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LETTER

Chemistry of electron deficient carbonyl metallate ions: gas phase reactions of [metal(CO)$_x$]$^-$, metal = Cr, Mn; $x = 3$, 4 and [metal(CO)$_y$]$^-$, metal = Fe, Ni; $y = 2$, 3 with carbon disulfide

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New insights into the gas phase reactions of electron deficient carbonyl metallate ions with a variety of organic and inorganic substrates have been provided recently from Fourier transform ion cyclotron resonance (FTICR) spectroscopic investigations [1–6]. By means of this technique with its facility for high resolution elemental identification of ions and the definition of primary and secondary ion/molecule reaction channels by the measurement of the temporal variations of ionic reaction product distributions, it is now possible to undertake detailed studies of the reactions of electron deficient and coordinatively unsaturated carbonyl metallate ions in the absence of solvation phenomena [7, 8]. In this connection, many simultaneous and consecutive reactions of 15–17 electron organometallic ions require examination for the longer (seconds) trapping times and at the higher mass resolution which can be provided by FTICR spectroscopy compared with the complementary flowing after glow (FA) technique [5, 9].

Carbon disulfide is known to be activated and complexed by most low oxidation state transition metals, and this solution phase chemistry has been comprehensively reviewed [10–13]. Theoretical studies have also been made of the bonding capabilities of CS$_2$ towards (neutral) transition metal fragments [14]. However little is known of the elementary gas phase reactions of CS$_2$ with electron deficient odd- or even-electron transition metal carbonylate ions. Results are now presented which focus on new reactions of CS$_2$ with the 13- and 15-electron radical anions [Cr(CO)$_3$]$^{.-}$ and [Cr(CO)$_4$]$^{.-}$; [Fe(CO)$_4$]$^{.-}$

and [Fe(CO)$_3$]$^{.-}$; the 14- and 16-electron species [Mn(CO)$_3$]$^-$ and [Mn(CO)$_4$]$^-$ along with the 15- and 17-electron radical anions [Ni(CO)$_2$]$^{.-}$ and [Ni(CO)$_3$]$^{.-}$.

Experimental

Experiments were performed in a Spectrospin CMS-47 FTICR spectrometer fitted with a 6 cm diameter × 6 cm cylindrical ICR cell, a 150 mm bore 4.7 Tesla superconducting magnet, a high vacuum system (base pressure $\leqslant 10^{-9}$ mbar) pumped by a Balzers TPU-330 turbomolecular pump and a Bruker Aspect 3000 computer. More detailed features of this instrument have been described previously [15, 16]. Reagents were admitted to the ICR cell via a 40 °C temperature regulated inlet system fitted with Balzers precision leak valves type BDV-035. The ICR cell temperature was somewhat above ambient, *c.* 30 °C, due to heating from the 4 cm remotely positioned cell filament. All pressures were measured with a magnetically shielded Balzers type IMR-132 ionization gauge positioned above the turbomolecular pump. However, the present absence of appropriate absolute pressure calibration instrumentation compatible with the prevailing low experimental pressures precluded accurate estimates of neutral particle densities in the cell. Hence, meaningful rate constant measurements could not be made.

Low energy ionization (5 eV) of Cr(CO)$_6$ and Fe(CO)$_5$ gave the ionic species by dissociative electron attachment in the following relative abundances Cr(CO)$_5$$^{.-}$ 100%, Cr(CO)$_4$$^{.-}$ 10%, Cr(CO)$_3$$^{.-}$ 10%; Fe(CO)$_4$$^{.-}$ 100%, Fe(CO)$_3$$^{.-}$ 15%, Fe(CO)$_2$$^{.-}$ 5%. 10 eV ionization of Mn$_2$(CO)$_{10}$ and Ni(CO)$_4$ gave, respectively, Mn(CO)$_5$$^-$ 100%, Mn(CO)$_4$$^-$ 15%, Mn(CO)$_3$$^-$ 5%, and Ni(CO)$_3$$^{.-}$ 100%, Ni(CO)$_2$$^{.-}$ 5%, Ni(CO)$^{.-}$ 2%. These ionic products are consistent with previously reported negative ion mass spectra [17–23].

Selective ion ejections were performed in order that [metal(CO)$_x$]$^-$ ions could be trapped in the cell to react there with CS$_2$ for defined reaction times. Elemental compositions of reaction products were established by accurate ionic mass measurements [24, 25] and the most significant reaction channels were defined from the plots of the temporal variations in ionic product distributions ('time plots'). Pressure ratios of CS$_2$ to the neutral metal carbonyls of 5:1 were typically used with the indicated total cell pressure maintained at 2.5–3.0 × 10^{-7} mbar.

The metal carbonyls were obtained from Strem Chemicals Inc., Newburyport, MA, U.S.A. and carbon disulfide was May and Baker AR grade. All reagents

were subjected to multiple freeze, pump, thaw cycles before their admission into the inlet system of the FTICR spectrometer and compound purities were checked from their broad band positive ion mass spectra also obtained with the CMS-47 instrument.

Results and discussion

Table 1 lists the ionic product distributions for the reactions of CS_2 with the carbonyl metallate ions I–IV. Similar reaction products were given by the 13- and 14-electron ions I and III in their CS_2 reactions with the ions $[\text{metal} \cdot COCS_2]^-$ being formed in an associative ligand substitution pathway which is unlikely to involve a ligand charge transfer intermediate (EA $CS_2 = 0.51$ eV [26], $Cr(CO)_3 < EA$ $Fe(CO)_3 = 1.8$ eV [27]). The CS_2 ligand is envisaged as being η^2-complexed in these species which is consistent with the known existence of η^2-three-membered ring complexes involving CS_2 and manganese [11].

Figures 1–4 are 'time plots' and show the temporal variations in fractional ion abundances over extended trapping times for the CS_2 reactions of the terminal members of this series, i.e. I, II, VII, VIII. In particular Fig. 1 provides insights into the origins of $[\text{metal } CS_2]^-$, $[\text{metal}(CS_2)_2]^-$, $[\text{metal } S_2]^-$ and $[\text{metal } S]^-$ ions for the $[Cr(CO)_3]^-/CS_2$ system.

The initial primary reaction of CS_2 with $[Cr(CO)_3]^-$ involves CO ligand displacement which leads to the formation of both $[COCrCS_2]^-$ and $[CrCS_2]^-$. η^2-CS_2 neutral metal complexes are known to react further with CS_2 in the solution phase and can form head-to-tail bis(hetero-allene) dimers of the type $[L_x\text{metal} \cdot C_2S_4]$ containing a five-membered $[\text{metal} \cdot SCSC]$ heterocyclic ring [10, 13, 14, 28, 29]. In this gas phase study the species $[\text{metal}(CS_2)_2]^-$ or $[\text{metal } C_2S_4]^-$ can reasonably be attributed to the secondary reactions of the primary product ions $[CO \cdot \text{metal } CS_2]^-$ and $[\text{metal } CS_2]^-$ with CS_2 at the

longer trapping times during which the reactions were examined. The small yields of $[\text{metal } S_2]^-$, $[\text{metal } S]^-$ and $[CS \text{ metal } CS_2]^-$ seen in Fig. 1 can be inferred to originate from the slow decomposition of a $[\text{metal } C_2S_4]^-$ [30] intermediate by CS, CS_2, or S eliminations.

The 15- and 16-electron ions II and IV reacted somewhat differently with CS_2 compared with I and III. The primary reaction product ions $[(CO)_2\text{metal } CS_2]^-$, $[CO \text{ metal } CS_2]^-$ and $[\text{metal}(CS_2)]^-$ were formed in simultaneous ligand displacement/decarbonylation reaction channels [31]. Figure 2 indicates that such species react further with CS_2 in ligand displacement/decarbonylation reaction channels to yield a product $[Cr(CS_2)_2]^-$ or $[Cr(C_2S_4)]^-$ which is the likely decomposition precursor for the trithiocarbonate ion $[CrCS_3]^-$ [32] by CS elimination, and CrS_2^- by CS_2 elimination.

The 13-, 15- and 17-electron coordinatively unsaturated metal carbonylate species V–VII also formed novel product ions in their reactions with CS_2. Noteworthy are the adduct ions $[\text{metal}(CO)_2CS_2]^-$ given by both the 13- and 15-electron ions V and VII in their reactions with CS_2. Figure 3 assists in identifying the primary and secondary reaction channels for the reaction of VII and CS_2. Thus, interaction of the linear s^1d^{10} $Ni(CO)_2^-$ species (VII) [20] with CS_2 may be envisaged to proceed via end-on S-coordination or formation of an η^2 complex [10–13] with the electron rich C=S to give the vibrationally excited adduct species $[CS_2Ni(CO)_2]^-$ which reacts further with concomitant decarbonylation to give $[CO \cdot Ni(CS_2)_2]^-$ and the terminal product ion $[Ni(CS_2)_2]^-$. The neutral analogue of this latter species, viz. $[Ni(CS_2)_2]$, has been identified in matrix reactions of nickel atoms with CS_2, but precise interpretation of the bonding between the metal and CS_2 ligands is presently ambiguous [33].

The 13-electron linear species $Fe(CO)_2^-$ (V) likewise enters into adduct formation with CS_2 (Table 2) but other ions identified viz. $[FeCS_2]^-$, $[FeS_2]^-$

TABLE 1. Ionic product distributions for reactions of $[Cr(CO)_{3,4}]^-$ and $[Mn(CO)_{3,4}]^-$ with CS_2[a]

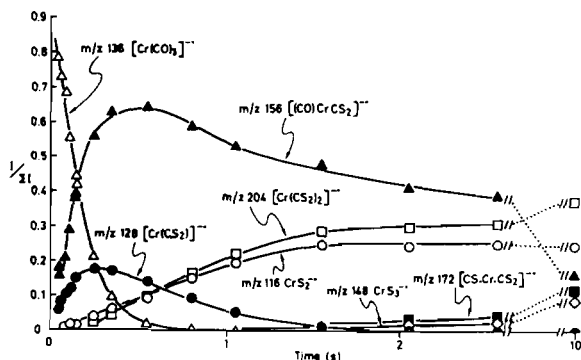| Product ions	Primary reactant ion			
	$[Cr(CO)_3]^-$ (I)[b]	$[Cr(CO)_4]^-$ (II)	$[Mn(CO)_3]^-$ (III)[c]	$[Mn(CO)_4]^-$ (IV)
$[\text{Metal}(CO)_3 \cdot CS_2]^-$				0.20
$[\text{Metal}(CO)_2 \cdot CS_2]^-$		0.66		0.38
$[\text{Metal}(CO) \cdot CS_2]^-$	0.53	0.16	0.24	0.09
$[\text{Metal} \cdot CS_2]^-$	0.05	0.06	0.51	0.28
$[\text{Metal} \cdot (CS_2)_2]^-$	0.22		0.20	0.04
$[\text{Metal} \cdot S_2]^-$	0.20	0.12		
$[\text{Metal} \cdot S]^-$			0.05	

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

Fig. 1. Temporal variations of ion abundances for the reactions of [Cr(CO)₃]⁻ with CS₂. ⁵²Cr isotope considered. $I/\Sigma I$ = ion abundance/sum of ion abundances.
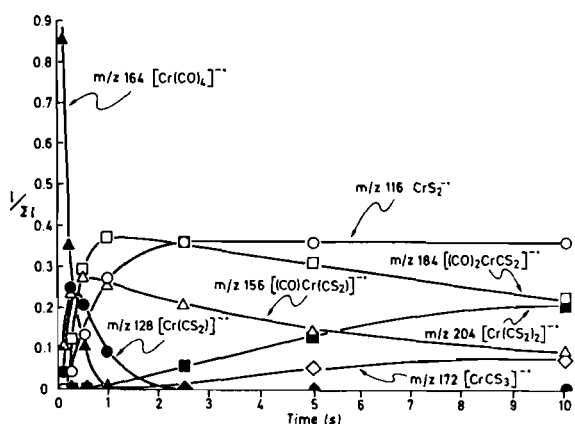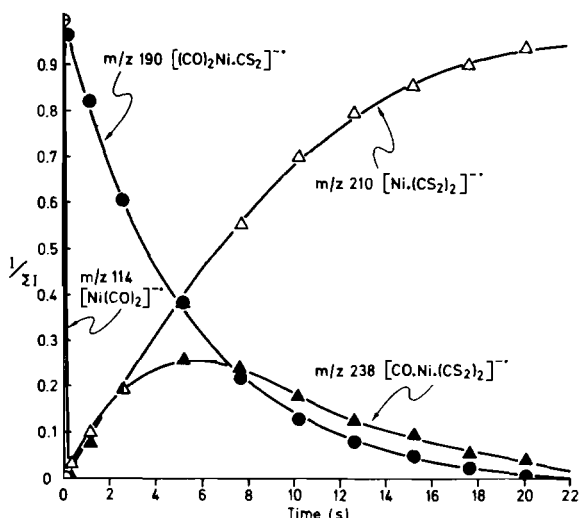

Fig. 2. Temporal variations of ion abundances for the reaction of [Cr(CO)₄]⁻ with CS₂. ⁵²Cr isotope considered. $I/\Sigma I$ = ion abundance/sum of ion abundances.

Fig. 3. Temporal variations of ion abundances for the reaction of [Ni(CO)₂]⁻ with CS₂. ⁵⁸Ni isotope considered. $I/\Sigma I$ = ion abundance/sum of ion abundances.

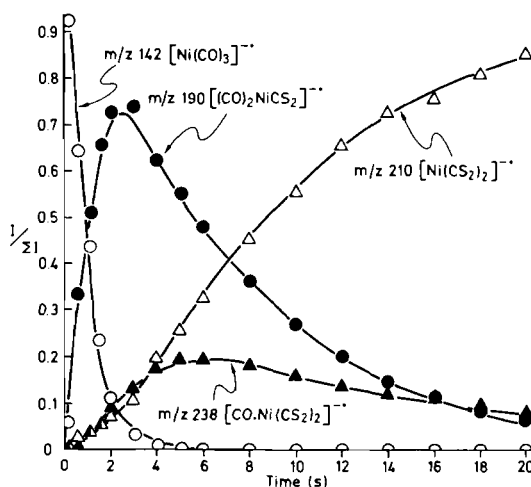
Fig. 4. Temporal variations of ion abundances for the reactions of [Ni(CO)₃]⁻ with CS₂. ⁵⁸Ni isotope considered. $I/\Sigma I$ = ion abundance/sum of ion abundances.

and [FeS]⁻ are the likely products of CO, CS and CS₂ eliminations from an [Fe(CS₂)₂]⁻ precursor. Whether the differences in reactivities of V and VII with CS₂ can be attributed to their electron affinity differences (EA Ni(CO)₂ = 0.643 eV, EA Fe(CO)₂ = 1.22 eV) or differing degrees of electron deficiency is not certain at this juncture.

The 15- and 17-electron ions VI and VIII also exhibited differences in their reactions with CS₂. Adduct ion formation did not occur between these coordinatively unsaturated species and CS₂. Moreover, no evidence was found for the reaction between CS₂ and the other 17-electron ions Cr(CO)₅⁻ and Fe(CO)₄⁻ and also, predictably, the 18-electron ion Mn(CO)₅⁻ even at trapping times of up to 5 s. It is noteworthy however, that [Ni(CO)₃]⁻ has recently been shown to react with organic substrates of high electron affinities for which a charge transfer mechanism from the metal to the ligands and involving a low energy 18-electron transition state, has been proposed [6].

Figure 4 indicates the reaction channels which lead to significant terminal product ions for the [Ni(CO)₃]⁻/CS₂ system. With an electron affinity of 1.077 eV for Ni(CO)₃ and D[Ni(CO)₂-CO]⁻ of (23±9) kcal mol⁻¹ versus D[Ni(CO)-CO]⁻ of (51±15) kcal mol⁻¹ for Ni(CO)₂⁻, simultaneous ligand exchange/decarbonylation reactions are consistent for the [Ni(CO)₃]⁻/CS₂ reaction. However, the structure of the stable terminal product ion [Ni(CS₂)₂]⁻ or [Ni(C₂S₄)]⁻ will be probed further by future pulsed collision induced decomposition (CID) experiments. The ionic products [FeCS₂]⁻, [FeS₂]⁻ and [FeS]⁻ from the reaction of VI with CS₂ can best be rationalized as decarbonylation

TABLE 2. Ionic product distributions for reactions of $[Fe(CO)_{2,3}]^{\cdot-}$ and $[Ni(CO)_{2,3}]^{\cdot-}$ with CS_2

Product ions	Primary reactant ion			
	$[Fe(CO)_2]^{\cdot-}$ (V)[b]	$[Fe(CO)_3]^{\cdot-}$ (VI)	$[Ni(CO)_2]^{\cdot-}$ (VII)[c]	$[Ni(CO)_3]^{\cdot-}$ (VIII)
$[Metal(CO)_2 \cdot CS_2]^{\cdot-}$	0.25	0.39	0.82	0.91
$[Metal(CO) \cdot (CS_2)_2]^{\cdot-}$			0.08	0.04
$[Metal(CO) \cdot CS_2]^{\cdot-}$	0.02	0.13		
$[Metal \cdot (CS_2)_2]^{\cdot-}$	0.02	0.05	0.10	0.04
$[Metal \cdot CS_2]^{\cdot-}$	0.65	0.35		
$[Metal \cdot S_2]^{\cdot-}$	0.06	0.05		
$[Metal \cdot S]^{\cdot-}$	0.01	0.01		

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

decomposition products and ions derived from a metal bis(heteroallene) dimer precursor [10].

These results show, however, that coordinatively unsaturated 13-, 14-, 15- and 17-electron ions are capable of undergoing a variety of reactions in a solvent free environment with a ligand of relatively low electron affinity and π-bonding capability as exemplified by CS_2.

Acknowledgement

References

1 I. K. Gregor, J. Organomet. Chem., 29 (1987) 201.
2 I. K. Gregor, Inorg. Chim. Acta, 132 (1987) 3.
3 I. K. Gregor, Org. Mass Spectrom., 22 (1987) 644.
4 I. K. Gregor, Org. Mass Spectrom., 24 (1989) 529.
5 R. R. Squires, Chem. Rev., 87 (1987) 623, and refs. therein.
6 Y. H. Pan and D. P. Ridge, J. Am. Chem. Soc., 111 (1989) 1150.
7 B. S. Freiser, in J. M. Farrar and W. H. Saunders Jr. (eds.), Techniques for the Study of Ion–Molecule Reactions, Wiley-Interscience, New York, 1988, Ch. II, p. 61.
8 M. V. Buchanan (ed.), Fourier Transform Mass Spectrometry, ACS Symposium Series 359, American Chemical Society, Washington, DC, 1987.
9 R. R. Squires, in D. H. Russell (ed.), Gas Phase Inorganic Chemistry, Plenum, New York, 1989, Ch. 2, p. 43.
10 J. A. Ibers, Chem. Soc. Rev., 11 (1982) 57.
11 I. S. Butler and A. E. Fenster, J. Organomet. Chem., 66 (1974) 161.
12 P. Y. Yaneff, Coord. Chem. Rev., 23 (1977) 183.
13 J. A. Cras and J. Willemse, in G. Wilkinson (ed.), Comprehensive Coordination Chemistry, Vol. 2, Pergamon, London, 1987, Ch. 16.4, p. 579.
14 C. Mealli, R. Hoffmann and A. Stockis, Inorg. Chem., 23 (1984) 56.
15 M. Allemann, Hp. Kellerhals and K.-P. Wanczek, Int. J. Mass Spectrom. Ion J. Phys., 46 (1983) 139.
16 L. J. de Koning, R. H. Fokkens, F. A. Pinkse and N. M. M. Nibbering, Int. J. Mass Spectrom. Ion Proc., 77 (1987) 95.
17 R. N. Compton and J. A. D. Stockdale, Int. J. Mass Spectrom. Ion Phys., 22 (1976) 47.
18 S. Pignataro, A. Foffani, F. Grasso and B. Cantone, Z. Phys. Chem., 47 (1965) 106.
19 R. C. Dunbar, J. F. Ennever and J. P. Fackler, Inorg. Chem., 12 (1973) 2734.
20 A. E. Stevens, C. S. Feigerle and W. C. Lineberger, J. Am. Chem. Soc., 104 (1982) 5026.
21 P. C. Engelking and W. C. Lineberger, J. Am. Chem. Soc., 101 (1979) 5569.
22 P. M. George and J. L. Beauchamp, J. Chem. Phys., 76 (1982) 2959.
23 W. K. Meckstroth and D. P. Ridge, J. Am. Chem. Soc., 107 (1985) 2281.
24 G. Klass, M. Allemann, P. Bischofburger and Hp. Kellerhals, Application Note II, Spectrospin AG, Fallanden, Switzerland, Nov. 1983.
25 A. G. Marshall, Acc. Chem. Res., 18 (1985) 316.
26 P. Kebarle and S. Chowdhury, Chem. Rev., 87 (1987) 513.
27 S. W. McElvany and J. Allison, Organometallics, 5 (1986) 416.
28 T. A. Gaffney and J. A. Ibers, Inorg. Chem., 21 (1982) 2851.
29 H. Werner, O. Kolb, R. Feser and U. Schubert, J. Organomet. Chem., 191 (1980) 283.
30 T. Herskovitz and L. J. Gugenberger, J. Am. Chem. Soc., 98 (1976) 1615.
31 J. A. S. Howell and P. M. Burkinshaw, Chem. Rev., 83 (1983) 557.
32 J. M. Burke and J. P. Fackler, Inorg. Chem., 11 (1972) 2744.
33 H. Huber, G. A. Ozin and W. J. Power, Inorg. Chem., 16 (1977) 2234.