Electrospray Tandem Mass Spectrometry of Oxo Complexes of Chromium, Manganese and Ruthenium

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Several oxometal species including MnO_4^-, $Cr_2O_7^{2-}$, CrO_3Cl^-, RuO_4^-, $RuO_2Cl_3^-$ and $[Ru(TMC)O_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) have been studied by electrospray tandem mass spectrometry; in each case the mass spectrum obtained from solution in acetonitrile shows the molecular ion as the base peak with a minimal degree of fragmentation.

Metal–oxo complexes have received much attention in recent years because of their use as stoichiometric and catalytic oxidants.[1] They are also involved in various enzymatic systems such as cytochrome P-450 and methane monooxygenase.[2] Characterizations of highly oxidizing metal oxo species by mass spectrometry using electron impact and fast atom bombardment ionization techniques have so far proven to be difficult because of the ease of reduction of these species. Moreover, metal oxo species are often unstable and difficult to isolate from solutions. MnO_2^-, MnO_3^- and MnO_4^- have been produced in the gas phase from manganese carbonyl compounds[3] and from heating a mixture of manganese oxide and potassium chromate to 1300–1500 K.[4] Electrospray mass spectrometry (ESMS) is a relatively new technique that has generated a lot of interest in the last few years mainly because of its successes in the study of large biomolecules such as proteins and oligonucleotides.[5] Its applications in the study of ionic metal species have also become increasingly important because the electrospray technique provides a mild method for transferring ions from solution to the gas phase with no apparent fragmentation. Only a few metal ions have been studied so far,[6] and they are all relatively stable with respect to reduction. To investigate if ESMS is also applicable to highly oxidizing transition-metal oxo complexes, we have chosen to study some oxo complexes of chromium, manganese and ruthenium. Chromates and permanganate are powerful oxidizing agents that have long been used in organic synthesis;[1] a wide variety of ruthenium oxo complexes in oxidation states ranging from IV to VIII have recently been found useful for stoichiometric and catalytic oxidation of various organic functional groups.[7]

Table 1 Electrospray mass spectral data[a]

Compound	Ions (*m*/*z*)
$KMnO_4$	MnO_4^- (119), $[MnO_4(MeCN)]^-$ (160), $[MnO_4(MeCN)_2]^-$ (201), $K(MnO_4)_2^-$ (277)
$(NBu_4)_2Cr_2O_7$	$Cr_2O_7^{2-}$ (108), CrO_4^- (116), $HCrO_4^-$ (117), CrO_3^- (100), $[Cr_2O_7(MeCN)]^{2-}$ (128.5), $[Cr_2O_7(MeCN)_2]^{2-}$ (149)
$Hpy[CrO_3Cl]$	CrO_3Cl^- (135)
$PPh_4[RuO_4]$	RuO_4^- (166)
$PPh_4[RuO_2Cl_3]$	$RuO_2Cl_3^-$ (241)
$[Ru(TMC)O_2](PF_6)_2$	$[Ru(TMC)O_2]^{2+}$ (195), $[Ru(TMC)O_2(MeCN)]^{2+}$ (215.5)
$[Ru(TMC)O_2](PF_6)_2$ + KI[b]	$[Ru(TMC)O(OH_2)]^{2+}$ (196)

[a] All spectra are collected in the negative-ion mode except for $[Ru(TMC)O_2](PF_6)_2$. Unless specified, solutions were *ca.* 1 mmol dm^{-3} in MeCN. [b] 0.5 mmol dm^{-3} Ru complex + *ca.* 5 mmol dm^{-3} KI. Mass spectrum taken after a reaction time of 20 min.

Table 2 Fragment ions of metal–oxo ions.[a]

Precursor ion (*m*/*z*)	Fragment ions (*m*/*z*)	E_{cm}/eV[b]
MnO_4^- (119)	MnO_3^- (103), MnO_2^- (87)	12.6
$Cr_2O_7^{2-}$ (108)	CrO_4^- (116), CrO_3^- (100), CrO_2^- (84)	6.3
CrO_3Cl^- (135)	CrO_2Cl^- (119), CrO_3^- (100), Cl^- (35)	9.1
RuO_4^- (166)	RuO_3^- (150), RuO_2^- (134)	9.7
$RuO_2Cl_3^-$ (239)	$RuOCl_3^-$ (223), $RuO_2Cl_2^-$ (204), RuO_2Cl^- (168), Cl^- (35)	5.7

[a] Ar was used as the collision gas. [b] The collision energy E_{cm} is calculated using the equation $E_{cm} = E_{lab}\,[M_{Ar}/(M_{Ar} + M_{ion})]$ where E_{lab} is the collision energy in laboratory frame.

Table 1 shows the electrospray mass spectral data of the metal–oxo species.† Although the spectra reported were obtained from solutions in acetonitrile, other solvents such as acetone and dichloromethane were found to work equally well. All peaks in the ES mass spectra are identified by means of the most abundant *m*/*z* value within the isotopic mass distribution. Table 2 shows the fragment ions of selected metal–oxo ions after collision-induced dissociation (CID). The mass spectrum of $KMnO_4$ shows an intense MnO_4^- ion. There are also less abundant but highly reproducible solvated ions $[MnO_4(MeCN)]^-$ and $[MnO_4(MeCN)_2]^-$, as well as the dimer $[MnO_4\text{–}K\text{–}MnO_4]^-$. As expected in ESMS, little or no fragmentation of permanganate was observed. The CID of MnO_4^- yields the ions MnO_3^- and MnO_2^- arising from apparently successive loss of oxygen atoms.

Two chromium oxo complexes were investigated: $(NBu^n_4)_2Cr_2O_7$ and $Hpy[CrO_3Cl]$ (Hpy = pyridinium). The mass spectrum of $(NBu^n_4)_2Cr_2O_7$ shows $Cr_2O_7^{2-}$ as the base ion together with less intense solvated ions $[Cr_2O_7(MeCN)]^{2-}$ and $[Cr_2O_7(MeCN)_2]^{2-}$ (Fig. 1). There is good agreement between the experimental and calculated chromium isotopic mass distribution; the Cr isotopic peaks are separated by 0.5 *m*/*z* units as expected for a doubly charged ion. CrO_3^- and CrO_4^-, product ions of a CID reaction (see later) in the lens region are also evident. In addition, there is also the ion $HCrO_4^-$ which is most likely due to the following equilibrium involving water present in the solvent [eqn. (1)].

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^- \qquad (1)$$

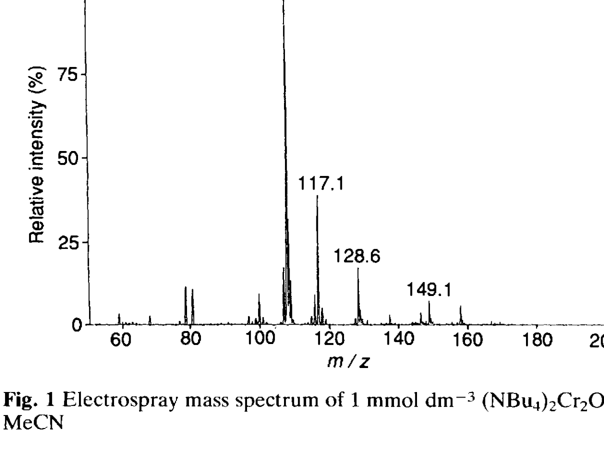

Fig. 1 Electrospray mass spectrum of 1 mmol dm^{-3} $(NBu_4)_2Cr_2O_7$ in MeCN

The CID of $Cr_2O_7^{2-}$ shows the ions CrO_4^- and CrO_3^- as well as the much less intense CrO_2^-. At low collision energies (E_{cm} < 3 V) the abundances of CrO_4^- and CrO_3^- are approximately the same, in accordance with the two ions being produced from the cleavage of a bridging Cr–O bond in $Cr_2O_7^{2-}$ $\{[O_3Cr–O–CrO_3]^{2-}\}$. Under higher collision energies, the intensity of CrO_4^- becomes lower than that of CrO_3^-; this is a consequence of CrO_4^- being converted to CrO_3^- through loss of an oxygen atom (as confirmed by CID of CrO_4^- in an MS^3 experiment). The detection of CrO_4^- is of interest because the ion may be interpreted to contain Cr in the highly unusual oxidation state of +7. An alternative and may be a more realistic formalism is to regard the species as Cr^{VI} with one O^- (radical ion) and three O^{2-} ligands. In the ES mass spectrum of Hpy[CrO_3Cl], the only peak present is the molecular ion CrO_3Cl^-. The CID shows the ions CrO_2Cl^- and CrO_3^- formed from loss of O and Cl respectively. The Cl^- ion was also observed, suggesting that the Cr–Cl bond is also cleaved heterolytically.

In the case of ruthenium, we have chosen RuO_4^-, an anionic ruthenium(VII) species; $RuO_2Cl_3^-$, an anionic ruthenium(VI) species; and $[Ru(TMC)O_2]^{2+}$ (TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), a cationic ruthenium(VI) species; as representatives of the high-valent ruthenium oxo complexes.[7] The mass spectra of all three ruthenium oxo complexes show the molecular ions as base peaks. Again there is good agreement between experimental and calculated isotopic mass distribution, and no fragment ions are observed. In the case of the doubly charged $[Ru(TMC)O_2]^{2+}$ ion, low intensities of the solvated species $[Ru(TMC)O_2(MeCN)]^{2+}$ are also observed (Fig. 2). The CID of RuO_4^- shows the ions RuO_3^- and RuO_2^- resulting from loss of oxygen atoms. The CID of $RuO_2Cl_3^-$ shows the major product ions $RuO_2Cl_2^-$, RuO_2Cl^- and Cl^- arising from homolytic and heterolytic cleavage of Ru–Cl bonds. $RuOCl_3^-$ is also present as a minor product.

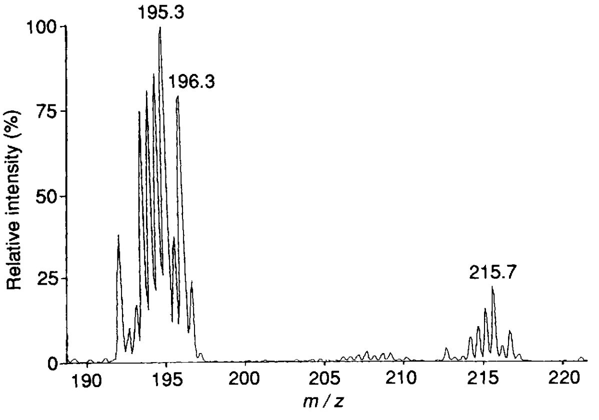

Fig. 2 Electrospray mass spectrum of 1 mmol dm^{-3} $[Ru(TMC)O_2](PF_6)_2$ in MeCN

To demonstrate the usefulness of ESMS in studying oxidation reactions by metal–oxo species, an aqueous solution of $[Ru(TMC)O_2](PF_6)_2$ was treated with excess potassium iodide and the ES mass spectra before and after the reaction were compared. The base peak was shifted from *m/z* 195 to 196, consistent with the reduction of $[Ru^{VI}(TMC)O_2]^{2+}$ to $[Ru^{IV}(TMC)O(OH_2)]^{2+}$, whose formation had been confirmed by UV–VIS spectrophotometry.[9]

In conclusion, electrospray mass spectra of highly oxidizing ionic metal–oxo species can be readily obtained with apparently little or no sign of degradation. ESMS is thus a potentially valuable technique for characterizing and studying the reactivities of metal–oxo species.

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† Experiments were performed on a SCIEX TAGA Model 6000E triple quadrupole mass spectrometer, which has as upper limit of *m/z* ≈ 1400. For details of the set-up see ref. 8.

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