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, C_3F_6 and C_4F_8 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_2F_4	C_3F_6	C_4F_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

(1) $R—CF_2—CF_2—CF_2· \longrightarrow R—CF_2· + CF_2=CF_2$

(2) $2CF_2 = CF_2 \begin{cases} \text{CF}_2—\text{CF}_2 \\ | \quad | \longrightarrow \text{CF}_2—\text{CF}_2 \\ \text{CF}_2· \text{ CF}_2· \\ \nearrow \\ \searrow \\ C_3F_6 + ·CF_2· \end{cases}$

(3) $CF_2=CF_2 + ·CF_2· \longrightarrow C_3F_6$

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 C_2F_4 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]

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.

The Formation of Tervalent Manganese in Strong Sulfuric Acid Solution[1]

BY JOHN F. G. HICKS, JR., AND EDWARD KROCKMALSKI

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

mechanism. In effect, his proposed reaction is the disproportionation of manganese dioxide, thus: $5MnO_2 + 4H^+ = 2MnO_4^- + 3Mn^{++} + 2H_2O$. 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]

On the other hand, much is known which indicates tervalent manganese as the coloring agent. Manganic ion is responsible for the color of the manganese purple[4] glasses, and it forms complex ions[5] in water solution which are deep red to purple. Furthermore, Carius[6] prepared manganic sulfate from manganese dioxide and concentrated sulfuric acid and Frank[7] prepared it from the decomposition of permanganate in concentrated sulfuric acid solution. Both associated the violet color with manganic sulfate.

Experimental

To confirm that the violet color is due specifically to manganic and not to permanganate ions, the following experiments were performed:

The violet concentrated sulfuric acid solution, upon dilution or neutralization with ammonia, changes through varying degrees of red and brown to colorless, with the precipitation of manganese dioxide. These changes are reversible and by adding concentrated sulfuric acid the manganese dioxide is redissolved, forming a deep red solution, or the violet one, if the neutralization has been carried out without too much dilution. The brown precipitate was identified as manganese dioxide by titration with ferrous sulfate, then conversion to permanganate and retitration. The precipitation was carried out at a pH ranging from 0.3 to 1.0 and, under these conditions, 5.9, 5.8, 5.9 and 6.1 mg. of manganese were found assuming manganese dioxide against respectively 6.1, 6.0, 6.1 and 6.3 mg. found as resulting permanganate. Identical behavior was observed whether the violet solution was prepared from crude manganese ore, reagent material or freshly precipitated manganese dioxide, prepared by adding the theoretical quantity of manganous sulfate to a neutral solution of potassium permanganate.

Five ml. of 0.01 M permanganate solution was added to 25 ml. of concentrated sulfuric acid. The characteristic light olive green color resulted. (Frank[7] says this is due to the formation of $(MnO_3)_2SO_4$.) Thus concentrated sulfuric acid destroys the characteristic permanganate color regardless of reduction, and 2 ml. of water added to this solution leaves the olive green essentially unchanged. (However, the permanganate color is regained if 20 ml. of water is added.) This solution was heated to fuming and after a few minutes the color changed to the violet in question and then to colorless. At this last stage, the manganese was all in the bivalent,[8] or, under these conditions, the stable equilibrium state.

Manganese dioxide was precipitated according to the reaction, $2H_2O + 2MnO_4^- + 3Mn^{++} = 5MnO_2 + 4H^+$, by adding 0.075 millimole of manganous sulfate to 0.05 millimole of potassium permanganate. Keeping the solution cold, 25 ml. of concentrated sulfuric acid was added. Continuous agitation for a few minutes left the manganese dioxide undissolved, but immediately upon adding 0.125

millimole of additional manganous sulfate, solution was complete and the color was the same deep violet. Thus strong sulfuric acid reverses the characteristic reaction[9] of manganic ion: $2Mn^{+++} + 2H_2O = MnO_2 + Mn^{++} + 4H^+$. Hydrogen ion concentrations above 10 N prevent the hydrolysis even at boiling temperatures.

A series of three determinations were carried out as follows: Five ml. of 0.01 M permanganate solution was added to 25 ml. of concentrated sulfuric acid, keeping the solution cool. Ferrous sulfate solution (0.05 M) was then added until the olive green color had changed to a distinct violet. After noting the buret reading, the titration was continued to a colorless end-point as a check on the amount of permanganate thermally decomposed. (The loss in oxidizing power of permanganate can be kept below 10% if the solution is not allowed to become too warm during the dilution of the concentrated acid.) The ratios of the volume of ferrous sulfate solution required to produce the violet end-point to that required to go from violet to colorless were 3.3, 3.9 and 3.8. This ratio should be 4 if manganic ion is formed and then destroyed according to the reactions: $MnO_3^+ + 6H^+ + 4Fe^{++} = Mn^{+++} + 4Fe^{+++} + 3H_2O$ and $Mn^{+++} + Fe^{++} = Mn^{++} + Fe^{+++}$. Because of the lack of sharpness at the end-points, the agreement is as good as can be expected. We have corrected for the loss of oxidizing power due to the thermal decomposition of the permanganate.

Three similar experiments using 0.10 M manganous sulfate to reduce the permanganate to manganic ion and then ferrous sulfate to reduce this to manganous were made. In this case, five times the amount of manganic ion is formed according to the reaction $MnO_3^+ + 6H^+ + 4Mn^{++} = 5Mn^{+++} + 3H_2O$, and thus the ratio of moles of added manganous sulfate to ferrous sulfate should be $^4/_5$; found 0.73, 0.69 and 0.73, after correction for thermal decomposition of permanganate. The discrepancy is again considered to be entirely explained by the lack of sharpness of the end-points, especially the intermediate one, since a pronounced violet color always appears before all the septavalent manganese has been consumed.

Five ml. of 0.01 M permanganate was added to 25 ml. of concd. sulfuric acid keeping the solution cold and then 2 ml. of 0.10 M manganous sulfate added to that, giving the violet solution. This solution was diluted and neutralized to a pH ranging between 0.3 and 1.0, the manganese dioxide filtered out and manganese determined in the filtrate and precipitate. The ratios of the number of gram-atoms of manganese found in the filtrate to those found in the precipitate were 1.26, 1.27, 1.26 and 1.16. If, however, the reduction of permanganate to manganic ion by manganous ion is carried out in 12 N sulfuric acid to suppress the thermal decomposition of permanganate, the ratios obtained are 1.01, 0.97 and 0.99. The violet color, therefore, is due to manganic ion and not permanganate. Since the standard oxidizing potentials of both the manganic-manganous and the permanganate-manganous couples are about 1.51 v.,[10] the reducing agents used by Heath[2] will not distinguish between permanganate and manganic ion.

Summary

The violet color obtained when manganese dioxide is fumed with concentrated sulfuric acid is due to the formation of manganic ion as an intermediate in the reaction $2MnO_2 + 4H^+ = 2Mn^{++} + 2H_2O + O_2$.

(4) Morey, "The Properties of Glass," Reinhold Publishing Corp., New York, N. Y., 1938, p. 436; Hoffman, *Sprechsaal*, **69**, 534 (1946).

(5) See, for example, Launer, THIS JOURNAL, **54**, 2597 (1932); Cartledge and Ericks, *ibid.*, **58**, 206 (1936); Muller and Kopp, *Z. anorg. Chem.*, **68**, 160 (1910); Meyer and Mark, *ibid.*, **133**, 325 (1924), for discussions of the oxalate, fluoride and phosphate complexes." Additional references to the original literature may be found in Pascal, "Traite de Chimie Minerale," Massons, Paris, 1933, IX, and Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1932, XII.

(6) Carius, *Ann.*, **98**, 53 (1956).

(7) Frank, *J. prakt. Chem.*, [2] **36**, 31 ,451 (1887).

(8) See Mellor, footnote 5, pp. 255, 401, 428.

(9) Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., N. Y., 1929, p. 292.

(10) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938.