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Gas-phase chemistry of first transition series carbonyl metallate ions: reactions with ^{13}C-labelled carbonyl sulfide

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Abstract

Fourier transform ion cyclotron resonance (FTICR) spectroscopic methods have been applied to examine the gas phase reactions of the metal carbonyl anions $[\mathrm{metal(CO)_4}]^-$, metal = Cr, Mn; $[\mathrm{metal(CO)_3}]^-$, metal = Cr, Mn, Fe; and $[\mathrm{metal(CO)_2}]^-$, metal = Fe, Ni with ^{13}C-labelled carbonyl sulfide. Measurements of temporal variations of ionic product distributions have allowed mechanisms to be proposed to account for the formation of both carbonylated and decarbonylated metal–S bonded ionic reaction products which derive from $^{13}\mathrm{C{=}S}$ cleavages in $[(\mathrm{CO})_x\cdot\mathrm{metal}\cdot\eta^2\text{-}\mathrm{S^{13}CO}]^-$ intermediates.

Introduction

Electron deficient and coordinatively unsaturated first transition series carbonyl metallate ions, $[\mathrm{metal}\cdot(\mathrm{CO})_x]^-$ have been shown recently to display considerable variation in their gas phase reactions with both organic and inorganic substrates [1–10]. New insights into this chemistry have been made possible by the application of both Fourier transform ion cyclotron resonance (FTICR) and flowing afterglow (FA) spectroscopic techniques. These methods enable detailed mechanistic and kinetic studies to be made of ion/molecule reactions in the gas phase [11–16]. FTICR studies in particular, have the facility for examining trapped-ion/molecule reactions for long periods (seconds) and at low pressures (10^{-9}–10^{-7} mbar) within ICR cells thereby enabling fundamental simultaneous and/or consecutive reaction channels, along with reaction intermediates and products, to be identified from time-resolved mass spectral measurements [11–15].

Carbon disulfide, carbonyl sulfide and carbon dioxide in the solution phase, display great diversity in their reactions at complexed transition metal centres [17–25]. In contrast to the chemistry given by metal–$\mathrm{CS_2}$ complexes, the solution phase chemistry of metal–OCS complexes is often dominated by reactions which involve cleavage of the C=S bond [21]. However, there is little experimental data available which focuses on the reactions of these $\mathrm{C_1}$ molecules at electron deficient anionic transition metal centres in the gas phase and in the absence of complicating solvation phenomena. Nevertheless, a recent preliminary account of the gas phase reactions of carbon disulfide with $[\mathrm{metal}\cdot(\mathrm{CO})_x]^-$ ions has attempted to redress this sparsity of chemical detail, particularly with respect to the definition of simultaneous and consecutive reaction channels for a number of $[\mathrm{metal}\cdot(\mathrm{CO})_x]^-/\mathrm{CS_2}$ systems (with metal = Cr, Mn, Fe, Ni) for ion trapping times of up to 20 s [2].

In order to identify unequivocally the elementary gas phase reactions of carbonyl sulfide with odd- or even-electron transition metal carbonylate ions this study has used exclusively the ^{13}C-labelled ligand $\mathrm{O^{13}CS}$. Results are now presented which describe new reactions of $\mathrm{O^{13}CS}$ with the 13- and 15-electron radical anions $[\mathrm{Cr(CO)_3}]^-$ and $[\mathrm{Cr(CO)_4}]^-$; $[\mathrm{Fe(CO)_2}]^-$ and $[\mathrm{Fe(CO)_3}]^-$; the 14- and 16-electron species $[\mathrm{Mn(CO)_3}]^-$ and $[\mathrm{Mn(CO)_4}]^-$ together with the 15-electron ion $[\mathrm{Ni(CO)_2}]^-$.

Experimental

All ion/molecule reactions described here were performed in a 6 cm diameter ×6 cm cylindrical cell of a Spectrospin CMS-47 FTICR spectrometer, details and performance characteristics of which have previously been well documented [26, 27]. The cell temperature was maintained at somewhat above ambient (*c.* 30–35 °C) due to heating from a 4 cm remotely positioned rhenium filament. Pressures were measured by a Balzers IMR-132 ionization gauge positioned in

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TABLE 1. Ionic product distributions for reactions of $[Cr(CO)_{3,4}]^-$ and $[Mn(CO)_{3,4}]^-$ with $O^{13}CS$[a]

Product ions	Primary reactant ion			
	$[Cr(CO)_3]^{-b}$ I	$[Cr(CO)_4]^{-b}$ II	$[Mn(CO)_3]^{-c}$ III	$[Mn(CO)_4]^{-c}$ IV
$[(CO)_2\cdot metal\cdot S^{13}CO]^-$		0.55	0.24	0.57
$[(CO)_3\cdot metal\cdot S]^-$	0.33	0.45	0.17	0.43
$[CO\cdot metal\cdot S^{13}CO]^-$			0.25	
$[(CO)_2\cdot metal\cdot S]^-$	0.63	<0.01	0.33	
$[CO\cdot metal\cdot S]^-$	0.04			

[a] Reaction times of 1 s. [b] Based on ^{52}Cr. [c] Based on ^{55}Mn.

proximity (c. 10 cm) to the Balzers TPU-330 turbomolecular pump. As previously reported, accurate estimates of low pressures and hence of neutral particle densities in the ICR cell precluded the acquisition of meaningful ion/molecule rate coefficients [2].

Low energy ionization (5–10 eV) of neutral metal carbonyls to give, by dissociative electron attachment, the various electron deficient metal carbonyl anions have been previously described [2]. Trapped electrons were ejected from the ICR cell after the electron beam pulse (25 ms) by the application of an oscillating electric field across the trapping plates (5–10 ms at c. 2 V_p amplitude, 4.2 MHz and -2.5 V trapping voltage). Mass selected $[metal\cdot(CO)_x]^-$ ions were trapped after the application of broad band excitation pulses to eject other extraneous ions from the cell, and translational excitation of these ions was minimized by the use of lowest possible r.f. fields. Neutral reactants were admitted to the ICR cell in the pressure ratio of 1/1 to the neutral metal carbonyl and to a total indicated pressure of $8–9\times10^{-8}$ mbar. Apart from those reactions otherwise indicated, reaction delays of 1 s were used to establish the tabulated ionic product distributions. Elemental compositions of all ionic reaction products were obtained from accurate mass measurements. Ion/molecule reaction channels were deduced from either the results of selective ion ejections or plots of the temporal variations of ionic product distributions (‘time-plots’) for reaction times of up to 3 s.

The metal carbonyls were obtained from either Strem Chemicals Inc., Newburyport, MA, USA or Aldrich. Carbonyl sulfide, 99% ^{13}C was obtained from Cambridge Isotope Laboratories, Woburn, MA, USA and its isotopic purity was verified and regularly checked from its positive ion mass spectra run on the CMS-47 FTICR spectrometer.

Results and discussion

Ionic product distribution data for the reactions of the tri- and tetracarbonyl metallate ions of chromium and manganese, respectively I–IV, with $O^{13}CS$ are listed in Table 1. As the 15- and 16-electron ions II and IV gave closely similar product distributions for reaction delays of 1 s a representative ‘time-plot’ is given in Fig. 1 for the $[Cr(CO)_4]^-/O^{13}CS$ system. The rate of reaction of II with $O^{13}CS$ was approximately twice that observed for the $[Mn(CO)_4]^-/O^{13}CS$ system.

The reaction of II and IV with $O^{13}CS$ is envisaged to proceed via a bimolecular reaction and formation of a six-coordinate η^2-$S^{13}CO$ excited ion/molecule complex which decomposes to form multiple products by

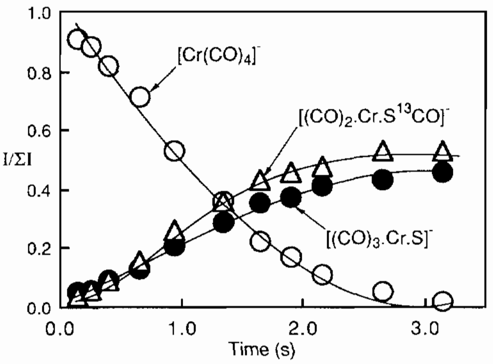


Fig. 1. Temporal variations of ion abundances for the reaction of $[Cr(CO)_4]^-$ with $O^{13}CS$. $I/\Sigma I$ = Ion abundance/sum of ion abundances ^{52}Cr considered.

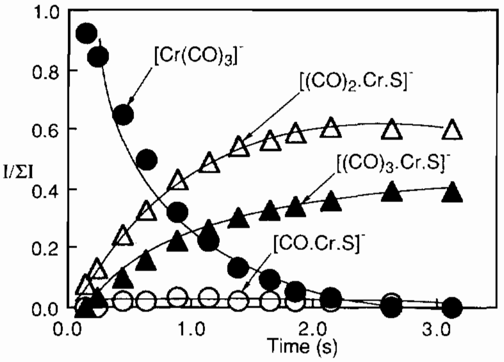


Fig. 2. Temporal variations of ion abundances for the reaction of $[Cr(CO)_3]^-$ with $O^{13}CS$. $I/\Sigma I$ = Ion abundance/sum of ion abundances. ^{52}Cr considered.

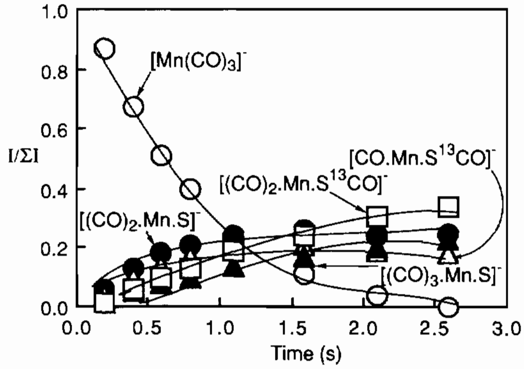


Fig. 3. Temporal variations of ion abundances for the reaction of $Mn(CO)_3]^-$ with $O^{13}CS$. $I/\Sigma I$ = Ion abundance/sum of ion abundances. ^{55}Mn considered.

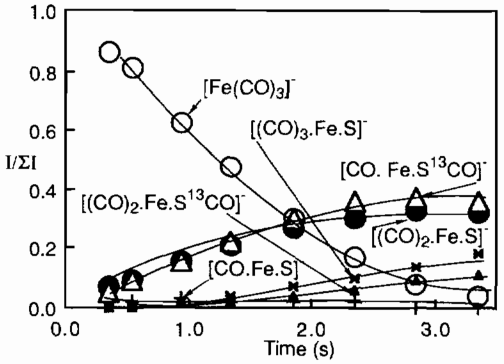


Fig. 4. Temporal variations of ion abundances for the reaction of $[Fe(CO)_3]^-$ with $O^{13}CS$. $I/\Sigma I$ = Ion abundance/sum of ion abundances. ^{56}Fe considered.

elimination of CO and ^{13}CO. Terminal four-coordinate ionic products, $[(CO)_2 \cdot metal \cdot S^{13}CO]^-$ and $[(CO)_3 \cdot metal \cdot S]^-$, respectively, were identified for these systems. Metal·η^2-C=S bonding in metal–carbonyl sulfide complexes is already well established from solution and solid phase experimental data [21, 22]. Whereas the bond energies in unlabelled carbonyl sulfide are 73.3 and 157.5 kcal mol^{-1} for the S=C and C=O bonds, respectively [28, 29], the weakening of the $^{13}C=S$ linkage concomitant with the formation of a stronger metal–S bond after complexation of $O^{13}CS$ with the metal centre is seen as sufficient to promote elimination of ^{13}CO from the $[(CO)_4 \cdot metal \cdot \eta^2\text{-}S^{13}CO]^-$ intermediate to give the terminal $[(CO)_3 \cdot metal \cdot S]^-$ product.

The product distribution data and complementary 'time-plot' for reaction of the 13-electron ion $[Cr(CO)_3]^-$ with $O^{13}CS$ (Table 1 and Fig. 2) indicate that multiple products, viz. $[(CO)_3CrS]^-$, $[(CO)_2CrS]^-$ together with the minor species $[COCrS]^-$, are formed via an initial bimolecular encounter followed by neutral losses of CO and ^{13}CO from a presumed five-coordinate $[(CO)_3 \cdot metal \cdot \eta^2\text{-}S^{13}CO]^-$ excited ion/molecule complex.

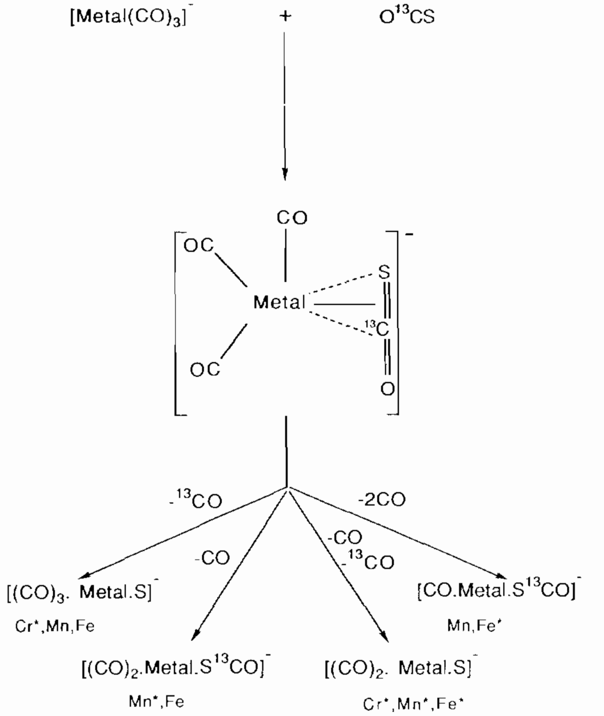
However the reactivities of the 14- and 15-electron ions $[Mn(CO)_3]^-$ and $[Fe(CO)_3]^-$ with $O^{13}CS$ display similarities which are evident in the product distribution 'time-plots' of Figs. 3 and 4 and Tables 1 and 2. These data may be rationalized in terms of competing reaction channels shown in Scheme 1. The origins of the major three- and four-coordinate ionic products formed after 3 s reaction delays are also identified from Scheme 1. Electron affinities of (0.46±0.2) eV for OCS [31] and (1.8±0.2) eV for $Fe(CO)_3$ together with a value of (1.4–2.0) eV for $D[Fe(CO)_2\text{–}CO]^-$ [30] are consistent with the absence of identifiable charge exchange species in the spectra and also the facile elimination of ^{12}CO ligands from the metal centre of the five-coordinate intermediate complex (Scheme 1).

The coordinatively unsaturated and linear 13- and 15-electron ions V and VII [30, 32] reacted differently with $O^{13}CS$, Table 2. Whereas $[Ni(CO)_2]^-$ (**VII**) gave the principal product ion $[(CO)_2NiS]^-$ and the minor species $[CONiS]^{\cdot-}$ as a consequence of ^{13}CO and CO elimination from a $[(CO)_2 \cdot metal \cdot \eta^2\text{-}S^{13}CO]^-$ complex, novel secondary reactions were observed for the

TABLE 2. Ionic product distributions for reactions of $[Fe(CO)_{2,3}]^-$ and $[Ni(CO)_2]^-$ with $O^{13}CS$[a]

Product ions	Primary reactant ion		
	$[Fe(CO)_2]^{-b}$ V	$[Fe(CO)_3]^{-b}$ VI	$[Ni(CO)_2]^{-c}$ VII
$[(CO)_2 \cdot metal \cdot S^{13}CO]^-$		0.05	
$[(CO)_3 \cdot metal \cdot S]^-$		0.10	
$[CO \cdot metal \cdot S^{13}CO]^-$		0.43	
$[(CO)_2 \cdot metal \cdot S]^-$	0.03	0.36	0.96
$[CO \cdot metal \cdot S]^-$	0.73	0.07	0.04
$[^{13}CO \cdot metal \cdot S_2]^-$	0.11		
$[CO \cdot metal \cdot S_2]^-$	0.03		
$[metal \cdot S_2]^-$	0.10		

[a] Reaction times of 1 s. [b] Based on ^{56}Fe. [c] Based on ^{58}Ni.



*Major ionic products after 3s reaction delays.
Very low abundances of [CO.Metal.S]- were detected for Metal=Cr, Fe.

Scheme 1.

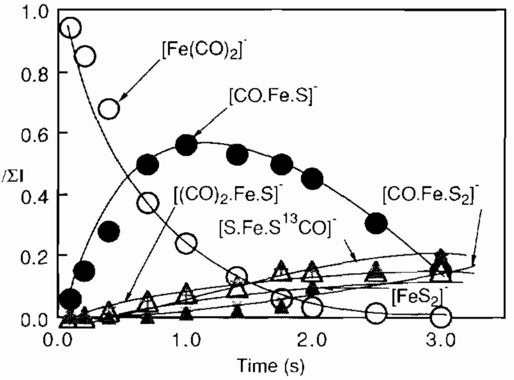
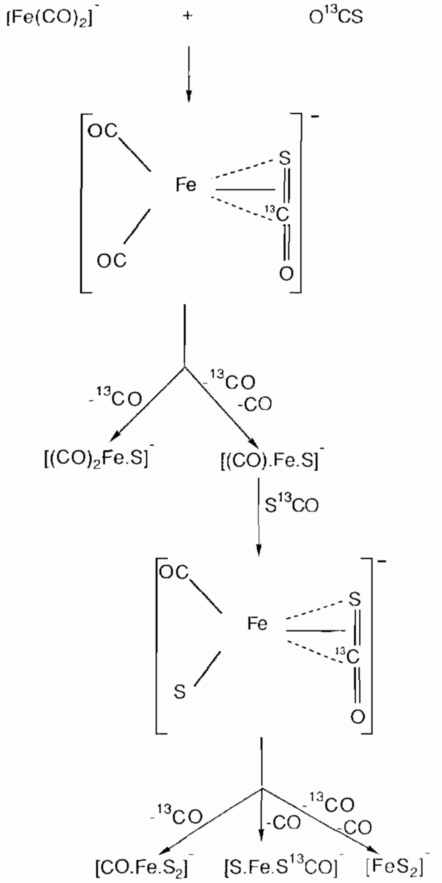


Fig. 5. Temporal variations of ion abundances for the reaction of $[Fe(CO)_2]^-$ with $O^{13}CS$. $I/\Sigma I$ = Ion abundance/sum of ion abundances. ^{56}Fe considered.

$[Fe(CO)_2]^-/O^{13}CS$ system at ion trapping times of up to 3 s (Fig. 5). The data from Fig. 5 and Table 2 for this system allow a mechanism to be proposed (Scheme 2) to indicate competing reaction channels for the reactive intermediate $[CO\cdot Fe\cdot S]^-$ in its further reactions with $O^{13}CS$ which result in the formation of terminal ionic species containing two S atoms. Significantly, use of the labelled ligand $O^{13}CS$ has provided evidence for the non-existence of a reductive disproportionation pathway of $O^{13}CS$ to give a $[metal\cdot\eta^2\text{-}S_2{}^{13}CO]^-$ dithiocarbonate species coordinated through two sulfur atoms [18].



Scheme 2.

Although the sparse thermochemical data base applicable to these and similar systems precludes a detailed analysis, differences in the electronegativities of these $[metal(CO)_2]$ species and the metal–CO bond strengths of their ions are noteworthy [30, 32]. Whilst the electronegativity of $Fe(CO)_2$, (1.0 ± 0.3) eV, differs from that of $Ni(CO)_2$, (1.22 ± 0.02) eV, the more significant differences in $D[CO\cdot metal\text{–}CO]^-$ of 1.0 ± 0.65 eV for **V**, as against 2.21 ± 0.65 eV for **VII** [30, 32], may be taken, at least in part, to indicate the availability of a more facile CO elimination channel for **V** to form the coordinatively unsaturated and reactive intermediate $[CO\cdot Fe\cdot S]^-$. This latter species has been identified previously as the sole ionic product ion in a flowing afterglow study of the reaction between $[Fe(CO)_2]^-$ and H_2S [33]. FeS^- ions have also been identified recently as products of Fe^- oxidative insertions into the C–S bonds of thiols and also from gas phase reactions of Fe^- with CS_2 and organic disulfides [34].

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