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INTERPRETATION OF THE MASS SPECTRA OF SUBSTITUTED CHROMIUM AND TUNGSTEN CARBONYLS BY MEANS OF APPEARANCE POTENTIAL MEASUREMENTS

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Summary

The 50 eV mass spectra of $M(CO)_5PR_3$ complexes (M = Cr and W; R = OCH_3, OC_2H_5, n-C_4H_9, O-n-C_4H_9 and C_6H_5) have been determined. The chromium derivatives and the $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(C_6H_5)_3$ tungsten derivatives show ions predominantly formed by CO elimination. This behaviour is related to the higher activation energy for the rupture of P—R compared with that of M—CO bonds.

The spectra of the P(n-C_4H_9)$_3$ and P(O-n-C_4H_9)$_3$ tungsten derivatives, on the other hand, are dominated by ions obtained by partial fragmentation of the heteroligands. The heptacoordination capability of tungsten, the length of the R chain, and energetic factors are responsible for the appearance of these new fragmentation pathways.

Introduction

The 50 eV mass spectra of substituted transition metal carbonyl complexes are dominated by ions obtained via successive loss of carbon monoxide. Ions formed by partial fragmentation of the complexed heteroligands are less abundant, while loss of heteroligands is only seldom observed [1,2].

During an investigation of some $M(CO)_5L$ complexes [3] rather unusual fragmentation patterns were found when M = Mo or W and L = $P(C_2H_5)_3$, P(n-C_4H_9)$_3$ and P(O-n-C_4H_9)$_3$. In these, extensive fragmentation of the L ligand was the predominant feature of the spectra and the CO cascade loss was

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TABLE 1

RELATIVE INTENSITIES OF PEAKS IN THE HIGH MASS REGION OF THE MASS SPECTRA (50 eV) OF $M(CO)_5L$ COMPLEXES

	M^+	M^+-CO	M^+-R	M^+-2CO	M^+-R-CO	M^+-3CO	$M^+-HR-2CO$	M^+-4CO	$M^+-R-3CO$	M^+-5CO	$M^+-R-4CO$
$Cr(CO)_6$ [a]	42	6		5		6		51		100	
$Cr(CO)_5P(OCH_3)_3$	24	2	6	3	5	5	1	39	3	100	4
$Cr(CO)_5P(OC_2H_5)_3$	13	1	7	3	6	3	1	34	3	100	5
$Cr(CO)_5P(n\text{-}C_4H_9)_3$	5	⩽1	⩽1	⩽1	⩽1	2	⩽1	14		100	
$Cr(CO)_5P(O\text{-}n\text{-}C_4H_9)_3$	6		3 3 [b]		⩽1	⩽1		20		100	
$Cr(CO)_5P(C_6H_5)_3$	9	6		11		5		8		100	
$W(CO)_6$ [a]	64	10		40		100		46		45	
$W(CO)_5P(OCH_3)_3$	82	13	24	88	17	100	9	39	12	92	9
$W(CO)_5P(OC_2H_5)_3$	65	5	20	100	13	76	2	10	14	86	5
$W(CO)_5P(n\text{-}C_4H_9)_3$	37	18	100 [c]		94 [c] 35 [d]		35 [d]		70 [d]		
$W(CO)_5P(O\text{-}n\text{-}C_4H_9)_3$	52		15 14 [b] 100 [c] 20 [d] 16 [e]	19	26 [c] 43 [d]	11					
$W(CO)_5P(C_6H_5)_3$	34	42		9		100		3		97	

[a] From ref. 6. [b] R = m/e 42. [c] R = m/e 58. [d] R = m/e 60. [e] R = m/e 73.

TABLE 2

AE'S (eV) FOR THE FORMATION OF THE MORE SIGNIFICANT IONS FROM $M(CO)_5L$ COMPLEXES

M	L	IP [a]	M^+ − Co	M^+ − 2CO	M^+ − 3CO	M^+ − 4CO	M^+ − 5CO	M^+ −R	M^+ − (R+CO)
Cr	CO [b]	8.18	1.0	1.8	2.4	3.4	5.1		
	$P(OCH_3)_3$	7.80	0.45	0.87	1.6	2.3	3.7	3.0 [c]	4.12 [c]
	$P(OC_2H_5)_3$	7.62	0.7	1.2	1.6	2.4	4.2	3.5 [d]	
	$P(n\text{-}C_4H_9)_3$	7.35	0.9	1.2	1.5	2.3	3.7		
	$P(C_6H_5)_3$	7.36	1.1	1.7	1.9	2.3	3.5		
W	CO [b]	8.45	1.5	3.3	5.1	7.6	10.0		
	$P(OCH_3)_3$	7.96	1.0	1.8	3.1	4.3	5.1	3.2 [c]	5.0 [c]
	$P(OC_2H_5)_3$	7.80	1.6	2.7	3.5		4.4	3.7 [d]	4.7 [d]
	$P(n\text{-}C_4H_9)_3$	7.63	1.8					3.1 [e]	4.2 [e]
	$P(C_6H_5)_3$	7.5	1.0	1.6	2.0				

[a] From ref. 10. [b] From ref. 6. [c] R = OCH_3. [d] R = OC_2H_5. [e] R = m/e 58.

of low intensity or absent. The corresponding chromium complexes showed normal cracking patterns.

The recent use [4] of energetic data in the elucidation of mass spectral features, prompted us to measure the appearance potentials (AP) of the more significant ions formed from some $M(CO)_5PR_3$ complexes (M = Cr and W). The study was non confined to the carbonyls whose fragmentation is unusual, some "well behaved" complexes also being examined. The comparison of Cr with W complexes should provide the key for the interpretation of the striking differences in the cracking patterns of the two series.

Results and discussion

Table 1 lists the relative intensities of the ions $M(CO)_nPR_m$ ($n = 0 - 5$, $m = 2, 3$) present in the 50 eV mass spectra of the $M(CO)_5PR_3$ complexes (M = Cr or W; R = OCH_3, OC_2H_5, n-C_4H_9, O-n-C_4H_9 and C_6H_5), together with the relevant data for the unsubstituted complexes*.

The mass spectra of the chromium complexes resemble that of $Cr(CO)_6$, showing chiefly ions obtained by successive loss of neutral CO groups from the molecular ion. The total relative intensity of the ions formed by elimination of an R· radical from the phosphinic ligand ranges from 0 to 11% in the mass spectral region investigated. Similar behaviour is shown by the tungsten complexes when PR_3 is $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(C_6H_5)_3$. In these cases also, the $[W(CO)_nPR_2]^+$ ions represent a few percent (0 - 15%) of the total ion current. Striking differences are found when PR_3 = P(n-C_4H_9)$_3$ and P(O-n-C_4H_9)$_3$. The relevant features of these spectra are: (i) the expected CO cascade loss up to $[WPR_3]^+$ ion is incomplete, and generally of low intensity; (ii) ions obtained by partial fragmentation of the heteroligand account for about 80% of the total ion current; these ions arise by detachment of neutral fragments (F) from the ligand of *m/e* 42,58 and 60, followed by losses of *m/e* 28**. The values of the masses of the neutral fragments suggest that stable molecules are always formed in this kind of fragmentation, which is not observed in the free ligands [5].

Table 2 shows the values of activation energy, AE (the differences between the appearance and ionization potentials), which represent ionic bond energies. The AE values for the formation of $[Cr(CO)_nPR_3]^+$ ions ($n = 1 - 4$) range from 0.5 to 2.4 eV, while those for the formation of the $[M - (R + n\ CO)]^+$ ions range from 3.0 to 4.4 eV. This shows that the fragmentation of the heteroligands competes with processes which require much lower AE's; it thus contributes no more than 10% to the total ion current***.

From Table 2 it is also evident that in both series of complexes the AE's for the loss of the first CO group increase with the donor ability of PR_3. This is due to the increasing charge density on the central metal, which enhances the π-bonding contribution in the M—CO bonds. Moreover, as previously found for

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* At lower *m/e* values the assignment of the spectra becomes uncertain moreover the presence of thermal decomposition products can not be excluded.

In some cases very intense metastable ions for the processes $[M]^+ \rightarrow [M{-}F]^+$ have been observed.

*** Note that all the ions observed in the chromium derivatives are formed by simple bond cleavages.

the unsubstituted carbonyls [6], the ionic M—CO bond energy increases markedly from Cr to W for corresponding ions. As a consequence of these effects, the AE's for the loss of CO groups increase so much that new ligand fragmentations can occur when the tungsten derivatives contain the more basic ligands. These novel fragmentations so drastically reduce the probability of CO cleavage that complete CO cascade loss is not observed. This does not fully account, however, for the different behaviour of $P(n\text{-}C_4H_9)_3$ and $P(O\text{-}n\text{-}C_4H_9)_3$ derivatives on going from chromium to tungsten, nor for the "normal" behaviour of the other phosphinic ligands complexed to tungsten. It is thus apparent that the above trends of the AE's, which mainly depend on the M—CO bond strength, are not sufficient to rationalize the mass spectra, and that other factors which lower the AE's of the anomalous fragmentations must operate. We think that the presence of a long chain R sustituent on the phosphorus atom and the ability of the central metal to form heptacoordinate species are important factors in this regard. In fact the most important new fragmentation path is the elimination of neutral fragment of *m/e* 58, corresponding to C_4H_{10} (see footnote ** on page 211); it is formed by P—R (or PO—R) bond cleavage plus abstraction of H from another R. The resultant unpaired electron in the R chain can interact with that on the central metal atom to form a new bond [2]. The formation of the resultant ring is favoured if R is a long chain and if the central metal is capable of heptacoordination. It is relevant to note that heptacoordinate intermediates have been invoked to explain the occurrence of second-order kinetics for hexacoordinated tungsten carbonyls in a solution reaction in which the corresponding chromium complexes react exclusively by a first-order path [8].

Last we comment briefly on the fragmentation reactions of the free and complexed ligands. AE's for the lower energy processes observed in the free ligands are shown in Table 3. The P—R cleavage reaction is the only process in common with the complexed ligands. This fragmentation requires AE's higher by about 1 eV in the complexes; this could be interpreted by considering that in the molecular ion of the complex the positive charge is located mainly on the central metal atom. This effect strengthens P—R bonds with respect to the free ligand molecular ion, where the positive charge is nearer to the bond which is cleaved. The other fragmentations observed in the free ligands involve hydrogen rearrangements on the phosphorus atom; such processes are prevented in the complexes because the phosphorus lone pair is used in the bond with the

TABLE 3

AE'S (eV) FOR THE FORMATION OF THE MORE SIGNIFICANT IONS FROM THE FREE LIGANDS

Ion	Ligand				
	$P(O\text{-}n\text{-}C_4H_9)_3$	$P(OC_2H_5)_3$	$P(OCH_3)_3$	$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)_3$
$[HPR_2OH]^+$	0.5	1.4			
$[HPR(OH)_2]^+$	1.2	2.5			
$[PR_2]^+$	2.8	2.7	2.2		~7.0
$[M - CH_3]^+$			1.5		
$[HPOCH_3]$			0.6		
$[(C_4H_9)_2P(C_2H_4)]^+$				2.0	
$[HP(C_4H_9)_2]^+$				0.4	
$[HP(C_4H_9)(C_2H_5)]^+$				1.7	

central metal. The very high AE for the detachment of a C_6H_5 group from the $P(C_6H_5)_3$ is responsible for the absence of ligand fragmentation in the $M(CO)_5P(C_6H_5)_3$ complexes despite the highly basic character of this ligand.

Experimental

The measurements were performed with an Atlas CH4 mass spectrometer. Appearance potentials were evaluated by Warren's method [9], the reproducibility being within ± 0.2 eV. Samples were introduced via the direct insertion probe. Molecular ionization potentials, previously measured [10], and the IP for Xe were used to calibrate the electron energy scale. The samples were prepared according to procedures described in the literature.

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