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Application of Cyclic Voltammetry to Rhodium Syngas Catalyst Precursor Systems

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Introduction

There has been a major resurgence of interest in transition metal cluster chemistry [1] since the first disclosures of ethylene glycol from synthesis gas using rhodium carbonyl systems as catalysts [2]. Despite the intense interest and major importance of this process, we still do not have a clear understanding of the nature of the species present in solutions under catalytically-active conditions – above 200 °C and with several hundred atmospheres of synthesis gas (CO + H_2). High pressure infrared [3] and NMR [4] data have recently been obtained on rhodium compounds which are precursors to catalytically-active systems. Infrared data have also been collected at elevated temperatures. Both approaches have limitations, in particular the complexity of polynuclear carbonyl absorptions and pressure broadening (IR) and the fluxionality of systems and timescale for observation (NMR). Although the data now available have not thus far been able to identify the catalyst species, the merit of such *in situ* examinations of catalysts under operating conditions has received much discussion [5]. Clearly the complexity of these cluster systems especially under forcing conditions [3, 6] has limited progress towards an understanding of the species present and processes involved, and new *in situ* techniques are required to provide complementary solution-phase data on these complex systems.

In this communication, we wish to report our work with such a technique. We have now investigated the cyclic voltammetry (CV) of several rhodium clusters which are syngas catalyst precursors [2].

Experimental

$[Bu_4N][Rh_{12}(CO)_{30}]$ was prepared under carbon monoxide by a well-established procedure [7]. Bu_4NPF_6 was prepared by the addition of KPF_6 to Bu_4NCl and recrystallized at least twice from ethanol. Tetrahydrofuran solvent was distilled off $LiAlH_4$ or K/Na alloy immediately before use (see below). Cyclic voltammograms were recorded for 10^{-3} *M* solutions using a PAR electrochemistry system with a Model 175 Universal Programmer and Model 173 Potentiostat/Galvanostat with Model 176 current to voltage converter, X–Y recorder and Tektronix 5115 storage oscilloscope. All data reported here were obtained using an anaerobic cell into which THF solvent was vacuum distilled after anaerobic introduction of the backing electrolyte and rhodium complex. Nitrogen and carbon monoxide were scavenged by bubbling through THF containing anthraquinone over Na/Hg amalgam prior to entry into the cell. Coulometry and preparative experiments were carried out in a three-compartment H cell. Peak potentials (Ep) quoted) within this paper are *versus* a silver Ag wire reference electrode. For the process Ru(bipy)$_3^{2+}$ → Ru(bipy)$_3^{+}$ in THF under our experimental conditions $E^\circ = (E_p^c + E_p^a)/2 = -0.90$ V *versus* Ag wire.

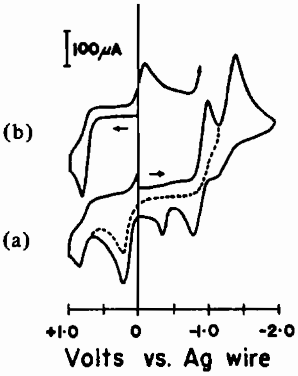

Fig. 1. (a) Cyclic voltammogram (2 V/sec) of $[NBu_4][Rh_{12}(CO)_{30}]$ in THF at room temperature (0.05 *M* NBu_4PF_6 as backing electrolyte). Broken line indicates voltammogram when reduction sweep was limited to −1.2 V. (b) Cyclic voltammogram recorded with initial sweep to positive potential.

Results and Discussion

Figure 1 represents the cyclic voltammogram of $[NBu_4]_2[Rh_{12}CO_{30}]$ under nitrogen in THF solvent with 0.05 *M* Bu_4NPF_6 as backing electrolyte. This CV was obtained reproducibly only if oxygen and water were rigorously excluded (see Experimental). Two reductions are observed at −1.00 and −1.45 V upon initially sweeping to negative potential. Coulo-

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metry at −1.15 V established that this reduction of $Rh_{12}(CO)_{30}^{2-}$ was a two electron process. The green anion $Rh_6(CO)_{15}^{2-}$ was identified in the catholyte solution by infrared spectroscopy [8]. When the reduction peak at −1.00 V was swept rapidly (2.0 V/sec) at −40 ℃* a small return oxidation peak was observed at −0.86 V, indicating that the fragmentation process to $Rh_6(CO)_{15}^{2-}$ is slower at lower temperatures, permitting some reverse oxidation of $Rh_{12}(CO)_{30}^{4-}$ which we calculate [9] has a halflife of approximately 50 milliseconds at −40 ℃. A return oxidation peak at +0.20 V was observed in the cyclic voltammogram only after sweeping through the reduction peak at −1.00 V (see Fig. 1, trace (b)) indicating that at +0.20 V we are observing oxidation of the electrochemical product, $Rh_6(CO)_{15}^{2-}$. Similarly, the reduction peak observed at −1.45 V (irreversible as low as −50 ℃), is best attributed to reduction of electrochemically produced species, since $Rh_{12}(CO)_{30}^{2-}$ itself is so readily ruptured through two electron reduction at −1.00 V.

The other major feature in the cyclic voltammogram of $Rh_{12}(CO)_{30}^{2-}$ is an oxidation at +0.80 V involving two electrons (from comparison with the height of the reduction peak at −1.00 V) When the +0.8 V region was swept rapidly (2.0 V/sec) at −40 ℃ a minor return reduction peak was observed at +0.70 V. Our data indicated [9] that the halflife of the oxidation product, $Rh_{12}(CO)_{30}$, is approximately 60 milliseconds at −40 ℃. Controlled oxidation at +0.85 V produced a brown solution which exhibited the following infrared νCO absorptions (acetonitrile solution, cm^{-1}) 2091ms, 2062s, 2020ms, 1998s,sh, 1988vs, 1960w,sh, 1812w, 1770vs, 1720m.

The above data for $Rh_{12}(CO)_{30}^{2-}$ can be summarized in the following scheme:

$$\begin{tikzcd}
Rh_{12}(CO)_{30}^{2-} \arrow[r, "+2e", "-1.00V\ \ A"'] \arrow[d, "D"', "\begin{array}{l}-2e\\+0.80V\end{array}"] & {[Rh_{12}(CO)_{30}^{4-}]} \arrow[r, "k=14.5\,s^{-1}", "B"'] & 2Rh_6(CO)_{15}^{2-} \arrow[d, "C", "\begin{array}{r}+ne\\-1.45\ V\end{array}"'] \\
{[Rh_{12}(CO)_{30}]} \arrow[d, "E"', "k = 11.5\ s^{-1}"] & & \text{products} \\
\text{products} & &
\end{tikzcd} \qquad (1)$$

Reduction of $Rh_6(CO)_{25}^{2-}$ is known [6] to yield $Rh_6(CO)_{14}^{4-}$, and hence the latter may be a product from step C. Our infrared data indicate that the final oxidation products from step E do not include $Rh_6(CO)_{16}$, although this cluster was identified earlier [6] as an oxidation product of $Rh_{12}(CO)_{30}^{2-}$.

In summary, our electrochemical data indicate that reduction or oxidation of $Rh_{12}(CO)_{30}^{2-}$ results in facile and rapid chemical transformations. The lack of reversibility of the reduction and oxidation of $Rh_{12}(CO)_{30}^{2-}$ is due to rapid structural rearrangements (involving scissions of metal–metal bonds in at least the case of reduction). This type of cluster fragmentation involving metal–metal cleavage during electrochemical processes is well established in the literature [10–14]. Thus for $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, well defined recuction steps are observed which are both chemically and electrochemically irreversible as low as −78 ℃ [11]. Similarly, $PhCCo_3(CO)_8PPh_3$ and $PtCo_2(CO)_8PPh_3$ fragment after one electron reductions [12, 13]:

$$\begin{tikzcd}
PhCCo_3(CO)_8PPh_3 \arrow[r, "e"] & {[PhCCo_3(CO)_8PPh_3^{\cdot-}]} \arrow[d] \\
& Co(CO)_4^- + \text{products}
\end{tikzcd} \qquad (2)$$

$$\begin{tikzcd}
PtCo_2(CO)_8PPh_3 \arrow[r, "e"] & {[\ [PtCo_2(CO)_8PPh_3]^{\cdot-}} \arrow[d] \\
& Co(CO)_4^- + [PtCo(CO)_4PPh_3]^{\cdot}
\end{tikzcd} \qquad (3)$$

The dimer product, $[PtCo(CO)_4PPh_3]_2$, was isolated from the latter reaction [13]. On the other hand, $Fe_3(CO)_{12}$ and the clusters $YCCo_3(CO)_9$ have reversible one electron reductions to radical anions, although there is fragmentation after further reduction to the respective dianions [11, 12].

Clearly, the 'electron reservoir' concept for metal clusters [15] is dependent upon the cluster system and the types of ligands involved [16]. The rapid rearrangements we have observed for $Rh_{12}(CO)_{30}^{4-}$ and $Rh_{12}(CO)_{30}$ parallel the lability established for the solution phase chemistry [6] including fluxional properties [19] of the parent $Rh_{12}(CO)_{30}^{2-}$.

An important, although until recently poorly understood [6, 8, 20] reaction of $Rh_{12}(CO)_{30}^{2-}$ is with carbon monoxide. The product of this reaction was labelled $Rh_{12}(CO)_{34}^{2-}$ for many years [6], since approximately four equivalents of carbon monoxide are absorbed per $Rh_{12}(CO)_{30}^{2-}$ unit. Recently, controlled precipitation of the product from this reaction at −78 ℃ yielded crystals of a new five vertex system, $Rh_5(CO)_{15}^-$ (isolated as the PPN salt). We have been able to monitor this complex transformation *in situ* at low temperatures using cyclic voltammetry. Figure 2 is the cyclic voltammogram recorded of the burgundy-red solu-

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*There are minor shifts in peak positions at lower temperatures; thus at −40 ℃ there are reductions at −0.30, −1.09, −1.42 V and oxidations at −0.71, −0.46, +0.35 and +0.80 V, in addition to minor return oxidation and reduction peaks at −0.86 and +0.70 V, respectively.

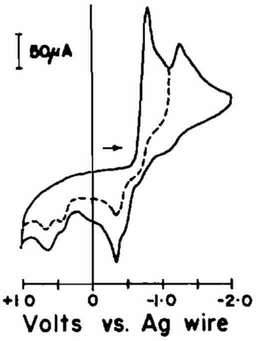

Fig. 2. Cyclic voltammogram (2 V/sec) of product from 0.5 hour reaction of $[NBu_4][Rh_{12}(CO)_{30}]$ with carbon monoxide at –50 °C (0.1 *M* Bu_4NPF_6 backing electrolyte). Broken line indicates voltammogram recorded when reduction sweep was limited to –1.1 V.

tion resulting from 0.5 hours reaction of violet-purple $Rh_{12}(CO)_{30}^{2-}$ with carbon monoxide at –50 °C. Two new reduction waves are observed at –0.80 and –1.26 V, with major oxidations at –0.33 and –0.64 V. Minor vestiges of the major features of the $Rh_{12}(CO)_{30}^{2-}$ system (two reductions and an oxidation) are evident. The reduction of $Rh_5(CO)_{15}^-$ at –0.80 V is a two-electron process by comparison (in Figs. 1 and 2) of the current carried to that of $Rh_{12}(CO)_{30}^{2-}$ reduction (also a two-electron process, *vide infra*) in the cyclic voltammogram before the carbon monoxide reaction. The process is irreversible at –50 °C·

$$Rh_5(CO)_{15}^- \xrightarrow{-0.80\,V} Rh_5(CO)_{15}^{3-} \rightarrow \text{products} \qquad (4)$$

As with the precursor $Rh_{12}(CO)_{30}^{2-}$ system, the other reduction wave at more negative potential (–1.30 V) and return oxidation waves are best attributed to electrochemically-active products from the rearrangements of $Rh_5(CO)_{15}^{3-}$. This was confirmed for the oxidation features at +0.6 V, which were not observed when positive potential was swept initially.

The purpose of this communication has been to indicate the potential and scope of the application of cyclic voltammetry to rhodium cluster systems which are closely related to catalysts for selective syngas conversion. The technique is clearly applicable as an *in situ* monitor of these systems. Our work is continuing in this area with other rhodium clusters and also with these catalyst precursors under the elevated temperature and syngas pressure conditions used to produce polyhydric alcohols such as ethylene glycol.

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16 In addition to the examples quoted above, the clusters $YCCo_3(CO)_{9-n}L_n$, L = R_3P, $(RO)_3P$ or RNC, exhibit irreversible one electron oxidations when n = 2 which become reversible when n = 3 [12]. Further, the clusters $Ni_6(\eta^5\text{-}C_5H_5)_6$ [17] and $Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4$ [18] both exhibit fully reversible peaks for one-electron reductions and up to two-electron oxidations.
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