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Selective fluorination of dichloromethane by highest oxidation state transition-metal oxide fluorides [☆]

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Abstract

In contrast to the reactivity of high oxidation state binary transition-metal fluorides with organic solvents, many transition-metal oxide fluorides do not react with CH_2Cl_2. Only the highest oxidation state species react, at temperatures below room temperature, via Cl–F exchange with >90% selectivity, affording unstable high oxidation state chloro complexes which decompose to chlorine and lower oxidation state species.

Keywords: Selective fluorination; Dichloromethane; Transition-metal oxide fluorides; ESR spectroscopy

1. Introduction

Chromium oxide fluorides, of varying and uncertain composition, are widely reported in the patent literature to act as halogen exchange [2] or HF addition catalysts [3] in the preparation of fluoro- and chlorofluoro-carbons. Surprisingly, therefore, the reactions of other transition-metal oxide fluorides with organic substrates have received scant attention; only the vanadium oxide fluoride, VOF_3, with BF_3 or CF_3CO_2H, is known to catalyse the oxidative cyclisation of, for example, propenoates [4], lactams [5] and isoquinolines [6]. Our observations [7] that binary transition-metal fluorides are selective fluorinating agents and the reported reactivity of the CrO_xF_y system [2,3] suggested that reactions of other oxide fluorides with C_1 and C_2 hydro-halocarbons might be significant. Here, we describe the reactions of a range of transition-metal oxide fluorides with dichloromethane as a model compound.

2. Experimental details

Vanadium oxide trifluoride (Johnson Matthey Ltd.) was sublimed under dynamic vacuum and stored in a dry box before use. $MoOF_4$ and WOF_4 [8], CrO_2F_2 and $CrOF_4$ [9], $ReOF_5$ [10], ReO_2F_3, OsO_2F_3 and OsO_3F_2 [11], and $OsOF_5$ [12] were all prepared by literature procedures and stored either in pre-fluorinated closed FEP containers in a dry box for solid samples or in pre-fluorinated nickel containers closed by a brass bellows valve for volatile samples. $ReOF_4$ was prepared by a modification of the procedure described by Yagodin et al. [13] in which $ReOF_5$ was transferred in vacuum on to a stoichiometric amount of rhenium powder in a pre-fluorinated autoclave (stainless steel, 100 cm^3 volume) and heated to 473 K for 16 h with the lid cooled by a steady flow of water. On cooling to room temperature, the ReF_6 by-product was removed under static vacuum and the autoclave transferred to the dry box where the blue $ReOF_4$ was removed from the lid and stored in a pre-fluorinated FEP tube. ReO_3F was prepared from the reaction of $KReO_4$ with IF_5 at 371 K as described by Aynsley and Hare [14] but it should be noted that, under scrupulously anhydrous conditions, this reaction does not proceed and it is necessary to add a catalytic amount of anhydrous hydrogen fluoride (AHF).

Identification of the organic products and HF was carried out by ^1H and ^{19}F NMR spectroscopies at 300.13 and 282.41 MHz, respectively, on a Bruker AM300 MHz spectrometer with a 5-mm bore selective probe. Samples were sealed in 4-mm o.d. FEP (polytetrafluoroethylene/perfluoropropylene) tubes as described previously [15], which were placed co-axially in 5-mm o.d. precision glass NMR tubes containing a small amount of acetone-d_6 as lock substance. Analysis of the inorganic products was carried out by IR spectroscopy on a Digilab FTS40 spectrometer and by X-band ESR spectros-

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[☆] See also Ref. [1].

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Table 1
Products of the fluorination of CH_2Cl_2

	Wt. [a] of metal oxide fluoride (g)	Wt. [a] of solvent (g)	Products [b]						Inorganic residue
			CH_2ClF	CH_2F_2	$CHCl_2F$	$CHClF_2$	CF_2Cl_2	HF	
$ReOF_5$	0.0731 (0.526)	0.4377 (5.15)	82.0	7.4	1.7	3.6	–	5.3	$ReOCl_4$
$ReOF_4$	0.0378 (0.136)	0.5038 (9.63)	96.8	1.8	0.5	–	0.2	0.7	$ReOCl_4$
OsO_3F_2	0.0314 (0.114)	0.8185 (5.93)	79.6	10.0	5.2	–	–	5.2	'OsO_2'
OsO_2F_3	0.0480 (0.172)	0.7063 (8.31)	84.8	13.4	0.3	0.6	–	0.9	'OsO_2'
$OsOF_5$	0.0521 (0.173)	0.3842 (4.52)	82.0	6.8	2.3	3.0	0.2	5.7	'OsO_2'

[a] No. of mmol in parentheses.
[b] Mol%.

copy on a Bruker ER 200D instrument with facilities for variable temperature control. Spectra were standardised against a sample of diphenylpicrylhydrazyl (dpph). Samples were held in pre-fluorinated 4-mm o.d. FEP tubes.

In a typical experiment, the oxide fluoride (ca. 0.1–0.3 mmol) was loaded, either in a dry box for solid samples or by vacuum transfer for vapours, into a pre-fluorinated FEP reactor (4-mm o.d., 1.5-cm^3 total volume) fitted with a PTFE valve. A large excess of dichloromethane (typically 0.4 cm^3) was added by vacuum transfer, and the reaction tube allowed to warm slowly to room temperature. After the reaction had finished, the organic products were transferred to a second FEP tube which was heat-sealed under vacuum for NMR investigation and the solid residue transferred to the dry box for manipulation.

3. Results and discussion

As observed in the fluorination of CH_2Cl_2 with highest oxidation state binary transition-metal fluorides, the d^n-configuration determines the reactivity of the transition-metal oxide fluorides (Table 1). In the reactions of binary fluorides, two types of reaction have been observed [7]; for d^0 species hydrogen–fluorine exchange occurs selectively, for d^n species halogen–fluorine exchange occurs selectively. In contrast, all the transition-metal oxide fluorides that react with dichloromethane do so by halogen exchange, indicating that hydrogen exchange involving HF generation and reduction of the metal is significantly less favourable for the oxide fluorides than for the binary fluorides. Furthermore, even the most reactive d^0 species, $ReOF_5$ and OsO_3F_2, react orders of magnitude more slowly than binary fluorides or the d^1 oxide fluorides of the same metals, suggesting that the presence of d electrons aids halogen exchange. Other less reactive d^0 species, such as VOF_3, CrO_2F_2, $CrOF_4$, $MoOF_4$, WOF_4, MnO_3F, ReO_3F or ReO_2F_3, do not undergo reaction with CH_2Cl_2. The non-reactivity of the Cr^{VI} oxide fluorides is particularly noteworthy and suggests that the industrial CrO_xF_y catalysts may not contain Cr^{VI} exclusively.

All the available fluorine from OsO_3F_2 reacts with dichloromethane within 5 min at room temperature via chlorine–fluorine exchange (ca. 95% selectivity – the remainder is hydrogen–fluorine exchange); the involatile, inorganic residue is insoluble in all common solvents and exhibits no IR-active Os–F or Os–Cl stretches. There are no isolable osmium(VIII) chloro complexes and, although the chlorine–fluorine exchange implies the formation of an osmium(VIII) chloro intermediate, this subsequently decomposes to give elemental chlorine and an intractable lower oxidation-state osmium oxide. Similar organic reaction products are obtained in the reaction of $ReOF_5$ and CH_2Cl_2 (ca. 95% chlorine–fluorine exchange), but the rate of reaction has allowed us to investigate the reaction pathway further. $ReOF_5$ dissolves in CH_2Cl_2 to give a yellow solution which slowly turns red over a 12 h period. Vacuum transfer of the organic material yields a colourless solution whose ^{19}F NMR spectrum shows exclusively chlorine–fluorine exchange, but only ca. 40% of the available fluorine is exchanged. The residue after the vacuum transfer is an involatile red oil which decomposed rapidly at room temperature. Monitoring the contents of the reaction tube by ESR spectroscopy during this initial 12 h period indicated that a novel single d^1 [rhenium(VI)] species had been generated [Fig. 1(a)]. As the reaction continued, the concentration of this product decreased, the solution turned green and a second d^1 rhenium species, identified in solution as $ReOCl_4$ by ESR spectroscopy was produced [Fig. 1(b)] [16]. After 24 h, no further products were observed. All the available fluorine had been exchanged and the solid inorganic residue was confirmed as $ReOCl_4$ by IR spectroscopy. The presumed initial Re^{VII} product decomposes by loss of chlorine to give the red product, a mixed oxide chloride fluoride of rhenium(VI), which subsequently reacts further to give $ReOCl_4$.

The d^1 oxide fluorides, $ReOF_4$, $OsOF_5$ and OsO_2F_3, react instantaneously as the CH_2Cl_2 melts, to give > 90% chlorine–

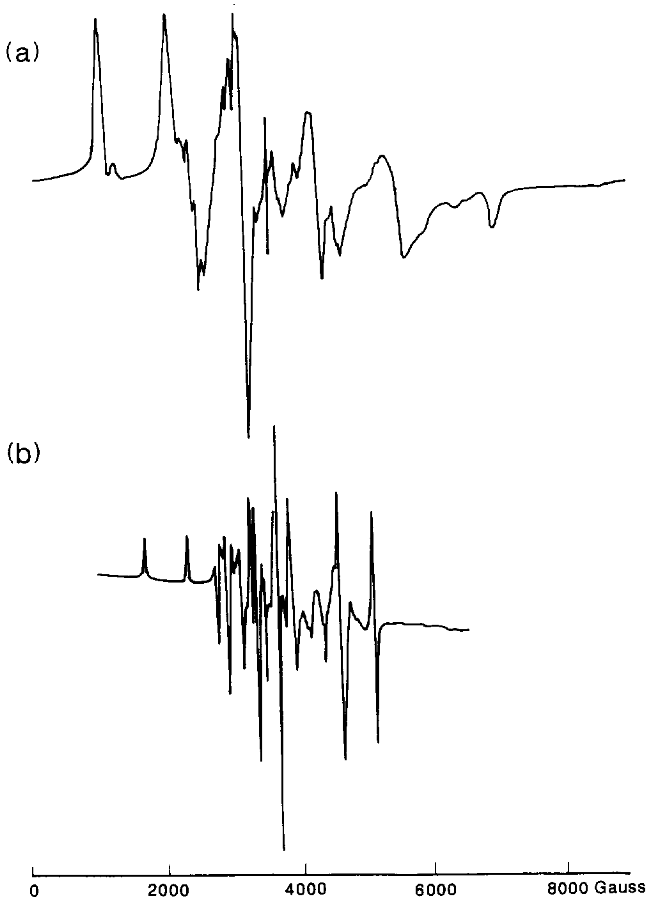

Fig. 1. X-band ESR spectra at 77 K of the products of the reaction of $ReOF_5$ with CH_2Cl_2. (a) Red solution after 12 h at room temperature; (b) green solution after 72 h at room temperature.

fluorine exchange consuming all the available fluorine. $ReOF_4$ yields exclusively green $ReOCl_4$ (the reaction proceeds too quickly to observe any intermediates), and the osmium reagents give chlorine and intractable non-stoichiometric low oxidation-state osmium oxides or oxide chlorides.

4. Conclusion

The oxide fluorides $ReOF_5$, $ReOF_4$, OsO_3F_2, OsO_2F_3 and $OsOF_5$ react with dichloromethane by chlorine–fluorine exchange with >90% selectivity; less reactive transition-metal oxide fluorides do not react even over extended periods of time. The mechanism can only be probed for the reaction with $ReOF_5$, which indicates fluorine–chlorine exchange at the metal centre accompanied by metal reduction. This is not surprising since chloro complexes of these metals in very high oxidation states are rare.

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