practically the same conductance, which is markedly greater than that of the iodide ion[2g] (6%). In ethylene chloride, the conductances of the iodide,[6] bromide and chloride[2h] ions stand in the ratio of the numbers 1:1.12:1.30. In this connection, we may recall the very low conductance of the sodium, lithium and fluoride ions in pyridine.

The highest conductance measured for any ion in pyridine is 52.6 for the nitrate ion containing four atoms; that of the chloride ion is 51.4. The perchlorate ion, with five atoms, has a conductance of 47.6.[2g] In ethylene chloride, the perchlorate and the nitrate[2c] ions have practically the same conductance, 40.0 and 40.1, respectively.

In pyridine, the choline ion ($HOC_2H_4 \cdot Me_3N^+$) with seven atoms has a conductance of 33.4, the conductance of the ethyltrimethylammonium ion (6 atoms) is 41.8.[2h] In ethylene chloride, the conductance of the choline ion is 40.4 while that of the ethyltrimethylammonium ion is 42.1.[2d] In nitrobenzene, the two ions have the same conductance, 17.1.[2i]

We have already pointed out that conductances in pyridine are generally higher than in ethylene chloride although the latter solvent has the lower viscosity. There is another marked difference between the two solvents. In ethylene chloride, positive and negative ions containing the same number of atoms and of similar structure have approximately the same conductance. Thus, the conductance of the BF_4^- ion is 42.7,[2f] while that of the tetramethylammonium ion is 42.6[2c]; that of the perchlorate ion is 40.0. In pyridine, the conductance of the perchlorate ion is 47.6[2g] while that of the tetramethylammonium ion is 43.0.[2h] In ethylene chloride the conductance values for the acetate and chloroacetate ions, are, respectively, 39.4 and 35.3; in pyridine, they are 51.8 and 50.1.

It appears that while positive and negative ions of the same size and similar structure have approximately the same conductance in ethylene chloride, the negative ions have a markedly greater conductance than positive ions in pyridine.

The conductance of an ion is determined by its interaction with the dipole molecules of the solvent medium. It is doubtful if the term "size" has physical meaning here.

PROVIDENCE, R. I. RECEIVED DECEMBER 14, 1950

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[6] H. L. Pickering and C. A. Kraus, THIS JOURNAL, **71**, 3288 (1949).

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

Perfluoroalkyl Halides Prepared from Silver Perfluoro-fatty Acid Salts. I. Perfluoroalkyl Iodides

BY MURRAY HAUPTSCHEIN AND ARISTID V. GROSSE

A general method for the synthesis of perfluoroalkyl iodides and diiodides by the action of iodine on the corresponding silver perfluoro-fatty acid salt is described. The preparation of iodotrifluoromethane, iodopentafluoroethane, and the new compounds 1-iodoheptafluoropropane and 1,3-diiodohexafluoropropane are reported as representative examples. Various physical constants and the infrared spectra of the latter three compounds are given.

We wish to report an extension and generalization of the method recently reported by Henne and Finnegan[1] for the preparation of iodotrifluoromethane. The present paper deals with the preparation of the important perfluoroalkyl iodides, but the method has also been demonstrated to be equally well adapted to the preparation of perfluoroalkyl chlorides and bromides which will be published in future papers.

Iodotrifluoromethane, iodopentafluoroethane, 1-iodoheptafluoropropane and 1,3-diiodohexafluoropropane have been synthesized by reaction with silver trifluoroacetate, silver pentafluoropropionate, silver heptafluoro-*n*-butyrate and silver hexafluoroglutarate, respectively, in the presence of an excess of iodine. The latter two representative reactions are given by the equations

$$CF_3CF_2CF_2CO_2Ag + I_2 \longrightarrow CF_3CF_2CF_2I + AgI + CO_2 \quad (1)$$

and

$$AgO_2CCF_2CF_2CF_2CO_2Ag + 2I_2 \longrightarrow ICF_2CF_2CF_2I + 2AgI + 2CO_2 \quad (2)$$

Preliminary attempts were made to carry out these degradations in refluxing chlorobenzene. However, practically no carbon dioxide gas was generated, and the principal products appeared to be the free perfluoro acid and *p*-iodochlorobenzene formed presumably from the attack of the perfluoroacyl radicals on the solvent by abstraction of a hydrogen atom and iodination of the aromatic nucleus. It was found, however, that by the controlled thermal decomposition of the dry silver salt and a ten per cent. excess of iodine, *in the absence of a solvent*, iodotrifluoromethane, iodopentafluoroethane, 1-iodoheptafluoropropane[2] and 1,3-diiodohexafluoropropane were formed in 95, 86, 87–93 and 18% yield, respectively. In the latter case, evidence is presented in the experimental section which indicates strongly that the reaction proceeded to a large extent by a route different from that shown in equation 2, with the production of perfluorobutyrolactone. The formation of the product can be easily accounted for by the cyclization of the gamma iodo salt, $ICF_2CF_2CF_2CO_2Ag$, to form silver iodide and the lactone. The physical constants of the perfluoroalkyl iodides are presented in Table I, and the infrared spectra[3] are shown in Figs. 1, 2 and 3. As

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[1] A. L. Henne and W. G. Finnegan, THIS JOURNAL, **72**, 3806 (1950). Our work has been carried out independently of these investigators.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949), found that 1-iodoheptafluoropropane was one of the products formed in the reaction of iodotrifluoromethane with tetrafluoroethylene, but no physical constants were reported.

[3] Determined with a Baird Associates Infrared Recording Spectrophotometer by Samuel P. Sadtler and Sons, Inc., Philadelphia.

TABLE I

PHYSICAL PROPERTIES

Compound	F.p., °C.	B.p., °C.	n^{20}_D	d^{20}_4	d^0_4	$\Delta d/\Delta t$	*MR* Found[a]	*MR* Calcd.[b]	AR_F[c]
$CF_3CF_2CF_2I$	....	41.2	1.3272	2.0626[d]	2.1306	−0.00340[g]	29.13	29.76	1.14
$ICF_2CF_2CF_2I$	(*ca.*) −25	131	1.4516	2.5812	2.6302	− .00245[h]	42.19	42.43	1.19
CF_3CF_2I	....	12.5	1.339(0°)	2.0850[e]	2.1605[e]	− .00377[i]	(23.80)[f]	24.89	(1.01)[f]

[a] *MR* (Found) denotes the molecular refraction calculated by Lorentz–Lorenz formula. [b] *MR* (Calcd.) denotes the molecular refraction calculated by adding the customary increments for C, I and F, using $AR_F = 1.23$ which is the best value for fluorine in fluorocarbons only. [c] AR_F is the atomic refraction for fluorine, obtained from *MR* (Found) by subtracting the customary increments for C and I. [d] The density measurements were made by E. A. Nodiff of the Research Institute. [e] Measured in special sealed pycnometer. [f] Value is only approximate because the measured n^0_D is approximate. [g] Average temperature coefficient of density in g./(cc.)(°C.) over the temperature range 0–28.5°. [h] Over the temperature range 0–26.7°. [i] Over the temperature range 0–23.5°.

would be expected for these fluorocarbon derivatives, the spectra show relatively little absorption below 7.0 microns. The fact that sharp and intense absorption bands are found at 7.52 microns for C_2F_5I and C_3F_7I but not for I-$(CF_2)_3$-I may be due to the presence of the $-CF_3$ group in the former cases. The generally strong absorption in the region from 8.0 to 8.9 microns present in all cases is characteristic of fluorocarbon spectra. The reactions of these perfluoroalkyl iodides are being investigated.

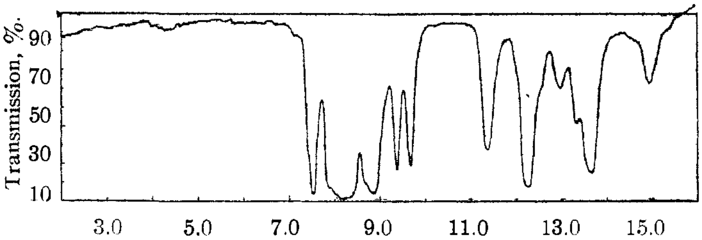

Fig. 1.—Infrared absorption spectrum of 1-iodoheptafluoropropane (cell thickness 0.01 mm.).

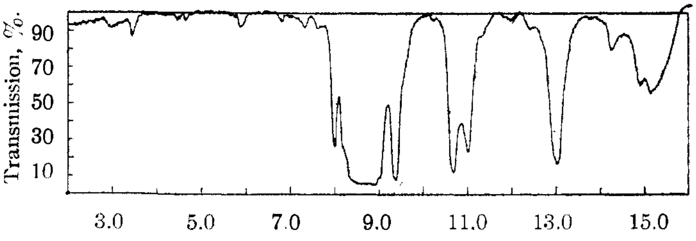

Fig. 2.—Infrared absorption spectrum of 1,1-diiodohexafluoropropane (cell thickness 0.01 mm.).

Experimental

Preparation of the Silver Salts.—All of the silver salts were prepared in nearly quantitative yields by the method described below for silver *n*-heptafluorobutyrate. The melting points of the analytically pure salts are recorded for the first time. Silver pentafluoropropionate and silver perfluoroglutarate are new compounds.

Silver *n*-heptafluorobutyrate was prepared by adding a slight excess of silver oxide with stirring to an aqueous solution of heptafluorobutyric acid (Minnesota Mining and Manufacturing Company) kept at 50–60°. The unreacted silver oxide was filtered off, and the clear solution was subjected to a number of evaporations and crystallizations which yielded several crops of pure white silver salt, which were dried over phosphorus pentoxide. An average yield of 95% of dry crystalline salt, m.p. 292–294° (melting to a clear liquid), was obtained. It was analyzed for silver by the Volhard method. *Anal.* Calcd. for $C_4F_7O_2Ag$: Ag, 33.62. Found: Ag, 33.65. Silver trifluoroacetate, m.p. 251–255°, was used. *Anal.* Calcd. for $C_2F_3O_2Ag$: Ag, 48.84. Found: Ag, 48.76. Silver pentafluoropropionate melted at 240.5–242.5°. *Anal.* Calcd. for $C_3F_5O_2Ag$: Ag, 39.82. Found: Ag, 39.79.

Perfluoroglutaric acid was prepared by the alkaline oxidation of $\overline{\mathrm{CCl{=}CClCF_2CF_2CF_2}}$ (Hooker Electrochemical Company) according to the method of Henne and Zimmerschied[4] in 87% yield. The acid was converted to the white crystalline silver salt which did not melt at 300°.

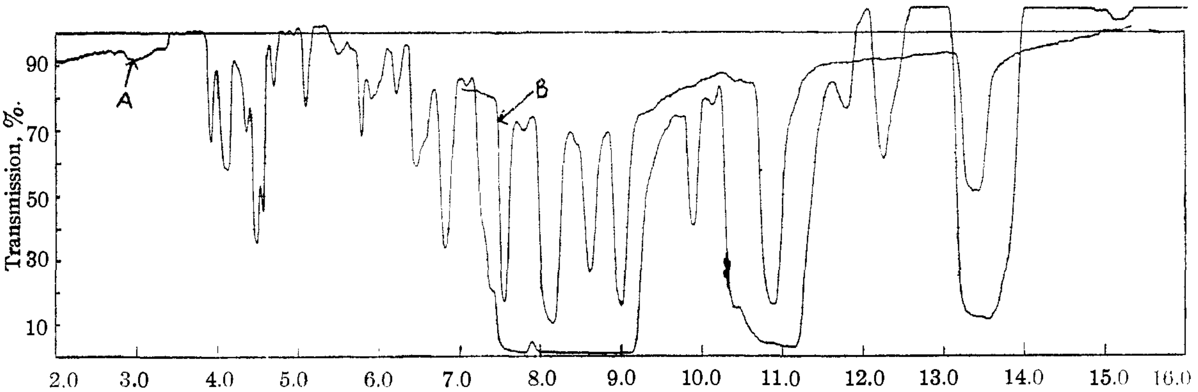

Fig. 3.—Infrared absorption spectrum of iodopentafluoroethane (Curve A is for vapor at 760 mm.; Curve B is for vapor diluted with dry nitrogen gas; a 5-cm. cell was used in both cases).

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(4) A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, 67, 1235 (1945).

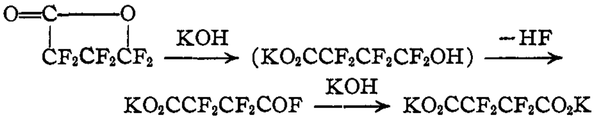
Anal. Calcd. for $C_5F_6O_4Ag_2$: Ag, 47.54. Found: Ag, 47.48.

Reaction of Silver *n*-Heptafluorobutyrate with Iodine.—A well-dispersed mixture of finely powdered dry silver salt (7.03 g. or 0.0219 mole) and powdered iodine (5.71 g. or 0.0225 mole) was sealed in a 150-ml. Pyrex bulb, and heated at 100° for 24 hours with occasional shaking. The bulb was then cooled to room temperature, and subsequently opened to a system for measuring the amount of carbon dioxide generated, which was found to be approximately 90% of theory based on equation (1). The silver iodide formed amounted to 5.1 g. or 99% of theory. A yield of 6.0 g. of pure 1-iodoheptafluoropropane was obtained corresponding to 93%. Although this technique was excellent for small scale operations, it was preferable to carry out this reaction at atmospheric pressure for any large-scale reaction. For this purpose a special reaction flask of 500-ml. capacity was designed, equipped with a sealed on tube 11 cm. high and 18 mm. in diameter above which was sealed on a Dry Ice reflux condenser. The flask was also equipped with a sealed Hershberg stirrer and an entrance tube for "sweeping out" the volatile product with dry nitrogen when desired. The "Dry Ice refluxer" was connected to a Pyrex trap immersed in a Dry Ice–acetone mixture to which was attached a sulfuric acid bubbler which indicated the rate of evolution of carbon dioxide. In operation, most of the flask was immersed in a boiling water-bath, and as the reaction proceeded the liquid iodide formed was observed to reflux in increasing quantity. Some iodine would sublime in the 11-cm. tube, but most of it could be returned to the reaction flask by gentle heating with a flame to melt the iodine. After a period of time the bubbling of carbon dioxide would decrease and it was found that the rate of reaction could be increased considerably by simply sweeping all of the fluorocarbon iodide by a stream of dry nitrogen into the cooled trap connected to the system. In this manner the reaction was easily controlled. In one run 74.0 g. (0.23 mole) of powdered silver salt was thoroughly mixed with 64.4 g. (10% excess) of powdered iodine, and the reaction was completed after three hours at 100°. The theoretical amount of silver iodide and 59.1 g. (86.7% yield) of pure 1-iodoheptafluoropropane were formed. Purification was accomplished by treating the crude product (62.4 g.) with "molecular" silver to remove any free iodine and with anhydrous potassium fluoride to remove any water or hydrogen fluoride which may have been present. The purified product was transferred under vacuum to a fractionating unit and was found to boil at 40–42° (mostly 41.2° at 760 mm.). C_3F_7I distills as a water-white liquid, but when exposed to air and light turns slowly pink. *Anal.*[5] Calcd. for C_3F_7I: C, 12.18; I, 42.90; mol. wt., 296.0. Found: C, 12.27; I, 43.19; mol. wt., 296.7.

Reaction of Silver Perfluoroglutarate with Iodine.—Preparation of 1,3-diiodohexafluoropropane was accomplished similarly in the special reaction flask described above. The reaction did not commence until heated to 120° in an oil-bath, and it tended to escape control so that it was necessary at one point to cool the reaction flask with cold water. There was obtained 7.78 g. (18.2% yield) of the diiodide which boiled at 131° at 760 mm.

Anal.[5] Calcd. for $C_3F_6I_2$: C, 8.92; I, 62.85; mol. wt., 403.9. Found: C, 9.02; I, 61.83; mol. wt., 405.5.

On exposure to air and light, $ICF_2CF_2CF_2I$ turns slowly pink and then purple. In addition 11.5 g. of a gaseous compound was isolated of estimated boiling point in the neighborhood of 0°. This compound was extremely reactive and caused considerable etching of the apparatus in the presence of atmospheric moisture. It reacted immediately when bubbled through water or 10% potassium hydroxide solution. Acidification of the latter solution with concentrated sulfuric acid, extraction with ether, and subsequent evaporation of the ethereal layer yielded a white crystalline solid which was shown to be a strong organic acid soluble in acetone but only slightly soluble in benzene. It melted at 84–85° and had a neutral equivalent of 96.9. Pure perfluorosuccinic acid melts at 86.5–87.4°[6] and has a theoretical neutral equivalent of 95.0. Thus the white solid was undoubtedly perfluorosuccinic acid. All these considerations made it very probable that the original reactive gaseous compound was perfluorobutyrolactone which should easily hydrolyze as follows to form perfluorosuccinic acid.



Preparation of Iodotrifluoromethane.—By the same method iodotrifluoromethane was prepared at about 120° in 95% yield.

Preparation of Iodopentafluoroethane.—Employing the same special reaction flask, the controlled degradation of silver pentafluoropropionate in the presence of a 10% excess of iodine at 100° resulted in the formation of an 85.8% yield of iodopentafluoroethane, b.p. 12.5° at 760 mm., mol. wt. found 242, calcd. 246; lit. b.p. 13°.[7]

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[5] Analysis by Clark Microanalytical Laboratory, Urbana, Illinois.

[6] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

[7] H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2948 (1949).