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Thermal Degradation of Polymers. IV. Poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole[*]

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Summary

The thermal decomposition of poly-2,2'-(*m*-phenylene)-5,5'-bibenzimidazole has been investigated at temperatures to 916°C. Mass-spectrometric thermal analysis (MTA), supported by elemental analysis of residues at various stages of a thermogravimetric analysis, was used to determine product distribution as a function of temperature. Below 550°C, the major product is water. Above 550°C, degradation of the heterocyclic structure to hydrogen cyanide, ammonia, carbon monoxide, and water begins. Hydrogen and methane probably are formed from decomposition and condensation of the carbocyclic structure. Activation energies for the formation of each major product were derived from the MTA data. The average of these is somewhat temperature-dependent but agrees within experimental error with the value of 44 ± 11 kcal obtained from isothermal kinetics. A mechanism involving initial hydrolysis of the polymer to an amine-substituted polyamide is postulated. Subsequent homolytic reactions account for formation of the major products.

Aromatic polybenzimidazoles are of interest as resin systems for high-temperature applications. Polymers derived from isophthalic acid derivatives and 3,3'-diaminobenzidine appear to have the most satisfactory combination of mechanical properties and thermal stability for many applications. Thermogravimetric analyses and infrared spectra of films heated in inert atmosphere have been reported (*1*). The TGA data show that decomposition begins at about 500°C and proceeds rapidly in the 550 to 900°C region, leav-

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[*] Presented at the 150th Meeting of the American Chemical Society, Atlantic City, N.J., September 1965.

ing a 75% residual char. The infrared spectra do not indicate any marked changes in structure below 400°C. General deterioration of the spectrum with heating above 500°C precludes the derivation of useful information about decomposition mechanisms from spectral data. As the first steps in determining the mechanism we therefore applied two techniques that had proven useful in the determination of degradation mechanisms of phenolic resins: mass-spectrometric thermal analysis (*2*) and elemental analysis of residual chars (*3*).

EXPERIMENTAL

Polymer Synthesis

Polymers were prepared from diphenyl isophthalate and 3,3′-diaminobenzidine according to the general procedure of Marvel and Vogel (*1*), with minor variations. Polymer A was prepared by being heated for 3 hr at 300°C under nitrogen, then for 3 hr at 300°C in vacuum, giving a molding powder, which was pressed for 2 hr at 400°C under 2000 psi (autogenous) pressure. Material for the MTA was filed from the molded cylinder. Polymer B was prepared by being heated for 30 min at 260°C under nitrogen, then for 2 hr at 330°C in vacuum, and finally for 1 hr at 400°C under nitrogen. Polymer C was a film 0.0006 in. thick (prepared from a dimethyl sulfoxide solution of polymer B); it was air-dried in a forced-draft oven for 1 to 2 hr at 150°C and then aged in air for 58 hr at 300°C.

Pyrolysis–Gas Chromatography

A powdered sample of polymer A was pyrolyzed at 800°C in a Perkin-Elmer (tube furnace) pyrolysis accessory. After separation on a silica-gel column, products were identified by mass spectrometry as they eluted. Pyrolysis products were methane, carbon monoxide, hydrogen cyanide, carbon dioxide, and hydrogen. Water was the only additional product observed when a Carbowax column was used.

Mass-Spectrometric Thermal Analysis (MTA) (*2,4*)

Samples were placed in the Knudsen cell inlet of the Bendix Time-of Flight Mass Spectrometer and heated at a linear rate (poly-

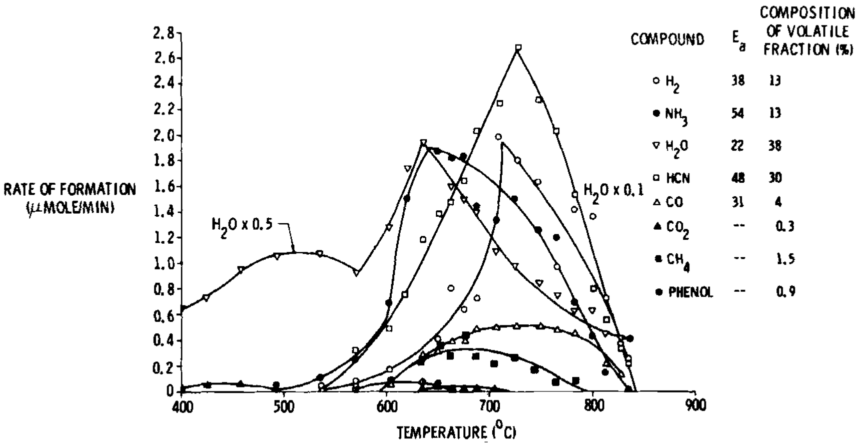

FIG. 1. MTA of molded polymer (A).

mer A, 15.5 mg and 20°C/min; polymer B, 2.5 mg and 25°C/min after 30-min heating at 520°C; polymer C, 1.6 mg and 20°C/min). Spectra from mass 1 to 120 were determined each minute. Then the heights of the peaks characteristic of each major product were measured. These were corrected for contributions due to fragments of higher-molecular-weight products. With the aid of suitable cali-

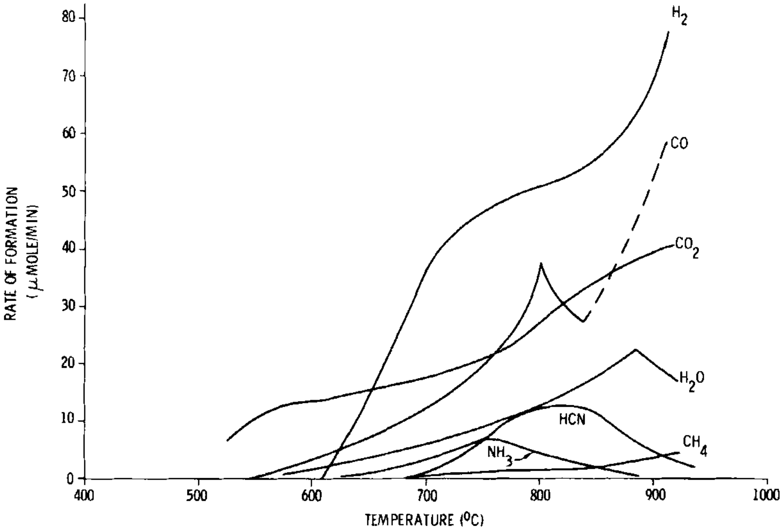

FIG. 2. MTA of polymer B (after 520° aging).

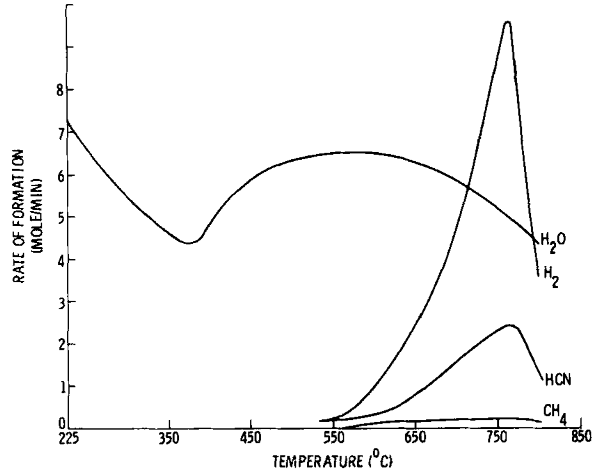

FIG. 3. MTA of air-aged polymer (C).

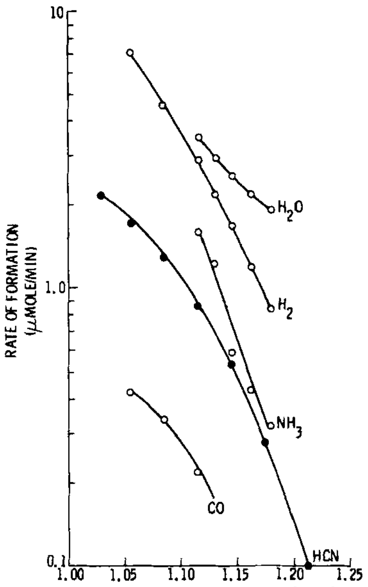

FIG. 4. Temperature dependence of polybenzimidazole pyrolysis (polymer A).

bration factors relative rates of formation were calculated.[*] Figures 1 to 3 show the MTA curves. Figure 4 shows Arrhenius plots for reactions of the molded polymer to the major decomposition products.

Isothermal Kinetics

Isothermal-kinetic studies were performed by placing powdered samples of polymer A in the Knudsen cell crucible, evacuating, heating at the maximal rate (100 to 150°C/min) to the desired temperature (560 to 604°C), then maintaining temperature (±2°C), and scanning spectra at intervals of 0.5 to 5 min. Semilogarithmic line plots of peak height versus time were obtained for each product. Curves for the various products were approximately parallel, indicating that a general decomposition of the polymer was taking place. From these curves half-lives and rate constants were deter-

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[*] The calibration factor for hydrogen cyanide is taken as an average of several molecules containing two to six atoms. Safety considerations prevented the use of HCN in a quantity sufficient for calibration.

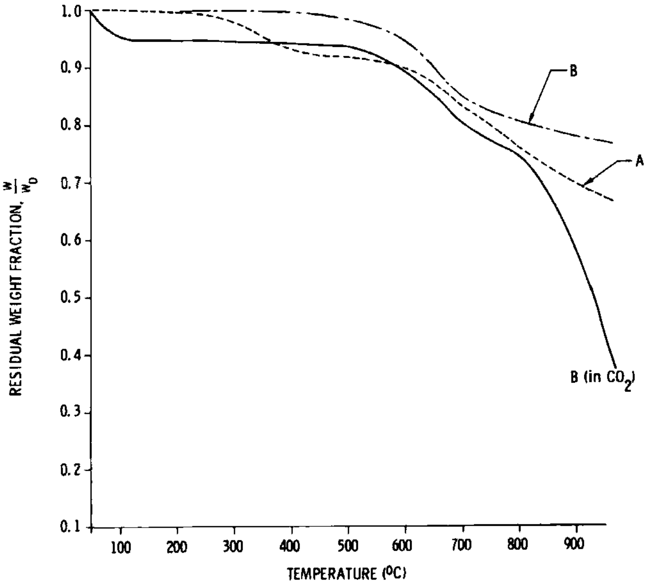

FIG. 5. TGA of polybenzimidazoles.

mined, and an average rate constant was calculated (Table 1). An activation energy of 44 ± 11 kcal was derived.

Thermogravimetric Analysis

The TGA apparatus, based on a Cahn electrobalance (3), was used at a heating of 3.3°C/min with argon on carbon dioxide atmosphere. Typical thermograms are shown in Fig. 5. Decomposition kinetics were derived from the slope of the thermograms by taking tangents at successive points. The rate *dw*/*dt* was divided by the active weight $W_t - W_{\text{residue}}$, to give rate constants. Figure 6 shows the Arrhenius plots based on the thermograms in argon.

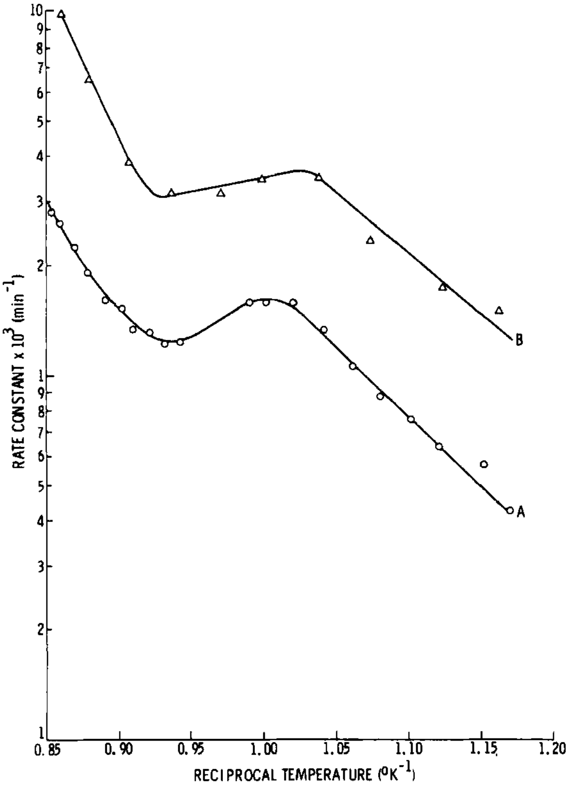

FIG. 6. Rate constants for decomposition of polybenzimidazole polymers (A and B).

TABLE 1

Temp., °C	Av. rate constant, min^{-1}
560	0.060
570	0.089
579	0.108
604	0.200

Elemental Analysis of Residue

Polymer B was predried at 150°C in vacuum. An approximately 150-mg sample was weighed into a small thin-walled Inconel crucible and then heated at a 3.4°C/min rate in argon atmosphere in the apparatus described previously (3), until the desired residual weight fraction remained. The sample was then detached from the electrobalance and quenched by being dropped to a point 5.5 in. below the furnace and immediately adjacent to the argon inlet tube. Elemental analyses of the residues were obtained. Results are shown in Table 2.

DISCUSSION

Kinetics

The determination of kinetic data from thermogravimetry for a high-temperature polymer having a high residual char presents

TABLE 2

Elemental Analysis of Polybenzimidazole Residues

Temp., °C	Residual weight fraction	C, %	H, %	N, %
25	1.000	73.46	4.28	11.12
319	0.990	73.77	4.02	11.90
487	0.983	73.66	4.13	12.05
586	0.968	73.60	3.94	11.34
606	0.947	75.49	3.18	11.61
670	0.895	77.12	2.75	10.35
730	0.854	77.84	1.81	5.41
817	0.813	77.82	1.52	3.74
916	0.771	80.58	1.07	2.50

a formidable problem. The "active fraction" depends on the residual weight fraction, but for aromatic polybenzimidazoles weight loss is not complete even at 1000°C. The problem is compounded, because the polymers are hygroscopic and resistant to drying, so the initial weight is also uncertain. Moreover, when degradation proceeds via sequential reactions, the activation energy is temperature-dependent.

Activation energies for formation of each product (Fig. 1) were determined from the Arrhenius plot (Fig. 3) and used for determining an average activation energy. The average activation energy was somewhat temperature-dependent (Fig. 7). The activation energy for formation of water above 550°C could not be determined accurately from the MTA of polymer A, because the evolution of chemically bonded water from postcuring of the polymer was not completed before decomposition began. The activation energy for water was therefore derived from the MTA of polymer B, determined after the sample had been maintained at 520°C for 30 min (until the peak at *m*/*e* 18 had decreased almost to the background value).

The Arrhenius plot, based on the thermogram of the molded polymer (curve A in Fig. 6), indicates a complex reaction. Below 720°C an activation energy of 18 kcal is observed; above this temperature the rate constant decreases, then an activation energy of 34 kcal is observed in the high-temperature region. These data are consistent with a two-stage reaction, in which the final dehydration

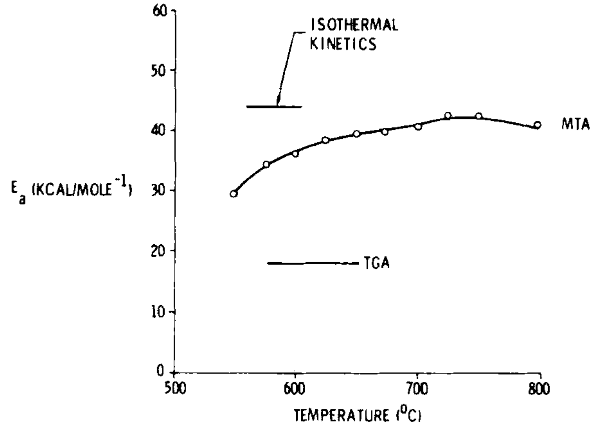

FIG. 7. Temperature dependence of activation energy (polymer A).

step of the polymerization is the principal low-temperature reaction. This is accompanied by slow degradation, which becomes the predominant reaction when polymerization is completed. Calculation of the activation energy for polybenzimidazole formation from the rate data of Wrasidlo and Levine (5) gives a value of 17 ± 3, which is certainly in good agreement with the lower-temperature reaction. The value of 34 kcal for the degradation activation energy is within the probable error of the values determined by MTA or isothermal effluent-gas analysis. Degradation of the polymer cured at atmospheric pressure (curve B in Fig. 6) apparently proceeds at a faster rate. Curves A and B are parallel. The twofold difference in rate is actually a function of the residual weight fraction (at 900°C), which differs in the two polymers. Polymer B lost only 20% of its weight on heating to 900°C, against the 32% weight loss of polymer A. This is best explained as a difference in water removal during cure.

Product Analysis

There was a distinct difference in thermal stability and decomposition products between the molded and powder-cured resins. The molded polybenzimidazole was only about 50% dehydrated to a heteroaromatic structure (6). There appeared to be a fairly high concentration of end groups, as shown by the carbon dioxide and phenol evolution. Relatively large amounts of water, hydrogen cyanide, ammonia, and hydrogen were formed, with lesser amounts of carbon monoxide and methane (Fig. 1). The thoroughly aged film gave principally hydrogen, smaller amounts of water and hydrogen cyanide, and a little methane. The water background varied during the experiment. The curve for water includes background and is of qualitative value only. Because of the small sample size it is possible that traces of ammonia and carbon monoxide were present but indistinguishable from air background or water and methane peaks. The cured powder, which was largely aromatized (80 to 90%, based on TGA), formed large amounts of hydrogen and carbon oxides, and lesser amounts of water, hydrogen cyanide, ammonia, and methane. The formation of oxygenated products in major quantities from a relatively well cured polymer, even after 0.5 hr of heating at 520°C in vacuum, strongly suggests that water of hydration reacts with the polymer by addition to the heterocyclic ring. This would involve reversal of the final polymerization step. The preceding steps are presumably also reversible, but two factors would tend to prevent hydrolysis to monomers. First, there is an excess of polymer, not of water. Second, at the high temperature required for hydrolysis of the benzimidazole structure aromatic amides are well above their decomposition temperature and would pyrolyze preferentially.

Below 550°C the only significant product observed in the MTA is water. Above 550°C degradation begins. The paucity of volatile products containing both carbon and hydrogen strongly suggests that the carbocyclic rings are retained in the char structure. This is supported by the elemental analysis, which shows a sharp rise in carbon content but a corresponding drop in hydrogen and nitrogen content between 600 and 900°C. The 70 to 80% residual weight fraction also corresponds to loss of the components of the heterocyclic ring.

The elemental analyses taken at various stages of the heating program generally confirm the MTA data. Nitrogen values were low, owing to incomplete oxidation (5 min at 900°C in CO_2 atmosphere). From the TGA run in carbon dioxide it became obvious that the rate of oxidation was too low for complete combustion during the Dumas nitrogen determination. Nevertheless, the data were used for caluclation of the composition of the volatile products, since pyrolysis under reproducible conditions would leave about the same percentage of nitrogen in the char.

Calculation of the composition of gases evolved from polymer B was performed by means of the data in Table 2. Over a given temperature range the changes in the amounts of elements present in the residue (weight fraction times percentage) must represent the amounts evolved (Table 3). In the range 25 to 487°C water must be the main product, with perhaps some organic compound. From 487

TABLE 3

Composition of Effluent Gas

Temp., range, °C	Gram-atoms lost per 100-g sample			
	C	N	H	O
25–487	0.09	0	0.22	0.07
487–606	0.08	0.06	1.05	0.05
606–916	0.78	0.64	2.18	—

to 606°C the analytical data are consistent with formation of hydrogen, some hydrogen cyanide being likely. From 606 to 916°C the analytical data are consistent with formation of hydrogen cyanide, hydrogen, and methane. These conclusions particularly agree with the data from the mass-spectrometric thermal analysis of polymer C (Fig. 3).

Mechanism

From these studies sufficient information is now available on polybenzimidazole degradation to justify the presentation of a mechanism (Fig. 8). It must account for the following data:

1. The over-all activation energy is 30 to 41 kcal (Fig. 7).
2. Activation energies for formation of the major products range from 22 to 54.
3. Maximal rates do not occur at the same temperature for each product.
4. The polymer containing more water gives a lower residual weight.
5. Oxygenated products are formed from a polymer containing only carbon, hydrogen, and nitrogen.
6. Aging of the polymer at 520°C changes the ratio of products.
7. Air aging does not greatly increase the proportion of oxygenated products formed during subsequent thermal decomposition.
8. The residue is enriched in carbon and depleted in nitrogen and hydrogen at elevated temperatures.
9. The residual weight at 800 to 1000°C is 70 to 80% of the initial weight.

The initial (slow) step (1) involves hydrolysis or ring opening, or both, of the hydroxyimidazoline to the tautomeric amide structures. This reaction, accompanied by cross-linking via amide interchange, may account for the decrease in solubility observed on heating of the polymer at 450 to 500°C. An alternative explanation is cross-linking via a benzene to a biphenyl type of coupling (7). Absorbed and entrapped water is present even in well-cured polybenzimidazoles. Since the activation energy is much lower than the energy for homolytic scission of any of the bonds in the polybenzimidazole structure, free radical formation at this stage is precluded. The product mixture is generally similar to the product of aromatic amides (8), especially in the MTA run after 520°C aging, making a hydrolytic mechanism most likely.

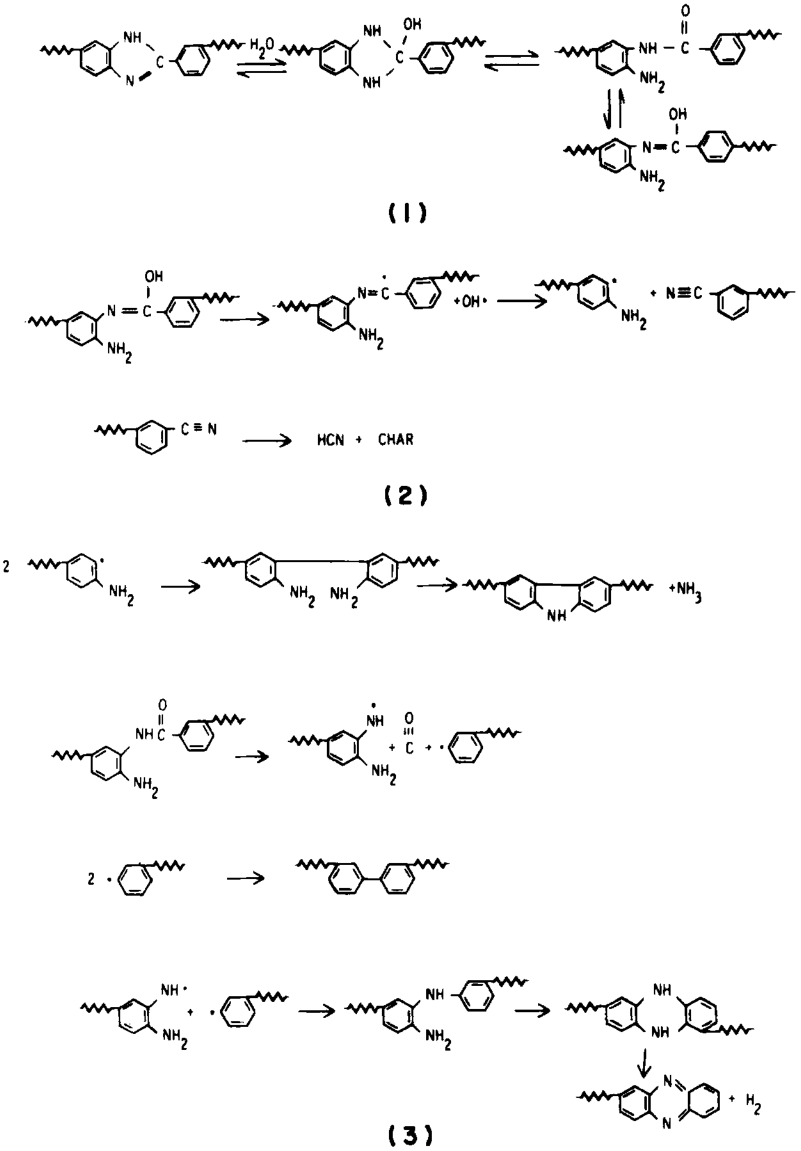

FIG. 8. Postulated mechanisms for thermal degradation of poly-2,2′-(*m*-phenylene)-5,5′-bibenzimidazole.

Hydrolysis is then followed by decomposition of the amide structure via at least two homolytic pathways. The imide tautomer decomposes to *o*-aminophenyl radicals, benzonitrile structures, and hydroxyl radical (**2**). The hydroxyl radical may abstract hydrogen to form water. The degradation of benzonitrile to hydrogen cyanide has been reported (9). Coupling of two *o*-aminophenyl radicals gives a 2,2′-diaminobiphenyl structure, which degrades with loss of ammonia to carbazole or anthracene structures (*10*). The carbonyl tautomer is postulated as the source of carbon monoxide. The suggested scheme (**3**) involves elimination of carbon monoxide, leaving phenyl and *o*-aminophenylamine radicals. Coupling of these would lead to a carbon–nitrogen residue with a ladder polymer structure. Further condensation of the polycyclic rings into a graphitic char is probably the principal reaction leading to hydrogen. The activation energy for formation of hydrogen, 38 kcal/mole, is similar to that reported in phenolic resins (2), 29 to 32 kcal/mole, for which a similar mechanism has been suggested (*11*).

An alternative mechanism (Fig. 9) merits consideration: phthalic anhydride and benzo-2,1,3-selenadiazole, formally similar to benzimidazole, have been shown to give benzyne on pyrolysis (*12*) or electron impact (*12,13*). Subsequent reactions of benzyne would form biphenyl or naphthalene structures. Benzonitrile moieties and

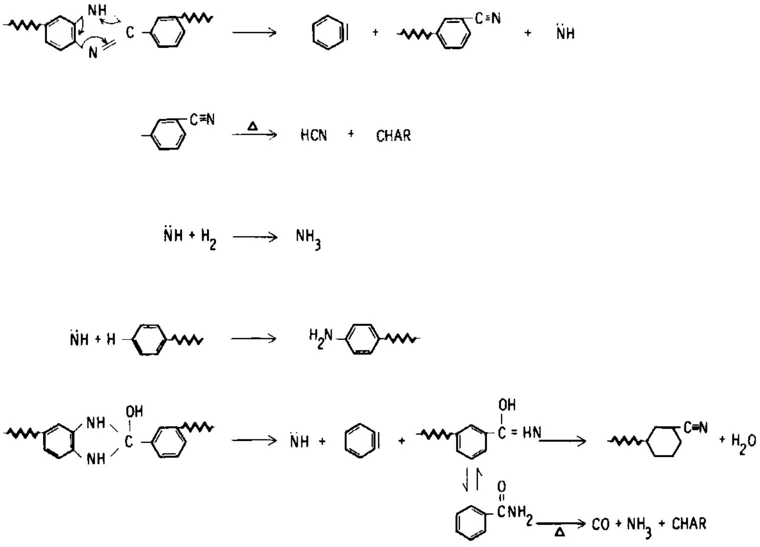

FIG. 9. Polybenzimidazole decomposition via benzyne intermediates.

nitrene would also be formed from benzimidazoles. Insertion reactions of nitrene could lead to ammonia or amines. The hydrated polymer would give benzyne, nitrene, and benzamide moieties. Dehydration of the amide to nitrile and water would be competitive with pyrolysis to carbon monoxide and ammonia.

It would be predicted from this mechanism that more carbon monoxide and ammonia but less hydrogen cyanide would be formed from the polymer with higher water content (A). The well-cured polymer (B), however, actually gave a higher percentage of carbon monoxide and less hydrogen cyanide. For this reason we consider the benzyne mechanism less likely. Unfortunately, evidence of the nature of the intermediates could not be obtained from infrared examination of the polymer. Although we attempted to find trace quantities of monomeric materials having functional groups similar to those postulated, no evidence of their formation could be obtained. Friedman (*14*) has obtained evidence of benzonitrile and phthalonitriles, aniline, phenylenediamine, and benzimidazoles or cyanoanilines from mass spectrometric examination of polybenzimidazole pyrolysis products, but these are consistent with both mechanisms. It is possible that the degree of branching or of cure left a larger proportion of end groups in the polymers used in his investigation, leading to higher concentrations of these products. Differences in configuration or construction materials of the apparatus might also be a factor. For substantiation of the postulated mechanism comparative studies of the pyrolysis of model compounds would be desirable, so that activation parameters for benzonitrile and diaminobiphenyl pyrolysis could be determined or initial pyrolysis products of the diphenylbibenzimidazole system identified.

Acknowledgments

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Zusammenfassung

Die thermische Zersetzung von Poly-2,2′-(*m*-phenylen)-5,5′-bibenzimidazol wurde bei Temperaturen bis zu 916°C untersucht. Massenspektrometrische thermische Analyse (MTA) in Zusammenhang mit Elementaranalysen der Rückstände während verschiedener Stufen der thermogravimetrischen Analyse wurden als Methoden benutzt, um die Produktverteilung als Funktion der Temperatur zu bestimmen. Unterhalb von 550° bestand das Hauptprodukt aus Wasser. Oberhalb von 550° beginnt der Abbau der heterocyclischen Struktur zu Blausäure, Ammoniak, Kohlendioxid und Wasser. Wasserstoff und Methan bilden sich wahrscheinlich durch Zersetzung und Kondensation carbocyclischer Strukturen. Aus den MTA Daten lassen sich die Aktivierungsenergien der Bildung jedes der Hauptprodukte ableiten. Deren Mittelwerte sind etwas temperaturabhängig, stimmen aber innerhalb der Fehlergrenze mit dem aus isothermischen kinetischen Studien erhaltenen Wert von 44 ± 11 kcal überein. Ein Mechanismus wird postuliert der anfängliche Hydrolyse des Polymeren zu einem aminsubstituierten Polyamid einschliesst. Nachfolgende homolytische Reaktionen sind für die Bildung der Hauptptrodukte verantwortlich.

Résumé

On étudie la décomposition thermique du poly-2,2′-(*m*-phenylène)-5,5′-bibenzimidazole aux températures allant jusqu' à 916°C. L'analyse spectrométrique thermique de masse (MTA), supportée par l'analyse élémentaire des residues aux stades divers de l'analyse thermogravimétrique a été utilisée pour la détermination de la distribution des produits en fonction de la température. Au-dessus de 550°C commence la dégradation de la structure hétérocyclique en acide cyanhydrique, ammoniaque, oxyde de carbone et eau. Au-dessous de 550°C l'eau est le produit principal. L'hydrogène et le méthane sont probablement formés de la décomposition et de la condensation de la structure carbocyclique. À partir de données de MTA on déduit les énergies d'activation de la formation de chaque produit principal. Leur valeur moyenne dépend légèrement de la témperature, mais est en accord avec les limites d'erreur experiméntale de 44 ± 11 kcal obtenue de résultats de cinétiques isothérmiques. Un mécanisme d'hydrolyse initiale du polymère en un polyamide aminosubstitué est postulé. Les réactions homolytiques subséquentes sont responsables de la formation des produits principaux.

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