

Negative Ion Mass Spectra of Organometallic Compounds; Electron Capture-induced Decarbonylation of an Ester Group in a π -Arene Metal Carbonyl

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Summary Secondary electron capture by (π -methyl benzoate)tricarbonylchromium yields a molecular anion which undergoes decarbonylation and further loss of three CO groups; in addition, Cr^- ions have been identified in the 70 eV negative ion mass spectrum of this compound.

RECENT reports^{1,2} have indicated that a considerable number of organic and inorganic compounds can accept an electron in a secondary electron capture process to produce molecular anions which may then undergo relatively simple fragmentations.

However, for electron capture to occur in simple organic esters, it is apparently necessary for a stabilizing substituent to be present in the molecule. Thus, Bowie and his co-workers³ have incorporated a conjugated dicarbonyl unit in such compounds which has permitted electron capture to proceed, yielding intense molecular anions, from which fragmentations particular to the ester group can occur.

We now report for the first time a novel related electron capture involving (π -methyl benzoate)tricarbonylchromium $[\text{CrMeO}_2\text{CC}_6\text{H}_4(\text{CO})_3]$. We have observed electron capture in the gas phase by this compound resulting in the decarbonylation of the ester group. In addition, Cr^- ions have been detected in the 70 eV negative ion mass spectrum of this compound.

These results are important since we have been unable to effect secondary electron capture, under our instrumental conditions, in methyl benzoate or (π -benzene)tricarbonylchromium alone.

TABLE
Negative ion mass spectrum of $[\text{CrMeO}_2\text{CC}_6\text{H}_4(\text{CO})_3]$

	Relative abundances (%) ^a
$[M]^-$	34.3
$[M - \text{CH}_3]^-$	0.2
$[M - \text{CO}]^-$	100
$[M - \text{CO} - \text{CH}_3]$..	0.3
$[M - 2\text{CO}]^-$	1.8
$[M - 2\text{CO} - \text{CH}_3]^-$..	0.1
$[M - 3\text{CO}]^-$	3.2
$[M - 3\text{CO} - \text{CH}_3]^-$..	0.3
$[M - 4\text{CO}]^-$	4.0
$[\text{Cr}]^-$	0.6

^a Based on ^{52}Cr

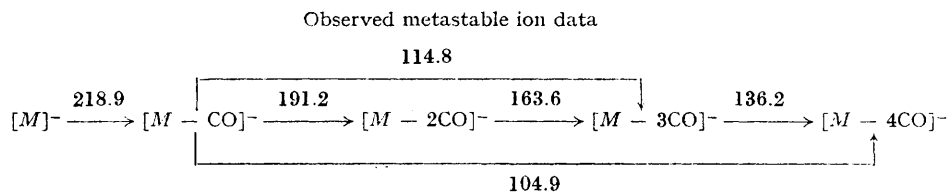
The 70 eV negative ion mass spectrum of $[\text{CrMeO}_2\text{CC}_6\text{H}_4(\text{CO})_3]$ (Table) yielded an intense molecular anion, together with simple fragments corresponding to the loss of CO and CH_3 groups. However, the principal fragments correspond to the loss of CO groups from the molecular anion, $[M]^-$. Significantly, four CO groups are lost from this ion and metastable data from the Table indicate that loss of one

CO group from the molecular anion yields the $[M - \text{CO}]^-$ ion, with 100% relative abundance, from which three CO groups are subsequently lost, giving $[M - 2\text{CO}]^-$, $[M - 3\text{CO}]^-$, and $[M - 4\text{CO}]^-$ ions with low abundances; respectively, 1.8, 3.2, and 4.0%. As three CO groups are bonded to the Cr atom in the molecule, we propose that, as a consequence of electron capture in the molecule, decarbonylation of the ester group has occurred to yield the $[M - \text{CO}]^-$ ion, from which simultaneous and consecutive loss of three CO groups has taken place. ^{13}C labelling studies of this and similar compounds are proceeding to establish unequivocally the origin of the first CO group lost from the molecular anion.

of the Cr^- ions reported here indicates a similar mechanism with secondary electrons involved.

(π -Benzoic acid)tricarbonylchromium, prepared by hydrolysis⁶ of the methyl ester, also gave a 70 eV negative ion mass spectrum with similar major fragments to those reported here for the ester. Decarbonylation of the carboxylic acid group is also indicated from the metastable ion data, and in addition, Cr^- ions were identified in the spectrum. Two previous reports of fragmentation of a carboxylic acid and its corresponding methyl ester in π -bonded arene metal carbonyls were made, but these were observed in positive ion mass spectrometric studies.⁷

The negative ion spectra were obtained with a modified



Another novel ion observed in the spectrum, and identified by its cluster, is the Cr^- ion. Cr^- ions have been reported previously⁴ and have resulted from dissociative electron capture processes involving $[\text{Cr}(\text{CO})_6]$. We have reported^{2,5} examples where reductions in the oxidation states of metals have occurred as a result of secondary electron capture, and preliminary work on the specific origin

Hitachi Perkin-Elmer RMU-6L mass spectrometer under similar conditions to those previously described.¹

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