altered, and probably in such a way as to influence particularly the poisoning that normally occurs during synthesis. By the proper choice of such additives, it appears possible to obtain further information about the nature of the catalysts involved and the mechanisms of the surface reactions occurring, and to modify catalysts so as to improve oil yields, increase catalyst stability, and to extend the range of synthesis temperatures.

PROVIDENCE, RHODE ISLAND RECEIVED AUGUST 20, 1951

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Properties and Reactions of Perfluorobutyrolactone

BY MURRAY HAUPTSCHEIN, CHARLES S. STOKES AND ARISTID V. GROSSE

Various physical and chemical properties of perfluorobutyrolactone are described. This novel type lactone reacts with water, ethanol, ammonia, hydrogen iodide and ethyl mercaptan to form the perfluorosuccinic acid, ethyl ester, amide, mixed acyl fluoride–acyl iodide and dibasic thiol ester, respectively. The latter derivative is the first member of a new class of compounds to be reported. A general mechanism for these reactions has been elucidated. The method of formation of perfluorobutyrolactone was shown not to be general. Perfluorovalerolactone was not detected in the corresponding reaction of silver perfluoroadipate with iodine, 1,4-diiodoöctafluorobutane being the only organic product isolated. Several infrared spectra are given and discussed.

In a previous communication[1] we had presented evidence which proved that perfluorobutyrolactone was the main product formed by the thermal degradation of silver hexafluoroglutarate with an excess of iodine. We have now actually isolated this perfluorolactone, b.p. 18°, m.p. −59°, $d^{-32.4}_4$ 1.6646, $d^{-42.2}_4$ 1.6889, in a very pure state under rigorously anhydrous conditions. The infrared absorption spectrum (Fig. 1) is relatively simple and demonstrates the absence of any hydrogen in the molecule. The sharp and intense band at 5.34 microns is indubitably due to the lactone carbonyl group. The normal hydrocarbon lactones have a band at 5.5–5.7 microns and there is therefore a shift to shorter wave lengths in the case of the fluorocarbon analogs.

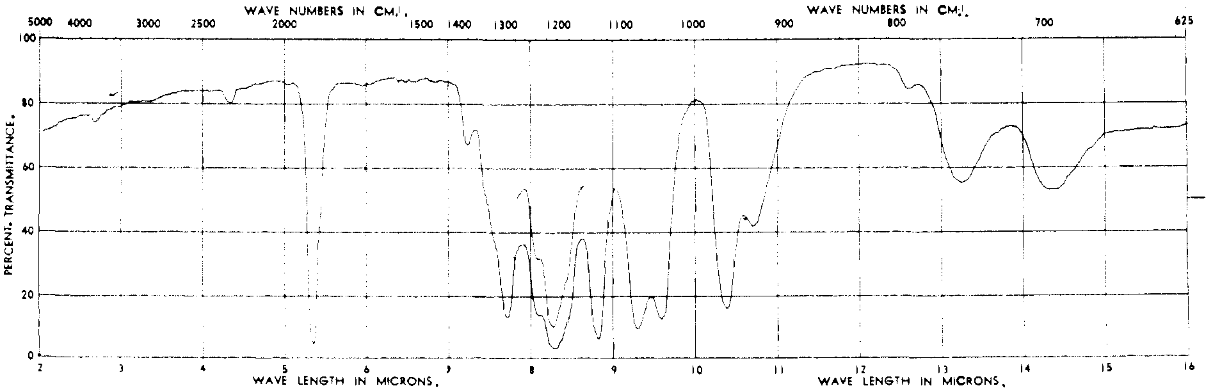
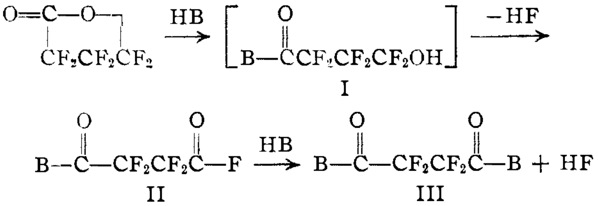


Fig. 1.—Infrared absorption spectrum of perfluorobutyrolactone determined with a Baird Associates Infrared Double Beam Recording Spectrophotometer of Samuel P. Sadtler and Sons, Inc., Philadelphia. A 5-cm. gas cell consisting of sodium chloride prisms in which all optics were sealed with paraffin wax was used. The cell was first flushed out with dry nitrogen gas to exclude moisture, and the anhydrous lactone was distilled into the cell at atmospheric pressure.

It is of interest to mention at this point that the thermal degradation of silver perfluoroadipate with iodine did not yield any perfluorovalerolactone, but proceeded in the "normal" manner to form the corresponding diiodide, $ICF_2CF_2CF_2CF_2I$,[2] b.p. 150°, m.p. −9°, d^{27}_4 2.4739, d^{0}_4 2.5466, $n^{26.2}_D$ 1.4273, n^{0}_D 1.4401, MR_D found 46.98, AR_F 1.19.

The infrared spectrum of this perfluoro diiodide (Fig. 2) is quite similar to that of 1,3-diiodohexafluoropropane.[1]

The highly reactive perfluorobutyrolactone has been allowed to react with water, ethanol, ammonia, hydrogen iodide and ethyl mercaptan to form products that are accounted for by the following general mechanism.



When B corresponded to OH, OC_2H_5, NH_2 and SC_2H_5, $HOOC–CF_2CF_2–COOH$, $C_2H_5O–OC–CF_2CF_2COOC_2H_5$, $H_2NOCCF_2CF_2CONH_2$ and $C_2H_5S–$

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(1) M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951). See also M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 848 (1952).

(2) R. N. Haszeldine, *Nature*, **167**, 139 (1951), found that 1,4-diiodoöctafluorobutane was one of the products formed in the addition polymerization of tetrafluoroethylene and tetrafluorodiiodoethane, but no physical constants were reported.

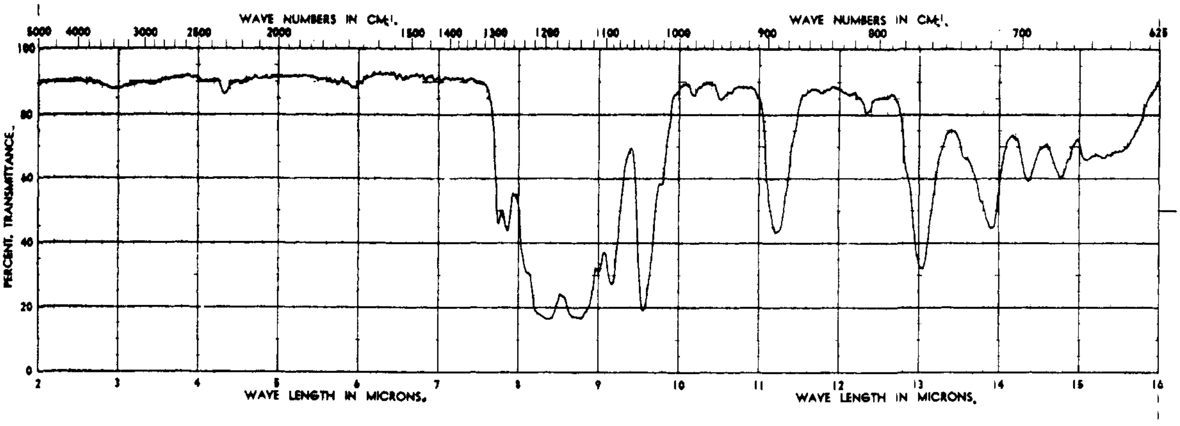


Fig. 2.—Infrared absorption spectrum of 1,4-diiodoöctafluorobutane taken in 0.01-mm. liquid cell.

$OC{-}CF_2CF_2COSC_2H_5$ were formed, respectively, in practically quantitative yields at room temperature or below. Formula III was the product actually isolated in all of these cases. When B equals I, formula II ($IOCCF_2CF_2COF$) was formed, which on the addition of water rapidly hydrolyzed to tetrafluorosuccinic acid (corresponding to III). The hydrogen iodide reaction was considerably slower than the other four reactions.

The reaction with water was determined quantitatively. It is observed that one mole of perfluorobutyrolactone should form four equivalents of acid, *i.e.*, one mole of the dibasic tetrafluorosuccinic acid and two moles of hydrofluoric acid. On titration with alkali of a mole of lactone there was actually found a total of 4.0 equivalents of acid. Furthermore, 2.0 moles of fluoride ion (HF) was shown to be present. The remaining 2 equivalents of acid was proven to be tetrafluorosuccinic acid (1 mole). These results can be applied with equal validity to the other reactions since in all cases the only products formed were various derivatives of tetrafluorosuccinic acid and hydrogen fluoride or SiF_4 from the reaction with glass (ammonium fluoride in the case of the ammonia reaction).

The compound diethyl dithioltetrafluorosucci-

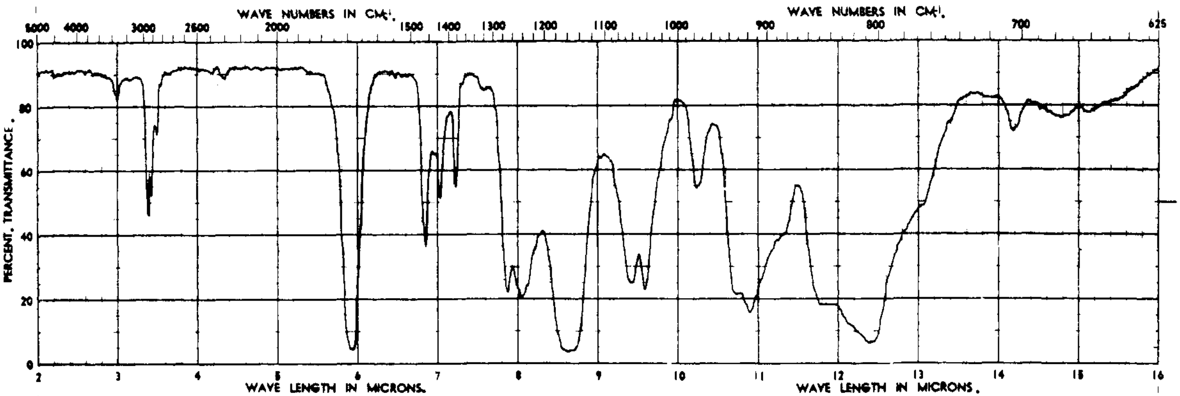


Fig. 3.—Infrared absorption spectrum of diethyl dithiotetrafluorosuccinate taken in 0.01-mm. liquid cell.

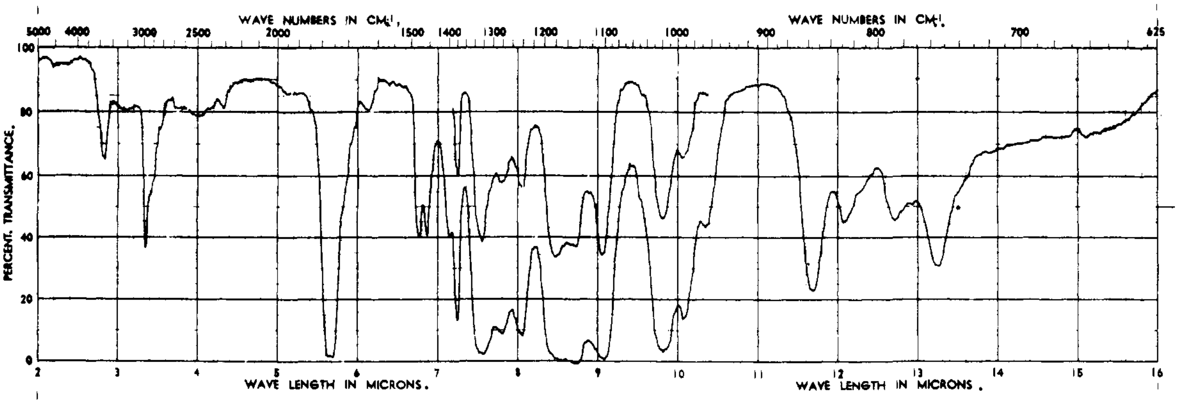


Fig. 4.—Infrared absorption spectrum of diethyl tetrafluorosuccinate taken in 0.01-mm. liquid cell (top curves taken in 0.005-mm. liquid cell).

nate is the first thiol ester of a perfluorodibasic acid to be reported. It boils at 108° at 8 mm., m.p. *ca.* 10°, n^{19}D 1.4519, n^{40}D 1.4428. It forms an insoluble lower layer in water or 5% aqueous potassium hydroxide. It is of interest to compare the infrared absorption spectrum of this thiol ester (Fig. 3) with that of diethyl tetrafluorosuccinate (Fig. 4). The sharp band at 5.93 microns in Fig. 3 corresponds to the thiol ester carbonyl group. The ethyl ester itself has a sharp absorption band at 5.68 microns. Three bands which are present only in the fluorothiol ester at 10.9, 12.4 and 14.18 microns may be due to the presence of sulfur in this compound only.

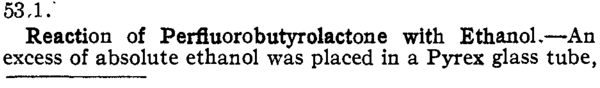
Experimental

Preparation of Perfluorobutyrolactone.—Perfluorobutyrolactone was prepared by the reaction of silver perfluoroglutarate with iodine at a temperature of approximately 120° as described previously.[1] The theoretical amount of AgI was formed and the yield of lactone varied from 44 to 56% in several runs. The other product, 1,3-diiodohexafluoropropane, was formed in 10–18.2% yield. The lactone was treated with anhydrous potassium fluoride to ensure the removal of traces of hydrogen fluoride and water, and then transferred *in vacuo* into a modified Booth–Podbielniak low temperature fractionating unit, in which the boiling point, freezing point and vapor density could be determined under rigorously anhydrous conditions. Aside from a small amount of product which boiled at −8 to 18°, almost all of the product was found to boil at 18°, f.p. −59°. The density of the liquid lactone was determined in a sealed dilatometer.

Anal.[3] Calcd. for $C_4F_6O_2$: mol. wt., 194; O, 16.49. Found: mol. wt., 194; O, 16.40, 16.62.

The pure, water-white, perfluorobutyrolactone was sealed *in vacuo* in several Pyrex tubes. The lactone is sensitive to even minute traces of water. At room temperature slight etching of the Pyrex glass was noticeable, but it could be eliminated by prior degassing with a mercury diffusion pump. Reaction with the glass could be avoided also by storage in Dry Ice at a temperature below the freezing point of the lactone, and by the addition of a small amount of anhydrous KF which served as a getter.

Reaction of Perfluorobutyrolactone with Water.—This reaction was determined quantitatively by titration with alkali and determining the ionizable fluorine as fluoride ion. The over-all reaction is



$$\text{O=C—O}\;\;\text{CF}_2\text{CF}_2\text{CF}_2 + 4\text{NaOH} \longrightarrow \text{NaO}_2\text{CCF}_2\text{CF}_2\text{CO}_2\text{Na} + 2\text{NaF} + 2\text{H}_2\text{O}$$

It was found that 1 mole of lactone corresponded to a total of 3.99 equivalents of acid and 1.96 equivalents of fluoride ion. The difference of 2.03 equivalents of acid corresponded to 1.015 moles of tetrafluorosuccinic acid. This acid was actually isolated[1] and the silver salt derivative was prepared by neutralization with silver oxide.

Anal. Calcd. for $C_4F_4O_4Ag_2$: Ag, 53.4. Found: Ag, 53.1.

Reaction of Perfluorobutyrolactone with Ethanol.—An excess of absolute ethanol was placed in a Pyrex glass tube, and perfluorobutyrolactone was transferred *in vacuo* to the liquid nitrogen cooled tube, which was then sealed off. An immediate reaction ensued upon warming up to the melting point of the reactants. There were formed in essentially quantitative yields hydrogen fluoride and diethyl tetrafluorosuccinate, b.p. 88° at 15 mm., $n^{28.2}$D 1.3642; known[4] b.p. 89° at 15 mm., n^{20}D 1.3690.

Reaction of Perfluorobutyrolactone with Ammonia.—In a similar manner perfluorobutyrolactone and dry liquid ammonia reacted immediately and quantitatively to form ammonium fluoride and tetrafluorosuccinamide. The ammonium fluoride was separated by extraction with water and the insoluble diamide melted at 258–259.5° after a single recrystallization from dioxane; known m.p. 259.8–260.3°,[5] 255–260°.[6]

Reaction of Perfluorobutyrolactone with Hydrogen Iodide.—Perfluorobutyrolactone was transferred *in vacuo* to a liquid nitrogen cooled Pyrex tube containing a slight excess of anhydrous hydrogen iodide, prepared by treating red phosphorus with iodine and water, drying over Drierite and redistilling. In contrast to the preceding experiments, no reaction was immediately evident in the sealed tube. Two immiscible layers were formed at temperatures up to 0°, but after standing at room temperature overnight, reaction was nearly complete. The two products formed were hydrogen fluoride and a liquid which fumed vigorously in air and boiled at a temperature higher than 120°. This impure product was shown to be $FOCCF_2CF_2COI$ by the following reactions. It reacted immediately with ammonia to form tetrafluorosuccinamide, m.p. 258°, NH_4F and NH_4I. Also, on addition of water it formed a lower layer which hydrolyzed very rapidly to form tetrafluorosuccinic acid, HF and HI. These reactions proved conclusively that the original liquid was the mixed acyl iodide–acyl fluoride of perfluorosuccinic acid.

Reaction of Perfluorobutyrolactone with Ethyl Mercaptan.—Perfluorobutyrolactone reacted with ethyl mercaptan (Columbia Organic Chemicals Co.) immediately and practically quantitatively, as described above for ethanol and ammonia, to form hydrogen fluoride and diethyl dithioltetrafluorosuccinate, $C_2H_5S\text{-}COCF_2CF_2CO\text{-}SC_2H_5$, b.p. 108° at 8 mm.

Anal. Calcd. for $C_8H_{10}S_2O_2F_4$: C, 34.52; H, 3.62. Found: C, 34.78; H, 3.48.

Reaction of Silver Perfluoroadipate with Iodine.—Silver perfluoroadipate was prepared by the neutralization of perfluoroadipic acid (courtesy of Minnesota Mining and Manufacturing Co.) with silver oxide in 96% yield. This new salt did not melt at 350°. *Anal.* Calcd. for $C_6F_8O_4Ag_2$: Ag, 42.82. Found: Ag, 42.81.

The reaction with iodine was carried out essentially by the previously described method.[1] There was isolated the theoretical amount of silver iodide and a 64.2% yield of $ICF_2CF_2CF_2CF_2I$ boiling at 148–150° (mostly 150°). The product turned pink on exposure to air and light.

Anal. Calcd. for $C_4F_8I_2$: C, 10.58; H, none; mol. wt., 454. Found: C, 10.62; H, none; mol. wt. (Victor Meyer) 452.[7]

Acknowledgment.—The authors wish to express their appreciation to the U. S. Air Force, Wright Air Development Center, for their financial support of this work.

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(3) Direct determination of oxygen by the elementary isotopic analysis method. See A. V. Grosse, S. G. Hindin and A. D. Kirshenbaum, *Anal. Chem.*, **21**, 386 (1949).

(4) A. L. Henne and W. J. Zimmerscheid, THIS JOURNAL, **69**, 281 (1947).

(5) A. L. Henne and W. F. Zimmer, *ibid.*, **73**, 1103 (1951).

(6) J. J. Padbury and E. L. Kropa, U. S. Patent 2,502,478 (April 4, 1950).

(7) All carbon and hydrogen microanalyses were done by Clark Microanalytical Laboratories, Urbana, Illinois.