Effect of Phosphoric Acid on Chemical Transformations during Nomex Pyrolysis

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The thermal degradation of Nomex [poly(*m*-phenylene isophthalamide)] impregnated with phosphoric acid has been investigated by the analysis of the corresponding pyrolysis products, which were fractionated into gases, liquids, and char. Gas chromatography (GC) and/or gas chromatography/mass spectrometry (GC/MS) were used to study the volatiles evolved whereas the solid residue was examined by elemental analysis and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). For the sake of comparison, a parallel study of unimpregnated Nomex was carried out in the same conditions. The main product of unimpregnated Nomex degradation in the conditions of this work was found to be *m*-benzenediamine, which is the result of a heterolytic process. Aromatic nitriles are also produced through homolytic reactions. Most of the products of impregnated Nomex degradation were also detected with its unimpregnated counterpart, except for isophthalic acid, carbon monoxide, and elemental phosphorus. Aromatic nitriles are the pre-eminent products from pyrolysis of unimpregnated Nomex, there being no trace of *m*-benzenediamine. Reaction mechanisms for impregnated Nomex degradation consistent with these findings are proposed, including a nonhomolytic process for the formation of nitriles in the presence of phosphoric acid.

1. Introduction

Phosphorus compounds, such as phosphoric acid, have been introduced into organic materials for various purposes: as inhibitors of carbon oxidation[1−4] and as activating reagents for the chemical activation of ligno-cellulosic precursors in order to lower carbonization temperatures and increase carbonization yields with respect to the alternative physical activation process.[5−11] The inhibition of carbon oxidation is due to the diminution of the reactive sites available, as these are blocked by phosphorus compounds. The beneficial effect on the activation process of lignocellulosic materials has also been satisfactorily explained by the chemical processes promoted by phosphorus compounds (particularly, phosphoric acid): that is, the hydrolysis and dehydratation

Scheme 1. Chemical Structure of Nomex
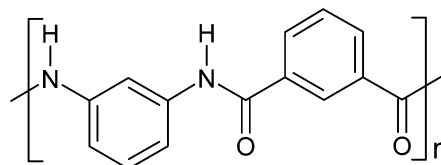
of the biopolymers that make up the lignocellulosic feedstocks at low temperatures, causing a redistribution of the precursor material, and cross-linking reactions at higher temperatures, which fix otherwise volatile products in solid residue.

Recently, it was discussed that the addition of small amounts of H_3PO_4 to the synthetic polymer poly(*m*-phenylene isophthalamide) (Scheme 1), known as Nomex (henceforth designated as Nomex), leads to a shift of the carbonization process to lower temperatures and an improvement of the carbon yield.[12] The explanations that are satisfactory for lignocellulosic materials, which are mixtures of biopolymers, are not applicable in this case. To establish the exact nature of the chemical processes involved, it is necessary to compare the mechanisms of thermal degradation of Nomex both with and without phosphoric acid. The characterization of the products evolved during the pyrolysis process would also be useful for the possible industrial production of the resulting activated carbon, as this would provide information about their possible recovery (if valuable) or disposal (if environmentally dangerous).

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In this work, the thermal degradation of Nomex fiber by itself and when impregnated with phosphoric acid has been comparatively studied. To this end, both the products evolved during pyrolysis and the resulting solid residue have been analyzed. Although previous studies on the thermal degradation of unimpregnated Nomex can be found in the literature,[13–18] these were not carried out in relation to the preparation of activated carbon fibers.

2. Experimental Section

2.1. Starting Materials. The starting material was commercially available crystalline Nomex *tow*, 2.2 dtf (decitex per filament). These fibers have a bilobular cross section with diameters of 5 μm (narrower section) and 16.8 μm (wider section). The impregnation was carried out in a rotary evaporator, using 10 g of Nomex and a 200 mL solution of phosphoric acid. The temperature was increased while stirring until the excess water had evaporated, which took 6 h. After this, the sample was dried under vacuum overnight at 110 °C. The concentration of phosphoric acid in the solution was adjusted to obtain impregnation ratios [(g of H_3PO_4/g of Nomex) × 100] of 2, 11, 75, and 120 wt %. Nomex impregnated to 75 wt % was chosen for further studies as this is an impregnation ratio typical of chemical activation.[5,9]

2.2. Preparation of Pyrolyzed Materials. TG measurements were performed in a CI Electronics microbalance. The samples (~50 mg) were heated from 25 to 1000 °C at a linear heating rate of 10 °C min^{-1} under an Ar (99.9990% pure by volume) flow of 50 cm^3 min^{-1}.

On the basis of the thermal analyses, the samples were pyrolyzed to different selected temperatures, which were chosen as being representative of the different stages of the degradation. Nomex samples (~2 g), both pure and impregnated (to 75 wt %), were introduced into a quartz reactor and a horizontal furnace where they were first dried (110 °C, 30 min) and then pyrolyzed. All the experiments were conducted by heating at 10 °C min^{-1} to the desired temperature in a 100 cm^3 min^{-1} Ar (99.9990% pure) flow. The process was effectively stopped by rapid cooling to room temperature. Samples prepared in this way will be referred to as N-*T* (in the case of unimpregnated Nomex) and NP-*T* (in the case of Nomex impregnated to 75 wt % with H_3PO_4), where *T* is the temperature of pyrolysis in °C.

Samples pyrolyzed in the presence of H_3PO_4 were Soxhlet-washed with distilled water to remove the excess of phosphates until conductivity in the washing liquids was below 3 μS cm^{-1} (measured in a pH/conductivity meter, Mettler-Toledo mod. MPC 227). The samples were then dried under vacuum at 110 °C for 12 h.

2.3. Solid Residues. For the samples pyrolyzed in the presence of phosphoric acid, the char yield was calculated from the mass of residue remaining after the excess of activating agent had been washed out and the amount of Nomex before impregnation. The starting material and the chars resulting from pyrolysis were studied by means of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). All the samples, both fresh and pyrolyzed, were cold-ground at 77 K

in a ball-mill in combination with a cooling attachment in which liquid nitrogen was the coolant. DRIFTS spectra were obtained in a Nicolet Magna IR560 spectrometer using a high-sensitivity MCT/A detector. Each spectrum is the result of co-adding 200 interferograms obtained at a resolution of 4 cm^{-1}.

The elemental analyses of C, H, O, and N were carried out in a LECO CHNS-932 microanalysis apparatus with a LECO VTF-900 accessory for oxygen analysis. The amount of P retained was photometrically determined by measuring the absorbance at 700 nm of molybdenum blue with a Helios Alpha double-beam UV/Vis spectrometer. The samples were first digested with hydrogen peroxide and nitric acid in a microwave furnace to yield phosphoric acid, which reacted with ammonium molybdate to give phosphomolybdic acid. The phosphomolybdic acid was reduced with tin(II) chloride to form molybdenum blue.

2.4. High-Boiling Point Volatiles. The recovery of high-boiling point volatiles was accomplished by dissolving the reaction products in ethanol (>99.8% pure), kept at 0 °C by an ice–water bath. The fraction of evolved products which coated the inside surface of the outlet of the quartz reactor and the connecting tubes was carefully rinsed from the walls with ethanol. The two solutions were mixed to form the high-boiling point volatiles fraction.

Some of the compounds detected were identified by comparing their retention times with those of standard compounds using an HP5890-II gas chromatograph equipped with a fused-silica capillary column (25 m × 0.22 mm i.d.) that was coated with SE-54 stationary phase and a high-sensitivity (10^{-12} mol) flame ionization detector. Helium (99.9995% pure) was used as a carrier gas (flow rate: 1.8 cm^3 min^{-1}). The furnace temperature was increased at a heating rate of 4 °C min^{-1} from 50 to 290 °C, where it was kept for 20 min. The injector and detector temperatures were 300 °C. The injection volume was 10 μL. A semiquantification was also performed.

The identification of high-boiling point volatiles was confirmed by GC/MS using a Finnigan Mat GCQ gas chromatograph equipped with a fused-silica capillary column (25 m × 0.22 mm i.d.) coated with HP-5MS stationary phase. The experimental conditions were the same as those used for the GC analysis. The mass range recorded was 50–500 amu. Identification was carried out by either comparing their mass spectra with those found in spectral libraries, if available, or by performing a complete study of their fragmentation pattern.

2.5. Low-Boiling Point Volatiles. Low-boiling point volatiles were retained in Pyrex ampules previously purged with Ar and kept under vacuum until the moment when they were connected (for ~5 s) to the outlet of the reactor at the desired temperature.

The products collected in this way were quantified by GC, using an HP5890-II gas chromatograph equipped with a thermal conductivity detector. Two different columns were used: a molecular sieve 13X column (45/60 mesh; 0.914 m × 2 mm i.d.) and a Porapak N column (80/100 mesh; 3.048 m × 2 mm i.d.). Helium (99.9995% pure) was used as the carrier gas (flow rate: 23 and 30 cm^3 min^{-1}, respectively, for the molecular sieve and the Porapak columns). The injector, furnace, and detector temperatures were 80, 50, and 220 °C, respectively. The injection volume was 100 μL.

Their identification and quantification were carried out by comparing them with the retention times and peak areas, respectively, of a standard gas mixture (% volumes: 82.03 H_2, 0.22 O_2, 5.07 N_2, 5.09 CH_4, 6 CO, 1 CO_2, 0.33 C_2H_4, 0.26 C_2H_6).

3. Results

3.1. Thermal Analysis Studies. Figure 1 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for the pyrolysis of pure Nomex and when impregnated with H_3PO_4.

As stated in previous studies,[18] this polymer thermally decomposes through different processes, namely: (i) breaking of the hydrogen bonds between polymeric

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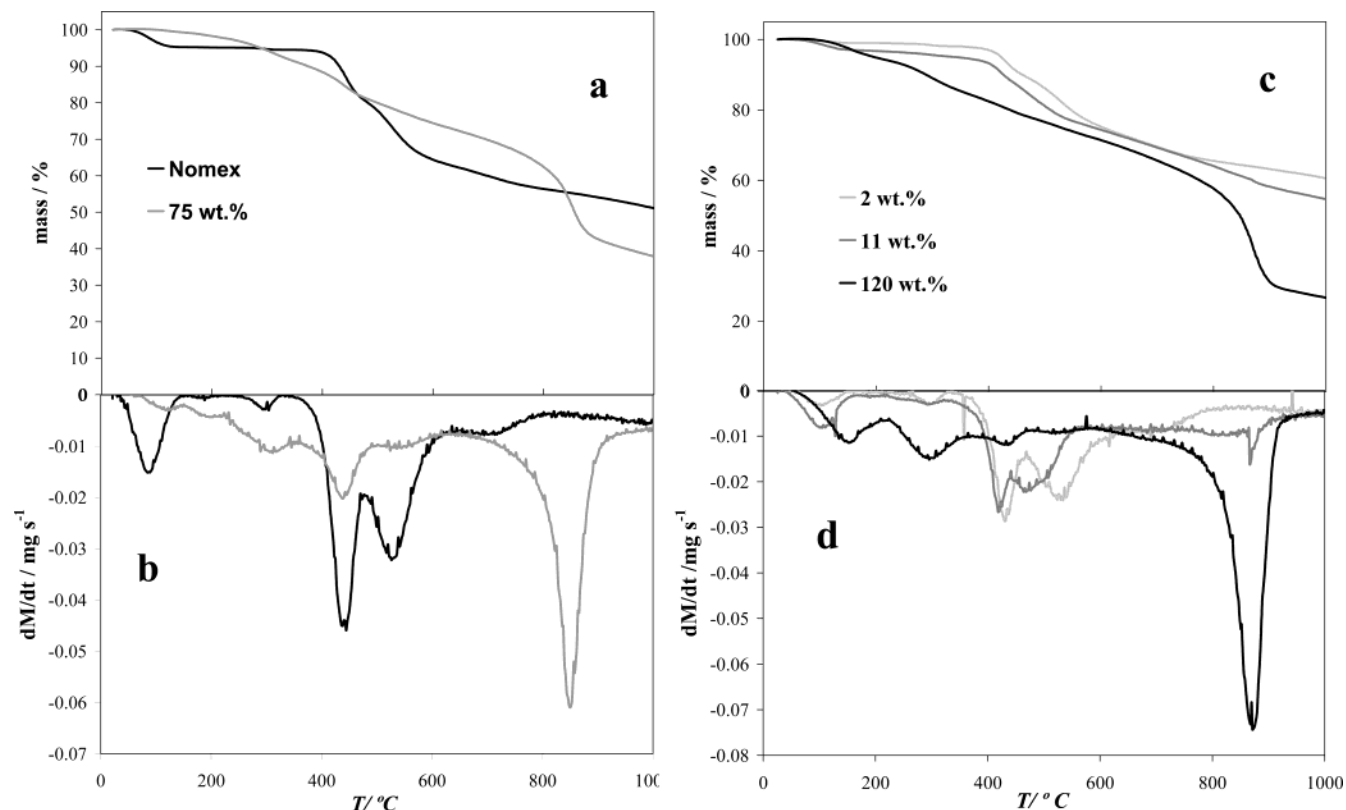
Figure 1. TG (a) and DTG (b) curves for Nomex fiber alone (black) or impregnated with 75 wt % H_3PO_4 (gray). TG (c) and DTG (d) of impregnated Nomex with impregnation ratios of 2% (pale gray), 11% (dark gray), and 120% (black).

chains ($\sim$270 °C); (ii) heterolytic rupture of the amide bonds (400−480 °C); and (iii) homolytic rupture of the amide bonds (480−600 °C). In the third step, polycondensation reactions also occur, generating the pseudographitic structure of the final carbon fiber. These three steps are clearly reflected in the corresponding DTG curve (Figure 1b). On the basis of the temperature intervals at which the different mass loss steps take place, several temperatures were selected for characterization of the products formed in these conditions (solid residues, high-boiling point, and low-boiling point volatiles) to trace the evolution of Nomex during pyrolysis. Thus, high-boiling point volatiles were collected at 450, 485, 545, 610, and 700 °C.

Nomex impregnated to 75 wt % H_3PO_4 presents a very different picture (Figure 1a,b). Contrary to its unimpregnated counterpart, no plateau is observed at any moment during the thermal treatment. Instead, there is a continuous loss of mass from the initial moisture release onward. In the temperature range where the most pronounced mass loss took place in the case of Nomex degradation (400−600 °C), only one faded first step is appreciable (400−500 °C), the most pronounced step occurring between ca. 700 and 890 °C. The different stages are better appreciated in the corresponding DTG curve. Apart from water loss, there are three steps in the degradation of the material covering temperature ranges from approximately 210 to 350 °C, 400 to 500 °C, and 700 to 890 °C. Correspondingly, the temperatures chosen in this case are 350, 500, 700, and 900 °C for the high-boiling point volatiles. For the low-boiling point volatiles, these temperatures plus those corresponding to maximum mass loss in each step were selected. The char yield around 550−800 °C is signifi-

cantly improved relative to that of unimpregnated Nomex, but it is smaller at 1000 °C due to the mass loss between 700 and 890 °C.

Table 1 reports the char yields for Nomex pyrolyzed at different temperatures. For the samples pyrolyzed in the presence of phosphoric acid, the char yield was calculated from the mass of residue remaining after washing relative to the mass of Nomex prior to impregnation. It can be seen that the impregnated samples show a detectable char yield above 550 °C, which confirms a significant increase in yield once the contribution of phosphoric acid to sample mass has been eliminated.

To illustrate the effect of the impregnation ratio on the degradation, some additional TG/DTG curves are presented in parts (c) and (d), respectively, of Figure 1. It can be observed how the two steps found in the 400−600 °C temperature range for pure Nomex collapse to just one and shift to lower temperatures as the impregnation ratio increases. The higher the impregnation ratio, the lower the temperature required to obtain a carbonaceous solid. It should be noted that the increase in yield for impregnated Nomex is observed even with impregnation ratios as low as 2 wt %.

3.2. Solid Residue. *3.2.1. Nomex.* A detailed characterization of the solid residues from Nomex pyrolysis by means of elemental analysis and DRIFTS spectroscopy at the temperatures studied in this work can be found elsewhere.[18] However, for the sake of comparison with the data obtained in the same conditions for H_3PO_4-impregnated Nomex, the corresponding data related to the pyrolysis temperatures under study are included in Table 1 and Figure 2a.

Table 1. Elemental Analyses of Nomex (Either Unimpregnated or Impregnated) Heat-Treated to Different Temperatures (Error <0.5%)

sample	char yield (wt %)	C (wt %)	H (wt %)	O (wt %)	N (wt %)	P (wt %)	C (at. %)	H (at. %)	O (at. %)	N (at. %)	P (at. %)
N-20	100.0	71.2	3.9	15.6	9.7		51.6	33.9	8.4	6.0	
N-452	86.3	69.5	4.1	13.9	9.5		50.8	35.6	7.6	6.0	
N-500	78.3	73.9	3.8	10.7	10.0		54.3	33.5	5.9	6.3	
N-550	70.2	76.5	4.1	6.3	10.2		53.0	35.3	3.4	6.3	
N-585	66.3	78.4	3.6	5.1	10.0		58.6	32.2	2.9	6.4	
N-650	62.7	79.8	3.5	5.8	9.0		60.0	30.9	3.3	5.8	
N-750	57.7	80.4	2.2	7.4	7.0		67.8	22.4	4.7	5.1	
NP-350	94.6	69.1	4.6	14.7	11.3	0.0	47.7	38.0	7.6	6.7	0.0
NP-400	89.7	69.0	3.9	11.7	12.2	0.0	51.0	34.7	6.5	7.7	0.0
NP-450	81.2	71.2	3.6	6.8	12.3	0.9	54.4	33.4	3.9	8.1	0.3
NP-500	75.7	70.9	3.3	10.1	10.9	0.8	55.5	31.0	6.0	7.3	0.2
NP-550	73.0	70.9	2.7	10.0	9.3	1.6	59.2	27.4	6.2	6.7	0.5
NP-600	68.2	70.4	2.3	12.4	8.0	1.7	61.2	24.2	8.1	6.0	0.6
NP-650	67.1	67.9	2.1	17.6	7.3	1.8	59.8	22.5	11.6	5.5	0.6
NP-700	62.7	66.4	2.1	20.1	6.6	2.3	58.6	22.3	13.3	5.0	0.8
NP-750	58.4	66.8	1.7	18.5	6.4	2.7	62.1	18.9	12.9	5.1	1.0
NP-800	56.8	67.8	1.4	16.7	6.1	2.8	65.5	16.3	12.1	5.1	1.0
NP-850	55.3	68.0	1.1	17.4	6.1	2.8	67.8	12.9	13.0	5.2	1.1
NP-950	42.9	71.3	1.5	20.5	4.4	2.0	65.4	16.3	14.1	3.5	0.7
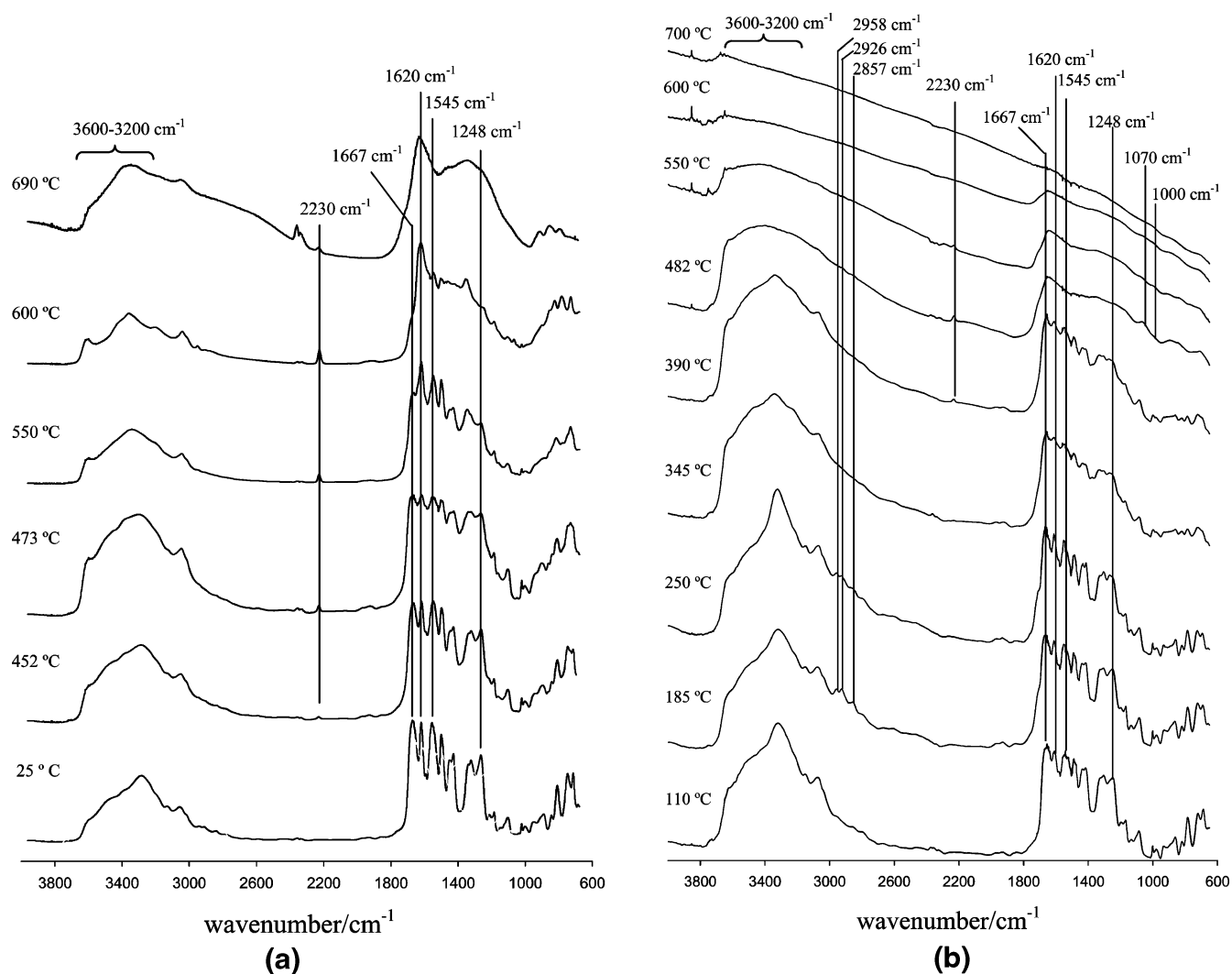
Figure 2. DRIFTS spectra of materials heat-treated to different temperatures: unimpregnated Nomex (a) and impregnated Nomex (b).

Nomex fiber does not contain inorganic impurities in any detectable quantity as confirmed by the fact that the analyzed elements (C, H, O, N) sum up 100 wt % within the limits of experimental error (Table 1). There is no significant change in the elemental composition of the sample until 550 °C. From then onward, as might be expected in any carbonization process, the C content in the sample gradually increases whereas that of H

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decreases. The N and O atomic percentages vary little during the whole process, these elements being largely retained.

The DRIFTS spectra (Figure 2a) clearly indicate the transformations undergone by the polymeric fiber: (i) in the first stage of the degradation (400−480 °C) the heterolytic rupture of amide bonds leads to the breaking of the polymeric chains into smaller fragments, leaving the spectrum of the fresh polymer unchanged except for the increase in intensity of the bands at 3600−3200 cm^{-1}, which is related to the end groups (carboxylic acids and primary amines); (ii) between 480 and 600 °C, the homolytic cleavage of the amide bond leads to the appearance of reaction products, which is reflected in the spectra by the disappearance of the band ascribed to the amide group (1667 cm^{-1}, amide I band; 1545 cm^{-1}, amide II band; and 1248 cm^{-1}, amide III band) and the appearance of the stretching band of the nitrile group (2230 cm^{-1}). In this step polycondensation reactions also take place, leading to an increase in the intensity of the band related to aromatic carbon bonds (1620 cm^{-1}); (iii) finally, at 690 °C, the spectrum is one that is typical of carbonaceous material.

3.2.2. Impregnated Nomex. Elemental analyses (C, H, N, O, P) for different temperatures of pyrolysis are also shown in Table 1. In contrast with unimpregnated Nomex there are noticeable changes in the elemental composition from the very beginning of the pyrolysis process, as the oxygen content significantly decreases in the lowest temperature range (350−450 °C). From then onward, it rises until this element reaches a value of around 12−14 at. % in the highest temperature range (700−950 °C), oxygen being retained to a greater extent than in the case of unimpregnated Nomex. P is not retained in the samples below 450 °C. From this temperature onward, the P content steadily increases, maximum retention taking place in the 700−850 °C temperature range. At higher temperatures, the relative P content decreases.

Figure 2b shows the DRIFTS spectra obtained for impregnated Nomex pyrolyzed at different temperatures. Nomex impregnated and dried at 110 °C shows a spectrum coincident with that of unimpregnated Nomex (Figure 2a), except for the higher intensity of the band centered around 3300 cm^{-1}, which reflects a greater abundance of terminal groups (carboxylic acids and primary amines) in the impregnated material.

There are no clear changes in the spectra upon thermal treatment up to 390 °C except for the appearance of three weak bands centered at 2958, 2926, and 2857 cm^{-1} in the spectra of the fibers up to 345 °C, which are clearly visible between 185 and 250 °C. Such bands have been found to appear in the spectra of condensed phase acids.[19] The nitrile group band (2230 cm^{-1}) appears at 390 °C. However, this band disappears, giving way to the spectrum typical of carbonaceous materials, at lower temperatures than in the unimpregnated Nomex (550−600 °C versus 700−750 °C).

At 700 °C, two shoulders around 1070 and 1000 cm^{-1}, already present at lower temperatures, remain in the spectrum for impregnated Nomex. These are not found in the unimpregnated counterpart at similar temperatures (see spectrum for 690 °C in Figure 2a). The first shoulder can be assigned to P−O symmetrical vibrations in a chain of P−O−P (polyphosphate). The formation of polyphosphates may explain the mass loss found in the TG curve for (unwashed) impregnated Nomex (see Figures 1a,b) between 210 and 350 °C. Indeed, heat treatment of orthophosphoric acid promotes condensation reactions which lead to the formation of pyrophosphoric acid (213 °C)[20,21] (loss of one water molecule) and, above 300 °C, metaphosphoric acid and other polyphosphate species with the loss of two or more water molecules.[22] As expected, the extent of this reaction increases with the impregnation ratio (see Figure 1). However, the DRIFTS spectra of the (washed) impregnated Nomex for the corresponding temperature range do not show these shoulders since polyphosphates do not link to the solid residue at such low temperatures, as evidenced by its 0% P content (see Table 1). The second shoulder can be assigned to P−O−P asymmetric stretching in polyphosphates, C−P−O^4 or P−O−C aromatic stretching or symmetrical stretching of PO$_2$ and PO$_3$ in phosphate carbon complexes.[23,24] The formation of such complexes is confirmed by the fact that the highest retention of P takes place in the 700−850 °C temperature range (Table 1) and by the fact that O and P retentions run in parallel, O being retained to a higher extent than in the unimpregnated counterpart. The DRIFTS spectra obtained for higher temperatures (up to 950 °C) yielded similar results. They are therefore not shown to avoid repetition.

3.3. High-Boiling Point Volatiles. *3.3.1. Nomex.* Figure 3a shows the chromatogram of the high-boiling point fraction collected for unimpregnated Nomex heat-treated to 700 °C. Table 2 shows the chromatographically detected products and the tentatively assigned compounds at different temperatures. Some of the pyrolysates remain unidentified. The quantitative analyses of such a complex mixture of products involve considerable difficulty. Thus, GC was used to perform semiquantitative analyses to provide an approximate idea of the relative proportions of a given product in the high-boiling point fraction. The high-boiling point volatiles fraction recovered at each temperature consists of the products evolved from the beginning of pyrolysis (110 °C) up to that specific temperature. Thus, the chromatogram for the highest temperature (Figure 3a) contains all the compounds found in the whole range of temperatures. The detected compounds are in good agreement with previous studies in the literature on products evolved during Nomex pyrolysis.[13−17] A total coincidence in their relative abundance is not to be expected as these are highly dependent on the conditions chosen for pyrolysis. However, the products found to be preponderant in this work are among the major

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Table 2. Tentative Assignation and Relative Abundance of Chromatographically Detected Products in the High-Boiling Point Fraction of Unimpregnated Nomex Heat-Treated to Different Temperatures

t_R/min	proposed compound	m/Z	% area $T =$ 450 °C	$T =$ 485 °C	$T =$ 545 °C	$T =$ 610 °C	$T =$ 700 °C
4.69	*N,N*-dimethylacetamide	87	22.22	7.46	4.90	4.11	3.53
9.12	aniline	93	4.35	5.31	3.01	3.85	3.31
9.22	benzonitrile	103			2.36	5.61	7.28
13.82	*m*-methylbenzonitrile	117			0.18	0.76	0.89
18.25	benzoic acid	122	12.49	14.89	9.76	6.70	3.59
20.23	*m*-benzenedicarbonitrile	128	0.17	1.07	4.55	8.08	8.69
21.18	*m*-benzenediamine	108	53.20	57.48	63.18	47.78	49.87
22.96	biphenyl	154			0.37	0.24	
23.22	*m*-aminebenzonitrile	118			0.40	1.36	1.61
28.14	*m*-cyanobenzoic acid	147		4.25	0.82		
28.64	fluorene	166			0.19	0.80	0.95
31.67	[1,1′-biphenyl]-X-carbonitrile	179			0.23	1.20	1.37
32.31	[1,1′-biphenyl]-X-amine	169	1.19		0.19	0.60	0.72
34.99	carbazole	167				0.42	0.69
37.50	*N*-phenyl benzamide	197	0.26	0.62	1.45	1.53	1.91
39.75	unidentified product	194		0.17	0.59	0.97	1.13
44.15	*N*-(*m*-cyanophenyl) benzamide	222	0.31	0.68	0.60	0.99	0.95
44.71	*N*-(*m*-aminophenyl) benzamide	212	3.70	5.93	4.71	8.97	9.38
50.49	*N*-(*m*-aminophenyl) *m*-cyanobenzamide	237	0.72	1.66	2.39	2.66	2.38
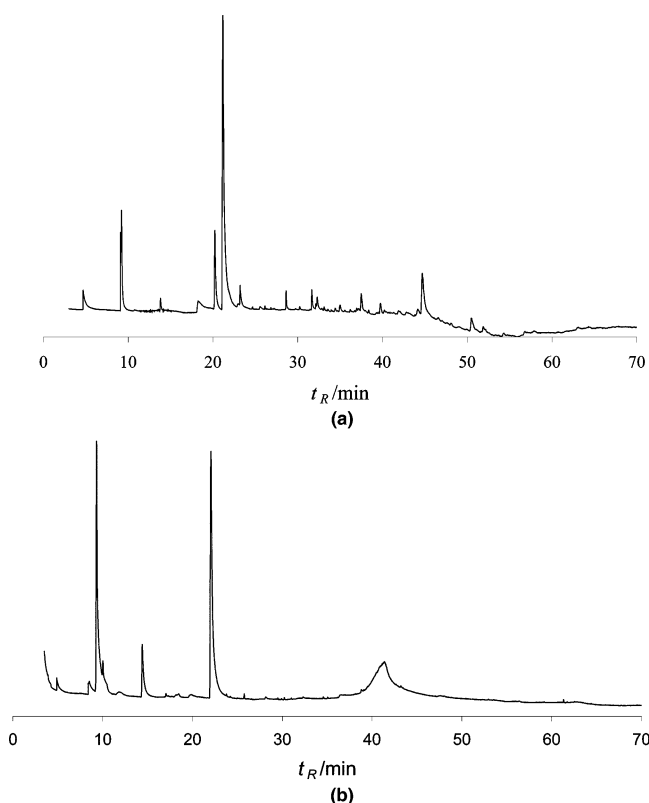
Figure 3. Chromatogram of the high-boiling point volatiles fraction resulting from Nomex pyrolysis up to 700 °C: unimpregnated (a) and impregnated Nomex (b).

ones found in the literature. In what follows, it is assumed that the mechanisms for their production are those generally accepted by the scientific community.[15,16,18]

The residual polymerization solvent used in Nomex production, *N,N*-dimethylacetamide, is released below the lowest temperature studied (boiling point: 165 °C), before the beginning of the degradation process. The evaporation of this solvent is barely appreciable in the TG curve (Figure 1a), but it can be observed in the corresponding DTG curve (Figure 1b) as a small minimum around the aforementioned boiling temperature.

The principal products detected were as follows: *m*-benzenediamine, benzoic acid, *N*-(*m*-aminophenyl) benzamide, *m*-benzenedicarbonitrile, benzonitrile, aniline, and *m*-cyanobenzoic acid. The most abundant degradation product at any of the temperatures studied (450–700 °C) was *m*-phenylenediamine. The corresponding monosubstituted derivative (aniline) is also evolved but to a lesser extent up to 610 °C. The formation of products containing one or two primary amine or carboxylic acid end groups has been attributed to the heterolytic degradation of chain end and penultimate amide groups,[15,16,18] in particular through hydrolytic reactions. Benzoic acid is released at temperatures below 545 °C. A carboxylic/nitrile structure is detected at a temperature of 485 °C, vanishing at higher temperatures.

The appearance of nitrile bonds comes from the homolytic rupture of the phenyl/NH bond.[15,16,18] Nitriles begin to evolve at 545 °C and their growing evolution from then on reflects a generalization of homolytic reactions at such temperatures. From this temperature onward, secondary reaction products from reactions between radicals, such as fluorene, carbazole, or biphenyl derivatives, appear in minor amounts. The results for 610 and 700 °C are rather similar, as might be expected in view of the minor mass loss that occurs between these two temperatures (Figure 1a).

3.3.2. Impregnated Nomex. Figure 3b shows the chromatogram of the high-boiling point pyrolytic products obtained from impregnated Nomex heat-treated to 700 °C. Table 3 gives semiquantitative results of the GC analysis of the pyrolysis products of the impregnated Nomex at different temperatures together with tentative assignations for these compounds.

All the products detected in the degradation of impregnated Nomex had also been previously identified in that of unimpregnated Nomex except for isophthalic acid. The fact that this compound is the preponderant product at 350 °C suggests that phosphoric acid catalyzes the hydrolysis of the amide bond due to the displacement of the weak isophthalic acid by the stronger H_3PO_4, causing depolymerization. This explains the appearance of the bands for a condensed phase acid in

Table 3. Relative Abundance and Tentatively Assigned Structures of the Pyrolysates Evolved during the Thermal Degradation of Impregnated Nomex

			% area		
t_R/min	proposed compound	m/Z	$T =$ 350 °C	$T =$ 500 °C	$T =$ 700 °C
4.71	*N,N*-dimethylacetamide	87	3.06	0.29	1.17
9.27	aniline	93	1.88	1.11	1.77
9.52	benzonitrile	103		4.83	20.14
14.40	*m*-methylbenzonitrile	117		1.10	5.28
18.48	benzoic acid	122	2.40	0.62	0.35
21.01	*m*-benzenedicarbonitrile	128	1.25	8.31	28.87
28.32	*m*-cyanobenzoic acid	147	0.27	0.20	0.18
41.28	isophthalic acid	166	84.23	80.17	35.61

the DRIFTS spectra of the impregnated Nomex up to 345 °C. At higher temperatures, this compound sublimes.

It is clear from the data in Table 3 that the relative importance of nitriles, due to the homolytic cleavage of the amide bond in the unimpregnated Nomex, is enhanced by the presence of phosphoric acid. Indeed, benzenedicarbonitrile, benzonitrile, and methylbenzonitrile prove to be the main products at 700 °C. On the other hand, products attributed to the heterolytic degradation of the terminal amine and penultimate amide groups are not observed in significant amounts. Furthermore, neither the major product evolved in the case of Nomex—*m*-benzenediamine—nor one of the principal ones—*N*-(*m*-aminophenyl) benzamide—appears among the detected products. Indeed, it is noteworthy that the composition of the liquid fraction of the pyrolysis products of the impregnated Nomex presents a lesser variety of compounds in comparison with that of the unimpregnated Nomex (compare Tables 2 and 3). Except for *m*-methylbenzonitrile, the minor products in the pyrolysis of the polymer (% area ≤ 2) do not appear in the case of its impregnated counterpart. Secondary reactions involving radicals seem to be hindered by the presence of the phosphoric acid.

A white precipitate appears in the ethanol solution of the volatiles recovered at temperatures above 700 °C. This white solid was dissolved in CS_2 and identified with the help of ^{31}P NMR (Bruker AC300 spectrometer, 300 MHz, acquisition time of 0.68 s, 18000 scans, 85% H_3PO_4 in aqueous solution as reference) as white phosphorus (P_4) corresponding to the appearance of a signal at −512 ppm.[25] This indicates that phosphorus vapor (P_4) is released as a result of the reduction of the phosphates present in the sample when this is subjected to high temperatures in the presence of carbon (indeed, elemental phosphorus is industrially obtained by heating mineral phosphates in an electrical furnace in the presence of carbon[26]). The loss of phosphorus compounds must be the cause of the greatest mass loss step in the TG curve (Figure 1a) when phosphates give way to phosphorus vapor. The elemental analysis (Table 1) and the DRIFTS spectra (Figure 2b) of the solid residues in the corresponding temperature range also support this. First of all, some linkage between phosphorus compounds and the polyaromatic structure occurs, raising the percentage of P retained by the solid residue (450−

(25) Gutowsky, H. S.; McCall, D. W. *J. Chem. Phys.* **1954**, *22*, 162−164.
(26) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: Elmsford, NY, 1984; p 554.

Table 4. Composition of the Low-Boiling Point Volatiles Fraction Collected during Nomex (Impregnated or Not) Pyrolysis at Different Temperatures

	% volume			
sample	H_2	CH_4	CO	CO_2
N-450				0.04
N-530				0.61
N-800	3.72	0.88		0.20
NP-275				0.03
NP-430				0.09
NP-500				0.73
NP-700	2.78	0.09	1.28	0.16
NP-850	2.40		4.58	3.61
NP-900	1.94		10.35	5.11

850 °C). After this, reduction of these phosphorus compounds takes place and P_4 is released, lowering the P content. The fact that the greatest retention of P occurs at 850 °C (Table 1), which is the very same temperature where the maximum mass loss takes place (Figure 1a,b), adds support to this interpretation: phosphorus compounds are reduced after linking with the carbonaceous substrate. In addition, the high retention of O at the higher pyrolysis temperatures (Table 1) indicates that some oxidation of the carbonaceous material occurs in parallel with the reduction of phosphorus compounds.

3.4. Low-Boiling Point Volatiles. *3.4.1. Nomex.* The composition of the low-boiling point volatiles fraction evolved from Nomex in percent volume of the gases detected in appreciable amounts (H_2, CH_4, CO, and CO_2) at three different pyrolysis temperatures (450, 530, and 800 °C) is offered in Table 4.

Of the gases studied in this work, CO_2 is the only one detected at the first two temperatures (450 and 530 °C). Its highest release takes place at 530 °C, decarboxylation processes being favored at these temperatures. This is consistent with the diminution of products containing a carboxylic end group (benzoic acid and *m*-cyanobenzoic acid) found in the high-boiling point fraction at 545 °C.

At 800 °C, H_2 and CH_4 are also evolved, which is to be expected from the aromatization processes taking place in the solid residue at such a temperature.

CO moieties were not found in any appreciable amounts under the conditions used in this study. CO (if present) is negligible. The same can be said for C_2H_4 and C_2H_6. Although other authors have found that CO is evolved in this process,[13,15] no quantitative data have been provided.

3.4.2. Impregnated Nomex. Table 4 includes the percent volumes of the gases released as a result of impregnated Nomex pyrolysis at different temperatures.

CO_2 is the only gas detected up to 700 °C and its evolution in this temperature range is analogous to that found in the case of the unimpregnated material. At 700 °C, H_2, CH_4, CO, and CO_2 are evolved in detectable amounts. This is in contrast with the case of unimpregnated Nomex, where CO release could not be detected at any of the temperatures studied. From 700 °C onward, CO and CO_2 evolve in increasing amounts, while the H_2 release drops, the CH_4 one disappearing altogether. Both the significant CO release and the drop in H_2 evolution could be related to the reduction of phosphorus compounds referred to above.

**Scheme 2. Hydrolysis of Nomex Polymer**
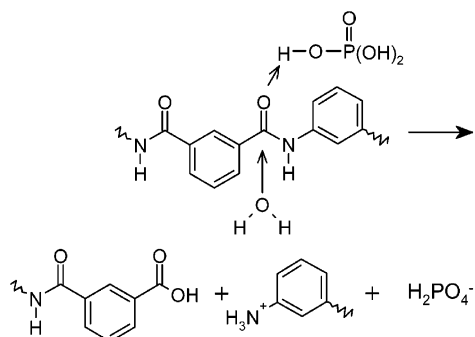
4. Discussion

From the results presented in this work, several observations regarding the mechanisms of the thermal transformation of the Nomex fiber impregnated with phosphoric acid can be made:

(i) First of all, impregnated Nomex is depolymerized at low temperatures (<350 °C) by the hydrolysis of the amide bond in the presence of a strong acid such as H_3PO_4. This is inferred both from the DRIFTS spectra, which reveal an increase in the intensity of the bands ascribed to terminal groups, and from the chromatographic results, which reveal the notable evolution of isophthalic acid (the diacidic monomer of Nomex) well before the beginning of the pyrolysis process proper. This evolution is reflected also in the significant drop in oxygen content in the solid residues at the lowest temperatures, whereas N remains almost invariable in the same temperature range.

Indeed, it is well-known that amides hydrolyze in acidic media to yield the corresponding carboxylic acid and amine. The corresponding mechanism for impregnated Nomex is presented in Scheme 2. It must be remembered that any moisture in the impregnated samples was eliminated before the beginning of the thermal treatment, as they were first dried overnight under vacuum at 110 °C and then predried in the reactor before every experiment (for 30 min at 110 °C). From the DRIFTS results, it can be seen that some hydrolysis has already taken place during the impregnation process, as the spectrum for impregnated Nomex (Figure 2b) reflects a higher amount of terminal groups than in the case of unimpregnated Nomex (Figure 2a). In this case, the water needed for hydrolysis to take place is provided by the aqueous solution of the phosphoric acid. In the subsequent thermal treatments, it must come either from the water which is hydrogen-bonded to the polymeric chains (<1 wt % in unimpregnated Nomex) and/or from phosphoric acid condensations to yield pyrophosphoric acid (213 °C) and other polyphosphate chains (~300 °C).

(ii) Nitrile formation is the main reaction that takes place during the principal degradation stage of the impregnated Nomex (between 400 and 500 °C), as the chromatographic results clearly show. In the case of the unimpregnated Nomex, nitriles are formed through homolytic breaking of the phenyl/NH bond. However, both the displacement of the main mass loss to lower temperatures and the absence of secondary products from reactions between radicals suggest that a homolytic mechanism is not very plausible in the case of impregnated Nomex.

**Scheme 3. Formation of Nitriles**
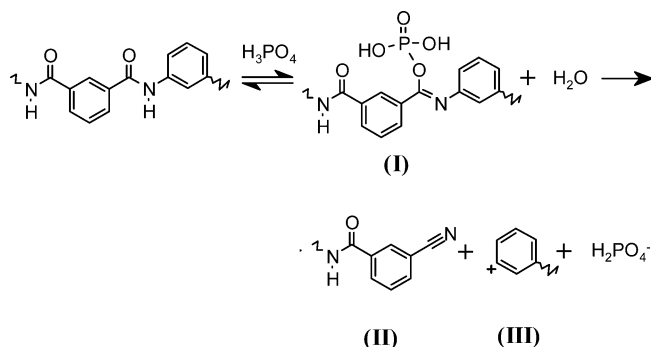
A possible mechanism for nitrile formation in the presence of phosphoric acid is shown in Scheme 3. The reaction starts with the formation of the O-phosphorylated imidate intermediate (product I) as a first step.[27] This is followed by the heterolytic rupture of the phenyl/N bond that accompanies the formation of the corresponding aromatic nitrile (product II), of an intermediate carbocation (product III) and finally the elimination of a phosphate group.

Another such reaction involving the remaining amide group of the first product (designated as product II) would lead to the formation of *m*-benzenedicarbonitrile, while the hydrolysis of this amide group would generate *m*-cyanobenzoic acid. The loss of nitrile by the former compound or the decarboxylation of the latter would yield benzonitrile. The formation of aniline could also be explained with the help of the reaction shown in Scheme 3, if a benzene ring with an amino terminal group were involved in the process instead of a monomer in the middle of the polymeric chain. Alternatively, this terminal monomer could undergo a hydrolysis from the penultimate amide group,[15] to yield *m*-benzenediamine, which was found to be the major product of unimpregnated Nomex degradation in the conditions used in this work. However, *m*-benzenediamine is not detected in the case of impregnated Nomex. This suggests that the reaction shown in Scheme 3 is the main reaction to occur in impregnated Nomex degradation, as a result of which nitriles and, to a minor extent, amines are formed. As indicated below, the low evolution of aromatic amines can be explained by different stabilization reactions (see Scheme 4) involving the intermediate carbocation, formed as shown in Scheme 3 and designated as product III.

(iii) The early formation of the chars when pyrolysis is carried out in the presence of H_3PO_4 is probably a consequence of the occurrence of cross-linking reactions. These reactions may involve the formation of phosphate and polyphosphate bridges[7] between chains. In fact, the phosphate (or polyphosphate) group of the intermediate product in the reaction shown in Scheme 3 (designated as product I) could be linked to other polymeric chains. Cross-linking could also be originated by the stabilization of the carbocation proposed as a product in the aforementioned reaction (product III in Scheme 3). Various possible stabilizations of this product are presented in Scheme 4: electrophilic aromatic substitutions on activated or deactivated aromatic rings (first and second possibilities, respectively) and nucleophilic

(27) Oberlander, E. A.; Tebby, J. C. *ARKIVOC* **2000**, *1*, 320–342.

Scheme 4. Cross-linking Reactions
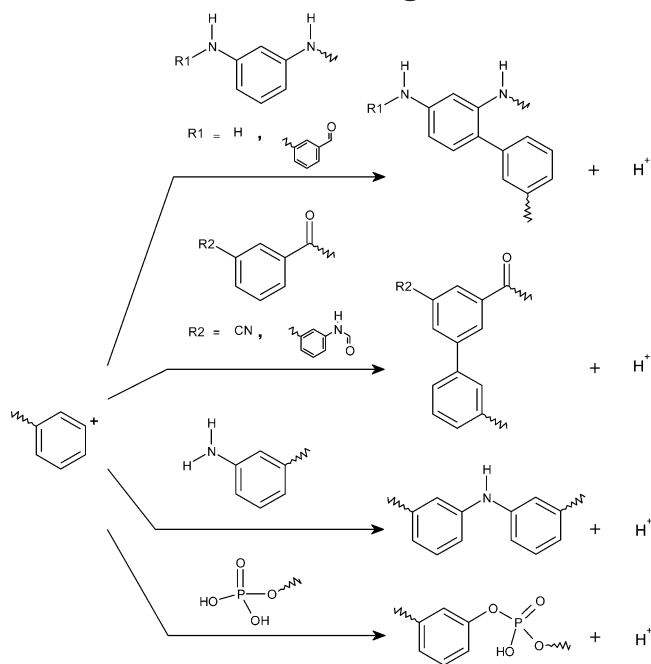
attack either by the nitrogen of the terminal amine groups (third possibility) or by the oxygen of the phosphate or polyphosphate groups (fourth possibility). In all four cases deprotonation follows. These stabilizations lead to cross-linking between the aromatic structures and so to the formation of char. Cross-linking reactions may account for the higher yields obtained for impregnated Nomex in relation to its unimpregnated counterpart above ~515 °C, due to the bonding of otherwise volatile materials into the solid residue.

It should also be pointed out that these reactions also clarify the poor evolution of amines during the impregnated Nomex degradation. Indeed, the terminal amine groups appear to be involved in two stabilizations of the carbocation (first and third possibilities in Scheme 3)

while, in the first one, the most activated aromatic rings (and, thus, the most reactive rings toward electrophilic substitution) are precisely those that they belong to (*m*-benzenediamine).

5. Conclusions

Degradation of phosphoric acid-impregnated Nomex has been investigated using GC to analyze its gaseous and liquid products and elemental analyses to examine the solid products in conjunction with DRIFTS at different temperatures chosen on the basis of TG studies. The results were compared with those obtained for unimpregnated Nomex in the same conditions. Hydrolysis of the amide bond at low temperatures is promoted by the presence of H_3PO_4. Almost all the products evolved in the degradation proper of the impregnated Nomex are also found in its unimpregnated counterpart. However, their relative abundance is different: while amine evolution is preponderant in the case of the unimpregnated polymer, it only occurs to a minor extent with H_3PO_4-impregnated Nomex, in which nitriles prevail as the principal products. Various reaction mechanisms consistent with these findings have been proposed, a nonhomolytic process involving the formation of nitriles in the presence of phosphoric acid being suggested as the most probable. At temperatures around 850 °C, P_4 is released as a result of the reduction of phosphorus compounds previously linked to the carbonaceous residue.

As a subsidiary product, isophthalic acid could be recovered in the first stages of pyrolysis of phosphoric acid-impregnated Nomex for the industrial production of activated carbon fibers by chemical activation of Nomex.

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