

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 ⁵²Cr

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

