NATIONAL BUREAU OF STANDARDS REPORT

10 691

FLASH PYROLYSIS OF POLYTETRAFLUOROETHYLENE

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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FLASH PYROLYSIS OF POLYTETRAFLUOROETHYLENE

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Abstract

Polytetrafluoroethylene was thermally decomposed using high energy fluxes from a molecular gas laser emitting energy at 10.6 μm for exposure times of up to 1.5 minutes. Two modes of decomposition were noted as evidenced by a change in stable decomposition products as determined by gas chromatography. Nine different low molecular weight (four or less carbon atoms) fluorocarbons have been detected. In vacuo the primary reaction is depolymerization to the monomer, C_2F_4. In nitrogen and helium atmospheres chain rupture is more complete to yield significant amounts of carbon and fluorocarbons CF_4, C_3F_6, and C_2F_6. Decomposition in nitrogen atmospheres and to a lesser extent in helium is accompanied by a stream of incandescent carbon emitting radiation in the visible region of the spectrum. It is postulated that in nitrogen atmospheres higher temperatures result with the formation of significant amounts of trifluoromethyl radical.

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1.0 INTRODUCTION

The thermal decomposition of polytetrafluoroethylene has been studied extensively and most recently reviewed by W. W. Wright in considerable detail (1). These studies have been carried out in inert atmospheres or vacuum. Most research has emphasized the kinetics of decomposition in vacuum. Pyrolysis generally has been studied under isothermal conditions or with a programmed rate of temperature increase. Decomposition in vacuum was shown to yield predominantly monomer decreasing from 95% at 500 °C to about 75% at 1200 °C. Increasing pressure appears to favor the dimer, C_4F_8, presumably formed from the gas phase dimerization of the monomer. The major product, tetrafluoroethylene, is assumed to form by chain unzipping. Isothermal pyrolysis in inert atmospheres studied in the 500-600 °C range, appears to proceed in the same way.

The present investigation extends the range of pyrolysis conditions into the high temperature region for inert atmospheres. The molecular gas laser provides a reproducible source of energy variable over a wide range of energy densities. The energy fluxes available allow pyrolysis studies up to and through the temperature ranges encountered in polymer combustion. Elucidation of the chemical mechanisms of pyrolysis requires a knowledge of the details of the polymer pyrolysis process under high temperature and oxidizing conditions encountered in combustion. Knowledge of the mechanism of pyrolysis of a "simple" polymer such as polytetrafluoroethylene should lead to an improved understanding of ignition, flashover, and smoke formation.

2.0 EXPERIMENTAL METHOD

2.1 Pyrolysis Cell

The pyrolysis experiments were carried out in a modified 10 cm x 2 cm pyrex cylindrical infrared gas cell. The cell was modified by addition of a 2 cm diameter side arm fitted with a 25 mm NaCl window to transmit the laser radiation. A rigid disc of polytetrafluoroethylene was positioned in the side arm approximately 1 cm from the NaCl window and cell evacuated to 0.13 N/m^2 (10^{-3} Torr) or less. For experiments involving inert atmospheres the cell was next filled with He or N_2 to a pressure of 67000 N/m^2 (500 Torr). This pressure was arbitrarily chosen so that the final pressure inside the cell would not be much above atmospheric pressure.

2.2 Radiation Source

A 130 watt molecular gas laser (CO_2) operated CW (continuous wave) provided a source of 10.6 μm radiation for the sample pyrolysis. The unfocused laser beam of 1.3 cm diameter was employed at a power density of 41 watts/cm^2.

2.3 Gas Analysis

In a typical experiment the sample disc of smaller diameter than the laser beam was irradiated for a specified time, usually less than 1 minute, and the cell was transferred to a double-beam infrared spectrophotometer and the absorption spectrum recorded in the range 650-4000 cm^{-1}.

A gas chromatograph equipped with a thermal conductivity detector was employed for separation and identification of gaseous pyrolysis products. A sampling valve with 2 ml loop was used in conjunction with a vacuum manifold for sample introduction. Fluorocarbons containing two or more carbon atoms were separated at 0 °C on a 540 cm column packed with Chromosorb W[1] (30-60 mesh) coated with 30 Wt% of 1H, 1H, 7H-dodecafluoroheptylacrylate (2). Due to the wide range in boiling points an additional column was required to resolve the tetrafluoromethane from nitrogen and traces of air. CF_4 and the C_2 fluorocarbons were separated at 22-24 °C on a 150 cm Porapak R[1] (80-100 mesh) column. Helium carrier gas (60 ml/min at 64 psig) was used with injector and detector temperature maintained at 22-23 °C. Detector current was 100 ma and recorder sensitivity was 1 mv full scale.

Qualitative identification of the pyrolysis products was made from the infrared spectrograms and a comparison of retention data for reference gases. The gases CF_4, C_2F_6, C_3F_6, cyclo - C_4F_8, C_4F_8-2 (mixture of cis and trans) and polytetrafluoroethylene, were of commercial origin. C_2F_4 was prepared by controlled heating of polytetrafluoroethylene in vacuum (3).

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[1] Certain commercial materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material identified is necessarily the best available for the purpose.

Quantitative determination of the components from peak areas of the chromatograms was evaluated with an electromechanical integrator. The area normalization method was used for estimating the concentration of individual components. This method assumes that the ratio of one peak area to the sum of all peak areas is proportional to the mole percent of a particular component. Individual response factors were not used (4). The ratio of the peak area for CF_4 to the areas of C_2F_4 and C_2F_6 resolved on Porapak R was used to correlate CF_4 concentration with the data obtained with the fluoracrylate column.

2.4 Ultraviolet Measurements

Ultraviolet spectra of the incandescent sample were obtained by igniting the sample in a quartz cell fitted with a NaCl window to admit the laser beam. A medium dispersion quartz spectrograph was employed and the spectra were photographically recorded on 1F and 1N 4 x 10 inch plates.

3.0 EXPERIMENTAL RESULTS

A series of typical laser pyrolyses are summarized in Table 1. Pyrolysis was carried out in vacuum, helium, and nitrogen. A representative gas chromatogram of a pyrolysis mixture in helium is shown in Figure 1. The identity of the two minor peaks, due to C_2F_2 and iso - C_4F_8, were not confirmed due to lack of reference gases (2). Duplicate chromatograms for identical sample mixtures were reproducible within ±1.5% for major components. To reduce thermal cleavage of the rock salt window due to the laser beam the longer exposures were not continuous. Sample weight loss ranged from 0.2 g to 0.3 g.

Infrared spectrograms obtained for all pyrolysis gas mixtures supplemented the gas chromatographic data. The structural similarity of the components and their large number limited the usefulness of the infrared spectrograms.

Comparison of the pyrolysis in nitrogen and vacuum shows a dramatic change both in appearance and composition of the products. Vacuum laser pyrolysis results in evolution of some white fluorocarbon deposit and over 90% C_2F_4. This agrees with earlier vacuum pyrolysis work where the method of heating was different (5). Only 1% of the dimer cyclo - C_4F_8 was formed and C_3F_6 was observed in higher concentrations than previously reported which suggests somewhat higher temperatures during the laser pyrolysis. No SiF_4 or oxygen containing compounds were observed.

Laser pyrolysis in nitrogen consistently results in a decrease in C_2F_4 from over 90% to 35% (Table 1). In addition large increases occur in C_2F_6, CF_4, and C_3F_6, from 0 to 30%, 0 to 30%, and 7 to 20% respectively. Also the higher molecular weight fluorocarbons, cyclo - C_4F_8, trans - C_4F_8-2, cis - C_4F_8-2, and iso - C_4F_8 appear. Visual observation indicates intense incandescence of the black carbon stream having the appearance of a flame. Pyrolysis in a helium atmosphere resembles the nitrogen pyrolysis but with a somewhat higher concentration of C_2F_4 and less incandescent carbon. Concentrations are somewhat variable due to slight variations in irradiation conditions.

Ultraviolet emission spectra of the incandescence indicated a continuum from about 9000 Å (the upper limit of the plate and optics) to about 4000 Å closely resembling spectra of diffusion flames rich in radiating carbon. Since the maximum duration of the emission is a few seconds other species possibly present in the flame in much lower concentrations would not be detected.

4.0 DISCUSSION

The details of the degradation mechanism for polytetrafluoroethylene in inert atmospheres has yet to be determined. The generally favored mechanism of random chain scission with unzipping of the polymer to form the monomer accounts for the laser pyrolysis products in vacuum (1,6). This mechanism assumes formation of the monomer C_2F_4 directly rather than by dimerization of CF_2. On the basis of calculations of bond dissociation energies Errede favors a primary reaction to form CF_2. The CF_2 radical on the basis of spectroscopic studies has been shown to be exceptionally stable with a lifetime in the millisecond range (8).

The laser pyrolysis in inert atmospheres results in a large decrease in C_2F_4 with the formation of an almost equal amount of C_2F_6 and significant amounts of CF_4, C_3F_6, and iso - C_4F_8. The intense incandescence in inert atmospheres and carbon formation suggest much higher temperatures are attained. These products not found in the vacuum pyrolysis could readily form from the CF_3 radical produced by fluorination of CF_2 produced as a primary step in the decomposition. The much higher temperatures would provide the necessary fluorine.

1. $CF_2 + F \rightarrow CF_3$
2. $2CF_3 \rightarrow C_2F_6$
3. $CF_3 + F \rightarrow CF_4$

Some of the C_2F_6, reaction 2, could result from direct fluorination of C_2F_4 formed by dimerization of CF_2. Infrared spectroscopic studies at low temperatures have shown that reactions 1, 2, 3 readily occur with negligible activation energies (9, 10).

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Table 1

Laser Pyrolysis Products of Polytetrafluoroethylene[1]

Atmosphere	Laser Exposure Time(sec)	Visual Observation	CF_4	C_2F_6	C_2F_4	C_2F_2	C_3F_6	cyclo-C_4F_8	trans-C_4F_8-2	cis-C_4F_8-2	iso-C_4F_8
vacuum	25	white deposit	-	-	92.0	-	7.2	0.8	not measured		
	45	white deposit	-	-	91.5	-	7.4	1.1	-	-	-
helium	25	black smoke, extensive incandescence	3.7	29.8	42.0	0.9	19.9	3.7	not measured		
	30	black smoke, extensive incandescence	2.1	25.0	42.4	0.8	21.0	3.7	0.4	0.5	4.1
nitrogen	30	black smoke, extensive incandescence	4.6	30.3	35.5	0.9	20.3	4.2	trace	trace	4.2
	45	black smoke, extensive incandescence	2.6	27.6	34.3	0.9	24.3	3.5	0.6	0.6	5.6

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[1] Results are expressed in mole percent.

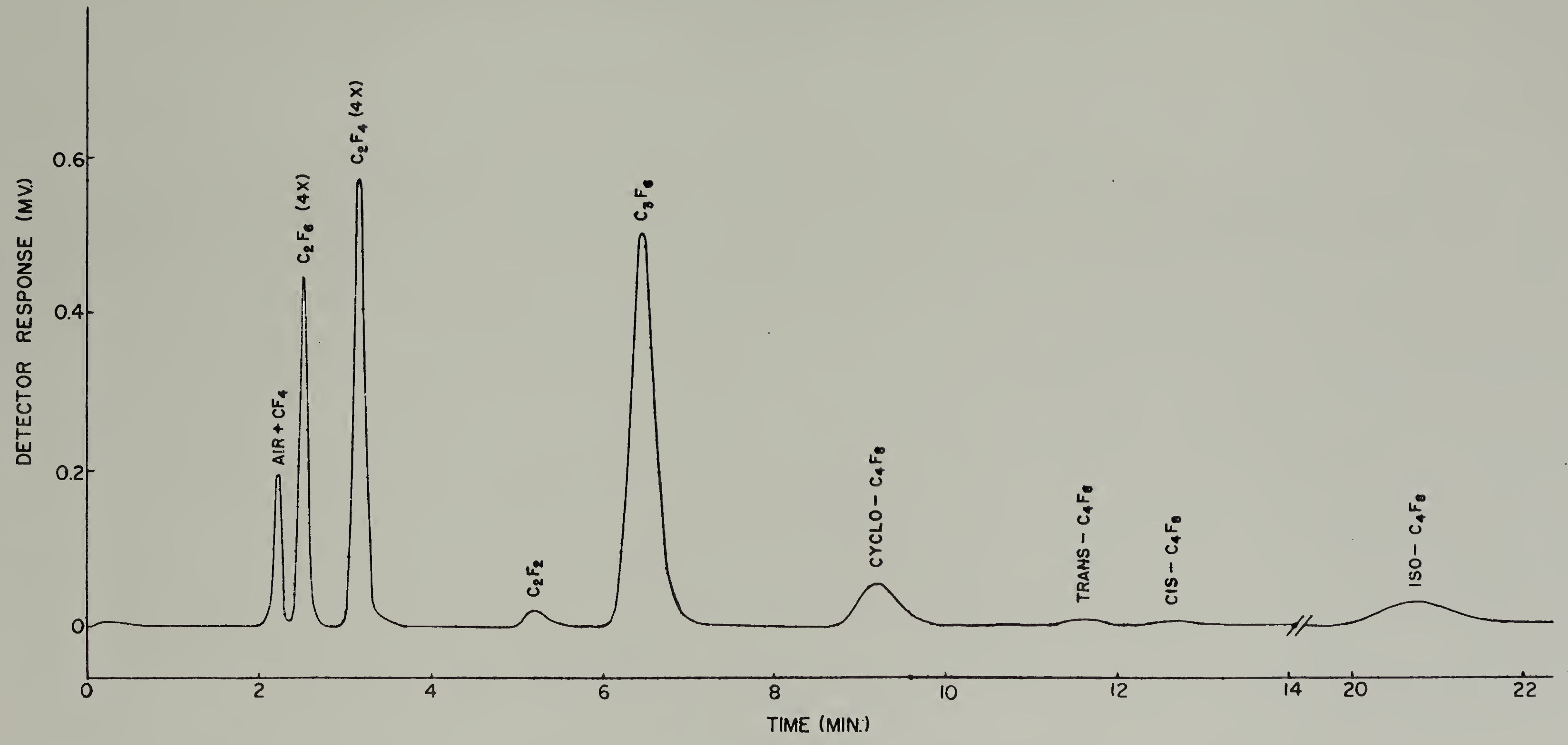
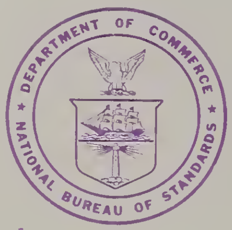


Figure 1

Chromatogram of polytetrafluoroethylene pyrolysis products in helium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