the complex is completely dissociated due to MoO_4^{2-} formation. Because of the more extensive formation of isopolytungstates, the pH range over which formation constants of W(VI) complexes can be measured is much smaller.[10] The results presented for the complexation of Mo(VI) and W(VI) by aspartic acid and glutamic acid indicate that the work of Singh and Srivastava[5] is incorrect, presumably because they did not account for the consumption of titrant, and thus the control of solution pH, by the isopolymolybdate and isopolytungstate equilibria.

Registry No. Aspartic acid, 6899-03-2; glutamic acid, 6899-05-4; MoO_4^{2-}, 14259-85-9; WO_4^{2-}, 14311-52-5; MoO_3L^{2-} (L = aspartic acid), 62005-75-8; MoO_3L^{2-} (L = glutamic acid), 62005-77-0.

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**Chemistry of Chromyl Fluoride.
5.[1] New Preparative Routes to CrO_2F_2**

Patrick J. Green and G. L. Gard*

The literature contains a number of reports on the synthesis of chromyl fluoride that involve the use of such reagents as fluorine,[2] hydrogen fluoride,[3] sulfur tetrafluoride,[4] cobalt trifluoride,[5] or iodine pentafluoride[6] in reaction with chromium trioxide. Treatment of chromyl chloride with fluorine[7] or chlorine monofluoride[8] also has been used to produce chromyl fluoride. These methods are useful for preparation of relatively small quantities of CrO_2F_2 but are not particularly practical for the production of the large amounts needed for chromyl fluoride reaction studies.

In this paper four new preparative routes to chromyl fluoride are presented, among which are the most convenient methods of synthesis yet reported.

Experimental Section

Chromium trioxide (Mallinkrodt, Reagent Grade) was thoroughly dried under vacuum before use. Chlorine monofluoride (Ozark-Mahoning) was used as received after its infrared spectrum showed no extraneous absorbances.[9] Carbonyl fluoride (PCR), tungsten hexafluoride (Ozark-Mahoning), and molybdenum hexafluoride (prepared by the method of Pitts and Jache[10]) were condensed over NaF to remove HF and then distilled into the reaction vessel. Sulfur hexafluoride (Matheson, 99.8%) was used as received.

Infrared spectra were taken on a Perkin-Elmer 467 infrared spectrophotometer. Gas-phase spectra were obtained with a Monel cell using either AgCl or KRS-5 windows. The path length of the cell was 8.25 cm. Chromyl fluoride analyses were done in the authors' laboratory by condensing and hydrolyzing a freshly prepared sample in a fused silica vessel. Hexavalent chromium was determined iodometrically, using standardized thiosulfate solution. Acidity was measured by titration with standard base using phenolphthalein indicator and is reported as milliequivalents of acid. One mole of chromyl fluoride hydrolyzes to yield 4 equiv of acid in the form of 2 mol of HF and 1 mol of H_2CrO_4. Other chemical analyses were performed by Beller Laboratories of Göttingen, West Germany. Molecular weight determination of gases was accomplished using the vapor density method.

Reaction of Chromium Trioxide and Chlorine Monofluoride. Dried CrO_3 (45 mmol) was added to a 100-ml stainless-steel reaction vessel in a drybox followed by the addition of 94 mmol of ClF at −196 °C. The reaction mixture was then warmed to 0 °C and kept at that temperature for 12 h after which time the vessel was evacuated at −196 °C. The only volatile product at this temperature was found to be O_2, identified by its molecular weight. (Requires: 32.0 g/mol. Found: 32.1 g/mol.) At −78 °C, the volatile products were ClF and ClO_2F, as identified by their characteristic infrared absorbances,[9,11] and Cl_2, identified as yellow-green liquid at −78 °C with approximately 100 mm of vapor pressure at that temperature. At room temperature, the only volatile product was CrO_2F_2, identified by its infrared spectrum.[12] The yield of CrO_2F_2 was 45 mmol or 100% based on CrO_3.

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 6.36 mequiv. Found: Cr, 42.43; acidity, 6.30 mequiv.

Following a procedure similar to that outlined above, 25 mmol of CrO_3 and 24 mmol of ClF were brought to 0 °C in a stainless-steel reaction vessel. Upon evacuation of the vessel at −196 °C, oxygen was removed. The infrared spectrum of the volatile products (at −78 °C) showed only ClO_2.[13] At room temperature the only volatile product was CrO_2F_2.

Reaction of Carbonyl Fluoride and Chromium Trioxide. To a 100-ml stainless-steel reaction vessel 9 mmol of dried CrO_3 was added. Carbonyl fluoride (24 mmol) was transferred into the vessel and the reaction mixture was heated to 185 °C for 12 h. Upon cooling the vessel to −78 °C and opening it to an evacuated −196 °C trap, white bands formed immediately in the liquid-nitrogen-cooled receiver. The trap contents were shown to be COF_2 and CO_2 by infrared analysis. The room-temperature volatile product was CrO_2F_2 as shown by its infrared spectrum. The yield of chromyl fluoride was 100% based on chromium trioxide.

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 4.16 mequiv. Found: Cr, 42.71; acidity, 4.15 mequiv.

In another run, using the above outlined procedure, 12 mmol of dried CrO_3 and 9 mmol of COF_2 were added to a reaction vessel and heated to 185 °C for 12 h. When the vessel was evacuated at −78 °C, the only volatile product observed in the infrared spectrum was CO_2. A molecular weight determination was performed on the −78 °C volatile product. (Requires: 44.0 g/mol. Found: 43.9 g/mol.) After evacuation at room temperature, which removed 9 mmol CrO_2F_2, the vessel was found to contain 3 mmol of unreacted CrO_3.

Reaction of Molybdenum Hexafluoride and Chromium Trioxide. To 24 mmol of CrO_3 contained in a 200-ml stainless-steel vessel 11 mmol of MoF_6 was added at −78 °C via vacuum distillation. The reaction vessel was heated to 125 °C for 12 h and then evacuated at room temperature. The only volatile product was found by infrared analysis to be chromyl fluoride. The weight loss indicated that the total amount of CrO_2F_2 produced was 11 mmol.
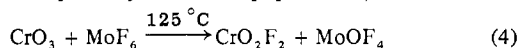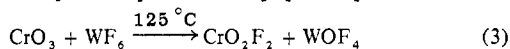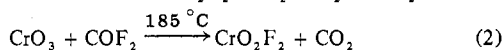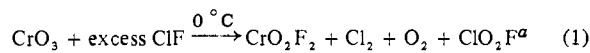
Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 6.01 mequiv. Found: Cr, 42.51; acidity, 5.92 mequiv.

Sublimation of the solid residue yielded a white solid which had a melting point of 95–97 °C. The reported melting point of $MoOF_4$ is 97 °C.[14]

Anal. Calcd for $MoOF_4$: Mo, 51.0; F, 40.4. Found: Mo, 51.0; F, 40.0. The yield was quantitative based on MoF_6.

In another experiment, 23.57 mmol of CrO_3 was placed in a 30-ml fused silica reaction vessel. The vessel was evacuated and 9.623 mmol of MoF_6 was vacuum distilled into the vessel and condensed at −78 °C. The reaction mixture was allowed to warm to room temperature and reddish-brown vapors were evident immediately upon melting of the MoF_6. The reaction mixture was stirred for 2 h at room temperature and the reddish-brown color of the vapors became increasingly intense. The vessel was evacuated at room temperature and chromyl fluoride and silicon tetrafluoride were the only volatile components to be observed in the infrared spectrum.

Notes

Scheme I. New Preparations of Chromyl Fluoride

$$CrO_3 + excess\ ClF \xrightarrow{0\ °C} CrO_2F_2 + Cl_2 + O_2 + ClO_2F^a \quad (1)$$

$$CrO_3 + COF_2 \xrightarrow{185\ °C} CrO_2F_2 + CO_2 \quad (2)$$

$$CrO_3 + WF_6 \xrightarrow{125\ °C} CrO_2F_2 + WOF_4 \quad (3)$$

$$CrO_3 + MoF_6 \xrightarrow{125\ °C} CrO_2F_2 + MoOF_4 \quad (4)$$

^{a} Equation is unbalanced. See Discussion.

Reaction of Tungsten Hexafluoride with Chromium Trioxide. To a 200-ml stainless-steel vessel was added 162 mmol of dried CrO_3 in a drybox. The vessel was then evacuated and 100 mmol of WF_6 was transferred via vacuum distillation and condensed at −78 °C. The reaction mixture was heated to 125 °C for 12 h. Upon opening the vessel to the vacuum line at room temperature, it was found that the only volatile material remaining was CrO_2F_2, as identified by its infrared spectrum. The yield of CrO_2F_2 was 110% based on eq 3 in Scheme I (see Discussion).

Anal. Calcd for CrO_2F_2: Cr, 42.62; acidity, 9.23 mequiv. Found: Cr, 41.95; acidity, 9.31 mequiv.

In another run, 10.55 mmol of CrO_3 was placed in a 30-ml fused silica reaction vessel. The vessel was evacuated and 75.78 mmol of WF_6 was transferred via vacuum distillation and condensed at −78 °C. The reaction mixture was then warmed to 45 °C where after 1 h red-brown vapors appeared above the liquid WF_6. The reaction was stirred overnight. When evacuated the only volatile materials indicated in the infrared spectrum were CrO_2F_2, WF_6, and SiF_4, leaving behind a gray-white solid. More WF_6 was added to the vessel and the solution was stirred for two additional hours at 60 °C. Red-brown vapors became evident immediately upon heating. The vessel was reevacuated, leaving an off-white powder. The powder was sublimed and the white crystalline sublimate was found to melt at 102–104 °C. WOF_4 has a reported melting point of 105 °C.[15]

Anal. Calcd for WOF_4: W, 66.6; F, 27.5. Found: W, 66.7; F, 27.7.

Reaction of Tungsten Oxide Tetrafluoride with Chromium Trioxide. To a 100-ml stainless-steel vessel 2 mmol of CrO_3 and 2 mmol of WOF_4 were added in a drybox. The vessel was then heated to 120 °C for 12 h. The room temperature volatile product was found to be CrO_2F_2 as shown by its characteristic infrared spectrum.

Reaction of Sulfur Hexafluoride and Chromium Trioxide. To 27 mmol of CrO_3 contained in a stainless steel vessel 35 mmol of SF_6 was added at −196 °C. The reaction mixture was then heated to 185 °C for 24 h. Evacuation of the vessel after heating yielded only SF_6. A similar reaction was run at 330 °C. No chromyl fluoride was produced.

Discussion

The reaction of chromium trioxide and the interhalogen fluorides BrF_3, BrF_5, or ClF_3 is reported to lead to chromium oxide trifluoride contaminated with the fluorinating agent with only a trace of chromyl fluoride produced.[16,17] We have found that excess ClF reacts with CrO_3 at 0 °C producing CrO_2F_2, O_2, ClO_2F, and Cl_2. When the molar ratio for ClF to CrO_3 is 1:1, CrO_2F_2, O_2, ClO_2, and Cl_2 are formed. Fawcett et al.[18] has reported the use of carbonyl fluoride as a fluorinating agent capable of converting carbonyl groups to gem-difluoro groups. In this work COF_2 was found to react with CrO_3 forming chromyl fluoride and carbon dioxide. In addition, it was discovered that chromium trioxide reacts with WF_6 or MoF_6 to produce chromyl fluoride and WOF_4 or $MoOF_4$, respectively. Sulfur hexafluoride was found not to react with chromium trioxide. These reactions are summarized in Scheme I.

Chlorine monofluoride and chromyl chloride react to form chlorine and chromyl fluoride[8] as would be predicted from what is known of the reactivity of ClF. The reaction of chromium trioxide with ClF is not so straightforward as evidenced in the finding of chloryl fluoride and chlorine dioxide among the products of the reaction; however, these products can be accounted for with the help of previous work.
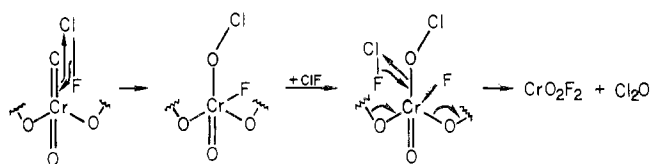

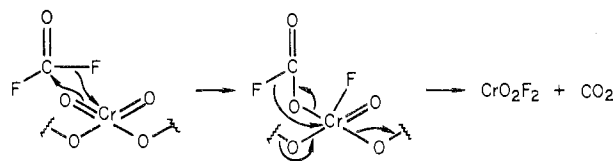**Figure 1.** Proposed mechanism of the reaction of CrO_3 and ClF at 0 °C.

Figure 2. Proposed mechanism of the reaction of CrO_3 and COF_2.

It has been shown that chlorine monofluoride adds across a double bond to oxygen to form a product having fluorine bonded to the central atom and chlorine bound to oxygen. Examples of this type of reactivity include the reaction of ClF and SO_3[19] which leads to chlorine fluorosulfate as well as the interaction of ClF and perfluorinated ketones[20] which form perfluorinated hypochlorites. In addition, ClF can also fluorinate oxides to form non-chlorine-containing products. The reactions of chlorine monofluoride with selenium dioxide[21] and tellurium dioxide[22] which yield the corresponding tetrafluorides are examples of this behavior. Other reactions of this type involve the production of WF_6[10] and UF_6[23] from ClF with WO_3 and UO_2F_2, respectively. In all the latter reactions chloryl fluoride (ClO_2F) was reported as a product of the reaction when ClF was in excess.

Christe[24] has shown that ClF reacts with dichlorine monoxide at −78 °C to form chloryl fluoride and chlorine. This reaction may well play an important part in the reaction of chlorine monofluoride and chromium trioxide as has been proposed for the interaction of ClF and SeO_2 by Lau and Passmore.[21] A mechanism for the interaction of ClF and CrO_3 is presented in Figure 1. The first step involves the addition of ClF across a chromium–oxygen double bond to form a chlorine fluorochromate intermediate which reacts with a second molecule of ClF to produce Cl_2O and CrO_2F_2. The dichlorine monoxide formed would not survive in the presence of ClF, but would be converted to ClO_2F and Cl_2. The oxygen found as a product of the reaction of ClF and CrO_3 could be produced as a result of the pressure-induced decomposition of the chlorine oxide by-products of the reaction. When excess CrO_3 was used, the only chlorine oxide detected was ClO_2, perhaps indicating that chloryl fluoride is formed and acts as a fluorinating agent to produce CrO_2F_2 from CrO_3. Chloryl fluoride has been shown to react with UF_4 to produce UF_5, UF_6, and ClO_2.[25]

The reaction of carbonyl fluoride and chromium trioxide goes to completion with the only detectable products being CrO_2F_2 and CO_2. A mechanism for the reaction can be found in Figure 2. The fluoroformate intermediate formed initially would probably rapidly rearrange to form the end products.

Chromium trioxide reacts with tungsten hexafluoride and molybdenum hexafluoride at a moderate temperature to form chromyl fluoride while sulfur hexafluoride does not react even at elevated temperatures above the decomposition temperature of chromium trioxide. The production of chromyl fluoride from the hexafluorides of molybdenum and tungsten and chromium trioxide provides the simplest and most convenient route to large quantities of CrO_2F_2 thus reported. An added feature of these processes is that the use of a high-pressure vessel is not required and the reaction can be run in a very dry fused silica vessel. Since the reactants consist of a

nonvolatile reagent and a volatile fluorinating agent which form a volatile and nonvolatile product, CrO_2F_2 and $MoOF_4$ or WOF_4, respectively, purification is greatly simplified. In addition, this provides a straightforward route to the oxide tetrafluorides of molybdenum and tungsten, which can be obtained pure via sublimation. The heating of a sample of CrO_3 mixed with WOF_4 to 120 °C leads to formation of chromyl fluoride. This accounts for a yield greater than 100% based on the reaction producing 1 mol of CrO_2F_2 per mol of WF_6.

In line with the reported relative reactivities of the two hexafluorides,[26] MoF_6 produced chromyl fluoride more readily than did WF_6.

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β-Diketonate Complexes of Iron(II)

S. D. Ittel

The preparation of transition metal β-diketonate complexes has typically been accomplished by direct reaction of the β-diketones with metal salts in the presence of base or by other similar reactions. In addition to these reactions which do not involve any change in the oxidation state of the metal,[1] there are examples of preparations where a derivative of a metal in a lower oxidation state has been prepared by reduction from a higher oxidation state by the diketone.[2] The reaction of

2,4-pentanedione with $Mo(C_2H_4)(DPPE)_2$ [DPPE = bis-1,2-(diphenylphosphino)ethane)] represents the first oxidative addition of a β-diketone to a transition metal.[3] The resultant 7-coordinate Mo(II) is the only reported hydrido complex containing both β-diketonate and tertiary phosphorus ligands. The more common, analogous alkyl complexes are known for iron,[4] cobalt,[5] nickel,[6,7] and platinum.[8] The molybdenum complex is also isolated from the aluminum alkyl reduction of $Mo^{III}(acac)_3$ (acac = 2,4-pentanedionato). The alkyl complexes of the other metals are typically isolated as intermediates or impurities in similar reductions.

The treatment of $Fe(acac)_3$ with $AlEt_3$ or $AlEt_2(OEt)$ in the presence of DPPE at 0 °C, in ether under an inert atmosphere, has been shown[9] to afford $Fe(DPPE)_2(C_2H_4)$. We have found that if the reaction is carried out at −78 °C and then allowed to warm to room temperature, the primary product isolated is $Fe(DPPE)_2H_2$. It has been reported[10] that when the reduction is carried out using AlR_3 where R is larger than ethyl, the only product isolated is the dihydride, presumably as a result of thermal decomposition of an unstable iron dialkyl. It may be assumed that the product of the low-temperature reduction is $Fe(DPPE)_2Et_2$, which decomposes upon warming to yield the dihydride and ethylene.

If the reduction is carried out at 0 °C with less aluminum alkyl, it is possible to isolate the paramagnetic compound $Fe^{II}(DPPE)(acac)_2$ (I). This is not a by-product as in the Mo reaction but is an intermediate and may be further reduced by addition of more aluminum alkyl.

The same product is isolated from the reaction of the β-diketone with Fe^0 in refluxing toluene according to the reaction

$$2Fe(DPPE)_2C_2H_4 + 2Hacac$$
$$\rightarrow Fe(DPPE)(acac)_2 + Fe(DPPE)_2H_2 + DPPE + 2C_2H_4 \qquad (1)$$

This reaction, formally a disproportionation, affords an alternative to the 7-coordination observed in the molybdenum system; both iron(II) species are 6-coordinate, 18-electron systems, and both the diketonate and the hydride are coordinated. The golden diketonate complex is easily separated from the reaction mixture and recrystallized from tetrahydrofuran.

The oxidative addition reaction can be repeated with other β-diketones to produce complexes of the type

Diketonate
abbreviation
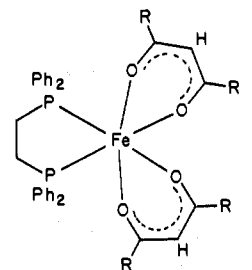
I, R = Me	acac
II, R = Ph	DBM
III, R = CF_3	$acacF_6$

Some idea as to the mechanism of reaction 1 can be obtained from the reaction of β-diketones with Fe^0 phosphite complexes.[11-13] When hexafluoro-2,4-pentanedione is reacted with FeL_5 where L = $P(OMe)_3$, an initial yellow product of the stoichiometry $[FeL_5H]^+[C_5F_6O_2H]^-$ can be isolated; the characteristic ^{31}P NMR spectrum of this material is identical with that of an authentic sample of FeL_5H^+.[11,14] This unstable compound reacts further to produce a red uncharacterized complex having coordinated β-diketonate. The initial hydride formation is to be expected because β-diketones are stronger