

A combined gas phase and surface study on electron induced decomposition of the heteronuclear FEBID precursor; $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$

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Synopsis Here we present a combined gas phase and surface study on electron induced decomposition of the heteronuclear FEBID precursor; $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$. Dissociative electron attachment and dissociative ionization of this compound in the gas phase is explored and discussed in context to controlled deposition experiments where the same compound is exposed to high-energy electrons, when adsorbed on a surface.

In recent years, a number of gas phase studies on the interaction of low energy electrons with organometallics have been conducted in conjunction with surface studies on deposit formation from thin layers of the same compounds adsorbed on surfaces and exposed to high-energy electrons [1]. The aim of these studies has primarily been to evaluate the potential of these compounds as precursor molecules in focused electron beam induced deposition (FEBID) [2] and to unravel the mechanisms behind deposit formation [1]. In this context, the combination of gas phase and surface experiments is advantageous as the former can deliver information on the extent and energy dependency of individual processes, while the latter elucidates the surface interactions and exposure to secondary electrons with an energy distribution similar to what is expected in FEBID instruments. The use of heteronuclear precursors is an attractive alternative to mixed gas or multiple gas inlet systems for the fabrication of alloy nanostructures, and recent experiments with $\text{HFeCo}_3(\text{CO})_{12}$ [3] achieved a typical metal purity of 80% with 1:3 FeCo ratio, clearly demonstrating the viability of this approach.

To follow this path and explore further heteronuclear precursor candidates, we have conducted gas phase studies on dissociative ionization and dissociative electron attachment to the heteronuclear organometallic $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ [5], a compound specifically synthesized for this purpose. Furthermore, the combination of the multiply coordinated cyclopentadienyl group, which is known to be a poor leaving group (see ref. 4 and refs therein), and the more labile CO ligands offers an excellent opportunity to compare these ligands in a heteronuclear architecture.

The two most intense fragments produced in DEA to by $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ are both formed via a low-lying resonance leading to a maximum in the ion yield near 0 eV. These channels are the loss of one CO, and the cleavage of the iron-manganese bond to form $\text{Mn}(\text{CO})_5^-$. Hence, both these channels are associated with a single bond rupture. Further CO loss is also observed in DEA, covering the formation of $[\text{M} -$

$\text{nCO}]^-$ over the range from $n = 2$ to $n = 6$. These channels are, however, orders of magnitude less efficient than the primary single bond rupture channels. No cyclopentadienyl loss is observed in DEA to this compound. In dissociative ionization, the fragmentation pattern observed are very different to these observed in DEA. At about 70 eV, the DI spectra is dominated by fragments formed through the loss of 5 and 6 CO ligands, the formation of the iron cyclopentadienyl fragments FeCp and $\text{FeCp}(\text{CO})_2^+$ and the bare metal Fe^+ and Mn^+ . Hence, the fragmentation through DI is much more extensive than through DEA.

Recently, surface science experiments were performed in the Fairbrother lab, wherein $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ was physisorbed onto gold and highly ordered pyrolytic carbon (HOPG) substrates under ultra-high vacuum (UHV) and irradiated with varying electron dose, while the surface composition was monitored using X-ray photoelectron spectroscopy (XPS). These studies show that the primary deposition pathway is through carbonyl loss, while no cyclopentadienyl loss is observed.

In the current contribution we discuss the efficiency of the DI vs. the DEA channels in conjunction with the decomposition pathways and deposit formation from thin layers of $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$ at surfaces.

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