



Scientific contribution

Chromyl Fluoride as a Strongman Representative of the Chromium (VI) Dioxodihalides Oxidizing Agent Family

Jeran Marko^{1,*}, Tramšek Melita¹, Tavčar Gašper^{1,2}

¹ Department of Inorganic Chemistry and Technology, "Jožef Stefan" Institute, Ljubljana, Slovenia

² "Jožef Stefan" International Postgraduate School, Ljubljana, Slovenia

* Correspondence: M.J.; marko.jeran@ijs.si

Abstract:

The chemistry of chromium (Cr) as a transition state element includes a variety of oxidation states and their specific colours. The general and most common oxidation states of chromium are (+6), (+3), and (+2). However, some stable compounds with (+5), (+4) and (+1) states are also known. The main species formed by chromium in the (+6) oxidation state are the chromate (CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions.

Chromium (VI) dioxodihalides represent a group of versatile oxidants that donate oxygen atoms to a variety of organic molecules. Chromium-oxotransition metal complexes in higher oxidation states have been used as models in biochemical studies, in particular to investigate how such systems can mimic biologically relevant mixed-function oxygenases and how the oxygen ligands interact in electrophilic reactions. The representative compound from this group of chromium compounds is chromyl fluoride (CrO_2F_2), which was mentioned after 1952, when its physical properties were precisely determined. It is a violet-red coloured crystalline solid that melts to an orange-red liquid at a temperature close to room temperature.

In this paper, two ways to prepare chromium fluoride are presented: (a) by reaction between its chloride analogues and gaseous fluorine and (b) by reaction between chromium(VI) oxide and anhydrous hydrogen fluoride. Raman spectroscopy was used to characterise the crude products directly in the FEP tube. Its physical properties and chemical reactivity pose a great challenge for synthesis. Special equipment is required for its production (e.g. a nickel vacuum line system).

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1. Introduction

1.1. Chromium compounds

Chromium (Cr) is a metal that is naturally found in the environment (soils, rocks, volcanic dusts, etc.) in two states: as trivalent Cr(III) and as hexavalent Cr(VI). The studies have shown that Cr(VI) compounds have almost 100 times higher toxicity than Cr(III) compounds (Hussain and Keçili, 2020). Chromium compounds are widely used in industry, e.g. for the production of dyes in the textile industry (potassium chromate, ammonium dichromate), for the production of printing inks, Cr-based paints, plastics (zinc chromate, sodium chromate, lead chromate and barium chromate) and as corrosion inhibitors (strontium chromate, zinc chromate and calcium chromate) (Hussain and Keçili, 2020).

Cr(VI) compounds are considered as highly toxic and industrial pollutants with dangerous effects on humans, including various diseases such as liver and kidney damage, respiratory and immune system problems (Hussain and Keçili, 2020; Cohen, et al.1993).

Chromium compounds are also important in organic synthetic chemistry. Their complexes are important as fluorinating reagents for the preparation of biologically active compounds for pharmaceuticals and agrochemicals (Haufe and Bruns, 2002). Some examples of enantioselective nucleophilic fluorination using chromosalen complexes as Lewis's acid catalysts for ring-opening *meso*-epoxidic compounds have been reported (**Figure 1**). However, these reactions lead to end products with an enantiomeric excess of only about 66% (Thornbury, et al. 2017).

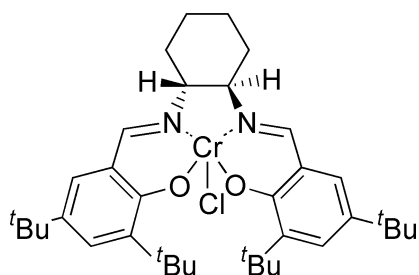


Figure 1. Jacobsen's enantiomerically pure (*R,R*)-(-)-(salen)chromium chloride complex for ring-opening epoxides in the presence of stoichiometric or slightly substoichiometric amounts (Haufe and Bruns, 2002).

1.2. Motivation for study of chromium(VI) dioxodihalides

Chromium(VI) dioxodihalides represent a group of versatile oxidants that donate oxygen atoms to a variety of organic molecules. These oxotransition metal complexes of chromium in higher oxidation states were taken as a model for the enzyme cytochrome P-450. The electronic structure of chromium(VI) dioxodichloride (**Figure 2**) was studied to determine the extent to which this remarkable system can mimic mixed-function oxygenases in biological systems and to determine the mechanism of oxygen ligand activity in electrophilic reactions (Torrent, et al. 1996).

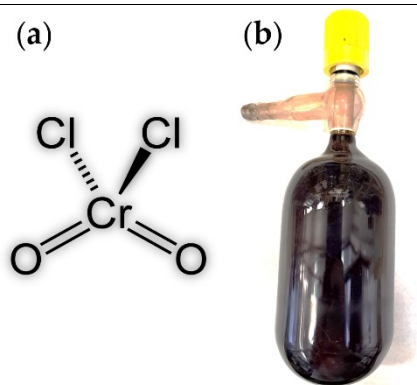


Figure 2. (a) Molecular structure of chromyl chloride, and (b) chromyl chloride as chemical reagent in a glass flask with Teflon valve.

In developing compounds with high oxidation efficiency and synthesising new materials, including materials with exceptionally high specific surface area (Tavčar and Skapin, 2019), researchers also faced various challenges in synthesis.

1.3. Chromyl fluoride (CrO_2F_2)

The literature dealing with chromyl compounds mainly reports on chromyl chloride (CrO_2Cl_2) and its reactions. The fluorinated analogue, called chromyl fluoride (CrO_2F_2), was mentioned after 1952, when its physical properties were accurately determined (Brown, et al. 1975). Infrared absorption spectra with tetrahedral structure and C_{2v} symmetry were derived from the gas phase (Brown, et al. 1976).

Brown et al. (1976) first reported the structural study of chromyl fluoride in liquid phase and presented solid phase data. The study revealed that liquid chromyl fluoride is mainly in the form of monomers with C_{2v} symmetry. The authors also confirmed the claim that the metal centres are polymerized via fluorine bridge bonds. More specifically, the solid phase forms polymers containing terminal Cr-O bonds.

Pure chromyl fluoride (**Figure 3**) reaches a pressure of 760 mm Hg as violet-red crystals at 22.6 °C and melts to an orange-red liquid at 31.6 °C. The vapor pressure at the triple point is 885 mm Hg (Engelbrecht and Grosse, 1951). Engelbrecht and Grosse (1951) noted that its solubility in HF at -78 °C is very low. Purification procedures took into account the fact that it forms stable and non-volatile triple addition compounds with HF and potassium or sodium fluoride (KF or NaF).

Because of its extreme reactivity with any type of organic compounds, care must be taken during handling. For example, at high temperatures, paraffinic gasses such as methane or butane ignite in its presence and burn with bright flame, producing smoke from chromium(III) oxide (Cr_2O_3) and chromium(III) fluoride (CrF_3) (Engelbrecht and Grosse, 1951).

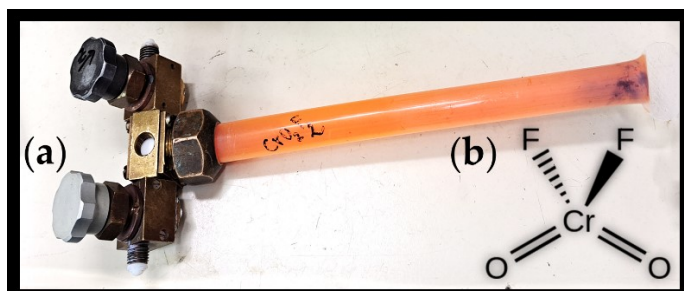


Figure 3. (a) Chromyl fluoride stored in fluorinated ethylene propylene (FEP) tube. Two valves on the container allow the reagent container to be connected to the nickel system. (b) Molecular structure of chromyl fluoride.



1.4. Method for the preparation of pure chromyl fluoride

Many of these preparation methods have been tried but proved undesirable for various reasons. The methods are often not suitable for small volumes, require difficult-to-handle reactants, or involve side reactions that lead to mixtures that are difficult to purify. Simple and robust synthesis methods that can produce a purer product were needed (Flesch and Svec, 1958; Gard and Williamson, 1986).

Chromyl fluoride can convert hydrocarbons to ketones and organic acids and is characterised by favourable conversion pathways to other chromium compounds, such as chromyl nitrate, which is easily prepared from CrO_2F_2 and sodium nitrate (NaNO_3). Years ago, it was necessary to work via dinitrogen pentoxide (N_2O_5) to produce chromyl nitrate (Gard and Williamson, 1986).

Because of the extreme reactivity of chromium fluoride with both glass and quartz, it was necessary in the past to work in a metal system. The success of Engelbrecht and Grosse's (1951) method allowed laboratory equipment such as traps and tubes made of silica-free glass and inert and transparent plastic material such as polychlorotrifluoroethylene (Kel-F), which allowed visual recording of reaction monitoring and detection of products without contamination. The method was based on chromium trioxide (CrO_3) reacting readily with anhydrous hydrogen fluoride (aHF) to form the desired chromyl fluoride (**Equation 1**).



The synthesis reaction (**Equation 1**) is reversible, and water can readily hydrolyze the fluoride back into the starting CrO_3 . The gaseous chromium fluoride hydrolyzes directly with water vapour to the usual smoky pink powder (Engelbrecht and Grosse, 1951). The studies of Engelbrecht and Grosse (1951) showed that when a high excess of anhydrous hydrogen fluoride (more than 10 moles of aHF per 1 mole of starting CrO_3) is used, a good yield of chromyl fluoride can easily be obtained (about 85% or more).

The general procedure presented by Flesch and Svec (1958) is to mix dry CrO_3 with dry CoF_3 , heat the mixture in a glass or all-metal vacuum system, and collect the product in a trap cooled in a bath of solid CO_2 -trichloroethylene slush.

Gard and Williamson (1986) prepared chromyl fluoride by the reaction between dry chromium(VI) oxide and carbonyl fluoride at a temperature of 185 °C (**Equation 2**). At -78 °C, the volatile components (CO_2 , COF_2) were removed under dynamic vacuum. The purple-red product was transferred to another (Hoke) stainless steel tube under vacuum. They obtained the product in >99% purity.



There are a number of literature reports on the synthesis of chromyl fluoride using reagents such as fluorine, hydrogen fluoride, sulphur tetrafluoride, cobalt trifluoride, or iodine pentafluoride for reaction with chromium trioxide. Treatment of chromyl chloride with fluorine or chlorine monofluoride (ClF) has also been used to produce chromyl fluoride. These methods are suitable for the preparation of relatively small amounts of CrO_2F_2 , but are not particularly practical for the preparation of the large amounts needed for chromium fluoride reaction studies (Green and Gard, 1977). The reaction of chromium trioxide with the interhalogen fluorides BrF_3 , BrF_5 , or ClF_3 produces chromium oxide trifluoride contaminated with the fluorinating agent, forming only a trace of chromium fluoride (Green and Gard, 1977; Clark and Sadana, 1964; Sharpe and Woolf, 1951).

Green and Grad (1977) found that an excess of ClF reacts with CrO_3 at 0 °C to form CrO_2F_2 , O_2 , ClO_2F , and Cl_2 . When the molar ratio of ClF to CrO_3 is 1:1, CrO_2F_2 , O_2 , ClO_2 , and Cl_2



formed. In the work of Green and Gard (1977), COF_2 was also found to react with CrO_3 to form chromyl fluoride and carbon dioxide. In addition, chromium trioxide was found to react with WF_6 or MoF_6 to form chromium fluoride and WOF_4 or MoOF_4 . It was found that sulphur hexafluoride does not react with chromium trioxide. These reactions are summarized in **Table 1**.

Table 1. Green and Gard (1977) reactions of chromyl fluoride preparations.

$\text{CrO}_3 + \text{ClF} (\text{excess}) \rightarrow \text{CrO}_2\text{F}_2 + \text{Cl}_2 + \text{O}_2 + \text{ClO}_2\text{F}$	$T = 0 \text{ }^\circ\text{C}$
$\text{CrO}_3 + \text{COF}_2 \rightarrow \text{CrO}_2\text{F}_2 + \text{CO}_2$	$T = 185 \text{ }^\circ\text{C}$
$\text{CrO}_3 + \text{WF}_6 \rightarrow \text{CrO}_2\text{F}_2 + \text{WOF}_4$	$T = 125 \text{ }^\circ\text{C}$
$\text{CrO}_3 + \text{MoF}_6 \rightarrow \text{CrO}_2\text{F}_2 + \text{MoOF}_4$	$T = 125 \text{ }^\circ\text{C}$

Chromium trioxide reacts with tungsten hexafluoride (WF_6) and molybdenum hexafluoride (MoF_6) at mild temperatures to form chromyl fluoride, while sulphur hexafluoride (SF_6) does not react even at temperatures above the decomposition temperature of chromium trioxide. The preparation of chromyl fluoride from molybdenum and tungsten hexafluoride and chromium trioxide is the simplest and most convenient route to large amounts of CrO_2F_2 reported to date. Another feature of these processes is that no high-pressure vessel is required and the reaction can be carried out in a very dry fused silica vessel. The synthesis of chromyl fluoride from molybdenum and tungsten hexafluoride and from chromium trioxide represents the simplest and most convenient route to large amounts of CrO_2F_2 known to date. Another advantage of this preparation method is that no high-pressure vessel is required and the reaction can be performed out in a very dry fused silica vessel. Since the reactants include of a non-volatile reagent and a volatile fluorinating agent, forming one volatile and one non-volatile product, CrO_2F_2 and MoOF_4 and WOF_4 , respectively, purification is much easier. Moreover, this provides an easy route to the oxide tetrafluorides of molybdenum and tungsten, which can be obtained pure by sublimation. Chromium fluoride formation can be achieved by heating a mixture of CrO_3 and WOF_4 to $120 \text{ }^\circ\text{C}$. The method leads to a (high) quantitative yield, assuming that 1 mol of CrO_2F_2 per mol of WF_6 was formed in the reaction (Green and Gard, 1977).

2. Methods

2.1 Anhydrous hydrogen fluoride (aHF)

Anhydrous hydrogen fluoride (aHF) (Linde AG, Pullach, Germany, 99.995%) was treated with potassium hexafluoronickelate(IV) (K_2NiF_6) (Advance Research Chemicals, Inc., 99.9%) for several days before use.

2.2 Synthesis of chromyl fluoride via chromyl chloride and fluorine

In 50 mL of a dried nickel reactor at $-196 \text{ }^\circ\text{C}$, 1.1 g (7.1 mmol) of chromyl chloride ($\geq 99.99\%$, Sigma-Aldrich, USA) was condensed. Then, the addition of fluorine (F_2 , 4 bar, approx. 7 mmol) (99.98%, Solvay Fluorand Derivate GmbH) was monitored by pressure-volume measurement

Then 4 bar (approx. 7 mmol) of gaseous fluorine (F_2) (99.98%, Solvay Fluorand Derivate GmbH) was carefully added to the reactor at room temperature. The reactor containing the reactants was heated to $200 \text{ }^\circ\text{C}$ overnight. The mixture was carefully cooled to room temperature, then to $-196 \text{ }^\circ\text{C}$, where excess fluorine was removed via natronkalk (Divelime, United Kingdom), and then to $-35 \text{ }^\circ\text{C}$ where chlorine was removed. 748.6 mg (6.1 mmol) of chromyl fluoride was isolated (87% yield).

2.3 Synthesis of chromyl fluoride via chromium(VI) oxide and anhydrous hydrogen fluoride

In a dry and air-free FEP tube at $-196 \text{ }^\circ\text{C}$, 5 mL (247.38 mmol) of anhydrous hydrogen fluoride (aHF) (Linde, Germany) was added to chromium(VI) oxide (3.0 g, 30.0 mmol,

CrO₃) (p.a., Merck, Germany). Reaction vessel was slowly warmed up to the room temperature and after approx. thirty minutes, the reaction mixture turns dark green and the gas phase of the product is formed. The reaction proceeded overnight at room temperature. The reaction mixture at room temperature was transferred into a new FEP tube, cooled at -196 °C. To the crude product, additional gaseous fluorine (F₂) (99.98%, Solvay Fluorand Derivate GmbH) was carefully added (approx. 2.8 bar, 5 mmol). The tube containing the reagents was shaken on 330 rpm (SciQuip, UK) overnight at room temperature. The crude mixture was cooled at -196 °C and the excessive fluorine was removed at vacuum line. The crude isolate of CrO₂F₂ contains HF. The mass balance of the reaction was not possible to determine due to the presence of the HF solvent. Nevertheless, for our purposes we do not need to remove HF. This substance is suitable as a reagent for other reactions that take place in the medium HF.

2.4 Raman spectroscopy

Raman spectra were recorded on a sample placed in an FEP tube at room temperature using the Horiba Jobin Yvon LabRam-HR spectrometer (resolution of 1 cm⁻¹) equipped with an Olympus BXFM-ILHS microscope. Samples were excited with the 632.8 nm emission line of a He-Ne laser.

3. Results

The result of synthesis of chromyl fluoride was confirmed by Raman spectroscopy. The data was compared with shifts according to the Brown et al. (1976).

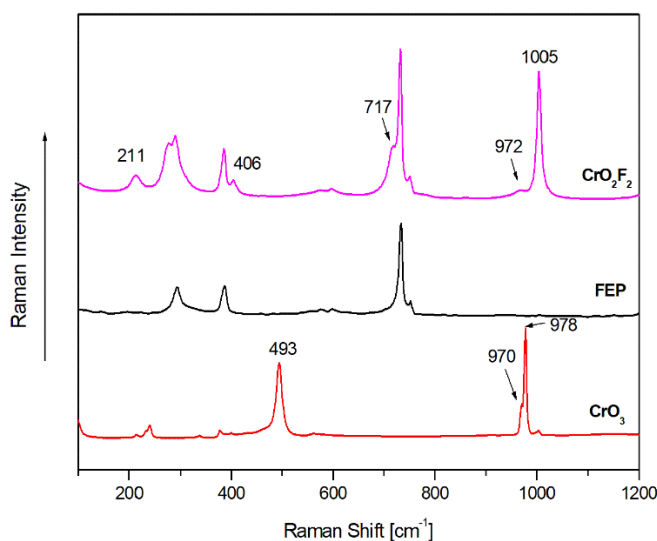


Figure 4. Raman spectra of the liquid phase of chromyl fluoride in an FEP tube, an empty FEP tube, and the starting material chromium (VI) oxide.

The results of Raman measurements show a comparison between the liquid phase of chromyl fluoride after its synthesis and chromium(VI) oxide as starting material (**Figure 4**). The strongest Raman peaks in the liquid phase at 1005 cm⁻¹, 717 cm⁻¹, and 406 cm⁻¹ confirm the presence of chromyl fluoride as a product. The reported data for the vibrational frequencies (Raman peak) for pure liquid CrO₂F₂ are 995 (intensity: 100) cm⁻¹, 708 (intensity: 75) cm⁻¹, 403 (intensity: 24) cm⁻¹, 220 (intensity: 29) cm⁻¹, and 275 (intensity: 58) cm⁻¹ (Brown, et al. 1975). However, the strongest peak of CrO₂F₂ dissolved in aHF was found at 1005 cm⁻¹ (Besida, et al. 1989), the shift being due to interaction with HF molecules. The small peak at 972 cm⁻¹ of chromyl fluoride indicates a trace of chromium(VI) oxide (John Wiley & Sons Inc, 2023). Its Raman spectra were recorded on object glass.



4. Conclusions

Chromyl fluoride is very useful as a reagent in various fields of research, especially in the preparation of new compounds. Its physical properties and chemical reactivity pose a great challenge to synthesis laboratories. Special equipment is needed for its production, in our case a nickel vacuum line system that allows safe production. Further studies on the use of this material will follow.

Characterization of the product was performed using Raman spectroscopy, which has proven to be a fast, simple and efficient method. It is a non-destructive technique that can be used to analyse samples in all states of aggregation. In addition, only a small amount of sample is required when measuring solids or liquids. In our case, the gaseous and liquid phases were successfully measured directly in the FEP tube.

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Conflicts of Interest: The authors declare no conflict of interest.

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