CATALYSIS OF THE OXIDATION OF 1,4-CYCLOHEXADIENE TO BENZENE BY ELECTROACTIVE BINUCLEAR RHODIUM COMPLEXES

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Electrochemical oxidation of $Rh_2(TMB)_4^{2+}$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) in the presence of 1,4-cyclohexadiene produces benzene and two protons. It is probable that a key step in the reaction is hydrogen-atom transfer from 1,4-cyclohexadiene to electrochemically generated $Rh_2(TMB)_4^{3+}$. The H-atom abstraction apparently is facilitated by the presence of a $d\sigma^*$ hole in the Rh_2^{3+} complex.

1. Introduction

Binuclear d^8 complexes readily undergo photochemical atom-transfer reactions [1,2]. The $^3(d\sigma^* p\sigma)$ excited states of these complexes possess a $d\sigma^*$ hole that facilitates atom transfer to one of the open coordination sites of the M_2 unit. We have now found that an electrochemically generated d^8-d^7 complex with a $d\sigma^*$ hole also is an H-atom abstraction agent. Here we report the results of a study of the electrochemical oxidation of $[Rh_2(TMB)_4](PF_6)_2$ (TMB = 2,5-diisocyano-2,5-dimethylhexane) in the presence of 1,4-cyclohexadiene.

2. Experimental

The d^8-d^8 complex $[Rh_2(TMB)_4](PF_6)_2$ was prepared as described previously [3]. Solvents were purified by standard methods [4,5]. 1,4-cyclohexadiene was distilled from $NaBH_4$ under argon, freeze-pump-thaw degassed, and stored under vacuum in the dark. Tetra-*n*-butyl ammonium hexafluorophosphate ($TBAPF_6$) was prepared by combining hot, saturated acetone solutions of NH_4PF_6 and TBAI. A large excess of distilled water was then added, and the solution was cooled and filtered. The precipitated $TBAPF_6$ was recrystallized three times from 95% ethanol.

Electrochemical experiments [cyclic voltammograms (CVs) and constant potential bulk electrolyses] employed a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, a model 175 universal programmer, and a model 179 digital coulometer. The CVs were plotted on a Houston Instruments Omniographic 2000 x, y-recorder. Volatile organics obtained from bulk electrolyses were analyzed on a Hewlett-Packard 5890A gas chromatograph. Absorption spectra were measured on a Shimadzu UV-260 spectrophotometer.

The cell geometry employed in the CV experiments has been described by Fox [6]. CVs were measured on argon-blanketed dichloromethane solutions containing 0.1 M $TBAPF_6$ and 10^{-3} M Rh_2^{2+} (working electrode: BAS Pt button or BAS glassy carbon; auxiliary electrode: Pt wire; SSCE reference). The Pt button electrode was prepared following a standard procedure [7]. The glassy carbon electrode was polished with 0.3 μm α-alumina slurry, sonicated in purified water for 15 min, and rinsed with dichloromethane.

Constant potential bulk electrolysis experiments were done in an H-tube type cell at either a Pt basket or a pyrolytic graphite working electrode [10^{-3} M Rh_2^{2+}; 0.1 M $TBAPF_6$; CH_2Cl_2 (Ar)]. The H-tube cell was modified so that CVs of bulk electrolysis samples could be measured directly (BAS Pt button or BAS glassy carbon working electrode). The auxiliary (Pt basket) electrode was separated from the working electrode by a medium-porosity, sintered-glass frit.

3. Results and discussion

The CV of $[Rh_2(TMB)_4](PF_6)_2$ in dichloromethane solution is shown in fig. 1. The ΔE value (the separation between the anodic and cathodic peaks) for the first oxidation wave increases from 95 mV at a sweep rate of 20 mV/s to 160 mV at 500 mV/s; however, the $E_{1/2}$ value of 0.74 V (SSCE) is independent of sweep rate, indicative of a quasi-reversible electron-transfer process [8,9]. Based on analogy to other Rh(I) dimers [10–12], the first oxidation wave represents the conversion of $Rh_2(TMB)_4^{2+}$ to $Rh_2(TMB)_4^{3+}$. The second oxidation wave corresponds to the formation of a two-electron oxidized product [the associated reduction is at ~ 0.58 V (SSCE)]. Addition of CH_3CN to the CH_2Cl_2 solution produced a 2-fold increase in the anodic current with only a slight (30 mV) cathodic shift in the first oxidation wave. No other oxidation feature was observed to 1.5 V (SSCE), and no cathodic wave similar to that found in CH_2Cl_2 was seen.

Electrochemical oxidation of $Rh_2(TMB)_4^{2+}$ in the presence of 1,4-cyclohexadiene exhibited enhanced anodic current; this behavior coupled with the disappearance of the cathodic wave in the return scan indicate a catalytic process (fig. 1) [13]. [No electrochemical activity was observed in the potential range

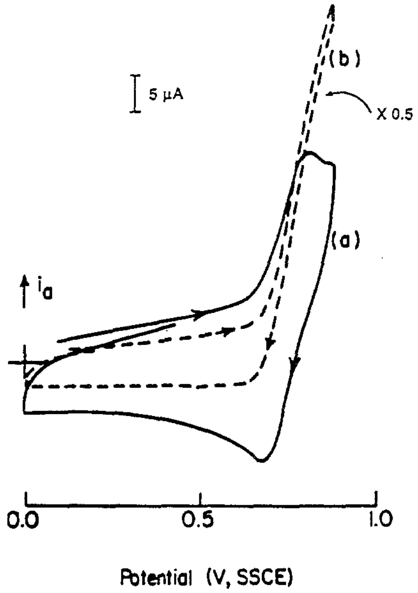

Fig. 1. Cyclic voltammogram of a dichloromethane solution (0.1 M $TBAPF_6$) of (a) $[Rh_2(TMB)_4](PF_6)_2$ (1 mM); (b) CV of the same solution with a 20-fold excess of 1,4-cyclohexadiene.

investigated for solutions of 1,4-cyclohexadiene in the absence of $Rh_2(TMB)_4^{2+}$]. Exhaustive electrolysis of a red dichloromethane solution of $[Rh_2(TMB)_4](PF_6)_2$, $TBAPF_6$, and 1,4-cyclohexadiene (20-fold excess) gave a clear, light-red solution; analysis of this solution by gas chromatography (gc) revealed the formation of benzene with the loss of 1,4-cyclohexadiene. The stoichiometry of the process as determined from the coulometry and gc analysis is given in eq. (1).

$$C_6H_8 \rightarrow C_6H_6 + 2H^+ + 2e^- \qquad (1)$$

The production of protons in the electrolysis solution was determined by cyclic voltammetry at a Pt button electrode and by the decrease in pH of a water extract of the CH_2Cl_2 solution.

The maximum number of turnovers observed for the oxidation of 1,4-cyclohexadiene is limited by the amount of substrate relative to solvent. With a 20-fold excess of 1,4-cyclohexadiene to $[Rh_2(TMB)_4](PF_6)_2$, a maximum of 9 turnovers was found. A yellow solid containing $Rh_2(TMB)_4Cl_2^{2+}$ [14] was isolated from the final electrolysis solution. The d^7-d^7 dichloro complex terminates the catalytic reaction.

By analogy to d^8-d^8 $^3(d\sigma^*p\sigma)$ photochemistry [1,2], it is likely that the $Rh_2(TMB)_4^{2+}$-catalyzed electrochemical oxidation of 1,4-cyclohexadiene (RH_2) to benzene (R) involves hydrogen-atom transfer from RH_2 to electrochemically generated $Rh_2(TMB)_4^{3+}$ (Rh_2^{3+}). Although the details of the overall reaction scheme are not known, the following steps could be included:

$$\mathrm{Rh_2^{2+} \rightleftarrows Rh_2^{3+} = e^-} \tag{2}$$

$$\mathrm{Rh_2^{3+} + RH_2 \rightleftarrows [Rh_2^{3+}, RH_2]} \tag{3}$$

$$\mathrm{[Rh_2^{3+}, RH_2] \rightarrow [Rh_2H^{3+}, RH\cdot] \rightarrow Rh_2^{2+} + H^+ + RH\cdot} \tag{4}$$

$$\mathrm{Rh_2^{3+} + RH\cdot \rightarrow Rh_2^{2+} + R + H^+} \tag{5}$$

$$\mathrm{2RH\cdot \rightarrow R + RH_2\cdot} \tag{6}$$

In the above scheme, H-atom abstraction from RH_2 in the complex $[Rh_2^{3+}, RH_2]$ generates $[Rh_2H^{3+}, RH\cdot]$, which could give Rh_2^{2+}, H^+, and $RH\cdot$ (reaction 4) [15]. Further oxidation of $RH\cdot$ (reaction 5) or disproportionation (reaction 6) would produce R.

Another route to R could involve a dimer of Rh_2^{3+} (reaction 7):

$$\mathrm{2Rh_2^{3+} \rightleftarrows [Rh_2^{3+}, Rh_2^{3+}]}.$$

It is known that $Rh_2b_4^{3+}$ (b = 1,3-diisocyanopropane) dimerizes through formation of a Rh_2^{3+}-Rh_2^{3+} bond [16,17], and it is reasonable to propose that $Rh_2(TMB)_4^{3+}$ (although sterically encumbered at the axial sites) could associate weakly in the same manner (strong Rh_2^{3+}-Rh_2^{3+} bond formation in this case is disfavored by intercomplex TMB-TMB interactions) [17]. A weak $[Rh_2^{3+}, Rh_2^{3+}]$ complex could abstract two hydrogen atoms from RH_2 to give R directly (reaction 8):

$$\mathrm{[Rh_2^{3+}, Rh_2^{3+}] + RH_2 \rightarrow [Rh_2^{3+}(RH_2)Rh_2^{3+}] \rightarrow 2Rh_2^{2+} + R + 2H^+}. \tag{8}$$

We favor the dimer mechanism for the two-electron oxidation of RH_2 (reaction 8) because it does not require potentially unfavorable steps such as the generation and release of $RH\cdot$ (reaction 4). In future work, we intend to investigate other electrochemically generated d^8-d^7 complexes with an emphasis on elucidating the role of weakly coupled $[d^8\text{-}d^7, d^7\text{-}d^8]$ species in reactions with substrates. It is worth noting that a $[d^8\text{-}d^7, d^7\text{-}d^8]$ complex is electronically analogous to the Rh(II)-porphyrin pair proposed by Sherry and Wayland [18] to be the active species in a methane C-H bond cleavage reaction.

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