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Mild fluorination of oxo-anions; a clean route to Group 6 and 7 transition metal oxide fluorides

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Abstract

The reactions of mild fluorinating agents with transition metal oxo-anions have been used to provide new synthetic routes to MnO_3F, ReO_3F, CrO_2F_2, MoO_2F_2 and WO_2F_2.

Keywords: Oxo-anions; Fluorination; Metal oxide fluoride

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1. Introduction

The usual routes to transition metal oxide fluorides involve either fluorination of metal oxides with elemental fluorine [1] or other fluorinating agents [2], or direct heating of the metal in fluorine/oxygen mixtures [3]. These methods, while generally straightforward if the appropriate facilities are available, can result in a number of products which can be difficult to separate, and typically require high reaction temperatures and pressures. A number of more specialist synthetic routes are available for certain particular compounds [4], but these are not of general applicability.

An alternative route to transition metal oxide fluorides involves the action of mild fluorinating agents on high oxidation-state transition metal oxo-anions. This type of reaction has been known for a considerable time; in 1954, Engelbrecht and Grosse [5] reported the formation of dark-green MnO_3F by the reaction of $KMnO_4$ with IF_5. A few years later, the analogous reaction of $KReO_4$ with IF_5 to yield ReO_3F was reported [6]. More recently, the final member of this series, TcO_3F, was prepared by the reaction of ammonium pertechnetate with an excess of anhydrous HF [7]. Surprisingly, since oxo-anions of a number of transition metals are known and are either commercially available or can be readily prepared, there have been no reports in the literature of a systematic extension of these synthetic routes to other transition metal oxo-anion systems. The attraction of these routes lies in the fact that, since the metal species are already in high oxidation-states, powerful oxidative fluorination reagents can be avoided. Here, we report the reactions of alkali–metal oxo-anions of the transition metals of Groups 6, 7 and 8 with the fluorinating agents IF_5, IF_7, anhydrous HF and XeF_2.

2. Experimental

Caution: the reactions of manganese oxo-anions with many fluorinating agents result in the production of dark green MnO_3F liquid. This is shock sensitive and can spontaneously detonate even in moderate quantities. Suitable protective clothing should be worn and great care must be exercised when dealing with this material.

The starting materials, K_2CrO_4 (Fisons), $KReO_4$, Na_2MoO_4 and Na_2WO_4 (Aldrich), $KMnO_4$ (May and Baker) and $KRuO_4$ (Johnson Matthey) were used as supplied after drying in an oven for 24 h; $KOsO_4$ [8], K_2MnO_4 [9], K_3MnO_4 [10] and K_2FeO_4 [11] were prepared by literature routes. Xenon difluoride was prepared by the photolytic reaction of elemental xenon and fluorine [12], HF (Fluorochem) was vacuum distilled, dried under 1 atm fluorine gas and stored over dried BiF_5 in Kel-F(polychlorotrifluoroethylene) storage vessels [13]. IF_5 (Fluorochem) was used as supplied after treatment with elemental fluorine at 1 atm at room temperature overnight. IF_7 was prepared by the fluorination of IF_5 with fluorine at 290°C [14] and stored in a nickel can closed with a brass bellows valve. Arcton 133a (CF_3CH_2Cl; ICI) was used as supplied.

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Analysis of the reaction products was carried out by IR spectroscopy of solids or solids mulled in sodium-dried Nujol held between KBr plates on a Perkin-Elmer PE580 instrument; Raman spectroscopy on powdered samples in prefluorinated and evacuated glass capillaries on a Coderg T800 spectrometer equipped with a Coherent Radiation Laboratories Model 52 argon ion laser; and ^{19}F NMR spectroscopy of solutions on a Bruker AM300 instrument operating at 282.41 MHz.

All room temperature reactions were carried out on a millimolar scale in pre-passivated 4 or 6 mm o.d. FEP (perfluoroethylene–propylene copolymer) heat-sealed tubes fitted with PTFE valves (Production Techniques) attached to an all-metal vacuum line. Pre-dried solid starting materials were weighed into the FEP tubes in a dry box, before evacuation of the tubes on the vacuum line. Volatile reagents were then added by vacuum transfer, usually at −196°C, and the mixtures allowed to warm slowly to room temperature and left to stand for 16 h. Higher-temperature reactions were carried out in nickel reactors (10 cm^3 volume) equipped with a gold gasket seal, reagents being loaded as outlined above for FEP reactors. Solid products were transferred to the dry box for characterisation while volatile reagents/solvents and products were separated by vacuum transfer and the products stored in either pre-passivated FEP or nickel containers.

3. Results and discussion

When potassium chromate reacts with an excess of mild fluorinating agents such as HF or IF_5 at room temperature, or with IF_5 at elevated temperatures, dark red chromyl fluoride, CrO_2F_2, (identified from its gas phase infrared and solution ^{19}F NMR spectrum) is produced in quantitative yield in each case. That is, all of the chromium of the potassium chromate is converted to CrO_2F_2. In contrast, when XeF_2 in Arcton 133a solution is used, fluorination does not occur and the chromate–dichromate equilibrium is shifted in favour of the dichromate ion.

Neither alkali–metal molybdates nor tungstates react with HF or IF_5 at room temperature. However, the Raman spectrum recorded on the product of the reaction between IF_5 and Na_2MoO_4 when heated to 120°C for 20 h exhibits peaks corresponding to those previously reported for MoO_2F_2 [15]. The product of reaction between K_2WO_4 and IF_5 under similar conditions also exhibits a number of peaks in the Raman spectrum, typically at 975, 902, 765 and 385 cm^{-1}. These do not correspond to starting material, nor to WOF_4 [16], but indicate the presence of terminal W=O and W–F moieties, suggesting that WO_2F_2 is generated.

Dark green, shock-sensitive, MnO_3F (identified by its characteristic gas-phase IR spectrum) [17] results when $KMnO_4$ is combined with an excess of either HF or IF_5 at room temperature. The reactions were carried out stoichiometrically (e.g., see Eq. (1)) but, to ensure that no residual fluorinating agent remained, the volatile products were transferred at 0°C on to $KMnO_4$ in a second reactor.

$$KMnO_4 + IF_5 \rightarrow MnO_3F + IOF_3 + KF \qquad (1)$$

If this procedure, in which potassium permanganate is in overall excess, is used then pure MnO_3F results. This may be vacuum sublimed out of the reactor at 0°C leaving behind the excess of permanganate and KF and IOF_3 by-products. Aynsley and Hair [6] reported that in the reaction of $KMnO_4$ with IF_5 "an explosion always occurs if the potassium permanganate is in excess." In our hands, the procedure outlined above did not give rise to such explosions. Attempts to force further fluorination were unsuccessful, and only MnO_3F is generated by the reaction of $KMnO_4$ with IF_5 at 100°C in a nickel reactor. Similarly, if IF_7 or XeF_2 are used as fluorinating agents in dichloromethane or Arcton 133a solution, MnO_3F is produced. The reactions of the lower oxidation-state oxo-anions, K_2MnO_4 and K_3MnO_4, with HF or IF_5, surprisingly, result in generation of Mn(VIII) and the exclusive production of MnO_3F.

In contrast, neither IF_5 nor HF react with $KReO_4$ at room temperature to yield any fluorine-containing compounds as demonstrated by IR and NMR spectroscopic studies. Furthermore, contrary to the literature report [6], even at temperatures up to 200°C, potassium perrhenate and IF_5 do not react. However, when a trace amount of HF is added to the reaction mixture and the mixture is heated to 100°C, ReO_3F generation occurs as previously reported. By contrast, when $KReO_4$ is mixed with XeF_2 in Arcton 133a solution, a slow reaction ensues, ultimately yielding ReO_3F, as evidenced by its IR spectrum [18], recorded after removal of the solvent.

Reactions involving the Group 8 transition metal species $KRuO_4$ and $KOsO_4$ were generally less successful than the reactions of their Group 6 and 7 counterparts. The reactions of these complexes with IF_5 and XeF_2 resulted in the production of the tetroxides RuO_4 and OsO_4 as identified by their IR and Raman spectra, whereas reaction with HF resulted in reduction to the black oxides, RuO_2 and OsO_2. When K_2FeO_4 is combined with IF_5, reaction occurs resulting in the formation of a dark unstable solid, from which it is possible to sublime a small amount of a brown material. This material proved impossible to isolate or identify.

4. Conclusion

The reactions of transition metal oxo-anions with mild fluorinating agents is a route to transition metal oxide fluorides. Although no new complexes have been prepared, this work demonstrates that the route is a simple and clean preparative procedure.

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