CHEMISTRY AND REACTIVITY OF METAL CLUSTER CARBONYL RADICAL ANIONS

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ABSTRACT. Metal carbonyl clusters generally undergo one-electron reduction to reactive radical anions. Reactivity is dependent on the nuclearity of the cluster and whether capping or bridging groups 'clamp' the metal-metal bonds. Because nucleophilic substitution on the radical anion is fast even the most unstable anions can participate in efficient electron transfer chain catalysis. Illustrative examples using C2Co2, C3M and M3 clusters are given and the influence of the nucleophile on the chain length and possible mechanisms highlighted. Selective substitution, isomerization and metal-metal bond formation are attractive features of ETC reactions. Synthetic and catalytic possibilities using electrogeneration of reactive cluster fragments are discussed.

1. REDOX CHEMISTRY OF METAL CLUSTER CARBONYLS.

The application of metal carbonyl clusters to electron transfer reactions arose from our work on carbyne-capped clusters, particularly RCo3(CO)9, 1. It was evident from the chemistry of these molecules that the delocalized bonding in the CCo3 core provided a 'push-pull' mechanism for the transfer of charge via the capping group.1, 2 Theoretical and spectroscopic data from other work3 suggested that most
metal carbonyl clusters had metal-centred delocalized cores so we embarked on a systematic survey of the redox properties of carbonyl clusters, the only previous work in this area being that of Dessy and co-workers.

Because of the electron acceptor properties of the CO ligands and the low energy, metal-centred LUMO, the majority of metal carbonyl clusters undergo facile one-electron reduction to radical anions. Detailed spectroscopic studies on C\textsubscript{2}M\textsubscript{2}, CM\textsubscript{3}, and M\textsubscript{4} radical anions have confirmed the a\textsuperscript{2\text{*}} metal-centred LUMO. Subsequent electron transfer behaviour and stability of the radical anions is dependent on the structural type, metal and temperature. Scheme 1.

\begin{align*}
\text{cluster} + e & \rightarrow \text{cluster}^{-} \quad \text{stable but reactive} \\
\text{e} & \rightarrow \text{decomposition} \quad \text{(1)} \\
\text{cluster}^{-} \rightarrow \text{cluster}^{-} & \rightarrow \text{fragmentation} \quad \text{(2)} \\
\text{cluster}^{-} & \rightarrow \text{cluster}^{-}\text{e} \rightarrow \text{cluster}^{2-} \rightarrow \text{bond opening} \\
\text{cluster}^{-} & \rightarrow \text{cluster}^{-}\text{e} \rightarrow \text{cluster}^{2-} \rightarrow \text{ligand loss} \quad \text{(4)} \\
\text{L} & \rightarrow \text{cluster}^{-}\text{e} \rightarrow \text{cluster}^{2-} \rightarrow \text{ligand loss} \quad \text{(5)}
\end{align*}

\textbf{Scheme 1}

Maximum stability of the radical anions occurs with the capped metal clusters (e.g. C\textsubscript{2}M\textsubscript{2}, P\textsubscript{2}Fe\textsubscript{3}, PCO\textsubscript{3}) or where the metal-metal bond is 'clamped' by a suitable bridging group as in 3. Stability decreases with heterometal cores or if the CO groups are replaced by weaker \pi-acceptors (e.g. H\textsuperscript{-}, PR\textsubscript{3}). Unless a structural change occurs, the addition of a second electron leads to decomposition. path 3 of Scheme 1; when conproportionation is fast a relatively high concentration of radical anion may be maintained at the electrode surface. Non-capped.