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THE MASS SPECTRA OF SOME METAL CARBONYL COMPLEXES OF TRIS(DIMETHYLAMINO)PHOSPHINE

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SUMMARY

Mass spectral data for several metal carbonyl complexes of tris(dimethylamino)phosphine have been obtained. These data include fragmentation patterns of the molecules (studied as a function of pressure, temperature and ionizing energy), and ionization and appearance potential measurements. From the latter information the average bond dissociation energies of the metal–carbonyl bond in these complexes were estimated. The results are compared to the semi-quantitative data for these phosphines reported by King. Studies of the fragmentation patterns as a function of energy (clastograms) indicate that several of the fragmentation reactions involve the production of more than one neutral fragment.

INTRODUCTION

King[1] has recently published a paper reporting the fragmentation patterns of some metal carbonyl complexes of tris(dimethylamino)phosphine. In this report, he also presents a ratio method for estimating, semi-quantitatively, the metal–carbonyl bond strength. Since this method has general utility and is easily employed in many mass spectral studies, it was of interest to carry out a detailed mass spectral study on these compounds and determine the bond energy values from appearance potential data, and compare these values to the ones estimated by King[1].

In our study, the fragmentation patterns were studied as a function of energy. These clastograms are useful in elucidating ion source processes and verifying the processes proposed by King from metastable transitions. As a degree of caution, the fragmentation patterns were checked for temperature and pressure dependence. The temperature check assures that the compounds are not being thermally decomposed in the ion source, while pressure dependence studies provide information on possible ion-molecule or charge-exchange reactions.

EXPERIMENTAL

All experiments reported here were conducted on a modified Bendix T-O-F Model 12-107 mass spectrometer which has been described previously[2]. The samples

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were introduced directly into the ion source with an NRL-designed direct insertion probe with low temperature capabilities similar to the probe described by Haddon *et al.*[3]. This probe was employed to check for thermal decomposition of the metal carbonyl complexes of tris(dimethylamino)phosphine by observing the fragmentation patterns over a temperature range of −60° to 250°. While the volatility of these compounds was not sufficient for spectra observation over this entire temperature range, once the temperature of the probe was high enough for spectra to be obtained, no substantial changes in the fragmentation patterns were observed throughout the remainder of this temperature range. Therefore, it is concluded that the molecules did not undergo thermal decomposition.

Ion currents from these metal carbonyls were determined as a function of the pressure read on a discharge gauge installed on the ion source housing. A plot of this data showed all the ion currents varied linearly with the ion source pressure throughout the pressure range employed. Thus, we conclude that no ion-molecule or charge-exchange reactions are taking place.

The Bendix mass spectrometer was employed in these studies primarily because of its open ion source, cool temperature (approximately 30°) and the rapidity with which the appearance potential data can be obtained. The advantages and disadvantages of this technique have been thoroughly discussed both by ourselves[4] and by others[5]. Warren's[6] method of extrapolated differences was employed to evaluate the appearance potential data. To estimate the accuracy of the appearance potential data, the following procedures were employed: two rare gases were introduced with each sample; first, the ionization potential of one rare gas and the appearance potential of an ion from the metal carbonyl complex were measured simultaneously, then the ionization efficiency curves of the second rare gas and the same ion were measured together, and finally, the ionization potentials of the two rare gases were measured simultaneously. Using this technique, the absolute accuracy was estimated to be ±0.5V; this rather large uncertainty is probably due to the complexity of the ion source reactions involved. However, the reproducibility of the measurements was better than ±0.05 (standard deviation of the mean of 10 measurements).

RESULTS AND DISCUSSION

Fragmentation pattern

Since King[1] has reported the fragmentation of these complexes in detail, their patterns will not be given in this report. Instead, the spectra of only two complexes are given in Tables 1 and 2 and are compared with the data reported by King[1]. The spectra have been normalized to the same *m/e* value used by King[1] to facilitate comparison. These data clearly point out the degree to which spectra can be reproduced from drastically different instruments using ion sources and direct insertion probes operating at different temperatures. Similar agreement with King's data was obtained for all of the complexes studied. Actually, the spectra reported here agree slightly better with King's values when the temperatures of the probe and ion source used in this study are increased. However, we prefer the cooler temperatures for the energetic measurements, which is the primary reason this study was conducted. The cooler ion source may be the reason that the higher *m/e* values reported here are more intense compared to the values reported by King[1].

TABLE 1

FRAGMENTATION PATTERN OF $[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3$[a]

Ion	*Rel. intensity (this work)*	*Rel. intensity (ref. 1)*
$[(CH_3)_2N]_3PFe(CO)_3P[N(CH_3)_2]_3^+$	169	90
$[(CH_3)_2N]_3PFe(CO)_2P[N(CH_3)_2]_2^+$	7	3.8
$[(CH_3)_2N]_2PFe(CO)_3P[N(CH_3)_2]_3^+$	22	13
$[(CH_3)_2N]_3PFe(CO)P[N(CH_3)_2]_3^+$	129	130
$[(CH_3)_2N]_2PFe(CO)_2P[N(CH_3)_2]_3^+$	—	0.6
$[(CH_3)_2N]_3PFeP[N(CH_3)_2]_3^+$	321	290
$[(CH_3)_2N]_2PFeCOP[N(CH_3)_2]_3^+$	7	5.1
$[(CH_3)_2N]_3PFePH[N(CH_3)_2]_2^+$	47	51
$[(CH_3)_2N]_2PFe(CO)PH[N(CH_3)_2]_2^+$	—	2.6
$[(CH_3)_2N]_2PHFePH[N(CH_3)_2]_2^+$	12	13
$[(CH_3)_2N]_2PFePH[N(CH_3)_2]_2^+$	17	9.0
$[(CH_3)_2N]_2PFeP[N(CH_3)_2]_2^+$	5	5.1
$[(CH_3)_2N]_4PFe^+$	76	60
$(CH_3)_2NPHFePH[N(CH_3)_2]_2^+$	12	9.0
$(CH_3)_2NPHFeP[N(CH_3)_2]_2^+$	14	6.4
$[(CH_3)_2N]_3PFeCO^+$	24	6.4
$[(CH_3)_2N]PFe^+$	100	100
$[(CH_3)_2N]_2PHFe^+$	90	51
$[(CH_3)_2N]_3P$	26	57
$(CH_3)_2NFeCH_2NCH_3^+$	49	33
$(CH_3NCH_2)_2Fe^+$	40	56
$[(CH_3)N]_2P^+$	520	400
$(CH_3)_2NFe^+$	44	33.4
$(CH_3)_2NPH^+$	374	260
CH_3NP^+	33	44

[a] Based on the ^{56}Fe isotope.

Ionization potentials, appearance potentials, and bond energy values

The ionization potentials and appearance potentials of the complexes studied are delineated in Table 3. Previous results for a variety of carbonyl compounds[7,8,9,10] have shown that the average ionic bond energy obtained from appearance potential data is equal to the average neutral bond energies within ±0.3 eV. Assuming this postulate holds for the compounds reported here, the bond energies for the metal carbonyl complexes of tris(dimethylamino)phosphine may be estimated using the technique described by Junk *et al.*[7].

The bond energies calculated by this method for the cleavage of the first metal–carbonyl bond are cited in Table 4 together with King's[1] ratio of the [Parent−44]/[Parent−28]+[P−44] ion currents. King used these ratios to estimate, semi-quantitatively, the relative metal–carbonyl bond strengths. Higher values of the ratio [P−44]/[P−44]+[P−28] imply a greater metal–carbon bond strength in a series of carbonyl compounds. As can be seen from the data presented in Table 4, King's hypothesis holds for the comparison of the metal–carbonyl bond energies of the Cr, Mo, and W compounds (all Group VIA metals) and for comparison of the same energy in the two iron complexes. However, the rule fails when metal–carbonyl bond energies of the iron compounds are compared to the same values for the complexes of the

TABLE 2

FRAGMENTATION PATTERN OF $[(CH_3)_2N]_3PMO(CO)_5$[a]

Ion	*Rel. intensity (this work)*	*Rel. intensity (ref. 1)*
$[(CH_3)_2N]PMo(CO)_5^+$	32	11
$[(CH_3)_2N]_3PMo(CO)_4^+$	16	28
$[(CH_3)_2N]_2PMo(CO)_5^+$	5	1.9
$[(CH_3)_2N]PMo(CO)_3^+$	5	11
$[(CH_3)_2N]_2PMo(CO)_4^+$	5	5
$[(CH_3)_2N]_3PMo(CO)_2^+$	9	8.1
$[(CH_3)_2N]_2PMo(CO)_3^+$	4	5
$[(CH_3)_2N]_3PMoCO^+$	3	1.9
$[(CH_3)_2N]_2PMo(CO)_2^+$	7	10
$[(CH_3)_2N]_3PMo^+$	100	100
$[(CH_3)_2N]_2PMo(CO)^+$	6	3.7
$[(CH_3)_2N]_2PHMo^+$	7	< 3
$(CH_3)_2NP(CH_2NCH_2)Mo^+$	48	42
$PCH_2NCH_2Mo^+$	10	16
$(CH_3)_2NMoCH_2NCH_3^+$	—	~7
$(CH_3NCH_2)_2Mo^+$	12	~7
$CH_3NCH_2MoCH_2NCH_2^+$	—	~3
$(CH_3)_2NMo^+$	—	~5
$CH_3NCH_2Mo^+$	7	4
Mo^+	5	< 2
$[(CH_3)_2N]_3PO_2^+$	—	13
$[(CH_3)_2N]_3P^+$	20	44
$[(CH_3)_2N]_2P^+$	198	290
$[(CH_3)_2N]_3P^{2+}$	—	4.4
$(CH_3)_2NPH^+$	200	240
CH_3NP^+	26	51

[a] Based on the ^{98}Mo isotope.

Group VIA metals. Thus, from this limited data it appears that King's ratio method may be usable for estimating the relative M–CO bond energy for complexes with the same main group metals; however, it does not seem to be valid for a comparison between similar compounds when the metal atoms of the complexes are not in the same group.

King's study[1] presented evidence based on observed metastable transitions for the simultaneous loss of two carbonyl groups from $\{[(CH_3)_2N]P\}_2Fe(CO)_3^+$. This was an unusual elimination reaction for metal carbonyls and it was of interest to see if such an elimination could be corroborated by an independent method. The use of the clastogram method, developed by Kiser[11], appeared to be a suitable check. This method, based on the quasi-equilibrium theory of mass spectra, delineates which ions are fragmenting and forming other ions. Plots of the fractional abundances of the various ions of the molecule against the electron energy (clastograms) indicate that not only does $\{[(CH_3)_2N]_3P\}_2Fe(CO)_3^+$ lose two carbonyl groups[1], but the ion, $\{[(CH_3)_2N]_3P\}_2Fe(CO)_2^+$ also loses two carbonyl groups in a single step. Similar processes were also observed for the decomposition of the ion, $[(CH_3)_2N]_3PFe(CO)_4^+$, which were not observed by King[1], namely:

$$[(CH_3)_2N]_3PFe(CO)_4^+ \rightarrow [(CH_3)_2N]_3PFe(CO)_2^+ + 2CO$$

$$[(CH_3)_2N]_3PFe(CO)_3^+ \rightarrow [(CH_3)_2N]_3PFe(CO)^+ + 2CO$$

$$[(CH_3)_2N]_3PFe(CO)_2^+ \rightarrow [(CH_3)_2N]_3PFe^+ + 2CO$$

None of the Group VIA compounds exhibit this trend; this again emphasizes the

TABLE 3

ENERGETIC DATA FOR THE METAL CARBONYL COMPLEXES OF TRIS(DIMETHYLAMINO)-PHOSPHINE (TDP) (IN eV)

Ion	*M*			
	Cr	*Mo*	*W*	*Fe*
Di-substituted phosphine complexes				
$(TDP)_2M(CO)_4^+$	6.5	6.8	5.5	—
$(TDP)_2M(CO)_3^+$	9.5	11.1	10.3	7.7
$(TDP)_2M(CO)_2^+$	—	11.2	12.2	9.7
$(TDP)_2M(CO)^+$	—	14.0	—	10.2
$(TDP)_2M^+$	—	14.8	10.7	11.7
$TDP\,M^+$	11.0	16.1	—	—
TDP^+	—	10.1	—	—
M^+	22.2	15.3	—	—
Mono-substituted phosphine complexes				
$(TDP)M(CO)_5^+$	6.6	5.7	—	—
$(TDP)M(CO)_4^+$	7.6	7.8	—	9.0
$(TDP)M(CO)_3^+$	8.6	9.6	—	9.4
$(TDP)M(CO)_2^+$	—	9.9	—	9.8
$(TDP)M(CO)^+$	9.8	12.1	—	10.2
$(TDP)M^+$	12.5	10.3	—	10.2
M^+	22.3	18.4	—	17.0

TABLE 4

BOND ENERGIES OF METAL CARBONYL COMPLEXES OF TRIS (DIMETHYLAMINO)-PHOSPHINE

Compound	*Bond energy (eV) of the first M–CO bond*	[*P*-44]/[*P*-44]+[*P*-28][a]
$[(CH_3)_2N]_3PCr(CO)_5$	1.0	(0.06)
$\{[(CH_3)_2N]_3P\}_2Cr(CO)_4$	3.0	(0.16)
$[(CH_3)_2N]_3PMo(CO)_5$	2.1	(0.09)
$\{[(CH_3)_2N]_3P\}_2Mo(CO)_4$	4.3	(0.22)
$\{[(CH_3)_2N]_3P\}_2W(CO)_4$	4.8	(0.9)
$[(CH_3)_2N]_3PFe(CO)_4$	0.4	(0.13)
$\{[(CH_3)_2N]_3P\}_2Fe(CO)_3$	2.00	(0.77)

[a] Values of the ratio of the ion intensities [P−44]/[P−44]+[P−28] for the phosphine complexes study taken from ref. 1. This suggests the smaller the ratio, the weaker the M–CO bond energy where [P−44] and [P−28] correspond to the intensities of ions 44 and 28 mass units less than the molecular weight ions, respectively.

difference between the iron and Group VIA complexes noted earlier in the bond energy correlations. We also attempted to verify King's observation of the loss of PH_3 from the iron compounds using our neutral fragment mass spectrometer[12]. Unfortunately, the sensitivity of this instrument was not sufficient to detect PH_3, and hence, it was not possible for us to confirm this interesting fragmentation.

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