Observations of Polymetal Carbonyl Cations in the Mass Spectra of the Group VI Metal Hexacarbonyls

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Summary Secondary ions, $M_m(CO)_n^+$, considered to arise from ion–molecule reactions, have been observed in the mass spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ at 10^{-5}—10^{-6} Torr at 35—100°, depending upon m (1—3 for Cr, 1—2 for Mo, and 1—4 for W) the value of n is 0—14

Two reports of secondary ions arising from ion–molecule reactions during mass spectral studies of transition-metal carbonyl derivatives have appeared [1,2] In addition, secondary ions, $M_m(CO)_n^+$ have been observed in the mass spectra of the unsubstituted Group VIB metal carbonyls [3] Experiments which indicate the origin of these polymetal carbonyl cations are described in this report

Mass spectra were obtained with a Hitachi–Perkin–Elmer model RMU-6E instrument The electron multiplier was employed for detection and spectra were recorded with a Honeywell visicorder model 1508 $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were sublimed prior to use Their mass spectra showed no significant impurities Except where noted, samples were volatilized from a glass ampoule attached to the gas inlet system In order to avoid thermal decomposition of the metal hexacarbonyls, the maximum respective inlet, oven, and source temperatures were for $Cr(CO)_6$, 60 80 and 60°, for $Mo(CO)_6$, 35, 35, and 40°, for $W(CO)_6$, 100, 100, and 100° The pressures reported in the Tables

were measured with an ionization gauge tube situated prior to the pumping system of the electrostatic sector

The relative abundances of species observed for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ under the conditions indicated are presented in Table 1 Since each of these metals has several isotopes, the relative abundance of each $M_m(CO)_n^+$ ion was calculated from the sum of intensities at all masses which would contribute to that ion thereby assuring meaningful numbers when comparing two ions containing different numbers of metals Although the relative abundances of the polymetal carbonyl cations are low, they may be observed readily with the electron multiplier

There are four explanations which might account for these observed polymetal carbonyl cations (i) polymerization by way of thermal decomposition, (ii) presence of unknown polymetal carbonyl compounds in the samples, (iii) condensation of molecules upon adiabatic expansion through the molecular leak, (iv) ion–molecule reactions

Firstly, instrument temperatures were maintained at levels such that thermal decomposition should not have occurred [4,5]

In regard to (ii), each of these compounds has been shown to be monomeric in the gas phase[6] with no tendency towards polymerization Of particular interest towards this point is an experiment in which gaseous $Cr(CO)_6$ in the gas reservoir was allowed to mix with gaseous $Mo(CO)_6$ in the gas inlet system The mass spectrum of this mixture was

scanned and found to contain not only dimolybdenum and dichromium carbonyl cations but mixed dicarbonyl cations, i.e. $CrMo(CO)_n^+$ (where $n = 5$—7), as well. Inasmuch as each of the metal hexacarbonyls was shown to be pure by earlier mass spectral scans, these heterometal carbonyl species must be formed only within this instrument.

formation of the various $M_m(CO)_n^+$ ($m > 1$) listed in Table 1 also takes place as a result of ion–molecule reactions. Although exact pressure measurements are not possible with this system, we have been able to show that the relative intensities of the various $W_2(CO)_n^+$ are directly proportional to the square of the relative intensity of

TABLE 1

Abundance of positive ions in the mass spectra of the Group VIB metal hexacarbonyls

Chromium				(Ionizing voltage = 50 eV; pressure = 4×10^{-6} Torr)										
$n =$		12	11	10	9	8	7	6	5	4	3	2	1	0
$Cr_3(CO)_n^+$		0·08	0·02	0·01	0·01	0·03	0·04	0·01	—	—	—	—	—	—
$Cr_2(CO)_n^+$		—	0·01	0·03	0·04	0·07	1·97	3·37	1·87	2·22	1·07	0·80	—	—
$Cr(CO)_n^+$		—	—	—	—	—	—	55·5	4·71	5·69	8·09	100·0	63·5	77·1
$Cr(CO)_n^{2+}$		—	—	—	—	—	—	—	1·07	3·29	3·73	13·5	8·89	0·53

Additional monopositive ions: $Cr(CO)C$, 4·27; CrO, 3·91; CrC, 11·7.

Molybdenum				(Ionizing voltage = 50 eV; pressure = 5×10^{-6} Torr)										
$n =$		12	11	10	9	8	7	6	5	4	3	2	1	0
$Mo_2(CO)_n^+$ ..		—	0·02	0·04	0·10	0·14	1·25	0·70	0·87	0·19	0·14	—	—	—
$Mo_2(CO)_nC^+$ ..		—	—	—	—	—	—	—	0·04	0·11	0·09	—	—	—
$Mo(CO)_n^+$ ..		—	—	—	—	—	—	56·5	9·01	13·5	100·0	72·5	72·2	87·4
$Mo(CO)_nC^+$ ..		—	—	—	—	—	—	—	—	0·09	0·44	1·09	4·33	19·8
$Mo(CO)_n^{2+}$ ..		—	—	—	—	—	—	1·15	0·72	0·60	2·29	1·93	1·07	0·07

Additional ions: (+1) $Mo(CO)_2O$, 0·11; $Mo(CO)O$, 0·68; MoO, 4·72.

(+2) $Mo(CO)_2C$, 0·12; $Mo(CO)C$, 0·49; MoC, 0·05.

Tungsten					(Ionizing voltage = 40 eV; pressure = $1·5 \times 10^{-5}$ Torr)									
$n =$	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0
$W_4(CO)_n^+$	<0·10	<0·40	<0·50	<0·20	<0·10	—	—	—	—	—	—	—	—	—	—
$W_3(CO)_n^+$	<0·10	<0·20	<0·20	1·27	2·00	2·67	1·24	0·28	<0·10	—	—	—	—	—	—
$W_2(CO)_n^+$	—	—	—	0·32	0·36	3·15	12·4	22·5	10·8	11·7	9·48	1·77	0·50	—	—
$W_2(CO)_nC^+$	—	—	—	—	—	—	—	—	<0·30	1·01	2·12	1·86	0·90	—	—
$W(CO)_n^+$	—	—	—	—	—	—	—	—	67·5	8·09	43·4	100·0	52·9	61·6	44·5
$W(CO)_nC^+$	—	—	—	—	—	—	—	—	—	—	0·20	0·99	1·63	9·23	12·7
$W(CO)_n^{2+}$	—	—	—	—	—	—	—	—	0·77	0·67	0·95	1·82	1·46	0·37	—

Additional monopositive ions: $W_4(CO)_{12}C$, <0·10; $W_3(CO)_7C$, 0·39; $W_3(CO)_6C$, 0·26
$W(CO)_2O$, 0·18; $W(CO)O$, 0·40; WO, 4·02; WC_2, 0·92.

Concerning suggestion (iii), although we cannot prove that none of the polymetal carbonyl cations is formed by condensation of the molecules upon adiabatic expansion through the molecular leak, we have carried out an allied experiment which demonstrates that polymeric metal carbonyl ions can be formed directly in the ion source. In particular, the simultaneous introduction into the ion source of the relatively involatile $Me_3NW(CO)_5$, through the direct insertion probe, and $Cr(CO)_6$, from the gas inlet system, produced a number of ions, including $Me_3NWCr(CO)_n^+$ (where $n = 3$—6), which were not observed for either pure sample under identical source conditions. This is in effect a crude double beam experiment and the heterometal carbonyl cations could not have resulted from polymerization at the molecular leak of the gas inlet system. Further, $W_2(CO)_n^+$ (where $n = 4$—10) were also generated in this reaction, although the relative intensities were different than had been seen for $W(CO)_6$ inserted through the gas inlet system. Studies involving direct insertion of the parent hexacarbonyls were not feasible owing to their very high volatilities.

The formation of the $Me_3NWCr(CO)_n^+$ ions most likely occurs by way of ion–molecule reactions. We feel that the

$W(CO)_6^+$. A similar dependence was noted recently for the formation of $(C_5H_5)_2M_2(CO)_n^+$ (where M=V, Mn, or Co) from the corresponding parent $(C_5H_5)M(CO)_x$.[2]

TABLE 2

Metastable processes observed for $^{52}Cr(CO)_6$

			Calcd.	Exptl.
1.	$Cr(CO)_6^+ \rightarrow Cr(CO)_5^+ + CO$	..	167·5	167·6
2.	$\rightarrow Cr(CO)_4^+ + CO$	..	140·0	140·1
3.	$\rightarrow Cr(CO)_3^+ + CO$	..	112·7	112·8
4.	$\rightarrow Cr(CO)_2^+ + CO$	..	85·7	85·6
5.	$\rightarrow Cr(CO)^+ + CO$	..	59·2	59·2
6.	$\rightarrow Cr^+ + CO$	.. ..	33·7	33·7
7.	$Cr_2(CO)_7^+ \rightarrow Cr_2(CO)_6^+ + CO$	..	246·6	246·7
8.	$Cr_2(CO)_7^+ \rightarrow Cr(CO)_5^+ + Cr(CO)_2$	..	122·9	122·6
9.	$Cr_2(CO)_6^+ \rightarrow Cr^+ + Cr(CO)_6$	..	9·9	9·9
10.	$Cr_2(CO)_2^+ \rightarrow Cr^+ + Cr(CO)_2$	..	16·9	16·9

Metastable peaks were observed readily only for chromium hexacarbonyl and are listed in Table 2 together with the processes they indicate. The usual stepwise decomposition of the parent is seen readily.[7] For the polymetallic

chromium carbonyl cations, however, additional decomposition paths are available. Thus, in addition to a stepwise loss of CO groups, as indicated by process 7, decomposition by loss of a metal-containing fragment, as shown in reactions 8—10, is also possible.

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