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Determination of the Thermal Decomposition Products of Terephthalic Acid by Using Curie-Point Pyrolyzer

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The thermal decomposition behavior of terephthalic acid (TA) was investigated by thermogravimetry/differential thermal analysis (TG/DTA) and Curie-point pyrolysis. TG/DTA analysis showed that TA is sublimed at 276°C prior to decomposition. Pyrolysis studies were carried out at various temperatures ranging from 160 to 764°C. Decomposition products were analyzed and their structures were determined by gas chromatography–mass spectrometry (GC-MS). A total of 11 degradation products were identified at 764°C, whereas no peak was observed below 445°C. Benzene, benzoic acid, and 1,1'-biphenyl were identified as the major decomposition products, and other degradation products such as toluene, benzophenone, diphenylmethane, styrene, benzaldehyde, phenol, 9H-fluorene, and 9-phenyl 9H-fluorene were also detected. A pyrolysis mechanism was proposed based on the findings.

Keywords: decomposition, gas chromatography, mass spectroscopy, pyrotechnics, smoke, thermal

INTRODUCTION

Smokes are widely exploited as visual obscurants. Smokes are suspensions of solid particles in gaseous media. They have low vapor pressures and collapse slowly under gravity. Smokes are divided into two categories: pyrotechnic and nonpyrotechnic. Pyrotechnics are frequently used for obscuring objects, signaling friendly forces, and marking positions. They are also used in fireworks, airbag inflators, and special effects devices for the entertainment industry (Eslami and Hosseini 2011). Pyrotechnic smokes have different colors. Among these, white smokes are the most powerful for screening applications (Greenholt n.d.). Military-purpose smoke compositions include white phosphorous (WP), red phosphorous (RP), hexachloroethane (HC), and terephthalic acid (TA). Phosphorous-based compositions pose a risk of harming nearby personnel or damaging buildings because of high combustion temperatures (>500°C). Furthermore, they are respiratory irritants and lead to the formation of acidic water vapor and highly toxic gases, such as phosphine. HC-based compositions contain hexachloroethane, aluminum powder, and zinc oxide. Upon combustion, HC-based smoke compositions produce zinc chloride, which causes gross pathological pulmonary

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diseases and might even lead to death due to pulmonary edema (Lombardi 2012). Smoke compositions derived from HC are suspect human carcinogens due to their toxic combustion products like zinc chloride, hydrogen chloride, arsenic, cadmium salts, hexachlorobenzene, hexachloroethane, perchloroethylene, carbon tetrachloride, and trichloroethylene. A number of human deaths due to overexposure have been reported in the past (Eaton, Lopinto, and Palmer 1994).

TA is an important chemical intermediate in the plastics industry. It has been extensively used in the production of polyesters, coatings, adhesives, fibers, dyes, plastic films (Ding and Li 2003; L. Wang, Zhou, and Zeng 2003; Z. J. Wang et al. 2011), and training smoke formulations (Muse, Anthony, and Bergmann 1997). Annually, 12 million tons of TA is produced in China (Z. J. Wang et al. 2011). TA smoke was developed by the U.S. Army for training purposes as a low-toxicity alternative to HC smoke. TA-based composition has lower toxicity and shorter burning time compared to HC smoke (Muse, Anthony, and Bergmann 1997). In addition to low toxicity (Thompson et al. 1988), TA smoke is nonmutagenic (Lee, Muse, and Brown 1988), nongenotoxic (Gong, Xu, and Wang 1999), and environmentally benign (Chester, Kumas and Haley 1994). Though some TA decomposition products such as benzene, biphenyl, toluene, and carbon monoxide have been reported in the literature (Muse et al. 1995; Muse, Anthony, and Bergmann 1997; Kumagai et al. 2011a, 2011b), minor decomposition products have not been characterized.

Thermal analysis methods provide information on the thermal decomposition and ignition temperatures of pyrotechnic compositions (Berger et al. 1997; Charsley, Laye, and Brown, 2003; Hosseini, Pourmortazavi, and Hajimirsadeghi 2005; Roduit et al. 2006; Eslami, Hosseini, and Pourmortazavi 2008; Gunawan and Zhang 2009). Differential thermal analysis (DTA) coupled with thermogravimetry (TG) is a well-known method for thermal characterization of pyrotechnics.

In this work, we identify all decomposition products formed by the pyrolysis of TA in a Curie-point pyrolyzer subjected to temperatures ranging between 160 and 764°C in an inert atmosphere. Pyrolysis products were analyzed by gas chromatography and mass spectrometry and identified by comparing the mass spectra of decomposition products to those of the reference materials. The focus is on the determination of minor thermal decomposition products. Finally, a decomposition mechanism is proposed on the basis of the pyrograms at various temperatures.

EXPERIMENTAL

Materials

TA (98%) was obtained from Merck (Darmstadt, Germany). Analytical standards were purchased from Sigma-Aldrich (St. Louis, MO, USA) for benzene (99%), benzaldehyde (98%), phenol (99%), acetophenone (98%), benzoic acid (98%), benzophenone (99%), and 9-phenyl 9H-fluorene (99%). Toluene (99%) and 1,1-biphenyl (99%) were purchased from Merck. Diphenylmethane (99%) was from Alfa Aesar (Karlsruhe, Germany). The retention times of reference materials were used for validation.

Instrumentation

Thermogravimetric Analysis

Thermogravimetric analysis was performed on a SEIKO SII TG/DTA 7300 (Seiko Instruments, Chiba, Japan) at a heating rate of $10^{\circ}\text{C min}^{-1}$ from 20 to 700°C . The experiment was carried out with an approximately 10 mg sample heated under a flow of nitrogen (200 mL/min).

Py-GC/MS Analysis

A schematic diagram of the system, consisting of a Curie-point pyrolyzer (JCI-22S, Japan Analytical Industry, Tokyo, Japan) and a gas chromatograph (Agilent 6850, Agilent Technologies, Santa Clara, CA, USA) interfaced to an Agilent 5973 inert mass selective detector, is shown in Figure 1.

A sample (maximum 0.1 mg) was wrapped in a pyrofoil ($9 \times 20 \times 0.05\text{ mm}$) with a known Curie-point temperature (160, 358, 445, 590, 670, and 764°C) and placed in a glass sample tube (inside diameter 4.5 mm, outside diameter 6 mm, length 36 mm). This sample tube was then inserted into a probe. The inside of the probe was preheated to 150°C after purge was completed. When the gas chromatograph–mass spectrometer (GC-MS) was ready for analysis, the probe needle was inserted into the GC injection port and the pyrolyzed gas was introduced into the GC-MS.

The GC parameters were as follows: column HP-5MS ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) with temperature program of 50°C for 3 min followed by a gradient to 150°C at $5^{\circ}\text{C min}^{-1}$; 290°C at $10^{\circ}\text{C min}^{-1}$. Helium at 1 mL/min was used as the carrier gas. The separated pyrolyzates from the GC were transferred into the mass spectrometer via a heated interface maintained at 290°C .

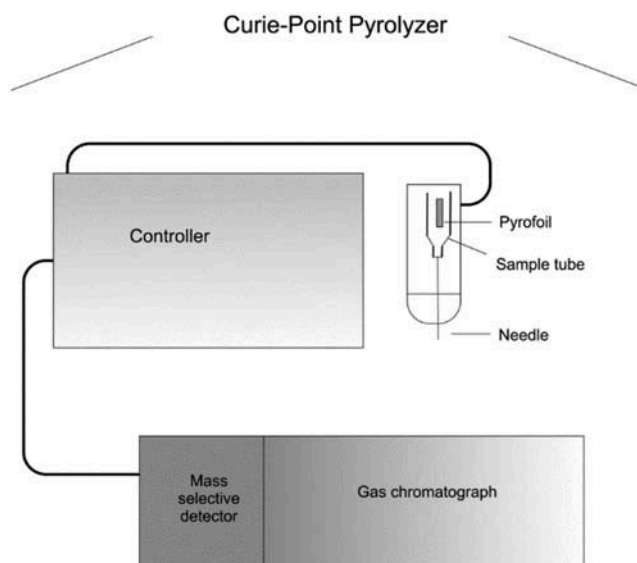


FIGURE 1 Schematic diagram of Py-GC/MS system.

Electron impact ionization was used (70 eV) and mass spectra were collected over the range of 25–550 m/z . Postexperimental data analysis (peak integration) was done using Wiley7Nist05.L software (Agilent Technologies). All pyrolysis tests were repeated three times at each pyrolysis temperature to ensure reproducibility. In order to simplify the quantification procedure, the percentage peak area of each pyrolysate is used. The area percentage is calculated by dividing each peak area by the total peak area and is proportional to the pyrolysate concentration.

RESULTS AND DISCUSSION

TG/DTA Analysis

The thermal characteristics of TA were examined in a nitrogen atmosphere using TG/DTA. DTA and TG curves for TA are shown in Figure 2.

TG analysis shows that TA is stable up to 276°C and completely decomposes at 382°C. TA sublimates prior to decomposition. The rapid weight loss and the primary peak at 373°C are due to the sublimation of TA, and the secondary peak at 543°C is attributed to the trace thermal decomposition. TG/DTA analysis provides data only on the thermal stability of TA. In order to obtain a detailed understanding of the temperature, mechanism, and products of thermal decomposition, pyrolysis (Py)-GC/MS analysis was carried out.

Py-GC/MS Analysis

In order to obtain information on the thermal decomposition products of TA, a Curie-point pyrolyzer was used. The Curie-point pyrolyzer has advantages such as high heating rate, good heat transfer between the heating element and the sample, precise temperature

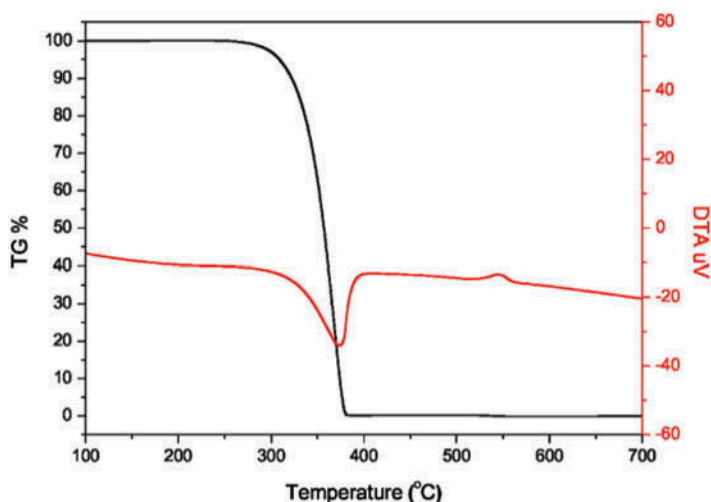


FIGURE 2 TG/DTA curve of terephthalic acid.

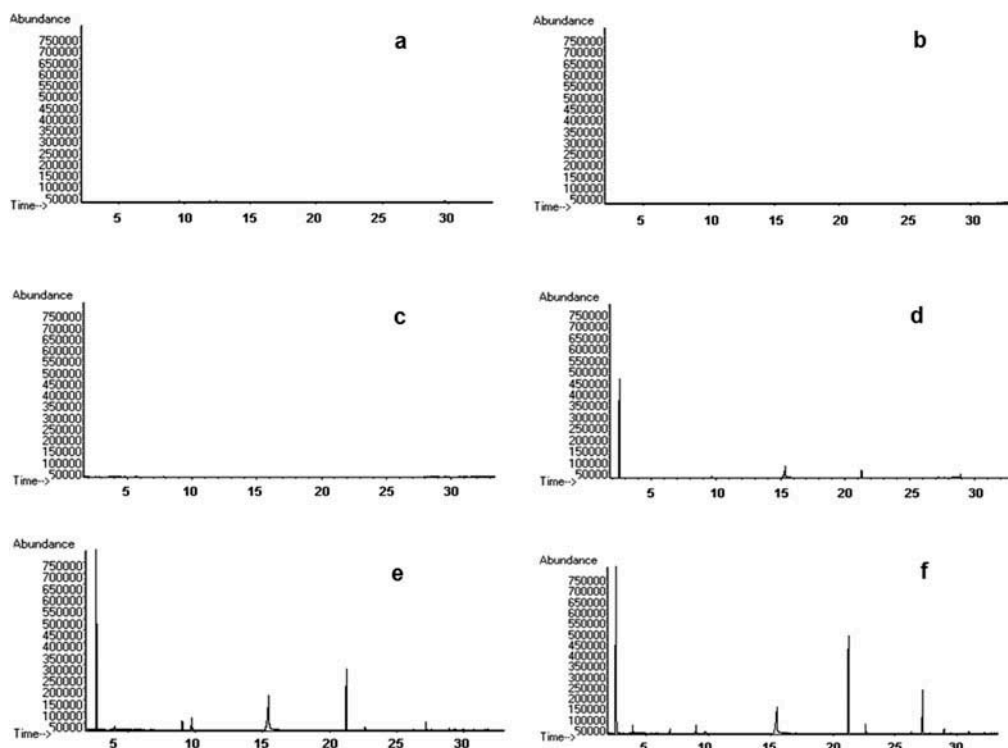


FIGURE 3 Pyrograms of TPA at (a) 160°C, (b) 358°C, (c) 445°C, (d) 590°C, (e) 670°C, and (f) 764°C.

control, reproducible temperature profiles, and the use of a small quantity sample (Lin, Chang, and Rei, 1986). The total ion chromatograms obtained at various pyrolysis temperatures are shown in Figure 3. The pyrograms at relatively low temperatures exhibited no peak. However, increasing the pyrolysis temperature to 590°C leads to decomposition, as evidenced by the appearance of five peaks in the pyrograms. At the highest pyrolysis temperature, six more peaks appeared in the chromatogram.

Identification and quantification of decomposition products are given in Table 1. Identification of the degradation products was accomplished by comparing the retention times and the mass spectra of the pyrolysate peaks to those of the reference materials under the same conditions. Boiling points of pyrolysis components are correlated with their retention times. The quantification procedure is performed by the normalization of the pyrolysate peak areas at all temperatures. As shown in Table 1, benzene, benzoic acid, and 1,1'-biphenyl are the major decomposition products. Percentage decomposition is not calculated because the TA peak does not appear under GC-MS analysis conditions at any pyrolysis temperature. Figure 4 shows the relation between the pyrolysis temperature and the concentration of the major pyrolysates. Benzene and 1,1'-biphenyl contents increase with increasing pyrolysis temperature, whereas benzoic acid content decreases with increasing temperature. This is due to the further pyrolysis of benzoic acid with increasing temperature.

TABLE 1
Identification of pyrolysis products

No.	Compound	MW ^a (g/mol)	BP ^b (°C)	t _R ^c (min)	Area (%)					
					160°C	358°C	445°C	590°C	670°C	764°C
1	Benzene ^d	78.2	80	2.5	— ^e	—	—	62.2	69.9	73.6
2	Toluene ^d	92.1	110	3.9	—	—	—	—	0.5	0.6
3	Styrene ^d	104.1	145	6.8	—	—	—	—	—	0.4
4	Benzaldehyde	106.1	178	9.0	—	—	—	—	1.3	0.9
5	Phenol ^d	94.1	182	9.7	—	—	—	1.9	2.2	0.4
6	Benzoic acid	122.1	249	15.5	—	—	—	25.4	15.3	8.1
7	1,1'-Biphenyl ^d	154.2	255	21.2	—	—	—	7.3	8.6	10.5
8	Diphenylmethane	168.2	264	22.6	—	—	—	—	0.5	0.9
9	9H-Fluorene	166.2	295	26.2	—	—	—	—	0.2	0.2
10	Benzophenone	182.2	305	27.2	—	—	—	—	1.9	3.9
11	9-Phenyl 9H-fluorene	242.3	378	28.9	—	—	—	3.2	0.5	0.6

^aMolecular weight.
^bBoiling point.
^cRetention time.
^dCompound has an exposure guideline from the National Institute for Occupational Safety and Health.
^eNot detected.

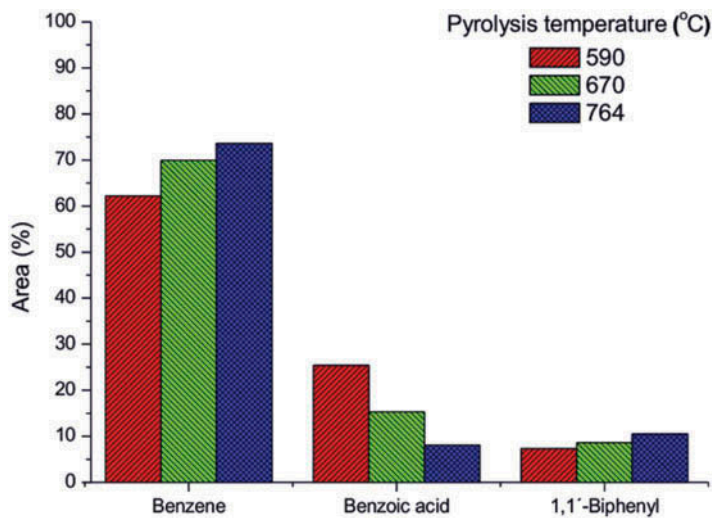


FIGURE 4 Content of major pyrolysates at different pyrolysis temperatures.

Figure 5 shows the change in the amount of the minor pyrolysates at different pyrolysis temperatures. The peak areas of benzophenone and diphenylmethane increase with increasing pyrolysis temperature, whereas those of benzaldehyde, 9-phenyl 9H-fluorene,

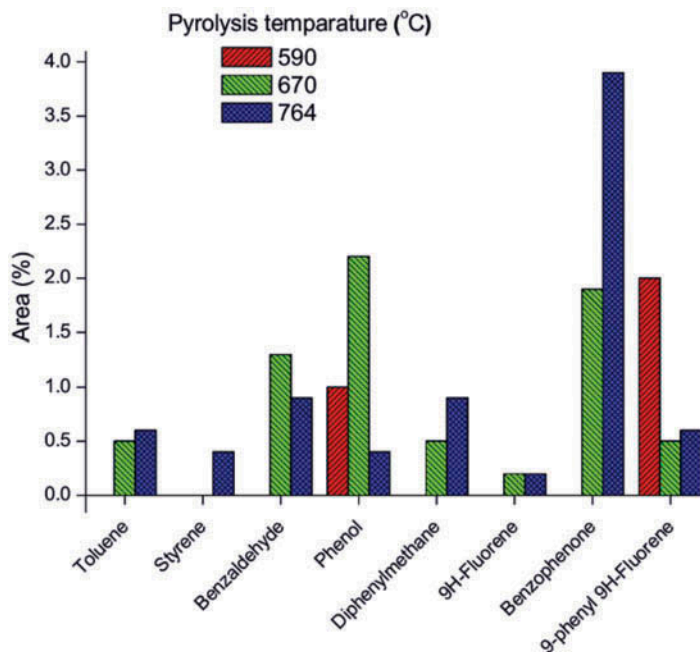
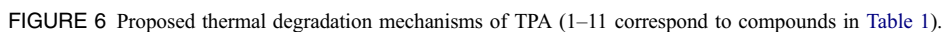


FIGURE 5 Content of minor pyrolysates at high pyrolysis temperature.

and phenol decrease. Benzaldehyde, 9-phenyl 9H-fluorene, and phenol may further decompose and transform. The peak areas of toluene and 9H-fluorene do not change significantly with the pyrolysis temperature. Styrene was observed only at the highest temperature.

The proposed degradation mechanism of TA is summarized in Figure 6. Degradation reactions are proposed on the basis of Py-GC/MS results at different temperatures. The most probable mechanism involves the reactions of the intermediate radicals that are formed at high temperatures via a free radical mechanism. Above 590°C, TA may first decompose to benzoic acid by the elimination of one molecule of COOH. Benzoic acid may further pyrolyze and decompose to smaller compounds. Benzene is the smallest decomposition product of TA. Phenol formation is due to the elimination of CO from benzoic acid. Benzaldehyde could be formed by the elimination of OH from benzoic acid. Decomposition of benzaldehyde could generate styrene. Toluene might be formed by the interaction of phenyl and methyl radicals. Although TA has only one aromatic ring, decomposition products with two and three aromatic rings are identified at high temperatures. This can be a result of the polymerization of some radicals that are produced during pyrolysis. The formation of 1,1'-biphenyl, benzophenone, diphenylmethane, 9H-fluorene, and 9-phenyl 9H-fluorene may arise from the recombination of radicals with two or three aromatic rings.



This study provides information on the thermal decomposition products and mechanism of TA. The thermal stability of TA was studied by TG/DTA and Py-GC/MS analysis. TG/DTA showed a rapid weight loss between 276 and 382°C due to sublimation. The decomposition temperature and products of TA were identified by Curie-point pyrolysis. No decomposition product was observed in the pyrograms between 160 and 445°C, whereas between 590 and 764°C, 11 pyrolysates were identified and quantified. Their concentrations in the total mixture varied from 0.2 to 73.6%. The major decomposition products were benzene, benzoic acid, and 1,1'-biphenyl. Based on Py-GC/MS analysis, the proposed pyrolysis reactions can account for the change in the contents of the pyrolysates with temperature variation. Decomposition products are hydrocarbons and oxygenated compounds. Some of

the decomposition products are toxic substances. The National Institute for Occupational Safety and Health (2005) has developed for 6 of the 11 identified pyrolysates. It is suggested that TA-based pyrotechnic mixtures should be dispersed at temperatures lower than 445°C to avoid the formation of toxic substances.

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