ammonia–ammonium salt buffers containing various anions were not significantly different. The half-wave potentials for Co(III) to Co(II) and for Co(II) to Co(0) were similar in all of the solutions, and only trivial differences in the polarographic maxima were observed.

Sulfate Systems.—Oxidation of Co(II) in sulfate media required use of the membrane cell. The oxidation was not quantitative (yields up to 30%) and current efficiencies were low (around 20%).

Different Co(III) complexes were indicated spectrophotometrically. In all of the sulfate solutions, Co(II) showed a single absorption peak at 510 mμ. After electrolytic oxidation of 0.01 M $CoSO_4$ in 0.1 M H_2SO_4–0.01 to 1 M Na_2SO_4, two other peaks were observed at 610 mμ (previously reported for cobalt(III) sulfate) and at 406 mμ (unreported). The Co(III) was not very stable, because both polarographic current at -0.6 v and absorbances at 406 and 610 mμ decreased similarly with time. Half-times for Co(III) decay at room temperature were highly dependent upon the composition of the medium: 100 min in 0.1 M H_2SO_4–1 M Na_2SO_4; 75 min in 0.1 M H_2SO_4; 20 min in 0.1 M Na_2SO_4; and 12 min in 0.01 M Na_2SO_4. When 0.01 M cobalt(II) sulfate alone was oxidized without any supporting electrolyte, the half-time for decay was only about 3 min, long enough to observe polarographically, but not long enough to permit collection for absorbance measurements.

When prepared in 0.1 M H_2SO_4 alone, without any Na_2SO_4, the short-wavelength peak occurred at 387 mμ, which decreased and shifted to 406 mμ as decay occurred, indicating the existence of still another Co(III) complex.

Acetate Systems.—Quantitative oxidation of Co(II) in acetate solutions was obtained with the porous glass cell, giving a green Co(III) complex with a small absorption peak at 600 mμ and a larger peak at 344 mμ. When prepared by oxidation of 0.002 M $Co(NO_3)_2$ in 0.2 M HOAc–0.5 M NaOAc (pH 4.88), polarographic measurement showed the green Co(III) complex to be quite stable: only 50% reduction was observed after 48 hr.

Partial reduction of the green complex was catalyzed by passage through Dowex 50W or through Dowex 1, but that part of the green complex that was not reduced was not retained on either resin, in accord with previous observations.[10] Some workers have proposed a neutral trisacetate complex,[11] while others have proposed a polymeric hydroxy-bridged acetate complex.[10] In an unsuccessful attempt to determine the ratio of cobalt to acetate in the green complex, it was interestingly found that a mixed bed of Dowex 50W and Dowex 1 catalyzed the exchange of free C^{14}-labeled acetate in solution with acetate bound in the complex even more rapidly than the reduction.

Other Co(III) complexes were also obtained in acetate media. Electrolytic oxidation of 0.002 M $Co(NO_3)_2$ in 0.5 M NaOAc (pH 6.22) gave a fine brown precipitate, but the colorless supernate contained Co(III) (measured polarographically) which was strongly held on Dowex 1, indicating an anionic species. After elution with 1 M NaCl, the cobalt was shown polarographically to be still in the trivalent state. Electrolytic oxidation of 0.002 M $Co(NO_3)_2$ in 0.003 M HOAc–0.008 M NaOAc (pH 3.58) also gave a colorless Co(III) complex, but no precipitate. The complex was retained on Dowex 1, but not strongly at all; it was eluted with only slight tailing by the dilute acetate buffer, and 1 M NaCl was not required for elution.

Acid Systems.—Co(III) species could be prepared even in 0.1 M $HClO_4$ and 0.1 M HNO_3 although the yields were quite small (around 15%), even with the membrane cell. The Co(III) was detected with the flow-through dropping-mercury electrode located about 20 sec downstream from the oxidizing cell. Further characterization of the Co(III) species was not attempted; their instability did not permit collection of the oxidizing cell effluent for batch spectrophotometric or polarographic analysis.

Conclusions

Continuous electrolysis cells are described in which Co(II) may be rapidly oxidized to Co(III) complexes at controlled potential, and in solutions of controlled composition, at concentrations sufficient to permit separation, characterization, and quantitation by conventional ion-exchange, spectrophotometric, and polarographic methods. Oxidation times are about 1 min. Co(III) complexes (some hitherto unreported) can be prepared in acid ($HClO_4$, H_2SO_4, HNO_3) and in buffered (acetate, ammonia) solutions. Anodic oxidation in flowing systems with continuous sensing devices should permit study of relatively short-lived Co(III) complexes.

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CONTRIBUTION FROM GENERAL CHEMICAL RESEARCH
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The Chemistry of Bis(monofluorocarbonyl) Peroxide: Generation of the Fluoroformyl Radical and Synthesis of Fluoroformylsulfuryl Fluoride

BY W. B. FOX AND G. FRANZ

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Arvia, *et al.*, recently reported that the reaction of fluorine, carbon monoxide, and excess oxygen affords a novel compound $C_2F_2O_4$, to which the structure corresponding to bis(monofluorocarbonyl) peroxide, FC(O)OOC(O)F, was assigned.[1-4] We have examined this unusual material and obtained additional evidence for the proposed peroxide structure through nmr, esr, and chemical studies. Photolysis of the peroxide produces the expected FC(O)O· radical, which may be "trapped" by reaction with SO_2, leading to the formation of fluoroformylsulfuryl fluoride, $FC(O)OSO_2F$. The infrared spectrum of the latter compound and the electronegativity of the FC(O)O group are discussed.

Results and Discussion

Although the compound $C_2F_2O_4$ was formulated as the symmetrical peroxide FC(O)OOC(O)F by Arvia, *et al.*, the evidence cited by them (oxidizing power, chemical reactivity,[3] infrared spectrum[4]) was not unambiguous. However, the F^{19} nmr spectrum of $C_2F_2O_4$ obtained in our work strongly supports the original postulate of a symmetrical peroxide. The spectrum consists of a single, sharp, temperature-independent (+25 to −30°) resonance at ϕ +34.4, indicative of equivalent fluorines bonded to carbon rather than oxygen.[5] Excluding improbable configurations with both fluorines bonded to the same carbon atom, the only structure consistent with the data is that of the symmetrical peroxide.

In an effort to determine whether bis(monofluorocarbonyl) peroxide would undergo the facile O–O bond homolysis typical of peroxides, a sample of the material was photolyzed at low temperature in the resonance cavity of an esr spectrometer. The resulting spectrum, a highly anisotropic doublet, was tentatively assigned to the FC(O)O· radical. Although the spectrum might have arisen from other paramagnetic species (FC(O)·, for example), the existence of FC(O)O· was supported by the formation of CO_2 and the new compound fluoroformylsulfuryl fluoride in high yield when the peroxide was photolyzed in the presence of sulfur dioxide

$$FC(O)OOC(O)F + SO_2 \longrightarrow FC(O)OSO_2F + CO_2$$

It seems likely that the primary step in the reaction is homolytic cleavage of the peroxide, followed by the subsequent reactions indicated. Alternative pathways

$$FC(O)OOC(O)F + h\nu \longrightarrow 2FC(O)O\cdot$$

$$FC(O)\cdot + SO_2 \longrightarrow FC(O)OSO_2\cdot$$

$$FC(O)OSO_2\cdot + \begin{array}{c} FC(O)O\cdot \\ \text{or} \\ FC(O)OOC(O)F \end{array} \longrightarrow FC(O)OSO_2F + \begin{array}{c} CO_2 \\ \text{or} \\ CO_2 + FC(O)O\cdot \end{array}$$

involving the intermediate $FSO_2\cdot$ radical cannot be decisively ruled out, but the absence of SO_2F_2 as a product suggests that $FSO_2\cdot$ is not an important intermediate in this system.[6]

The infrared spectrum of fluoroformylsulfuryl fluoride in the NaCl region contains strong bands at 1500 and 1258 cm^{-1}, attributable to asymmetric and symmetric S=O stretching vibrations of the FSO_2O group. Robinson[7] has tabulated data indicating that these modes in FSO_2OX compounds may be expected in the regions 1445–1510 cm^{-1} (asymmetric S=O) and 1230–1260 cm^{-1} (symmetric S=O) when X is a highly electronegative group. A strong absorption at 855 cm^{-1} was assigned to S—F stretching of the FSO_2O group by comparison with assignments for this mode in SO_3F_2[8] (852 cm^{-1}), SO_2F_2[9] (848 cm^{-1}), and NF_2OSO_2F[9] (840 cm^{-1}). Other strong bands found at 1910 and 1190 cm^{-1} were assigned to C=O and C—F of the FCO group.[10,11] A medium intensity band at 757 cm^{-1} may be due to S—O stretching of the S—O—X group, since this mode is considered to give frequencies close to this value.[12] It has been assigned at 778 cm^{-1} in NF_2OSO_2F[9] and 787 cm^{-1} in CH_3OSO_2F.[13] Additional bands in the spectrum of fluoroformylsulfuryl fluoride were observed at 1975 cm^{-1} (weak, unassigned), 992 cm^{-1} (strong, possibly C—O stretch[4]), and 816 cm^{-1} (medium, unassigned).

The frequencies of the S=O stretching vibrations of $FC(O)OSO_2F$ are of interest in that they provide a basis for qualitatively assessing the electronegativity of the FC(O)O group. Several authors have pointed out that, since $-SO_2-$ symmetric and asymmetric stretching frequencies are essentially free from mass and coupling effects, these frequencies will depend on the electronegativities of the attached groups.[9,14,15] The more electronegative the attached groups, the higher will be the S=O stretching frequencies. Although the use of S=O frequencies for precise evaluation of group electronegativites may be complicated by the occurrence of double bonding between sulfur and the groups in question, a relative order of electronegativities can probably be estimated from the spectra. For example, changes in S=O frequencies were used to arrive at the electronegativity sequence $F > OF > CF_3 > OR \simeq OH > Cl$, etc.[7] Since there are now available a number of additional FSO_2X compounds for which S=O frequencies are known, and since the X group electronegativities have been independently estimated, it is of interest to reexamine the frequency–electronegativity relationship. For simplicity, the arithmetic means of asymmetric and symmetric S=O

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[5] (a) The F^{19} nmr resonance of the FC(O)O group has been observed in the region of ϕ 10–15: F. Fawcett, C. Tullock, and D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962). (b) The F^{19} nmr chemical shifts for the OF group in carbon-bonded hypofluorites lie in the range ϕ −139 to −154: G. Cady and C. Merrill, *ibid.*, **84**, 2260 (1962); J. Prager and P. Thompson, *Ibid.*, **87**, 230 (1965).

[6] Intermediate $FSO_2\cdot$ radicals in reactions of N_2F_4 with SO_2 were found to produce substantial amounts of by-product SO_2F_2 along with the desired F_2NSO_2F: M. Lustig, C. Bumgardner, F. Johnson, and J. Ruff, *Inorg. Chem.*, **3**, 1165 (1964).

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stretching frequencies for FSO_2X compounds were tablulated and compared with available data on the X electronegativities. The data are shown in Table I.

TABLE I

X in FSO_2X	Av of asym and sym S=O freq, cm^{-1}	Electronegativity of X
F	1385[a]	4.0[b]
CF_3O	1383[c]	
FC(O)O	1379	
FO	1374[8]	3.4, 3.7[d]
NF_2O	1371[9]	
NF_2	1369[6]	3.3,[e] 3.6[d]
CF_3	1351[15]	3.3,[f] 3.4[d]
CH_3O	1350[g]	3.0[f]
N_3	1346[h]	2.8[i]

[a] W. Perkins and M. Wilson, *J. Chem. Phys.*, **20**, 1791 (1952). [b] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 90. [c] W. VanMeter and G. Cady, *J. Am. Chem. Soc.*, **82**, 6005 (1960). [d] J. Huheey, *J. Phys. Chem.*, **68**, 3073 (1964). [e] R. Ettinger, *ibid.*, **67**, 1558 (1963). [f] J. Bell, J. Heisler, H. Tannenbaum, and J. Goldenson, *J. Am. Chem. Soc.*, **76**, 5185 (1954). [g] J. Roberts and G. Cady, *ibid.*, **81**, 4166 (1959). [h] J. Ruff, *Inorg. Chem.*, **4**, 567 (1965). [i] A. Clifford, *J. Phys. Chem.*, **63**, 1227 (1959).

Although the occurrence of double bonding between sulfur and fluorine may reduce the extent of S=O bonding, (thereby tending to decrease the S=O frequencies), this effect should be roughly the same for the models chosen since all except N_3SO_2F have S—F stretching frequencies in the narrow range 840–855 cm^{-1}. (The S—F stretching frequency of N_3SO_2F[16] is at 827 cm^{-1}.) The extent of double bonding between sulfur and the atom bonded to it in the X group of FSO_2X cannot be determined from available data, but is presumed to be small for the electronegative groups chosen here.

The infrared data suggest that the FC(O)O group ranks quite high on the electronegativity scale, being quite close to fluorine itself. The order of electronegativities suggested by the data is: $F > CF_3O > FC(O)O > FO > NF_2O > NF_2 > CF_3 \simeq CH_3O > N_3$.

Experimental Section

Materials.—Bis(monofluorocarbonyl) peroxide was prepared by the method of Arvia[3] and purified by vacuum-train fractionation through traps held at −78 and −196°. The material collected at −78° was identified by infrared spectroscopy as the peroxide. Sulfur dioxide (Matheson Company) was used directly from the cylinder.

Esr Spectrum.—A sample of bis(monofluorocarbonyl) peroxide was cooled to −196° in a quartz-windowed resonance cavity of a Varian V-4500 esr spectrometer and irradiated with a high-pressure mercury lamp. The resulting spectrum consisted of an anisotropic doublet (hyperfine splitting ~15–20 gauss, *g* value not determined). Accurate splitting values could not be obtained since the line width was nearly as large as the hyperfine splitting. The radical species appeared to be relatively stable, the signal intensity diminishing very little over a period of 5 min after the radiation was discontinued.

Preparation of $FC(O)OSO_2F$.—Sulfur dioxide (11 mmoles) and bis(monofluorocarbonyl) peroxide (11 mmoles) were condensed into a 1-l. Pyrex flask and allowed to stand at 25° for 2 days. No reaction occurred under these conditions. The mixture was then irradiated for 15 hr with a 360-w high-pressure mercury lamp, and the products were separated by fractional codistillation.[17] Subsequent infrared and mass spectral analysis of the fractions showed that, apart from small amounts of unreacted starting materials (*ca.* 10%), the major products were $FC(O)OSO_2F$ (*ca.* 8 mmoles, 70% yield), CO_2 (*ca.* 8 mmoles), and a small amount of SiF_4. Fluoroformylsulfuryl fluoride samples could be stored in thoroughly dried and flamed Pyrex vessels for up to 1 week with little change, but the material was easily decomposed by moisture.

Analysis.—Weighed samples of $FC(O)OSO_2F$ were digested with 25% NaOH solution for 12 hr at 100° to ensure complete hydrolysis. Sulfur and fluorine were then determined by conventional procedures.

Anal. Calcd for CO_4SF_2: S, 21.9; F, 26.0. Found: S, 23.0; F, 24.5.

Infrared Spectrum.—The spectrum of gaseous $FC(O)OSO_2F$ over the range 700–4000 cm^{-1} was recorded with a Perkin-Elmer Infracord spectrometer. A 10-cm gas cell fitted with NaCl windows was employed, with sample pressure ranging from 8 to 15 mm.

Nmr Spectra.—A Varian Model V-4302 spectrometer was used for the F^{19} nmr spectra. The spectrum of pure $FC(O)OSO_2F$ was measured at 25°, and that of FC(O)OOC(O)F was measured at −30 and +25°. Trichlorofluoromethane was used as an external reference.[18]

The F^{19} nmr spectrum of pure $FC(O)OSO_2F$ consists of a sharp doublet at ϕ +13.5 (C–F) and another doublet of equal intensity at ϕ −37.0 (S–F). The spin–spin coupling constant between the two types of fluorine atoms is 10 cps. In the somewhat related F–C–O–S–F bond and space system of $C_2F_5OSF_5$, Merrill found coupling constants to be 3 and 10 cps between $-CF_2-$ group fluorines and the axial and basal fluorines, respectively, of the SF_5 group.[19]

Physical Properties of $FC(O)OSO_2F$. (A) Molecular Weight.—The molecular weight was determined by vapor density at 760 mm and 25°, assuming ideal gas behavior. A value of 135 was found (calcd 146.1), the low value being attributed to the presence of lower molecular weight materials formed by reaction of the compound with traces of moisture in an inadequately dried glass system.

(B) Vapor Pressure.—The vapor pressure of $FC(O)OSO_2F$ was measured in a carefully flamed and dried vacuum system employing a conventional mercury manometer. The values obtained were 44.5 mm at −23.0°, 75.0 mm at −12.5°, 133.0 mm at 0.0°, 213.2 mm at 11.0°, and 338.5 mm at 23.0°. Infrared and mass spectral analyses confirmed that the composition of the fluoroformylsulfuryl fluoride sample underwent no change in the course of the measurements. The vapor pressure between 23.0 and −23.0° can be expressed by the equation

$$\log P_{\text{mm}} = 7.3239 - \frac{1420}{T}$$

(C) Mass Spectrum.—A Consolidated Electrodynamics Corp. Model 21-202 spectrometer with an ionization potential of 70 v was used. The inlet system and cycloid tube were at ambient temperature. The mass number, species (and relative abundance) of the most prominent peaks for $FC(O)OSO_2F$ are as follows: 146, $FC(O)OSO_2F^+$ (1.2); 83, SO_2F^+ (14.4); 80, SO_3^+ (0.1); 67, SOF^+ (3.7); 64, SO_2^+ (5.8); 63, CO_2F^+ (0.1); 51, SF^+ (0.6); 47, COF^+ (55.7); 44, CO_2^+ (100.0).

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results and to Miss R. Juurik for the chemical analyses. This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-30-069-ORD-2638.

Correspondence

The Isolation of Pentacyanonickelate(II) Salts

Sir:

Extensive and repeated investigations[1] have been made on the aqueous solution chemistry of the system $Ni(II)-CN^-$, and it now appears certain that the intense orange-red color of such solutions containing excess CN^- is due to the species $Ni(CN)_5^{3-}$. However, it had not been possible to isolate compounds of this anion. For example, the statement is made,[1] "... no Ni(II) cyanides have been isolated containing more than four CN^- per Ni(II); $K_2Ni(CN)_4$ is obtained from Ni(II) solutions saturated with KCN, even though the principal species in solution is $Ni(CN)_5^{3-}$." Assuming that this five-coordination persists in the solid state, we wish to report the isolation of salts of this anion. To the best of our knowledge this is the first time that a crystalline compound has been isolated of a five-coordinated Ni(II) complex containing only unidentate ligands.[2]

Before describing the rather simple syntheses of these salts, it may be worthwhile to mention the reasoning used to design these experiments. It is well recognized by coordination chemists that difficult-to-isolate complex ions can often be obtained by the use of large counterions. Almost always as a last resort, one can use $(C_6H_5)_4As^+$ and $(C_6H_5)_4B^-$ to isolate complex anions and cations, respectively. It is also known that greater success may be had if the large counterion one uses has a charge that is identical with that of the metal complex ion one wishes to isolate. For example, it is generally better to use PF_6^- to isolate monovalent complexes and SiF_6^{2-} to isolate divalent complexes. Dwyer[3] and his students have had considerable success using this simple approach for the resolution of optically active metal complexes. One can make the following empirical generalization: *metal complex ions that are difficult to isolate can often be isolated as salts of large ions having the same but opposite charge.*

Our first attempts to isolate salts of $Ni(CN)_5^{3-}$ were made using $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$, but these attempts failed. One of the difficulties was that in *ca.* 4 *M* CN^- the Co(III) ammines react with the replacement of ammine by CN^-. From previous studies[4] on the mechanisms of reactions of Co(III) complexes, it appeared that this reactivity was due to the presence of catalytic amounts of Co(II) and/or that the base hydrolyses of Co(III) are very rapid. In contrast to this, the corresponding Cr(III) complexes were expected to be stable under these conditions because of the unfavorable potential for the formation of Cr(II) and because Cr(III) ammines are less susceptible to base hydrolysis.[5] This was borne out by an examination of the visible absorption spectrum of a solution of $[Cr(NH_3)_6]^{3+}$ in *ca.* 4 *M* CN^-, which does not change at room temperature over a period of 6 hr.

The compound $[Cr(NH_3)_6][Ni(CN)_5]\cdot 2H_2O$ was prepared five times, and the compound $[Cr(en)_3][Ni(CN)_5]\cdot 2H_2O$ was prepared three times. In each case the product obtained analyzed correctly for the dihydrate salt, and in each case it was possible to remove both molecules of water at room temperature under high vacuum over a period of 24 hr. Slight variations were made in all of these preparations, and the best results were obtained with $[Cr(en)_3]^{3+}$ because its salt is less soluble. Described here are optimum conditions for the isolation of the $[Cr(NH_3)_6]^{3+}$ compound.

To a solution containing 4.0 g of $K_2Ni(CN)_4\cdot H_2O$ and 15 g of KCN in 20 ml of water at room temperature was added 20 ml of a solution containing 4.0 g of $[Cr(NH_3)_6]Cl_3\cdot H_2O$. After stirring, the solution was placed in a refrigerator at *ca.* $-5°$ and allowed to stand overnight. The orange-red crystals that separated were collected on a suction filter, and the mother liquor was carefully removed by suction, but the crystals were not washed. The air-dried product weighed 2.5 g (45% yield).

Anal. Calcd for $CrNiC_5H_{22}N_{11}O_2$: Cr, 13.73; Ni, 15.48; C, 15.84; H, 5.85; N, 40.64, O, 8.45. Found: Cr, 14.2; Ni, 15.1; C, 16.0; H, 5.80; N, 41.1; O, 8.1 (from weight loss assuming loss of H_2O). After the removal of the water of hydration, we have: *Anal.* Calcd for $CrNiC_5H_{18}N_{11}$: C, 17.51; H, 5.29. Found: C, 17.3; H, 5.1.

The infrared spectrum of solid $[Cr(NH_3)_6][Ni(CN)_5]$ in the C–N stretching region has three sharp absorption bands (2130 (m), 2100 (vs), and 2070 (s) cm^{-1}) which are in fair agreement with the bands (2123, 2103, and 2083 cm^{-1}) reported for the species in solution. The ultraviolet reflectance spectrum of the solid also appears to show the disappearance of the absorption band at 308 mμ due to $Ni(CN)_4^{2-}$, but the results are

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