The electroactive species in the catalysis of cyclohexadiene to benzene by $Rh_2(TM4)_4^{+2}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane)

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Upon further investigation of the recently reported electrocatalytic oxidation of 1,4-cyclohexadiene to benzene by $Rh_2(TM4)_4^{+2}$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane), we have obtained data which strongly implicates the $2e^-$ oxidized d^7-d^7 complex as the electroactive species. This contrasts with the original report which suggested that the $1e^-$ oxidized d^7-d^8 radical acted as the key species via hydrogen atom abstraction from 1,4-cyclohexadiene. A possible mechanism for the catalysis is proposed.

Keywords: Electrocatalytic oxidation of 1,4-cyclohexadiene; binuclear rhodium complexes; IR spectroelectrochemistry

1. Introduction

In a recent communication [1], Smith and Gray reported the electrocatalytic oxidation of 1,4-cyclohexadiene to benzene by the binuclear rhodium complex $[Rh_2(TM4)_4][PF_6]_2$ (TM4 = 2,5-diisocyano-2,5-dimethylhexane), (eq. (1)):

$$C_6H_8 \xrightarrow{Rh_2(TM4)_4^{+2}} C_6H_6 + 2H^+ + 2e^-. \tag{1}$$

Based on the electrochemistry of $[Rh_2(TM4)_4][PF_6]_2$ in 0.1 *M* $TBA^+PF_6^-/CH_2Cl_2$(TBA^+ = *n*-tetrabutylammonium) in the presence of excess 1,4-cyclohexadiene, they suggested that the catalytic cycle was initiated upon the $1e^-$ oxidation of $Rh_2(TM4)_4^{+2}$ to $Rh_2(TM4)_4^{+3}$. They further proposed that an important step in the cycle entailed hydrogen atom transfer from 1,4-cyclohexadiene to either the electrochemically generated d^7-d^8 radical or a d^8-d^7-d^7-d^8 dimer of the $Rh_2(TM4)_4^{+3}$ species. In this paper we present our results of

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additional studies which show that under the above conditions $Rh_2(TM4)_4^{+3}$ is in equilibrium with $Rh_2(TM4)_4^{+2}$ and $Rh_2(TM4)_4^{4+}$. Our data suggests that the $2e^-$ oxidized, d^7-d^7 complex is the catalytically active species in this system.

2. Experimental

$[Rh_2(TM4)_4][PF_6]_2$, $[Rh_2(TM4)_4][TFPB]_2$($TFPB^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate), and TBA^+TFPB^- were prepared by literature procedures [2–4]. $TBA^+ClO_4^-$ and $TBA^+PF_6^-$ were purchased from Southwestern Analytical and used as received. 1,4-cyclohexadiene (Aldrich) was distilled from $NaBH_4$ under argon prior to use.

All electrochemical experiments were performed with a Bioanalytical Systems (BAS) Model 100 electrochemical analyzer. Cyclic voltammetry (CV) was performed at 20 ± 2°C with a normal three-electrode configuration consisting of a highly polished glassy-carbon-disk working electrode ($A = 0.07$ cm^2), and an AgCl/Ag reference electrode containing 1.0 *M* KCl. The working compartment of the electrochemical cell was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.1 *M* solution of supporting electrolyte. Bulk electrolyses were performed by substituting a Pt mesh electrode for the glassy carbon electrode in the cell described above. IR spectroelectrochemistry was performed as described in ref. [3].

The dichloromethane (Fischer, HPLC grade) used for all electrochemical experiments was distilled from P_2O_5. Electrolyte solutions were prepared and stored over activated 4 Å molecular sieves, and were passed down a short column of activated alumina immediately prior to use.

3. Results and discussion

As reported in the original communication, $Rh_2(TM4)_4^{+2}$ undergoes a quasi-reversible $1e^-$ oxidation centered at +0.74 V (vs. SSCE) followed by a second, irreversible $1e^-$ oxidation which displays a cathodic return at +0.58 V in 0.1 *M* $TBA^+PF_6^-$ [1]. We confirm that addition of 1,4-cyclohexadiene to this solution results in the electrocatalytic oxidation of cyclohexadiene to benzene upon sweeping the potential past the first redox process of $Rh_2(TM4)_4^{+2}$. In light of the recent reports of photochemically induced atom-transfer to the $d\sigma^*$ hole of excited-state d^8-d^8 complexes [5,6], this observation led to the proposal that a key step in the catalytic cycle involved hydrogen atom transfer from cyclohexadiene to the electrochemically generated $d\sigma^*$ hole of the $Rh_2(TM4)_4^{+3}$ radical. Alternatively, it was suggested that the reaction may proceed in a concerted step via the weak coupling of two $Rh_2(TM4)_4^{+3}$ radicals and 1,4-cyclohexadiene, by

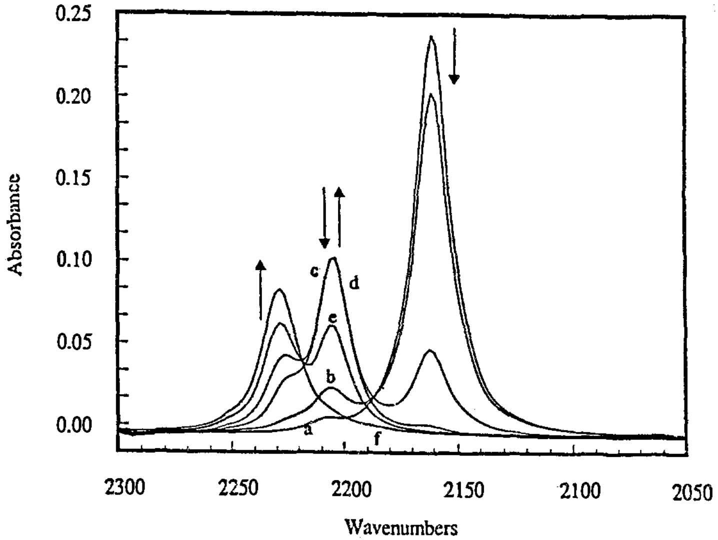

Fig. 1. IR spectroelectrochemical oxidation of $[Rh_2(TM4)_4][PF_6]_2$ in 0.1 *M* $TBA^+PF_6^-/CH_2Cl_2$ at ca. +0.7 V vs. SSCE. The absorbance at 2202 cm^{-1} due to the d^7-d^8 radical initially grows in (a–c), reaches a maximum value midway through the electrolysis (d), and eventually disappears (e–f).

analogy to the proposed Rh(II) porphyrin dimer reported by Sherry and Wayland [7] to activate the C-H bonds of methane.

We propose a third explanation, however, which involves oxidation of 1,4-cyclohexadiene by the $2e^-$ oxidized d^7-d^7 complex, $Rh_2(TM4)_4^{+4}$. Work performed in our laboratory since the initial communication has shown that the d^7-d^8 $Rh_2(TM4)_4^{+3}$ radical undergoes a ligand induced disproportionation, according to eq. (2).

$$2Rh_2(TM4)_4^{+3} + 2L \overset{K_{disp}}{\rightleftharpoons} Rh_2(TM4)_4^{+2} + Rh_2(TM4)_4L_2^{+4} \tag{2}$$

$$K'_{disp} = \frac{\left[Rh_2(TM4)_4^{+2}\right]\left[Rh_2(TM4)_4L_2^{+4}\right]}{\left[Rh_2(TM4)_4^{+3}\right]^2}. \tag{3}$$

The magnitude of the disproportionation equilibrium constant, K'_{disp} (eq. (3)), is highly dependant on the coordinating ability of L, ranging from $K'_{disp} > 10^6$ for $L = Cl^-$ to $K_{disp} < 10^{-10}$ for $L = TFPB^-$ [3].

Fig. 1 shows the IR spectroelectrochemical oxidation of $Rh_2(TM4)_4^{+2}$ in 0.1 *M* $TBA^+PF_6^-$ at a potential just positive of the formal $Rh_2(TM4)_4^{+3}$/ $Rh_2(TM4)_4^{+2}$ couple. The initial stretch at 2164 cm^{-1} due to $Rh_2(TM4)_4^{+2}$ ultimately gives way to the band at 2228 cm^{-1} due to the $2e^-$ oxidation product $Rh_2(TM4)_4(PF_6)_2^{+2}$; the stretch due to $Rh_2(TM4)_4^{+3}$ (2202 cm^{-1}) is observed only transiently. From this data we calculate that K'_{disp} is equal to ca. 0.1 at 25°C

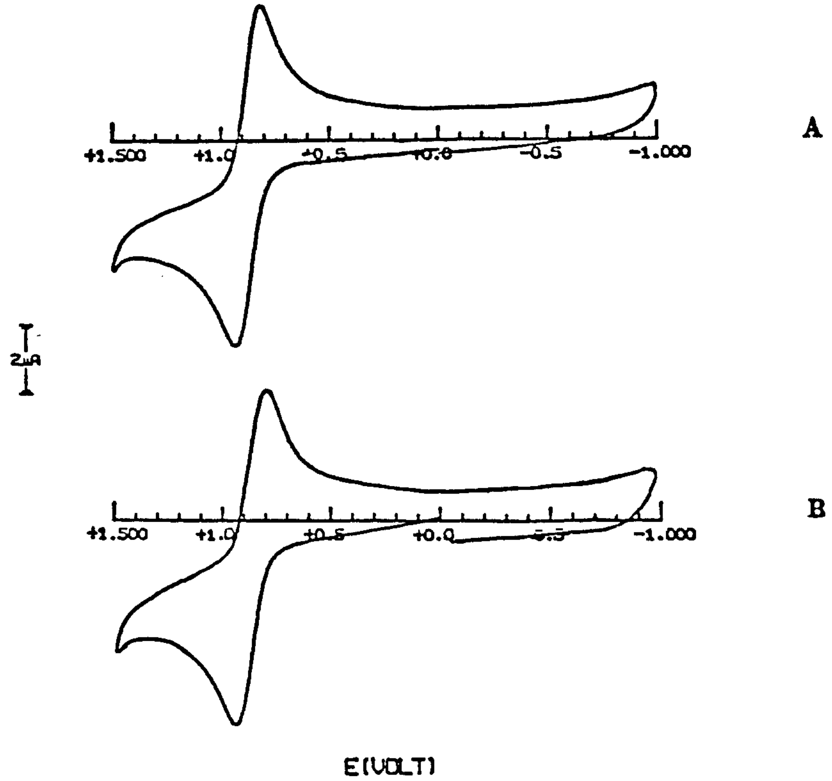

Fig. 2. (A) Cyclic voltammogram of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 *M* TBA^+TFPB^-/CH_2Cl_2. (B) CV of the same solution in the presence of of 1,4-cyclohexadiene.

[3]. This equilibrium provides a mechanism for the generation of the d^7-d^7 oxidation product even at the onset of anodic current for the first $1e^-$ process.

The possibility that the electroactive electronic state of the metal is the d^7-d^7 complex rather than the d^7-d^8 radical is attractive from both mechanistic and energetic considerations. UV-vis and IR spectroelectrochemical experiments on similar d^8-d^8 binuclear complexes have shown that while the d^7-d^7 species strongly binds ligands in the axial positions, the d^7-d^8 radicals show very little propensity to coordinate nucleophiles [8,9]. Moreover, considering the thermodynamic redox potentials of $Rh_2(TM4)_4^{+2}$, the d^7-d^7 electronic state of $Rh_2(TM4)_4^{+4}$ is a potent $2e^-$ oxidant.

In order to test whether the d^7-d^8 radical is able to initiate the catalytic cycle under conditions in which no $Rh_2(TM4)_4^{+4}$ is generated, we investigated the electrochemistry of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 *M* TBA^+TFPB^- as the supporting electrolyte. As previously reported, $Rh_2(TM4)_4^{+2}$ exhibits only a single $1e^-$ quasi-reversible oxidation to $Rh_2(TM4)_4^{+3}$ in this medium with no evidence of disproportionation [3]. Fig. 2 shows the CV of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 *M* TBA^+TFPB^-/CH_2Cl_2 in the presence of a 20-fold excess of 1,4-cyclo-

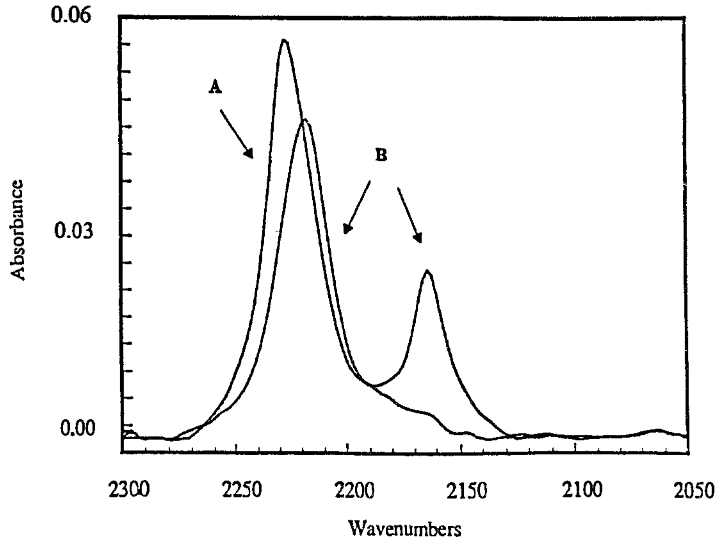

Fig. 3. (a) IR spectrum of $Rh_2(TM4)_4(ClO_4)_2^{+2}$ as generated via bulk electrolysis of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 *M* $TBA^+ClO_4^-/CH_2Cl_2$. (b) IR spectrum of the above solution after the addition of excess 1,4-cyclohexadiene.

hexadiene; no current enhancement indicative of a catalytic process is observed. Moreover, bulk electrolysis of this solution resulted in the passage of only one equivalent of charge, with the concomitant precipitation of $[Rh_2(TM4)_4][TFPB]_3$.

Having observed no catalytic activity from the d^7-d^8 radical, we generated a solution of the d^7-d^7 complex $Rh_2(TM4)_4(ClO_4)_2^{+2}$ via bulk electrolysis of $[Rh_2(TM4)_4][TFPB]_2$ in 0.1 *M* $TBA^+ClO_4^-$ [10]. Fig. 3 shows the IR spectra of that solution before and after addition of excess 1,4-cyclohexadiene. The addition of cyclohexadiene affects a color change from yellow to red, as well as the appearance of IR bands at 2164 cm^{-1} ($Rh_2(TM4)_4^{+2}$) and 2216 cm^{-1} ($Rh_2(TM4)_4Cl_2^{+2}$). At the end of the reaction, the original stretch at 2225 cm^{-1} due to $Rh_2(TM4)_4(ClO_4)_2^{+2}$ is no longer present. The formation of $Rh_2(TM4)_4Cl_2^{+2}$ is in accordance with the observation of Smith and Gray that the catalytic cycle terminates with the complexation of Cl^- to the $Rh_2(TM4)_4^{+4}$ core.

To explain these observations, we propose a general mechanism for the electrocatalytic oxidation of cyclohexadiene to benzene, as outlined in Scheme 1. While the exact details of the catalysis remain in question, our data strongly suggest that important steps involve the disproportionation of $Rh_2(TM4)_4^{+3}$ by PF_6^-, association of 1,4-cyclohexadiene to the resulting d^7-d^7 oxidation product, and electron transfer into $Rh_2(TM4)_4^{+4}$ by cyclohexadiene to generate benzene and the d^8-d^8 starting material.

$$Rh_2(TM4)_4^{+2} \rightarrow Rh_2(TM4)_4^{+3} + e^- \qquad (4)$$

$$2Rh_2(TM4)_4^{+3} + 2PF_6^- \overset{K_{disp}}{\rightleftharpoons} Rh_2(TM4)_4^{+2} + Rh_2(TM4)_4(PF_6)_2^{+2} \qquad (5)$$

$$\mathrm{Rh_2(TM4)_4(PF_6)_2^{+2} + C_6H_8 \rightarrow \left[Rh_2(TM4)_4(PF_6)_2^{+2},\, C_6H_8\right]} \tag{6}$$

$$\mathrm{\left[Rh_2(TM4)_4(PF_6)_2^{+2},\, C_6H_8\right] \rightarrow} \\ \mathrm{\rightarrow Rh_2(TM4)_4^{+2} + C_6H_6 + 2H^+ + 2PF_6^-} \tag{7}$$

Scheme 1.

It is worth noting that the rate of catalysis is significantly slower in the presence of 0.1 *M* ClO_4^- than in 0.1 *M* PF_6^-, even though the disproportionation constant in perchlorate is more than two orders of magnitude greater than in hexaflurophosphate [11]. Presumably, this effect is caused by the larger binding constant of ClO_4^- to $Rh_2(TM4)_4^{+4}$, which inhibits association between substrate and catalyst (step 6 in Scheme 1). In similar fashion chloride apparently binds tightly enough to exclude cyclohexadiene entirely.

Our preliminary UV-vis and IR spectroelectrochemical studies of this reaction have revealed the build-up of several intermediates during the course of the catalysis. We are currently attempting to characterize these species, as well as to investigate the catalytic activity of other, potentially stronger electrochemically generated d^7-d^7 oxidants toward a variety of substrates.

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[11] The cyclic voltammogram of $Rh_2(TM4)_4^{+2}$ in 0.1 *M* $TBA^+ClO_4^-$ exhibits a quasi-reversible $2e^-$ oxidation. At 25°C, $K'_{disp} = 18$ [3]. Addition of 1,4-cyclohexadiene to this solution causes only a slight anodic current enhancement; however, exhaustive bulk electrolysis past the $Rh_2(TM4)_4(ClO_4)_2^{+2}/Rh_2(TM4)_4^{+2}$ couple turns the catalysis over an average of 5 times.