Journal of Fluorine Chemistry, *24* (1984) 443–450
Received: April 11, 1983; accepted: May 20, 1983

HIGH OXIDATION STATE TRANSITION METAL PERFLUOROGLUTARATES

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SUMMARY

The reaction of bifunctional perfluorinated acid anhydrides with CrO_3, K_2CrO_4, and Na_2MoO_4 results in the formation of new high oxidation state transition metal perfluoroglutarates.

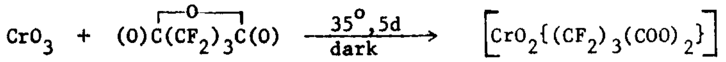
INTRODUCTION

Fluorinated acid anhydrides, $(R_fCO)_2O$, are known to add across Cr=O bonds in chromium trioxide or chromates to yield chromyl and chromyl-salt derivatives [1,2]. Analogous Mo and W chemistry is known [2]. Similar action by bifunctional perfluorinated acid anhydrides might lead to either chelated or polymeric chromyl systems. The present results with perfluoroglutaric and perfluorosuccinic anhydrides suggest that the polymeric forms are strongly favored.

0022-1139/84/$3.00

RESULTS AND DISCUSSION

Under carefully controlled conditions, it was found that CrO_3 with excess perfluoroglutaric anhydride (PFGAn) will form chromyl perfluoroglutarate in nearly quantitative yield:



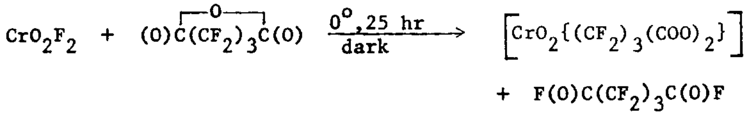
$$CrO_3 + (O)\overset{\overline{\quad O \quad}}{C(CF_2)_3C}(O) \xrightarrow[\text{dark}]{35^o,5d} \left[CrO_2\{(CF_2)_3(COO)_2\}\right]$$

This new chromyl compound is a brown solid that is extremely hygroscopic, which hydrolyzes to a yellow chromic acid solution:

$$\left[CrO_2\{(CF_2)_3(COO)_2\}\right] + 2H_2O \longrightarrow H_2CrO_4 + HOOC(CF_2)_3COOH$$

Chromyl perfluoroglutarate is strongly oxidizing and at room temperature it ignites acetone and methanol. It is insoluble in CS_2 and perfluoroalkane-70, and is only slightly soluble in CCl_4. When it is heated slowly, decomposition occurs above 80^o but rapid heating results in explosive decomposition around 70^o-90^o, which produces CO_2, COF_2, and CF_3COF among other products.

Since chromyl trifluoroacetate may be prepared <u>via</u> the reaction of CrO_2F_2 with trifluoroacetic anhydride [3] , an attempt was made to prepare chromyl perfluoroglutarate in a like fashion:

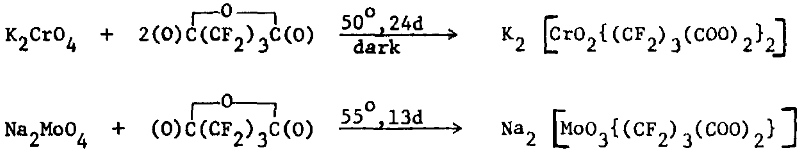


$$CrO_2F_2 + (O)\overset{\overline{\quad O \quad}}{C(CF_2)_3C}(O) \xrightarrow[\text{dark}]{0^o,25\ hr} \left[CrO_2\{(CF_2)_3(COO)_2\}\right] + F(O)C(CF_2)_3C(O)F$$

The above reaction did occur, but chromyl perfluoroglutarate was produced in an impure state.

Perfluorosuccinic anhydride (PFSAn) also reacts with CrO_3 to produce the dark brown solid, $\left[CrO_2\{(CF_2)_2(COO)_2\}\right]$, in about 87% yield. Chromyl perfluorosuccinate is slightly soluble in CCl_4, but due to its unpredictable explosive nature, attempts to isolate and study this compound further were abandoned.

The reaction of PFGAn with K_2CrO_4 and Na_2MoO_4 were also studied. Surprisingly, two moles reacted per mole of K_2CrO_4 while with Na_2MoO_4 only one mole added:



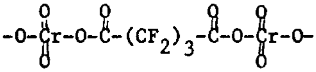
$$K_2CrO_4 \;+\; 2(O)\overset{O}{\overbrace{C(CF_2)_3C}}(O) \xrightarrow[\text{dark}]{50^{o},24d} K_2\left[CrO_2\{(CF_2)_3(COO)_2\}_2\right]$$

$$Na_2MoO_4 \;+\; (O)\overset{O}{\overbrace{C(CF_2)_3C}}(O) \xrightarrow{55^{o},13d} Na_2\left[MoO_3\{(CF_2)_3(COO)_2\}\right]$$

The chromium salt product was a green hygroscopic solid that hydrolyzes to a yellow solution; on heating it turns brown and melts at $\sim 150^{o}$. With trifluoroacetic anhydride, $(CF_3CO)_2O$, K_2CrO_4 and Na_2MoO_4 formed $K_2CrO_2(CF_3COO)_4$ and $Na_2MoO_2(CF_3COO)_4$, respectively [2].

The infrared spectrum of chromyl perfluoroglutarate contains bands at 1780, 1655, and 1415 cm^{-1}; the first two bands are attributable to the ν asym(COO) while the latter is assigned as νsym(COO). Also, the (C-C) stretching frequency is located at 815 cm^{-1}. These assignments are in accord with those found for Ir(III) perfluoroglutarates [4]. The bands appearing in the 1255-1055 region are attributable to C-F stretching modes [5]. The chromium oxygen (Cr=O) asymmetric and symmetric modes are found at 970 and 950 cm^{-1}, respectively. In chromyl trifluoroacetate these bands were unresolved at 960 cm^{-1} [1]. It is interesting to point out that for CrO_3 the broad absorption band at 969 cm^{-1} represents the stretching frequency for the Cr=O groups while the band at 893 cm^{-1} is assigned to the (Cr-O-Cr) stretching mode [6].

In a similar fashion, the infrared spectrum of chromyl perfluorosuccinate may be assigned: 1750 and 1665 cm^{-1} $\left[\nu asym(COO)\right]$, 1420 cm^{-1} $\left[\nu sym(COO)\right]$, 1240-1130 cm^{-1} (ν C-F), 986 and 940 cm^{-1} (ν asym and ν sym Cr=O).

The low solubility, low volatility and infrared data suggest that chromyl perfluoroglutarate is a polymer with possibly a chain type structure, i.e.  $-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr}}}}-O-\overset{O}{\overset{\|}{C}}-(CF_2)_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{Cr}}}}-O-$. The perfluoroglutarate groups are bidentate bridging in character, much like the bridging oxygens in chromium trioxide. It is interesting to note that the ligands (F, CF_3COO, SO_3F, NO_3, CF_3SO_3) in their respective chromyl compounds also act as bridging ligands [7].

The ultraviolet/visible spectra for $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$ and $\left[CrO_2\{(CF_2)_2(COO)_2\}\right]$ in CCl_4 are similar to those reported for other chromyl compounds [1].

The infrared spectrum of $K_2\left[CrO_2\{(CF_2)_3(COO)_2\}_2\right]$ is similar to that found for $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$ except that the absorption bands due to Cr=O stretching are absent. The Cr-O-C stretching frequency is assigned to the band at 957 cm^{-1}; in $K_2CrO_2(CF_3COO)_4$ this band was observed at 940 cm^{-1} [2]. In $Na_2\left[MoO_3\{(CF_2)_3(COO)_2\}\right]$ the band at 945 cm^{-1} is probably the stretching frequency for Mo=O; for K_2MoOCl_5 the Mo=O is located at 967 cm^{-1} [6].

EXPERIMENTAL

The compounds used in this work were obtained from commercial sources; CrO_3 (Baker), K_2CrO_4, CCl_4 (spectral grade), $Na_2MoO_4\cdot 2H_2O$ (Mallinckrodt), (PFGAn), (PFSAn) (PCR). Perfluoroalkane-70 is a mixture of $F(CF_2)_nF$ (b.p. 70–80°) and was purchased from PCR. All solids were reagent grade and were thoroughly dried before use. The remaining chemicals (except for CCl_4) were vacuum distilled prior to use. Chromyl fluoride was prepared by the methods of Green and Gard [8].

Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum manifold equipped with a Televac vacuum gauge and mercury manometer connected to the manifold.

The infrared spectra were recorded on a Perkin-Elmer 467 infrared spectrophotometer. Infrared spectra of gaseous samples were obtained with a Monel cell (AgCl windows) equipped with a Whitney brass valve. The path length of the cell was 8.25 cm. The spectra of solid samples were obtained either neat between KRS-5 windows or as KBr pellets and were calibrated with polystyrene film.

The ultraviolet spectra were recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The samples were dissolved in spectro-quality CCl_4 (Mallinckrodt). The path length of the cell was 1.00 cm. The X-ray powder spectra were obtained using an XRD-5 General Electric Camera. Nickel-filtered Cu Kα radiation was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot H_2O$) in which the calculated d values agreed with the published ASTM values. Only the very strong (vs), strong (s), medium (m) and weak to medium (wm) intensity lines are reported in this paper. The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenolphthalein indicator. Standard analyses were performed by Beller Laboratory, Göttingen, West Germany.

Reaction of CrO_3 with PFGAn

To a 100 ml Pyrex glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 8.58 mmol of dried CrO_3 and 112 mmol of perfluoroglutaric anhydride (PFGAn) were added. The reaction mixture was protected from light and heated with stirring at 35° for 5 d. The material volatile at 0° was pumped away through a trap cooled to -196° (no non-condensable gases were present). A tan-brown solid product, 8.51 mmol of $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$ was formed in 99% yield; expl. dec. ∿ 80°. The uv/vis spectrum in CCl_4 contained two bands at 407 and 275 nm. The infrared spectrum has bands (cm^{-1}): 1780(s), 1655(s,b), 1415(m,br), 1255(m), 1170(vs), 1055(m), 970(s), 950(s), 905(m), 815(m), 700(s,br), 565(m), 325(w), 280(w). The X-ray powder spectrum gave the following d values (in Å) with their respective intensities: 11.13(s), 8.37(m), 7.54(m), 6.51(wm), 4.95(s), 4.55(s), 4.18(vs), 3.84(s), 3.43(s), 2.87(s), 2.39(wm), 2.34(wm), 2.25(wm), 2.19(m).

Anal. Calcd for $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$: Cr, 16.15; C, 18.65; F, 35.40. Found: Cr, 17.67; C, 17.01; F, 35.10; also Cr, 16.13 via iodometry, 16.10 via acidity (based on Eq. 2).

Reaction of CrO_2F_2 with PFGAn

To a 100 ml quartz vessel equipped with a Kontes Teflon valve and a Teflon stirring bar, 18.7 mmol of PFGAn and 5.36 mmol of CrO_2F_2 were added. The reaction mixture was protected from light and stirred at 0° (25 hr). During this time the red-brown vapors of CrO_2F_2 disappeared and the solution became dark-brown. The materials volatile at 0° were pumped away through a trap cooled to -196°. An infrared spectrum showed that PFGAn and perfluoroglutaryl fluoride were present. A dark-brown product, 5.34 mmol of $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$ was formed in 99% yield. The infrared spectrum was similar to that found for $\left[CrO_2\{(CF_2)_3(COO)_2\}\right]$ prepared from CrO_3 and PFGAn.

Reaction of CrO_3 with PFSAn

To a 100 ml Pyrex glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 4.25 mmol of dried CrO_3 and 32.81 mmol of perfluorosuccinic anhydride were added. The reaction mixture was protected from light and heated with stirring at 25-45° for 4 d. The material volatile at room temperature was pumped away through a trap cooled to -196° (no non-condensable gases were present). A brown solid product, 3.70 mmol of $[CrO_2\{(CF_2)_2(COO)_2\}]$ was formed in 87% yield; the solid did not melt but slowly decomposed upon heating (<u>caution</u> - rapid heating or storage results in unpredictable explosive decomposition). The infrared spectrum has bands (cm^{-1}): 1750(m), 1665(s,b), 1420(m,b), 1240(m), 1170(m), 1130(s), 986(m), 940(s,b). The uv/vis spectrum in CCl_4 contained two bands at 394 and 276 nm. Chromyl perfluorosuccinate reacts with water to form a yellow chromate solution; it is slightly soluble in CCl_4. Due to its instability, further studies were not carried out.

Reaction of K_2CrO_4 with PFGAn

To a 100 ml Pyrex glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 2.69 mmol of K_2CrO_4 and 42.47 mmol of PFGAn, were added. After 24 d at 50° (in the dark) the materials volatile at room temperature were pumped away through a trap cooled to -196°. The volatile material was only PFGAn. A green solid, 2.70 mmol of $K_2[CrO_2\{(CF_2)_3(COO)_2\}_2]$ was formed in 100% yield; m.p. ~ 150°. The infrared spectrum has bands (cm^{-1}); 1780(s), 1650(m,br), 1430(m,br), 1325(w), 1283(w), 1262(m), 1180(s,br), 1155(s), 1051(m), 957(m), 919(w), 894(m), 818(w), 789(w), 757(w), 737(w), 630(w). The X-ray powder spectrum gave the following d values (in Å) with their respective intensities: 19.53(m), 7.52(m), 6.20(m), 5.53(s), 5.29(vs), 5.16(vs), 4.62(w), 4.31(s), 3.88(s), 2.57(m), 2.30(m).

Anal. Calcd for $K_2[CrO_2\{(CF_2)_3(COO)_2\}_2]$: Cr, 8.15; C, 18.82; F, 35.72. Found: Cr, 9.8; C, 16.95; F, 33.00; also Cr, 8.34 via iodometry.

Reaction of Na_2MoO_4 with PFGAn

To a 100 ml Pyrex glass vessel equipped with a Kontes Teflon valve and Teflon stirring bar, 2.47 mmol of Na_2MoO_4 and 36.8 mmol of PFGAn were added. The reaction mixture was protected from light and heated with stirring at 55° (13 d). The materials volatile at room temperature were pumped away through a trap cooled to -196°; the only volatile material was PFGAn. A white (light green tinge) solid, 2.49 mmol of $Na_2[MoO_3\{(CF_2)_3(COO)_2\}]$ was formed in ∿100% yield; dec. > 125°. The infrared spectrum has bands (cm^{-1}): 1765(m), 1670(vs), 1420(m), 1400(m), 1282(w), 1245(s), 1210(s), 1160(vs), 1115(w), 1075(w), 1056(m), 945(s,br), 830(m), 785(w), 750(m), 630(m,br), 550(m), 505(m).

Anal. Calcd for $Na_2[MoO_3\{(CF_2)_3(COO)_2\}]$: Na, 10.74; Mo, 22.42; C, 14.03; F, 26.63. Found: Na, 10.80; Mo, 21.40; C, 13.47; F, 26.30.

ACKNOWLEDGEMENT

We wish gratefully to acknowledge the support of the donors of the Petroleum Research Fund administered by the American Chemical Society.

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