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Electrochemical Investigation of Kinetic and Thermodynamic Aspects of Oxidation and Reduction of Mononuclear and Binuclear Rhodium Dithiocarbamate and Diselenocarbamate Complexes

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Oxidative controlled-potential electrolysis of $Rh(RR'dtc)_3$ (RR'dtc = dithiocarbamate) in dichloromethane at platinum electrodes leads to the formation of the binuclear complexes $[Rh_2(RR'dtc)_5]^+$. The use of platinum microelectrodes and very fast scan rate cyclic voltammetry (submillisecond time domain) shows that the formally rhodium(IV) complex $[Rh(RR'dtc)_3]^+$ is formed as an intermediate that rapidly dimerizes to $[Rh_2(RR'dtc)_6]^{2+}$. An internal redox reaction finally leads to the formation of stable $[Rh_2(RR'dtc)_5]^+$. Rate constants for the dimerization process have been calculated and are 1000 times faster than those for the cobalt analogues. Electrochemical oxidation of $Rh(Et_2dsc)_3$ (Et_2dsc = diethyldiselenocarbamate) occurs at considerably less positive potentials than for $Rh(RR'dtc)_3$, but proceeds via the same mechanism. The electrochemical oxidation process at mercury electrodes for both $Rh(RR'dtc)_3$ and $Rh(Et_2dsc)_3$ occurs at potentials different from those observed at platinum and involves oxidation of the mercury electrode to generate mixed rhodium–mercury complexes that decompose to $[Rh_2(RR'dtc)_5]^+$ and mercury dithiocarbamate (or diselenocarbamate) complexes on the time scale of controlled-potential electrolysis. $Rh(RR'dtc)_3$ and $Rh(Et_2dsc)_3$ undergo chemically irreversible two-electron reductions at very negative potentials with extremely rapid loss of ligand to generate a Rh(I) species. Oxidation of $[Rh_2(RR'dtc)_5]^+$ at platinum electrodes generates $[Rh_2(RR'dtc)_5]^{2+}$ as a transient intermediate whereas the compound $Rh_2(RR'dtc)_5$ produced by reduction of $[Rh_2(RR'dtc)_5]^+$ has no inherent stability and is converted on the voltammetric time scale to $Rh(RR'dtc)_3$ and $Rh(RR'dtc)_2$. Parallel behavior is observed for oxidation and reduction of $[Rh_2(Et_2dsc)_5]^+$.

Introduction

The chemistry and electrochemistry of transition-metal dithiocarbamate (RR'dtc) complexes have been studied extensively,[3-8] but there are relatively few reports on metal dialkyldiselenocarbamate (RR'dsc) complexes.

Recently we have systematically examined the redox behavior of cobalt dithiocarbamate[9-11] and diselenocarbamate[12] complexes. In these studies we rationalized to relationship between the formally Co(IV) complexes $[Co(RR'dtc)_3]^+$ and the binuclear Co(III) species $[Co_2(RR'dtc)_5]^+$. A logical extension of the cobalt work is to study complexes of rhodium where again some confusion is present in the literature as to whether $[Rh(RR'dtc)_3]^+$ or $[Rh_2(RR'dtc)_5]^+$ complexes are the products of oxidation of $Rh(RR'dtc)_3$. The work reported on $Rh(RR'dtc)_3$ complexes has mainly concerned preparations,[13-15] electronic spectra,[16] structure determinations,[17-19] proton NMR spectroscopy[20-22] and mass spectrometry.[23] However, Gahan et al.[15] claimed to have prepared a rhodium(IV) dithiocarbamate complex, $[Rh(RR'dtc)_3]^+$, by chemical oxidation of $Rh(RR'dtc)_3$, but later work by Hendrickson and Martin[24] suggests that the product is the rhodium(III) complex $[Rh_2(RR'dtc)_5]^+$. The electrochemistry of $Rh(n\text{-}Bu_2dtc)_3$ in acetone at platinum electrodes has been studied by Thewissen and co-workers,[25] and a brief mention of the oxidation of $Rh(Me_2dtc)_3$ and reduction of $[Rh_2(Me_2Rdtc)_5]^+$ is given by Hendrickson.[24] However, neither of these studies elucidate details of the relationship between the formation of $[Rh(RR'dtc)_3]^+$ and $[Rh_2(RR'dtc)_5]^+$. The electrochemical reduction of a series of rhodium(III) dithiocarbamates has been investigated in a range of solvents.[25,26] Studies on $Rh(RR'dsc)_3$ complexes are restricted to reports on their preparations in a paper by Jensen[27] and brief mentions in other works,[28,29] but no studies of their redox behavior are available.

In the present investigation we have synthesized $Rh(RR'dtc)_3$, $[Rh_2(RR'dtc)_5]^+$, $Rh(Et_2dsc)_3$, and $[Rh_2(Et_2dsc)_5]^+$. Cyclic voltammetry at conventionally sized platinum and mercury electrodes and very fast scan rate voltammetric techniques at platinum microelectrodes have lead to a detailed understanding of the redox properties of these complexes and the redox-controlled relationships between the species.

Nomenclature. The following abbreviations will be used throughout this paper: RR'dtc = dithiocarbamate, pyrrdtc = pyrrolidine-*N*-carbodithioate, morphdtc = morpholine-*N*-carbodithioate, RR'dsc = diselenocarbamate.

Experimental Section

Preparations. $Rh(RR'dtc)_3$ complexes were prepared by modified literature methods.[3,4] Stoichiometric amounts of sodium hydroxide, amine (RR'NH), and carbon disulfide were reacted in cold aqueous

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solution to produce the sodium dithiocarbamate, NaRR'dtc. Solid $RhCl_3$ was added to this solution to form Rh(RR'dtc)$_3$. Purification was by Soxhlet extraction using chloroform or dichloromethane, followed by column chromatography on alumina using dichloromethane as the eluant.

An analogous method cannot be used for the preparations of diselenocarbamates since carbon diselenide polymerizes in alkaline media.[30] A cold ethereal solution of CSe_2 was added very slowly with stirring to a cold solution of diethylamine, the mole ratio of CSe_2 to amine being close to 1:2 with the amine in slight excess. The resulting yellow solid, $(Et_2NH_2)(Et_2dsc)$, was filtered, dried and then dissolved in water. Addition of $RhCl_3$ with stirring yielded a precipitate of crude $Rh(Et_2dsc)_3$, which was then purified in the same manner as for Rh(RR'dtc)$_3$. Anal. Calcd $Rh(Et_2dsc)_3$: C, 21.7; H, 3.7; N, 5.1; Se, 57.1. Found: C, 21.7; H, 3.6; N, 4.9; Se, 55.0. Analyses were performed by the Australian Microanalytical Service (Amdel) except for selenium, which was determined by atomic absorption spectrometry at Deakin University on a GBC 903 instrument.

$[Rh_2(Et_2dtc)_5]BF_4$ was prepared by adding an excess of $BF_3{\cdot}OEt_2$ very slowly with stirring to $Rh(Et_2dtc)_3$ in benzene (solution or slurry) in the presence of oxygen using a method related to that of Martin et al.[24] The reaction mixture was stirred thoroughly, left open to the air, and set aside to evaporate to dryness (usually overnight). A dark orange sticky solid or oil was obtained. The crude product was extracted with dichloromethane and filtered and the filtrate again allowed to evaporate to dryness. The resulting solid or oil of $[Rh_2(Et_2dtc)_5]BF_4$ and (usually) $Rh(Et_2dtc)_3$ was further purified by dissolving it in the minimum quantity of dichloromethane, slowly adding diethyl ether until precipitation commenced, and then cooling to 0 °C in an ice/water bath. Washing with benzene followed by the recrystallization procedure (sometimes a number of times) ultimately produced an orange-red solid, which was shown to be analytically pure. $[Rh_2(Et_2dtc)_5]PF_6$ was made by oxidation of $Rh(Et_2dtc)_3$ with $NOPF_6$ by using the same purification and isolation techniques as described above. Other $[Rh_2(RR'dtc)_5]^+$ compounds and the $[Rh_2(Et_2dsc)_5]^+$ cation were prepared in situ by electrochemical oxidation of Rh(RR'dtc)$_3$ and $Rh(Et_2dsc)_3$, respectively (see text).

Electrochemical Instrumentation. Unless stated otherwise, electrochemical measurements were made at (20 ± 1) °C in dichloromethane (0.1 M Bu_4NClO_4). Solutions were degassed with solvent-saturated nitrogen, and a continuous stream of nitrogen was passed over the solutions while measurements were being performed. The supporting electrolytes were of electrochemical grade and were dried over P_2O_5 in a vacuum desiccator. All other chemicals were of AR grade. Slow scan rate polarographic and voltammetric measurements with a three-electrode format were carried out by using a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer. Both dropping and hanging mercury and platinum disk electrodes of conventional size were used as the working electrode with a platinum-wire auxiliary electrode. Potentials were measured against a Ag/AgCl (saturated LiCl; CH_2Cl_2) reference electrode. This electrode was frequently calibrated against the $[Fe(C_5H_5)_2]^+/Fe(C_5H_5)_2$ redox couple by using a 10^{-3} M solution of $Fe(C_5H_5)_2$. The reversible half-wave potential $E^r_{1/2}$ of this ferrocene standard at 20 °C was 0.48 ± 0.02 V versus Ag/AgCl in dichloromethane. When positive feedback circuitry was used to minimize the effect of uncompensated resistance or low temperatures, a platinum-wire quasi-reference electrode was employed. Positive feedback circuitry was applied by using a PAR polarographic analyzer interface accessory Model 174/50 and adjusted with the aid of a Tektronix Model 5103N oscilloscope. The response for all slow scan rate experiments was recorded on a Houston Instruments Omnigraphic 2000 XY recorder.

Fast scan rate cyclic voltammetric experiments (>500 mV s^{-1}) were performed at platinum microdisk electrodes by using a PAR Model 175 universal programmer and a very simple current follower based on a OP-37 operational amplifier with a 1 MΩ resistor in the feedback loop. Experiments at microelectrodes were performed in a two-electrode rather than a three-electrode mode.[31] Data were acquired with a Gould Type 4035 digital storage oscilloscope and then transferred to a Houston Instruments Omnigraphic 2000 XY recorder. A variety of platinum microdisk electrodes ranging in size from 0.5 to 25 μm in radius were used as the working electrode. The construction of these electrodes is related to methods described elsewhere.[31] A platinum-wire quasi-reference electrode was employed in fast scan rate experiments. Potentials versus this quasi-reference electrode were converted to the Ag/AgCl reference scale via reference to the ferrocene oxidation potential. Microelectrodes were polished by using a 0.05 μm alumina/water slurry on a polishing cloth (Buehler). Occasionally it was found advantageous to immerse the electrode in a 50:50 mixture of concentrated nitric and sulfuric acids, then rinse with ethanol, and dry thoroughly. All microelectrode experiments were performed in an aluminum Faraday cage.

Table I. Voltammetric Data for Oxidation and Reduction of 1 × 10^{-3} M Rh(RR'dtc)$_3$ and $Rh(Et_2dsc)_3$ Solutions in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

Rh(RR'dtc)$_3$		oxidation		reduction		
					at Hg	
R	R'	at Pt[a] E_p^{ox},[b] V	at Hg[a] E_p^{ox},[b] V	at Pt[a] E_p^{red},[b] V	E_p^{red},[a,b] V	E_p^{red},[b,c] V
Me	Me	1.13	0.47 (0.59)[d]	−2.02	−1.90	−1.77
Et	Et	1.12	0.52	−2.11	−1.97[e]	−1.82
i-Pr	*i*-Pr	1.02	0.48	−2.23	−2.1[f]	−2.03[f]
morph		1.22	0.54 (0.71)[d]	−2.02	−1.80	−1.71
pyrr		1.11	0.44 (0.63)[d]	−2.04	−1.88	−1.77
$Rh(Et_2dsc)_3$		0.78	0.30	−2.13	−1.99	−1.89

[a] Scan rate 200 mV s^{-1}. [b] V vs Ag/AgCl; E_p^{ox} = oxidation peak potential; E_p^{red} = reduction peak potential. [c] Differential-pulse polarography, drop time 0.5 s, pulse amplitude 50 mV, scan rate 2 mV s^{-1}. [d] Two peaks are present—the presence of adsorption is indicated. [e] Value only approximate due to close proximity of the solvent reduction limit. [f] Shoulder on the solvent reduction limit.

Controlled-potential electrolysis experiments were performed at a platinum-gauze or mercury-pool working electrode by using a PAR Model 173 potentiostat/galvanostat in conjunction with a Model 179 digital coulometer. In these experiments, the auxiliary electrode was platinum gauze separated from the test solution by a salt bridge containing a porous Vycor frit. The reference electrode was the same Ag/AgCl electrode as used for slow scan rate voltammetric measurements.

Results and Discussion

A. Rh(RR'dtc)$_3$ and $Rh(Et_2dsc)_3$. Oxidation at Platinum Electrodes. Oxidative cyclic voltammograms of Rh(RR'dtc)$_3$ in dichloromethane at conventional-sized platinum electrodes at scan rates up to 500 mV s^{-1} show a well-defined irreversible oxidation wave for each compound, and Table I summarizes the data. This process has characteristics similar to those reported for oxidation of $Rh(Bu_2dtc)_3$ in acetone.[25] A second oxidation wave at more positive potentials is detected with difficulty near the solvent limit for concentrated solutions and corresponds to oxidation of $[Rh_2(RR'dtc)_5]^+$ (see later). For $Rh(Et_2dtc)_3$, scanning in the negative direction after switching the potential at potentials more positive than the first oxidation process reveals the presence of small reduction peaks at approximately −0.10 and −1.0 V vs Ag/AgCl (Figure 1a). These peaks correspond to reduction of species formed via ligand oxidation and the binuclear species $[Rh_2(Et_2dtc)_5]^+$ (see later), respectively. The oxidation processes are still irreversible at −78 °C except that for Rh(*i*-Pr$_2$dtc)$_3$, which gives a partially reversible response (Figure 1b). Thus, at least for Rh(*i*-Pr$_2$dtc)$_3$, a formally Rh(IV) dithiocarbamate species [Rh(*i*-Pr$_2$dtc)$_3$]$^+$ is detected on the conventional cyclic voltammetry time scale, but only at low temperature and a scan rate of 500 mV s^{-1}.

Oxidative controlled-potential electrolysis at a platinum electrode of all the rhodium dithiocarbamate complexes in dichloromethane occurs with the transfer of 1.0 ± 0.1 electron per molecule. Cyclic voltammograms recorded after the electrolysis show no wave due to oxidation of Rh(RR'dtc)$_3$, but there is the irreversible oxidation wave approximately 500 mV more positive than that for the oxidation of Rh(RR'dtc)$_3$. This wave remains irreversible at low temperatures except for, again, the case of Rh(*i*-Pr$_2$dtc)$_3$. An analytically pure sample of $[Rh_2(Et_2dtc)_5]BF_4$ gives an oxidative response that is identical within experimental error with that shown by the product of bulk electrochemical oxidation of $Rh(Et_2dtc)_3$.

Overall, these results suggest initial oxidation of Rh(RR'dtc)$_3$ to the rhodium(IV) complex [Rh(RR'dtc)$_3$]$^+$ followed by dimerization and an internal redox reaction to give the rhodium(III)

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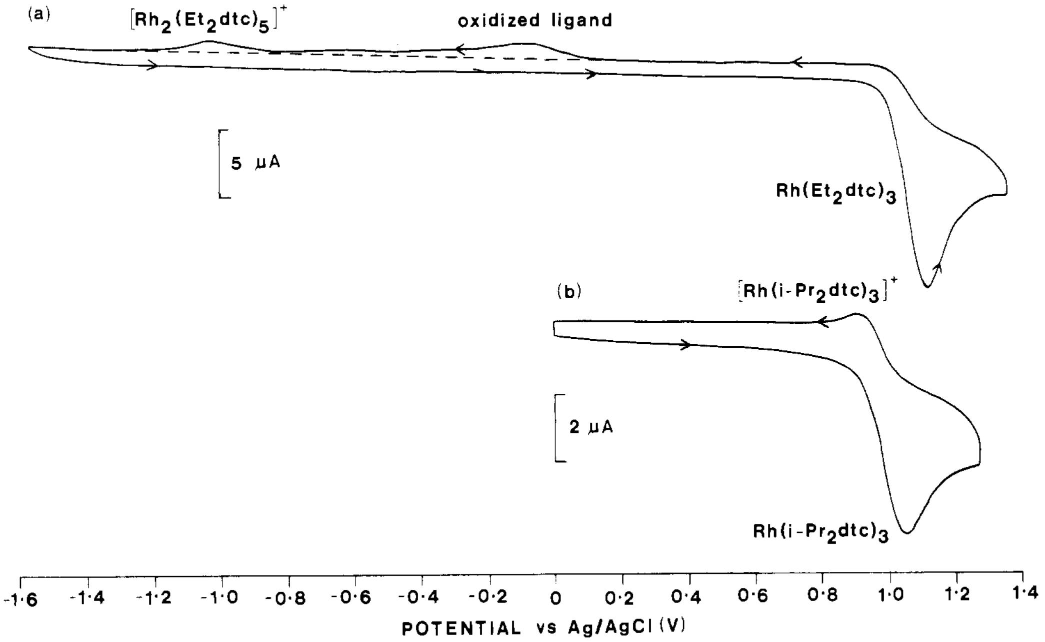

Figure 1. Cyclic voltammograms (scan rate 500 mV s^{-1}) at a platinum electrode in dichloromethane (0.1 M Bu_4NClO_4) for oxidation of (a) 10^{-3} M $Rh(Et_2dtc)_3$ at 20 °C and (b) 10^{-3} M $Rh(i\text{-}Pr_2dtc)_3$ at −70 °C. The dashed line indicates solvent background.

binuclear complex $[Rh_2(RR'dtc)_5]^+$ and an oxidized form of the ligand. If the proposed mechanism is correct, then very fast scan cyclic voltammetry should lead to observation of a reversible $[Rh(RR'dtc)_3]^+/Rh(RR'dtc)_3$ redox couple for all compounds if conditions can be achieved where the dimerization reaction following charge transfer is no longer important on the electrochemical time scale. At conventional electrodes scan rates are usually limited to less than 50 V s^{-1}, but at microelectrodes scan rates on the order of 100 000 V s^{-1} have been recorded[32] (i.e. in the submillisecond time domain). Figure 2 shows the cyclic voltammograms at a platinum microelectrode for the oxidation of 10^{-2} M $Rh(Et_2dtc)_3$ in dichloromethane (1.0 M TBAP) at different scan rates. As the scan rate increases, the voltammograms become more reversible, and at 2000 V s^{-1}, there is a well-defined reverse peak corresponding to the formation of $[Rh(Et_2dtc)_3]^+$. Figure 3a shows the cyclic voltammogram at a microelectrode for oxidation of 10^{-2} M $Rh(Et_2dtc)_3$ in dichloromethane at 5000 V s^{-1}, while Figure 3b depicts the cyclic voltammogram for the oxidation of 10^{-3} M $Rh(Et_2dtc)_3$ at 500 V s^{-1}. Comparing the two cyclic voltammograms, it can be seen that they have approximately the same degree of reversibility. The scan rate and concentration dependence are entirely consistent with theory for a second-order chemical reaction coupled to electron transfer (i.e. electron transfer followed by dimerization).[33] A plausible mechanism for oxidation of $Rh(RR'dtc)_3$ complexes at platinum electrodes therefore appears to be

$$Rh(RR'dtc)_3 \rightleftharpoons [Rh(RR'dtc)_3]^+ + e^- \qquad (1)$$

$$2[Rh(RR'dtc)_3]^+ \rightarrow [Rh_2(RR'dtc)_6]^{2+} \qquad (2)$$

$$[Rh_2(RR'dtc)_6]^{2+} \rightarrow [Rh_2(RR'dtc)_5]^+ + \tfrac{1}{2}[R_2R'_2bitt]^{2+} + S \qquad (3)$$

where $[R_2R'_2bitt]^{2+}$ is the 3,5-bis(*N*,*N*-dialkyliminio)-1,2,4-trithiolane dication.[7,34] This is the same mechanism as proposed for the oxidation of $Co(RR'dtc)_3$ complexes.[11] The only differences are that the rate of dimerization is much faster in the case of rhodium compared to cobalt and that the rhodium complexes are oxidized at a more positive potential than their cobalt analogues. Digital simulations of the theory for dimerization were undertaken and indicate the rate constant for the dimerization step for $[Rh(Et_2dtc)_3]^+$ (eq 2) is on the order of 10^6 M^{-1} s^{-1}, which is more than 1000 times higher than that for the corresponding cobalt complex. The high ohmic *iR* drop and charging current present at very high scan rates in dichloromethane preclude highly accurate calculations of the second-order rate constant.

With the use of microelectrodes and sufficiently fast scan rates, a reversible (or partly reversible) cyclic voltammogram was observed for all the $Rh(RR'dtc)_3$ complexes studied. Depending on the RR′ groups different scan rates are needed to achieve similar degrees of reversibility. Results demonstrate that $[Rh(i\text{-}Pr_2dtc)_3]^+$ is the most stable cation and $[Rh(pyrrdtc)_3]^+$ the least stable with $[Rh(Et_2dtc)_3]^+$ and the other complexes having intermediate stability. In all cases the rate of dimerization is about 10^3 times faster than that for the corresponding cobalt complex. Rhodium(IV) complexes are not common,[35,36] but our work at fast scan rates at microelectrodes show that rhodium(IV) dithiocarbamates do exist, but only as short-lived intermediates. Interestingly, they are less stable than their cobalt(IV) analogues, which is unexpected as higher oxidation states are usually favored by the heavier transition metals.

The oxidative behavior of $Rh(Et_2dsc)_3$ at platinum in dichloromethane is entirely analogous to that of $Rh(Et_2dtc)_3$. An irreversible oxidation wave is observed at 0.80 V vs Ag/AgCl (scan rate 500 mV s^{-1}), which is about 300 mV less positive than that for the oxidation of $Rh(Et_2dtc)_3$. This difference in potential between dtc and dsc complexes has been observed before[12] and appears to be a general phenomenon. A second oxidation wave due to oxidation of $[Rh_2(Et_2dsc)_5]^+$ is observed at 1.1 V vs Ag/AgCl and is irreversible under all conditions studied. The use of microelectrodes and fast scan rate voltammetry shows that the first oxidation wave for $Rh(Et_2dsc)_3$ becomes reversible at fast scan rates. For the same concentrations, similar scan rates are required for $Rh(Et_2dtc)_3$ and $Rh(Et_2dsc)_3$ to achieve similar degrees of reversibility, suggesting similar rates for the proposed dimerization step.

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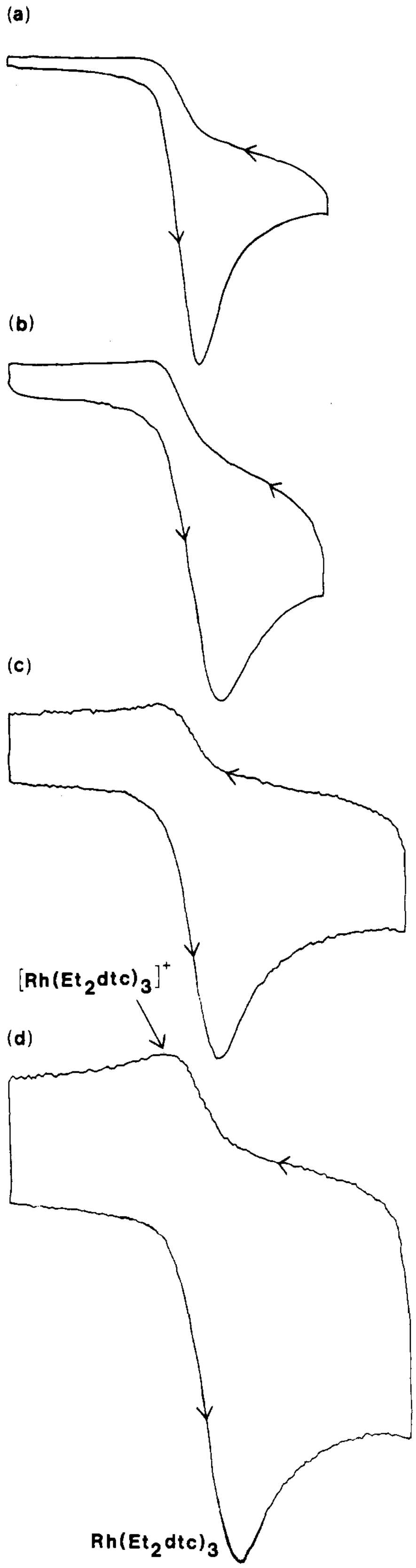

Figure 2. Cyclic voltammograms at platinum microelectrodes in dichloromethane at 20 °C for oxidation of 10^{-2} M $Rh(Et_2dtc)_3$ at various scan rates: (a) 50 V s^{-1}, electrode 25-μm radius, 0.5 M Bu_4NClO_4; (b) 500 V s^{-1}, electrode 25-μm radius, 0.5 M Bu_4NClO_4; (c) 1000 V s^{-1}, electrode 5-μm radius, 1.0 M Bu_4NClO_4; (d) 2000 V s^{-1}, electrode 5-μm radius, 1.0 M Bu_4NClO_4.

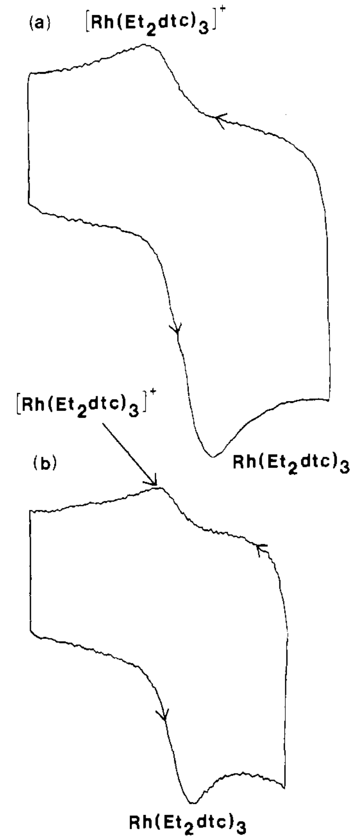

Figure 3. Cyclic voltammograms at a platinum microelectrode in dichloromethane at 20 °C for the oxidation of $Rh(Et_2dtc)_3$: (a) 10^{-2} M, scan rate 5000 V s^{-1}, electrode 5-μm radius, 1.0 M Bu_4NClO_4; (b) 10^{-3} M, scan rate 500 mV s^{-1}, electrode 25-μm radius, 0.5 M Bu_4NClO_4.

Oxidation controlled-potential electrolysis of the orange $Rh(Et_2dsc)_3$ at +0.95 V vs Ag/AgCl at a platinum electrode occurs with the transfer of 1.0 ± 0.1 electron/molecule. Cyclic voltammograms after electorlysis show no wave for the oxidation of $Rh(Et_2dsc)_3$, but the second wave at approximately 1.1 V vs Ag/AgCl remains. Thus the oxidative behavior of $Rh(Et_2dsc)_3$ at platinum electrodes is entirely analogous to that of $Rh(Et_2dtc)_3$ apart from the shift in potential.

Oxidative Processes at Mercury Electrodes. Electrochemical oxidation in the presence of $Rh(RR'dtc)_3$ complexes at mercury electrodes in dichloromethane occurs at potentials very different from those at platinum electrodes. In cyclic voltammograms at a hanging mercury drop electrode, the number of waves and their shape, size, and degree of reversibility all vary depending on the dithiocarbamate ligand. The oxidation process at the dropping mercury electrode is very complicated, and the characteristics of the dc waves also vary considerably between the compounds. Adsorption effects preclude accurate $E_{1/2}$ values (half-wave potentials) being obtained from dc polarograms, but E_p values (peak potentials) from differential-pulse polarograms are summarized in Table I.

Oxidative controlled-potential electrolysis of a dichloromethane solution containing $Rh(Et_2dtc)_3$ at +0.65 V vs Ag/AgCl at a mercury-pool electrode occurs with the transfer of 0.9 ± 0.2 electron/molecule. Cyclic voltammograms recorded at mercury electrodes after the electrolysis (Figure 4a) show a reduction wave at a very negative potential where $Rh(Et_2dtc)_3$ is reduced (see later), together with several other small reduction waves. The reversible wave at approximately −0.6 V vs Ag/AgCl increases in size if the oxidized solution is allowed to stand. This is the potential for the reversible couple of $Hg(Et_2dtc)_2$ at mercury electrodes,[37,38] and therefore $Hg(Et_2dtc)_2$ is deduced to be an eventual product of the oxidation process associated with $Rh(Et_2dtc)_3$ at mercury electrodes. The reduction process at −1.0

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(37) Bond, A. M.; Colton, R.; Dillon, M. L.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1984**, *23*, 2883.

(38) Bond, A. M.; Colton, R.; Hollenkamp, A. F.; Hoskins, B. F.; McGregor, K. *J. Am. Chem. Soc.* **1987**, *109*, 1969.

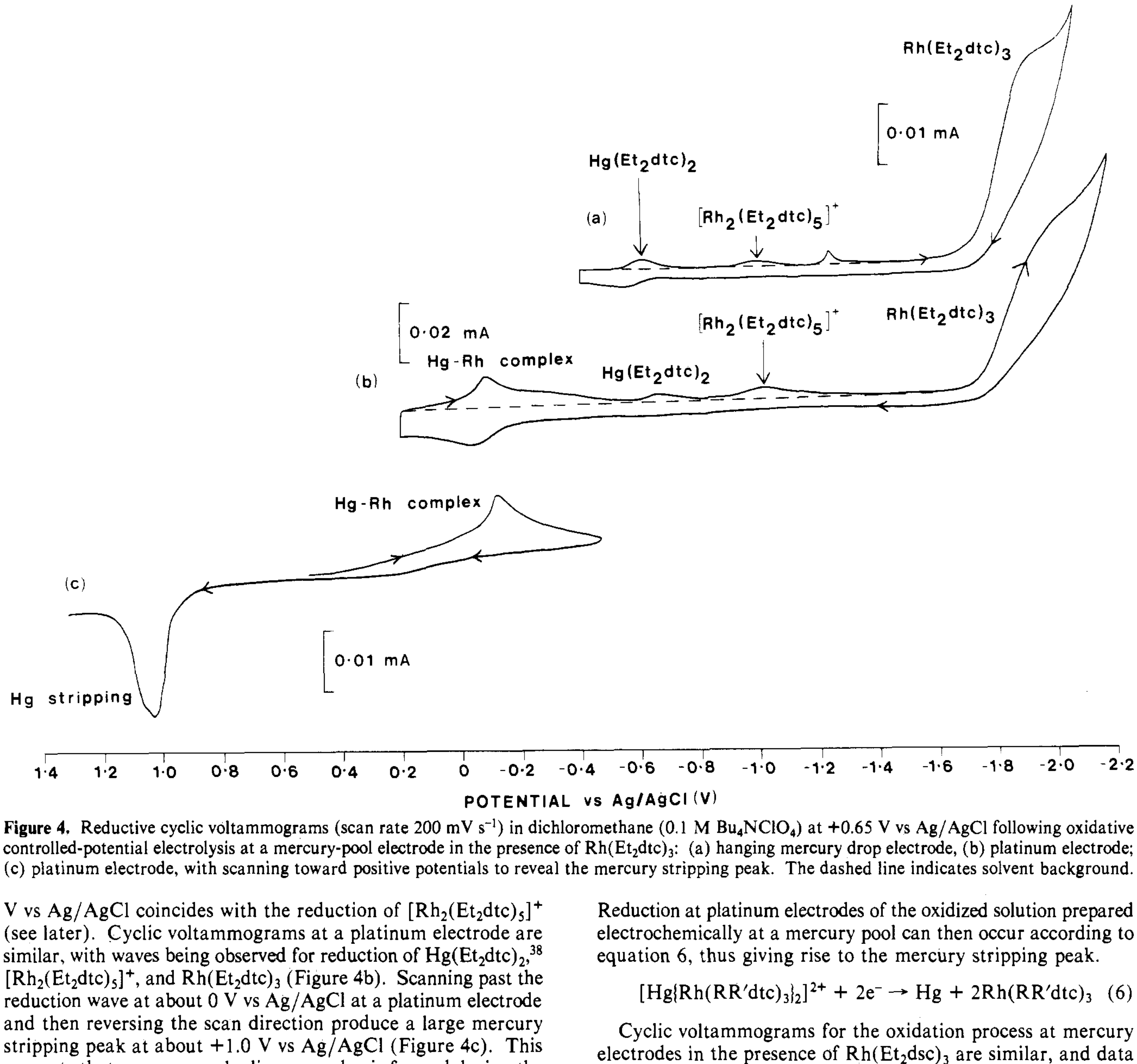

Figure 4. Reductive cyclic voltammograms (scan rate 200 mV s^{-1}) in dichloromethane (0.1 M Bu_4NClO_4) at +0.65 V vs Ag/AgCl following oxidative controlled-potential electrolysis at a mercury-pool electrode in the presence of $Rh(Et_2dtc)_3$: (a) hanging mercury drop electrode, (b) platinum electrode; (c) platinum electrode, with scanning toward positive potentials to reveal the mercury stripping peak. The dashed line indicates solvent background.

V vs Ag/AgCl coincides with the reduction of $[Rh_2(Et_2dtc)_5]^+$ (see later). Cyclic voltammograms at a platinum electrode are similar, with waves being observed for reduction of $Hg(Et_2dtc)_2$,[38] $[Rh_2(Et_2dtc)_5]^+$, and $Rh(Et_2dtc)_3$ (Figure 4b). Scanning past the reduction wave at about 0 V vs Ag/AgCl at a platinum electrode and then reversing the scan direction produce a large mercury stripping peak at about +1.0 V vs Ag/AgCl (Figure 4c). This suggests that a mercury–rhodium complex is formed during the oxidative electrolysis at a mercury electrode that is reduced at 0 V vs Ag/AgCl, resulting in elemental mercury being plated onto the platinum electrode. That is, the oxidation process at a mercury electrode involves oxidation of the mercury rather than oxidation of $Rh(RR'dtc)_3$. Support for this suggestion is provided by the interaction of mercury(I) perchlorate and $Rh(Et_2dtc)_3$ in dichloromethane, which produces elemental mercury and a solution whose cyclic voltammograms are similar to those of the electrochemically oxidized (at mercury) solution of $Rh(Et_2dtc)_3$.

Reductive controlled-potential electrolysis at −0.30 V vs Ag/AgCl at a platinum electrode after oxidation of $Rh(Et_2dtc)_3$ at a mercury-pool electrode corresponds approximately to a one-electron process. Cyclic voltammograms after this experiment show that $Rh(Et_2dtc)_3$ is partially regenerated. All of the above data suggest that a mercury–rhodium complex is formed from the oxidation process observed at a mercury electrode. Unfortunately, the mercury–rhodium complex is too unstable to allow its isolation and complete characterization. An equation consistent with the oxidation process observed at mercury electrodes is

$$2Rh(RR'dtc)_3 + Hg \rightleftharpoons [Hg\{Rh(RR'dtc)_3\}_2]^{2+} + 2e^- \quad (4)$$

The chemical reaction with mercury(I) is consistent with the process

$$2Rh(RR'dtc)_3 + Hg_2^{2+} \rightleftharpoons [Hg\{Rh(RR'dtc)_3\}_2]^{2+} + Hg \quad (5)$$

Reduction at platinum electrodes of the oxidized solution prepared electrochemically at a mercury pool can then occur according to equation 6, thus giving rise to the mercury stripping peak.

$$[Hg\{Rh(RR'dtc)_3\}_2]^{2+} + 2e^- \rightarrow Hg + 2Rh(RR'dtc)_3 \quad (6)$$

Cyclic voltammograms for the oxidation process at mercury electrodes in the presence of $Rh(Et_2dsc)_3$ are similar, and data are summarized in Table I. The oxidation process occurs at a less positive potential than is the case for the $Rh(RR'dtc)_3$ compound.

Reduction at Platinum Electrodes. Electrochemical reduction of $Rh(RR'dtc)_3$ complexes in dichloromethane at platinum electrodes shows a single irreversible process over the temperature range +20 to −78 °C. On the reverse scans the cyclic voltammograms show oxidation waves due to oxidation of released dithiocarbamate ligand to form thiuram disulfides.[25] The close proximity of the wave to the solvent reduction limit makes it difficult to measure $Rh(RR'dtc)_3$ reduction peak potentials accurately, but approximate values are given in Table I. The proximity of the solvent limit also makes it difficult to perform quantitative controlled-potential electrolysis, so the number of electrons involved in the process cannot be determined by this method. Consideration of the usual oxidation states of rhodium suggests this is a two-electron-reduction process with $[Rh(dtc)_2]^-$ being the likely product.[25,35,36]

$$Rh(RR'dtc)_3 + 2e^- \rightarrow [Rh(RR'dtc)_2]^- + [RR'dtc]^- \quad (7)$$

Reduction of $Rh(Et_2dsc)_3$ occurs at a potential similar to that of its dithiocarbamate analogue (Table I). Since the reduction processes are irreversible, the potentials have no thermodynamic significance, but it is still surprising that the reduction potentials are similar while the oxidation potentials differ by about 300 mV.

Table II. Cyclic Voltammetric Data[a] for Oxidation and Reduction of $[Rh_2(RR'dtc)_5]^+$ and $[Rh_2(Et_2dsc)_5]^+$ in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C at a Platinum Electrode

$[Rh_2(RR'dtc)_5]^+$		oxidation	reduction	
R	R'	E_p^{ox},[b,c] V	E_p^{red},[b] V	
Me	Me	1.60	−0.97	−2.04[d]
Et	Et	1.60	−1.03	−2.11[d]
i-Pr	*i*-Pr	1.50	−1.32	−2.23[d]
morph		1.64	−0.90	−2.02[d]
pyrr		1.56	−1.02	−2.04[d]
$[Rh_2(Et_2dsc)_5]^+$		1.09	−1.19	−2.13[d]

[a] Scan rate 200 mV s^{-1}. [b] V vs Ag/AgCl. [c] Values only approximate due to the close proximity of the solvent oxidation limit. [d] These peaks are due to reduction of $Rh(RR'dtc)_3$ or $Rh(RR'dsc)_3$ formed at the electrode surface.

Reduction at Mercury Electrodes. Electrochemical reductions of $Rh(RR'dtc)_3$ complexes in dichloromethane at mercury electrodes occur at slightly less negative potentials than those at platinum electrodes, but the processes are in general similar to those observed at platinum electrodes, implying that mercury does not participate in the reduction process. Reduction potentials are given in Table I. Results for $Rh(RR'dtc)_3$ reduction at mercury electrodes appear to be solvent dependent with two waves being reported in dimethylformamide,[26b] where $Rh(RR'dtc)_2$ is proposed as a stable intermediate.

Cyclic voltammograms for reduction of $Rh(RR'dtc)_3$ in dichloromethane at a hanging mercury drop electrode show a new chemically reversible process on second and subsequent scans at approximately −0.6 V vs Ag/AgCl, which corresponds to the processes[37]

$$2[RR'dtc]^- + 2Hg \rightleftharpoons 2Hg(RR'dtc) + 2e^- \qquad (8)$$

$$2Hg(RR'dtc) \rightleftharpoons Hg(RR'dtc)_2 + Hg \qquad (9)$$

This result confirms that dithiocarbamate ligand is released in the reduction process for $Rh(RR'dtc)_3$ at both mercury and platinum electrodes. Reduction of $Rh(Et_2dsc)_3$ at a mercury electrode is generally similar to that described for $Rh(RR'dtc)_3$.

B. $[Rh_2(RR'dtc)_5]^+$. Oxidation at Platinum Electrodes. $[Rh_2(Et_2dtc)_5]BF_4$ was isolated as a pure solid, but the other $[Rh_2(RR'dtc)_5]^+$ cations and $[Rh_2(Et_2dsc)_5]^+$ were generated in solution by controlled-potential electrolysis and their electrochemistry investigated directly on these solutions.

Electrochemical oxidation of $[Rh_2(RR'dtc)_5]^+$ in dichloromethane at platinum electrodes occurs near the solvent limit and is chemically irreversible at room temperature. The waves remain irreversible at −78 °C with the exception of that for $[Rh_2(i\text{-}Pr_2dtc)_5]^+$, which is partially reversible at −78 °C at a scan rate of 500 mV s^{-1}. The product of oxidation can therefore be assumed to be the unstable complex $[Rh_2(RR'dtc)_5]^{2+}$. $[Rh_2(Et_2dtc)_5]^+$ is oxidized at a potential approximately 500 mV more positive than that for $Rh(Et_2dtc)_3$. Table II summarizes the electrochemical data for $[Rh_2(RR'dtc)_5]^+$ complexes at platinum electrodes. $[Rh_2(Et_2dsc)_5]^+$ behaves similarly and is oxidized irreversibly at a potential approximately 500 mV less positive than that required to oxidize $[Rh_2(Et_2dtc)_5]^+$.

Oxidation Processes at Mercury Electrodes. No oxidation waves were observed at mercury electrodes in the presence of $[Rh_2(RR'dtc)_5]^+$ or $[Rh_2(Et_2dsc)_5]^+$ before the normal onset of the oxidation of the mercury electrode.

Reduction at Platinum Electrodes. Reduction of $[Rh_2(RR'dtc)_5]^+$ is characterized by two reduction steps. The first is at about −1.0 V vs Ag/AgCl, and the second at more negative potentials has peak potentials and characteristics similar to those described earlier for the reduction of $Rh(RR'dtc)_3$. Providing that the first reduction wave is included in the scan, reverse scans show the oxidation wave for $Rh(RR'dtc)_3$, thus confirming that $Rh(RR'dtc)_3$ is rapidly released after reduction of $[Rh_2(RR'dtc)_5]^+$. $[Rh_2(Et_2dsc)_5]^+$ behaves similarly, and data are given in Table II.

Reduction at Mercury Electrodes. Reductions of $[Rh_2(RR'dtc)_5]^+$ and $[Rh_2(Et_2dsc)_5]^+$ in dichloromethane are more complex at a mercury electrode than at platinum. The two waves that appear at platinum are apparent in the cyclic voltammograms at mercury together with other smaller responses which are due to adsorption and exchange reactions with the mercury electrode. The first reduction process for $[Rh_2(RR'dtc)_5]^+$ on a long time scale experiment at both mercury and platinum electrodes is likely to occur as in eq 10, with the unstable $Rh(RR'dtc)_2$ being formed on the shorter time scale.

$$[Rh_2(RR'dtc)_5]^+ + 2e^- \rightarrow Rh(RR'dtc)_3 + [Rh(RR'dtc)_2]^- \qquad (10)$$

Conclusions

In general terms, the oxidation processes of $Rh(RR'dtc)_3$ and $Rh(RR'dsc)_3$ complexes at a platinum electrode are similar to the previously reported oxidations of their cobalt analogues, although surprisingly rhodium(IV) dithiocarbamates are less stable than their cobalt analogues. This work proves conclusively that both chemical and electrochemical oxidations of $Rh(RR'dtc)_3$ produce $[Rh_2(RR'dtc)_5]^+$ as the only stable product, and the claimed isolation[15] of Rh(IV) compounds of the $[Rh(RR'dtc)_3]^+$ cation in the solid state cannot be substantiated. Reduction processes for both $Rh(RR'dtc)_3$ and $Co(RR'dtc)_3$ also are related in the sense that loss of ligand occurs in both cases. However, reduction processes are very solvent dependent. This work also illustrates the power of very fast cyclic voltammetry in the study of fast chemical reactions following electron transfer.

Registry No. $Rh(Me_2dtc)_3$, 33991-55-8; $Rh(Et_2dtc)_3$, 31656-14-1; $Rh(i\text{-}Pr_2dtc)_3$, 107311-51-3; $Rh(Et_2dsc)_3$, 19497-07-5; $[Rh_2(Et_2dtc)_5]^+$, 117469-89-3; CH_2Cl_2, 75-09-2; $[Rh_2(Me_2dtc)_5]^+$, 59109-45-4; $[Rh_2(i\text{-}Pr_2dtc)_5]^+$, 117497-42-4; $[Rh_2(Et_2dsc)_5]^+$, 117497-43-5; $[Hg\{Rh(Me_2dtc)_3\}_2]^{2+}$, 117469-93-9; $[Hg\{Rh(Et_2dtc)_3\}_2]^{2+}$, 117497-44-6; $[Hg\{Rh(i\text{-}Pr_2dtc)_3\}_2]^{2+}$, 117469-94-0; $[Rh(Me_2dtc)_2]^-$, 117469-90-6; $[Rh(Et_2dtc)_2]^-$, 117469-91-7; $[Rh(i\text{-}Pr_2dtc)_2]^-$, 117469-92-8; $[Me_2dtc]^-$, 7234-39-1; $[Et_2dtc]^-$, 392-74-5; $[i\text{-}Pr_2dtc]^-$, 22296-17-9; Pt, 7440-06-4; Hg, 7439-97-6.