PYROLYSIS PRODUCTS OF POLYTETRAFLUOROETHYLENE AND POLYFLUOROETHYLENEPROPYLENE WITH REFERENCE TO INHALATION TOXICITY

HEIHACHIRO ARITO and REISUKE SODA

National Institute of Industrial Health, Ministry of Labour, Kawasaki, Japan

Abstract—Analysis of pyrolysis products of polytetrafluoroethylene (PTFE) and polyfluoroethylenepropylene (PFEP) and the influence of pyrolysis conditions on the pyrolysis products were investigated to evaluate the inhalation toxicity of those pyrolysis products. Both polymers were pyrolysed at various temperatures in a flow of nitrogen and air, either dry or humid. The pyrolysis products were analysed by infrared spectrometry and combined gas chromatography-mass spectrometry. In pyrolysis of both polymers in a nitrogen stream, octofluoroisobutylene was identified in addition to the main products such as tetrafluoroethylene, hexafluoropropylene and octofluorocyclobutane. The main pyrolysis products of both polymers in an air stream were carbonyl fluoride and trifluoroacetyl fluoride. Tetrafluoroethylene and hexafluoropropylene were far less in quantity but octofluoroisobutylene was found only with PFEP. Perfluoroalkanes were produced by oxidative pyrolysis of PTFE at high temperature. Effect of water vapour in the gas flow on the product formation was significant only in oxidative pyrolysis. In the presence of water vapour, carbonyl fluoride was converted into hydrogen fluoride and carbon dioxide, while trifluoroacetyl fluoride was converted to trifluoroacetic acid and hydrogen fluoride.

POLYTETRAFLUOROETHYLENE (PTFE) has been widely used as a heat-resistant and chemically stable polymer. It has excellent electrical resistance and low friction. Polyfluoroethylenepropylene (PFEP) is also a useful polymer and its properties are superior to PTFE, particularly in a moulding process, because its melting temperature is lower. These fluorocarbon plastics are said to be non-toxic in ordinary use. When they are subjected to a relatively high temperature, pyrolysis products evolve. Some of them are very hazardous and responsible for so-called polymer fume fever which is caused by the fine particulate matter (HARRIS, 1959). Several investigators have been concerned with the gaseous components of the pyrolysis products as the toxic agents. SCHEEL *et al.* (1968) have shown that carbonyl fluoride is the most and main toxic substance in the products of pyrolysis of PTFE in an air stream. OKAMURA (1970) made histo-pathological examinations of the organs of mice exposed to the monomers and thermal decomposition products of some fluorocarbon polymers and suggested that octofluoroisobutylene and some other unidentified compounds showed severe toxicity. However, she has not positively identified octofluoroisobutylene in the pyrolysis products.

In investigating the toxicity of pyrolysis products of fluorocarbon polymers, it is important to identify not only the main pyrolysis products but also very toxic by-products which may be present in small quantity. In our Institute, the toxicity of the pyrolysis products of PTFE and PFEP has been studied and it has been found that the gaseous products as well as the particulate matter play an important role in their biological effects. In an attempt to identify the gaseous components responsible for the

toxicity of the pyrolysis products, PTFE and PFEP were subjected to pyrolysis in various atmospheres and temperatures, and their thermal decomposition products were analysed. In addition to the products such as tetrafluoroethylene, hexafluoro-propylene and octofluorocyclobutane which have been reported so far, octofluoroiso-butylene and trifluoroacetyl fluoride were positively found in the pyrolysis products. In the oxidative atmosphere, a wide variety of products are formed in pyrolysis.

EXPERIMENTAL

Materials

Commercial sheets of PTFE* and PFEP† (manufactured by Daikin Co. Ltd and E. I. duPont de Nemours & Co., respectively) were used in the present study. The sheets were 0.5 mm thick and were divided to make uniform test pieces of 44 mm by 17 mm. Air and nitrogen were supplied from gas cylinders and purified through molecular sieve and silica gel. Calcium hydroxide used was reagent grade.

Pyrolysis apparatus

The pyrolysis apparatus used in this study is schematically drawn in Fig. 1. A stain-less steel boat 50 mm long × 20 mm wide × 10 mm high × 1.0 mm thick was used for mounting a test piece of polymer sheet, and this was subjected to pyrolysis in a cylindri-cal tube also made of stainless steel. Fused silica or other materials which might be attacked by the pyrolysis products must, of course, be avoided. The inner diameter of the tube was 30 mm at the inlet of gas flow and 10 mm at the outlet and the total length was 120 cm. The tube was heated with a 1.2 kW electric furnace. The pyrolysis tempera-ture was monitored using an almel–chromel thermocouple on the boat and was con-trolled by the electric current supplied to the furnace. The lead line of the thermocouple was covered with a zirconia insulator and then sheathed in a stainless steel tube.

Experimental procedure

Pyrolysis was carried out in a constant gas flow of 2.0 l/min to purge the pyrolysis products into a sampling port. Four kinds of gas stream were used: dry air, dry nitro-gen, wet air and wet nitrogen. The wet gas stream was prepared by passing the dry gas over the surface of warm water in a flask heated at 60°C. With the temperature constant at the desired level, the boat mounting a test piece was placed into a uniformly-heated part of the cylindrical tube for a given time. The purging gas was exhausted through a fluorocarbon plastic flask of 300 ml from which a certain portion of the effluent was drawn to collect the pyrolysis gases into the sampling device with a diaphragm pump. The flow rate of sampling was 200 ml/min. Sampling time was determined by consider-ing pyrolysis temperature and the analytical method. It was 10 to 15 min at 650°C and 105 min at 450°C for infrared spectrometry, and 3 min at 600°C and 10 min at 500°C for combined gas chromatography–mass spectrometry.

Collection of pyrolysis products

Two kinds of sampling devices were used for collection of the gaseous pyrolysis products. The device used for infrared spectrometric analysis consisted of a train of

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* Density 2.17gcm^{-3}; M.W. $3 \times 10^6 \sim 10 \times 10^6$.
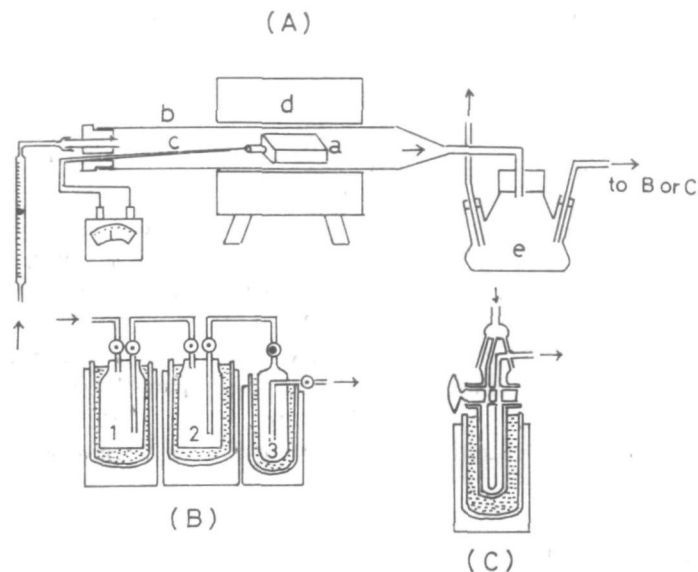† Density 2.15gcm^{-3}; M.W. several million.

(A)

FIG. 1. Schematic diagram of apparatus used in this study. The arrows indicate the direction of gas flow.

(A) Pyrolysis apparatus and sampling port.
   a—stainless steel boat mounting a test piece of polymer; b—cylindrical tube of stainless steel; c—almel–chromel thermocouple and its lead lines; d—electric furnace; e—300 ml fluorocarbon plastic flask as a sampling port.
(B) Sampling device for infrared spectrometry.
   1 and 2—fluorocarbon plastic vessels cooled by powdered dry ice and liquid nitrogen, respectively; 3—glass vessel cooled by liquid nitrogen.
(C) A gas sampling tube for combined gas chromatography–mass spectrometry; the glass sampling tube is cooled by liquid oxygen.

three vessels as shown in Fig. 1B. The first and the second vessel, which were made of fluorocarbon plastics, were cooled by powdered dry ice and liquid oxygen, respectively. The third vessel was cooled by liquid nitrogen. The refrigerants, of course, need to be used with care. The gases collected in each sampling vessel were transferred to an evacuated gas cell and then submitted to the infrared spectrometric analysis. Fig. 1C shows another sampling device used for the combined gas chromatography–mass spectrometry. The glass sampling tube was cooled by liquid oxygen to collect the pyrolysis gases and then warmed to room temperature to introduce the gases into the gas chromatograph. The sampling tube was designed to introduce the collected gases directly into the chromatographic column with a glass connector.

Analytical instruments and their operating conditions

Infrared spectra were recorded by a Hitachi EPI G2 spectrometer with a 10 cm gas cell. A combined gas chromatograph–mass spectrometer of Shimadzu-LKB 9000 type was used. The gas chromatographic column was stainless steel tubing 3 m long × 3 mm in diameter, packed with Porapak Q, 80–100 mesh. Column temperature was linearly programmed at 4°C/min from 50°C to 230°C. Gas chromatograms were obtained by a total ion monitor at 20 eV, while mass spectra were scanned at 70 eV and sometimes at

20 eV to confirm the results at 70 eV. The temperature of a separator and an ion source of the mass spectrometer was kept constant at 300°C.

RESULTS

Pyrolysis was carried out at temperatures ranging from 450°C to 650°C for PTFE and only at 400°C for PFEP. The pyrolysis products in the humid gas stream were analysed only by infrared spectrometry, because large amounts of water condensed in a glass tube made it difficult to collect the gaseous products into the sampling tube for the combined gas chromatography–mass spectrometry. Identification by the combined gas chromatography–mass spectrometry was performed by comparison of the observed mass spectra with those of authentic compounds cited in the literature (CORNU and MASSOT, 1966). Table 1A summarizes identification of pyrolysis products of PTFE both in air and nitrogen stream and Table 1B summarizes that of PFEP. Relative retention times of gas chromatographic peaks for the identified compounds are given in Table 1A.

Pyrolysis in the nitrogen stream

The main pyrolysis products of PTFE in the nitrogen stream were tetrafluoroethylene, hexafluoropropylene and octofluorocyclobutane at pyrolysis temperatures of 500–650°C. The former two compounds were also found with PTFE at the lower temperature of 450°C and with PFEP at 400°C; they were identified clearly by both analytical methods. Tetrafluoroethylene, hexafluoropropylene and octofluorocyclobutane were identified by using their characteristic bands (NIELSEN and CLAASSEN, 1950; 1952; CLAASSEN, 1950). The patterns of the infrared spectra of pyrolysis products of PTFE in the nitrogen stream were essentially identical in pyrolysis temperatures from 450°C to 650°C. A very small gas chromatographic peak of 1.16 in relative retention time was identified as octofluoroisobutylene and the observed mass spectrum corresponding to the chromatographic peak is presented in Table 2. Octofluoroisobutylene was clearly found in the pyrolysis products of both PTFE and PFEP in the nitrogen but it was so minute in quantity that the characteristic infrared bands could not be observed. The pyrolysis products of both PTFE and PFEP in the humid nitrogen stream were the same as those in dry nitrogen.

Pyrolysis in the air stream

Oxidative pyrolysis of both PTFE and PFEP in the air stream gave a wide variety of pyrolysis products as compared with those in the nitrogen stream. Constituents of pyrolysis products of PTFE varied depending on the pyrolysis temperature, as shown in Table 1A. It was found from the intense infrared bands (NIELSEN *et al.*, 1952) that carbonyl fluoride was a main pyrolysis product of PTFE in the dry air stream. When the pyrolysis temperature exceeded 550°C, some new bands appeared in the infrared spectra of pyrolysis products of PTFE. From those observed bands, carbon tetrafluoride, hexafluoroethane and silicon tetrafluoride were identified (WOLTZ and NIELSEN, 1952; NIELSEN *et al.*, 1948; JONES *et al.*, 1951). In addition to the above three compounds, octofluoro-*n*-propane and decafluoro-*n*-butane were found to be present in pyrolysis products of PTFE by combined gas chromatography–mass spectrometry. Table 2 shows another mass spectrum corresponding to a gas chromatographic peak of 0.42

TABLE 1. IDENTIFICATION OF PYROLYSIS PRODUCTS IN NITROGEN AND AIR STREAMS EITHER DRY OR HUMID, BY INFRARED SPECTROMETRY (IR) AND COMBINED GAS CHROMATOGRAPHY–MASS SPECTROMETRY (GC–MS)

A. PTFE

Carrier gas	Dry (or humid) nitrogen stream					Dry (or humid) air stream					Relative retention time
Pyrolysis temperature (°C)	650	600	550	500	450	650	600	550	500	470	
Analytical instrument	IR	GC–MS	IR	GC–MS	IR	IR	GC–MS	IR	GC–MS	IR	
CF_4						+	+	+(+)			0.13
SiF_4						+	+	+(+)	+	(+)	0.24
COF_2						+	+	+(+)	+	+	0.24
CO_2						+	+	+(+)	+	+(+)	0.24
$CF_3—CF_3$						+	+				0.31
$CF_2=CF_2$	+	+	+(+)	+	+			(+)	+	(+)	0.41
CF_3COF						+	+				0.42
$CF_3—CF_2—CF_3$						+					0.62
$CF_3—CF=CF_2$	+	+	+(+)	+	+			(+)	+	(+)	0.75
cyclic C_4F_8	+	+	+(+)	+			+	+	+		1.00
$CF_3—(CF_2)_2—CF_3$							+				1.09
$(CF_3)_2C=CF_2$		+		+							1.16

+ indicates that the compound is positively found in the pyrolysis products.

TABLE 1B. PFEP
(Pyrolysis temperature, 400°C)

Carrier gas	Nitrogen stream		Air stream	
	dry (humid)	dry	dry (humid)	dry
Analytical instrument	IR	GC–MS	IR	GC–MS
SiF_4			+(+)	+
COF_2			+(+)	
CO_2			+(+)	+
$CF_2=CF_2$	+(+)	+	(+)	+
CF_3COF			+(+)	+
$CF_3-CF=CF_2$	+(+)	+	+(+)	+
$(CF_3)_2C=CF_2$		+		+ .

TABLE 2. THE OBSERVED MASS SPECTRA ASSIGNED TO OCTOFLUOROISOBUTYLENE AND TRIFLUOROACETYL FLUORIDE IN THE PYROLYSIS PRODUCTS OF PTFE AND PFEP

$(CF_3)_2C=CF_2$			CF_3COF		
m/e	R.A.*	Ions assigned	m/e	R.A.*	Ions assigned
69	100	CF_3^+	69	100	CF_3^+
181	60.6	$C_4F_7^+$	50	31	CF_2^+
93	39.4	$C_3F_3^+$	47	29	COF^+
31	18.2	CF^+	31	11	CF^+
200	17.6	$C_4F_8^+$	97	4.9	CF_3CO^+
131	14.5	$C_3F_5^+$	81	0.88	CF_3C^+
112	12.7	$C_3F_4^+$	116	0.83	CF_3COF^+
100	9.7	$C_2F_4^+$			
150	5.6	$C_3F_6^+$			
50	4.2	CF_2^+			

* Abbreviation: Relative abundance.

in the relative retention time which appeared in the pyrolysis products of both PTFE and PFEP in the air stream. It was identified as trifluoroacetyl fluoride, although the standard mass spectrum was not available in the literature. Presence of trifluoroacetyl fluoride was also supported from its characteristic bands (Loos and LORD, 1965) in an infrared spectrum of pyrolysis products of PTFE at 650°C. Small quantities of tetra-fluoroethylene and hexafluoropropylene were found in the oxidative pyrolysis of PTFE at 500°C only by the combined gas chromatography–mass spectrometry but they were not detected at temperatures higher than 550°C.

The oxidative pyrolysis of PFEP gave different patterns in both infrared spectra and gas chromatograms from those of PTFE. The band intensity of trifluoroacetyl fluoride from PFEP increased appreciably compared with that from PTFE. The bands of carbonyl fluoride and hexafluoropropylene were clearly found, while tetrafluoroethylene was not detected. It was found by the combined gas chromatography–mass spectrometry that octofluoroisobutylene was produced even in the oxidative pyrolysis of PFEP, although it was not found in that of PTFE.

In the humid air stream, PTFE pyrolysis showed that band intensity of carbon dioxide was enhanced greatly, while that of carbonyl fluoride decreased significantly at 550°C and disappeared at 500°C. This trend was also observed in the PFEP pyrolysis in the humid air stream. The PFEP pyrolysis in the wet air stream produced watery droplets of strong acidity on the wall of the first sampling vessel cooled by powdered dry ice. To those droplets, a solution of calcium hydroxide was added and the resultant precipitate was filtered out. The infrared spectrum of the precipitate showed bands of calcium fluoride and the spectrum of the filtrate was identical to that of calcium trifluoroacetate. These results indicate that the carbonyl fluoride produced in pyrolysis reacted with water vapour to form hydrogen fluoride and carbon dioxide in the humid air stream, while trifluoroacetyl fluoride formed trifluoroacetic acid and hydrogen fluoride.

DISCUSSION

Pyrolysis of PTFE has been extensively studied under vacuum and inert gas atmosphere, the primary concern being the main reaction products such as tetrafluoroethylene, hexafluoropropylene and octofluorocyclobutane (MADORSKY et al., 1953; SIEGLE et al., 1964; JELLINEK and KACHI, 1965; LEWIS and NAYLOR, 1947). However, little attention has been given to the oxidative pyrolysis and formation of by-products such as octofluoroisobutylene and trifluoroacetyl fluoride. The present study confirmed the presence of octofluoroisobutylene in non-oxidative pyrolysis of PTFE and in both oxidative and non-oxidative pyrolysis of PFEP. Oxygen in the air stream apparently suppressed the formation of octofluoroisobutylene in PTFE pyrolysis but did not completely prevent its formation from PFEP pyrolysis. Although a mechanism of octofluoroisobutylene formation is not clearly shown, it can be stated that some of the free radicals produced initially in the thermal decomposition of PTFE recombine with each other to form octofluoroisobutylene in the non-oxidative atmosphere, while they are oxidized to carbonyl fluoride in the oxidative pyrolysis. It can be estimated from band intensities of infrared spectra and peak heights of gas chromatograms that tetrafluoroethylene was the most abundant product, hexafluoropropylene the second and octofluorocyclobutane the third in the non-oxidative pyrolysis of PTFE in this study. LEWIS and NAYLOR (1947) reported that weight percent of the pyrolysis products of PTFE under normal atmospheric pressure was 15% for tetrafluoroethylene, 25% for hexafluoropropylene and 59% for octofluorocyclobutane. The discrepancy between the results obtained by us and those by Lewis and Naylor may be atttributed to the difference in the pyrolysis system. Pyrolysis was performed in a gas flow in this study, while Lewis used a closed system in which tetrafluoroethylene formed initially would undergo further reaction to increase the amounts of hexafluoropropylene and octofluorocyclobutane. In this context, it can be speculated that octofluoroisobutylene, an extremely toxic substance is produced more abundantly in a stagnant inert gas atmosphere than in a dynamic gas flow. The octofluoroisobutylene formation is very significant with respect to the toxicological study of thermal decomposition products of fluorocarbon polymers. This compound is reported to be extremely toxic and its lethal concentration is ten times lower than that of phosgene (CLAYTON, JR., 1968).

Carbonyl fluoride is found to be a main pyrolysis product in oxidative pyrolysis of both PTFE and PFEP. This finding is in good agreement with the results of KUPEL et al. (1964), COLEMAN et al. (1968) and PACIOREK et al. (1973). Trifluoroacetyl fluoride is

also a main pyrolysis product of PFEP but it is produced less abundantly with PTFE. Production of carbonyl fluoride and trifluoroacetyl fluoride would result from oxidation of the free radicals CF_2: and CF_3CF:, respectively. Perfluoroalkanes such as carbon tetrafluoride, hexafluoroethane and octofluoropropane and so on are produced in the oxidative pyrolysis of PTFE when pyrolysis temperature is raised. Carbon tetrafluoride is considered to result from the following disproportionation reaction, since carbonyl fluoride becomes labile at higher temperatures:

$$2COF_2 \rightarrow CF_4 + CO_2.$$

Our finding on carbon tetrafluoride formation agrees well with the result (AMPHLETT and DACEY, 1971) that rate of carbon tetrafluoride formation in this reaction becomes greater with increase in temperature. Hexafluoroethane and other higher perfluoro-alkanes may presumably be formed by reaction of the corresponding perfluoroalkenes with labile carbonyl fluoride in high temperature. Silicon tetrafluoride which occurs in pyrolysis in air stream may result from reaction of hydrogen fluoride with a glass wall of the infrared gas cell and the gas sampling tube used for both analyses.

The effect of water vapour in carrier gas on formation of the pyrolysis products is observed distinctively in the oxidative pyrolysis. Water vapour would react with carbonyl fluoride and trifluoroacetyl fluoride as indicated below.

$$COF_2 + H_2O \rightarrow CO_2 + 2HF,$$

$$CF_3COF + H_2O \rightarrow CF_3COOH + HF.$$
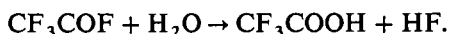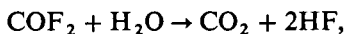
Those two processes are supported by the evidence that carbon dioxide increases greatly in the PTFE pyrolysis in humid air stream, while carbonyl fluoride decreases significantly and that calcium trifluoroacetate was present in the filtrate of the reaction products of the pyrolysate with calcium hydroxide solution. When the pyrolysis products containing carbonyl fluoride and trifluoroacetyl fluoride are inhaled into the respiratory tract covered with mucous fluid, those two compounds could be converted as indicated above. Trifluoroacetic acid is not too toxic but would irritate the upper respiratory tract upon inhalation, since it is as strongly acidic as other mineral acids (KAUCK and DIESSLIN, 1951).

WARITZ and KWON (1968) suggested that for industrial hygiene reasons a supply of inert gas should be provided in the vicinity of plant using PTFE at high temperatures. The inert gas supply is very effective in preventing the formation of carbonyl fluoride and trifluoroacetyl fluoride but on the other hand causes the formation of very toxic octofluoroisobutylene particularly in a stagnant gas. The present study suggests that due precaution should be taken to prevent toxic gas formation during the heating of fluorocarbon polymers in industrial use and also during treatment of solid waste containing fluorocarbon polymers in a community incinerator.

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