Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Johnston, T. H. and Gaulin, C. A.(1969) 'Thermal Decomposition of Polyimides in Vacuum', Journal of Macromolecular Science, Part A, 3: 6, 1161 — 1182

To link to this Article: DOI: 10.1080/10601326908051943

URL: http://dx.doi.org/10.1080/10601326908051943

J. MACROMOL. SCI.–CHEM., A3(6), pp. 1161-1182, October, 1969

Thermal Decomposition of Polyimides in Vacuum

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SUMMARY

The decomposition in vacuum of a cured polyimide resin (Skybond 700) was studied in detail using simultaneous mass spectral and differential thermal analysis. These data were complemented with kinetic studies of the polymer and selected model imides. The mechanisms involved in the decomposition of Skybond 700 at moderate temperatures were determined using the combined results. It was discovered that the major endotherm seen in the thermogram was due to three simultaneous reactions: 1) Rupture of the benzophenone carbonyl bond to yield CO, 2) rupture of the imide bond to yield CO, and 3) rupture of the imide bond to yield CO_2. Reaction 3 is in conflict with previous studies where CO_2 was reported to arise from impurities in the polymer. The imide linkage as a source of CO_2 was substantiated by studying the degradation of model imide compounds. The decomposition rate of each of the models, in the vapor phase, was found to be first order, as was the rate of formation of CO_2. It was then postulated that CO_2 is formed in the decomposition of the imide linkage by an intromolecular rearrangement through an ionic isomeric intermediate. Reaction rates were determined for the models, and the activation energies for each of the competing decomposition reactions for N-phenylphthalimide, the model most closely related to the polymer imide linkage, were calculated.

INTRODUCTION

The severity of the environment to which manned and ballistic reentry vehicles are currently being exposed has focused attention on higher-performance thermal protection materials. Among these, the nitrogen-containing heterocyclic polymers have appeared most attractive because of their extreme thermal stabilities. Examples of this class of polymer are the polyimides and polybenzimidazoles. As part of a continuing program intended to provide a basic understanding of ablative processes and to supply data for incorporation into analytical models which predict ablation performance, a study of the mechanisms and rates of thermal degradation of these polymer types was initiated.

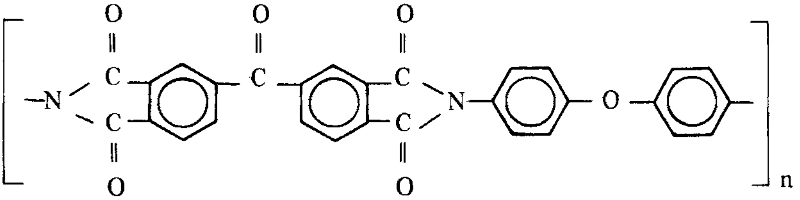
This paper is concerned with the pyrolysis of a polyimide resin and imide compounds used as models of the polyimide structure. Specifically, this study was restricted to the decomposition of Monsanto's Skybond 700, which was selected because of its fabrication characteristics.

In previous publications, analysis of the gaseous decomposition products of various polyimides showed that carbon monoxide and carbon dioxide accounted for about 80-90 mole % of the gases evolved [1, 2, 3]. The presence of carbon dioxide after pyrolysis in air is easily explained. This is not the case for thermal decomposition in a vacuum environment. Bruck [1] reported substantial quantities of CO_2 in the pyrolysis of H-film. H-film differs from Skybond 700 principally in that pyromellitic dianhydride instead of benzophenone dianhydride is used as a reactant. Bruck's analysis of the condensable decomposition gases shows that water is also a significant product (8.0 mole %). The presumption was that carbon dioxide is solely a by-product from the decomposition of incompletely cyclized polypyromellitamic acid and that it is formed by decarboxylation and by hydrolytic scission of the amide groups. Bruck also assumed that carbon monoxide is the only gaseous oxygen product evolved from the decomposition of the imide groups and other oxygen-containing components of the polymer. He reported that the ratio of CO to CO_2 at 610°C from purified H-film was 3 to 1. The decomposition of duPont's H-film has also been studied by others [2]. These studies showed that at 540°C carbon monoxide and carbon dioxide were the important gaseous products (93 mole %) in a ratio of 1.67 to 1. Water constituted only 1.2 mole %.

The present study initially employed a mass-thermal analysis method to investigate the decomposition products of Skybond 700. In the mass spectral analysis the evolution of substantial quantities of CO_2 at high temperatures appeared to be inconsistent with the assumption that it originated from polyamic acid impurities. Accordingly this investigation was extended to determine the reaction kinetics and mechanisms involved in the decomposition of imide groups in polyimide polymers. Three model imide compounds in addition to the polymer were decomposed with time as the only variable.

MATERIALS

The Skybond 700 resin, obtained from Monsanto Corporation, was cured in an air oven for a total of 16 hr at 25°C increments, between 200 and 372°C. These temperatures are typical of those in current use for preparation of laminates with this resin, and significant amounts of oxidative degradation are not expected to occur under these conditions [4]. Infrared analysis of the resulting polymers showed that free carboxylic acid was not present and that amide and amine nitrogen-to-hydrogen bonds were present in a quantity representative of polymer chain termination groups. The polymer was extracted with dimethylformamide, and an infrared spectrum showed that the extracted material was not of an organic nature. The cured polymer has the general structure:



Eastman Organic Chemicals phthalimide and methylphthalimide C.P. grade were used without further purification. Elemental analysis and melting point range determinations proved the compounds to be sufficiently pure for kinetic considerations. N-phenylphthalimide was prepared by reacting phthalic anhydride with aniline. It was purified by recrystallization from ligroin. The melting point and elemental analysis of the resulting imide indicated it was 99+% pure. However, since even a 1% variation in oxygen content corresponds to at least 5% N-phenylphthalamic acid, a free carboxyl determination was made by a two-phase extraction potentiometric titration.

The compound was determined to contain less than 1% N-phenylphthalamic acid. Matheson Company research grade CO, CO_2, and H_2 were used without purification for quantitative calibrations.

EXPERIMENTAL METHODS

The study was initially carried out using a differential thermal analyzer (the duPont Model 900) to control the temperature program and record the decomposition endotherm. A special cell was designed and built to operate in high vacuum and in the temperature range from ambient to 1200°C. Platinum-platinum/rhodium thermocouples were embedded in the reference material and samples, which were contained in platinum cups. Fine Al_2O_3 powder was used as the reference material. The polymer sample was ground with Al_2O_3 to form a 10% by weight mixture. Approximately 5 mg of the mixture were used as the sample size. A temperature program of 5-10°C/min was used to degrade the samples, and initial operating pressures were generally on the order of 10^{-6} Torr. Each sample was preconditioned in vacuum in the apparatus at 200°C for 1-2 hr to eliminate outgassing effects.

During operation, the DTA cell was attached through a specially designed molecular beam-forming device to a high-resolution mass spectrometer (the double-focusing CEC Model 110B). The design of the cell and beam-former are described elsewhere [5]. As the sample decomposed, the thermal response was detected by the DTA and simultaneously the mass spectra of the decomposition products were recorded. In one experiment the volatile products were scanned electromagnetically over the range 12-200 amu every 3 min at an ionization potential of 70 eV. For this work, a resolution of 1:3000 sufficed and ambiguities due to interference from similar masses were eliminated. In a second experiment, the mass spectrometer was focused for mass 2 and scanned electrostatically for detection of hydrogen every 2 min using 70-eV electrons for ionization.

With the current apparatus, it was not possible to carry out a mass spectral-DTA study on the model compounds because their vapor pressure did not permit decomposition in the high-vacuum mass-thermal analysis cell. However, it is possible to design a modification of this cell to permit decomposition and simultaneous mass analysis of volatile materials, and such a cell is being assembled currently.

For the kinetic studies, weighed samples of the imides and polymer were placed in 13-mm quartz tubes, equipped with break seal, through a necked-down sidearm. The tubes were evacuated at 10^{-4} mm mercury for 2 hr and then sealed off. They were subsequently placed in a closed-end clamshell furnace which had been preheated to the desired temperature. After the prescribed decomposition period, the tubes were placed on a vacuum line. The seals were broken, and the gases were passed through a liquid nitrogen-cooled trap. Hydrogen and carbon monoxide were the only noncondensable products found at this temperature. The gases were transferred with a Toeppler pump to a measured volume where the pressure was recorded. A sample of the gas was then analyzed with a Beckman gas chromatograph, Model IIA, using an activated molecular sieve 5 Å column. Precalibration with Matheson CO and H_2 enabled the concentration of carbon monoxide and hydrogen to be calculated. The liquid nitrogen trap was warmed to -76°C with a dry-ice acetone bath. The gases evolved at this temperature were analyzed with the procedure previously described except that a silica gel column was used on the chromatograph. The concentration of CO_2 was calculated from this aliquot.

The residues in the sample tube were extracted with chloroform into 10-ml volumetric flasks. The infrared spectra between 5 and 6 μ were recorded on a Beckman IR4. This is the region where the imide carbonyl coupling absorption occurs [6]. The wavelengths used for quantitative analysis of the residues were: for N-methylphthalimide 5.63 μ and for N-phenylphthalimide 5.60 μ. The phthalimide residues were extracted with methanol and analyzed at 5.62 μ. The residue of the polymer could not be analyzed.

RESULTS AND DISCUSSION

Exploratory investigation was carried out using a DTA apparatus for controlled programming of the pyrolysis of Skybond 700 with a continuous analysis by high-resolution mass spectrometry of the product gases after the method of Gaulin et al. [5]. Interpretation of the data obtained from this investigation revealed a sequential decomposition reaction path involving various groups in the polymer. The volatile decomposition products were H_2, CO, CO_2, H_2O, HCN, and minor quantities of benzonitrile, benzene, methane, and ammonia. Figure 1 shows a composite spectrum of these products at their peak intensities without regard to temperature. In Fig. 2, the ion currents from the mass spectral data for the major products are plotted as a function of the decomposition temperature of the polymer. A separate plot for

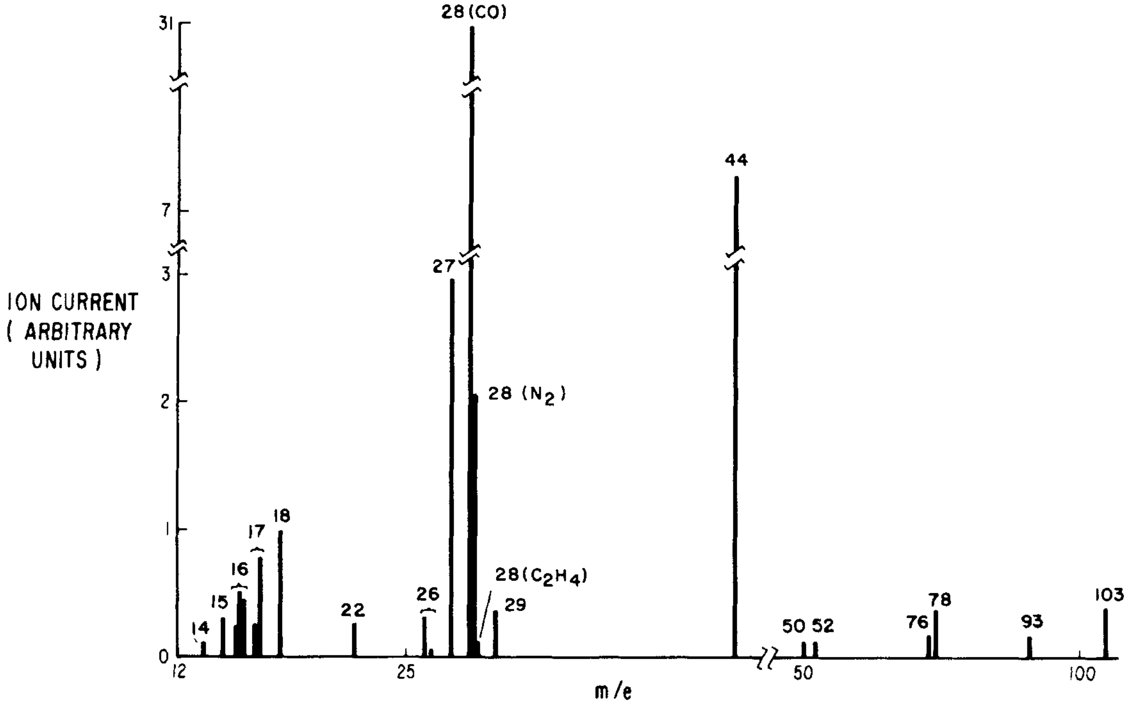


Fig. 1. Mass spectrum of Skybond 700 decomposition products.

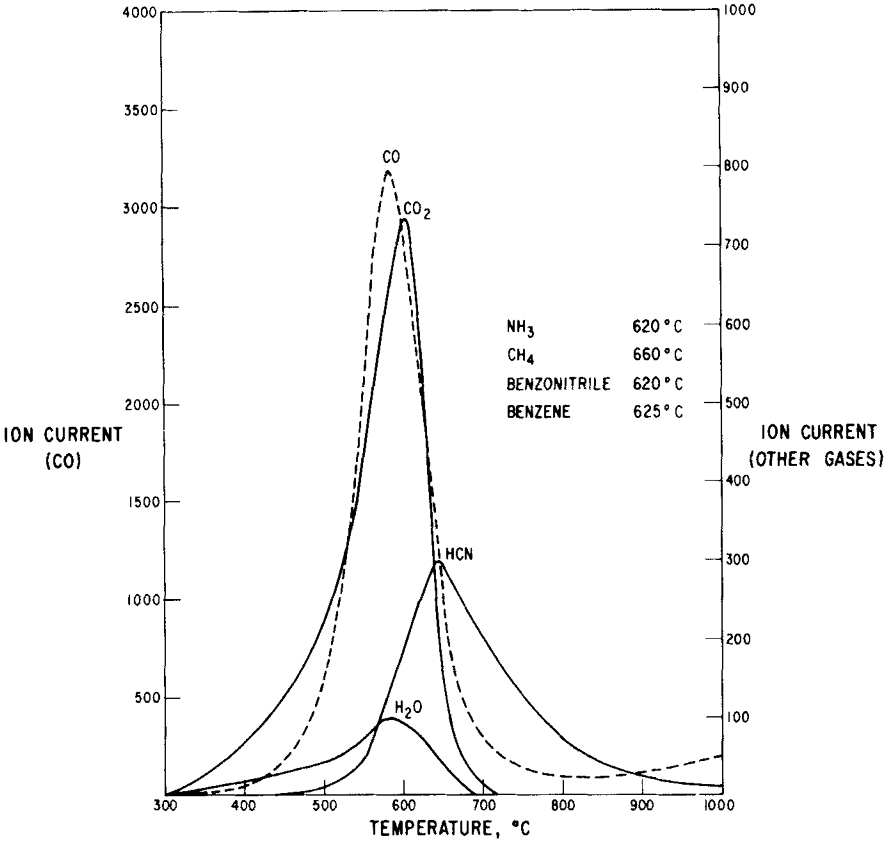


Fig. 2. Mass spectral intensities of the decomposition products of Skybond 700 vs. temperature.

hydrogen appears in Fig. 3. Figure 4 shows the corresponding thermogram determined simultaneously with the mass spectrum. Similarities between the mass spectral intensities and the peaks in the thermogram permit certain correlations between the two sets of data. One of the first products to appear was carbon dioxide. At moderate temperatures (e.g., 300-500°C) it proved to be only a minor product. At higher temperatures (e.g., 500-700°C) carbon dioxide became a major product and seemed to evolve simultaneously with the decomposition of the imide group. Water also appears early as a minor product. At the low temperatures both CO_2 and H_2O probably result, as postulated by Bruck, from ring closure and

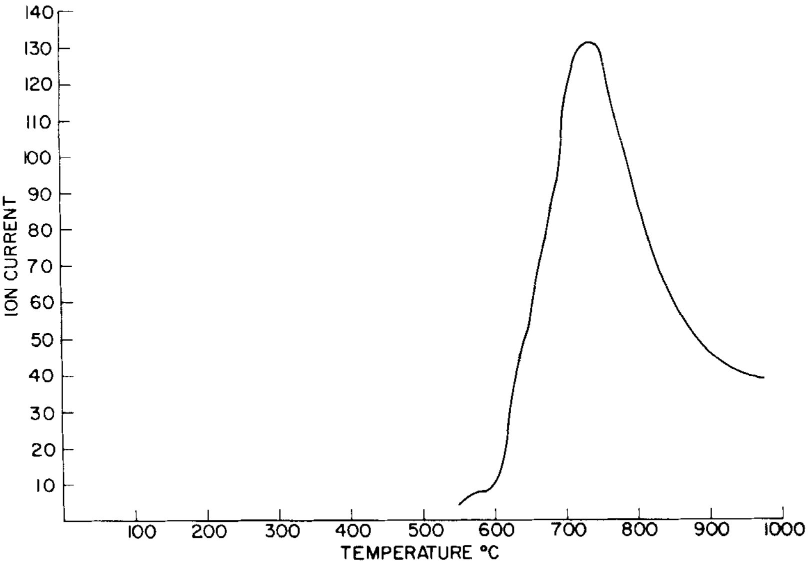


Fig. 3. Mass spectral intensities of hydrogen from Skybond 700 vs. temperature.

decomposition of polyamic acid groups. This is seen in the mass spectrometry results as a gradual increase in these components between 300 and 500°C and similarly in the thermogram as a weak, broad inflection in the same temperature range. From 500 to 605°C, CO and CO_2 are the major products formed, as determined by the mass spectrometer. This temperature range corresponds to that of the major endotherm in the thermogram, which has its maximum intensity at 600°C. At these temperatures carbon monoxide can arise from degradation of the benzophenone substructure, from the phenyl ether, or from the imide ring. Subsequent infrared studies of the degradation of Skybond 700 film at 550°C show that benzophenone decomposes rapidly in this temperature region, the imide bond slowly decomposes, and the ether linkage remains intact.

Assuming that CO_2 arises from decomposition of the imide bond, the relative slopes of the CO and CO_2 peaks at 550°C indicate that a bond other than the imide is rupturing simultaneously to yield CO. This is in agreement with the infrared study, which shows the disappearance of a carbonyl band (6.05 μ) in the polymer at 550°C. This reaction is much more rapid than the imide decomposition, with the result that the peak

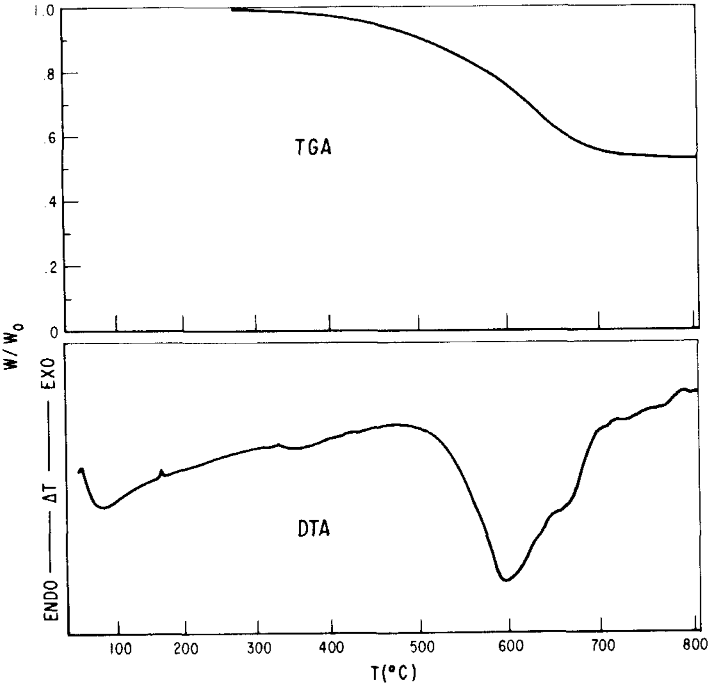


Fig. 4. TGA and DTA of Skybond 700 in vacuum.

for CO is reached at 585°C as opposed to 605°C for CO_2. A plot of the relative ion current ratio of CO versus CO_2 (Fig. 5) places the decomposition peak for the benzophenone carbonyl at 560°C. Above 600°C the primary products are CO_2, CO, benzonitrile, benzene, hydrogen, ammonia, methane, and hydrogen cyanide. At these temperatures, the CO_2 intensity decreases rapidly and disappears at 700°C. The intensity of the carbon monoxide peak diminishes rapidly, rises again as the ether linkages decompose, and continues to evolve past 1000°C. Hydrogen cyanide is a major product which peaks at 650°C and, like CO, continues to evolve past 1000°C. This is seen in both the mass spectrum and in the thermogram, the latter showing a pronounced inflection at 655°C. Significant quantities of HCN in the volatile product are not surprising since elemental analysis of the residue remaining after treatment at 1000°C shows that the concentration of nitrogen in the char is approximately 50% of its concentration in the polymer. The decomposition products of the aromatic

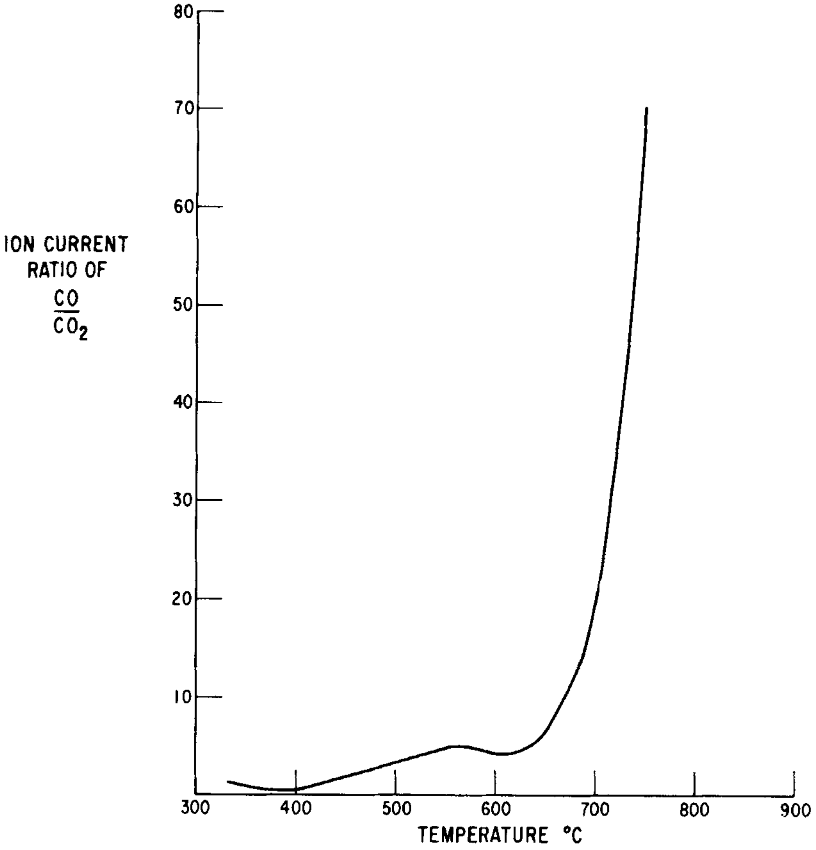


Fig. 5. Ion current ratio of CO/CO_2 vs. temperature.

groups also show up in the region 600-700°C. The ion current peaks for benzonitrile and ammonia are at 620°C, benzene is at 625°C, methane is at 660°C, and hydrogen is a major product at the high temperatures, peaking at 750°C.

The source and the mechanism for the formation of carbon dioxide could not be determined from the mass spectral study. However, there are at least three possible mechanisms. It could be formed 1) in the decomposition of incompletely cyclized polyamic acid, as proposed by Bruck, 2) by decomposition of the polyimide through an intermolecular oxygen transfer, or 3) by an intramolecular rearrangement. Since it

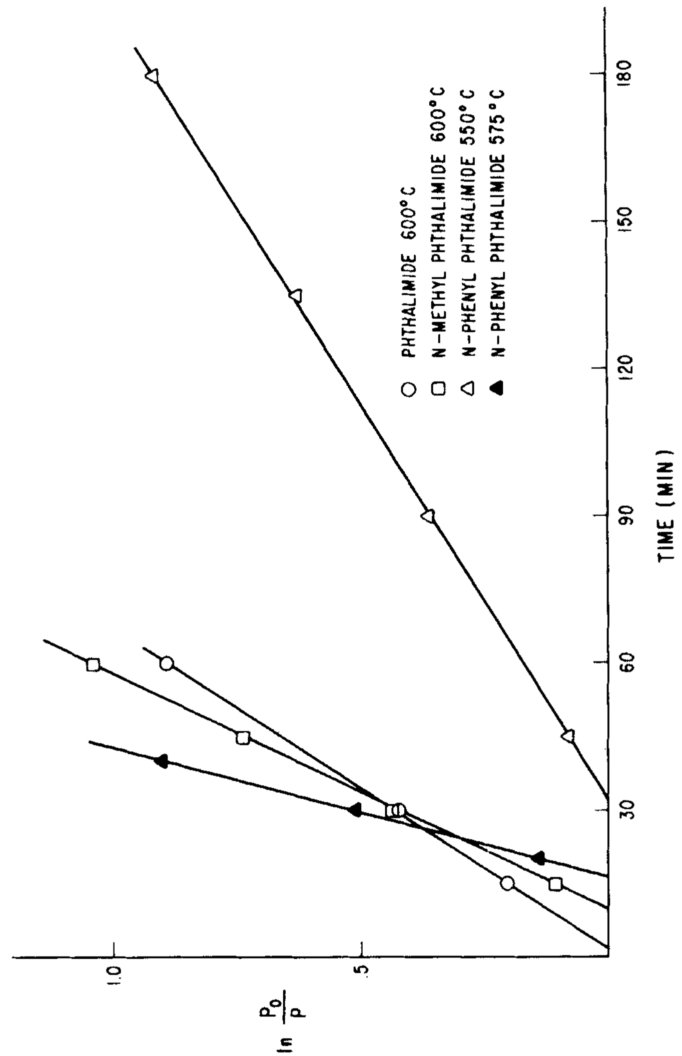


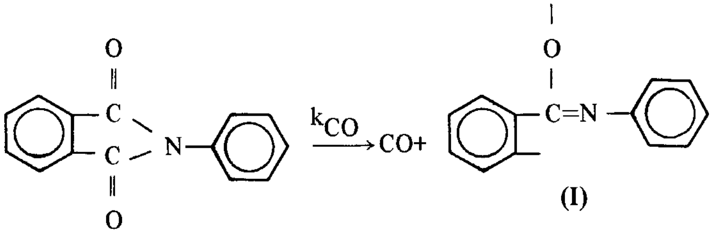
Fig. 6. First-order decomposition plots of imide compounds.

would be difficult to characterize the polymer completely, and since multiple sources of oxygen are present, it was decided to resort to the use of model compounds to elucidate the source of CO_2. Among the possible model compounds, N-phenylphthalimide is the simplest structural representation.

Since the vapor pressure of phenylphthalimide was too high to pyrolize in the DTA apparatus, it was necessary to carry out the pyrolysis in sealed quartz tubes under essentially isothermal conditions. The temperatures for the degradation studies were chosen where data could be obtained over a reasonable time span. Only the two gaseous oxygenated products and the amount of undecomposed imide were quantitatively determined. Time plus these three variables were all that were needed for a kinetic study. Other products were identified, but no attempt was made to achieve a mass balance.

A plot of the logarithm of the ratio of initial to final amounts of N-phenylphthalimide versus time yields a straight line, indicating a first-order decomposition reaction for this material in the vapor phase (Fig. 6). The induction period as seen in the plot is the time span needed for the system to reach thermal equilibrium. The fact that the reaction is first order indicates that the degradation of N-phenylphthalimide proceeds through a unimolecular process rather than an intermolecular collision. The complete reaction scheme at 550°C most probably occurs as follows:

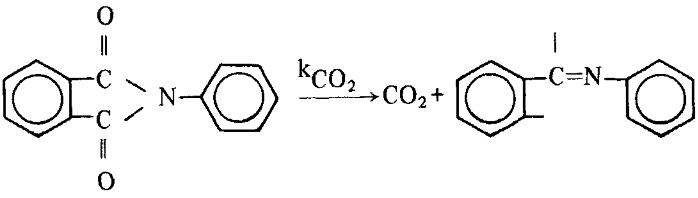
1.



(I)

1a. $I \longrightarrow CO + \text{char} + HCN + H_2 + \text{minor products}$

1b. $I + \text{free radicals} \longrightarrow \text{stabilized oxygenated product}$ **(II)**

2. 

(II)

The presence of **(II)** was first suspected when a mass balance could not be obtained between the oxygen content of the decomposed N-phenylphthalimide determined by infrared and the oxygen content of the gaseous products determined chromatographically. The ratio of CO and CO_2 to the decomposed imide at any temperature remained constant with time. Thus, it appeared that the tarry residue contained an oxygenated product which was necessary to complete the decomposition scheme for the formation of CO. Attempts to isolate and identify **(II)** failed. It could not be extracted from the residue, and the infrared spectrum of the residue was not sufficiently defined to identify oxygen-to-carbon absorption. The decomposition was then conducted for 24 hr to ensure complete reaction. The gaseous products were analyzed along with the residue. The imide had completely decomposed but the percentage of oxygen in the residue remained the same. Other samples were decomposed at 550°C for 24 hr. They were then heated at temperatures of 575, 600, and 625°C for 2 hr. At 575°C no further oxygen was evolved from the residue. At 600°C the CO yield was slightly higher. At 625°C virtually all of **(II)** decomposed to yield CO and a satisfactory oxygen mass balance. Apparently the N-phenyl group stabilizes the initial radical **(I)** through the resonance configuration depicted to enable a certain fraction to react with other radicals in the systems, reaction lb. The decomposition temperature of **(II)**, > 600°C, favors an aromatic ether structural representation for **(II)** rather than an amide linkage which decomposes at much lower temperatures. The remaining fraction of **(I)** simultaneously decomposes to release the other carbonyl group as carbon monoxide, reaction la. Reactions la and lb are very rapid compared with reaction 1. The existence of **(I)** shows that CO is formed through cleavage of the imide ring.

Kinetic considerations and reaction rates were calculated using the equations:

$$k_{CO} + k_{CO_2} = \ln \frac{p_o}{p} t^{-1} \qquad (1)$$

$$(CO_2) = \frac{k_{CO_2}}{k_{CO} + k_{CO_2}} \; p_o \; [1 - e^{-(k_{CO} + k_{CO_2})t}] \qquad (2)$$

where k_{CO} and k_{CO_2} are the reaction rates for the mechanisms involving the formation of CO and CO_2, respectively; p_o and p are the initial and final concentrations of the imide; t is time; (CO_2) is the final amount of CO_2 formed in millimoles (mM); and the quantity $p_o \; [1 - e^{-(k_{CO} + k_{CO_2})t}]$ is equal to the amount of imide decomposed in mM. Thus, Eq. (2) can be written:

$$k_{CO_2} = \frac{(CO_2)(k_{CO_2} + k_{CO})}{p_o - p}$$

The ratio $k_{1a}/(k_{1a} + k_{1b})$ was calculated using the equation:

$$\frac{(CO)}{(CO_2)} = \frac{k_{CO}(1 + \frac{k_{1a}}{k_{1a} + k_{1b}})}{k_{CO_2}} \qquad (3)$$

The values obtained for the reaction rates are listed in Table 2 along with the k_{CO}/k_{CO_2} ratios.

Plotting the CO and CO_2 concentrations versus Δp (Fig. 7) shows that both reactions 1 and 2 are first order. Thus, the formation of CO_2 proceeds through a mechanism involving either internal oxygen transfer or intramolecular rearrangement. Benzene and benzonitrile are also formed during the decomposition through reaction with free hydrogen radicals or by hydrogen abstraction. The presence of benzene makes it seem likely that the mechanism for the formation of CO_2 involves a cleavage of the nitrogen-to-phenyl bond.

The activation energies for reactions 1 and 2 were determined by conducting a study of the decomposition at two temperatures, 550 and 575°C. The activation energy calculated for reaction 1 is 90 kcal, and for reaction 2 it is 107 kcal. The higher value obtained for reaction 2 is consistent with a cleavage of the nitrogen-to-phenyl bond as the mechanism for the formation of CO_2.

The ratio $k_{1a}/(k_{1a} + k_{1b})$ increases rapidly with temperature. At 550°C only 18% of (I) decomposes, while at 575°C 77% decomposes. Extrapolation to 600°C indicates that stabilization of (I) does not occur.

To ascertain that CO_2 is indeed formed from the degradation of the

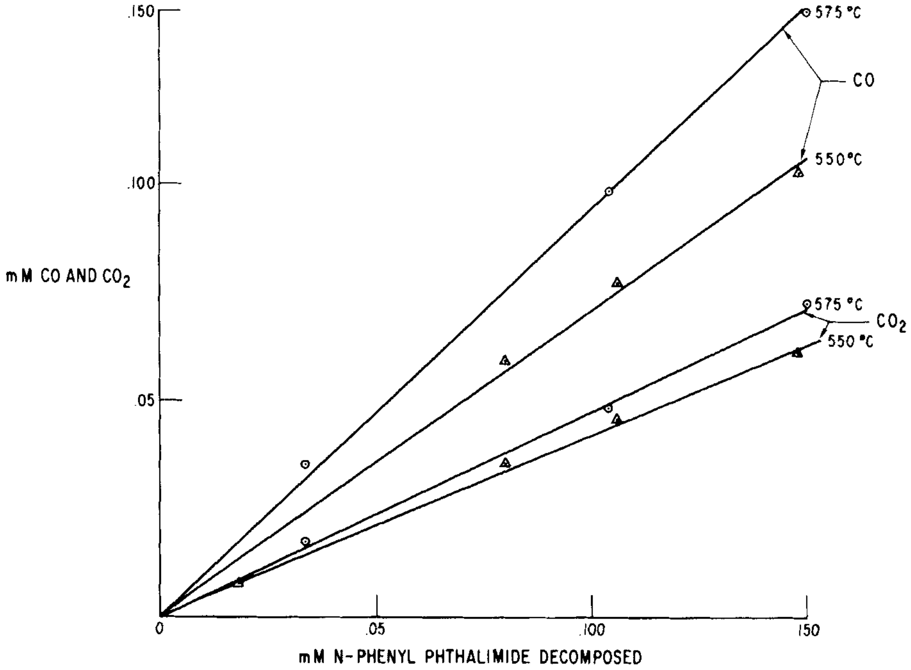
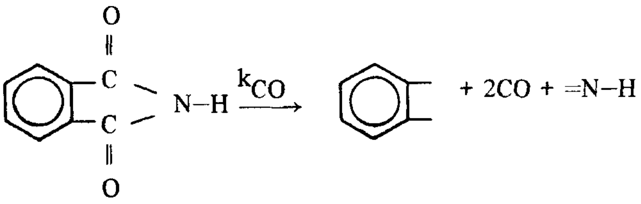


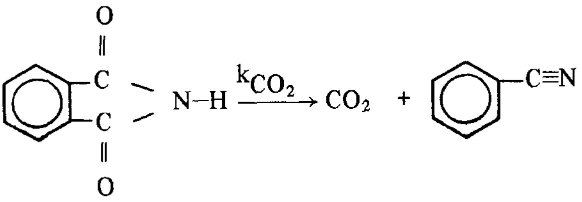
Fig. 7. First-order plots of CO and CO_2 formation from N-phenylphthalimide.

imide bond, the decomposition kinetics of phthalimide and N-methylphthalimide were studied. It was also possible that this study might yield some information relating to the mechanism involved in the formation of CO_2. Both compounds seemed to be much more thermally stable than N-phenylphthalimide. Reasonable rate data were obtained at 600°C. The decomposition of phthalimide could be represented by the following reactions:

3.



4.

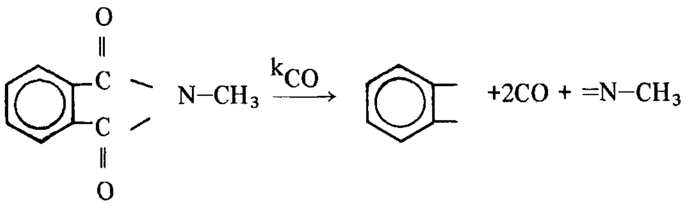


As in the N-phenylphthalimide decomposition, these reactions are first order for CO and CO_2 production. Since the ratio k_{CO}/k_{CO_2} is 0.25, reaction 4 is predominant.

The formation of carbon monoxide from the decomposition of phthalimide does not involve a stable oxygenated intermediate at 600°C. The two carbonyl groups are released simultaneously. Trial runs at 550°C indicated the same results, but the rate of reaction at this temperature was too slow to permit a quantitative study. Very little char is formed from the decomposition, probably because reaction 4 is the preferred route. Hydrogen was not observed as a product; nor was benzene. Benzonitrile was a major product in the vapor, which could account in part for the absence of hydrogen due to reaction with the free radical.

Methyl phthalimide could decompose according to the following reaction schemes.

5.



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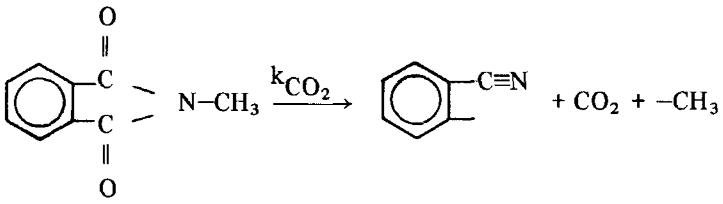


As in the previous two imides, the decomposition reaction was first order. However, with the methyl substituent the reaction for the formation of CO is predominant. Benzonitrile could not be detected and methane was conspicuously absent. Hydrogen was present in large amounts, which would

Table 1

	N-phenylphthalimide						
Sample size, mM	0.237	0.264	0.229	0.248	0.256	0.260	0.253
Temperature, °C	550	550	550	550	575	575	575
Time in furnace, min	45	90	135	180	20	30	40
Residue, mM	0.219	0.184	0.123	0.100	0.222	0.156	0.103
Amount decomposed, mM	0.018	080	0.106	0.148	0.0338	0.104	0.150
CO formed, mM	0.0128	0.059	0.0768	0.102	0.035	0.098	0.129
CO_2 formed, mM	0.0078	0.035	0.0453	0.0605	0.017	0.048	0.064
Ratio CO/CO_2	1.64	1.68	1.69	1.68	2.06	2.04	2.02
Corrected time, sec/10^3	0.78	3.48	6.18	8.88	0.222	0.882	1.422

	N-methylphthalimide				Phthalimide			Skybond 700		
Sample size, mM	0.343	0.365	0.323	0.251	0.383	0.419	0.474	0.208	0.211	0.202
Temperature, °C	600	600	600	600	600	600	600	550	550	550
Time in furnace, min	15	15	45	60	15	30	60	90	135	240
Residue, mM	0.308	0.241	0.156	0.089	0.309	0.272	0.193	–	–	–
Amount decomposed, mM	0.0353	0.124	0.167	0.162	0.0743	0.147	0.281	–	–	–
CO formed mM	0.047	0.193	0.252	0.243	0.029	0.054	0.108	0.373	0.363	0.369
CO_2 formed, mM	0.0078	0.032	0.042	0.041	0.058	0.119	0.226	0.250	0.252	0.243
Ratio CO/CO_2	6.03	6.04	6.00	5.93	0.50	0.45	0.48	1.49	1.44	1.52
Corrected time, sec/10^3	0.300	1.2	2.1	3.0	0.786	1.686	3.49	–	–	–

Table 2

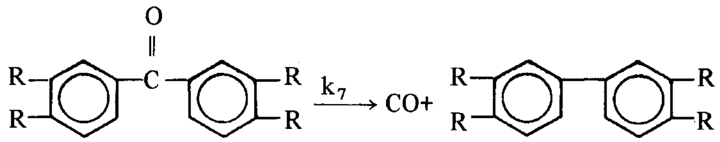
Compound	Temp. °C	Reaction rate (sec^{-1}) Constants	Ratio k_{CO}/k_{CO_2}
N-phenylphthalimide	550	$k_{CO} = 5.99 \times 10^{-5}$	
		$k_{CO} = 4.23 \times 10^{-5}$	1.42
	575	$k_{CO} = 3.37 \times 10^{-4}$	
		$k_{CO_2} = 2.92 \times 10^{-4}$	1.15
(extrapolated)	600	$k_{CO} = 1.55 \times 10^{-3}$	
		$k_{CO_2} = 1.8 \times 10^{-3}$	.86
Phthalimide	600	$k_{CO} = 5.3 \times 10^{-5}$	
		$k_{CO} = 2.12 \times 10^{-}4$	0.25
N-methylphthalimide	600	$k_{CO} = 2.69 \times 10^{-4}$	
		$k_{CO_2} = 8.73 \times 10^{-5}$	3.06
Skybond 700	550	–	0.67

account for the large quantity of char formed. The data and reaction rates for these imides are listed in Tables 1 and 2.

A complete comparative kinetic analysis of the polymer could not be made since two sources of CO were decomposing at the same time, and a quantitative analysis of the various oxygen groups in the residue with infrared was impossible. Accordingly, the polymer was decomposed at 550°C to correspond to the N-phenylphthalimide. The decomposition was carried to completion and for a time period beyond completion to determine if secondary decomposition products were being formed at this temperature. In this way a quantitative analysis of the gaseous oxygen products could be made. The experimental data are shown in Table 1.

From the data in Table 1 it appears that three initial reactions occur almost simultaneously in the decomposition of Skybond 700.

7.



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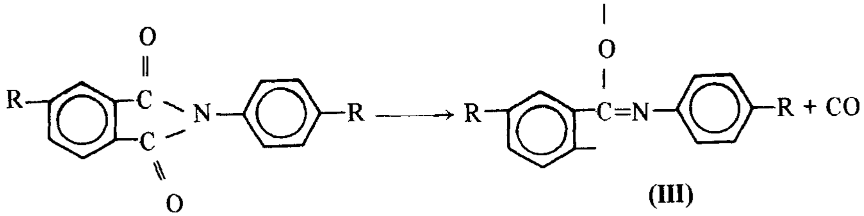

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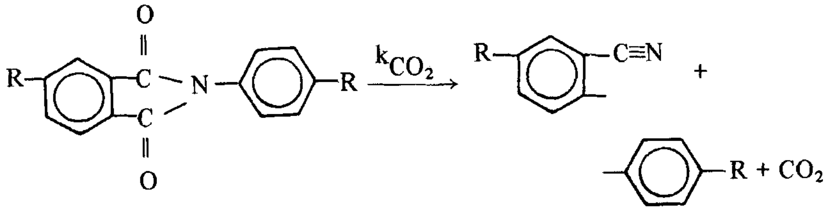
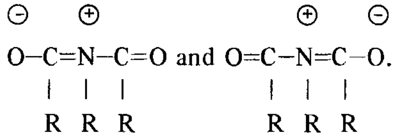


Reaction 1a is very important in interpreting the results obtained from the degradation of the polymer. In a gas-state decomposition, as in the decomposition of phenylphthalimide, reaction sites are not localized and small changes in temperature markedly affect the lifetime of **(I)**. The end result is that a large portion of **(I)** thermally decomposes before it can enter into a stabilizing collision reaction. The polymer, being a linear chain and partially cross-linked in the solid state at comparable temperatures, is not affected by these factors, as shown in reaction 8 where the intermediate, **(III)**, is ultimately stabilized.

Reaction 7 is readily observable in the infrared region at 6.05 μ and proceeds at a much faster rate than the imide decomposition. A reasonable oxygen mass balance can then be obtained subtracting the mM of CO formed from reaction 7 from the total mM of CO formed. This is possible since the data at 550°C show that the decomposition reactions of the polymer at this temperature have essentially gone to completion in the allotted time. The total mM of oxygen present in the polymer were calculated using the molecular weight of the monomeric unit. The remaining CO versus the CO_2 formed gives a ratio of 0.67 for k_8/k_9. Essentially complete stabilization of **(III)** in reaction 8 is evident as opposed to only partial stabilization of **(I)** in the model compound vapor. The stabilized intermediate of reaction 8 is responsible to a great extent for the retention of the polymer configuration until higher temperatures where the char is formed.

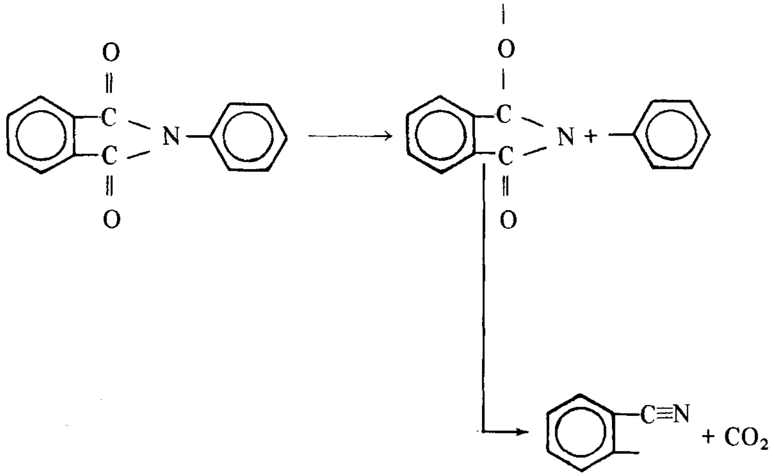
It is reasonable to assume at this point that the mechanism for the formation of CO in an imide decomposition involves scission of the imide ring to release either one or two of the carbonyl groups. The mechanism for the formation of CO_2 is not as easy to characterize. The ratio k_{CO}/k_{CO_2} increases as the nitrogen substituent is changed from H < phenoxy phenyl < phenyl < methyl, phenoxy phenyl being the substituent in the polymer. Of all the imides studied, phthalimide gives the greatest amount of CO_2 when decomposed. Phthalimide differs from the other imides chiefly in the ionic isomeric structures within the imide itself,



$$\overset{\ominus}{O}-\underset{R}{C}=\underset{R}{\overset{\oplus}{N}}-\underset{R}{C}=O \text{ and } O=\underset{R}{C}-\underset{R}{\overset{\oplus}{N}}=\underset{R}{C}-\overset{\ominus}{O}.$$

It is believed that these ionic structures are an integral part of the mechanism which favors the formation of CO_2. Stabilization of the ionic structures can occur in two ways: free radical stabilization, which occurs when the nitrogen substituent bond is broken, or stabilization due to the electron-donating characteristics of the nitrogen substituent. The principal feature common to both is that each requires an internal oxygen transfer to produce the CO_2.

Using N-phenylphthalimide to illustrate the desirable characteristics of each stabilizing mechanism, the following reaction would occur with scission of the nitrogen to phenyl bond:

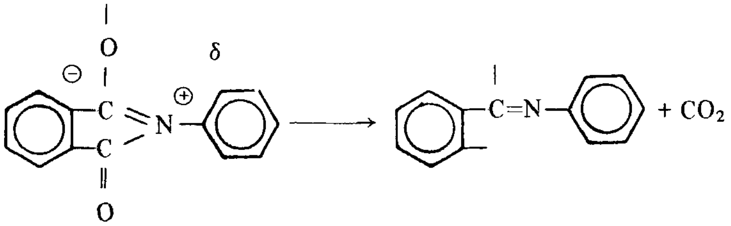


10.

In the first step, breaking of the nitrogen-to-phenyl bond leads to a resonance-stabilized free radical which gives a favorable configuration for the internal transfer of oxygen. N-phenylphthalimide itself has an extremely planar imide-to-phenyl spatial orientation which, because of its highly strained nature, would not be conducive to the internal transfer that takes place. Hydrogen abstraction by the phenyl and benzonitrile radicals can account for the presence of benzene and benzonitrile in the products. Subsequent polymerization of the major fraction of the benzonitrile radical also explains the retention of nitrogen in the polymer residue below 600°C. The activation energy of 107 kcal for this reaction seems reasonable for the cleavage of the nitrogen-to-phenyl bond. Since the bond energies are not known for each substituent, there is no way of correlating them with the series found for the k_{CO}/k_{CO_2} ratios. However, a few kcal difference for each substituent would have a significant effect on the k_{CO}/k_{CO_2} ratio.

The second route depends on a partial charge transfer from the N-substituent and has the advantage of preserving chain integrity.

11.



The work of Matsuo [6] supports this mechanism, which rationalizes both nitrogen retention and high char yield in the polymer. According to Matsuo, investigation of the longest-wavelength absorptions in the electronic spectra of imides reveals that the extent of electron donation from the nitrogen atom to the carbonyl groups increases as the substituent is changed in the order of hydrogen, alkyl, and aryl groups. The stabilization of the ionic structures of the imide system is also directly affected by the electronic nature of a substituent on the aryl groups, the one having the greatest effect being the p-phenoxy group. The order of the series experimentally derived in this study corresponds to his observations with the exception of the hydrogen in phthalimide. However, this is a labile hydrogen which in the gas phase migrates between the oxygen and nitrogen and could account for the discrepancy.

Regardless of which mechanism is assumed, it appears that the imide ring is a primary source of CO_2 and that this reaction is competitive in rate with ring scission to produce CO, with the former accounting for about 50% of the decomposition of N-phenylphthalimide at 600°C.

In the case of Skybond 700, the early appearance of CO_2 and H_2O in small quantities probably arises, as postulated by Bruck, from ring, closure, decarboxylation of polyamic acid groups, and hydrolytic scission of the imide ring. By extraction of polyamic acid from his H-film with DMF, Bruck was able to reduce the amount of CO_2, H_2O, NH_3, and HCN significantly, which added to the credibility of his interpretation. In the case of Skybond 700, however, water was a minor product, which indicated a low percentage of polyamic acid groups and largely eliminated the possibility of hydrolytic scission. Furthermore, HCN becomes more predominant at temperatures greater than those used by Bruck (600°C), which explains why, after purification, he did not observe HCN. Even after extraction Bruck observed a large amount of CO_2, which he explained as originating from impurities ($\approx$ 23%) still in the polymer. In the present work, results with simple nonpolymeric model compounds indicate that the CO_2 originates from the imide ring probably by an intramolecular rearrangement. It is clear, then, that the CO_2 yield may not be used to calculate the amount of impurities present in a heterocyclic polymer system.

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Accepted by editor May 22, 1968
Received for publication July 3, 1969