problem due to the influence of TIP in opposition to σ withdrawal. The net effect can be changed simply by methylation at N-1 for the C-4 resonance, whereas the C-2 resonance always is shifted downfield. This is not always true for pyridines and pyrazines at adjacent positions.

The 2,5-dimethylimidazole ligand coordinates with only the C-2 position in the hindered orientation as a matter of necessity for Co(III) and Ru(II). The Ru(III) complex, obtained an oxidation of the parent $(NH_3)_5RuL^{2+}$ species, displays LMCT spectra which may be related to the HOMO's of imidazole rings. The imidazolato form seems to have altered the energies of the n and π_2 orbitals sufficiently that three bands are detected for the n, π_2, and π_1 to π_d transitions. The near-equivalence of n and π_2 for less substituted imidazoles has not produced splitting of n and π_2 previously.

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Registry No. $[(NH_3)_5CoOH_2](ClO_4)_3$, 13820-81-0; $(NH_3)_5Co(Me_2SO)^{3+}$, 44915-85-7; $[(NH_3)_5CoCl]Cl_2$, 13859-51-3; $[(NH_3)_5RhCl]Cl_2$, 13820-95-6; $[(NH_3)_5IrCl]Cl_2$, 15742-38-8; $[(NH_3)_5Co^{III}O_3SCF_3](O_3SCF_3)_2$, 75522-50-8; $[(NH_3)_5Rh^{III}O_3SCF_3](O_3SCF_3)_2$, 84254-57-9; $[(NH_3)_5Ir^{III}O_3SCF_3](O_3SCF_3)_2$, 84254-59-1; $(NH_3)_5Co^{III}(imH)^{3+}$, 38716-02-8; $(NH_3)_5Rh^{III}(imH)^{3+}$, 87571-37-7; $(NH_3)_5Ru^{III}(imH)^{3+}$, 80593-52-8; $(NH_3)_5Ir^{III}(imH)^{3+}$, 87571-40-2; $(NH_3)_5Co^{III}(2\text{-MeimH})^{3+}$, 89955-97-5; $(NH_3)_5Co^{III}(2,5\text{-Me}_2\text{imH})^{3+}$, 89922-03-2; $(NH_3)_5Ru^{III}(2,5\text{-Me}_2\text{imH})^{3+}$, 89922-04-3; $(NH_3)_5Co(5\text{-MeimH})^{3+}$, 89922-05-4; $(NH_3)_5Co(4\text{-MeimH})^{3+}$, 89955-98-6.

Contribution from the Division of Chemical and Physical Sciences,
Deakin University, Victoria 3217, Australia

Influence of Oxygen Insertion on the Electrochemistry of Chromium(III) Dithiocarbamate Complexes

A. M. BOND* and G. G. WALLACE

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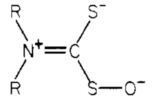
Dithiocarbamate (dtc) complexes of chromium(III) containing oxygen-expanded ligands, odtc, can be synthesized. With pyrrolidine-*N*-carbodithioate ([pdtc]$^-$) as the dithiocarbamate ligand, the electrochemistry of both $Cr(pdtc)_3$ and $Cr(pdtc)_2(opdtc)$ has been examined in detail. On the basis of studies employing cyclic and differential-pulse voltammetry at platinum, gold, and glassy-carbon electrodes in methanol, acetone, acetonitrile, and dichloromethane, it has been shown that the formally chromium(IV) complex, $[Cr(pdtc)_2(opdtc)]^+$, is kinetically more stable than $[Cr(pdtc)_3]^+$. Thermodynamically, the same stability order also applies in the sense that $Cr(pdtc)_2(opdtc)$ is easier to oxidize than $Cr(pdtc)_3$. The enhanced stability is attributed to the increased importance of the resonance form containing a partial positive charge on the nitrogen atom gained by oxygen insertion (i). The related structural form (ii) is frequently associated with stabilization of high-oxidation-state dithiocarbamate complexes. Polarographic reduction of the complexes at mercury electrodes demonstrates that [opdtc]$^-$ is a strongly coordinated ligand since [pdtc]$^-$ is preferentially lost in forming Cr(pdtc)(opdtc). The reduction processes are defined by the following equations: (i) $Cr(pdtc)_2(opdtc) + e^- \rightleftharpoons [Cr(pdtc)_2(opdtc)]^-$; (ii) $[Cr(pdtc)_2(opdtc)]^- \rightarrow Cr(pdtc)(opdtc) + [pdtc]^-$; (iii) $2Cr(pdtc)(opdtc) \rightarrow Cr(pdtc)_2 + Cr(opdtc)_2$; (iv) $Cr(pdtc)_2 + 2e^- \rightarrow Cr(0) + 2[pdtc]^-$; (v) $Cr(opdtc)_2 + 2e^- \rightarrow Cr(0) + 2[opdtc]^-$. Exchange reactions with mercury are also important at mercury electrodes. Other aspects of the redox behavior of $Cr(pdtc)_3$ and $Cr(pdtc)_2(opdtc)$ are also presented as well as a brief report on the redox behavior of the diethyldithiocarbamate analogues.



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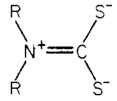

ii

Introduction

Transition-metal dithiocarbamate complexes have been the subject of numerous electrochemical investigations[1-4] because of their ability to exist as stable entities in a wide variety of oxidation states. For example, the electrochemistry of a range of chromium(III) dithiocarbamate complexes $Cr(dtc)_3$ (Figure 1A) has been considered,[5-8] with both oxidation and reduction processes being noted. The products resulting from oxidation of chromium(III) dithiocarbamates have not been isolated, and even though the electrode process is chemically irreversible in most solvents, it has been assumed by simple analogy with other metal dithiocarbamates that a chromium(IV) species $[Cr(dtc)_3]^+$ is produced. Reduction processes also have not been adequately characterized in most studies, although there seems little doubt that a chromium(II) dithiocarbamate is the product of the first reduction step.

Recently a new type of chromium(III) dithiocarbamate (Figure 1B), $Cr(dtc)_2(odtc)$, incorporating chelate-ring expansion by oxygen insertion has been prepared and characterized.[9] In this complex, the chromium is still formally in oxidation state III and resembles other metal dithiolato complexes that have undergone ring expansion by insertion of a sulfur atom.[10,11] Comparison of the electrochemical oxidation of the normal and sulfur-rich complexes[11] was said to lead to more reversible oxidation for the sulfur-rich complexes. Although data presented in the original work actually do not support this conclusion, Fackler has more recently shown that at very fast scan rates, under conditions of cyclic voltammetry,

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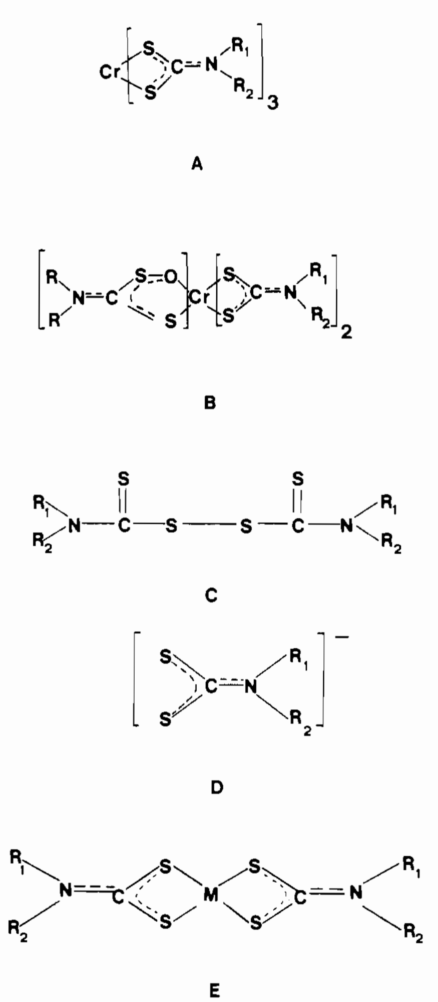

Figure 1. Structures of various complexes used in this work: (A) $Cr(dtc)_3$ (when $R_1 = R_2$ = ethyl, the diethyl complex is referred to as $Cr(dedtc)_3$; when R_1 and R_2 are both derived from the heterocyclic amine pyrrolidine, the complex is referred to as $Cr(pdtc)_3$); (B) $Cr(dtc)_2(odtc)_2$ (nomenclature as in A leads to $Cr(dedtc)_2(odedtc)$ and $Cr(pdtc)_2(opdtc)$); (C) thiuram disulfide (nomenclature as in A leads to dedtc-dedtc and pdtc-pdtc); (D) dithiocarbamate anion (nomenclature as in A leads to $[dedtc]^-$ and $[pdtc]^-$); (E) $M(dtc)_2$ (M = Hg, Cu) (nomenclature as in A leads to $Hg(dedtc)_2$, $Hg(pdtc)_2$, $Cu(dedtc)_2$, and $Cu(pdtc)_2$).

the sulfur-rich species appear to be associated with a more chemically reversible oxidation process,[12] implying that sulfur insertion leads to a greater kinetic stability of products.

In other studies,[13,14] the replacement of sulfur by oxygen coordination has been shown to have both thermodynamic and kinetic consequences.

In this work a detailed investigation of the electrochemistry of both $Cr(pdtc)_3$ and $Cr(pdtc)_2(opdtc)$ has been undertaken where $[pdtc]^-$ is pyrrolidine dithiocarbamate. This ligand should be named as pyrrolidine-*N*-carbodithioate, but we have retained the commonly used name. The electrochemistry has been examined in various solvents and at various working electrodes to assess the effect of the oxygen insertion on redox properties.

Experimental Section

Preparation and Purification of Compounds. (i) $Cr(pdtc)_3$ was prepared in the usual manner.[1-4]

(ii) $Cr(pdtc)_2(opdtc)$ was prepared by reaction of ammonium pyrrolidine dithiocarbamate with $K_2Cr_2O_7$ in the mole ratio 3:1.[9] The green precipitate that formed immediately on mixing of the reagents was filtered off, dried, and dissolved in dichloromethane. It was then purified by chromatography on silica to separate the three reaction products, namely $Cr(pdtc)_3$, $Cr(pdtc)_2(opdtc)$, and the oxidized ligand thiuram disulfide (Figure 1C), pdtc–pdtc.

(iii) $Cr(dedtc)_3$ and (iv) $Cr(dedtc)_2(odedtc)$ were prepared and characterized as for the pyrrolidine dithiocarbamate complexes.

Standard solutions for electrochemical experiments were prepared in (i) acetonitrile (0.1 M Et_4NClO_4 (TEAP)), (ii) acetone (0.1 M TEAP), (iii) methanol (0.05 M TEAP), and (iv) dichloromethane (0.1 M Bu_4NClO_4 (TBAP)).

Mass Spectra of $Cr(pdtc)_3$ and $Cr(pdtc)_2(optdc)$. The mass spectra gave parent – ion peaks consistent with the expected formulations: $Cr(pdtc)_3$, *m/e* 490; $Cr(pdtc)_2(opdtc)$, *m/e* 506. The mass spectral data in addition to analytical data obtained using high-performance liquid chromatography (HPLC) with UV detection (λ = 254 nm) were taken as evidence that both compounds had been prepared in pure form.[15]

Instrumentation

Voltammograms and polarograms were recorded on an EG & G Princeton Applied Research (PAR) Corp. (Princeton, NJ) Model 174A polarographic analyzer. Solid gold, platinum, and glassy-carbon working electrodes were obtained from Metrohm (Herisau, Switzerland). A hanging-mercury-drop electrode, HMDE, was used for cyclic voltammetry at mercury electrodes and a conventional dropping-mercury electrode for DC polarograms. Glassy-carbon auxiliary and a Ag/AgCl (saturated LiCl/acetone) reference electrodes were employed in conjunction with the working electrodes in all voltammetric and polarographic experiments.

Coulometric data in dichloromethane were obtained by using a PAR Model 173 potentiostat/galvanostat in conjunction with a PAR Model 179 digital coulometer. A platinum-gauze working electrode was employed with a platinum auxiliary (separated by a porous Vycor plug from electrolyte solution) and a Ag/AgCl (saturated LiCl/CH_2Cl_2) reference electrode.

The chromatographic equipment used for analytical work and product identification was a Waters Associates (Milford, MA) Model 6000A solvent delivery system used in conjunction with a U6K injector and a Model 450 variable-wavelength detector (λ set at 254 nm). The analytical column employed was a C-18 μ Bondapak column obtained from Waters (length 30 cm, i.d. = 3.9 mm). A solution consisting of 70% acetonitrile/30% acetate buffer (0.02 M, pH 5.8) effects separation of $Cr(pdtc)_3$, $Cr(pdtc)_2(opdtc)$, and pdtc-pdtc on this column. The preparative column used was packed with silica resin (Spherisorb SGP) from Phase Separation Ltd. (Clwyd, U.K.) (particle size 8 μm, length 23 cm, internal diameter (i.d.) 1 cm). The solvent used to dissolve the prepared mixture and subsequently separate it on the column was CH_2Cl_2 (0.01% CH_3OH).

Unless otherwise stated, experiments were performed at 22 ± 1 °C. All solutions were degassed with nitrogen prior to electrochemical experiments.

Mass spectra were obtained with a Finnigan 3000 series gas chromatography/mass spectrometer.

Results and Discussion

(A) Electrochemical Reduction and Oxidation of $Cr(pdtc)_3$. Electrochemical data from cyclic voltammetric experiments are summarized in Table I while Table II contains polarographic data in dichloromethane.

(1) Oxidation. $Cr(pdtc)_3$ is oxidized at considerably more positive potentials than many other metal dithiocarbamates.[1-4] The product is therefore likely to be reactive. At platinum, glassy-carbon, and gold solid electrodes one oxidation response is observed under conditions of cyclic voltammetry in methanol, acetone, acetonitrile, and dichloromethane. The oxidation process shows no sign of chemical reversibility, under conditions of cyclic voltammetry at scan rates $\leq$500 mV s^{-1}, in the more polar solvents (methanol, acetonitrile). However, a reduction process on the reverse sweep is observed as the

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Table I. Cyclic Voltammetric Data for Oxidation and Reduction of 3×10^{-4} M $Cr(pdtc)_3$ in Various Solvents[a]

	oxidn								redn							
	gold		platinum		glassy carbon		mercury		gold		platinum		glassy carbon		mercury	
solvent	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}
dichloromethane	+1.01	+0.91	+1.03	+0.91	+1.00	+0.90	+0.54	+0.48	−1.76	*c*	−1.80	*c*	−1.82	*c*	−0.70	−0.56
							+0.75	+0.60							−1.62	−1.44
acetone	+1.02	+0.94[b]	+1.04	+0.90[b]	+1.02	+0.92[b]	+0.58	+0.50		+0.26		+0.26		+0.35	−2.12	*c*
							+0.68	+0.62	−1.43	*c*	−1.52	*c*	−1.56	−1.40[b]	−0.52	−0.44
															−1.40	−1.33
acetonitrile	+1.05	*c*	+1.05	*c*	+1.02	*c*	+0.46	+0.40		+0.24		+0.24		+0.30	*e*	*c*
							+0.62	+0.56	−1.48	*c*	−1.52	*c*	−1.44	*c*	−0.60	−0.52
															−1.40	−1.34
methanol	+0.98	*c*	+0.99	*c*	+0.97	*c*	+0.36	+0.29		+0.20		+0.22		+0.28	*e*	*c*
									d	*d*	*d*	*d*	−1.20	*c*	−0.40	−0.28
															−1.20	*c*
														+0.28	*d*	

[a] Conditions: 22 °C, scan rate 200 mV s^{-1}. E_p^{ox} = oxidation peak potential (V vs. Ag/AgCl (saturated LiCl/acetone)); E_p^{red} = reduction peak potential (V vs. Ag/AgCl (saturated LiCl/acetone)). [b] Ratio of oxidation to reduction currents not unity, implying process not chemically reversible under specified conditions. [c] No current observed on reverse scan, implying electrode process is chemically irreversible. [d] No response observed due to limited negative potential range available in methanol. [e] Third process observed at apparoximately −2.0 V, best characterized in dichloromethane.

Table II. Polarographic $E_{1/2}$ Values for Oxidation and Reduction of Chromium Complexes in Dichloromethane[a]

	$E_{1/2}$, V vs. Ag/AgCl				
			redn		
compd	oxidn		I	II	III
$Cr(pdtc)_3$	+0.48	+0.64	−0.66	−1.56	−1.96
$Cr(pdtc)_2(opdtc)$	*b*	*b*	−0.66	−1.56	−1.86, −1.96

[a] Conditions: 22 °C, drop time 0.5 s. [b] Unresolved responses covering the potential range +0.40–+0.70 V.

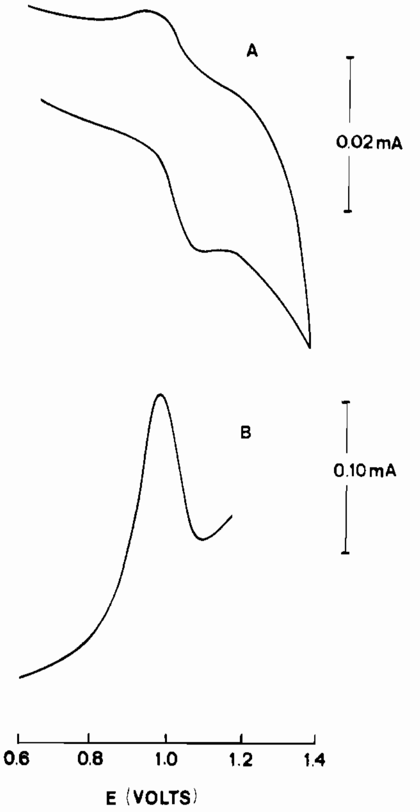

Figure 2. Oxidation of 2×10^{-4} M $Cr(pdtc)_3$ in dichloromethane (0.1 M TBAP) at 22 °C at a glassy-carbon electrode: (A) cyclic voltammogram with a scan rate of 200 mV s^{-1}; (B) differential-pulse voltammetry with a pulse amplitude of 100 mV and duration between pulses of 0.5 s.

solvent polarity decreases (Figure 2A). At low temperatures or fast scan rates in dichloromethane a chemically reversible response is found, which is consistent with the formation of $[Cr(pdtc)_3]^+$ (eq 1) at the electrode surface. That is, a

$$Cr(pdtc)_3 \rightleftharpoons [Cr(pdtc)_3]^+ + e^- \qquad (1)$$

chemically reversible oxidation process can be observed with short time scale experiments in inert solvents where insufficient time is available for decomposition of the formally chromium(IV) cation. Differential-pulse voltammograms show a well-defined response for the oxidation of $Cr(pdtc)_3$ at all solid electrodes (Figure 2B). This response corresponds to the process observed under conditions of cyclic voltammetry. In methanol, under conditions of differential-pulse voltammetry, an additional oxidation wave is observed at more positive potentials than for oxidation of $Cr(pdtc)_3$. $Cr(pdtc)_3$ is relatively insoluble in methanol, and the substantially increased analytical sensitivity of the differential-pulse method relative to cyclic voltammetry accounts for the lack of observation with cyclic voltammetry. The second response appears to correspond to oxidation of the dimer, pdtc-pdtc (Figure 1C), since this response increases when the solution is spiked with an

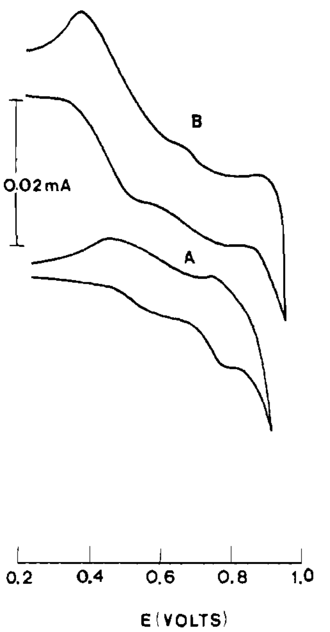

Figure 3. Cyclic voltammograms at a scan rate of 200 mV s^{-1} showing oxidation responses at the hanging-mercury-drop electrode in CH_2Cl_2 (0.1 M TBAP) at 22 °C: (A) 7×10^{-4} M $Cr(pdtc)_3$; (B) 7×10^{-4} M $Cr(pdtc)_2(opdtc)$.

authentic sample of pdtc-pdtc. Any $[pdtc]^-$ (Figure 1D) released at the electrode surface would be immediately oxidized to the dimer at the potential where $Cr(pdtc)_3$ is oxidized. The stability of $[Cr(pdtc)_3]^+$ in coordinating solvents such as methanol is markedly less than in noncoordinating solvents such as CH_2Cl_2 so a reasonable postulate is that reactions of the kind

$$Cr(pdtc)_3 \rightleftharpoons [Cr(pdtc)_3]^+ + e^- \quad (2)$$

$$[Cr(pdtc)_3]^+ + xMeOH \rightarrow [Cr(pdtc)_{3-x}(MeOH)_x]^{(1+x)+} + x[pdtc]^- \quad (3)$$

$$[Cr(pdtc)_{3-x}(MeOH)_x]^{(1+x)+} \rightarrow product(s) \quad (4)$$

$$2[pdtc]^- \rightarrow pdtc\text{-}pdtc + 2e^- \quad (5)$$

may occur. However, $[pdtc]^-$ is itself not completely stable in methanol under the conditions of the electrochemical experiment so the origin of the dimer is not entirely certain.

Two oxidation processes (Figure 3) are observed with cyclic voltammetry at the HMDE or DC polarograms at the DME, but at very different potentials to any of the responses at platinum, glassy-carbon, or gold electrodes (Table I), implying that this response may involve mercury compound formation and/or mercury exchange. This suggestion is supported by the fact that the complex $Hg(pdtc)_2$ (Figure 1E) also gives two oxidation responses at similar potentials[16] as found with $Cr(dtc)_3$. The process

$$2Cr(pdtc)_3 + Hg \rightleftharpoons Hg(pdtc)_2 + 2Cr(pdtc)_2 \quad (6)$$

would therefore appear to be important at the electrode surface. This is also confirmed by reduction studies as described later.

(2) Reduction. Under the experimental conditions specified in Table I and with a concentration of 3×10^{-4} M, reduction data at solid electrodes are consistent with a chemically irreversible reduction in all solvents, with one exception. At a glassy-carbon electrode and in acetone, an oxidative current response on the reverse scan of the cyclic voltammogram is evident as shown in Figure 4. Presumably, surface attachment of the $[Cr(pdtc)_3]^-$ complex occurs at this electrode surface in acetone, leading to stabilization of the product. Glassy-carbon electrodes can have functional groups on the surface, giving rise to chemically modified pathways.[17] At greater concentrations of the $Cr(pdtc)_3$ complex ($>10^{-3}$ M) signs of chemical reversibility are also indicated, particularly in CH_2Cl_2, implying that the breakdown of $[Cr(pdtc)_3]^-$ is catalyzed by the presence of low concentrations of water, oxygen, or other impurity. A response corresponding to free ligand oxidation ($2[pdtc]^- \rightarrow pdtc\text{-}pdtc + 2e^-$) was observed on the reverse scan of the cyclic voltammograms for the chemically irreversible reduction process (Figure 5), indicating that a ligand is released on reduction of the complex. This is the response noted at about 0.25 V in Table I. The electrode process at solid electrodes is therefore readily defined by eq 7 and 8 at other solid electrodes in dichloromethane, acetone, and acetonitrile, with the reaction 8 subject to catalysis by water.

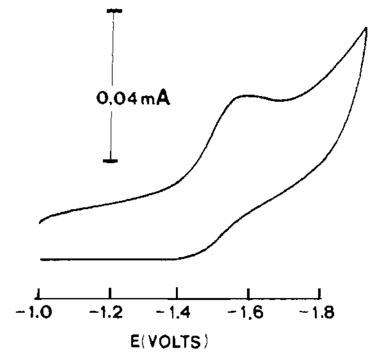

Figure 4. Reduction of 7×10^{-4} M $Cr(pdtc)_3$ in acetone (0.1 M TEAP) at a glassy-carbon electrode at 22 °C using cyclic voltammetry with a scan rate of 200 mV s^{-1}.

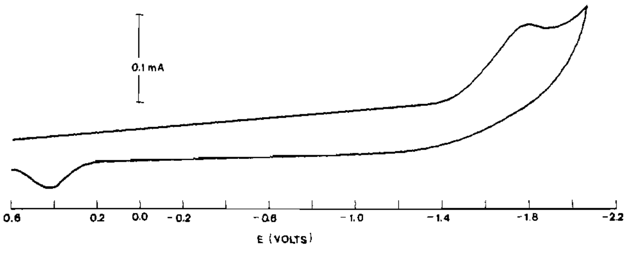

Figure 5. Reduction of 10^{-3} M $Cr(pdtc)_3$ in CH_2Cl_2 (0.1 M TBAP) at a glassy-carbon electrode at 22 °C using cyclic voltammetry with a scan rate of 500 mV s^{-1}.

$$Cr(pdtc)_3 + e^- \rightleftharpoons [Cr(pdtc)_3]^- \quad (7)$$

$$[Cr(pdtc)_3]^- \rightarrow Cr(pdtc)_2 + [pdtc]^- \quad (8)$$

At a hanging-mercury-drop electrode, three major reduction responses are observed (Figure 6). Figure 7 is a dc polarogram of $Cr(pdtc)_3$ in dichloromethane again showing three reduction steps. The first reduction response (least negative) is chemically irreversible in all solvents, under conditions of cyclic voltammetry with a scan rate of 500 mV s^{-1} at a HMDE. Plots of drop time of a DME vs. potential, under gravity-controlled conditions indicate a substantial degree of adsorption is associated with the electrode processes at mercury electrodes over a wide potential range. The degree of chemical reversibility of the second wave is increased with decreasing solvent polarity, showing that $[Cr(pdtc)_3]^-$ has some stability at mercury electrodes (adsorption stabilized) that is similar to the stabilization at glassy-carbon electrodes in acetone noted above. Under differential-pulse polarographic conditions, the

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[16] Bond, A. M.; Colton, R.; Dillon, M.; Moir, J.; Page, D. *Inorg. Chem.*, in press.

[17] Anderson, C. W.; Lung, K. R. *J. Electrochem. Soc.* **1982**, *129*, 2505 and references cited therein.

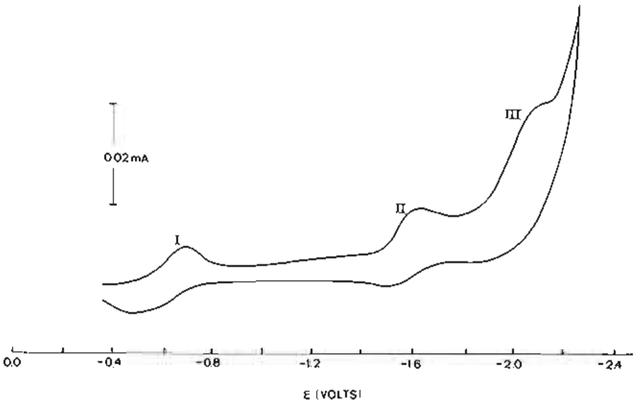

Figure 6. Reduction of 5×10^{-4} M $Cr(pdtc)_3$ in CH_2Cl_2 (0.1 M TBAP) at a hanging-mercury-drop electrode using cyclic voltammetry with a scan rate of 200 mV s^{-1}.

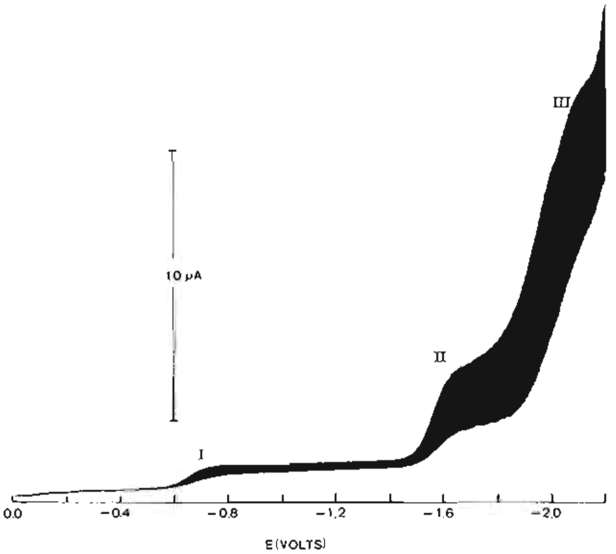

Figure 7. Dc polarogram for reduction of 8×10^{-4} M $Cr(pdtc)_3$ in CH_2Cl_2 (0.1 M TBAP) at 22 °C using a drop time of 0.5 s.

first (least negative) response increases on addition of free ligand $[pdtc]^-$ or $Hg(pdtc)_2$ to the solution. However, as comparison of Figures 8 and 9 show, the response of $Cr(pdtc)_3$ and $Hg(pdtc)_2$ are not identical, indicating that this response is due to ligand exchange between chromium and mercury with subsequent reduction of $Hg(pdtc)_2$ and not from free $Hg(pdtc)_2$ in solution.

Equations 9 and 10 omit complexities arising from other

$$Hg + 2Cr(pdtc)_3 \rightleftharpoons Hg(pdtc)_2 + 2Cr(pdtc)_2 \qquad (9)$$

$$Hg(pdtc)_2 + 2e^- \rightleftharpoons Hg + 2[pdtc]^- \qquad (10)$$

exchange and redox cross-sections that are thermodynamically allowed and presumably occur. Equation 10 is written in its simplest overall form. Undoubtedly this reduction proceeds through mercury (I) intermediates.[18] The polarography of iodate in the presence of $[dtc]^-$ occurs in a similar fashion.[19]

$$IO_3^- + 3Hg + 6[dtc]^- + 6H^+ \rightleftharpoons 3Hg(dtc)_2 + I^- + 3H_2O \qquad (11)$$

$$Hg(dtc)_2 + 2e^- \rightleftharpoons Hg + 2[dtc]^- \qquad (12)$$

The two responses occurring at more negative potentials on mercury electrodes can be ascribed to reduction of the metal center in the $Cr(pdtc)_3$ complex to generate a chromium(II) complex and elemental chromium, respectively.

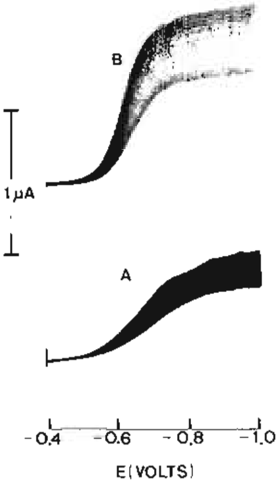

Figure 8. Dc polarogram for first reduction process of $Cr(pdtc)_3$ (A) and reduction of $Hg(pdtc)_2$ (B) in CH_2Cl_2 (0.1 M TBAP) at 22 °C using a drop time of 0.5 s.

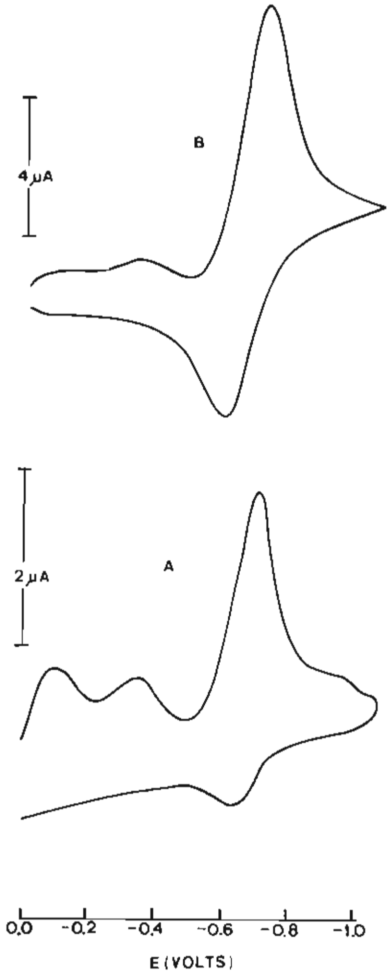

Figure 9. Cyclic voltammograms for first reduction process of $Cr(pdtc)_3$ (A) and reduction of $Hg(pdtc)_2$ (B) in CH_2Cl_2 (0.1 M TBAP) at 22 °C using a scan rate of 500 mV s^{-1}.

$$Cr(pdtc)_3 + e^- \rightleftharpoons [Cr(pdtc)_3]^- \qquad (13a)$$

$$[Cr(pdtc)_3]^- \rightarrow Cr(pdtc)_2 + [pdtc]^- \qquad (13b)$$

$$Cr(pdtc)_2 + 2e^- \rightarrow Cr(0) + 2[pdtc]^- \qquad (14)$$

The magnitude of the process described by the reverse of eq 10 progressively increases in cyclic voltammograms as the

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[18] Bond, A. M.; Casey, A. T.; Thackeray, J. R. *Inorg. Chem.* **1974**, *13*, 84.

[19] Toropova, V. F.; Polyakov, Yu. N.; Movchan, N. I. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **1979**, *22*, 302; *Chem. Abstr.* **1979**, *91*, 32424*m*.

potential is switched to potentials more negative than the $E_{1/2}$ values of the second and third processes, respectively, confirming that ligand is lost on reduction as per eq 13b and 14.

(3) Controlled-Potential Oxidative Electrolysis at Platinum Electrodes in Dichloromethane. Electrolysis of a 5 × 10^{-4} M $Cr(pdtc)_3$ solution in dichloromethane was carried out at +1.20 V vs. Ag/AgCl by using a platinum working electrode. During the course of the electrolysis, the solution lost its characteristic blue color and became clear. Cyclic voltammograms were recorded before and after exhaustive oxidation of the $Cr(pdtc)_3$ solution. The oxidation and reduction reponses observed prior to electrolysis disappeared, and no electrochemical responses were observed at the end of the electrolysis. Injection of the oxidized solution into an analytical HPLC system with spectrophotometric detection, which can separate and detect $[pdtc]^-$, pdtc-pdtc, or $Cr(pdtc)_3$, gave negative results for these possible products. Oxidation of $Cr(pdtc)_3$ gave an *n* value of 5 ± 1 electrons/mol, indicating a multiple electron process possibly involving the oxidation of $[pdtc]^-$ and/or pdtc-pdtc released after initial formation of $[Cr(pdtc)_3]^+$. At the positive potentials required for oxidation of $Cr(pdtc)_3$, these species are also oxidized so this result would be expected. Our results, implying a multielectron process on the synthetic time scale, are consistent with data in ref 6 but not with that of ref 7 where controlled-potential electrolysis experiments were claimed to give an *n* value equal to 1 electron.

(4) Comparison with Oxidation and Reduction of $Cu(dedtc)_2$. Normal-pulse voltammograms for oxidation or reduction of 5 × 10^{-4} M solutions of either $Cu(dedtc)_2$ (Figure 1E) or $Cr(pdtc)_3$ at the same platinum electrode gave identical limiting currents, within the limit of experimental error, in CH_2Cl_2. Since it has been well established[20] that both the oxidation and reduction of $Cu(dedtc)_2$ are one-electron steps (eq 15 and 16), it can be assumed that both the oxidation and

$$Cu(dedtc)_2 \rightleftharpoons [Cu(dedtc)_2]^+ + e^- \qquad (15)$$

$$Cu(dedtc)_2 + e^- \rightleftharpoons [Cu(dedtc)_2]^- \qquad (16)$$

reduction of the chromium complexes at platinum electrodes are also one-electron steps on the time scale of voltammetric experiments. The longer time scale of controlled-potential electrolysis oxidative experiments are therefore unambiguously demonstrated to involve additional steps.

(B) Electrochemical Oxidation and Reduction of $Cr(pdtc)_2(opdtc)$. Data for reduction and oxidation are summarized in Tables II and III.

(1) Oxidation. The degree of chemical reversibility of the oxidation response for the $Cr(pdtc)_2(opdtc)$ complex is increased significantly in all solvents compared with $Cr(pdtc)_3$. Inclusion of an oxygen atom also affects the thermodynamics in that $E_{1/2}$ ($\approx E°$) for reaction in eq 17 is slightly more positive

$$Cr(pdtc)_2(opdtc) \rightleftharpoons [Cr(pdtc)_2(opdtc)]^+ + e^- \qquad (17)$$

than that for eq 1. In all solvents a second uncharacterized oxidation wave is observed at more positive potentials (Figure 10). It is a broad drawn-out wave that is not always well-defined under conditions of cyclic voltammetry, and the differential-pulse response shows it to be a complicated single process or more likely two unresolved processes. The reduction response at about +0.40 V (Table III) seen on the reverse scan of cyclic voltammograms is attributed to a product of this more positive oxidation process(es). Clearly different reaction pathways occur after formation of $[Cr(pdtc)_2(opdtc)]^+$ than was the case with $[Cr(pdtc)_3]^+$. The uncharacterized processes may involve oxidation of $[Cr(pdtc)_2(opdtc)]^+$ to Cr(V) and/or Cr(VI) complex(es). The presence of an oxygen group is likely to stabilize the higher oxidation states. However, ligand-based oxidation processes cannot be ruled out in view of the known ease of oxidation of this class of ligand.

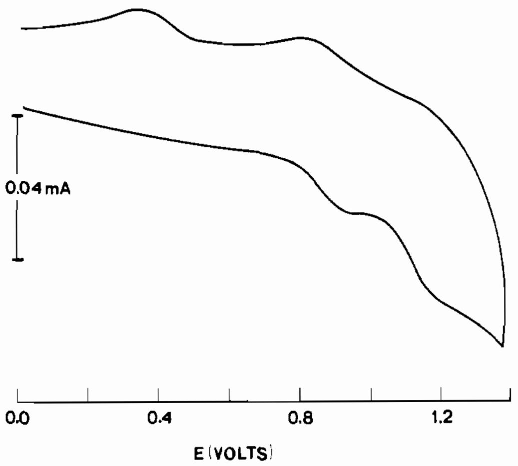

Figure 10. Oxidation of 5 × 10^{-4} M $Cr(pdtc)_2(opdtc)$ in CH_2Cl_2 (0.1 M TBAP) at 22 °C using cyclic voltammetry at a glassy-carbon electrode with a scan rate of 500 mV s^{-1}.

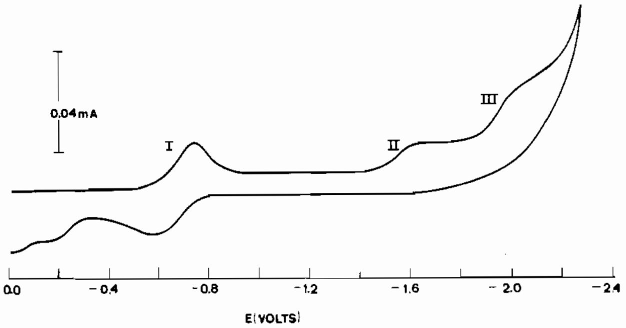

Figure 11. Reduction of 7 × 10^{-4} M $Cr(pdtc)_2(opdtc)$ in CH_2Cl_2 (0.1 M TBAP) at 22 °C using cyclic voltammetry at a hanging-mercury-drop electrode with a scan rate of 500 mV s^{-1}.

Oxidation at Hg under conditions of cyclic voltammetry produces three (unresolved) responses for $Cr(pdtc)_2(opdtc)$. These processes are undoubtedly related to those observed with $Cr(pdtc)_3$. Dc polarograms confirm that these processes correspond to those obtained with $Hg(pdtc)_2$ and that exchange reactions occur as was the case with $Cr(pdtc)_3$ at mercury electrodes. The response implies that an exchange process with mercury produce $Hg(pdtc)_2$, $Hg(opdtc)_2$, and Hg(pdtc)(opdtc) complexes.

(2) Reduction. All reduction responses at solid electrodes are irreversible (in the range of concentrations employed, 10^{-3}–10^{-4} M). Reduction potentials are similar to those of $Cr(pdtc)_3$, and release of ligand on reduction is also observed as evidenced by an oxidation response at potentials expected for oxidation of $[pdtc]^-$ or probably that for the unknown ligand $[opdtc]^-$ on the reverse scan of cyclic voltammograms. The redox behavior of the oxygen-containing ligand is unknown, so that unambiguous identification as to whether the reduction process is

$$Cr(pdtc)_2(opdtc) + e^- \rightarrow Cr(pdtc)_2 + [opdtc]^- \qquad (18)$$

or

$$Cr(pdtc)_2(opdtc) + e^- \rightarrow Cr(pdtc)(opdtc) + [pdtc]^- \qquad (19)$$

or

$$2Cr(pdtc)_2(opdtc) + 2e^- \rightarrow Cr(pdtc)_2 + Cr(opdtc)_2 + 2[pdtc]^- \qquad (20)$$

is not possible from data at platinum electrode. Cyclic voltammograms for reduction of $Cr(pdtc)_2(opdtc)$ (Figure 11) at a mercury electrode are similar to those of $Cr(pdtc)_3$ (Figure

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[20] Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1976**, *15*, 2115.

Table III. Cyclic Voltammetric Data for Oxidation and Reduction of 3 × 10⁻⁴ M $Cr(pdtc)_2(opdtc)$ in Various Solvents[a]

	oxidn								redn							
	gold		platinum		glassy carbon		mercury		gold		platinum		glassy carbon		mercury	
solvent	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}
dichloromethane	+0.90	+0.78	+0.90	+0.80	+0.92	+0.84	+0.56	+0.40	−1.67	*c*	−1.64	*c*	−1.66	*c*	−0.66	−0.50
	+1.20	+0.40	+1.20	+0.40	+1.20	+0.40	+0.70	+0.60							−1.64	*c*
										+0.25		+0.25		+0.35	−2.06	*c*
acetone	+1.00	+0.90	+0.98	+0.90	+1.00	+0.96	+0.52	+0.44	−1.48	*c*	−1.40	*c*	−1.50	*c*	−0.56	−0.60
					+1.19	+0.30	+0.68	+0.62							−1.60	*c*
										+0.24		+0.24		+0.30	*e*	*c*
acetonitrile	+0.97	+0.90	+1.00	+0.90	+1.00	+0.92	+0.46	+0.40	−1.47	*c*	−1.64	*c*	−1.60	*c*	−0.66	−0.60
					+1.24		+0.68	+0.60							−1.46	*c*
										+0.20		+0.20		+0.28	*e*	*c*
methanol	+0.93	*c*	+0.94	*c*	+0.90	*c*	+0.37	+0.29	*d*	*d*	*d*	*d*	−1.56	*c*	−0.47	−0.40
	+1.20	*c*			+1.11	*c*	+0.60	+0.50						+0.30	−1.26	*c*

[a] Conditions and footnotes *c*–*e* same as in Table I.

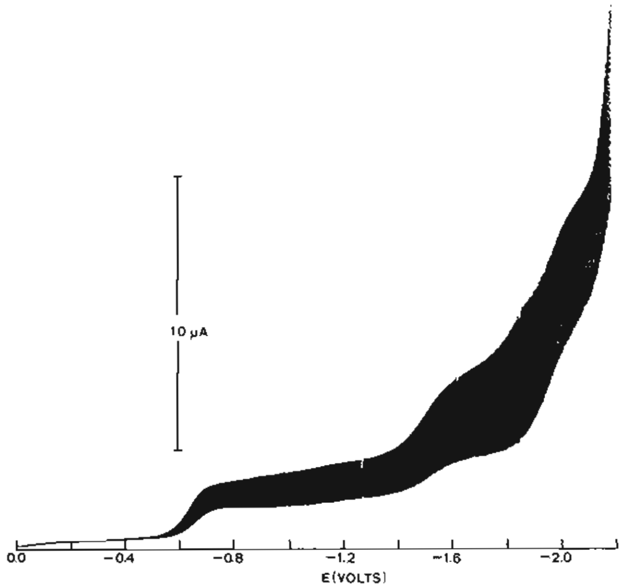


Figure 12. Dc polarogram for reduction of 7 × 10⁻⁴ M $Cr(pdtc)_2(opdtc)$ in CH_2Cl_2 (0.1 M TBAP) at 22 °C using a drop time of 0.5 s.

6). However, dc polarograms (Figures 7 and 12) demonstrate that significant differences apply. Thus, the ratios of wave heights are quite different; the $Cr(III) + e^- \rightarrow Cr(II)$ wave does not become reversible even in the more nonpolar solvents, and the most negative response appears to be split into two processes of equal height. The poloargraphic data are consistent with the hypothesis that, on reduction, $[pdtc]^-$ rather than $[opdtc]^-$ is released and that the kinetically labile chromium(II) mixed-ligand complex thus formed is in equilibrium with an exchange process. That is, the reduction step can be described by eq 21–25.

$$Cr(pdtc)_2(opdtc) + e^- \rightleftharpoons [Cr(pdtc)(opdtc)]^- \quad (21)$$

$$[Cr(pdtc)_2(opdtc)]^- \xrightleftharpoons{\text{fast}} Cr(pdtc)(opdtc) + [pdtc]^- \quad (22)$$

$$2Cr(pdtc)(opdtc) \rightleftharpoons Cr(pdtc)_2 + Cr(opdtc)_2 \quad (23)$$

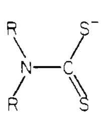
$$Cr(opdtc)_2 + 2e^- \rightarrow Cr(0) + 2[opdtc]^- \quad (24)$$

$$Cr(pdtc)_2 + 2e^- \rightarrow Cr(0) + 2[pdtc]^- \quad (25)$$

(3) Controlled-Potential Oxidative Electrolysis at Platinum Electrodes in Dichloromethane. Controlled-potential oxidative electrolysis was performed under identical conditions as described for $Cr(pdtc)_3$, at a platinum electrode. In dichloromethane, the characteristic green color of the $Cr(pdtc)_2(opdtc)$ solution disappeared during the course of the electrolysis as did the original oxidation and reduction responses on the cyclic voltammograms. None of the previously designated chromium or ligand compounds could be identified as products by cyclic voltammetry or the analytical HPLC system with UV/visible spectrophotometric detection. An *n* value of 2.5 ± 0.5 electrons was obtained as compared to 5 ± 1 electrons for $Cr(pdtc)_3$, confirming the previous suggestion that the reaction pathway for decomposition of $[Cr(pdtc)_2(opdtc)]^+$ is different from that for $[Cr(pdtc)_3]^+$. Normal-pulse voltammetry of $Cr(pdtc)_2(opdtc)$ compared with that of $Cr(dedtc)_2$ produced equivalent limiting currents per unit concentration, again supporting the hypothesis that on the short electrochemical time scale the oxidation process is a one-electron step whereas with longer time experiments multielectron steps are occurring.

Conclusions

Insertion of oxygen into the dithiocarbamate ligand to produce the $Cr(pdtc)_2(opdtc)$ complex significantly alters the kinetics of the electrode processes. Thus, $[Cr(pdtc)_2(opdtc)]^+$, the initial product formed on oxidation of $Cr(pdtc)_2(opdtc)$, is substantially more stable in the kinetic sense than $[Cr(pdtc)_3]^+$, which is derived from $Cr(pdtc)_3$. On electrochemical reduction of $Cr(pdtc)_2(opdtc)$, $[pdtc]^-$ is preferentially released to generate the complex Cr(pdtc)(opdtc), indicating the considerable kinetic stability of $[opdtc]^-$ when coordinated to chromium. Thermodynamically, differences between the $Cr(pdtc)_2(opdtc)$ and $Cr(pdtc)_3$ complexes are not very large with respect to redox potentials. However, $Cr(pdtc)_2(opdtc)$ is easier to oxidize than $Cr(pdtc)_3$ so that thermodynamically, as well as kinetically, enhanced stability of the chromium(IV) species is obtained by the oxygen insertion. A less detailed study of analogous diethyldithiocarbamate complexes shows the same overall pattern of behavior, indicating some generality may apply to these observations. Other workers[1-4] have shown that the dithiocarbamate ion may be represented by resonance forms I–III, where resonance form III is claimed to be the most dominant the higher the oxidation state of the metal.[1-4] The increased stability with inclusion of an oxygen atom is possibly



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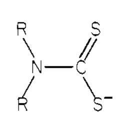

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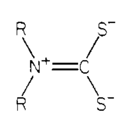
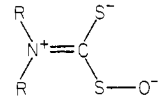


III

due to stabilization of the analogous resonance form IV.



IV

Acknowledgment. The contribution of the Australian Research Grants Scheme is providing financial support for this work is gratefully acknowledged.

Registry No. $Cr(pdtc)_3$, 38532-19-3; $Cr(pdtc)_2(opdtc)$, 89437-75-2; $Hg(pdtc)_2$, 41060-60-0; $K_2Cr_2O_7$, 7778-50-9; Au, 7440-57-5; Pt, 7440-06-4; C, 7440-44-0; Hg, 7439-97-6; ammonium pyrrolidine dithiocarbamate, 5108-96-3.

Contribution from the Institute for Physical Chemistry,
University of Frankfurt, 6000 Frankfurt/Main, Federal Republic of Germany

Kinetics and Mechanism of Some Fast Substitution Reactions of a Series of Methyl-Substituted dien Complexes of Palladium(II) in Aqueous Solution[1]

E. L. J. BREET† and R. VAN ELDIK*

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The kinetics of the substitution reactions of $Pd(1,4,7\text{-}Me_3dien)Cl^+$, $Pd(1,1,7,7\text{-}Me_4dien)Cl^+$, and $Pd(1,1,4,7,7\text{-}Me_5dien)Cl^+$ by OH^- and I^- were studied as a function of [entering ligand], temperature, and pressure up to 1 kbar. The rate constants for both the solvolysis and direct substitution paths decrease significantly with increasing steric hindrance. For the Me_3dien and Me_4dien complexes, they exhibit meaningful $[OH^-]$ dependencies, and the corresponding volumes of activation (+21 ± 2 and +25 ± 4 $cm^3\ mol^{-1}$, respectively) provide strong evidence for a conjugate-base substitution process. The results are discussed in comparison with those previously reported for a corresponding series of ethyl-substituted dien complexes.

Introduction

Although substitution reactions of square-planar complexes in general, and of Pt(II) and Pd(II) in particular, have received much attention from various investigators over the last two decades, the interest in such reactions continues uninterruptedly as demonstrated by the significant number of contributions appearing annually. This interest mainly focuses on the effect of steric hindrance, chelation of ligands, antitumor activity, and substituents of biological importance. Our own interest originated in the remarkable effect of steric hindrance on simple substitution processes, which was originally interpreted[2-4] as evidence for a change from an associative to a dissociative reaction mode with increasing steric hindrance.

We recently reported[5] kinetic data and temperature and pressure parameters for some substitution reactions of dien (diethylenetriamine) and a series of ethyl-substituted dien complexes of palladium(II) in aqueous solution. A significant $[OH^-]$ dependence of the observed rate constant was found for one of the complexes, viz. $Pd(1,1,7,7\text{-}Et_4dien)Cl^+$, in agreement with earlier observations.[2,3] The accompanying activation parameters differed markedly from those reported for other substitution reactions of this complex[6-8] and required the suggestion of a conjugate-base mechanism[3,5] to account for the extraordinary kinetic behavior. The present investigation was undertaken to extend the previously studied[5] series of palladium(II) complexes, viz. dien, Et_3dien (1,1,4 and 1,4,7 isomers), $1,1,7,7\text{-}Et_4dien$, $4\text{-}Me\text{-}1,1,7,7\text{-}Et_4dien$, and $1,1,4,7,7\text{-}Et_5dien$, to include some methyl-substituted complexes, viz. $1,4,7\text{-}Me_3dien$, $1,1,7,7\text{-}Me_4dien$, and $1,1,4,7,7\text{-}Me_5dien$, in order to establish whether a similar $[OH^-]$ dependence exists for one of these species. Additionally, the data enable an overall comparison of the substitution behavior of a wide range of palladium(II)-substituted dien complexes, emphasizing the role played by steric hindrance during such processes.

Experimental Section

The complexes $[Pd(1,4,7\text{-}Me_3dien)Cl_2]HCl$, $[Pd(1,1,7,7\text{-}Me_4dien)Cl]ClO_4$, and $[Pd(1,1,4,7,7\text{-}Me_5dien)Cl]ClO_4$ were prepared as described before.[3,9,10] Analytical data for these complexes and

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† On leave from the Research Unit for Chemical Kinetics, Potchefstroom University for C.H.E., 2520 Potchefstroom, Republic of South Africa.

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