Journal of Organometallic Chemistry, 212 (1981) 369—372
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XXV *. DISSOCIATIVE ELECTRON CAPTURE BY MOLECULES OF π-ARENECHROMIUM TRICARBONYL COMPLEXES

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(Received December 2nd, 1980)

Summary

Mass spectra of the negative ions η^6-LCr(CO)$_3$, where L = benzene, thiophene, indene, fluorene or azofluorene, have been studied. The formation of the negative ions proceeds in three resonance regions with maxima at 0 to 0.8 eV, 1.8 to 4.7 eV and 6.0 to 8.4 eV. In the mass spectrum of thiophenechromium tricarbonyl, the $SCr(CO)_3]^-$ ion is present, which is formed through a π—σ isomerization stage. In the $[M - H]^-$ ion of indenechromium tricarbonyl a process of re-coordination of the chromium atom from the benzene to the cyclopentadienyl ring is observed.

In contrast to the mass spectrometry of positive ions, mass spectrometry of negative ions of the dissociative electron capture (DEC) of π-complexes of transition metals is little developed [1].DEC mass spectra of metallocenes Cp_2M (M = Fe, Co, Ni, Mg) [2] and of derivatives of cyclopentadienyltitanium halides [3,4] have been studied. Cyclopentadienylmetal carbonyl complexes, CpM-$(CO)_n$, of cobalt, manganese and vanadium, as well as of some of their derivatives, have been studied by the secondary electron capture method [5]. Mass spectra of negative ions of two arenechromium tricarbonyl complexes, $ROOCC_6H_4Cr(CO)_3$ (R = H, CH_3), obtained with an electron energy of about 70 eV, are given in ref. 6.

In the present work, electron capture by molecules of π-arenechromium tricarbonyl complexes I—V with the formation of negative ions has been studied.

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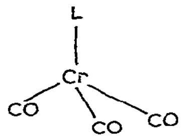
* For part XXIV, see ref. 9.



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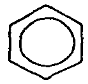

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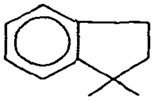

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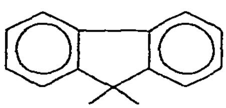

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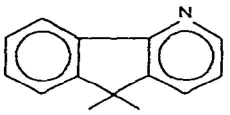


(V)

As can be seen from the Table 1, the formation of negative ions in three resonance regions with maxima at 0 to 0.8 eV, 1.8 to 4.7 eV and 6.0 to 8.4 eV, is characteristic for all the compounds studied.

Molecular negative ions are observed in compounds II—V (yield maxima being at 0 to 0.1 eV). Their average lifetimes with respect to the electron autoelimination in the ionic yield maxima are not long, amounting to ~30 μs for III and IV, ~56 μs for V and ~235 μs for II. The formation of molecular ions proceeds by way of vibration-excited Feschbach resonance. With an increase of the electron energy within the resonance peak the lifetime of the ions diminishes and a process of ion stabilization by the ejection of the CO group occurs (compounds I—III and V).

Ions $[ArCr(CO)_n]^-$ (n = 0—2) and $[Cr(CO)_n]^-$ (n = 0—3) are common in the DEC spectra of all the compounds, elimination of one or two carbonyl groups taking place in the first resonance region. Decarbonylation of $[ArCr(CO)_2]^-$ ions and elimination of the arene ligand with the formation of $[Cr(CO)_3]^-$ ions pro-

TABLE 1

MASS SPECTRA OF NEGATIVE IONS FROM DECOMPOSITION OF COMPOUNDS I—V [a]

Ions	I	II	III	IV	V
M^-		55.0(0.1)	2.7(0)	37.5(0)	30.0(0)
$[M—H]^-$			5.3(0.4) 2.7(3.0)		
$[M—CO]^-$	100(0.7) 100(1.8)	100(0.4)	71.0(0.8) 18.1(1.8)	100(3.0)	6.7(0.45) 3.7(2.3)
$[M—2CO]^-$	10.0(4.0)	10.0(2.2)	16.8(2.6)	2.25(3.8)	100(0.4) 1.2(2.7)
$[M—3CO]^-$	2.7(4.5)	3.0(3.1)	100(3.0) 19.4(4.6)	37.5(3.5)	4.2(2.9)
$[Cr(CO)_3]^-$	29.6(4.0)	3.0(3.1)	1.4(3.6)	0.7(4.0)	0.06(4.5)
$[Cr(CO)_2]^-$	2.7(4.7)				
	3.8(6.9) 3.9(7.7)	0.04(6.0)	0.8(7.1)	0.4(7.0)	
$[Cr(CO)]^-$	1.0(6.9) 1.0(7.7)		0.15(7.4)	0.1(7.0)	
Cr^-	3.8(7.0) 3.8(7.8)		0.32(7.6)	0.16(7.0)	0.06(6.4)
$[M—Cr(CO)_3—H]^-$			6.1(7.8)	3.7(7.0)	0.35(6.4)
$[SCr(CO)_3]^-$		2.0(0.4)			
$[C_6H_5Cr]^-$	3.0(8.4)				

[a] Relative intensities of peaks are indicated in the ionic yield maxima. Positions of the ionic yield maxima on the energy scale of the electrons (eV, ±0.05 eV) are in the parentheses.

ceeds at higher energies in the second resonance region. Successive elimination of carbonyl groups in indenechromium tricarbonyl is accompanied by formation of the corresponding metastable peaks. As the number of the carbonyl groups becomes smaller, peak maxima of ions $[C_9H_8Cr(CO)_n]^-$ shift towards higher energies:

$$\underset{1.8\ \text{eV}}{[C_9H_8Cr(CO)_2]^-} \overset{*}{\rightarrow} \underset{2.6\ \text{eV}}{[C_9H_8Cr(CO)]^-} \overset{*}{\rightarrow} \underset{3.0\ \text{eV}}{[C_9H_8Cr]^-}$$

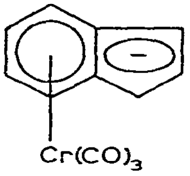
In the second resonance region the elimination of the arene ligand with the formation of $[Cr(CO)_3]^-$ ions competes with the decarbonylation. In this case the value of the $[ArCr]^-/[Cr(CO)_3]^-$ intensity ratio becomes two orders of magnitude higher as one goes from benzenechromium tricarbonyl to indenechromium tricarbonyl; this being indicative of a high stability of the $[C_9H_8Cr]^-$ ions as compared to the ion $[C_6H_6Cr]^-$. The ions $[Cr(CO)_n]^-$ (n = 0—2) are formed in the third resonance region at the energies of 6.9 to 7.8 eV. In the same energy region ions $[M - 3\ CO - H]^-$ are observed.

The ions considered above are present in the DEC mass spectra of all the complexes studied. For some compounds, in addition to these ions, the formation of specific fragments is seen. Such specific fragments are $[C_6H_5Cr]^-$ in the spectrum of I, $[SCr(CO)_3]^-$ in the spectrum of II and $[M - H]^-$ in the spectrum of III.

The ion $[C_6H_5Cr]^-$ is formed in the same resonance region (8.4 eV) as the ion Ph^- in the DEC spectrum of benzene [7]. However, the lifetime of the coordinated phenyl anion (τ = 444 μs) is one order of magnitude higher than the lifetime of the free ion Ph^- (τ = 47 μs), i.e. the phenyl anion becomes stabilized upon coordination with the atom of chromium.

In the spectrum of thiophenechromium tricarbonyl, $[SCr(CO)_3]^-$ ions are present in the first resonance region with an electron energy of 0.4 eV. These ions are formed from molecular ions as a result of migration of the atom of sulphur to the chromium atom, with subsequent ejection of one butadiene molecule or of two acetylene molecules. A similar rearrangement with the formation of $[SCr(CO)_n]^+$ ions (n = 0—2) was also observed by us in the mass spectrum of positive ions of thiophenechromium tricarbonyl [8]. It is probable that this process proceeds through a π—σ isomerization stage of the thiophenechromium tricarbonyl complex.

Contrary to the case with benzenechromium tricarbonyl, in the spectrum of indenechromium tricarbonyl $[M - H]^-$ ions are present, being formed in two resonance regions at 0.4 eV and 3.0 eV. Elimination of the hydrogen atom leads to the formation of a stable indenyl anion which may be coordinated with the chromium atom, both in the benzene and cyclopentadienyl rings. Each type of coordination must correspond with a particular structure (A and B). The ion $[M - H]^-$ in the first and second resonance regions probably corresponds to structure A and B, respectively. One cannot, however, exclude the possibility of the existence of structure C, in which the negative charge is localized at the chromium atom.



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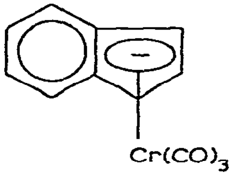

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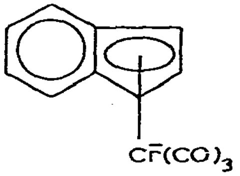

(C)

Experimental

The experiment was carried out on a modified MX-1306 mass spectrometer, made suitable for studying dissociative electron capture of organic molecules. The energy distribution of the electrons was 0.3 eV at half-height, the energy scale of the electrons was calibrated in terms of the yield of SF_6^- ions from SF_6 and $C_6H_5^-$ ions from C_6H_6.

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