

## NEGATIVE ION MASS SPECTRA OF SOME CLASSES OF METAL CARBONYL HALIDES

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### Summary

The negative-ion mass spectra at 70 eV of the compounds  $\text{Re}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{Mn}(\text{CO})_5\text{X}$  ( $\text{Br}, \text{I}$ ),  $\text{Re}_2(\text{CO})_8\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{Mn}_2(\text{CO})_8\text{Br}_2$  and  $\text{Rh}_2(\text{CO})_4\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are reported. The negative molecular ions are absent and the current is mainly transported by fragments due to the loss of carbonyl groups. In the spectra of the bimetallic compounds a rather high intensity is displayed by ionic species containing the two halide substituents. The variations in the ionic abundances are related to the change of the metal–CO bond strength, while the nature of X seems to play a minor role.

### Introduction

In recent years increasing interest has been paid to the mass spectrometric studies of negative ions [1–5]. This is to be ascribed mainly to the fact that they offer information complementary to that from positive-ion mass spectrometry [2]. For some classes of compounds, moreover, the negative-ion mass spectra obtained in an electron impact ion source at 70 eV, display abundant molecular ions, which are weak or not detectable in the corresponding positive-ion mass spectra [6–9].

Moreover, much interest in the behaviour of the gaseous negative ions has arisen from the increasing utilisation of chemical ionisation negative-ion mass spectrometry as a very sensitive analytical tool for some classes of compounds [10].

As part of an investigation on the negative-ion mass spectra of organic [9,11,12] and metal-containing compounds [13–15], we report and discuss here the negative-ion mass spectra of the compounds  $\text{Re}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{Mn}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ),  $\text{Re}_2(\text{CO})_8\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ),  $\text{Mn}_2(\text{CO})_8\text{Br}_2$  and  $\text{Rh}_2(\text{CO})_4\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).

## Results and discussion

The negative-ion mass spectra at 70 eV of the monometal compounds  $\text{Re}(\text{CO})_5\text{X}$ , where  $\text{X} = \text{Cl}, \text{Br}, \text{I}$  and  $\text{Mn}(\text{CO})_5\text{X}$ , where  $\text{X} = \text{Br}, \text{I}$ , are reported in Table 1. All the spectra are devoid of the negative molecular ion, as is usual for most carbonylmetal derivatives, and the fragments, formed by loss of carbonyl groups, contain the halide ligand.  $[\text{M} - \text{CO}]^-$  is the base peak in the spectra of  $\text{Re}(\text{CO})_5\text{Br}$  and  $\text{Re}(\text{CO})_5\text{I}$  and shows a high intensity in that of  $\text{Re}(\text{CO})_5\text{Cl}$ , whereas it displays a rather lower intensity in the spectra of manganese compounds, where  $[\text{M} - 2\text{CO}]^-$  is the base peak. Variation of  $\text{X}$  both in rhenium and in manganese compounds does not affect the fragment abundances much.

In Table 2 the negative-ion mass spectra of  $\text{Re}_2(\text{CO})_8\text{X}_2$ , where  $\text{X}$  is  $\text{Cl}, \text{Br}, \text{I}$  and of  $\text{Mn}_2(\text{CO})_8\text{Br}_2$  are reported. The main feature in these spectra is the absence of the  $[\text{M} - \text{CO}]^-$  fragment ions in addition to that of the  $[\text{M}]^-$  ions. In the spectra of  $\text{Re}_2(\text{CO})_8\text{X}_2$  compounds the nature of the halogen as a minor influence on the ion abundances. The  $[\text{M} - 2\text{CO}]^-$  ions have the highest intensity in the spectra of the rhenium compounds whereas the current transported by the other bimetallic fragments is rather low. In contrast, a good intensity is shown by the  $[\text{Re}(\text{CO})_3\text{X}_2]^-$  fragments. The feature of even-electron species and the presence of the two halide substituents give  $[\text{Re}(\text{CO})_3\text{X}_2]^-$  a higher stability than that of  $[\text{Re}(\text{CO})_4\text{X}]^-$  and  $[\text{Re}(\text{CO})_3\text{X}]^-$ , which are also present in the spectra of  $\text{Re}_2(\text{CO})_8\text{X}_2$ . The negative-ion mass spectrum of  $\text{Mn}_2(\text{CO})_8\text{Br}_2$  displays weak intensities for the  $[\text{M} - 2\text{CO}]^-$ ,  $[\text{M} - 3\text{CO}]^-$  and  $[\text{Mn}(\text{CO})_3\text{Br}_2]^-$  ions and a high intensity for  $[\text{M} - 4\text{CO}]^-$ , which is the base peak.

Under electron impact at 70 eV,  $\text{Rh}_2(\text{CO})_4\text{X}_2$  compounds, where  $\text{X}$  is  $\text{Cl}, \text{Br}, \text{I}$ , show the negative ion fragmentation patterns reported in Table 3.  $[\text{M} - 2\text{CO}]^-$  is the base peak for all the three compounds, whereas weak abundances are displayed by  $[\text{M} - \text{CO}]^-$  ions and  $[\text{M}]^-$  are absent, as usual. Weak  $[\text{RhX}_2]^-$  fragments are also present.

For all these classes of compounds  $[\text{M}]^-$  is not stable, and the presence of halogen substituents does not cause any enhancement in this respect. On the other hand, in the negative ion mass spectra of halogenated organic compounds  $[\text{M}]^-$  is detectable only when a number of fluorine atoms are present in cyclic compounds, such as perfluorocyclobutadiene [16–18] or in compounds containing electron withdrawing functional groups, such as hexafluoroacetone

TABLE 1

NEGATIVE ION MASS SPECTRA (PERCENTAGE ABUNDANCES) OF  $\text{Re}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) AND  $\text{Mn}(\text{CO})_5\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) AT 70 eV

Ion	$\text{Re}(\text{CO})_5\text{Cl}$	$\text{Re}(\text{CO})_5\text{Br}$	$\text{Re}(\text{CO})_5\text{I}$	$\text{Mn}(\text{CO})_5\text{Br}$	$\text{Mn}(\text{CO})_5\text{I}$
$[\text{M} - \text{CO}]^-$	67	100	100	25	30
$[\text{M} - 2\text{CO}]^-$	100	68	72	100	100
$[\text{M} - 3\text{CO}]^-$	85	55	27	21	14
$[\text{M} - 4\text{CO}]^-$	25	7	4	41	10
$[\text{M} - 5\text{CO}]^-$	2	1		42	7

TABLE 2

NEGATIVE ION MASS SPECTRA (PERCENTAGE ABUNDANCES) OF  $M'_2(\text{CO})_8\text{X}_2$  ( $M' = \text{Re}$  AND  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $M' = \text{Mn}$  AND  $\text{X} = \text{Br}$ ) AT 70 eV

Ion	$\text{Re}_2(\text{CO})_8\text{Cl}_2$	$\text{Re}_2(\text{CO})_8\text{Br}_2$	$\text{Re}_2(\text{CO})_8\text{I}_2$	$\text{Mn}_2(\text{CO})_8\text{Br}_2$
$[M - 2 \text{CO}]^{--}$	100	100	100	14
$[M - 3 \text{CO}]^{--}$	28	25	41	6
$[M - 4 \text{CO}]^{--}$	19	18	21	100
$[M - 5 \text{CO}]^{--}$	8	12	9	39
$[M - 6 \text{CO}]^{--}$	4	4		18
$[M'(\text{CO})_3\text{X}_2]^-$	55	90	33	17
$[M'(\text{CO})_4\text{X}]^{--}$	8	7	7	2
$[M'(\text{CO})_3\text{X}]^{--}$	3	5	4	1

[19–20]. It could also have been expected that the compounds with halide bridges would display behaviour similar to metal chelates, which give abundant negative molecular ions. However, this is not the case, since the compounds  $M'_2(\text{CO})_8\text{X}_2$ , we have examined do not exhibit any  $[M]^{--}$ .

In all these spectra the ion intensities also show a pattern analogous to that above described in the range of electron energy typical of dissociative attachment processes. Moreover, at low electron energy, metastable transitions are observed for the successive loss of carbonyl groups from ions in the highest mass region. From these observations we suggest that at 70 eV also the dominant process is the dissociative attachment, which gives, as primary product,  $[M - \text{CO}]^{--}$  in the spectra of  $\text{Re}(\text{CO})_5\text{X}$ ,  $\text{Mn}(\text{CO})_5\text{X}$  and  $\text{Rh}_2(\text{CO})_4\text{X}_2$  and  $[M - 2 \text{CO}]^{--}$  in the spectra of  $\text{Re}_2(\text{CO})_8\text{X}_2$  and  $\text{Mn}_2(\text{CO})_8\text{X}_2$ . Then the fragmentation of these primary ions occurs by loss of carbonyl groups in successive steps.

The pattern of the ion intensities in the spectra reported in Table 1 suggests that the major influence is played by the nature of the metal atom and consequently by the relative metal–CO bond strength. The energy lost in the elimination of one carbonyl group by  $\text{Re}(\text{CO})_5\text{X}$  is sufficient to stabilise  $[M - \text{CO}]^{--}$  strongly, since the Re–CO bond strength is high, whereas elimination of two carbonyl groups must occur to give the base peak in the manganese compounds. The change, as a function of X, of the Re–CO bond strength, obtained by electron impact studies [21] and from CO exchange data in  $S_N1$  reactions [22] shows a decrease in the order  $\text{Re}(\text{CO})_5\text{I} > \text{Re}(\text{CO})_5\text{Br} > \text{Re}(\text{CO})_5\text{Cl}$ . The

TABLE 3

NEGATIVE ION MASS SPECTRA (PERCENTAGE ABUNDANCES) OF  $\text{Rh}_2(\text{CO})_4\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) AT 70 eV

Ion	$\text{Rh}_2(\text{CO})_4\text{Cl}_2$	$\text{Rh}_2(\text{CO})_4\text{Br}_2$	$\text{Rh}_2(\text{CO})_4\text{I}_2$
$[M - \text{CO}]^{--}$	5	7	7
$[M - 2 \text{CO}]^{--}$	100	100	100
$[M - 3 \text{CO}]^{--}$	32	36	35
$[M - 4 \text{CO}]^{--}$	2	5	9
$[\text{RhX}_2]$	4	6	2

abundance values of  $[M - CO]^{-}$  and  $[M - 2 CO]^{-}$  of  $Re(CO)_5Cl$ , which indicate some minor influence of the halide ligand, are in accord with this sequence.

Values of metal-CO bond energies of  $Re_2(CO)_8X_2$  and  $Mn_2(CO)_8X_2$  are not available, and this prevents rationalization of the fragmentation pattern reported in Table 2, even though the strong effect of the metal suggests that analogous factors are responsible for the observed behaviour. A major difference of these spectra when compared with positive-ion mass spectra [23] is the very strong tendency to retain the halogen atoms, which is evidenced by the presence of  $[Re(CO)_3X_2]^{-}$ ,  $[Mn(CO)_3Br_2]^{-}$  and  $[RhX_2]^{-}$  ions.

## Experimental

All the compounds examined were prepared as described in the literature.

The mass spectra were recorded on a single-focusing Hitachi RMU 6H mass spectrometer with a trap current of 20  $\mu A$  when the ionising energy was 70 eV. The samples were introduced into the ion source through a direct inlet system and the sample pressure was  $2 \times 10^{-6}$ – $3 \times 10^{-6}$  Torr. Perfluorokerosene,  $Cr(CO)_6$ ,  $Mo(CO)_6$  and  $W(CO)_6$  were used as mass reference standards.

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