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Oxidation of Some Transition Metal Carbonyls by Peroxydisulfuryl Difluoride

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The simple oxidation of metal carbonyls has received little recognition despite the attention given to the general areas of carbonyl chemistry. As early as 1905, it was observed that the interaction of $Fe(CO)_5$ with Cl_2 or Br_2 led to very pure $FeCl_2$ or $FeBr_2$, respectively.[1] Later workers[2,3] were able to control this reaction and the first carbonyl halides were produced:

$$Fe(CO)_5 + X_2 = Fe(CO)_4X_2 + CO \qquad X = Br, Cl, I \tag{1}$$

Subsequent work with the simple carbonyls of cobalt,[4] nickel,[4] chromium,[5] manganese,[6] and vanadium[7] showed that with the halogens oxidation occurs to produce a metal halide and occasionally a carbonyl halide.

Peroxydisulfuryl difluoride ($S_2O_6F_2$) has been shown to react with the carbonyls of Mo[8] and W[9] to produce $MoO_2(SO_3F)_2$ and $WO(SO_3F)_4$, respectively. The fact that $S_2O_6F_2$ oxidizes the metal atom in $Mo(CO)_6$ or $W(CO)_6$ to its highest oxidation state suggests that other first-row carbonyls may behave similarly, leading to high-valent metal fluorosulfates.

We found that $S_2O_6F_2$ reacts with the simple carbonyls of vanadium, chromium, manganese, iron, and cobalt producing the following fluorosulfates: $VO(SO_3F)_3$, $Cr(SO_3F)_3$, $FeO(SO_3F)$, $Fe(CO)_4(SO_3F)_2$, $Co(SO_3F)_2$, $Mn(SO_3F)_4$.

$VO(SO_3F)_3$ is a dark red solid that is highly sensitive to moist air. It dissolves in water to give a yellow solution and in Me_2SO (dimethyl sulfoxide) to give an orange solution which rapidly decomposes to a blue solution. Previous workers[10] found $VO(SO_3F)_3$ to be a viscous red liquid, probably due to traces of $S_2O_6F_2$ or $VOCl_3$ which can only be removed by prolonged pumping. $Cr(SO_3F)_3$, a green solid, has been previously prepared in our laboratories by the reaction of CrF_5 with SO_3.[11] $FeO(SO_3F)$ is a light brown solid which is very sensitive to moist air. It is only slightly soluble in Me_2SO. $Fe(CO)_4(SO_3F)_2$ is a yellow solid which decomposes slowly in the dark at room temperature. It dissolves in donor solvents such as ether, acetone, and water with the evolution of a gas, presumably CO. It is insoluble in hexane, petroleum ether, or benzene. At 100 °C, the compound is quantitatively decomposed to $Fe(SO_3F)_2$ and CO. $Fe(SO_3F)_2$ has been previously reported.[12] $Mn(SO_3F)_4$ is a gray-brown solid that is highly sensitive to moisture. It is hydrolyzed to a black solid by water but is readily soluble in Me_2SO producing a wine red solution which decomposes in several hours to a very faint pink solution containing Mn(II). $Co(SO_3F)_2$ is a purple solid that is sensitive to moist air and has been previously reported.[12]

The infrared spectrum of $VO(SO_3F)_3$ contains more absorption bands than may be ascribed to any one type fluorosulfate group. For either monodentate-bound SO_3F groups or bidentate SO_3F groups (either bridging or chelating) nine fundamental infrared bands are expected. For $VO(SO_3F)_3$ a bidentate SO_3F group is present since SO bands at 1350 and 1160 cm^{-1}, characteristic of a bidentate SO_3F group,[13,14] are present in the spectrum. The third SO band, usually found near 1080 cm^{-1}, is probably buried under either one of the broad overlapping bands centered at 1160 and 950 cm^{-1}. A monodentate SO_3F group is also present, as characteristic SO bands are observed at 1410 and 1240 cm^{-1}; again the third SO band, usually found near 985 cm^{-1},[15] is probably buried under either one of the broad overlapping bands centered at 1160 and 950 cm^{-1}. The broad band at 950 cm^{-1} probably contains the V=O stretching frequency.[16] The presence of more than one type of SO_3F group is further supported by the presence of two bands in the 800–900-cm^{-1} region, where only S–F stretching modes occur in fluorosulfates.

For the compound $FeO(SO_3F)$, the strong bands at 1355 and 1110 cm^{-1} suggest that a bidentate SO_3F group is present. The third SO stretching frequency is probably buried by the very broad peak at 1110 cm^{-1}. The strong band at 1000 cm^{-1} probably contains the Fe–O stretching frequency, while the 835 cm^{-1} band is attributed to the S–F stretching mode. The positions of the other SO_3F modes agree with those found for other fluorosulfates containing bidentate fluorosulfates.[13]

The infrared spectrum of $Mn(SO_3F)_4$ shows the presence of monodentate and bidentate fluorosulfate groups. The characteristic SO bands at 1430, 1240, and 1055 cm^{-1} are attributed to the monodentate SO_3F group while the SO bands at 1370, 1180, and 1100 cm^{-1} are assigned to the bidentate SO_3F group. The presence of more than one type of SO_3F group is further supported by the presence of two bands in the 800–905-cm^{-1} region, where only S–F stretching modes occur in fluorosulfates.

Experimental Section

Peroxydisulfuryl difluoride ($S_2O_6F_2$) was obtained as a gift from Professor F. Aubke, Department of Chemistry, University of British Columbia. An infrared spectrum and vapor-phase molecular weight determination showed the material to be of high purity. All the carbonyls were purchased from Alpha Ventron. $Co_2(CO)_8$ and $Mn_2(CO)_8$ of 95% purity were handled under nitrogen and used as received. $Fe(CO)_5$ of 98% purity was vacuum distilled directly into the reaction vessel and was protected from light at all times. $Cr(CO)_6$ of 95% purity was used as received. $V(CO)_6$ of 90% purity was handled under helium in a glovebag. Perfluoroheptane (C_7F_{16}) was obtained from PCR Research Chemicals. It was vacuum distilled from phosphorus pentoxide before use.

Infrared spectra were taken on a Perkin-Elmer 467 infrared spectrophotometer. Solid samples were measured as thin smears between thallium bromide iodide (KRS-5) windows. Gaseous samples were contained in a Monel gas cell fitted with AgCl windows and a Whitney brass valve. The gas cell had a path length of 8.25 cm. The infrared spectra were calibrated with polystyrene film.

The electronic spectra was recorded on a Cary Model 14 recording spectrophotometer (path length of cell was 1.00 cm).

The x-ray powder spectrum was obtained on a General Electric XRD-5 powder camera using Ni-filtered Cu Kα radiation. Exposure times were generally 4 h. The procedure was standardized using known compounds in which the calculated *d* values agreed with the published ASTM values. Only the very strong (vs), strong (s), and medium (m) intensity lines are reported in this paper.

Chemical analyses were performed by Beller Laboratories, Gottingen, West Germany.

The reaction vessels (Pyrex glass) used in the following synthetic runs had volumes of 80 or 100 mL and were equipped with a Kontes Teflon stopcock and a Teflon-covered stirring bar. The solid carbonyls were transferred to a reaction vessel under nitrogen or helium. Either $S_2O_6F_2$ or C_7F_{16} and $S_2O_6F_2$ were then added. After the reaction was complete, the volatile materials were removed, first at −78 °C and then at room temperature, by pumping through a trap cooled

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to −196 °C. The remaining solid in the reaction vessel was pumped on until constant weight was achieved. In some cases the weight of the solid product was slightly larger than theoretically possible. This was due to a small amount of $S_2O_6F_2$ being absorbed by the Teflon stirring bar. The effect seemed to be more pronounced when the solvent C_7F_{16} was used.

Preparation of $VO(SO_3F)_3$. To 0.205 mmol of $V(CO)_6$, 5.66 mmol of $S_2O_6F_2$ was added at −196 °C. After 3 h at 50 °C the reaction was complete and a viscous red liquid that was sparingly soluble in excess $S_2O_6F_2$ was produced. An infrared spectrum of the volatile materials at −78 °C showed CO_2, CO, and $S_2O_5F_2$ to be present. Prolonged pumping on the residue at room temperature yielded 0.202 mmol of solid $VO(SO_3F)_3$ in 98.5% yield.

To 0.955 mmol of $V(CO)_6$, 1.2 mmol of dry degassed C_7F_{16} and 16.71 mmol of $S_2O_6F_2$ were added. After 3 h at 60 °C a viscous red liquid, insoluble in C_7F_{16}, was formed. Infrared spectra of the volatile materials at room temperature showed $S_2O_5F_2$, CO_2, C_7F_{16}, and $S_2O_6F_2$ to be present. Prolonged pumping on the residue at room temperature yielded 0.927 mmol of solid $VO(SO_3F)_3$ in 97% yield. The solid melts at 102–104 °C and decomposes to a yellow solid at 190 °C. Its infrared spectrum showed the following bands (cm^{-1}): 1410 (m, sh), 1350 (s, sh), 1285 (s, vbr), 1240 (s, sh), 1160 (s, br), 950 (m–s, sh), 890 (m, sh), 815 (m), 720 (m, br), 620 (m, vbr), 570 (m), 560 (m), 495 (m, sh), 450 (m–w, br), 380 (w, br).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $VO(SO_3F)_3$: V, 13.99; S, 26.4; F, 15.7. Found: V, 14.04; S, 24.6; F, 16.0.

Preparation of $Cr(SO_3F)_3$. To 1.98 mmol of $Cr(CO)_6$, 19.55 mmol of $S_2O_6F_2$ was added. The mixture was warmed to room temperature and then heated to 60 °C for 20 days. A pale green solid that was insoluble in $S_2O_6F_2$ was formed. An infrared spectrum of the volatile material at −10 °C showed CO_2, $S_2O_5F_2$, and $S_2O_6F_2$ to be present. A pale green solid residue (2.06 mmol) of $Cr(SO_3F)_3$ was recovered in essentially 100% yield.

The infrared and electronic spectra of $Cr(SO_3F)_3$ prepared from $S_2O_6F_2$ and $Cr(CO)_6$ were found to agree with those of $Cr(SO_3F)_3$ prepared from CrF_5 and SO_3.[11] Further studies were not made.

Preparation of $FeO(SO_3F)$. To 2.89 mmol of $Fe(CO)_5$, 19.55 mmol of $S_2O_6F_2$ was added. A vigorous reaction occurred on warming to room temperature producing a brown solid. The reaction was complete after 1 h at room temperature. An infrared spectrum of the volatile material at room temperature showed CO, CO_2, $S_2O_5F_2$, and $S_2O_6F_2$ to be present. A tan solid product (2.94 mmol) of $FeO(SO_3F)$ was formed in 100% yield. $FeO(SO_3F)$ decomposed at 260 °C; UV (Me_2SO), 335 nm (s). Its infrared spectrum showed the following bands (cm^{-1}): 1440 (vw), 1355 (s), 1110 (s, vbr), 1000 (s, sh), 835 (s), 740 (w, sh), 660 (w, sh), 620 (s, sh), 570 (s), 550 (s), 420 (m), 320 (m).

The x-ray powder spectrum gave the following *d* values with their respective intensities: 9.12 (s), 4.70 (m), 4.03 (m), 3.73 (m), 3.28 (m), 3.21 (m) 10^{-1} nm.

Anal. Calcd for $FeO(SO_3F)$: Fe, 32.7; S, 18.7; F, 11.1. Found: Fe, 32.2; S, 18.3; F, 11.6.

Preparation of $Fe(CO)_4(SO_3F)_2$. To 1.84 mmol of $Fe(CO)_5$, 48.8 mmol of dry degassed C_7F_{16} and 22.4 mmol of $S_2O_6F_2$ were added. On warming to room temperature a reaction occurred and a bright yellow solid precipitated. After 2 h in the dark at room temperature, the reaction was complete. Removal of all volatile materials left behind 1.94 mmol of yellow solid, $Fe(CO)_4(SO_3F)_2$, in essentially 100% yield. The solid did not melt below 100 °C, but at 100 °C decomposed to $Fe(SO_3F)_2$ and CO. Its infrared spectrum showed the following bands (cm^{-1}): 2218 (m), 2200 (s), 2175 (s), 2140 (s), 1410 (s), 1340 (s), 1245 (s, sh), 1200 (s), 1150 (s, sh), 1040 (s), 920 (m, br), 785 (s), 615 (s–m), 600 (s), 580 (s), 520 (m), 430 (m, br), 400 (m).

A freshly prepared sample (0.576 mmol) of $Fe(CO)_4(SO_3F)_2$ was decomposed at 100 °C for 1 h. It produced 2.36 mmol of CO gas (mol wt: found, 27; theoretical, 28; the infrared spectrum agreed with the literature) and 0.562 mmol of the white solid, $Fe(SO_3F)_2$. The infrared spectrum of the white solid was identical with that of $Fe(SO_3F)_2$.

Anal. Calcd for $Fe(SO_3F)_2$: Fe, 22.0; S, 25.2; F, 14.9. Found: Fe, 22.2; S, 25.3; F, 14.5.

Preparation of $Mn(SO_3F)_4$. To 0.446 mmol of $Mn_2(CO)_{10}$, 16.29 mmol of $S_2O_6F_2$ was added. After 1 day at room temperature the reaction was complete. An infrared examination of the volatile materials at −78 °C showed CO, CO_2, $S_2O_5F_2$, and a small amount of SO_2F_2 to be present. A gray-brown solid product (0.850 mmol) of $Mn(SO_3F)_4$ was formed in 96% yield.

To 0.368 mmol of $Mn_2(CO)_{10}$, 37.3 mmol of dry-degassed C_7F_{16} and 20.0 mmol of $S_2O_6F_2$ were added. After 3 h, the reaction was complete. The infrared spectrum of the volatile material at room temperature showed CO_2, $S_2O_5F_2$, C_7F_{16}, and $S_2O_6F_2$ to be present. A gray-brown solid product (0.738 mmol), $Mn(SO_3F)_4$, was formed in essentially 100% yield. $Mn(SO_3F)_4$ decomposes without melting at 105 °C; UV (Me_2SO), 510 nm (ϵ 1.2×10^3) and 320 nm (ϵ 3.6×10^3). Its infrared spectrum showed the following bands (cm^{-1}): 1430 (m), 1370 (s), 1240 (s), 1180 (s), 1100 (s, sh), 1055 (s), 905 (m), 835 (m–s), 750 (m, sh), 640 (m), 575 (m), 555 (m), 435 (m, br), 350 (m).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $Mn(SO_3F)_4$: Mn, 12.17; S, 28.3; F, 16.8. Found: Mn, 12.96; S, 27.2; F, 16.0.

Preparation of $Co(SO_3F)_2$. To 0.739 mmol of $Co_2(CO)_8$, 11.5 mmol of $S_2O_6F_2$ was added. On warming, the reaction began and was complete within 6 h at room temperature. An infrared spectrum of the volatile materials at −78 °C showed CO, CO_2, and $S_2O_5F_2$ to be present. A purple solid product (1.42 mmol) was obtained in 96% yield.

The use of the solvent C_7F_{16} did not change the reaction. To 0.310 mmol of $Co_2(CO)_8$, 26.5 mmol of dry-degassed C_7F_{16} and 6.22 mmol of $S_2O_6F_2$ were added. After 1 h at room temperature the reaction was complete and 0.640 mmol of the purple solid product $Co(SO_3F)_2$ was formed in essentially 100% yield. $Co(SO_3F)_2$ decomposed to a brown solid at 110 °C: UV (Me_2SO), 690 (ϵ 40.1), 535 (ϵ 239), 420 (ϵ 20.0), 260 nm (ϵ 466).

The x-ray powder spectrum showed the solid to be amorphous.

Anal. Calcd for $Co(SO_3F)_2$: Co, 22.8; S, 24.9; F, 14.7. Found: Co, 23.1; S, 25.1; F, 13.8.

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Registry No. $VO(SO_3F)_3$, 65776-46-7; $Cr(SO_3F)_3$, 55136-41-9; $FeO(SO_3F)$, 65776-54-7; $Fe(CO)_4(SO_3F)_2$, 65776-53-6; $Fe(SO_3F)_2$, 14928-65-5; $Mn(SO_3F)_4$, 65776-45-6; $Co(SO_3F)_2$, 15059-58-2; $V(CO)_6$, 14024-00-1; $Cr(CO)_6$, 13007-92-6; $Fe(CO)_5$, 13463-40-6; $Mn_2(CO)_{10}$, 10170-69-1; $Co_2(CO)_8$, 12553-61-6; $S_2O_6F_2$, 13709-32-5.

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Matrix-Isolation Infrared and Electron Paramagnetic Resonance Spectroscopic Studies of the Reaction of Lithium with Silicon Tetrafluoride

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Since Troost[4] first predicted the existence of SiF_2 in 1871, there has been extensive research into the chemistry of this

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