

The Thermal Reactions of Bis-(4-nitroanilino)-sulfone
and p-Benzoquinone dioxime-acid Mixtures

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INTRODUCTION

It is known that nitroaniline compounds when heated in the presence of concentrated sulfuric acid undergo an abrupt reaction to give voluminous amounts of a black material and gases.¹⁻³

The amount of acid required to promote the reaction varies over a wide range of percentages.^{4, 5} The temperature of reaction and yield of black material for this reaction, as measured by TGA at 3°C/min. under nitrogen, seemed to be independent of the amount of acid used.⁵

We wish to report that p-benzoquinone dioxime, when heated in the presence of concentrated sulfuric or phosphoric acid and bis-(4-nitroanilino)-sulfone when heated without acid, react in a similar way to give low density black material and gases.

DISCUSSION

The dehydration and self-condensation of benzoquinone dioxime by acid can lead to a ladder polymer (II). The bis-(4-nitroanilino)-sulfone (III) on thermal dissociation with condensation can also lead to a similar type ladder polymer (II).

Sketch
(a)

The benzoquinone dioxime-acid reaction was carried out over a range of weight percentages (Table I). The yield of black material and temperature of reaction, as measured by thermogravimetric analysis at 3°C/min. under nitrogen, was independent of the amount of acid except when a large excess of sulfuric acid was used (sample J-6). Here a resinous material formed without a voluminous expansion or abrupt weight change on

Table I

the TGA. The reaction temperatures, listed in Table I, are taken as the temperatures at which an abrupt weight change occurs during the thermogravimetric analyses experiments (Figure 1). The reaction temperature for all cases was approximately 110°C except for sample J-1 which reacted at 138°C. The material yield at the end of reaction was approximately 50% in all the sulfuric acid mixtures except for sample J-1 (Table I) which yielded 72%. The phosphoric acid mixtures gave higher yields of material after reaction (Table I) than those with sulfuric acid. The reaction temperature for the bis-(4-nitroanilino)-sulfone was higher than that of the benzoquinone dioxime-acid admixture (180°C). The yield for this reaction was approximately 50 percent, the same as for the dioxime-sulfuric acid case.

Fig. 1

The thermal stability of these classes of residues is illustrated in Figure 2 (TGA under nitrogen at 3°C/min). The residue shows little weight loss up to a temperature of 500°C. The weight loss at 100°C was attributed to absorbed water on the material and not a thermal degradation of the material. The residues exhibit great hygroscopicity, undoubtedly due to the large surface area.

Fig. 2

The insolubility of the residues obtained in these reactions precludes the use of all usual techniques for structural verification. Elemental analysis of the residue material was obtained and is listed in Table II. Assuming that the material was polymeric in nature, empirical formulas were calculated for the residues after the thermal reaction. The analytical data used to establish the empirical formulas were corrected for the pendant groups which were not considered a part of the repeating units in the ladder polymer (II). These pendant groups were $-\text{SO}_3^-$, $-\text{PO}_4^-$, and $\text{C}_6\text{H}_5\text{N}_2\text{O}_4\text{S}-$ corresponding to either the sulfur or phosphorous content in the elemental analyses. The corrected analytical data, with empirical formulas and molecular weights are listed in Table III. Molecular structures for the polymer backbones were assembled

Table II

Table III

using the corrected analytical data and empirical formulas using the recurring units IV through VIII.

These units are derivable from the starting materials by condensation, dehydration, rearrangement, and ring closure to varying degrees. The actual structure probably is a combination of open and closed ring structures as shown in V. Assuming that complete ring closure did not occur at the relatively low activation temperatures (to 170°C), a sample, J-3I, was heated under vacuum at 400°C to obtain further ring closure. Elemental analysis of this material shows a decrease in oxygen and hydrogen and an empirical formula close to that of structure VI (sample J-3II). However, complete ring structure did not occur. Another possibility which can occur under these conditions is that of hydrolysis of some of the oxime groups to give ladder polymers containing intermittent nitrogen-oxygen bridge structures IX and X (polyphenoxazines).^{6,7}

EXPERIMENTAL

Sketch
(b)

Preparation of bis-(1-nitroanilino)-sulfone. This compound was prepared by reacting p-nitroaniline and sulfuryl chloride in pyridine solution at -10°C to +10°C according to the method of Parnell.⁸ The melting point was 197-8°C (literature value is 195-197°C). An infrared spectrum was obtained and supported the assigned structure.

p-benzoquinone dioxime-sulfuric acid admixtures (J1-J6). To 1.38 g of p-benzoquinone dioxime was added slowly, while stirring, concentrated sulfuric acid in the weighed amount as indicated in Table I. The admixtures ranged in physical appearance from powders, for low acid weight, to a paste as the amount of acid was increased. Care must be exercised in adding the sulfuric acid in order to prevent premature exothermic reaction.

p-benzoquinone dioxime-phosphoric acid admixtures (P1-P3). To 1.38 g of p-benzoquinone dioxime was added slowly, while stirring, 85 percent phosphoric acid in the weighed amounts as indicated in Table 1. The admixtures were dark viscous pastes.

POLYMERS

Self-condensation of bis-(4-nitroanilino)-sulfone. The monomer was placed in a glass beaker and heated to a temperature of about 200°C on a hot plate. Abrupt reaction occurs with evolution of copious amounts of gases and black polymer residue. The black polymer is placed in an oven at 175-185 C for a period of one hour to insure complete reaction. The polymer is then removed from the beaker, ground and dispersed in dilute sodium hydroxide. The residue is filtered, washed with approximately 500 ml of dilute sodium hydroxide, neutralized with dilute hydrochloric acid, water-washed and finally acetone washed. The residue is then dried for 24 hours at 120°C under vacuum prior to analysis.

Self-condensation of p-benzoquinone-dioxime sulfuric acid mixture. The same procedure was followed as that for the bis-(4-nitroanilino)-sulfone except that the initial temperature on the hot plate was approximately 150°C to initiate polymerization and gaseous evolution.

Heating of polymer with uncyclized units to get ring closure. In a sublimation unit, 2 g of the J-3I polymer was heated under vacuum (0.5-5 mm Hg). In the first hour the temperature was raised to 250°C, in the second hour to 380°-390°C, and then for the next three hours was maintained at 390°C. Sample J-3IH.

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TABLE I
 Thermogravimetric Analysis
 N₂ atmosphere, 3°C/min.

Sample*	Weight Composition	T°C act.	Y _C (est), %
F-1	—	180	48
J-6	1.38 g dioxime 3.92 g sulfuric acid	—	—
J-1	1.38 g dioxime 1.96 g sulfuric acid	138	72
J-2	1.38 g dioxime 0.98 g sulfuric acid	111	52
J-3	1.38 g dioxime 0.66 sulfuric acid	108	49
J-4	1.38 g dioxime 0.51 g sulfuric acid	110	50
J-5	1.38 g dioxime 0.392 g sulfuric acid	111	50
P-1	1.38 g dioxime 4.62 g phosphoric acid	110	80
P-2	1.38 g dioxime 2.31 g phosphoric acid	105	76
P-3	1.38 g dioxime 1.15 g phosphoric acid	115	67

*F refers to bis-(4 nitroanilino)sulfone, J to benzoquinone dioxime-sulfuric acid mixtures,
 P to benzoquinone dioxime-phosphoric acid mixtures.

TABLE II
Elemental Analyses for Self-Condensation Polymers

Sample	Origin.	C	H	O	N	S
F-1I	bis(nitroanilino)-sulfone	62.49	1.94	12.50	20.95	3.07
	1.38 g QD					
J-6I	+3.92 g H ₂ SO ₄	57.61	1.97	22.63	14.41	3.12
J-1I	+1.96 g H ₂ SO ₄	54.30	2.17	21.15	16.25	5.84
J-2I	+0.98 g H ₂ SO ₄	54.08	2.43	20.46	17.19	6.32
J-3I	+0.66 g H ₂ SO ₄	55.89	2.60	18.92	17.86	5.57
J-4I	+0.51 g H ₂ SO ₄	56.56	2.58	17.61	19.35	4.72
J-6I	+0.39 g H ₂ SO ₄	58.55	2.54	15.38	19.15	4.64
J-3IH	J-3I, heated	61.78	1.48	9.04	25.70	0.92
		C	H	O	N	P
	1.38 g QD					
P1I	+4.62 g H ₃ PO ₄	61.81	2.43	17.08*	17.87	0.81
P-2I	+2.31 g H ₃ PO ₄	62.52	2.51	14.57*	19.65	0.75
P-3I	+1.15 g H ₃ PO ₄	62.15	2.39	11.52*	21.61	2.33

*Oxygen analysis by difference.

Analyses done by Huffman Laboratories, Wheatridge, Colorado.

TABLE III

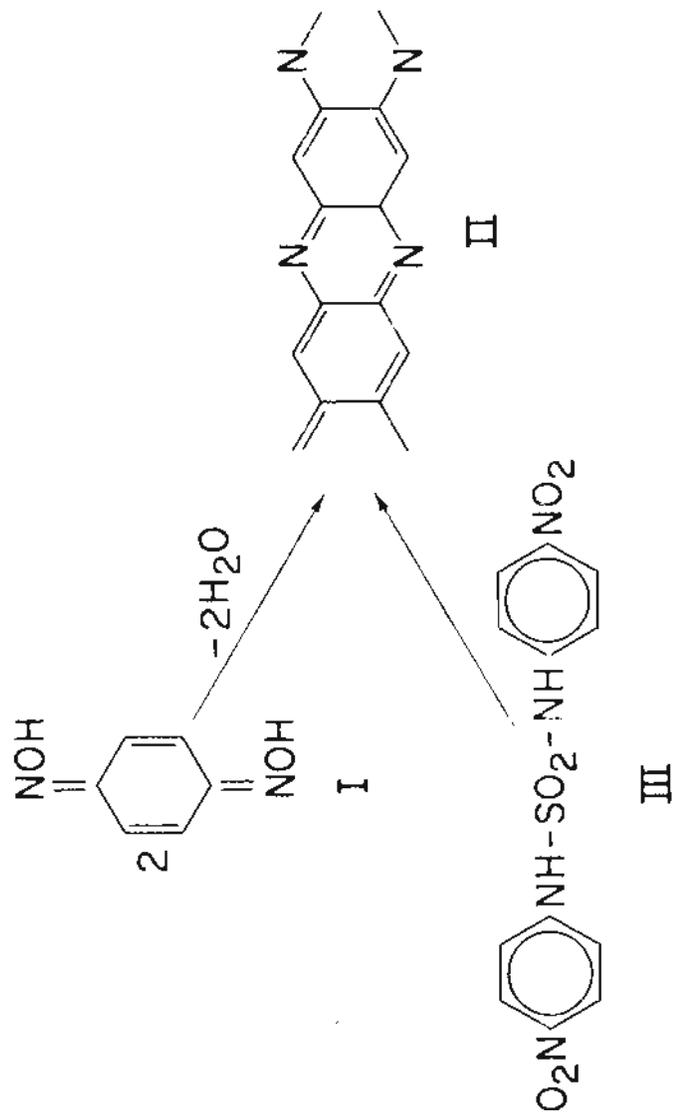
Corrected Analytical Data and Empirical Formulas for the Self-Condensation Polymers

Sample		Elemental Analysis				Calculation for Polymer Unit	Type
		C	H	O	N		
F-1I	Found:	69.45	1.82	7.88	21.13	$C_{60}H_{17}O_5N_{16}$	V or III
	Calcd:	63.9	1.82	7.65	21.6	MW = 1045.7	
J-6I	Found:	62.65	2.14	19.5	15.69	$C_{60}H_{25}O_{14}N_{13}$	V or III
	Calcd:	62.5	2.16	19.45	15.8	MW = 1151.8	
J-1I	Found:	63.8	2.55	14.6	19.1	$C_{54}H_{26}O_9N_{14}$	V or III
	Calcd:	63.9	2.56	14.2	19.3	MW = 1014.7	
J-2I	Found:	64.0	2.76	13.0	20.3	$C_{60}H_{30}O_9N_{16}$	V or III
	Calcd:	64.3	2.70	12.84	20.2	MW = 1120.9	
J-3I	Found:	64.2	3.00	12.15	20.50	$C_{36}H_{20}O_5N_{10}$	V or III
	Calcd:	64.3	2.98	11.9	20.9	MW = 672.4	
J-4I	Found:	63.55	2.90	11.72	21.74	$C_{54}H_{29}O_7N_{16}$	V or III
	Calcd:	63.9	2.90	11.0	22.2	MW = 1015.83	
J-5I	Found:	66.0	2.86	9.39	21.6	$C_{18}H_9O_2N_5$	V or III
	Calcd:	66.2	2.75	9.78	21.4	MW = 327.2	
P-1I	Found:	63.4	2.49	15.8	18.3	$C_{54}H_{25}O_{10}N_{13}$	V or III
	Calcd:	63.8	2.46	15.8	17.9	MW = 1015.8	
P-2I	Found:	63.99	2.57	13.33	20.11	$C_{60}H_{29}O_9N_{16}$	V or III
	Calcd:	64.3	2.61	12.86	20.19	MW = 1120.0	
P-3I	Found:	66.9	2.57	7.23	23.27	$C_{60}H_{28}O_5N_{18}$	V or III
	Calcd:	66.6	2.59	7.4	23.4	MW = 1080.0	
J-3IH	Found:	63.9	1.53	7.92	26.6	$C_{36}H_{12}O_3N_{12}$	VI or VII
	Calcd:	65.4	1.63	7.25	25.4		

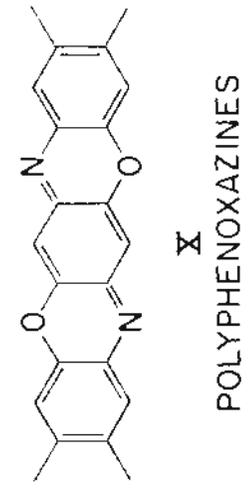
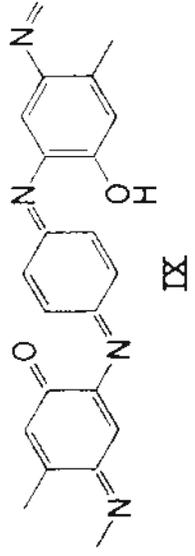
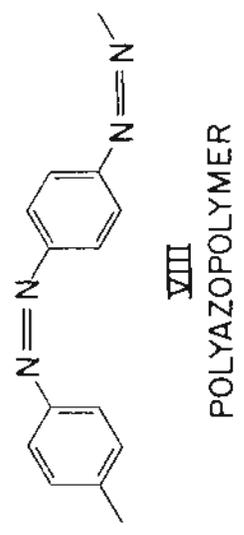
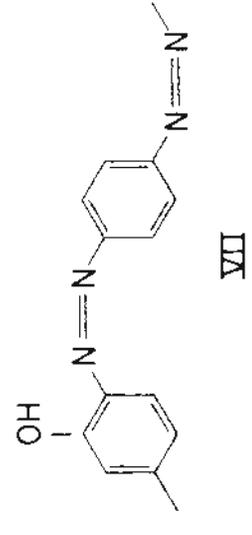
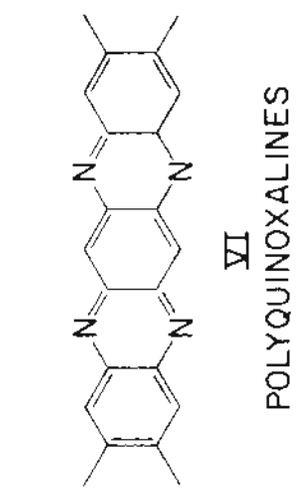
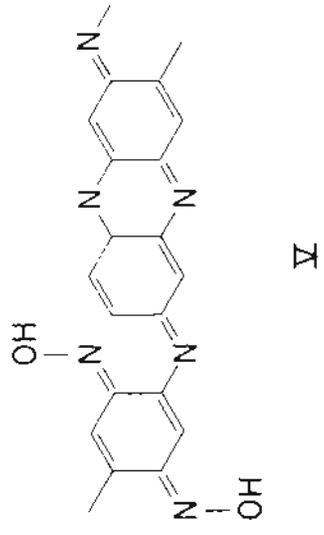
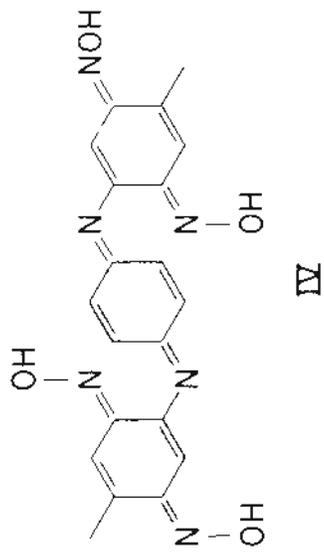
FIGURE TITLES

Fig. 1 Thermogram of sample J-3.

Fig. 2 Thermogram of sample J-3IH.



Sketch: (a)



Sketch. (b)

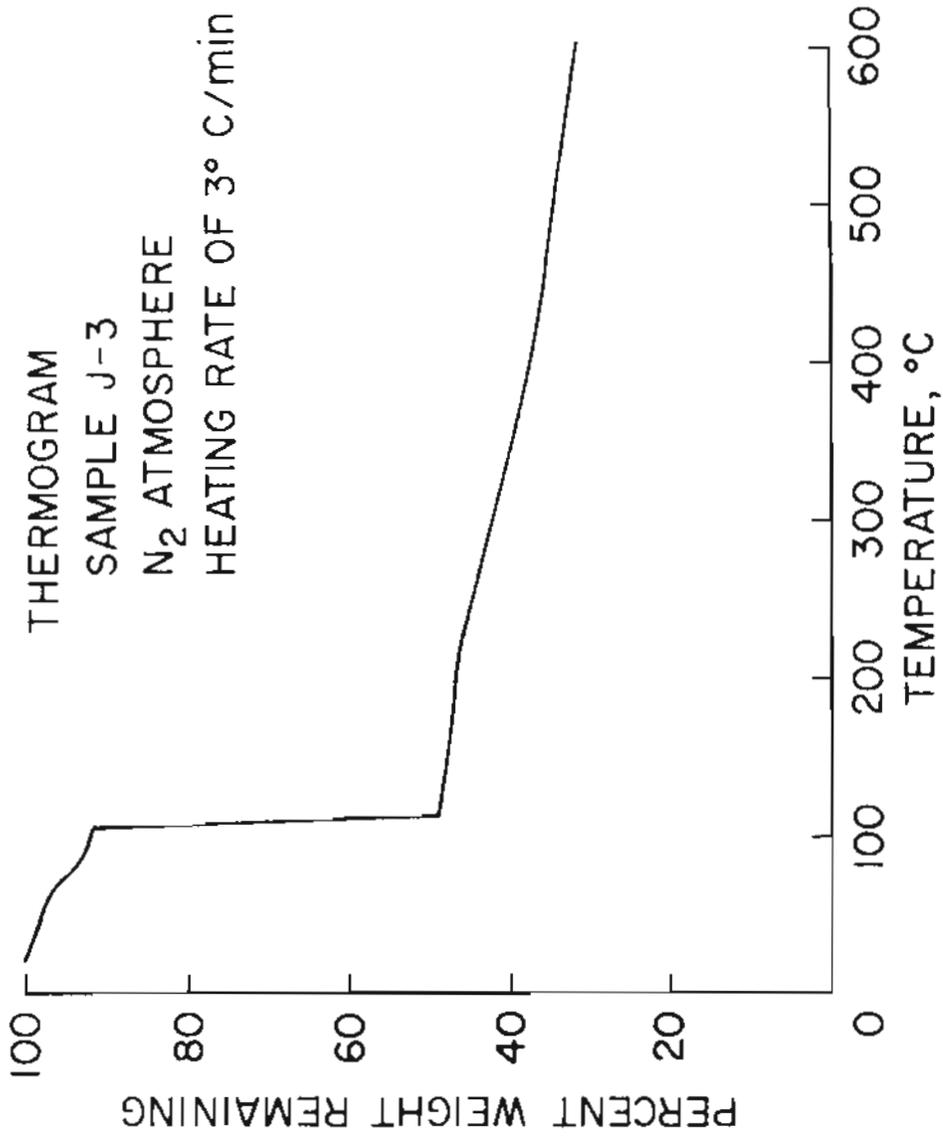


Fig. 1

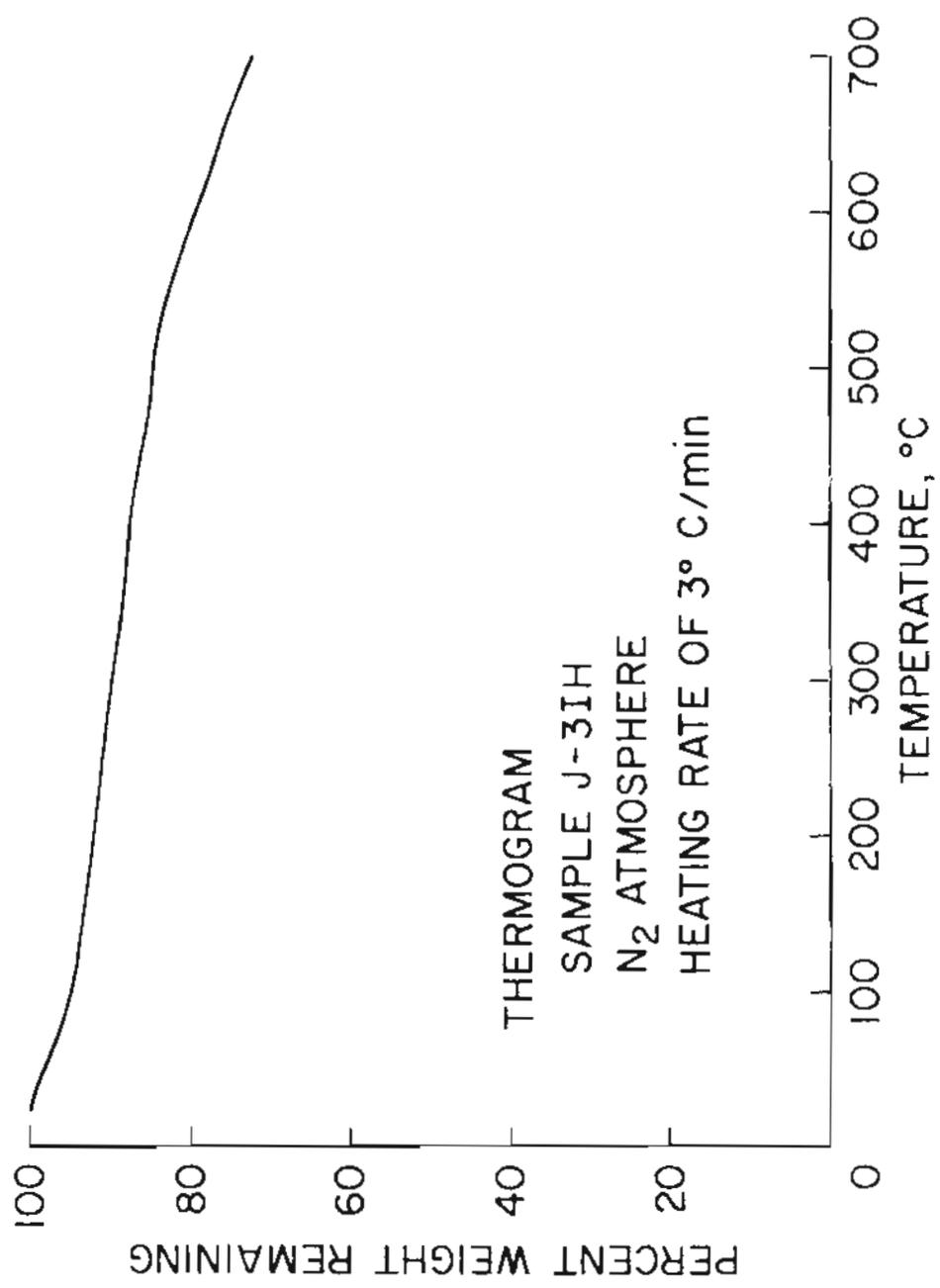


Fig. 2