

ION-MOLECULE REACTIONS OF CYCLOPENTADIENYL-TRICARBONYLMANGANESE DERIVATIVES WITH 18-CROWN-6 IN THE GAS PHASE

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(Received January 6th, 1984)

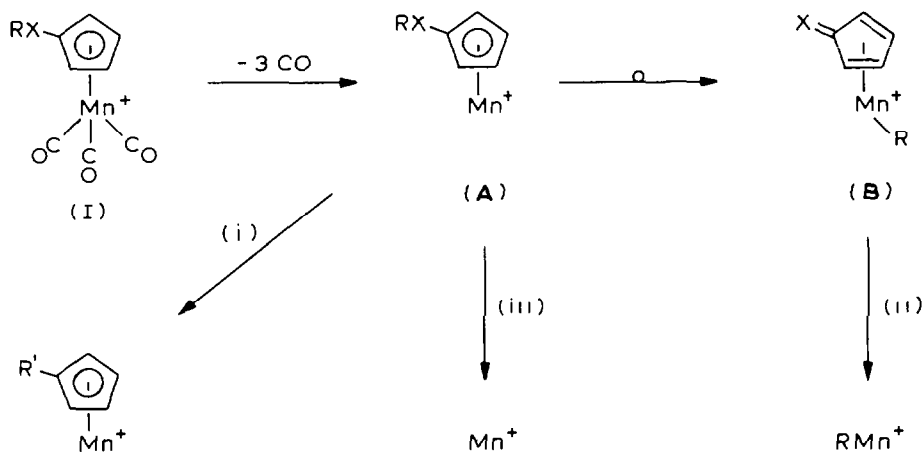
Summary

The ion-molecule reactions of 18-crown-6 (L) with ions produced from cymantrene and its derivatives under electron impact are studied. It is shown that $\text{RXC}_5\text{H}_4\text{MnL}^+$ ions (RX = the substituent in the cyclopentadienyl ring) can be produced by two reaction pathways: (i) by the addition of $\text{RXC}_5\text{H}_4\text{Mn}^+$ to crown ether; and (ii) by the exchange of carbonyl ligands in $\text{RXC}_5\text{H}_4\text{Mn}(\text{CO})_x^+$ ions ($x = 1-2$) for the macrocyclic molecule. The formation of RMnL^+ ions, where R = H, Me, Ph, OH, NMe_2 , proceeds via the substitution of $\text{C}_5\text{H}_4\text{X}$ in the isomerized form of the decarbonylated ions ($\text{RMn}^+\text{C}_5\text{H}_4\text{X}$) for L. The relative abundances of the $\text{RXC}_5\text{H}_4\text{MnL}^+$ and RMnL^+ ions provide information about the structure of the $\text{RXC}_5\text{H}_4\text{Mn}^+$ ions. The probability of synthesizing stable "sandwich" species of the $\text{C}_5\text{H}_5\text{Mn}(\text{crown})^+$ type in the condensed phase is predicted.

Macrocyclic polyethers (crown ethers) can form complexes with various metals both in condensed and gas phases [1–7]. The gas phase reactions of 18-crown-6 (L') and perhydrodibenzo-18-crown-6 (L'') with ions, formed from cymantrene (Ia) and its derivatives (Ib–Im) under electron impact, are discussed in the present work.

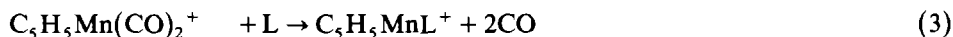
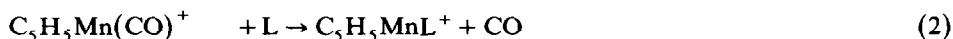
The mass spectra of cymantrene derivatives have been studied in refs. 8–10. The dissociation of molecular ions consists of the subsequent elimination of three carbonyl ligands with the formation of $\text{RXC}_5\text{H}_4\text{Mn}(\text{CO})_n^+$ type ions. Further decay of decarbonylated ions $\text{RXC}_5\text{H}_4\text{Mn}^+$ (A; Scheme 1) proceeds via three main routes: (i) elimination of neutral particles from the substituent with retention of the metal–cyclopentadienyl ring bond; (ii) migration of the substituent (or part of it) to manganese with the formation of ion B, which further decomposes into RMn^+ ions; and (iii) cleavage of the metal–ligand bond with the formation of Mn^+ ions.

Ions of the type $\text{RXC}_5\text{H}_4\text{MnL}^+$ (L = L' or L'') are present in the mass spectra obtained after simultaneous evaporation of the cymantrene derivatives Ia–Ih, Im or manganocene (II) and crown ethers in the ion source of the mass spectrometer



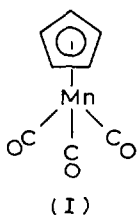
SCHEME 1

(Table 1). The molecular ions of cymantrene [11] and dicyclopentadienyl complexes [12–14] are not involved in the substitution reactions of the cyclopentadienyl ring or three carbonyl groups for a molecule of organic or organometallic compounds because of the coordination saturation of the central metal atom and the high stability of the $\text{C}_5\text{H}_5\text{-Mn}$ and $(\text{CO})_3\text{-Mn}$ bonds. Therefore in the case of manganocene, the formation of $\text{C}_5\text{H}_5\text{MnL}^+$ can proceed via addition of the macrocyclic molecule to the $\text{C}_5\text{H}_5\text{Mn}^+$ ion (reaction 1). Substitution of the carbonyl groups in the $\text{C}_5\text{H}_5\text{Mn}(\text{CO})^+$ ion (reaction 2) or of the two carbonyl ligands in the $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_2^+$ ion (reaction 3) can also be expected for cymantrene. In order to



evaluate the contribution of each of these processes to the formation of $\text{C}_5\text{H}_5\text{MnL}^+$ ions, we studied the ion-molecule reactions in a three-component mixture of manganocene, deuterocymantrene ($\text{C}_5\text{H}_{5-x}\text{D}_x\text{Mn}(\text{CO})_3$) and 18-crown-6. If

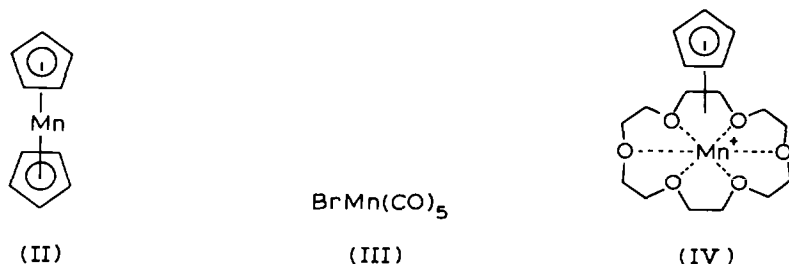
- (Ia, XR = H;
 Ib, XR = CN,
 Ic, XR = CHO;
 Id, XR = COCH₃,
 Ie, XR = COC₆H₅;
 If, XR = CH₂C₆H₅;
 Ig, XR = CH₂N(CH₃)₂,
 Ih, XR = CH(CH₃)NHCH₃,
 Ii, XR = CH₂OH;
 Ij, XR = CH(OH)CH₃,
 Ik, XR = CH(OH)C₆H₅;
 Il, XR = COOH;
 Im, XR = CH₂CH₂CH₂COOH)



$C_5H_5MnL^+$ ions are formed by reaction 1 only, in the mass spectrum of the mixture, the ion intensity ratio, $Z_2 = [C_5H_5MnL^+]/[C_5H_{5-x}D_xMnL^+]$, should be equal to that of $Z_1 = [C_5H_5Mn^+]/[C_5H_{5-x}D_xMn^+]$ *. However, Z_1 is approximately 1.3 times higher than Z_2 (Table 2). Besides, in the case of cymantrene, the value of $Z'_3 = [C_5H_5MnL^+]/[C_5H_5Mn^+] \cdot [L^+]$, characterizing the degree of $C_5H_5MnL^+$ ion formation, exceeds the analogous value for manganocene. The value of Z'_3 , increases as the energy of the ionizing electrons decreases, i.e. in parallel to the increase of $C_5H_5Mn(CO)_2^+$ and $C_5H_5MnCO^+$ ion concentrations respectively to $C_5H_5Mn^+$ ions (Table 2). These data show that $C_5H_5MnL^+$ ion formation proceeds both via addition (reaction 1) and via substitution of the carbonyl groups (reactions 2 and 3). The contribution of reaction 1 to the total concentration of $C_5H_5MnL^+$ ions is substantially greater than that of reactions 2 and 3.

In some cases, reaction 1 is the only one possible for $R'C_5H_4MnL^+$ ion formation. For example, $CH_3C_5H_4Mn(CO)_n^+$ ions with $n > 0$ are not observed in the mass spectrum of dimethylaminomethylcymantrene (Id) [8]. Nevertheless, $CH_3C_5H_4MnL^+$ ions give the most intense peak among the products of ion-molecule reactions (Table 1). Consequently, the appearance of such ions is conditioned by the interaction of $CH_3C_5H_4Mn^+$ ions present in the spectrum of this compound with the neutral crown ether molecule.

In contrast to the substituted cymantrenes Ib–Ih and Im, $RXC_5H_4MnL^+$ ions, containing a hydroxy group in the substituent, are not observed in the simultaneous evaporation of cymantrenylcarbinols Ii–Ik and crown ethers in the mass spectrometer. Such behavior of α -hydroxy derivatives is caused by the rapid isomerization of A ions (responsible for the formation of $RXC_5H_4MnL^+$ adducts) into the isomeric form, B (R = OH, see Scheme 1). The interaction of the latter with a macrocyclic



molecule proceeds via the substitution of the fulvene molecule and results in $HOMnL^+$ ion formation (reaction 4). Apparently, this is the only way to produce $HOMnL^+$ ions since these ions are present in the mass spectra obtained at low energies of ionizing electrons, i.e. under conditions excluding the formation of primary $HOMn^+$ ions. The formation of $C_6H_5MnL^+$ ions proceeds in the same way in the case of $C_6H_5XC_5H_4Mn(CO)_3$ (X = CO, CH₂), as well as for other ions of the $RMnL^+$ type (Table 1).



(Continued on p. 126)

* Cymantrene vapours with different concentrations of deuterium, introduced during the ion-molecule reaction, did not show an isotopic effect in $C_5H_5MnL^+$ ion formation.

TABLE 1

RELATIVE INTENSITIES OF THE ION-MOLECULE REACTION PRODUCTS OF CYMANTRENE DERIVATIVES (Ia–Im) AND MACROCYCLIC POLYETHERS (L' = 18-crown-6, L'' = perhydrodibenzo-18-crown-6)

Compound	Ion (<i>m/z</i> , relative intensities)		
	RXC ₅ H ₄ MnL ⁺	R'C ₅ H ₄ MnL ⁺	RMnL ⁺
Ia	C ₅ H ₅ MnL ⁺⁺ (384, 100) C ₅ H ₅ MnL ^{''+} (492, 100)		
Ib	NCC ₅ H ₄ MnL ⁺⁺ (409, 100)		
Ic	OHCC ₅ H ₄ MnL ⁺⁺ (412, 100)	–	HMnL ⁺⁺ (320, 10)
Id	AcC ₅ H ₄ MnL ⁺⁺ (426, 100) AcC ₅ H ₄ MnL ^{''+} (524, trace)	–	MeMnL ⁺⁺ (334, 80) MeMnL ^{''+} (334, trace)
Ie	BzC ₅ H ₄ MnL ⁺⁺ (488, 100) BzC ₅ H ₄ MnL ^{''+} (596, 100)	–	PhMnL ^{''+} (396, 20) PhMnL ⁺⁺ (504, 25)
If	PhCH ₂ C ₅ H ₄ MnL ⁺⁺ (474, 100)	–	PhMnL ⁺⁺ (396, 10)
Ig	Me ₂ NCH ₂ C ₅ H ₄ MnL ⁺⁺ (441, 30)	MeC ₅ H ₄ MnL ⁺⁺ (398, 100)	Me ₂ NMnL ⁺⁺ (353, 5) HMnL ⁺⁺ (320, 10)
Ih	MeNH(Me)C ₅ H ₄ MnL ⁺⁺ (455, 20)	EtC ₅ H ₄ MnL ⁺⁺ (412, 100) C ₂ H ₃ C ₅ H ₄ MnL ⁺⁺ (410, 20)	MeMnL ⁺⁺ (334, 5) HMnL ⁺⁺ (320, 5)
Ii	–	–	HOMnL ⁺⁺ (336, 100)
Ij	–	C ₂ H ₃ C ₅ H ₄ MnL ⁺⁺ (410, 50)	HOMnL ⁺⁺ (336, 100) HMnL ⁺⁺ (320, < 5)
Ik	–	–	HOMnL ⁺⁺ (336, 100)
Il	HOCC ₅ H ₄ MnL ⁺⁺ (428, 2)	C ₅ H ₅ MnL ⁺⁺ (384, 20)	HOMnL ⁺⁺ (336, 100)
Im	HOOC(CH ₂) ₃ C ₅ H ₄ MnL ⁺⁺ (470, 100)	(C ₄ H ₅ O)C ₅ H ₄ MnL ⁺⁺ (452, 10)	HOMnL ⁺⁺ (336, 15)
II	C ₅ H ₅ MnL ⁺⁺ (384, 100)		
III			BrMnL ⁺⁺ (398/400, 100) BrMnL ^{''+} (506/508, 100)

TABLE 2

ABUNDANCES OF SOME OF THE ION PEAKS IN THE MASS SPECTRA OF THE THREE-COMPONENT MIXTURE OF MANGANOCENE, DEUTEROCYMANTRENE^a AND 18-CROWN-6 AT 70 AND 12 V

Ion	Cp'Mn(CO) ₃ ⁺	Cp'Mn(CO) ₂ ⁺	Cp'MnCO ⁺	Cp'Mn ⁺	Cp ₂ Mn ⁺	CpMn ⁺	Cp'MnL ⁺	CpMnL ⁺	L ⁺ (<i>m/z</i> 133)
70 V	1580	280	1540	5850	4970	2300	16	5	90
12 V	^b	^b	1300	1300	^b	1100	27	11	45

	$Z_1 = \frac{\text{CpMn}^+}{\text{Cp}'\text{Mn}}$	$Z_2 = \frac{\text{CpMnL}^+}{\text{Cp}'\text{MnL}^+}$	$Z_3 = \frac{\text{CpMnL}^+}{\text{CpMn}^+ \cdot \text{L}^+}$	$Z'_3 = \frac{\text{Cp}'\text{MnL}^+}{\text{Cp}'\text{Mn}^+ \cdot \text{L}^+}$
70 V	0.4	0.3	2.4×10^{-5}	3.0×10^{-5}
12 V	1.0	0.4	2.2×10^{-4}	4.4×10^{-4}

^a Cp represents the unlabelled cyclopentadienyl ring (from manganocene); Cp', the deuterated cyclopentadienyl ligand (from deuterocymantrene). ^b Not measured.

RMnL^+ , $\text{RXC}_5\text{H}_4\text{MnL}^+$ ions and other products of ion-molecule reactions, formed in the simultaneous evaporation of crown ethers and cymantrene derivatives in the mass spectrometer, contain a manganese atom in the stable oxidative state +2. LMn^+ ions, where the metal atom could be in the unstable form +1, are not observed in spite of the high Mn^+ ion concentration. This fact is in agreement with data obtained earlier on the interaction of crown ethers with ions of thallium [4] and lanthanide complexes [5] in the gas phase.

Thus the results of the present work indicate rapid formation of complexes of type IV containing a Mn atom bound to a π -cyclopentadienyl ring and the crown ether molecule. Under the same conditions of the simultaneous evaporation of substituted cymantrenes or $\text{BrMn}(\text{CO})_5$, RMnL^+ ions (R = halogene or hydroxy group) analogous to the stable crown ether complexes with inorganic derivatives of transition metals [2,6] are observed. All these results shown that there is a principal possibility of type IV particles existing in the condensed phase.

Experimental

Mass spectra were recorded on an AEI MS-30 mass spectrometer at ionizing voltages of 8–70 V and ionization chamber temperatures of 200–250°C. For simultaneous evaporation of organometallic and organic compounds, the direct-inlet system was used at temperatures of 50–150°C depending on the volatility of the metallo complex. A vapour pressure of $\sim 10^{-4}$ Torr was used in the investigation of two- and three-component mixtures. In some cases, evaporation of the mixture was followed by “washing” of the ion source by vapours of the macrocyclic derivatives. Isotope ratios in the primary and cluster ions of type IV were calculated using the EC CM-3 computer system.

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