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MASS SPECTROMETRY OF π -COMPLEXES OF TRANSITION METALS

XVII *. ION—MOLECULE REACTION PRODUCTS IN MASS SPECTRA OF MIXTURES OF π -CYCLOPENTADIENYL- AND π -ARENEMETAL CARBONYLS WITH AROMATIC AND HETEROCYCLIC COMPOUNDS

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Summary

Ion—molecule reactions occur in the ionization chamber of a mass spectrometer during the combined vaporization of arenechromium tricarbonyls ($\text{ArCr}(\text{CO})_3$, $\text{Ar} = \text{C}_6\text{H}_6$, $\text{C}_6\text{H}_5\text{Cl}$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $\text{C}_4\text{H}_4\text{S}$, $\text{C}_4\text{H}_4\text{Se}$) and cyclopentadienylmetal carbonyls ($\text{C}_5\text{H}_4\text{RM}(\text{CO})_n$, M and $\text{R} = \text{Mn}, \text{H}; \text{Mn}, \text{Cl}; \text{Mn}, \text{Br}; \text{Mn}, \text{COCH}_3; \text{Re}, \text{H}; \text{V}, \text{H}$) with various aromatic and heterocyclic compounds (L). In all cases secondary ions of sandwich type $[\text{ArCrL}]^+$ or $[\text{C}_5\text{H}_4\text{RML}]^+$ containing a new metal—ligand bond are formed.

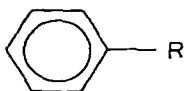
Transition metal π -complexes are characterized by the fact that ion—molecule reactions proceed even under ordinary conditions of mass spectral experiments at ionization chamber pressures of 10^{-4} – 10^{-5} Torr [2–11]. For example, the interaction of organometal ions formed by the fragmentation of π -complexes under electron impact with organic molecules having a centre suitable for complexing gives rise to fragments containing a new metal—ligand bond. These ion—molecule reactions were observed for cyclopentadienylmetal carbonyls [7,12,13], $\text{C}_5\text{H}_5\text{MC}_n\text{H}_n$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}; n = 6, 7$) [14], $\text{C}_5\text{H}_5\text{NiNO}$ [15], TiCl_4 [16] and ferrocene [1,17] and its derivatives [1].

This paper concerns ion—molecule reactions occurring in a mass spectrometer ionization chamber during the combined vaporization of arenechromium tricarbonyls (Ia–e) and cyclopentadienylmetal carbonyls (IIa–f) with various aromatic (IIIa–f) and heterocyclic compounds (IVa–c).

* For Part XVI, see ref. 1.

$\text{ArCr}(\text{CO})_3$ (Ar = C_6H_6 Ia; $\text{C}_6\text{H}_5\text{Cl}$, Ib; $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, Ic; $\text{C}_4\text{H}_4\text{S}$, Id; $\text{C}_4\text{H}_4\text{Se}$, Ie).

$\text{C}_5\text{H}_4\text{RM}(\text{CO})_n$, (M = Mn, R = H, Cl, Br, COCH_3 , $n = 3$, IIa–d; M = Re, R = H, $n = 3$, IIe; M = V, R = H, $n = 4$, IIf).

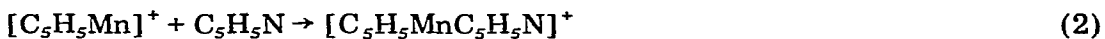
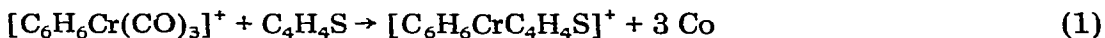


(R = H, IIIa; NH_2 , IIIb; Cl, IIIc; OH, IIId; CH_2Cl , IIIe; NO_2 , IIIf)

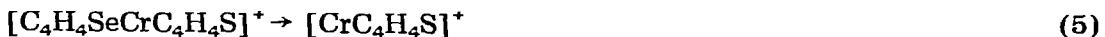
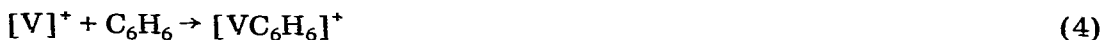


(X = CHN, IVa; S, IVb; NH, IVc)

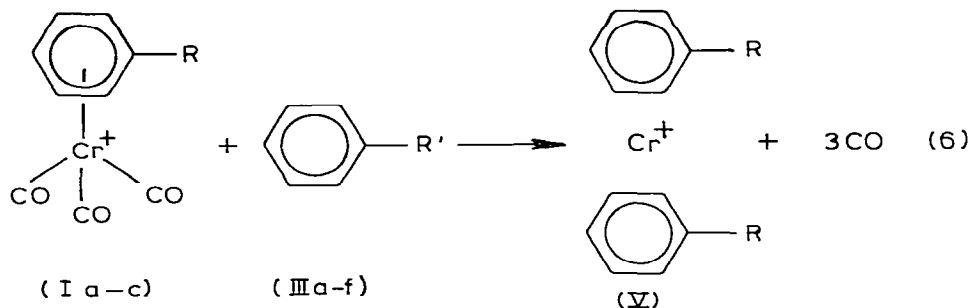
Secondary ions containing a new M–L bond (L = organic ligand) are present in the mass spectra of all the mixtures studied. The formation of these ions can be presented as a result of the substitution of three carbonyl groups in the molecular complex ion by an organic compound molecule [12] (reaction 1) or the addition of L to decarbonylated ions $[\text{ArCr}]^+$ and $[\text{C}_5\text{H}_4\text{RM}]^+$, formed on fragmentation of the starting complex under electron impact [14,17] (reaction 2).



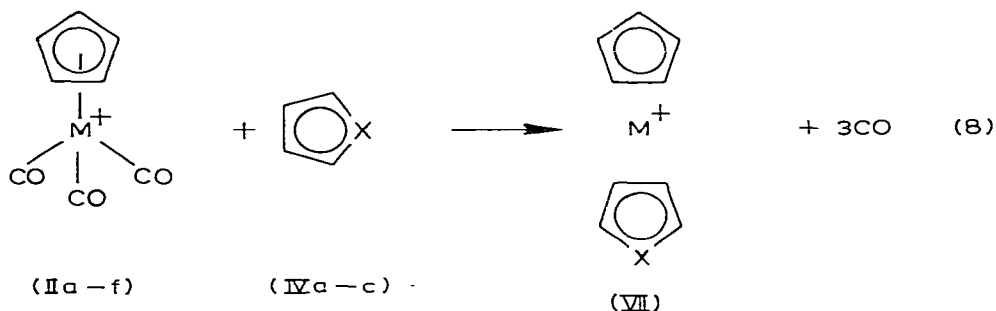
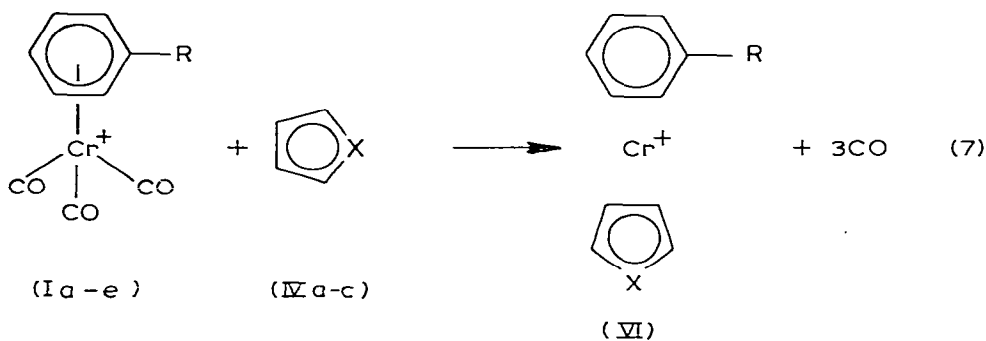
An analysis of the low-voltage mass spectra of a mixture of benzene with cyclopentadienylrhenium tricarbonyl indicated that the ion $[\text{C}_5\text{H}_5\text{ReC}_6\text{H}_6]^+$ was present in the spectrum even with ionizing voltages below the appearance energy for the ions $[\text{C}_5\text{H}_5\text{Re}]^+$. This is evidence for a dominant role of reaction 1 in the formation of $[\text{ArCrL}]^+$ and $[\text{C}_5\text{H}_4\text{RML}]^+$ ions. In the study of ion–molecule reactions taking place in mixtures of ferrocene with aromatic compounds it was established that the formation of $[\text{C}_5\text{H}_5\text{FeL}]^+$ follows exclusively via reaction 2 [17]. This may be due to the fact that to break the Cp–Fe bond in ferrocene (7.20 eV) a greater energy is required than to eliminate three carbonyl groups in the complexes under study (2.5–3.7 eV) [19,20]. Similarly, it was shown that the ions $[\text{LM}]^+$ can appear in a ligand interchange reaction with the ions $[\text{ArCr}]^+$ and $[\text{C}_5\text{H}_4\text{RM}]^+$ (reaction 3), as well as from a reaction involving the addition of an organic molecule to the metal ion (reaction 4). It may also be that some of the ions $[\text{LM}]^+$ are formed by dissociation of the ions $[\text{ArCrL}]^+$ and $[\text{C}_5\text{H}_4\text{RML}]^+$ according to reaction 5.



The secondary ions $[\text{ArCrL}]^+$ formed in the interaction of arenechromium tricarbonyls with aromatic compounds probably have the structure of bis-arene complexes V (reaction 6), since in this case it is difficult to suggest any other type of coordination.



In the ions $[\text{ArCrL}]^+$ and $[\text{C}_5\text{H}_4\text{RML}]^+$ coordination of the metal with the heterocyclic ligand may be both of the π -type with the formation of sandwich ions (type VI) and of the n-type at the expense of the unshared heterocycle electron pair [17]. One would then expect the appearance in the spectra of the ions $[\text{ArCrL}(\text{CO})_n]^+$ and $[\text{C}_5\text{H}_4\text{RML}(\text{CO})_n]^+$ ($n = 1, 2$). However, no such ions were observed in any spectrum of the mixtures I and II with heterocycles. From this, it may be assumed that the secondary ions containing the heterocyclic ligand L have the structure of a "doubledecker sandwich" (VI and VII, reactions 7 and 8).



Thus, gas phase ion—molecule reactions give rise to complexes with “unusual” ligands along with molecular ions of the known complexes, such as π -bisarene- and π -benzenecyclopentadienyl-metal derivatives. The most interesting ones of these are the molecular benzenechromonitrobenzene ion and the ions containing both the heterocyclic and the arene (cyclopentadienyl) ligands, or two heterocyclic ligands (for example, bistiophenochromium, selenophen-chromothiophen, pyridinechromothiophen). The presence of these ions in the mass spectra indicates the theoretical possibility of their existence as stable molecules (for example, bisbenzenechromium and cyclopentadienylbenzene-manganese) or, at least, as intermediate particles. It is possible, therefore, that these “unusual” complexes may be obtained under the usual conditions as neutral molecules or as ionic compounds. This assumption can be substantiated by a number of examples of synthesis of new types of complexes which were first observed as gas phase ion- or intra-molecular reaction products, such as the “triple-decker sandwich” $[(C_5H_5)_3Ni_2]^+$ [21], the salt $[C_5H_5Ni(diene)]^+X^-$ [22] and the salt π -pentamethylcyclopentadienyltin $[(CH_3)_5C_5Sn]^+X^-$ [23].

Experimental

The mass spectra were obtained on the AEI MS-30 mass spectrometer equipped with the DS-50 data acquisition system at ionizing voltages of 12, 20 and 70 V, ionization chamber temperature of 250°C and a pressure of 10^{-4} – 10^{-5} Torr. The complex and the organic compound were volatilized into an ionic source simultaneously with the use of a direct feed system and a heated glass system, respectively. The intensity of the secondary ions amounted to 0.1 to 8% of the intensity of the complex molecular ion. The intensity of the secondary ions is greatest at lowest ionizing voltages. The mass spectra of the mixtures Ia + IIIf, Ia + IVb and Ie + IVb were obtained on the MX-1310 mass spectrometer at ligand pressure of $\sim 8 \times 10^{-4}$ Torr.

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