perfluoro-fatty acids with perfluoroalkyl iodides, but without success.[1] In contrast to the ease of formation of esters by treating perfluoro-silver salts with *n*-alkyl iodides and diiodides,[2] the attempted preparation of *n*-perfluoropropyl-*n*-perfluorobutyrate by the reaction of silver *n*-perfluorobutyrate with *n*-perfluoropropyl iodide at 275–335°, in the absence of solvents, resulted in the formation of *n*-perfluorohexane, carbon dioxide and silver iodide according to the equation

$$CF_3CF_2CF_2I + CF_3CF_2CF_2CO_2Ag \longrightarrow n\text{-}C_6F_{14} + CO_2 + AgI \quad (1)$$

These results suggest a free radical mechanism with formation of $C_3F_7\cdot$ and $C_3F_7COO\cdot$. At the high temperature of the reaction, direct combination does not take place. The latter radical loses carbon dioxide, and the coupling product, $C_3F_7\text{–}C_3F_7$, is formed exclusively.

Experimental

The Reaction of *n*-Perfluoropropyl Iodide with Silver *n*-Perfluorobutyrate.—The reaction of perfluoropropyl iodide[1] and silver perfluorobutyrate[1] was carried out in nickel and silver pressure reactors at 275 and 335°, respectively. In both cases the only reaction products isolated were *n*-perfluorohexane, carbon dioxide and silver iodide in agreement with equation (1). Only possible traces of unreacted perfluoropropyl iodide were detected. *n*-Perfluorohexane boiled at 56°; mol. wt. found (Victor Meyer), 336; calcd., 338; known, b.p. 55.9–56.7°.[3]

The nickel reactor (100-cc. capacity) was of the rotating type and was partially filled with stainless steel balls. The silver reactor (16-cc. capacity) was filled with silver Raschig rings. Both vessels were equipped with Hoke valves. In a typical reaction, 7.5 g. (0.053 mole) of perfluoropropyl iodide was transferred *in vacuo* to the nickel reactor containing 8.4 g. (0.0262 mole) of finely powdered silver perfluorobutyrate. After heating this mixture at 275° for 10 hours, the Dry Ice-cooled reactor was opened to a similarly cooled glass collecting trap, and the temperature of the reactor was allowed to warm up slowly to *ca.* 25°. A large quantity of uncondensed carbon dioxide gas was collected in a barium hydroxide scrubber attached to the system. Finally all volatile products were transferred *in vacuo* to the collecting trap. This material (6.46 g.) was rectified in a micro fractionating column, and 5.65 g. (66% yield) of *n*-perfluorohexane, was collected. The yield of silver iodide was quantitative. A small scale run in the silver reactor at 335° for one hour, gave an almost quantitative yield of perfluorohexane.

At temperatures below 220° only a very slight reaction occurred in sealed Pyrex tubes. When anhydrous ethyl ether was used as a solvent, there were formed some *n*-perfluoropropyl hydride and a sizable fraction boiling at 70–100° which had a distinct ester odor and was only slightly soluble in water and dilute alkali (density < 1). No pure compound, however, could be isolated under these conditions.

The Reaction of 1,2-Dibromo-1-chlorotrifluoroethane with Silver *n*-Perfluorobutyrate.—The reaction of silver perfluorobutyrate with 1,2-dibromo-1-chlorotrifluoroethane (prepared by the photochemical bromination of chlorotrifluoroethylene) was carried out in glass and metal pressure reactors at temperatures of 100–200° and higher under a variety of conditions. The desired perfluorochloroester, trifluorochloroglycol diheptafluorobutyrate, was not obtained. When ethyl ether or dioxane was used as solvent, an insignificant amount of reaction occurred with some decomposition and loss of carbon dioxide. When an ethyl ether–heptafluorobutyric acid solvent mixture was employed, despite the formation of 50% silver bromide, evidence was found only for the formation of carbon dioxide, the olefin chlorotrifluoroethylene, and only possible traces of a higher boiling ester. Despite its reactivity, methanol was tried as a solvent because of its high solubilizing effect for the reactants. In this case the theoretical amount of silver bromide was isolated as well as a high yield of methyl *n*-heptafluorobutyrate,[4] b.p. 80–80.8° at 760 mm., n^{20}_{D} 1.293, formed by reaction with the solvent.

In the latter case, 15.0 g. of the dibromide, 36.5 g. of the silver salt and 70 ml. of methanol were heated together at 100° for 5 hours in a sealed Pyrex bulb. There were formed 20.2 g. of silver bromide, traces of chlorotrifluoroethylene, and after washing and drying with calcium chloride, 18.18 g. of pure methyl *n*-heptafluorobutyrate.

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(1) The perfluorinated inner ester, perfluorobutyrolactone, is the only completely fluorinated ester to be described to date. See M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951); M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 1974 (1952).

(2) M. Hauptschein and A. V. Grosse, *ibid.*, **73**, 5139 (1951); also M. Hauptschein, unpublished results.

(3) T. J. Brice in J. H. Simons, "Fluorine Chemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1950, p. 453. Also, J. H. Simons and W. H. Pearlson, 112th Meeting American Chemical Society, September, 1947.

(4) Minnesota Mining and Manufacturing Co. Brochure on Heptafluorobutyric Acid.

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Molecular Order in *n*-Heptane and *n*-Perfluoroheptane

BY J. H. HILDEBRAND AND G. J. ROTARIU

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Molecules of *n*-perfluoroheptane are undoubtedly far less flexible than those of *n*-heptane by reason of the size of the fluorine atoms, hence they can be expected to pack in a somewhat more orderly, parallel array in the liquid state, especially at lower temperatures. The liquids should differ like dry and cooked spaghetti. We sought evidence for this in a difference between their entropies of vaporization like the differences previously found between liquids with differing order due to molecular geometry.[1] According to the "Hildebrand Rule" liquids composed of highly symmetrical molecules all have the same entropy of vaporization per mole, Δs^v, when compared at temperatures where they have the same gas volume, v^g, but any degree of order in the liquid, whether the result of molecular association or simply of geometrical shape, leads to a higher entropy of vaporization as this order is destroyed.

We have reliable vapor pressure equations for *n*-heptane[2] and for *n*-perfluoroheptane.[3] Instead of obtaining their entropies of vaporization graphically from the slope of log p *vs.* log T plots, as heretofore, we differentiated the vapor pressure equations to obtain $\Delta s^v = R(\mathrm{d} \ln p/\mathrm{d} \ln T)$. Selecting 25° as the temperature of comparison for the heptane, we calculated 15° as the temperature at which the perfluoroheptane would vaporize to the same volume, 403 liters, assuming ideal gases, which introduces no significant discrepancy. Table I gives the resulting figures for Δs^v, and shows an excess of 1.6 entropy units for the perfluoroheptane. This seems reasonable when compared with the

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(1) J. H. Hildebrand, *J. Chem. Phys.*, **7**, 233 (1939).

(2) "Selected Values of Hydrocarbons," Circular of the National Bureau of Standards, C 461, 1947, p. 123.

(3) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

excess of 1.2 e.u. for *n*-hexane over diisopropyl at 49.5 liters.[1]

TABLE I

ENTROPY OF VAPORIZATION

	v_g = 403 lit.	*t*, °C.	v^g/v^l = 2703	*t*, °C.
C_7H_{16}	29.5	25	29.5	25
C_7F_{16}	31.1	15	32.4	7
Diff.	1.6		2.9	

Pitzer[4] has shown that in the case of molecules having radial intermolecular potentials of the same form, such as the rare gases, the entropies of vaporization are equal not at equal vapor volumes, v^g, but at equal ratios of vapor to liquid volume, v^g/v^l, but Hildebrand and Gilman[5] showed that in the case of polyatomic molecules with different liquid volumes the agreement is considerably better at equal v^g. The molal volume of perfluoroheptane is so much larger than that of heptane that a much lower temperature must be taken to make the comparison at equal v^g/v^l, 7° if the heptane is at 25°. Table I gives the comparison under these conditions. The difference in this case, 2.9 e.u., is, in our opinion, greater than is reasonable to expect from difference in order alone, and it furnishes another instance of the inferiority of the corresponding states rule as a basis for comparing polyatomic molecular species with potential fields so far from radial.

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[4] K. S. Pitzer, *J. Chem. Phys.*, **7**, 583 (1939).

[5] J. H. Hildebrand and T. S. Gilman, *ibid.*, **15**, 229 (1947).

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Correction Concerning Some Reported Derivatives of D-Talitol

BY C. S. HUDSON, M. L. WOLFROM AND T. Y. SHEN

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Barker and Bourne[1] have recently shown that data of the literature justify a belief that a dimethylene acetal which Hann, Haskins and Hudson[2] reported as 2,4:3,5-dimethylene-D-talitol is in reality the 2,4:3,5-dimethylene-allitol that Wolfrom, Lew and Goepp[3] prepared from authentic allitol. Upon receipt of this information from Messrs. Barker and Bourne by early letter, for which we express our appreciation, we examined the original samples from the two researches[2,3] by mixed melting point measurements and by X-ray diffraction diagrams. In like manner the respective original samples of two derivatives,[2,3] namely, the 1,6-diacetate and the 1,6-ditosylate, were also compared. In all cases the results show unequivocally that the reported "D-talitol" acetal is 2,4:3,5-dimethylene-allitol. In one of the researches[2] three additional derivatives of the acetal were reported as belonging in the D-talitol series; since the acetal is now known to be of the allitol series the names of these derivatives are be changed to 1,6-dibenzoyl-2,4:3,5-dimethylene-allitol (m.p. 188–189°), 1,6-didesoxy-2,4:3,5-dimethylene-allitol (m.p. 165–166°) and 1,6-didesoxy-1,6-diiodo-2,4:3,5-dimethylene-allitol (m.p. 219–220°). All the substances have *meso* configurations and are to be regarded as devoid of optical rotation; the very small specific rotations that were reported[2] are near the limits of observation. The recorded melting points[2,3] are essentially correct.

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[1] S. A. Barker and E. J. Bourne, *J. Chem. Soc.*, 905 (1952).

[2] R. M. Hann, W. T. Haskins and C. S. Hudson, THIS JOURNAL, **69**, 624 (1947).

[3] M. L. Wolfrom, B. W. Lew and R. M. Goepp, Jr., *ibid.*, **68**, 1443 (1946).

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The Heat of Combustion and Resonance Energy of Tropolone

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In 1945, Dewar predicted[1] that tropolone (2,4,6-cycloheptatriene-1-one-7-ol) would exhibit aromaticity and later made a theoretical estimate of its resonance energy.[2] Following its synthesis,[3] Dr. W. von E. Doering of the Hickrill Chemical Research Foundation suggested that an estimate of its resonance energy from heat of combustion data would be valuable and offered four grams of tropolone to this Laboratory. Consequently, and because of current interest in other related seven-membered cyclic compounds (*e.g.*, ref. 3b), heat of combustion measurements for tropolone[4] were included in the Bureau of Mines calorimetric program.

Material.—The sample had been prepared and purified according to ref. 3a and was then recrystallized from cyclohexane and sublimed three times. The method of purification and the carbon dioxide determinations (see table) suggest that the material (m.p. 51°) was of high purity. The material was non-hygroscopic and when compressed into briquets was not significantly volatile at room temperature.

The Apparatus and Its Calibration.—The apparatus (with the exception of the bomb) and combustion technique have been previously described.[5] The bomb used in this investigation was sealed with a pure gold gasket and had an internal volume of 0.374 l. The energy equivalent of the calorimeter was determined by combustion of benzoic acid (National Bureau of Standards Standard Sample 39g) having for its isothermal heat of combustion at 25° a value of $-\Delta U_B/M$ of 26.4338 abs. kj. g.$^{-1}$. Since the conditions in these experiments were not quite those of the standard bomb process, the N.B.S. value was corrected to 26.4306 abs. kj. g.$^{-1}$. Eight combustions of benzoic acid yielded an average value 3190.95 cal. deg.$^{-1}$ for the energy equivalent, S_B, of the system. The average deviation from the mean of these experiments was ±0.006% with a maximum spread of 0.025%.

Auxiliary Quantities.—Weights were corrected to a vacuum basis by use of a density value of 1.34 g. cc.$^{-1}$ for

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[1] M. J. S. Dewar, *Nature*, **155**, 50, 141, 451 (1945).

[2] M. J. S. Dewar, *ibid.*, **166**, 790 (1950).

[3] (a) W. von E. Doering and L. H. Knox, THIS JOURNAL, **72**, 2305 (1950); (b) **73**, 828 (1951); (c) J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *Chemistry and Industry*, 427 (1950); (d) R. D. Haworth and J. D. Hobson, *ibid.*, 441 (1950).

[4] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 503 (1951), have recently published a value of the heat of combustion of tropolone having a claimed accuracy of ±0.9 kcal./mole. This datum was obtained for them by G. R. Nicholson of Imperial Chemical Industries Limited. Because of the higher order of accuracy of the present work and because of the current great interest in tropolone, it has seemed desirable to record both the original and derived data of the combustion experiments performed in this Laboratory.

[5] W. N. Hubbard, J. W. Knowlton and H. M. Huffman, THIS JOURNAL, **70**, 3259 (1948).