superpressure apparatus[3] using a cell constructed of sodium chloride with a graphite heater. The cell was calibrated at room temperature with the bismuth 25.5- and 27-kbar and the barium 58-kbar transformations. Temperatures, uncorrected for pressure, were determined from a calibration of the high-pressure cell with a Pt—Pt-10% Rh thermocouple.[4]

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(3) H. T. Hall, *Rev. Sci. Instr.*, **31**, 125 (1960).

(4) NOTE ADDED IN PROOF.—S. Rundqvist and E. Larsson, *Acta Chem. Scand.*, **13**, 551 (1959), report that CoP_3 (a = 7.706 Å) is isostructural with $CoAs_3$.

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Trifluoromethylsulfinyl Fluoride[1]

BY EDWARD W. LAWLESS AND LUEDRIC D. HARMAN

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Trifluoromethylsulfinyl fluoride and other alkyl- or arylsulfinyl fluorides were reported[2] as minor by-products in the synthesis of the corresponding RSF_3 compounds, as a result of reaction with the glass apparatus or traces of moisture. Supporting data were given for benzenesulfinyl fluoride which was obtained[2] in good yield by the reaction of phenylsulfur trifluoride and benzaldehyde. The CF_3SF_3 was synthesized[2] by the reaction of gaseous CS_2 or $(CF_3S)_2CS$ with AgF_2. Both reactions were exothermic and gave a mixture of products: SF_4, CF_3SF_3, CF_3SF_5, and SF_6 from CS_2; and CF_3SF_3, $(CF_3)_2S_2$, CF_3SFO, and CF_3SF_5 from $(CF_3S)_2CS$. We wish to report improved syntheses of CF_3SF_3[2-4] and CF_3SFO and some properties of the latter.

In the present investigation, we have found that liquid bis(trifluoromethyl) disulfide will, in fact, readily react further with AgF_2. The products are CF_3SF_3, CF_3SF_5, and CF_3SFO. The formation of CF_3SF_5 can be minimized by allowing the reactants to warm from −10 to 25° over several hours and by avoiding a large excess of AgF_2.[5] The formation of CF_3SFO can be minimized by using rigorously anhydrous conditions and passivated, glass-free apparatus.

Trifluoromethylsulfinyl fluoride was obtained in good yield by simply storing small quantities of the product mixture in a glass bulb until all of the reactive CF_3SF_3 was eliminated by conversion to CF_3SFO and SiF_4. The CF_3SFO was purified by vacuum-line fractionation and identified by its gaseous molecular weight, ^{19}F nmr spectrum, mass spectrum, and an infrared spectrum, Figure 1, which is consistent with the proposed structure. The CF_3SFO is a white solid and colorless liquid or gas having a boiling point of approximately −9°. It appeared to be thermally stable in stainless steel at 135° and was unreactive with mercury at 25°. Gaseous CF_3SFO was stored in dry glass for 2 weeks without noticeable decomposition, but after 3 months in normal laboratory light all of the CF_3SFO was destroyed. Instability of sulfinyl fluorides in glass was previously noted.[2] The CF_3SFO is slowly hydrolyzed by water vapor at 25° with destruction of the CF_3 group. No reaction was observed between CsF and CF_3SFO at 120 or 135° and no complex which was stable at room temperature was formed when CF_3SFO and AsF_5 were held at −78°. The addition of F_2 to CF_3SFO at 25° produced a number of degradation products, but CF_3SO_2F and CF_4 were the major products observed from the reaction at −78°.

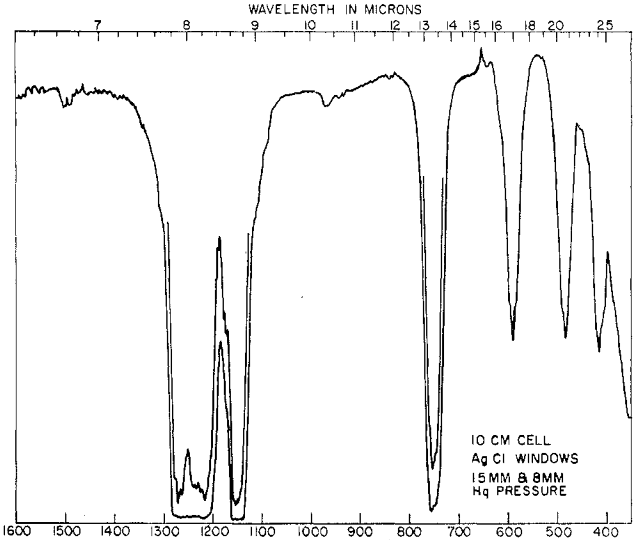

Figure 1.—Infrared spectrum of trifluoromethylsulfinyl fluoride.

Experimental Section

Preparation.—Silver difluoride (Alfa Inorganics, Inc.) and $(CF_3)_2S_2$ (Peninsular ChemResearch, Inc.) were allowed to react in a series of 11 runs utilizing 1–2 g of $(CF_3)_2S_2$ per run. The mole ratio of AgF_2 to $(CF_3)_2S_2$ was varied from 12:1 to 2:1. A valved 75-ml stainless steel cylinder was charged with AgF_2 in a drybox and the $(CF_3)_2S_2$ was condensed in at −196° in a vacuum line. Each reactant mixture was then held at a selected temperature in the range −78–50° for a time in the range 116–0.5 hr. Products were fractionated or transferred in either a glass or an all-metal and Kel-F vacuum line operating at <0.01 mm. In a typical run, the reactor was charged with an 8:1 mole ratio of AgF_2 to $(CF_3)_2S_2$, placed in a dewar containing ice, and allowed to warm to room temperature overnight. Infrared analysis of a small sample of the volatile products showed that the major product (~70%) was CF_3SF_3 with smaller amounts of CF_3SFO and CF_3SF_5 present. Quantitative ^{19}F nmr analysis (based on integration of the three CF_3 peaks) at −40° on all of the remaining volatile products gave the composition: 60% CF_3SF_3, 28% CF_3SFO, 10% CF_3SF_4, and *ca.* 2% SiF_4. No residual $(CF_3)_2S_2$ was detected by either method. However, reaction

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(1) This work was supported by the United States Air Force under Contract AF 33(615)-3954.

(2) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).

(3) E. A. Tyczkowski and L. A. Bigelow, *ibid.*, **75**, 3523 (1953).

(4) R. Dresdner, *ibid.*, **79**, 69 (1957).

(5) Once formed CF_3SF_5 is resistant to further fluorination by AgF_2 at 35°.

at the stoichiometric ratio of 6:1 at 0° or at an 8:1 ratio at the higher temperature of 25° always left unreacted $(CF_3)_2S_2$, since the formation of CF_3SF_5 uses excess AgF_2. At −15° only a very slight reaction had occurred after 18 hr and at −30° no reaction was detectable by infrared analysis after 116 hr.

Good yields of CF_3SFO were obtained by simply storing 1–2-g quantities of the product mixture in a 1-l. glass bulb for a few days until all of the CF_3SF_3 was converted to CF_3SFO and SiF_4. The CF_3SFO was purified by pumping off the CF_3SF_5 and SiF_4 at −111° (or more rapidly at −97°; however, some CF_3SFO also distils) followed by a distillation from a −86° trap which retains most of any residual $(CF_3)_2S_2$.

Analysis.—The CF_3SFO was identified by its molecular weight (calcd, 136; found, 137, by vapor density method), ^{19}F nmr spectrum (resonances in a 3:1 intensity ratio for CF_3 and SF at 84 and 26 ppm *vs.* external $CFCl_3$ at −50°), and mass spectrum (intensities were: CF_3^+, 100; SFO^+, 45; SO^+, 38; SF^+, 11; CF_2^+, 10; CF^+, 8; S^+, 6; CF_2S^+, 2; CF_3SO^+, 1; CF_3S^+, 0.6; CF_3SFO^+, 0.03 at 70 V). The infrared spectrum (Figure 1) has very strong bands at 1269 ($S \rightarrow O$ stretch), 1226 and 1151 (C–F stretch), and 752 cm^{-1} (S–F stretch, but probably coincident with a medium intensity C–S stretching band[6–8]), and it has medium intensity bands at 588, 481, and 412 cm^{-1}.

The CF_3SF_5 was identified by its infrared[9] and nmr[10] spectra. The CF_3SF_3 was identified by its ^{19}F nmr spectrum (CF_3 at 71 and SF_3 (exchange broadened[11]) at −30 ppm *vs.* $CFCl_3$ in an approximately 1:1 ratio), its reactivity with glass and moisture to give CF_3SFO, and its relative volatility.[3,4] No attempt was made to obtain a high-purity infrared sample, but the following bands of CF_3SF_3 were evident: 1242 vs and 1140 db, vs (C–F stretch), 850 s and 708 vs (S–F stretch),[12,13] 598 m and 517 m cm^{-1}. Other bands appear to be at 1265 and 750[6] cm^{-1} (where CF_3SFO impurities interfere) and at 560 w and 405–393 db cm^{-1}.

Infrared analysis was performed on a Beckman IR-12 spectrometer using a metal-valved Kel-F cell equipped with AgCl windows. Nuclear magnetic resonance studies were performed on a Varian Associates Model HA-100 spectrometer using Pyrex tubes. Mass spectral analysis was performed by Morgan-Schaeffer Corp., Montreal, Canada.

Reactions.—The hydrolysis of CF_3SFO by water vapor appears to give several products, depending on the conditions. Of particular interest is the observation of one or more compounds of low volatility characterized by carbonyl stretching frequencies in the 1740-cm^{-1} region and the C–H band around 2975 cm^{-1}. Other bands associated with this material were at 1370 ($S \rightarrow O$?), 1218 (PQR), and 532 (PQR) cm^{-1}. Hydrolysis in an infrared cell (Kel-F body, AgCl windows) left a nonvolatile material which apparently contained sulfonyl or sulfonate groups.

No reactions of CF_3SFO were observed when it was heated with activated[14–17] CsF (3 mmoles each in a 75-ml cylinder) for 4 hr at 120° and 16 hr at 135° or when held with AsF_5 (9.3 mmoles each in a Kel-F tube) for 48 hr at −78°. By comparison, SF_2O (unlike SF_4O[16,17]) also did not appear to react with CsF, but does react[15] with AsF_5 at −78° to give a solid complex (which is, however, completely dissociated at 25°, unlike the stable[18] complexes $SF_3^+AsF_6^-$ and $SF_3O^+AsF_6^-$). The CF_3SFO thus appears to be a poor or very weak fluoride acceptor or donor.

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[6] The conflicting assignments to C–S stretch and CF_3 deformation of medium intensity bands in the 750-cm^{-1} region for several CF_3S compounds have been reviewed.[7] The C–S bands in CH_3SO_2F, CH_3SO_2Cl, and $(CH_3)_2SO_2$ have been recently assigned[8] in this region, *i.e.*, outside the normal 600–700-cm^{-1} region for alkylsulfur compounds.

[7] J. K. Brown and K. J. Morgan, *Advan. Fluorine Chem.*, **4**, 303 (1965).

[8] M. Spoliti, S. M. Chackalackal, and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1092 (1967).

[9] D. F. Eggers, Jr., and H. E. Wright, *J. Chem. Phys.*, **35**, 1045 (1961).

[10] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

[11] The SF_2 and SF resonances of CF_3SF_3 have been resolved by 100 ppm at lower temperatures by E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964). The temperature dependence is analogous to that in F_4.

[12] The location of the S–F bands in CF_3SF_3 and $C_6H_5SF_3$[2] (807 cm^{-1}) suggests strongly that the compound reported as SF_3CF_2COOH[13] (which had an S–F band at 894 cm^{-1} and was remarkably stable to hydrolysis) is actually a pentafluorsulfur derivative (perhaps SF_5CH_2COOH).

[13] R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).

[14] Activation of cesium fluoride by vacuum drying a finely powdered sample at 150–170° for 2 hr, followed by a second regrinding in a drybox, has proved[15] quite satisfactory for the reaction[16,17] with SF_4O to give $Cs^+SF_5O^-$.

[15] E. W. Lawless, unpublished results.

[16] W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3939 (1960).

[17] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1962).

[18] F. Seel and O. Detmer, *Z. Anorg. Allgem. Chem.*, **301**, 8 (1959).

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An Analysis of the Ligand Field Spectrum of Pentacyanocobaltate(II)

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Increased interest in pentacoordination[2a] coupled with the interpretation[2b] of the esr spectrum of $Co(CN)_5^{3-}$ in terms of C_{4v} symmetry prompts us to communicate an analysis of the d-to-d spectrum of pentacyanocobaltate(II). All results have been obtained by diagonalizing the d^7 ligand field matrices[3] in the strong field basis for a field of C_{4v} symmetry.

Figure 1 depicts the splitting of the low-lying electronic states of O_h symmetry (far left) by the axial ligand field characteristic of a square-pyramidal structure. The negative values of the axial parameters Ds and Dt correspond to a weaker ligand field along the unique axis than in the equatorial plane due to the removal of an axial CN^- ligand. In this situation the ground-state electron configuration is $(e)^4(b_2)^2(a_1)^1(b_1)^0 = {}^2A_1$ as demanded by the observed g values.[4] Calculated and observed spectra are compared in Table I, and an assignment is given in terms of *approximate* one-electron transitions. In fitting the observed spectrum, the ratio C/B was fixed at the free ion value,[5] and a typical reduction in the Racah parameter B was introduced on the basis of the nephelauxetic effect.[6] Neglecting configuration interaction, the transition ${}^2A_1 \rightarrow {}^2A_2$ at 31.7 kK is independent of Ds and Dt at an energy $\Delta + 2B - C$. Having calculated an approximate Δ value in this way, the remaining three observed transitions fix the two parameters Ds and Dt within rather narrow limits. The figure shows that two additional states

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[1] National Science Foundation Graduate Fellow, 1965–1967.

[2] (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); (b) J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3356 (1967). Professor Gray has subsequently measured the absorption spectrum at several temperatures in order to rule out the possibility of any structural equilibrium. Thus, all observed bands are now known to be due to a C_{4v} anion.

[3] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967).

[4] The observed g values are incompatible with a ${}^2B_1$ ground state.

[5] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

[6] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).