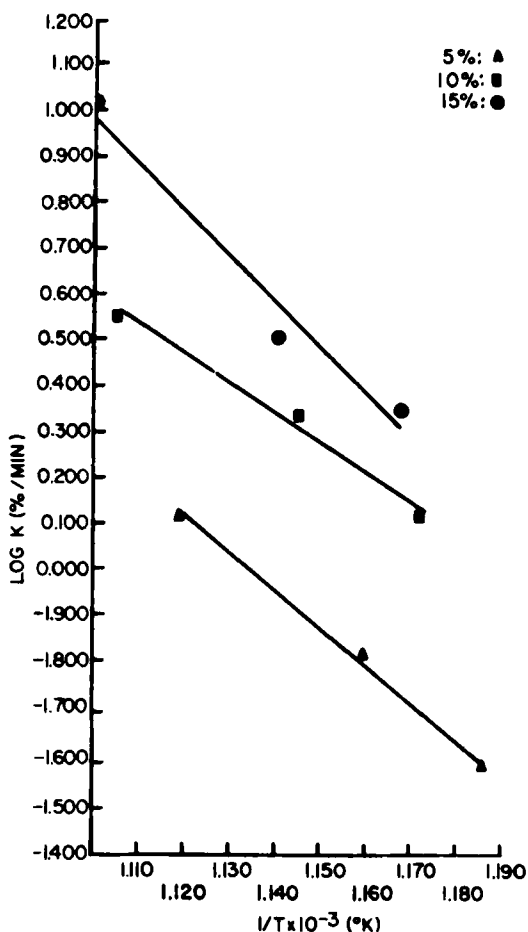


Fig. 3. Plot of the log of the rate constant ( $K$ ) vs. the reciprocal of the absolute temperature ( $1/T$ ) for polybenzimidazolone at 5, 10, and 15% decomposition.

The activation energy of the thermooxidative degradation of polybenzimidazolone was determined in the following way. Powdered samples of purified polymer (particle size of less than 200 mesh) were pyrolyzed in dry oxygen atmospheres at heating rates of 75, 150, and 270°C/hr in the temperature range of 25 to 700°. The samples degraded rapidly after approximately 15% weight loss. The corresponding TGA curves beyond

that point were very nearly perpendicular to the time coordinate and, therefore, analysis of the data was not attempted. However, the rate constants (expressed as per cent weight loss per minute) from 5, 10, and 15% reaction were easily obtained. A plot of the logarithms of the rate constants as a function of the reciprocal of the absolute temperature resulted in three straight lines (Fig. 3); from the slopes of these lines the value of the initial activation energy was found to be 35.5 kcal/mole (Table 1). Similar values were obtained from the thermooxidative degradation of structurally related polyimides [9, 10] polybenzimidazoles [12, 13], and polybenzimidazolones [14, 15]. A comparison of these data is illustrated in Table 2.

The activation energy of polybenzimidazolone under inert conditions is larger than that of the polymer systems compared in Table 2. This is probably due to the following factors: 1) the increased aromaticity of these polymers (relative to the imides); 2) the absence of a labile hydrogen atom (present in the imidazole ring system); and 3) the inherent stability associated with their semiladder structure. Under oxidative conditions less pronounced differences in stability are exhibited by all of the polymers under consideration. The convergence of activation energies is in keeping with the proposal that high energy reactions, such as thermooxidations, are much less selective toward subtle structural differences than reactions involving low-energy pathways.

A series of independent samples of Compound I were heated in either oxygen or helium for 30 min; the residues were carefully weighed to construct a thermal profile (Fig. 4) similar to the TGA curve (Fig. 3). As expected, 50% weight loss is shown at a lower temperature than determined from TGA data. Analyses of the residues obtained from these oxidations at 450° for each of the model compounds is shown in Table 3. The chars obtained from those model compounds which contained amine residues as end groups (II, III, V, and VII, Fig. 1) revealed large depletions in per cent carbon, hydrogen, and nitrogen; those models which had acid residues as end groups (I, IV, and VI, Fig. 1) revealed large losses in the per cent carbon while the nitrogen content either decreased by a relatively minor amount or increased. Although the extent of char formation varied considerably, the trends noted for the differences between acid end group and the amine end group models are clearly shown. The isomeric models (II and III) most clearly exemplify differences in char forming ability. The reason for this difference is not readily interpretable on structural grounds and speculation based on related literature is not possible at this time. The residues were also examined by infrared spectroscopy at various stages of degradation; the analyses revealed a gradual,

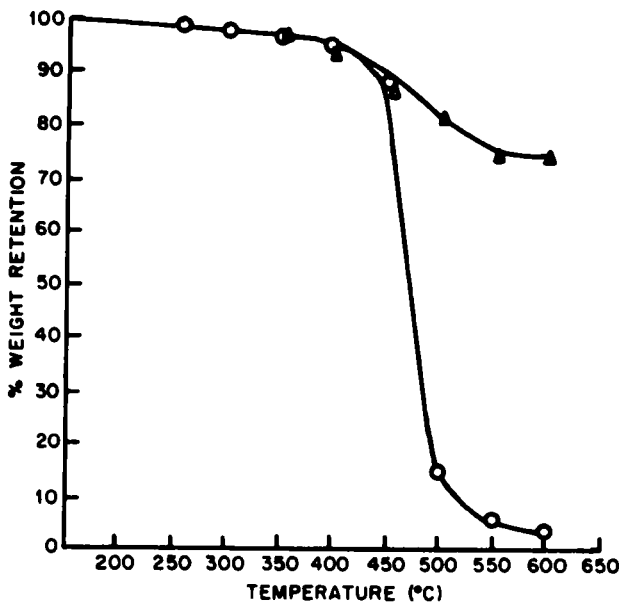


Fig. 4. Weight loss-temperature profile of Compound I in O<sub>2</sub> (○) and He (Δ).

uniform decrease and broadening of all bands in the spectra. Extraction of the residual materials with several organic solvents yielded only starting materials in decreasing quantities with increasingly degradation temperatures and time.

The occurrence of oxidative and thermal degradation was evidenced by differential thermal analyses (DTA) of the polymer and its model compounds (I-III) (Figs. 5-9). Under oxidative conditions broad exotherms were observed in the DTA curves of the materials (particularly Compound I). When the analyses were performed in an inert atmosphere, small positive drifting from the baselines are observed (Fig. 5). The differences are possibly due to a gradual change in the thermal conductivity of the materials. In high melting thermally stable organic systems, thermal conductivity changes have been interpreted as being the result of cross-linking and slight decomposition [11]. The susceptibility of these cross-linked and partially degraded residues toward oxygen, as expected, is enhanced by their radical character.

Although the exact nature of the radical and oxygenated residual species is speculative (cf. Ref. 1), that is, it has not been established whether oxygen is bonded to the residues in the classical sense, i.e., peroxidic and quinoid type intermediates, or loosely bound in a  $\pi$ -complex, it seems clear that

**Table 3.** Comparison of the Elemental Composition of the Model Compounds Before and After Oxidative Degradation (450°C for 30 min)

Compound	Elemental composition (%)			Residual composition (%)			Difference		
	C	H	N	C	H	N	$\Delta C$	$\Delta H$	$\Delta N$
I	80.36	3.35	10.25	75.63	3.06	10.17	- 5.70	- 8.60	- 1.00
II	75.60	2.81	13.34	47.96	1.69	9.72	-36.7	-39.8	-27.2
III	75.79	2.90	13.43	66.06	2.14	11.15	-12.6	-26.3	-17.1
IV	80.60	4.78	14.39	77.26	3.89	14.33	- 4.20	-18.6	- 0.40
V	77.40	4.44	18.08	30.57	1.62	10.07	-50.4	-64.4	-44.4
VI	79.16	3.75	5.20	71.51	2.39	6.71	- 9.50	-36.4	+12.9
VII	74.46	3.36	6.60	52.51	2.41	4.05	-29.5	-28.5	-39.5

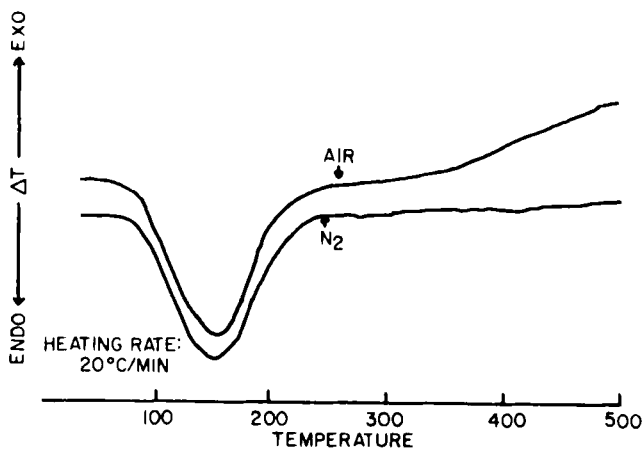


Fig. 5. DTA of polybenzimidazolone in N<sub>2</sub> and air.

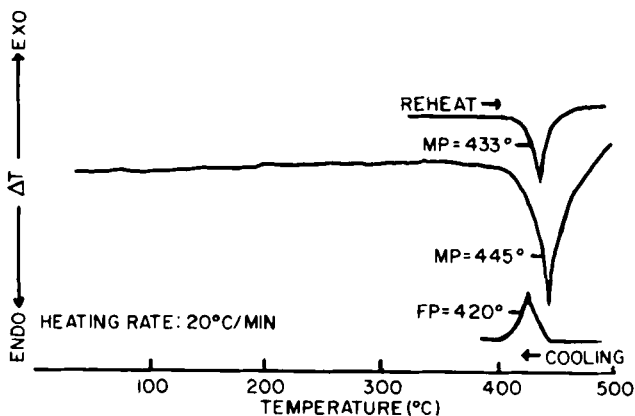


Fig. 6. DTA of Compound I in nitrogen.

whatever the intermediates may be, they are highly reactive species at the elevated degradation temperatures employed for degradation of these stable polymer systems. After the initial stage of reaction, the sudden increase in the reaction rate, as evidenced by the sharp increase in weight loss observed after reaching 18% degradation, can be attributed to a catastrophic, simultaneous decomposition of all oxygenated species. These reactions are accompanied by the production of the residual char. The cause of the collapse and

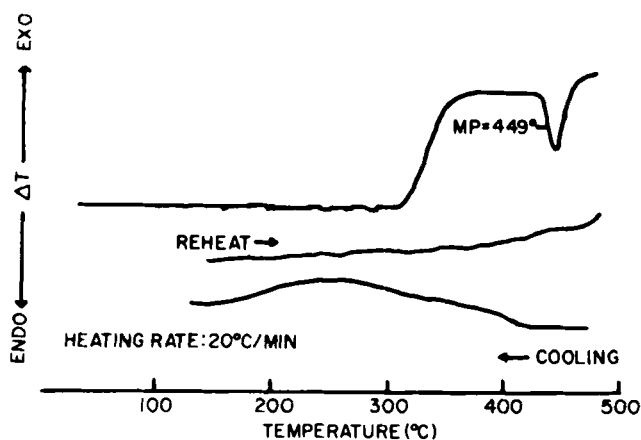
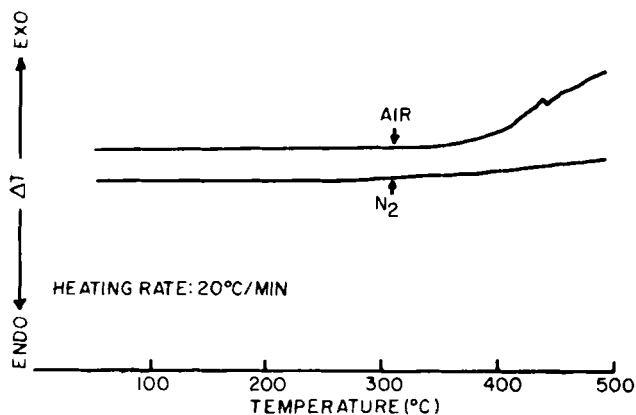


Fig. 7. DTA of Compound I in air.

Fig. 8. DTA of Compound II in  $N_2$  and air.

subsequent decomposition of the intermediate residues may be due to a series of secondary homolytic reactions initiated at the elevated temperatures and the exothermic decompositions of oxygenated species.

Separation of the gaseous degradation products from the oxidative pyrolysis of benzimidazolone polymer and Model Compounds I, II, III, IV, and VI was accomplished by the method previously described [1]. From chromatograms corresponding to various stages of degradation, the relative amounts of carbon dioxide and carbon monoxide were determined. Table 4 summarizes typical data for Compounds I, IV, and VI.

**Table 4.** Comparison of the Relative Amounts of Carbon Dioxide and Carbon Monoxide from the Thermooxidative Degradation of Model Compounds I, IV and VI as a Function of Time and Temperature

I				IV				VI			
CO <sub>2</sub> /CO	Time (min)	% Wt ret.	Temp. (°C)	CO <sub>2</sub> /CO	Time (min)	% Wt ret.	Temp. (°C)	CO <sub>2</sub> /CO	Time (min)	% Wt ret.	Temp. (°C)
2.46	10	98.0	400	1.10	10	91.0	400	—	—	—	—
2.34	20	96.4	400	2.16	20	87.2	400	0.794	20	94.9	400
2.87	30	96.0	400	2.19	30	86.4	400	0.917	30	96.4	400
4.27	40	95.6	400	2.50	40	74.8	400	1.08	40	97.1	400
—	—	—	—	—	—	—	—	1.18	50	95.6	400
—	—	—	—	—	—	—	—	1.21	60	95.3	400
—	30	98.7	300	—	—	—	—	—	—	—	—
—	30	96.5	350	—	—	—	—	—	—	—	—
2.87	30	96.0	400	2.19	30	86.4	400	0.917	30	96.4	400
7.84	30	88.5	450	2.50	30	41.2	450	3.73	30	94.5	450
4.64	30	15.0	500	2.03	30	4.26	500	2.60	20	2.85	500
11.7	30	6.0	550	—	—	—	—	—	—	—	—

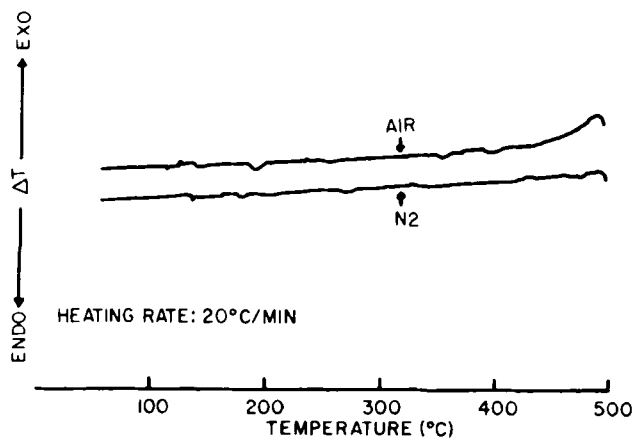


Fig. 9. DTA of Compound III in N<sub>2</sub> and air.

For comparison purposes with Compound I, Compounds IV and VI, the benzimidazole and benzimide models containing aromatic acid fragments as end groups were subjected to oxidative pyrolysis as a function of time and temperature. The ratio of carbon dioxide to carbon monoxide increased in a linear fashion with time at 400° in all cases. As expected, Model VI exhibited the lowest ratio values since it contains four carbonyl groups, all of which are capable of undergoing homolytic scission. Particularly striking was the gas ratio as a function of temperature for the benzimidazole and benzimide models; as was the case with Model I, these materials exhibited a sharp decrease in the value of the gas ratios at 500° relative to 450°.

As additional support of the postulate that much of the carbon monoxide produced in the initial stages of degradation arose from thermal scission of the carbonyl groups, Model Compounds I, IV, and VI were thermooxidatively degraded at several temperatures up to 20% decomposition (Table 5). At this point in the degradation, gas samples were taken, from the chromatographic data the molar values as well as the ratios of carbon dioxide to carbon monoxide were determined. It is reasonable to propose that if a non-oxidative degradation was actually occurring; then, as the temperature (and hence the thermal energy) was increased, the ratio of carbon dioxide to carbon monoxide should decrease for the same extent of degradation. Such a phenomena was, indeed, observed.

From the weight loss-temperature profile for Compound I (Fig. 4) it is clear that a pronounced exothermic degradation occurred in the 450 to 500°C temperature region. Figure 10 shows a marked change in the



**Table 5.** Comparison of the Gaseous Degradation Products from the Thermooxidative Degradation of Model Compounds I, IV, and VI at 20% Decomposition as a Function of Temperature

Compound	T (°C)	Moles CO <sub>2</sub> (× 10 <sup>-7</sup> )	Moles CO (× 10 <sup>-7</sup> )	Actual wt loss (%)	CO <sub>2</sub> /CO
I	500	34.4	20.8	22.0	1.65
	475	39.8	18.5	21.5	2.15
	450	37.9	14.5	22.0	2.61
	425	22.2	7.14	21.2	3.12
	400	—	—	—	—
				av	21.6
IV	500	14.9	7.37	21.2	2.02
	475	12.0	5.84	22.0	2.05
	450	9.81	10.1	20.6	0.950
	425	7.13	5.67	19.1	1.26
	400	4.26	2.36	19.8	1.82
				av	20.5
VI	500	36.7	24.0	22.4	1.73
	475	32.6	17.2	23.8	1.90
	450	17.9	8.56	21.0	2.09
	425	18.8	7.84	21.0	2.40
	400	—	—	—	—
				av	22.1

evolution of carbon dioxide and carbon monoxide in the same temperature region. Interestingly, the moles of carbon monoxide obtained from the 500° pyrolysis had increased by a factor of 11 relative to its value at 450°; the number of moles of carbon dioxide in the same temperature interval had

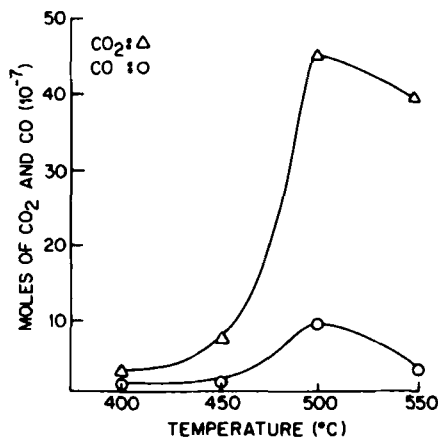


Fig. 10. Moles of CO<sub>2</sub> and CO as a function of temperature from the thermo-oxidative degradation of Compound I (30 min exposure).

undergone an almost seven-fold increase. This corresponds to the marked decrease in the ratio of carbon dioxide to carbon monoxide. At 550°, the amount of carbon monoxide decreased by about a third relative to its value at the previous temperature while the amount of carbon dioxide was reduced by a ninth; this resulted in a very sharp rise in the ratio of the gases.

These observations support a dual route for degradation in oxygen with thermal and thermooxidation occurring as competing processes. These results can be viewed as supporting evidence for the mechanisms proposed in our previous papers [1]. The conclusions pertaining to the route by which polybenzimidazolone systems undergo oxidative degradation at elevated temperature are:

- 1). Initially, thermal and oxidative degradation occur simultaneously.
- 2). It seems clear that attack by oxygen occurs at the amino-benzenoid moieties of these materials.
- 3). The formation of oxygenated species results in rapid catastrophic decomposition.
- 4). A cross-linked nitrogenous-carbon char is produced during the degradation which gradually and continuously degrades in the presence of oxygen at elevated temperatures.

## EXPERIMENTAL

### Thermogravimetric Analysis (TGA) of Polybenzimidazolone

The thermogravimetric analysis of the polymer in a dried oxygen flow stream (58.3 ml/min flow rate) was performed on a modified Cahn RH Electrobalance-TGA apparatus. Three samples (10 mg each) of polymer were pyrolyzed at heating rates of 75, 150, and 250°C/hr. By drawing tangents to these curves at 5, 10, and 15% reaction with the aid of a silvered mirror, the per cent weight loss as a function of time and the corresponding rate constants (%/min) were calculated. A plot of the  $\log_{10}$  of the rate constants versus the reciprocal of the absolute temperature (Fig. 3) gave three straight lines; from the slopes of these lines the value of the initial activation energy was calculated (Table 1).

### Differential Thermal Analysis

Differential thermal analyses behavior of polybenzimidazolone and Model Compounds I, II, and III were examined using a DuPont Model 900 DTA apparatus in air and nitrogen atmospheres at a heating rate of 20°C/min.

### Gas Chromatographic Examination of the Pyrolysis Gases

The apparatus used for the pyrolyses was described previously [1b]. Analyses of the gaseous products from the oxidative degradations were performed by passing them from the pyrolysis tube directly into a 25.3-ml gas sampling loop. The gas sampling loop was attached to an Aerograph 1525-B vapor phase chromatograph equipped with a 6 ft  $\times$   $\frac{1}{4}$  in. stainless steel column packed with 60-80 mesh Silica-Gel. By maintaining the column at Dry Ice-acetone temperatures, it was possible to separate and identify all of the effluent gases except cyanogen by comparison of their retention times with those of standard samples.

## ACKNOWLEDGMENTS

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