

The product which immediately precipitated was crystallized from absolute alcohol to a constant melting point of 128–130.5° (sintering at 126°).

Anal. Calcd. for $C_6H_5NO_4$: C, 40.8; H, 6.2. Found: C, 40.5; H, 6.3.

Allylamine Picrate.—Adding an ethereal solution of allylamine to an equimolar amount of picric acid in ether resulted in the immediate precipitation of the picrate. Three crystallizations from chloroform containing a small amount of absolute alcohol furnished small, matted, yellow-colored crystals melting at 141–141.5°.

Anal. Calcd. for $C_9H_{10}N_4O_7$: C, 37.8; H, 3.5. Found: C, 38.0; H, 3.5.

Benzenesulfonyl Derivative of Dibromopropylamine.—The benzenesulfonyl derivative of I was formed according

to the directions given for the preparation of the same derivative of II.² Recrystallization from alcohol yielded the alkali insoluble product VI, m. p. 89–90°.

Anal. Calcd. for $C_9H_{10}NO_2SBr$: C, 39.1; H, 3.7; N, 5.1. Found: C, 39.5; H, 3.5; N, 5.3.

Summary

The crystalline precipitate formed in ethereal solution of 2,3-dibromopropylamine is 2,3-dibromopropylamine hydrobromide and not II as previously reported. The debromination product is allylamine and not azacyclobutadiene.

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[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & COMPANY, INC.]

Pyrolysis of Polytetrafluoroethylene

BY E. E. LEWIS AND M. A. NAYLOR

Polytetrafluoroethylene is a new polymeric material possessing unusual heat stability and chemical inertness. A summary of its properties has been given by Renfrew and Lewis¹ and an attempt to explain these properties in terms of molecular structure has been given by Hanford and Joyce.²

Although the polymer is quite stable at the normal fabrication temperatures of 330 to 360°, it does undergo degradation if it is maintained at temperatures above 360° for extended periods of time. The extent and rate of this degradation increase as the temperature is raised. The materials obtained by cracking this polymer at 600 to 700° under reduced pressure are of particular interest because of their unexpected structure.^{3,4}

It is generally believed that the products formed by the polymerization of tetrafluoroethylene are straight chains having the structure $(-CF_2-CF_2-CF_2-CF_2-)_n$ terminated by as yet unidentified end-groups. If such is the case, one might expect the products of thermal cracking to have structural characteristics similar to those of the compounds obtained from the thermal cracking of high molecular weight straight chain hydrocarbons. This prediction would lead to the conclusion that the low molecular weight products formed should consist of straight- and branched-chain, saturated and unsaturated compounds along with carbon tetrafluoride. A broad range of molecular weights in the products would be expected.

Actually, however, the products obtained by cracking polytetrafluoroethylene at temperatures from 600 to 700° and at pressures between 5 and

760 mm. were of low molecular weight and consisted of C_2F_4 , C_3F_6 and C_4F_8 in varying quantities depending on conditions. Since the method of isolation employed, *i. e.*, Podbielniak distillation, is estimated to have accounted for 95 to 97% of the products formed, it is possible, of course, that small amounts of material of higher molecular weight and carbon tetrafluoride were formed but were not detected.

Experimental

The equipment used is shown in Fig. 1. The decomposition chamber consisted of a 54" length of $3/4$ " iron pipe with the middle 27 $1/2$ " section heated by three electrical resistance coils. Short lengths of galvanized-iron window screen were rolled into cylinders and then placed in the exit side of the heated zone of the pipe. Ground scrap polytetrafluoroethylene was fed from a hopper into the decomposition chamber by means of a hand-operated plunger. The decomposition products passed from the pipe through a glass tube into two or more vacuum flasks filled with glass wool and placed in series. The flasks removed solid particles that were being carried along in the gas stream. The filtered gas was compressed by means of a Model S Frigidaire refrigerating pump (driven by a $1/4$ h. p. motor) into either of two gas cylinders. The cylinders were kept at approximately atmospheric pressure by cooling them in a methanol and Dry Ice mixture. The pressure in the system was checked by two manometers on the vacuum side (one at the pipe exit and one immediately before the compressor) and by a compound gage on the pressure side. The temperature of the reaction zone was measured by three thermocouples brazed to the outside of the pipe. During a run, the product was directed into the larger of the two receivers until constant conditions of pressure and temperature had been established. The product was then diverted into the previously evacuated smaller cylinder and the analytical sample collected. For experiments at pressures too low to be maintained by the Frigidaire compressor, a Cenco Megavac pump was used. In this case, the sample was collected by immersing the two traps in liquid nitrogen. Pressure was controlled either by varying the rate of feed or by a throttling valve.

The sample for analysis was transferred to a Podbielniak still and distilled. Three fractions were obtained boiling at -76 , -29 and -6 °. These were identified as follows:

C_2F_4 .—This was the lowest boiling compound obtained from the pyrolysis. It was identified as tetrafluoroethylene

(1) M. M. Renfrew and E. E. Lewis, *Ind. Eng. Chem.*, **38**, 870 (1946).

(2) W. E. Hanford and R. M. Joyce, *THIS JOURNAL*, **68**, 2082 (1946).

(3) A. F. Benning, F. B. Downing and J. D. Park, U. S. Patent 2,394,581 (February 12, 1946).

(4) E. E. Lewis, U. S. Patent 2,406,153 (August 20, 1946).

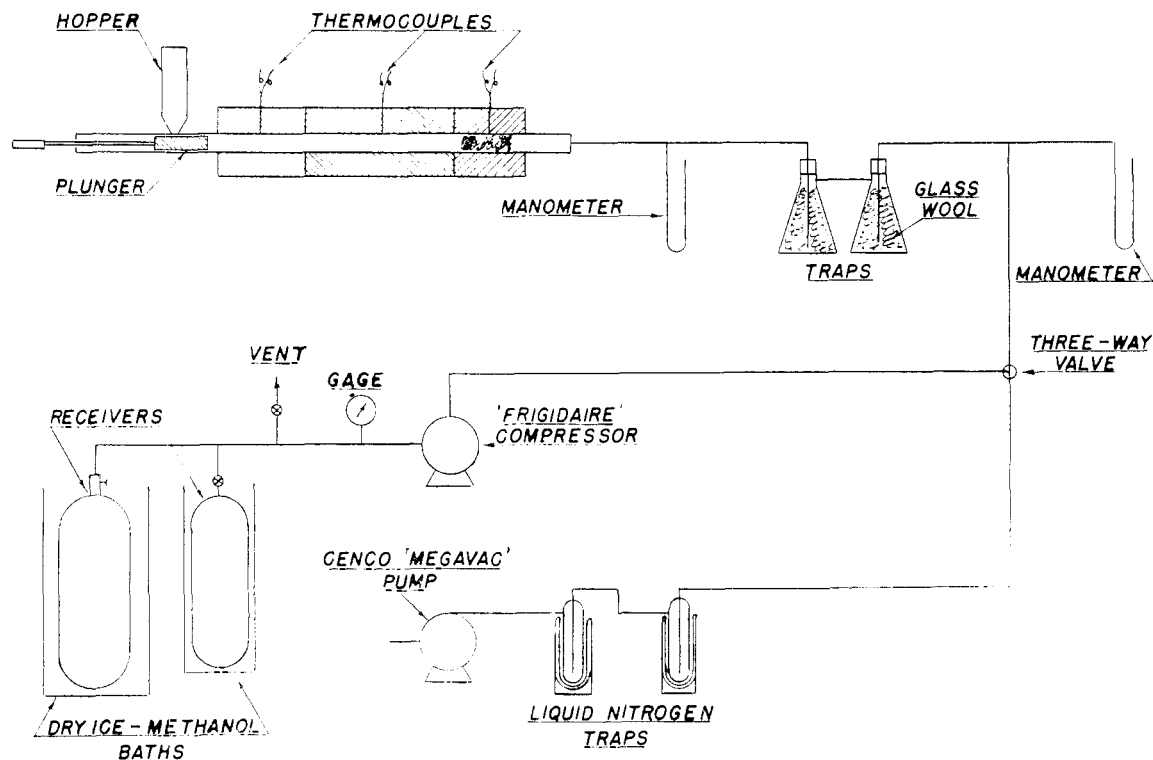


Fig. 1.—Apparatus for the pyrolysis of polytetrafluoroethylene.

by the following properties: b. p., found -76° , lit.⁵ -76.3° ; f. p., found -142° , lit.⁵ -142.5° ; mol. wt., found 101, calcd. 100. It was converted by direct chlorination to the 1,2-dichloride which boiled at 4° , lit.⁶ 3.8° .

C_3F_6 .—The second fraction was treated with chlorine under radiation at 3600 \AA . to yield a dichloride. The properties of the parent compound together with the dichloride are compared with the properties of hexafluoropropene and hexafluorocyclopropane and their chlorinated derivatives, 1,2-dichlorohexafluoropropane and 1,3-dichlorohexafluoropropane, in Table I.

TABLE I
PHYSICAL CONSTANTS

| | Boiling point, $^\circ\text{C}$. | Freezing point, $^\circ\text{C}$. | Mol. wt. | Index of refraction (n_D^{20}) |
|-------------------------------|-----------------------------------|------------------------------------|--------------|------------------------------------|
| C_3F_6 fraction | -29 | -150.6 | 148 | |
| Hexafluoropropene | -20.4^7 | -156.2^7 | 150 (calcd.) | |
| Hexafluorocyclopropane | -28^9 | | 150 (calcd.) | |
| C_3F_6 chlorination product | 35 | Glass at -130 | | 1.3041 |
| 1,2-Dichlorohexafluoropropane | 34.7^7 | -136^7 | | 1.3029 |
| 1,3-Dichlorohexafluoropropane | 35^8 | | | |

Attempts to oxidize the C_3F_6 with neutral potassium permanganate even at elevated temperatures and pressures resulted in the formation of only a very small amount of acidic material, which has not yet been identified. Although the physical constants observed for the C_3F_6 com-

pound seem to indicate that it is hexafluoropropene, its resistance to oxidation seems to favor the cyclic structure.⁸ At the present time we are unable to state which is the correct structure. Further work with the infrared or Raman spectra or with the oxidation product will be necessary.

C_4F_8 .—This fraction was identified as octafluorocyclobutane by the following properties: b. p., found -6° , lit.³ -5° ; f. p., found -50° , lit.⁹ -48° , mol. wt., found 202, calcd. 200. This compound would not de-

TABLE II

EFFECT OF PRESSURE ON THE PRODUCTS OF THE THERMAL DEGRADATION OF POLYTETRAFLUOROETHYLENE AT 600°

| Pressure, mm. | Weight per cent. of products | | |
|---------------|------------------------------|-------------------|-------------------|
| | C_2F_4 | C_3F_6 | C_4F_8 |
| 5 | 97 | ^a | ^a |
| 41 | 85.7 | 14.3 ^b | ^a |
| 55 | 84.1 | 15.9 ^b | ^a |
| 70 | 83.0 | 17.0 ^b | ^a |
| 150 | 76.5 | 15.4 | 8.1 ^b |
| 150 | 81.3 | 10.7 | 8.0 ^b |
| 150 | 80.3 | 14.5 | 5.2 ^b |
| 250 | 57.3 | 19.0 | 23.7 ^b |
| 350 | 34.1 | 21.7 | 44.2 ^b |
| 350 | 29.3 | 28.3 | 42.4 ^b |
| 350 | 32.5 | 22.3 | 45.2 ^b |
| 760 | 14.2 | 26.0 | 59.8 ^b |
| 760 | 15.9 | 25.7 | 58.4 ^b |

^a Indicates less than 4%. ^b Obtained by difference, no higher boiling compound detected.

(5) O. Rulf and O. Bretschneider, *Z. anorg. Chem.*, **210**, 173 (1933).
 (6) E. G. Locke, W. R. Brode and A. L. Henne, *THIS JOURNAL*, **56**, 1726 (1934).

(7) A. L. Henne and T. P. Wanlkes, *ibid.*, **68**, 496 (1946).

(8) A. L. Henne, R. P. Ruh and W. J. Zimmerschied; also A. V. Grosse and G. Cady; papers presented at the Chicago meeting of the American Chemical Society, September, 1946.

(9) J. Harmon, U. S. Patent 2,404,374 (July 23, 1946).

colorize aqueous potassium permanganate solution, nor would it react with chlorine in direct sunlight. Since both straight-chain and cyclic unsaturated fluorocarbons are known to be reactive to these reagents,⁸ we have concluded that this pyrolysis product is octafluorocyclobutane.

It may be seen from Table II that at a pressure of 5 mm. of mercury the product contained at least 97% of tetrafluoroethylene. As the pressure increased, the yield of tetrafluoroethylene decreased and, instead, C₃F₆ and C₄F₈ were formed in increasing proportions.

On the other hand, increasing the temperature from 600 to 700° had only a minor effect on the composition of the product.

TABLE III

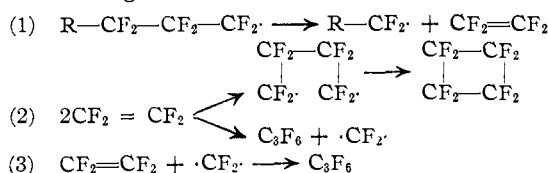
EFFECT OF TEMPERATURE ON THE PRODUCTS OF THERMAL DEGRADATION OF POLYTETRAFLUOROETHYLENE AT 41 MM.

| Temp., °C. | Weight per cent. of products | | |
|---------------|-------------------------------|-------------------------------|-------------------------------|
| | C ₂ F ₄ | C ₃ F ₆ | C ₄ F ₈ |
| 600 | 85.7 | 14.3 | <4 |
| 700 | 82.1 | 17.9 | <4 |

Discussion

The isolation of products only of low molecular weight from the cracking of polytetrafluoroethylene together with the pronounced dependence of the yield of each product on the pressure suggests two points. First, it seems that this polymer decomposes by splitting off units of the original monomer, tetrafluoroethylene, from a degrading fragment and, secondly, it appears that these monomer units are capable of undergoing secondary reactions, favored by increased pressure, to form compounds of higher molecular weight.

A possible mechanism may be represented in the following manner



Judging from the simplicity of these products it seems that very few carbon-fluorine bonds are broken by direct attack of an active fragment.

Such a view may be partially rationalized if bond strengths and polarizabilities are determining factors in such reactions,¹⁰ since the carbon-fluorine bond is one of the strongest single bonds encountered.^{7,11,12,13}

The suggestion that C₂F₄ units are selectively cracked off the degrading molecule is favored by the possibility of the close energy coupling between the endothermic cleavage reaction and the exothermic closing of the double bond to form tetrafluoroethylene.¹⁴ Such close coupling can result in a significant decrease in the energy requirements of this reaction. However, this is not possible with the cleavage of any other bond unless such splitting is followed by immediate ring closure. The steric requirements of this latter reaction reduce its probability considerably.

It is impossible to make any energy calculations for the above reactions since the actual strengths of the carbon-fluorine and carbon-carbon bonds in polyfluorides are not known with any degree of certainty.^{7,13}

Acknowledgment.—The authors wish to express their appreciation to Mr. R. E. James, Jr., for much of the experimental work reported here.

Summary

The thermal degradation of polytetrafluoroethylene has been carried out at 600 to 700° and at pressures of 5 to 760 mm.

A mechanism has been proposed to account for the fact that tetrafluoroethylene was formed in increasing amounts as the pressure was decreased and was the sole product at very low pressures.

(10) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 150-152.

(11) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

(12) H. A. Skinner, *Trans. Faraday Soc.*, **41**, 645 (1945).

(13) L. O. Brockway, *J. Chem. Phys.*, **41**, 185, 742 (1937).

(14) A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943.

ARLINGTON, N. J.

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The Formation of Tervalent Manganese in Strong Sulfuric Acid Solution¹

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Upon numerous occasions during analyses of pyrolusite and psilomelane and glasses containing manganese, the authors have observed the violet color which is the subject of a discussion by Heath,² who suggests that the violet solution, obtained by heating manganese dioxide with concentrated sulfuric acid, is due to permanganate and that this may be formed through a persulfate

(1) Contribution from the Department of Glass Technology, Corning Glass Works, Corning, N. Y., and The Analytical Laboratory Cia. Vidraria Santa Marina, São Paulo, Brasil.

(2) Division of Physical and Inorganic Chemistry of Am. Chem. Soc. Abstracts of papers presented at Chicago, Sept. 9-13, 1946, No. 103.

mechanism. In effect, his proposed reaction is the disproportionation of manganese dioxide, thus: $5\text{MnO}_2 + 4\text{H}^+ = 2\text{MnO}_4^- + 3\text{Mn}^{++} + 2\text{H}_2\text{O}$. This explanation is dissatisfying because common experience shows the reaction (in water) to proceed in the opposite direction, and both permanganate and persulfate to decompose upon fuming with sulfuric acid. Moreover, the naked eye can distinguish this color as being less red than that of permanganate.³

(3) We are indebted to Harrison P. Hood of the Corning Glass Works Research and Development Laboratory, who confirmed the color difference by means of the Hardy Color Analyzer.