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PROBING THE SELECTIVITY OF ELECTROGENERATED TRANSITION-METAL SITES

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Summary

The formation of complexes $[\text{MoL}_2(\text{dppe})_2]$, $[\text{MoL}'_2(\text{dppe})_2]$ and $[\text{MoLL}'(\text{dppe})_2]$ ($\text{L}=\text{CNBu}^t$, $\text{L}'=\text{CO}$) (by imposing a cathodic clamp beyond the reduction peak of $[\text{MoCl}_2(\text{dppe})_2]$ in the presence of L and L') was monitored by ramp-clamp reverse ramp voltammetry and, from the analysis of the product distribution, it was concluded that the unsaturated centres of the types $\{\text{Mo}(\text{dppe})_2\}$, $\{\text{MoL}(\text{dppe})_2\}$ and $\{\text{MoL}'(\text{dppe})_2\}$ discriminate (although equally) between the two substrates, the addition of CO at each site occurring 2.3 times as fast as the addition of CNBu^t to the corresponding site.

Introduction

Electrochemistry may be a valuable tool for the study of the electronic properties of transition metal centres and their ligands and may provide useful information on mechanistic studies. In the present work we wish to describe some preliminary results which show how a simple electrochemical technique (ramp-clamp-reverse ramp voltammetry - figure 1) may be applied on the detection of unstable intermediates in reactions and on the study of their relative affinity for electrochemically generated transition metal centres.

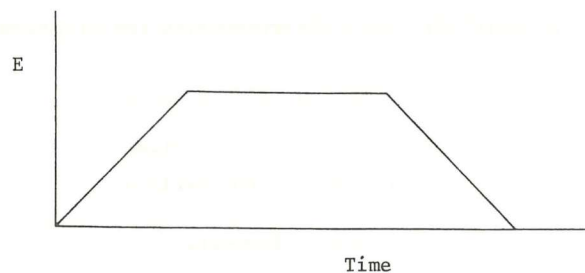


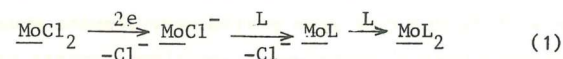
Figure 1 - Waveform for ramp-clamp-reverse ramp voltammetry

Results and Discussion

Electrochemical reduction of a transition metal complex with a chloride ligand may result in the cleavage of the metal-Cl bond and the exposure of an unsaturated coordination site which may bind a substrate.

We are particularly interested in molecules such as isocyanides, carbon monoxide, dinitrogen, di-hydrogen and acetylenes at Mo sites, since these substrates are known to interact with the molybdoenzyme nitrogenase. Here we focus on the co-substrates CNBu^t and CO at sites generated by electrochemical reduction of trans-[MoCl₂(Ph₂PCH₂CH₂PPh₂)₂], onwards denoted by [MoCl₂] where Mo stands for the trans-{Mo(Ph₂PCH₂CH₂PPh₂)₂} centre.

Complex [MoCl₂] is a known precursor of the bisdinitrogen complex trans-[Mo(N₂)₂] which is formed⁽¹⁾ by controlled potential electrolysis of the former in the presence of N₂. The pertinent features of the reduction of [MoCl₂] in the presence of a substrate L (such as N₂, CNBu^t or CO) involves the steps represented by equations (1):⁽¹⁾



Hence, by controlled potential electrolysis of [MoCl₂] at the cathodic peak, in the presence of a substrate, the complex undergoes a 2-electron reduction with cleavage of both Mo-Cl bonds and binding of two molecules of substrate; in this process, the metal-chloride bond rupture was shown⁽¹⁾ to be the rate limiting step. If the experiment is

carried out in the presence of two substrates (L and L'), complexes [MoL₂], [MoL'₂] and [MoLL'] are possible products, but only the more thermodynamically stable may be detected in the end of the electrolysis (> 30 minutes) [e.g., Mo(CNBu^t)₂ is the final product of the electrolysis in the presence of both CNBu^t and N₂].

However, through the application of the ramp-clamp-reverse ramp voltammetry to a solution of [MoCl₂] in the presence of both substrates, by imposing a cathodic clamp for ca.30s beyond the reduction peak, all the three possible products may be detected during the anodic sweep by their characteristic oxidation waves provided these are well separated (the substrates present considerably different P_L values)⁽²⁾ and the compounds are stable in the time-scale of the experiment (a few seconds).

Figure 2 shows a ramp-clamp voltammogram of [MoCl₂] in the presence of both CNBu^t and CO, and the generation of [Mo(CNBu^t)₂], [Mo(CO)₂] and [Mo(CO)(CNBu^t)] is evident; these complexes arise by the competitive reactions shown by the scheme which provides a simplified model for the analysis of the product distribution.

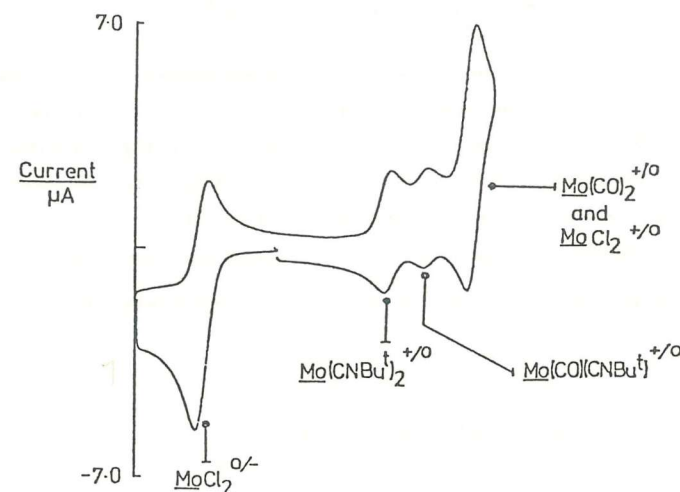
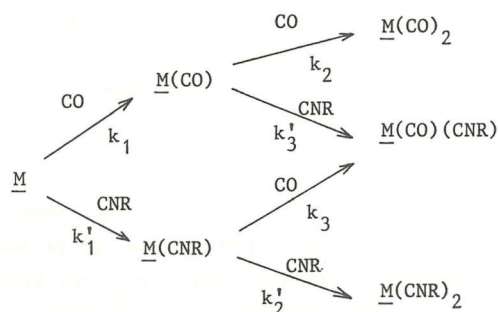


Fig.2-Ramp-clamp voltammogram of [MoCl₂] in the presence of CNBu^t and CO



Scheme - Addition reactions of CO and CNR to an unsaturated electrogenerated $\underline{\text{M}}$ centre

The peak-current for the oxidation of the product $[\underline{\text{Mo}}(\text{CNR})_2]$, i_p , was measured at various ratios of the substrate concentrations $[\text{CO}]/[\text{CNBu}^t]$; it is at a maximum, i_p^{max} , in the presence of CNBu^t and the absence of CO.

If the sites $\underline{\text{M}}$, $\underline{\text{M}}(\text{CO})$ and $\underline{\text{M}}(\text{CNR})$ are indiscriminate in their binding of substrates, the product distribution will be statistically related to $[\text{CO}]/[\text{CNBu}^t]$ through equation (2).

$$(i_p^{\text{max}}/i_p)^{1/2} - 1 = [\text{CO}]/[\text{CNBu}^t] \quad (2)$$

Figure 3 shows the corresponding dimensionless plot of the experimental data, but the slope is not unit (it is 2.3). This deviation is explained by the reaction of CO at each site occurring 2.3 times as fast as the reaction of CNBu^t with the corresponding site; moreover, the observed linear variation evidences that the three binding sites $\underline{\text{M}}$, $\underline{\text{M}}(\text{CO})$ and $\underline{\text{M}}(\text{CNR})$ discriminate equally between the two substrates.

These conclusions may be expressed by equations (3).

$$\frac{k_1}{k'_1} = \frac{k_2}{k'_2} = \frac{k_3}{k'_3} = \frac{k_{\text{CO}}}{k_{\text{CNR}}} = 2.3 \quad (3)$$

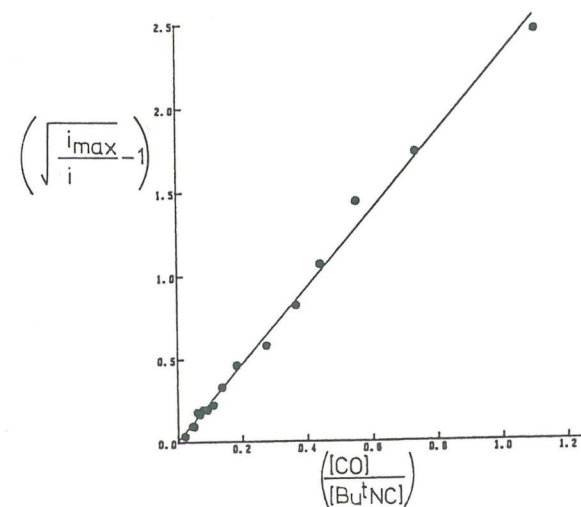


Figure 3 - Plot of $[(i_p^{\text{max}}/i_p)^{1/2} - 1]$ versus $[\text{CO}]/[\text{CNBu}^t]$ (see text)

We are extending this study to other substrates, such as N_2 and H_2 , and to other metal centres, namely derived from $[\text{MoCl}(\text{S}_2\text{CNET}_2)_2(\text{dppe})]^+$ which presents a single Mo-Cl bond, on the attempt to correlate the relative kinetic affinity of those substrates with their net electron donor/acceptor character and with the electronic properties (particularly the electron richness) of the binding metal centres.

Acknowledgements

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