The Influence of Source Temperature on the Mass Spectra of Metal Chelate Compounds

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THE application of mass spectrometry to metal chelate compounds is becoming increasingly important,[1] particularly as a method for determining molecular weights. These relatively involatile compounds are studied with mass spectrometers fitted with direct insertion probes, and usually spectra have been recorded at one insertion temperature only. We now report examples where significantly different spectra are obtained for the same compound at different insertion temperatures.

TABLE

[Relative abundances (%) based on metal containing fragments only]

	TiF_4,oxH		$TiF_2(\pi-C_5H_5)$ ox_2		$TiCl(\pi-C_5H_5)$ ox_2		$TiCl_2(\pi-C_5H_5)$ ox_2	
Fragment	180°	240°	190°	240°	180°[a]	260°[b]	190°	250°
Ti ox_3^+	—	—	—	15	—	10	25	70
TiX_2 ox_2^+	—	100	30	100	—	—	40	15
TiX ox_2^+	—	15	5	60	100	100	100	100
Ti ox_2^+	—	7	15	15	30	50	25	40
TiX_3 ox^+	100	30	—	—	—	—	—	—
TiX_2 ox^+	35	95	100	55	5	15	95	30
TiX ox^+	<5	5	5	5	10	20	40	35
TiO ox^+	<5	<5	<5	<5	10	15	40	30
Ti ox^+	<5	<5	<5	<5	5	5	25	10
Ti ox_2^{2+}	—	—	4	1	10	40	—	5
TiX_3^+	75	<5	—	—	—	—	—	—
TiX_2^+	20	<5	—	—	—	—	—	—
TiX^+	10	<5	5	<5	—	5	—	—

[a] Also a fragment corresponding to $(\pi-C_5H_5)$Ti ox_2^+ (25%).

[b] Also fragments corresponding to $(\pi-C_5H_5)$Ti ox_2^+ (30%), $(\pi-C_5H_5)$TiX ox^+ (5%), and $(\pi-C_5H_5)TiX^+$ (5%).

The mass spectra of over seventy compounds of the type $MY_{4-n}ke_n$ and MY_4,mkeH, where M = Ti, Ge, or Sn, keH = quinolin-8-ol (oxH), salicylaldehyde, or acetylacetone; Y = alkyl, alkoxy, aryloxy, cyclopentadienyl, or halogen; and $n = 1$—4, and $m = 1$ or 2, have been recorded. Some typical results are given in the Table.

The thermal decomposition of TiF_4,oxH is not unexpected. At a source temperature of 180° the fragment peak with highest *m/e* is TiF_3 ox^+ corresponding to loss of hydrogen fluoride; whilst at 240° the fragmentation pattern is consistent with thermal decomposition similar to that of $TiCl_4$, oxH.[2] The unexpected peak at *m/e* 478 due to the ion Ti ox_3^+ found in the spectra of TiF_2 ox_2 $(\pi-C_5H_5)$TiCl ox_2, and $TiCl_2$ ox_2 at higher insertion, temperatures was identified by precise mass measurements. Peaks due to the ions Ti ke_3^+ were also found in the spectra of all the other TiY_2 ke_2 compounds. It is unlikely that Ti ke_3^+ arises from impurities; and in the spectrum of $TiCl_2$ ox_2, at least, Ti ox_3^+ cannot arise by polymer fragmentation because the *X*-ray structure of $TiCl_2$ ox_2 indicates a monomer.[3]

The ion Ti ox_3^+ is probably formed by thermal decomposition during evaporation into the ion source. There are other examples[4] in which the peak with highest *m/e* has a molecular weight higher than that of the molecular ion of the parent chelate compound. We therefore recommend that when mass spectra of metal chelates are obtained with a direct insertion probe, studies should be made over a range of source temperatures, and that the results, if used for molecular-weight determinations, should be interpreted with caution.

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[1] G. M. Bancroft, C. Reichert, and J. B. Westmore, *Inorg. Chem.*, 1968, **7**, 870; E. P. Dudek and M. Barber, *ibid.*, M. J. Lacey, C. G. MacDonald, and J. S. Shannon, *Org. Mass Spectrometry*, 1968, **1**, 115; J. D. MacDonald and J. L. Margrove, *J. Less Common Metals*, 1968, **14**, 236; J. S. Shannon and J. M. Swan, *Chem. Comm.*, 1965, 33.

[2] M. J. Frazer and Z. Goffer, *J. Chem. Soc.*, 1966, 544.

[3] B. F. Studd and A. G. Swallow, *J. Chem. Soc.* (*A*), 1968, 1961.

[4] E. P. Dudek, E. Chaffee, and G. Dudek, *Inorg. Chem.*, 1968, **7**, 1257; J. R. Majer, M. J. A. Reade, and W. I. Stephen, *Talanta*, 1968, **15**, 373.