present here the results of measurements in the solvent *o*-chlorobenzotrifluoride at a temperature of 137.10°. The measurements were made with a Bingham-type viscometer in which flow times are measured as a function of driving pressure.

Experimental

The silicone oil constant temperature bath was electronically controlled at a temperature of 137.10 ± 0.02°. The viscometer was patterned after the one shown in ref. 2. with these modifications: (1) large stopcocks were placed in the arms approximately 10 cm. above A and M of the figure; and (2) a side arm containing a fritted glass disc and a 15-cc. bulb in which polymer and solvent were placed for dissolution was attached just above M. A weighed amount of polymer and 10 cc. (volume at 20°) of solvent were introduced into this bulb, a cap placed on the opening to the bulb and the stopcocks closed to keep solvent vapor from escaping. The solvent and polymer were left in the bulb until solution was complete. After solution, nitrogen gas under pressure was used to drive the solution through the fritted glass into the viscometer proper. Excess solution was withdrawn from the viscometer through a small stainless steel tube whose tip reached to point A in the left-hand arm. The solution was kept under an atmosphere of nitrogen at all times to prevent oxidation of the solvent.

A water manometer was used to determine driving pressure. Time of flow data as a function of driving pressure were obtained in the manner indicated in Appendix A of ref. 2. The viscometer was calibrated with water and sucrose solutions according to the methods outlined by Hall and Fuoss.[3] The volume of the dry bulb of the viscometer was 2.13 cc., the capillary radius was 0.015 cm., and the length of the capillary was approximately 10 cm.

Pressures were varied between 50 and 150 cm. of water in six approximately equal steps and the corresponding flow times recorded. In ref. 3 it is shown that the behavior of a solution in a Bingham-type viscometer can be expressed by the relationship

$$1/pt = A_0/\eta_\infty + (\kappa - \lambda)p \qquad (1)$$

in which p is the driving pressure, t is the flow time, A_0 is a constant depending only on viscometer dimensions, η_∞ is the viscosity of the solution at zero driving pressure (infinite time), and κ and λ are functions of viscometer dimensions and the nature of the solution. For the viscometer used A_0 was 9.57×10^{-7} poise-cm.^{2}/g. sec.

The polytrifluorochloroethylene used was made by the Kellogg Corporation. The three molecular weight ranges used were designated Kel-F 240, lot no. 124; Kel-F 270, lot no. 126 and Kel-F 300, lot no. 162-L.

Results and Discussion

Plots of $1/pt$ *vs.* p were constructed and the viscosities at zero rate of shear for various concentrations of the polymer obtained from the intercepts. From the viscosities the reduced viscosities were calculated and plotted in the usual fashion as a function of concentration. The plots are shown in Fig. 1. The viscosity of the solvent *o*-chlorobenzotrifluoride at 137.10° is 0.3595 centipoise. The density is 1.20.

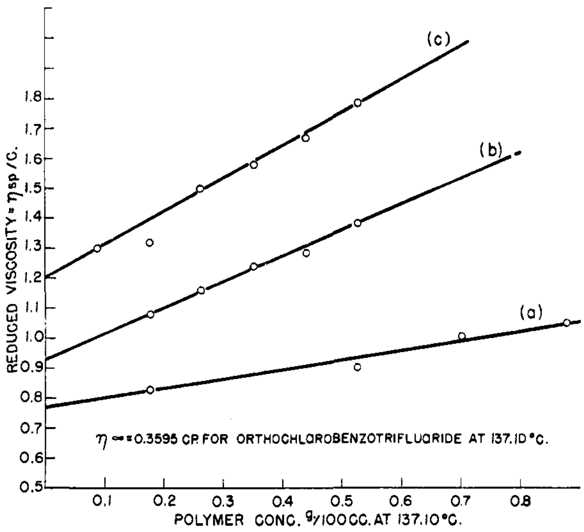

Fig. 1.—Reduced viscosity as a function of concentration for (a) Kel-F 240, (b) Kel-F 270 and (c) Kel-F 300 in orthochlorobenzotrifluoride at 137.10°.

Molecular weights of 56,500, 76,000 and 100,000 are given for Kel-F 240, 270 and 300, respectively, by Kaufman and Muthana.[1] The relationship between intrinsic viscosity $[\eta]$ (obtained from the intercepts in Fig. 1) and the molecular weight M is expressed by the equation[4]

$$[\eta] = KM^\alpha \qquad (2)$$

in which K is a constant and α is characteristic of the polymer and usually has a value between 0.3 and 1.2. Substituting the molecular weight values of Kaufman and Muthana into (2) and plotting log $[\eta]$ *vs.* log M gives values of 1.71×10^{-4} and 0.77 for K and α, respectively, when the concentration is expressed as grams of polymer per 100 cc. of solvent. The value of α is somewhat of an indication of chain stiffness. The value obtained here is midway between that for a flexible chain polymer such as a polyester and that of a stiff chain polymer such as a cellulose derivative. This is consistent with what might be expected when a Hirschfelder model of the polymer is examined. The model shows that some restriction to rotation about C–C bonds should be expected.

It was not possible to evaluate shear constants[3] for this polymer because of a reduction in the precision resulting from difficulties introduced by the high temperature.

The authors are indebted to Mr. R. J. Coswell for making some of the viscosity measurements.

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RECEIVED MAY 16, 1951

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[2] Eugene C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., Inc., New York, N. Y., Fig. 29, p. 76.

[3] H. T. Hall and R. M. Fuoss, THIS JOURNAL, **73**, 265 (1951).

[4] H. Mark, "Die feste Körper," Verlag S. Hirzel, Leipzig, 1948, p. 103.

Perfluoro-*n*-propyl Disulfide and Perfluoro-*n*-propyl Trisulfide

BY MURRAY HAUPTSCHEIN AND ARISTID V. GROSSE

Molten sulfur reacted with 1-iodoheptafluoropropane under pressure at 250° to form perfluoro-*n*-propyl disulfide, $(CF_3CF_2CF_2)_2S_2$, and perfluoro *n*-propyl trisulfide, $(CF_3CF_2CF_2)_2S_3$. This represents the first satisfactory synthesis of these novel type perfluoroalkyl sulfur compounds. In this connection it should be mentioned that Bennett, Brandt, Emeléus and Haszeldine[1] reported very recently that thiocarbonyl fluoride (CSF_2) was a main product of the reaction of sulfur with iodotrifluoromethane, although at the reaction temperature of 205° there could be isolated a readily

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[1] F. W. Bennett, G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *Nature*, **166**, 225 (1950).

TABLE I

PHYSICAL PROPERTIES

Compound	B.p., °C.	n^t_D	d^t_4	d^0_t	t, °C.	$\Delta d/\Delta t$	*MR* Found[a]	*MR* Calcd.[b]	AR_F[c]
$C_3F_7-S_2-C_3F_7$	122.2	1.3222	1.6940[d]	1.7531	28.0	-0.0021_1[e]	47.39	47.95	1.19
$C_3F_7-S_3-C_3F_7$	153	1.3600	1.6984	....	31.0	....	56.43	56.06	1.26

[a] *MR* (found) denotes the molecular refraction calculated by Lorentz–Lorenz formula. [b] *MR* (calcd.) denotes the molecular refraction calculated by adding the usual values for atomic refractions: C, 2.418; S (in disulfides), 8.11; and 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 S. [d] The density measurements were made by E. A. Nodiff of the Research Institute. [e] Average temperature coefficient of density in g./cc. (°C.) over the temperature range 0–30°.

hydrolyzable compound of molecular formula $C_2S_2F_6$, the structure of which was uncertain.

When 1-iodoheptafluoropropane was treated with a very large excess of sulfur at 250° in a sealed Pyrex bulb, a steady reaction ensued as evidenced by the liberation of iodine, some of which sublimed and recrystallized in the cooler stem of the bulb outside of the reaction zone. A trace of a gaseous material was obtained, and aside from small amounts of unreacted iodine and a product which was probably perfluoro-*n*-propyl monosulfide, $(CF_3CF_2CF_2)_2S$, boiling at approximately 90°, there were isolated two pure compounds boiling at 122.2 and 153° corresponding to perfluoro-*n*-propyl disulfide and perfluoro-*n*-propyl trisulfide in the respective yields of 47.0 and 18.7%. Iodine was formed in 94.6% yield which indicated that the disulfide and trisulfide were actually produced in an aggregate yield of over 90%, and that the smaller quantity of the two pure products actually isolated (total of 65.7%) was due to mechanical losses involved in the separation and purification processes. Equation (1) is a schematic representation of the reaction and Equation (2) represents the principal over-all reaction.

$$C_3F_7I + S \longrightarrow C_3F_7{-}S{-}C_3F_7 + C_3F_7{-}S{-}S{-}C_3F_7 + C_3F_7{-}S{-}S{-}S{-}C_3F_7 + I_2 \quad (1)$$

$$2C_3F_7I + 2S \longrightarrow C_3F_7{-}S{-}S{-}C_3F_7 + I_2 \quad (2)$$

It appears likely that the monosulfide was first formed, but that it reacted more readily than the original iodide with sulfur to form the disulfide in greatest yield.

The disulfide and trisulfide were both essentially insoluble in water and 10% potassium hydroxide. Analysis of the infrared spectra discussed below demonstrated that the perfluoropropyl group remained intact. It is thus most probable that

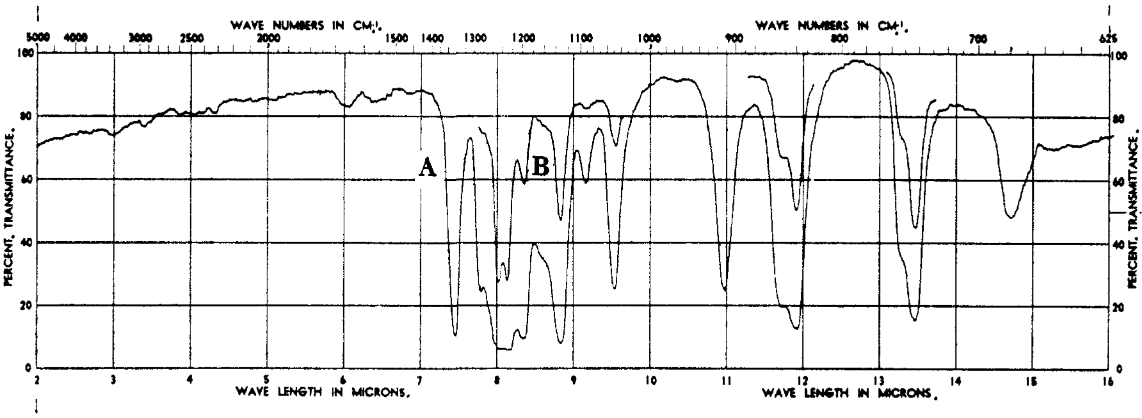

Fig. 1.—Infrared spectrum of perfluoropropyl disulfide (Curve A is for vapor at room temperature; Curve B is for vapor diluted with dry nitrogen gas. A 5-cm. cell was used in both cases.)

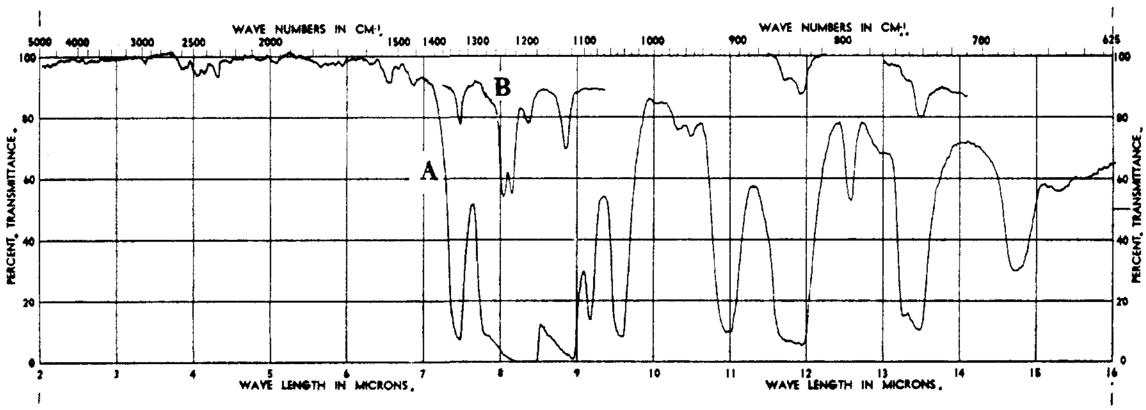

Fig. 2.—Infrared spectrum of perfluoropropyl trisulfide (Curve A is for liquid in cell of 0.01 mm. thickness; Curve B is for vapor in 5-mm. cell.)

the structural formulas assigned above were correct. The physical constants are presented in Table I, and the infrared spectra[2] are shown in Figs. 1 and 2. The infrared spectra for perfluoropropyl disulfide and trisulfide are almost identical and indicate the similarities in structure. The main difference is the presence of a band at 12.59 microns for the trisulfide, absent for the disulfide, which may be accounted for by the presence of the additional sulfur atom in the former. In comparing these spectra with that for 1-iodoheptafluoropropane,[3] the striking similarity of all spectra from 2 to 9 microns is excellent evidence for the presence of the C_3F_3– group in all three cases.

The chemical reactions of these perfluoro sulfur compounds are being studied.

Experimental

In a sealed Pyrex glass bulb of 500-ml. capacity, a mixture of 22.0 g. (0.0743 mole) of 1-iodoheptafluoropropane prepared as previously described[3] and 50 g. of elemental sulfur was carefully heated at 250° for 14 hours. Reaction was evidenced by the liberation of large amounts of free iodine. Traces of a gaseous product were noted when the Dry Ice cooled flask was unsealed. There was finally collected 8.9 g. of iodine and 12.78 g. of a liquid product by transferring under a vacuum of 0.5 mm. at temperatures up to 180°. Fractional distillation at 760 mm. pressure yielded several cuts: 0.5 g., b.p. 41–45° (unreacted C_3F_7I); 0.5 g., b.p. approximately 90° (probably $C_3F_7SC_3F_7$); 7.0 g., b.p. 120–123°, mostly 122.2°, ($C_3F_7S_2C_3F_7$); and 3.0 g., b.p. 152.5–153° ($C_3F_7S_3C_3F_7$). *Anal.*[4] Calcd. for $C_6F_{14}S_2$: C, 17.92; F, 66.14; mol. wt., 402.2. Found: C, 17.89; F, 66.18; mol. wt., 400.0. Calcd. for $C_6F_{14}S_3$: C, 16.59; F, 61.25; S, 22.15; mol. wt., 434.3. Found: C, 16.30; F, 61.30; S, 22.35; mol. wt., 434.2.

Acknowledgment.—The authors wish to express their sincere appreciation to the U. S. Air Force, Air Materiel Command for their financial support of this work.

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

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

[4] Microanalysis by Clark Microanalytical Laboratory, Urbana, Illinois. Molecular weights determined by Victor Meyer method.

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RECEIVED MAY 18, 1951

The Heat of Formation and Entropy of Aqueous Cuprous Ion

BY DONALD D. WAGMAN

The note by Hugus[1] has pointed out an error in the value of the entropy of aqueous cuprous ion in Table I–34 of the Selected Values of Chemical Thermodynamic Properties.[2] This value was calculated from the values for the heat and free energy of formation of the $Cu^+(aq)$ ion. In calculating the value of $\Delta H_f°$ we used the equilibrium data of Heinerth[3] on the reaction $^1/_2$ Cu (c) + $^1/_2Cu^{++}$ (aq) = Cu^+ (aq) measured as a function of temperature. However, the value ΔH = 9.4 kcal., calculated from the log K *vs.* $1/T$ plot, was erroneously assigned to the reaction Cu(c) + Cu^{++}(aq) = $2Cu^+$(aq). Utilizing the proper value of ΔH and the heat of formation of Cu^{++}(aq) = 15.39 kcal./mole[2] (calculated from other data[4–7]) we obtain the following corrected values for the formation of Cu^+(aq)

$$\mathrm{Cu(c)} + \mathrm{H^+(aq)} = \mathrm{Cu^+(aq)} + {}^1/_2\mathrm{H_2(g)}$$

$$\Delta H_f{}°_{298.16} = 17.1 \text{ kcal./mole}$$

$$\Delta F_f{}°_{298.16} = 12.0 \text{ kcal./mole}^{8,9}$$

$$\Delta S°_{298.16} = 17.1 \text{ cal./deg. mole}$$

Taking the entropies of H^+(aq), Cu(c), and $^1/_2H_2$(g) as 0, 7.96, and 15.61 cal./deg. mole,[2] respectively, we obtain

$$S°(\mathrm{Cu^+(aq)}) = 9.4 \text{ cal./deg. mole}$$

This value is in agreement with that of Hugus within the limits of uncertainty. The difference is due to the fact that we have assigned values to the heat and free energy of formation of the cupric ion Cu^{++}(aq) slightly different from those used by Latimer, Pitzer and Smith in their calculation of the entropy of the ion.[10,11]

The values of $\Delta H_f°$ in Table I–34 for Cu_2SO_4(aq) and $Cu(ClO_4)_2$(aq) should also be changed to −181.4 and −47.4 kcal./mole, respectively.

We wish to thank Mr. Hugus for calling attention to this error.

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[1] Z. Z. Hugus, THIS JOURNAL, **73**, 5459 (1951).

[2] Selected Values of Chemical Thermodynamic Properties, Series I, Table 34, National Bureau of Standards, Washington, D. C., (March 31, 1949).

[3] E. Heinerth, *Z. Elektrochem.*, **37**, 61 (1931).

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[7] A. Bouzat, *Ann. chim. phys.*, **29**, 305 (1903).

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[10] W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

[11] K. K. Kelley, Contributions to Theoretical Metallurgy. XI. Entropies of Inorganic Substances, U. S. Bureau of Mines Bull., No. 477 (1950).

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The Occurrence of Hydroxylysine in Proteins

BY LOIS WILEY INSKIP

Because of conflicting reports[1,2] in the literature on the occurrence of hydroxylysine in proteins, a search for hydroxylysine in the basic amino acid fractions of six protein hydrolysates was made by means of paper chromatography. Gelatin, known to contain about 1% hydroxylysine, was used as a control.

Two-dimensional chromatograms run in the phenol–collidine solvent system showed that hydroxylysine was present in gelatin, as was anticipated, but absent from casein, lactalbumin, glycinin and zein (gluten). Human hair contained a substance which moved on the chromatogram to a position very close to that occupied by hydroxylysine but which was probably cystine. Although cystine is usually decomposed during two-dimensional chromatography when phenol is used as the first solvent,[3] traces of it may be detected when it is

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[1] D. D. Van Slyke, A. Hiller and D. A. MacFadyen, *J. Biol. Chem.*, **141**, 681 (1941).

[2] P. Desnuelle and S. Antonin, *Biochem. et Biophys. Acta*, **1**, 50 (1947).

[3] C. E. Dent, *Biochem. J.*, **43**, 169 (1948).