

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Studies on the Thermal Decomposition of Silver Salts of Perfluorocarboxylic Acids¹

BY A. D. KIRSHENBAUM, A. G. STRENG AND MURRAY HAUPTSCHN

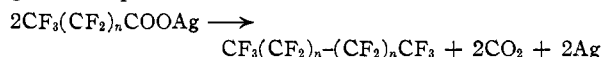
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A detailed investigation of the thermal decomposition of silver salts of perfluorocarboxylic acids has been made. Very high yields (80–95%) of coupling products are formed in accordance with the over-all equation: $2\text{CF}_3(\text{CF}_2)_n\text{COOAg} \rightarrow [\text{CF}_3(\text{CF}_2)_n]_2 + 2\text{CO}_2 + 2\text{Ag}$. The reaction has been studied, and the acid anhydride, $[\text{CF}_3(\text{CF}_2)_n\text{CO}]_2\text{O}$, and silver oxide have been shown to be important intermediates. The thermal decomposition of perfluorobutyric anhydride in the presence of silver oxide afforded an 85% yield of *n*-perfluorohexane. Under similar conditions, the hydrocarbon silver salt, silver acetate, decomposed almost entirely into acetic anhydride and silver oxide. The profound difference of the mode of action of heat on the silver and sodium salts of perfluorocarboxylic acids as well as on "hydrocarbon" and "fluorocarbon" anhydrides is discussed briefly.

Introduction

This paper reports the results of a comprehensive study of the action of heat on the silver salts of perfluorocarboxylic acids. Hals, Reid and Smith^{2a} and Haszeldine^{2b} have recently found that the sodium salts of perfluoro acids are pyrolyzed to yield perfluoro olefins and sodium fluoride in high yields. At the same time that the present work was first reported, La Zerte, Hals, Reid and Smith^{1b} found that varying yields of olefins were obtained also by the pyrolyses of other salts of perfluoro acids, particularly salts of the alkali and alkaline earth metals, *i.e.*, potassium, ammonium and barium. Kanewskaja and Shemiakin³ investigated the thermal decomposition of the silver salts of the "hydrocarbon" acids, acetic and benzoic acid. They found that the former salt yielded 4.7% acetic anhydride and 58.2% acetic acid, while the latter yielded benzoic acid and anhydride together with smaller amounts of other secondary products.

In contrast to these findings we have found that the thermal degradation of *silver* salts of *perfluoro* acids under varying conditions affords excellent yields of *coupling products* as represented by the general equation



The mechanism (or possible mechanisms) of this unusual degradation was clearly of interest, and accordingly a detailed study was initiated.

Experimental Techniques

Preparation of the Silver Salts.—Anhydrous silver perfluoroacetate, silver perfluoropropionate and silver *n*-perfluorobutyrate were prepared in analytically pure form by the method described previously.⁴ Mallinckrodt grade silver acetate was dried in an oven at approximately 80° and kept in a desiccator over phosphorus pentoxide.

Apparatus.—The apparatus employed for the study of the thermal degradation of the silver salts under autogenous pressures is illustrated in Fig. 1. It consisted essentially of a copper reaction vessel (3), the length of which was twelve inches and the diameter one inch, heated in an elec-

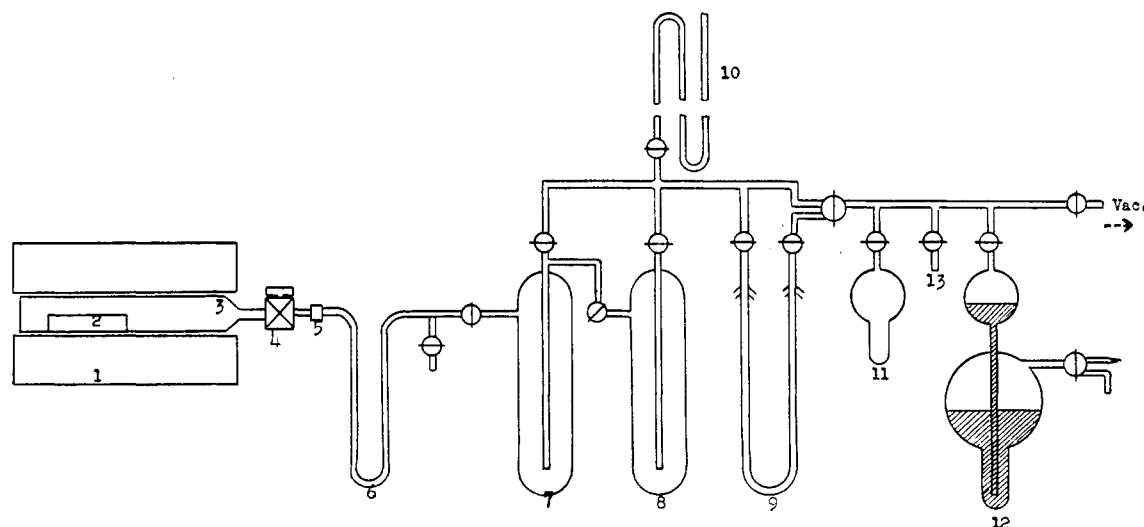


Fig. 1.—Thermal decomposition apparatus: 1, furnace; 2, boat + sample; 3, copper reaction tube; 4, Hoke needle valve; 5, glass-to-copper seal; 6, water ice trap; 7, Dry Ice trap; 8, liquid N₂ trap; 9, Ascarite tube; 10, Hg manometer; 11, bulb; 12, Toepler pump; 13, sample outlet.

(1) Presented at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 14 to 19, 1952. (a) Abstracts of Papers—Paper No. 40, p. 19K. (b) Abstracts of Papers—Paper No. 39, p. 19K.

(2) (a) L. J. Hals, T. S. Reid and G. H. Smith, *THIS JOURNAL*, **73**, 4054 (1951); (b) R. N. Haszeldine, *J. Chem. Soc.*, 4259 (1952).

(3) S. J. Kanewskaja and M. M. Shemiakin, *Ber.*, **69B**, 2152 (1936).

trically controlled furnace (1). The copper vessel was opened and closed by means of a Hoke needle valve (4) and connected to a Pyrex glass vacuum system by means of a glass to copper seal (5). The vacuum system included a water-ice U trap (6), a Dry Ice trap (7), a liquid nitrogen

(4) M. Hauptschein and A. V. Grosse, *THIS JOURNAL*, **73**, 2461 (1951).

TABLE I
 THERMAL DECOMPOSITION OF SILVER PERFLUOROBUTYRATE. DECOMPOSITION PRODUCTS, % CONVERSION^a

Con- ditions	Reaction time, hr.	T, °C.	(C ₃ F ₇ CO) ₂ O	C ₆ F ₁₄	CO ₂	CO	Ag	Ag ₂ O
P-C ^b	3-4	260-275	Trace	90-95	100	Trace	95	
P-C	3-4	400-450	..	85-90	95	None	100	
A-SQ ^c	3-4	375-450	5	90	...		97	2
A-SQ	3-4	375-450	5	95	...		100	Trace
A-SQ	3-4	375-450	35	65	...	Present	80	21
V-Q ^{d,f}	3	300-400 ^a	9	70	79	Present	65	25
V-C ^{e,f}	3	260-375	17	75	72		°	°
V-C ^f	3	250-275	13 (46) ^h	10 (36) ^h	12 (43) ^h	3 (11) ^h	Present	Present

^a The % conversions to C₆F₁₄, CO₂ and Ag are based on equation (4). The % conversions to (C₃F₇CO)₂O and Ag₂O are based on equation (1). ^b P-C = autogenous pressures in copper vessels. ^c A-SQ = "1-atm. argon" pressure in silver-lined quartz vessel. ^d V-Q = *in vacuo* in unlined quartz vessel. ^e V-C = *in vacuo* in copper vessel. ^f In these experiments unreacted silver salt was found to be present. ^g The total conversion to Ag + Ag₂O ≈ 100%. ^h Since 72% of silver salt was unreacted in this case, the actual yields of products, based on reacted salt, are those enclosed in parentheses.

trap (8), an Ascarite tube (9), an outlet (13) for connecting a sampling tube and a Toepler pump (12). In certain experiments the Ascarite tube was replaced by a trap containing a solution of barium hydroxide.

Procedures. (a) **Autogenous Pressures.**—Ten-gram samples were weighed into the copper boat (2) of Fig. 1, which was then placed into the copper reaction vessel. The vessel and the entire system were degassed at *ca.* 10⁻³ mm. for two hours. The evacuated reactor was sealed off and heated for three to four hours at temperatures varying from 260-450° for different experiments. The pressures developed under these autogenous conditions were estimated to be *ca.* 20-30 atmospheres.

(b) **One-Atmosphere Argon Pressure.**—Ten-gram samples in a platinum boat were inserted into a silver-lined quartz reactor. The system was evacuated as above, but then filled with one atmosphere of pure argon gas, closed off from the vacuum system and heated for 3-4 hours at 375-450°. The pressure was adjusted to 760 ± 50 mm. throughout the heating period by bleeding off gas into the various traps as excess pressure developed.

(c) ***In Vacuo.***—In these vacuum experiments copper or quartz reactors were filled with the charge, evacuated and left open to the entire vacuum system throughout the heating period.

The volatile and gaseous products were collected and separated in a conventional manner. Silver oxide was quantitatively separated from metallic silver by dissolving in excess ammonia and analyzing in the usual manner by precipitation of silver chloride. Any unreacted silver salt was separated from both silver and silver oxide by prior extraction with several portions of warm water.

Experimental Results

Pyrolysis of Silver *n*-Perfluorobutyrate at Autogenous Pressures.—A dozen experiments were carried out under these conditions and the results of two representative decompositions conducted at the extremes of the temperature ranges are tabulated in Table I. The *n*-perfluorohexane boiled at 56-57.5°; *n*_D²⁰ 1.251, 1.2511; mol. wt. found (Victor Meyer), 339, 338; calcd. 338; known⁵ for *n*-C₆F₁₄, b.p. 57.23°, *n*_D²⁰ 1.2515.

Pyrolysis of Silver *n*-Perfluorobutyrate at One Atmosphere Argon Pressure.—The results obtained under these conditions are summarized in Table I. The *n*-perfluorohexane boiled at 55-57°; mol. wt. found (Victor Meyer), 337, 340. The perfluorobutyric anhydride had a normal boiling point of *ca.* 110° as obtained from vapor pressure data; mol. wt. found (neutralization equivalent), 410 ± 5; calcd. 410; known⁶ for (CF₃(CF₂)₂CO)₂O, b.p. 107-107.5° (730 mm.).

Pyrolysis of Silver *n*-Perfluorobutyrate *in vacuo.*—Table I summarizes the results obtained under these conditions. The *n*-perfluorohexane boiled at 55-57.5°; mol. wt. found, 340, *n*_D²⁰ 1.2515. Perfluorobutyric anhydride was identified as described in the previous section.

Trace amounts of acid fluoride, but no perfluoropropene, were found in all cases. The acid fluoride fractions were all

combined and found to boil principally at 7-10°; known for C₃F₇COF, b.p. 7-7.5° (741 mm.).⁶ Perfluorobutyryl fluoride reacted with ammonia to give perfluorobutyramide, m.p. 103°; known for C₃F₇CONH₂, m.p. 105°.⁸ The yield of acid fluoride increased in certain experiments in which leaks developed, and the probability of the formation of the more volatile C₂F₅COF was indicated, but not verified.

The Thermal Decomposition of Perfluorobutyric Anhydride in the Presence of Silver Oxide.—Perfluorobutyric anhydride (6.35 g., 0.0155 mole) and silver oxide (3.00 g., 0.0129 mole) were added to the copper vessel and heated at 410-420° under autogenous pressures for four hours. An effective surface of silver oxide was produced by intimately dispersing it over copper wool. The results are tabulated below.

Reaction products	Wt., g.	Conversion, ^a %
(C ₃ F ₇ CO) ₂ O	Trace	...
C ₆ F ₁₄	4.41	84.5
Ag	2.79	100
Ag ₂ O	0	0
CO ₂	1.26	93 ^b
CO	0.065	15
Acid fluoride	<i>ca.</i> 0.68	<i>ca.</i> 10

^a Based on equation (2) and (3). The acid fluoride is formed, of course, through some side reaction. No more than a minute trace of olefin, however, was detected.

^b 15 mole % recovery of CO is equivalent to a total recovery of 7.5% CO₂ in equations (2) and (3).

The perfluorobutyric anhydride was purchased from Columbia Organic Chemicals Co. *n*-Perfluorohexane boiled at 55-57°; mol. wt. found, 338, *n*_D²⁰ 1.2514, in agreement with known values.⁵

Prior to this experiment, another run was carried out under similar conditions, except that a 200% excess of silver oxide was employed. In this case only a 52% conversion to perfluorohexane was obtained. The conversion to carbon dioxide was only 75% and relatively large amounts of acid fluoride (C₃F₇COF and/or C₂F₅COF) were formed. It had been previously noted in various experiments on the thermal decomposition of silver perfluorobutyrate that, when leaks developed in the system and some air inadvertently entered the reaction zone, lower yields of perfluorohexane and higher yields of acid fluorides were obtained. Apparently, oxygen in the air and excess silver oxide are responsible for secondary reactions, and are detrimental to the main degradation process.

Two experiments were also conducted on the thermal decomposition of perfluorobutyric anhydride in the *absence* of any silver oxide. The reactions were carried out at autogenous pressures at 400-435° for three hours. Evidence was obtained for the formation of C₆F₁₄, CO₂ and CO. However, due to laboratory mishaps, no quantitative data can be given. The recovery of appreciable amounts of unreacted anhydride and the formation of substantial quantities of side products, including acid fluorides, point to the fact that silver oxide is probably a favorable catalyst for this degradation as well as a definite reactant.

(5) V. E. Stiles and G. H. Cady, *THIS JOURNAL*, **74**, 3771 (1952).

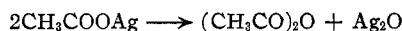
(6) Minnesota Mining and Manufacturing Co., Brochure on Heptafluorobutyric acid.

Pyrolysis of Silver Perfluoropropionate at Autogenous Pressures.—Four pyrolyses were carried out in a copper vessel at autogenous pressures for four hours at 400–440°. The conversions of *n*-perfluorobutane were 73, 76, 82 and 70% of theory, while the conversions to carbon dioxide and carbon monoxide were *ca.* 90 and 10%, respectively. The conversions to metallic silver and silver oxide were *ca.* 90–95% and 5–10%, respectively. The conversions to anhydride were only in the order of a few per cent. Traces of acid fluoride were found in all cases, while in two experiments minute traces of olefin (presumably C₂F₄) were detected.

n-C₄F₁₀ was found to boil at –2°; mol. wt. found (gas density balance), 238 ± 1; calcd., 238; known⁷ for *n*-C₄F₁₀, b.p. –1.7°.

Pyrolysis of Silver Perfluoroacetate at Autogenous Pressures.—The thermal decomposition of silver perfluoroacetate was conducted at 400–440° in the copper vessel at autogenous pressures. Except for the conversion to silver and silver oxide which was *ca.* 90 and 5%, respectively, the yields of volatile products could not be estimated accurately due to handling losses. In addition to the presence of traces of anhydride, small amounts of carbon monoxide, and large amounts of carbon dioxide, the main product was perfluoroethane, b.p. –78° (detd. from vapor pressure data); known b.p. for C₂F₆, –78.29°. No traces of an unsaturated compound were detected.

Pyrolysis of Silver Acetate.—The thermal decomposition of silver acetate (2.1077 g.) was carried out in the unlined quartz vessel under one-atmosphere argon pressure for 2.5 hours at 300–400° (2 hr. at 380–400°). There were isolated: *ca.* 0.6 g. (93%) of acetic anhydride, mol. wt. found (neutralization equivalent), 102 ± 2; calcd., 102; 1.41 g. (96%) of silver oxide, 0.012 g. of silver and 0.016 g. of carbon dioxide. The % conversions to the former two products are based on the reaction



The small quantities of metallic silver and carbon dioxide formed may have indicated that perhaps 1% of ethane was formed. A trace of a volatile liquid did condense in the liquid nitrogen trap and was shown to be unattacked by alkali, but was not identified further.

Thermal Degradation of Silver *n*-Perfluorobutyrate in the Presence of Sulfur.—Silver perfluorobutyrate (3.21 g., 0.010 mole) was intimately mixed with 3.6 g. (0.112 mole) of sulfur and heated in a Vycor glass test-tube at 255° for 30 minutes. The test-tube was attached first to a water-ice cooled trap and then to a Dry Ice refrigerated trap. Perfluorobutyric anhydride (1.91 g., 93%) was collected slowly in the former trap as a water-white colorless liquid which boiled at 106–108°. The latter trap contained a small amount of gas which boiled at *ca.* –10° (known for sulfur dioxide, b.p. –10°). No carbon dioxide was detected. The black molten residue was first extracted with carbon disulfide to remove unreacted sulfur and then exhaustively extracted with cold water. No traces of the soluble silver salt were found, indicating completeness of reaction. The black residue (1.2 g., theory for silver sulfide = 1.24 g.), was silver sulfide, although a small amount of silver oxide may also have been present.

Infrared Absorption Spectrum of *n*-Perfluorohexane.—The infrared spectrum was run on the Baird Associates infrared double beam recording spectrophotometer of Samuel P. Sadtler and Sons, Inc., Philadelphia. It was determined in the liquid phase in a sodium chloride cell of 0.01 mm. thickness. It agreed with the spectrum of a sample of *n*-perfluorohexane kindly supplied to us by Dr. W. H. Pearlson of Minnesota Mining and Manufacturing Company. The band at 7.46 microns is characteristic of the CF₃ group, in contrast to the CF₂ group of perfluoroalkanes.^{9,10} The principal absorption bands (in microns) are: 4.3, 7.46, 8, 8.25, 8.69, 9.04, 9.29, 9.5, 10.08, 10.80, 11.68, 12.24, 12.58, 13.2, 13.5, 13.65, 14.05.

(7) R. D. Fowler, J. M. Hamilton, J. S. Kasper, C. E. Weber, W. B. Burford and H. C. Anderson, *Ind. Eng. Chem.*, **39**, 375 (1947).

(8) E. L. Pace and J. G. Aston, *THIS JOURNAL*, **70**, 566 (1948).

(9) D. C. Smith, J. R. Nielsen, *et al.*, "Spectroscopic Properties of Fluorocarbons and Fluorinated Hydrocarbons," Naval Research Laboratory Report 3567, Washington, D. C., 1949.

(10) M. Hauptschein, C. S. Stokes and E. A. Nodiff, *THIS JOURNAL*, **74**, 4005 (1952).

Discussion and Mechanism

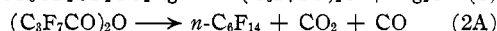
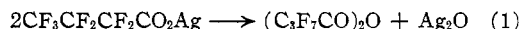
Initial experiments demonstrated conclusively that the pyrolyses of silver perfluoroacetate, silver perfluoropropionate and silver *n*-perfluorobutyrate at *ca.* 400° in closed copper reactors under autogenous pressures afforded excellent yields of perfluoroethane, *n*-perfluorobutane and *n*-perfluorohexane, respectively.

In order to shed some light on the mechanism of these thermal decompositions, a detailed study was made on the pyrolysis of silver *n*-perfluorobutyrate. At temperatures between 260 and 450° and at autogenous pressures, these pyrolyses afforded essentially stoichiometric yields of *n*-perfluorohexane, carbon dioxide and metallic silver in accordance with equation (4).

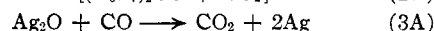
In two of the experiments carried out at "one-atmosphere argon," 90–95% conversions to perfluorohexane and 5% conversions to perfluorobutyric anhydride resulted. In a third run, however, there was only a 65% conversion to perfluorohexane, while a 35% conversion to the anhydride was obtained. Although the reason for this discrepancy is not known, it is significant that the total conversion to the hexane plus anhydride was approximately 100%. These findings pointed to the possibility of the anhydride being the precursor of perfluorohexane. The formation of silver oxide in addition to silver parallels roughly the formation of anhydride. Here again the total conversion to silver plus silver oxide was essentially 100%. Thus the possibility of silver oxide being an intermediate was also indicated.

It was next considered worthwhile to perform the pyrolyses *in vacuo* with the hope of isolating the intermediate products before further decomposition set in. Under these conditions increased amounts of perfluorobutyric anhydride and silver oxide were isolated. At the lowest temperature range the net yields of products, based on reacted salt, were 46 and 36% of anhydride and perfluorohexane, respectively. In most cases carbon monoxide was observed as a product of the decompositions, particularly when silver oxide was also shown to be present.

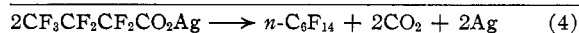
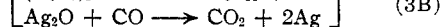
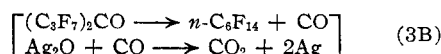
These findings suggest strongly that the principal degradation products are produced in accordance with the scheme



or

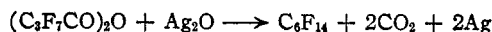


or



Although equation (1) has definitely been established as a primary step in the thermal decomposition, it has been indicated but not proved conclusively, as yet, that perfluorobutyric anhydride is in fact a precursor of perfluorohexane. In order to determine, unequivocally, that anhydride formation is an intermediate step and not a side reaction,

perfluorobutyric anhydride was thermally decomposed in the presence of silver oxide. An 84.5% yield of perfluorohexane was obtained, as well as the theoretical amounts of silver and carbon dioxide. The over-all reaction was thus

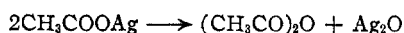


Actually a slight deficiency (84%) of silver oxide was used and it was informative to note that 15% of carbon monoxide (based on equation (2A)) was formed. This is precisely what should be expected if the carbon monoxide formed is oxidized by silver oxide in accordance with equation (3A), a reaction which is known to proceed easily. Thus, convincing evidence has been presented for steps (1), (2A) and (3A). The latter two steps may occur almost simultaneously, since silver oxide also appears to exert a favorably catalytic effect.

Although perfluorodipropyl ketone was not isolated at any time, the possibility of the second part of the degradation proceeding *via* equations (2B) and (3B) cannot be eliminated. In other words, the transient existence of the ketone as an intermediate in equation (2A) is not ruled out.

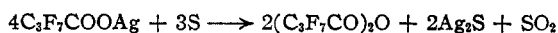
The incomplete oxidation of carbon monoxide by silver oxide may be accounted for as follows. Some of the silver oxide could be rendered ineffective due to being covered by the more plentiful metallic silver. It is significant that CO was found only when Ag_2O also was present.

The pyrolysis of the hydrocarbon silver salt, silver acetate, afforded very high yields of acetic anhydride and silver oxide in accordance with the equation



Kanewskaja and Shemiakin³ considered acetic anhydride to be the primary product of the decomposition, although their experimental conditions³ afforded only 5% anhydride, with a high yield of acetic acid apparently due to the ease of hydration of acetic anhydride. Under the rigorously anhydrous conditions employed in the present work this secondary reaction did not occur to any appreciable extent. It should also be added that no more than traces of the coupling product, ethane, were formed under our conditions, while none was reported by the previously mentioned investigators.³

Since sulfur is both a fairly good reducing and oxidizing agent, it was of interest to examine the thermal degradation of silver perfluorobutyrate in the presence of molten sulfur. It was also thought that this procedure might possibly afford a simple method for the synthesis of perfluoropropyl monosulfide. This compound was formed only in very small amounts by the reaction of 1-iodopropane with sulfur which yielded principally perfluoropropyl disulfide and trisulfide.¹¹ However, at a temperature of 255° this degradation proceeded in accordance with the over-all equation

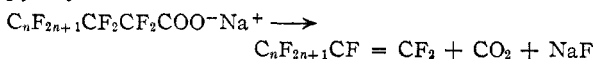


Haszeldine^{2b} obtained perfluoroacetic anhydride

(11) M. Hauptschein and A. V. Grosse, *THIS JOURNAL*, **73**, 5461 (1951).

by heating silver perfluoroacetate with sulfur at 300°. It would seem that sulfur and probably silver sulfide, in contrast to silver oxide, does not catalyze the further decomposition of the perfluoroanhydrides at these aforementioned temperatures. It is nevertheless possible that the first step in these degradations is also the formation of anhydride and silver oxide. The latter, however, is readily converted into silver sulfide by interaction with the excess sulfur always present.

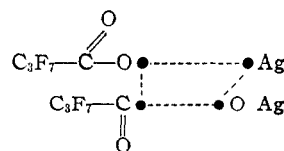
The profoundly different mode of thermal decomposition exhibited by silver and sodium salts of perfluorocarboxylic acids merits comment. The very highly polar links of the electrovalent sodium salt would favor heterolytic thermal decomposition. The affinity of the very electropositive sodium ion for the most electronegative fluoride ion (to form sodium fluoride) further reduces the activation energy necessary for heterolytic fission. The pyrolysis of the sodium salt²



probably involves the elimination of a beta fluoride ion from a perfluoroalkyl anion subsequent to (or perhaps simultaneous with) the "ionic" release of carbon dioxide, as proposed by Haszeldine.^{2b}

By way of contrast, silver has a much higher ionization potential than the alkali metals, and silver perfluorobutyrate, for example, must possess a considerable amount of covalent character as evidenced by its miscibility with organic solvents such as benzene. Homolytic thermal decomposition is clearly favored in this case. The formation of anhydride as shown in equation (1) may involve the transient formation of the free radicals, $\text{C}_3\text{F}_7\text{COO}\cdot + \cdot\text{Ag}$. The activated silver atom attacks the single-bonded oxygen of an adjacent molecule instantaneously, *i.e.*, radical displacement on oxygen, with liberation of silver oxide and simultaneous association of the transient $\text{C}_3\text{F}_7\text{CO}\cdot$ and $\text{C}_3\text{F}_7\text{COO}\cdot$ radicals.¹²

All of these steps would have to take place in the condensed phase almost simultaneously. It may also be possible that the thermally activated molecules undergo these rearrangements without primary dissociation as shown schematically by the transition complex



which breaks down into $(\text{C}_3\text{F}_7\text{CO})_2\text{O} + \text{Ag}_2\text{O}$.

It is of interest to compare the thermal decomposition of "fluorocarbon" anhydrides with that of the "hydrocarbon" anhydride, acetic anhydride. Szwarc and Murawski¹³ have shown that the de-

(12) It is recognized that the perfluoroacyl and -acyloxy radicals are decomposed easily under these pyrolytic conditions into perfluoropropyl radicals, carbon monoxide and carbon dioxide. Although our findings do not preclude the possibility that dimerization of the $\text{C}_3\text{F}_7\text{CO}\cdot$ radicals prior to the formation of the anhydride may occur concurrently, the significant quantity of anhydride actually isolated suggests that this explanation cannot account for most of the products obtained.

(13) M. Szwarc and J. Murawski, *Trans. Faraday Soc.*, **47**, 269 (1951).

composition of acetic anhydride is a truly unimolecular dissociation process forming ketene and acetic acid, and that the decomposition does not involve radicals. The vastly different nature of the decomposition of perfluorobutyric anhydride, for example, makes it likely, although not certain, that a radical mechanism is involved. Perfluorohexane may, accordingly, be formed as a result of the direct combination of the transient perfluoropropyl radicals in a ternary collision (with a solid or wall). Hodgins and Haines¹⁴ have shown that the reaction between atomic sodium and iodotrifluoromethane in a diffusion flame apparatus results in

(14) J. W. Hodgins and R. L. Haines, *Can. J. Chem.*, **30**, 473 (1952).

the formation of hexafluoroethane from the combination of two trifluoromethyl radicals.

Finally, from a synthetic standpoint, the thermal degradations of silver salts or of anhydrides of perfluoro acids, $C_nF_{2n+1}COOH$, afford excellent methods for the preparation of higher molecular weight fluorocarbons of known structure, $C_{2n}F_{4n+2}$, possessing even-numbered carbon atoms.¹⁵

Acknowledgment.—The authors wish to express their thanks to Dr. A. V. Grosse for his advice and stimulating interest, and to Mr. C. S. Stokes for technical assistance.

(15) For another, but less convenient, synthesis of this type see M. Hauptschein and A. V. Grosse, *THIS JOURNAL*, **74**, 4454 (1952).

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

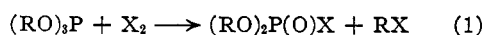
The Reactions of Phenyl Esters of Phosphorous Acid with Iodine¹

By JAMES P. FORSMAN AND DAVID LIPKIN

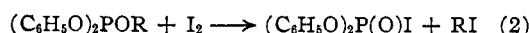
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The reactions of iodine with triphenyl phosphite, cyclohexyl diphenyl phosphite and 1,2:5,6-diisopropylidene-D-glucose 3-diphenylphosphite were investigated. In the case of all three esters an important reaction is the formation of phosphite polyiodides. Conditions for the reaction of the cyclohexyl ester were found, however, which lead to excellent yields of cyclohexyl iodide. Two phosphorus compounds of novel structure were obtained from the reaction of anhydrous ammonia with a solution of triphenyl phosphite and iodine.

Various investigators have studied the reactions of trialkyl phosphites with chlorine, bromine, iodine and cyanogen iodide.² The reactions are rapid and may be represented by the over-all equation



The reactions of triaryl phosphites with halogens have been investigated less extensively.³ The reaction of an aryl ester such as triphenyl phosphite with chlorine or bromine has been reported to yield the dichloride, $(C_6H_5O)_3PCl_2$, or dibromide, $(C_6H_5O)_3PBr_2$, respectively. The reaction of iodine with triaryl phosphites has not been reported previously in the literature. As a consequence of our interest in the synthetic possibilities of the reaction



we studied the reactions of iodine with triphenyl phosphite, cyclohexyl diphenyl phosphite and 1,2:5,6-diisopropylidene-D-glucose 3-diphenylphosphite.

Even in the case of the relatively simple triphenyl ester, the reaction with iodine is complex. Three unstable, crystalline products were isolated from this reaction, but only two of these could be identified. The latter proved to be the tetraiodide, $(C_6H_5O)_3PI_4$, and the enneaiodide, $(C_6H_5O)_3PI_9$. The expected diiodide, $(C_6H_5O)_3PI_2$, was not isolated and identified. The reaction of triphenyl phosphite with iodine in the presence of anhydrous

ammonia, under conditions such that precipitation of polyiodides does not take place, also yielded two new crystalline compounds, $(C_{18}H_{15}O_3P)_2NI_3$ and $(C_{18}H_{15}O_3P)_2NI$.

Polyiodides of unknown composition are formed in the reaction of iodine with the other two esters. Under suitable conditions, however, cyclohexyl diphenyl phosphite and iodine react almost quantitatively according to equation (2). On the other hand, reaction conditions leading to the formation of 3-iodo-3-deoxy-1,2:5,6-diisopropylidene-D-glucose from the glucose phosphite and iodine were not found.

Experimental⁴

Because of the nature of the reactions involved, scrupulously anhydrous conditions and equipment were used throughout this work. The chloroform and ethyl ether also were treated to remove alcohol. The petroleum ether used was a fraction boiling at 32–37° and the ligroin was a fraction boiling at 65–68°.

Preparation of Diphenyl Chlorophosphite.—To 857 g. (5.60 moles) of phenol (Mallinckrodt A. R. grade) in a round-bottom flask fitted with a dropping funnel, thermometer and condenser filled with Dry Ice, was gradually added 513 g. (3.74 moles) of phosphorus trichloride (Mallinckrodt A. R. grade). After the addition of the acid chloride to the phenol was completed (1–3 hr.), the funnel was replaced by a gas inlet tube through which a slow stream of dry nitrogen was introduced. The reaction mixture was then heated during the course of four hours to a temperature of 175° and kept at this temperature for one hour. Distillation at a rapid rate of the resulting mixture yielded 428 g. of a colorless liquid, b.p. 101–125° (0.15 mm.). Redistillation⁵ of this fraction through a one-meter column packed with glass helices gave 350 g. (50% yield based on phenol) of diphenyl chlorophosphite, b.p. 146.5–148.0° (4 mm.), n_D^{20} 1.5789.

(4) All boiling points are uncorrected. Melting points are corrected.
(5) Since diphenyl chlorophosphite disproportionates to phosphorus trichloride, phenyl dichlorophosphite and triphenyl phosphite, even on storage at –20°, it was always redistilled just prior to use.

(1) The material herein presented is taken from the Ph.D. thesis (Washington University, September, 1952) of James P. Forsman.

(2) (a) R. B. Fox and L. B. Lockhart, "The Chemistry of Organophosphorus Compounds," Naval Research Laboratory, Washington, D. C., 1948, p. 62; (b) W. Gerrard and N. H. Philip, *Research*, **1**, 477 (1948); (c) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 197–198.

(3) Reference 2c, pp. 325 and 329.