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MASS SPECTROMETRY OF π-COMPLEXES OF TRANSITION METALS

XXVI *. MASS SPECTRA FROM DISSOCIATIVE ELECTRON CAPTURE BY MONOSUBSTITUTED BENZENECHROMIUM TRICARBONYLS

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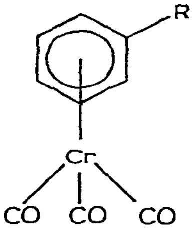
Summary

Mass spectra of negative ions η^6-$RC_6H_5Cr(CO)_3$, where R = H, Cl, F, I, OCH_3 or $N(CH_3)_2$, have been studied. Linear dependence of the first maxima of the resonance of $[M - CO]^-$ ions on Hammett constants σ_p has been established. For halogenated complexes a rearrangement process with the formation of the ions $[RCr(CO)_n]^-$ (n = 1—3) is characteristic.

In the present work we have studied the dissociative electron capture (DEC) by molecules of π-complexes of transition metals, namely, of monosubstituted derivatives of benzenechromium tricarbonyl



(I, R = Cl; II, R = F;
III, R = I; IV, R = H;
V, R = OCH_3; VI, R = $N(CH_3)_2$)

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* For part XXV, see ref. 3.

TABLE 1

MASS SPECTRA OF NEGATIVE IONS FROM DISSOCIATIVE ELECTRON CAPTURE OF MOLECULES OF $RC_6H_5Cr(CO)_3$

Ions	I R = Cl	II F	III I	IV H	V OCH_3	VI $N(CH_3)_2$
M^-	0.01(0)	0.4(0)				
$[M—CO]^-$	72.0(0.4)	100(0.55)	18.0(0.5)	100(0.7)	100(1.25)	100(1.8)
		13.5(2.75)		100(1.8)	95.0(1.8)	43.0(2.9)
$[M—(CO)_2]^-$	100(0.7)	43(3.4)	100(0.5)	100(4.0)		8.6(3.3)
$[M—(CO)_3]^-$	50.0(1.0)	2.2(3.8)	57.0(0.6)	2.7(4.5)	3.9(3.6)	1.1(3.9)
	5.8(3.5)		5.5(3.0)		0.8(8.6)	0.7(9.2)
$[M—CH_3]^-$					10.4(0.6)	0.36(3.5)
					4.5(2.6)	
$[M—CH_3—(CO)]^-$					95.0(3.3)	0.65(3.7)
						0.4(9.2)
$[M—CH_3—(CO)_2]^-$					6.1(3.6)	
$[M—CH_3—(CO)_3]^-$					5.5(5.7)	0.43(8.2)
$[RCr(CO)_3]^-$	0.13(3.8)	0.05(3.2)				
$[RCr(CO)_2]^-$	0.2(3.8)	0.1(3.3)				
$[Cr(CO)_3]^-$	0.08(3.8)	1.2(3.4)	0.35(4.0)	29.6(4.0)	13.0(3.6)	11.0(3.7)
$[Cr(CO)_2]^-$	0.01(7.9)	0.2(6.2)		2.7(4.7)	1.5(4.4)	0.8(4.6)
				3.8(6.9)	2.0(6.5)	2.5(6.5)
				3.9(7.7)		1.3(7.8)
$[Cr(CO)]^-$		0.05(6.8)		1.0(6.9)	0.65(7.0)	0.86(7.6)
				1.0(7.7)		
$C_6H_5Cr^-$				3.0(8.4)		0.3(8.0)
Cr^-	0.02(7.9)	0.15(7.8)		3.8(7.0)	2.0(7.6)	3.7(7.6)
				3.8(7.8)		

Relative intensities of the lines are given as effective ionic yield maxima. Energies of electrons at the ionic yield maxima are given in parentheses in eV, ±0.05 eV.

Negative molecular ions are formed only in the case of R = Cl and F; the effective yield of M^- ions is not high, and the lifetime with respect to the auto-elimination of the electron is 23 μs for the fluorinated benzenechromium tri-

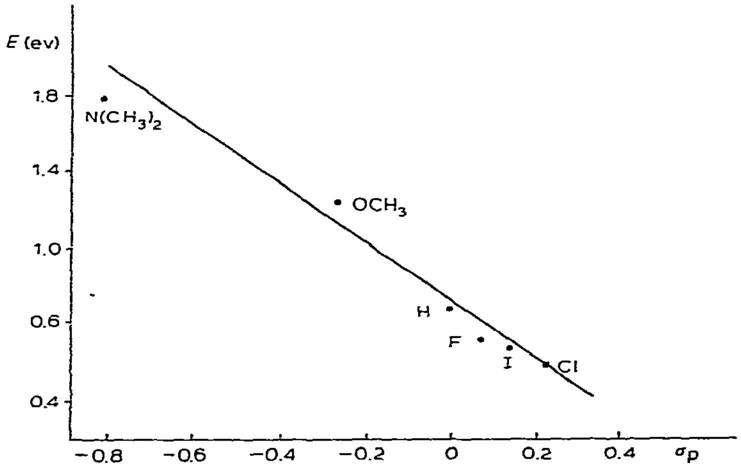

Fig. 1. Dependence of the first resonance maxima of the ions $[M — CO]^-$ on Hammett constants σ_p: $Y = -0.715X + 0.503$ ($r = 0.988$).

carbonyl and about 10 μs for the chlorinated benzenechromium tricarbonyl.

In the mass spectra of all the compounds studied the fragment ions $[RC_6H_5Cr(CO)_n]^-$ (n = 0—2) and $[Cr(CO)_n]^-$ (n = 0—3) are present; these are formed as a result of breakage of the metal—ligand bond with the ejection of carbonyl groups or of the arene ligand.

The main portion of the total ionic current (32 to 93%) is accounted for by $[M - CO]^-$ ions, which are formed in two resonance regions of 0.4 to 1.8 eV and 1.8 to 2.9 eV (see Table 1). As one goes from electron-accepting substituents to electron-donating ones, an increase of the values of the first maxima of the resonance of these ions is observed, in accordance with the Hammett equation (see Fig. 1). To a first approximation the values of the resonance maxima for a series of related compounds are proportional to the potentials of the appearance of the ion $[M - CO]^-$, which is equal to the sum of the energy of dissociation of the Cr—CO bond and of the electronic affinity of the fragment $[M - CO]$. Hence, the observed dependence is associated with an increase of $D(ArCr(CO)_2{-}CO)$ and/or with a decrease of the electronic affinity of the fragment $[M - CO]$ as one goes from the electron-accepting substituents to the electron-donating ones.

Successive decarbonylation of the negative molecular ion with the formation of the ions $[ArCr(CO)_n]^-$ (n = 0—2) in the first resonance region is characteristic only for chlorobenzenechromium tricarbonyl. Elimination of each subsequent carbonyl group leads to the 0.3 eV shift of the resonance maximum of the corresponding decarbonylated ion

$$[ClC_6H_5Cr(CO)_3]^- \xrightarrow{-CO} [M - CO]^- \xrightarrow{-CO} [M - (CO)_2]^- \xrightarrow[*]{-CO} [M - (CO)_3]^-$$

0 eV 0.4 eV 0.7 eV 0.8 eV 1.0 eV

The elimination of the third carbonyl group is accompanied by the formation of the corresponding metastable peak with a resonance maximum at 0.8 eV.

In the second resonance area of the electron capture (1.8 to 4.5 eV) two common processes take place: decarbonylation with the formation of the ions $[ArCr(CO)_n]^-$ (n = 0—2) and elimination of the arene ligand with the formation of the ions $[Cr(CO)_n]^-$ (n = 2, 3).

In the case of fluorine- and chlorine-containing complexes the Ar—Cr bond cleavage is accompanied by migration of the halogen atom to the chromium atom, with the formation of the ions $[RCr(CO)_3]^-$, $[RCr(CO)_2]^-$ and $[RCr(CO)]^-$.

Complexes V and VI are characterized not only by the decarbonylation but also by the elimination of the methyl group in the second resonance region with the formation of the ions $[M - CH_3 - (CO)_n]^-$ (n = 0—2, see Table 1). The high intensity of this process in V is due to the high stability of the resulting coordinated phenoxy anion.

Not more than 10% of the total ionic current is due to the ions that are formed at high energies of the electrons (from 6 to 10 eV). In this region of energies fragment ions which originate as a result of fragmentation of the complexes are present. Such fragment ions are $[Cr(CO)_n]^-$ (n = 0—2) in the spectra of I—VI and the ions corresponding to the elimination of the radicals $CH_3^{\cdot}$, $N(CH_3)_2^{\cdot}$ and of methane from dimethylanilinechromium tricarbonyl.

Positions of the resonance peaks for the formation of the $[M-H]^-$ ions in the spectrum of benzene and of the $[C_6H_5Cr]^-$ ions in the spectrum of benzene-chromium tricarbonyl are close: 8.0 and 8.4 eV [1]; this being, evidently, indicative of the similarity of the hydrogen atom elimination mechanism in both cases.

Experimental

The work was carried out on an MX-1303 mass spectrometer modified for recording negative ions [2].

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