The electrochemical behaviour of tris(N,N-disubstituted dithio-carbamato) complexes of ruthenium(III) in dimethylsulphoxide

MUSHTAQ AHMED* and ROBERT J MAGEE

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, 3083, Melbourne, Victoria, Australia

* Present address : Department of Chemistry, Queen Mary College, University of London, England

Abstract. The reduction at the mercury electrode of a series of ruthenium(III) dithiocarbamates in dimethylsulphoxide (DMSO) has been investigated using D.C. A.C. polarography, chronoamperometry, coulometry (controlled potential electrolysis) and cyclic voltammetry. Tris(N,N-disubstituted dithiocarbamato) complexes of ruthenium exhibit two one-electron polarographic waves in the potential range 0·00 to 2·20 volt relative to Ag/AgClO$_4$ (DMSO) reference electrode. The first reduction, at approximately − 0·950 volt, is quasi-reversible. The [Ru(II)(dAdtc)$_3$]$^-$ complexes resulting from this reduction are susceptible to dissociation, releasing the free dialkyldithiocarbamate anion.

Keywords. Electrochemical behaviour; tris(N,N-disubstituted dithiocarbamato); ruthenium(III); dimethylsulphoxide; polarography; chronoamperometry; coulometry; cyclic voltammetry.

1. Introduction

In recent yea s, there has been a growing interest in the electrochemistry of transition metal complexes of sulfur-containing ligands, such as the dithiocarbamates, with most workers, however, carrying out investigations at the platinum electrode (Hendrickson *et al* 1976; Brinkoff 1971; Cauquis and Lackenal 1973; Golding and Lehtonen 1974; Bond *et al* 1974) Randle *et al* (1976) showed that the electrochemical behaviour at the mercury electrode of copper(II) and nickel(II) dithiocarbamates was more complex and interesting than at the platinum electrode; this was confirmed by Vinh Hoa and Magee (1979), in studies with a series of cobalt (III) dithiocarbamates.

To extend the study of the electrochemistry of transition metal dithiocarbamates, investigations were carried out on a series of ruthenium(III) dithiocarbamates. Previously reported work on the electrochemical reactions of ruthenium(III) dithiocarbamate complexes is very sparse (Mattson *et al* 1976; Wheeler *et al* 1978).

Mattson *et al* (1976) carried out investigations on the oxidation of tris(N,N-disubstituted dithiocarbamato) complexes of ruthenium(III) using a rotating platinum electrode in DMF and acetonitrile. Half-wave potentials displayed a consistent dependence on the substituent groups.

In the present work, seven ruthenium(III) dithiocarbamate derivatives were examined, the dimethyl (Me$_2$dtc), diethyl (Et$_2$dtc), di-*n*-propyl (nPr$_2$dtc), di-*i*-propyl (iPr$_2$dtc), morphyl (morph dtc), piperidyl (pip dtc), and pyrrolydyl (pyrr dtc).

2. Experimental section

All the ruthenium(III) complexes were prepared according to Malatesta (1938, 1940), except as outlined below. RuCl$_3$·nH$_2$O was purified by twice stirring the solid with a concentrated HCl-ethanol solution and evaporating to dryness under a stream of nitrogen. The product was dissolved in absolute ethanol and treated with a stoichiometric amount of the sodium salt of the appropriate dithiocarbamate. The solid product was purified by column chromatography using silica gel and benzene as eluent (Duffy and Pignolet 1974). The purified solids were then recrystallised or separated from a dichloromethane-heptane solution by slow evaporation. It was observed that if the entire procedure is carried out under a nitrogen atmosphere, chromatography is unnecessary. The purity of the ruthenium complexes was checked by elemental analysis, infra-red and melting point determination. Table 1 contains analytical results for the ruthenium(III) dithiocarbamates synthesised. Dimethylsulphoxide was purified by the procedure recommended by Mann (1969) and stored over type 5A molecular sieves. Unless otherwise stated, the supporting electrolyte used throughout was 0·4 M NaClO$_4$. The sodium perchlorate used (BDH reagent grade) was recrystallised from triply distilled water and oven-dried at 200° C for several days. All potentials were measured against Ag/AgClO$_4$ (0·02M)/NaClO$_4$ (0·4M) reference electrode in dimethylsulphoxide (DMSO).

Table 1. Analytical data for the ruthenium(III) dithiocarbamates.

Compound	% Found				% Calculated				
	C	H	N	S	C	H	N	S	MP,° C
Ru(Me$_2$dtc)$_3$	25·06	4·24	8·66	..	23·41	3·93	9·10	41·67	>300
Ru(Et$_2$dtc)$_3$	33·41	5·54	7·59	35·00	33·01	5·54	7·70	35·24	242·5
Ru(nPr$_2$dtc)$_3$	40·10	6·59	6·56	..	40·03	6·72	6·67	30·54	174·5
Ru(iPr$_2$dtc)$_3$	40·49	6·70	6·46	29·90	40·03	6·72	6·67	30·54	219·5
Ru(Morp dtc)$_3$	30·59	4·30	6·76	..	30·65	4·12	7·15	32·73	>300
Ru(Pyrrol dtc)$_3$	31·42	4·32	6·77	..	33·38	4·48	7·78	35·64	>300
Ru(pip dtc)$_3$	37·37	5·57	7·34	..	37·15	5·20	7·22	33·06	>300

Analyses were performed by Australian Microanalytical Service.

2.1. *Electrochemical measurements*

A Princeton Applied Research (PAR) Model 170 Electrochemistry System was employed for the polarographic studies (DME) and the cyclic voltammetric and chronoamperometric work (HMDE). Potentials were recorded against $Ag/AgClO_4$, the auxiliary electrode being platinum.

Cyclic voltammograms were also recorded at platinum and gold electrodes, both being cleaned in conc. nitric acid prior to use and polarised at the anodic and cathodic limits before each experiment.

A.C. polarograms were also recorded on the PAR Model 170 instrument; a phase-sensitive read-out was used to give the in-phase component. A three-electrode system was used in all A.C. and D.C. work and, I.R. compensation was applied as required.

For constant potential coulometry with a mercury-pool electrode (diameter 4·6 cm), a Beckman Electroscan 30 instrument was employed. The auxiliary electrode was platinum and potentials were recorded relative to the $Ag/AgClO_4$ reference electrode.

All the electrochemical measurements were carried out at $25 \pm 0\cdot1^\circ$ C, solutions being degassed with pre-dried, oxygen-free nitrogen.

3. **Results and discussion**

3.1. *The polarographic behaviour of sodium N,N-dialkyldithiocarbamates*

In preliminary work, three sodium dialkyldithiocarbamates were examined polarographically, $NaMe_2dtc$, $NaEt_2dtc$, $NanPr_2dtc$. Each exhibited three oxidation waves characteristic of the $dAdtc^-$ anion. Two of these (waves 2 and 3) lay close together and were difficult to resolve; the main wave, wave 1, occurred around $-0\cdot83$ volt for all three compounds. The electrocapillary curve for $Na(Et_2dtc)$ (0·1 mM) showed a marked decrease in drop time in the potential region of wave 1 (figure 1), indicating that the compound and/or product of the anodic reaction is strongly adsorbed. A similar adsorption has been found in acetone (Bond *et al* 1973).

The reaction scheme for dialkyldithiocarbamate ligands in other media has been proposed as follows (Randle *et al* 1975) :

$$dAdtc^- + Hg^\circ \rightleftharpoons Hg(I) \ (dAdtc) + e$$

$$2Hg(I) \ (dAdtc) \rightleftharpoons Hg(II) \ d \ (Adtc)_2 + Hg^\circ,$$
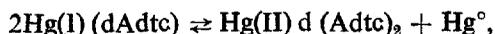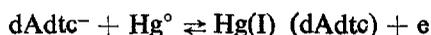
and it would appear that the same electrode process is responsible for wave I in DMSO.

Confirming the above mechanisms was the fact that polarograms of $Hg(Me_2dtc)_2$ and $Hg(Et_2dtc)_2$ in DMSO were found to be identical to those for the ligands, except that the wave corresponding to wave I was now clearly cathodic. When $NaEt_2dtc$ was added to a solution of $Hg(Et_2dtc)_2$ and the polarogram re-run, a composite cathodic/anodic wave resulted.

It is clear therefore, that the anodic wave I for the $dAdtc^-$ anions is due to oxidation of mercury rather than the ligand itself, the oxidation being followed by a step which produces $Hg(II)$ dialkyldithiocarbamate,
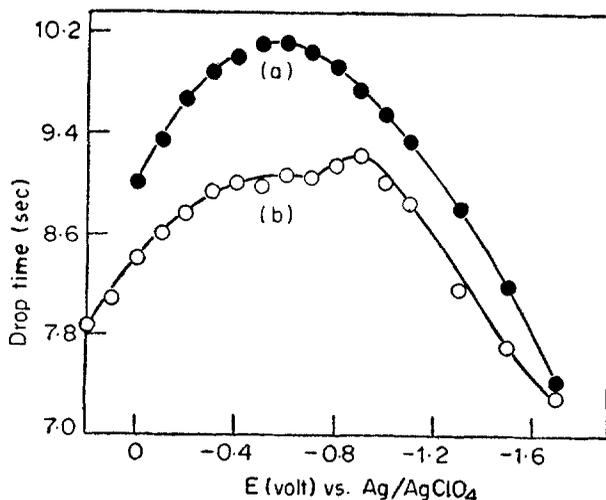
Figure 1. Electrocapillary curves for (A) 0·40 M NaClO₄. and (B) Na(Et₂dtc) (1·00 mM) O in DMSO. $T = 25°$ C; $h = 68·0$ cm; no Triton X − 100 added.

3.2. *Polarographic behaviour of ruthenium dithiocarbamates*

All the ruthenium dithiocarbamates gave similar polarograms with only one main reduction wave (wave I) being apparent (figures 2 and 3). One small post peak, (wave I[1]) was also observed at − 1·20 volt in all the polarograms. This post peak (wave I[1]) is discussed fully in the section on cyclic voltammetry. The stability of the ruthenium dithiocarbamates in DMSO was examined by observing the limiting current of Ru(Et₂dtc)₃ over an eight-day period. No decrease in limiting currents was observed, indicating that the ruthenium complexes were very stable in DMSO.

Wave I appeared to be diffusion controlled under polarographic conditions, e.g., limiting currents varied linearly with $\sqrt{h_{corr}}$. Temperature coefficients were in the range 1·763-2·060% per degree over a temperature interval 25° C to 54° C. Log-plot analyses of E against log $[i/(id − i)]$ gave linear plots for all compounds, but slopes indicate that the first reduction (wave I) shows considerable departure from reversible behaviour for each of the complexes examined. Table 2 lists some A.C. and D.C. polarographic parameters for wave I. The half-width $(\triangle E_{1/2})$ values clearly show that the electrode reaction is irreversible or quasireversible in most cases, and confirms the D.C. log-plot results.

As might be expected for a quasireversible electrode reaction the half-wave potential for wave I[$E_{1/2}$(I)] of Ru(Et₂dtc)₃, and presumably of the other compounds, is susceptible to change in the structure of the electrical double layer. Variation of the NaClO₄ concentration from 0·02 M to 1·50 M, in eight consecutive steps results in $E_{1/2}$ (I) shifting to more positive potentials from − 0·945 ± 0·001 volt to − 0·933 ± 0·011 volt. A positive shift in half-wave potential with increasing concentration of supporting electrolyte is expected, if the depolarising particle enters the inner part of the electrical double layer as either a neutral particle or with a negative end oriented towards the electrode.
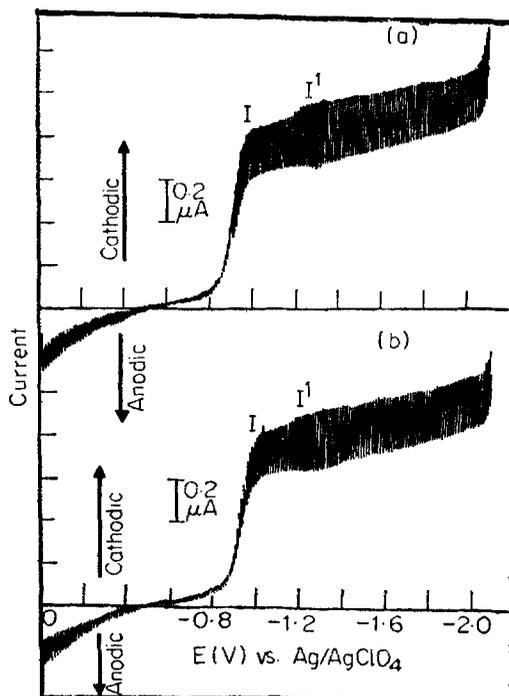
Figure 2. Polarograms of (A) $Ru(Me_2dtc)_3$ (1·008 mM), and (B) $Ru(Et_2dtc)_3$ (1·007 mM) in DMSO, 0·40 M $NaClO_4$. $T = 25°$ C; $h = 68·0$ cm; 0·008%., Triton X — 100 added.
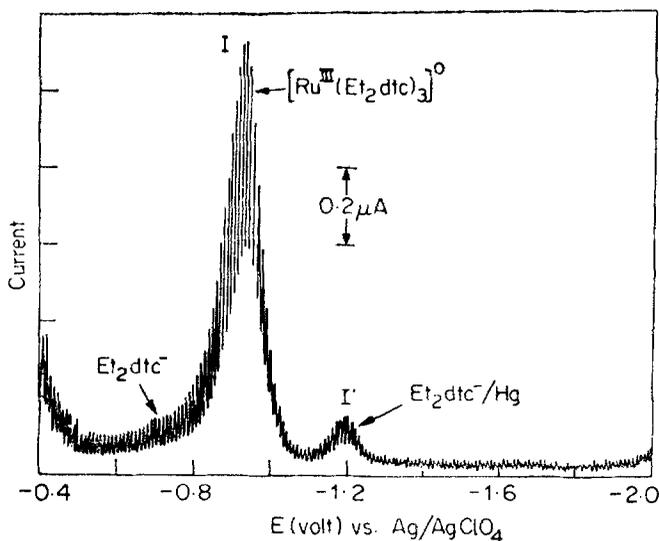
Figure 3. AC polarogram of $Ru(Et_2dtc)_3$ (0·397 mM), in presence of nitrogen in DMSO, and 0·40 M $NaClO_4$. $T = 25°$ C, $h = 68·0$ cm; no Triton X — 100 added. Frequency 400 Hz alternating potential 10 mV peak to peak.

Table 2. AC and DC polarographic data for the first reduction step of ruthenium(III) dithiocarbamates.

Complex	Conc. (mM)	$E_{1/2}$ (I) volts vs. ± 0.002 V	E_p (I) Ag/AgClO$_4$	Slope of plot E vs log $[i/i_d - i]$	$\triangle E_{1/2}$* half-(mV)
Ru(Me$_2$dtc)$_3$	0.197	-0.925	-0.932 ± 0.003	0.075 ± 0.001	90
Ru(Et$_2$dtc)$_3$	0.199	-0.970	-0.971 ± 0.005	-0.082 ± 0.001	90
Ru(nPr$_2$dtc)$_3$	0.206	-0.960	-0.960 ± 0.002	-0.924 ± 0.005	90
Ru(iPr$_2$dtc)$_3$	0.211	-1.010	-1.032 ± 0.002	-0.770 ± 0.002	110
Ru(morph dtc)$_3$	0.402	-0.850	-0.850 ± 0.002	-0.133 ± 0.001	110
Ru(pyrrol dtc)$_3$	1.008	-0.930	..	-0.098 ± 0.009	100
Ru(pip dtc)$_3$	0.993	-0.930	-0.920 ± 0.001	-0.098 ± 0.004	..

On varying the size of the supporting electrolyte cations along the series potassium, sodium, lithium and magnesium perchlorate, the $E_{1/2}$(I) for the reduction of Ru(Et$_2$dtc)$_3$ moved steadily from -0.943 ± 0.004 volt for LiClO$_4$ (0.40 M), and -0.941 ± 0.008 volt for KClO$_4$ (0.40 M), to -0.927 ± 0.004 volt for Mg(ClO$_4$)$_2$ (0.40 M). This positive shift in $E_{1/2}$ (I) with increasing charge to size ratio of the support cation is the reverse of that expected for a neutral depolariser or one entering the double layer with a negative end oriented toward the electrode (Vlcek 1960).

In dimethylsulphoxide, comparison of the potentials of the first reduction step of ruthenium(III) dithiocarbamates can only be made under conditions of carefully controlled supporting electrolyte concentration. The half-wave potentials of wave I were all found to lie on the negative arm of the electrocapillary curve for mercury in the solvent-support system. Hence, the ruthenium complexes undergo reduction at a negatively charged electrode.

Chronoamperometric reduction of each ruthenium complex at the hanging mercury drop electrode (HMDE) again demonstrated diffusion control of wave I, linear plots of i against $t^{-1/2}$ being obtained in DMSO for electrolysis times t as long as 20 sec. The diffusion coefficient D of each ruthenium dithiocarbamate was calculated from the slopes of the respective plots of i against $t^{-1/2}$ (table 3).

3.3. *Cyclic voltammetric behaviour of the ruthenium(III) dithiocarbamate*

Each of the ruthenium complexes displayed a similar voltammogram (figure 4c). consisting of seven peaks, four cathodic reduction peaks and three anodic oxidation peaks.* The small most positive cathodic wave (wave [1]I) obtained at -0.34 volt may correspond to reduction involving the Hg^{II} (dAdtc)$_2$ or Hg(I) (Et$_2$dtc).

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* Waves have been designated by adding superscripts to the main wave numeral, the position of the superscript defining the position of additional waves with respect to the main waves. Thus, wave [1]I occurs on the anodic side of wave I on the cathodic scan.

Table 3. Diffusion coefficients of the Ruthenium(III) dithiocarbamates in dimethyl sulphoxide from chronoamperometry.

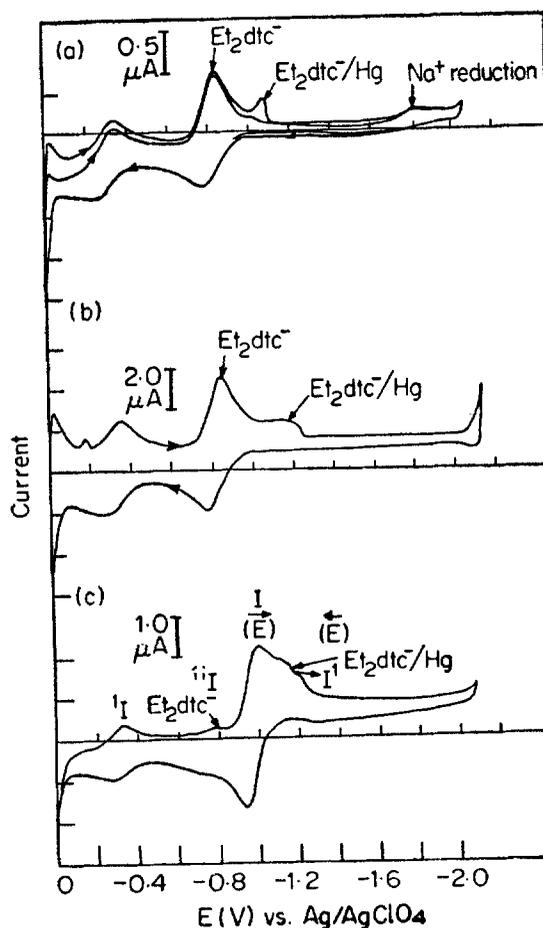| Compound	Conc. (mM)	Slope of i vs $t^{-1/2}$ plot ($\mu As^{1/2}$)	D cm^2 s$^-$ ($\times 10^{+6}$)
Ru(Me$_2$dtc)$_3$	0·197	0·8965	2·016
Ru(Et$_2$dtc)$_3$	0·199	0·7798	1·495
Ru(nPr$_2$dtc)$_3$	0·206	0·7881	1·425
Ru(iPr$_2$dtc)$_3$	0·211	0·5194	0·580
Ru(Morp dtc)$_3$	0·211	0·9602	2·016
Ru(Pryy dtc)$_3$	0·256	0·9151	1·244
Ru(pip dtc)$_3$	0·230	0·5900	0·640

Figure 4. Cyclic voltammograms at H.M.D.E. (scan rate − 0·050 V/s, $T = 25°$ C) in DMSO, 0·40 M NaClO$_4$ in presence of nitrogen. (A) Na (Et$_2$dtc) (0·40 M); (B) Hg (Et$_2$dtc)$_2$ (0·40 M); (C) Ru(Et$_2$dtc)$_3$ (0·397 mM).

It was observed that no peak was obtained on the anodic scan for post-wave (wave I^1). This post-peak (wave I^1) together with two pre-peaks (wave ^1I and wave ^{11}I) is discussed later.

3.3a. *Wave I* : In agreement with the results of polarography and chrono-amperometry, cyclic voltammetric studies also indicated that the electron transfer is essentially a quasireversible (in most of the cases), diffusion controlled process for each dithiocarbamate. Diffusion control, at least up to a scan rate of around $0 \cdot 005$ V/s, is shown by the constancy of i_{p_c} (I) (plane)/$V^{1/2}$, and the peak potentials of E_{p_c} (I) and E_{p_a} (I) with scan rate. The constancy of peak potentials and the value of $\triangle E_p$ (I) $[E_{p_a}$ (I) $- E_{p_c}$ (I)] of around $0 \cdot 062$ V (in most cases) at least up to a scan rate $0 \cdot 005$ V/s illustrate polarographic reversibility. However, depar-ture from reversible behaviour at higher scan rates is shown by the shift in peak potentials and the consequent increase in $\triangle E_p$ (I) values (Nicholson and Shain 1964). The increase in i_{p_a}(I)/i_{p_c}(I) with increasing scan rate again shows that the reaction is becoming irreversible at higher scan rates.

3.3b. *Nature of wave* ^1I : This pre-wave (wave ^1I) was more pronounced when working at low concentrations. The peak current ratio i_{p_c}(^1I)/i_{p_c} (I) was deter-mined from the cyclic voltammograms and was found not to increase with increas-ing scan rate. Peak current also did not increase with scan rate. For all the ruthe-nium complexes, wave ^1I did not show sharp symmetry. Further the value calcu-lated for Ru(Et$_2$dtc)$_3$ was found to be $[E_{p_{c_{1/2}}}(^1I) - E_{p_c}(^1I)] = -0 \cdot 241$ volt at $V = 0 \cdot 002$ V/s, which is not typical of an adsorption wave.

Much more convincing evidence concerning the nature of wave ^1I came from the addition of Hg^{11} (Et$_2$dtc)$_2$ to the solution, when the peak, obtained at $-0 \cdot 34$ volt became well pronounced.

3.3c. *Nature of wave* ^{11}I : The second pre-wave (wave ^{11}I) (figure 4C) was observed at $-0 \cdot 80$ volt. The peak current ratio i_{p_c}(^{11}I)/i_{p_c} (I) was determined from the cyclic voltammograms and was found not to increase with increasing scan rate. The peak current also did not increase with scan rate and the sharp symmetry of a pre-wave (wave ^{11}I) was not present. The value calculated for Ru(Et$_2$dtc)$_3$ gave the following result: $[E_{p_{c_{1/2}}}(^{11}I_3) - E_{p_c}(^{11}I)] = -0 \cdot 40$ volt at $0 \cdot 020$ V/s which is also not typical of adsorption.

To investigate the nature of wave ^{11}I, a sample of Ru(Et$_2$dtc)$_3$ was chosen together with the corresponding NaEt$_2$dtc. The solution of the sodium diethyldithio-carbamate ($1 \cdot 0$ mM) was then run on the cyclic voltammetric scale from anodic to cathodic between the limits of $0 \cdot 00$ volt and $-1 \cdot 20$ volt at $0 \cdot 050$ V/s under nitrogen. Three peaks were obtained, the first at $-0 \cdot 39$ volt; the second at $-0 \cdot 84$ volt; and third at $-1 \cdot 08$ volt. The first peak at $-0 \cdot 39$ volt is probably due to the reduction of Hg(I)(Et$_2$ dtc), i.e.,

$$Hg(I) (Et_2dtc) + e \rightarrow Hg° + Et_2dtc^-,$$
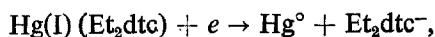
following the chemical reaction $[Hg(II) (Et_2dtc)_2]° + Hg° \rightarrow 2Hg(I) (Et_2dtc)$. The second peak at $-0 \cdot 84$ volt could be due to the reduction of the ligand itself, while the third peak may be due to fact that the chemical reaction $[Hg(II) (Et_2dtc)_2] + Hg° \rightarrow 2[Hg(I) (Et_2dtc)]°$ may not go to completion and some of the Hg(II) complex

may, therefore, be left to reduce at the more negative potential. In this connection, it is significant that the cyclic voltammograms of $Na_2(Et_2dtc)$ and $Hg(Et_2dtc)_2$ are remarkably similar.
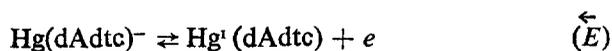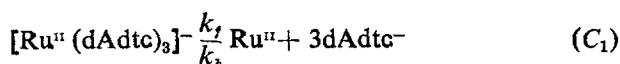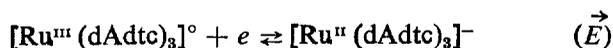
The solution of $Ru(Et_2dtc)_3$ (1·0 mM) was now run on the cyclic voltammetric scale from 0·00 volt to − 2·10 volt in the presence of the sodium diethyldithiocarbamate. The peak at − 0·84 volt (wave [11]I) became more pronounced. Thus, it would appear that the cyclic voltammetric behaviour of the complexes is caused by release of the Et_2dtc^- anion before electron transfer (see also cyclic voltammetry at the platinum and gold electrodes as discussed below).

3.3d. *The nature of the post-wave (wave I^1)* : All the usual tests indicated that this wave also was not a typical adsorption wave; for example $[E_{pc1/2}(I^1) − E_{pc}(I^1)]$ = 0·082 volt at 0·020 V/s.

To investigate the nature of wave I^1, a sample of $Ru(Et_2dtc)_3$ was chosen, together with the corresponding $Hg(II)(Et_2dtc)_2$. The cyclic voltammogram of $Hg^{II}(Et_2dtc)_2$ (0·40 mM) at 0·050 V/s in the presence of nitrogen was examined and found to be identical to that of the Et_2dtc^- anion.

A solution of $Ru(Et_2dtc)_3$ (0·60 mM) was then run on the cyclic voltammetric scale along with $Hg^{II}(Et_2dtc)_2$. The peak obtained at − 1·160 volt increased. Again it is possible that this wave, which is rather broad, is due, at least in part, to the same cause, as mentioned above i.e., reduction of some of the $[Hg(II)(Et_2dtc)_2]$ complex still remaining.

The complete reaction mechanism of the electrode processes for the ruthenium complexes associated with the reduction step may now be written as shown in the following reaction scheme.

$$[Ru^{III}(dAdtc)_3]^° + e \rightleftarrows [Ru^{II}(dAdtc)_3]^- \qquad (\overrightarrow{E})$$

$$[Ru^{II}(dAdtc)_3]^- \frac{k_f}{k_b} Ru^{II} + 3dAdtc^- \qquad (C_1)$$

$$Hg(dAdtc)^- \rightleftarrows Hg^I(dAdtc) + e \qquad (\overleftarrow{E})$$

$$2Hg^I(dAdtc) \overset{rapid}{\rightleftharpoons} Hg^{II}(dAdtc)_2 + Hg^° \qquad (C_2)$$
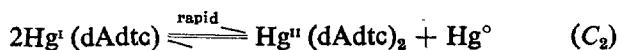
where $(\overrightarrow{E})$ represents an electrochemical reduction step; (C_1) a subsequent chemical reaction; $(\overleftarrow{E})$ a resulting oxidation step; and (C_2) a further chemical reaction. k_f and k_b are the forward and backward rate constants. The terminology $\overrightarrow{E}\overleftarrow{C}\overleftarrow{E}$ was introduced by Feldberg and Jeftic (1972) and has been extended here to $\overrightarrow{E}C_1$ $\overleftarrow{E}C_2$ to account for the further chemical step (C_2).

In terms of the above mechanism, the shape of wave I may be readily explained. The half-wave $(E_{1/2})$ potential of $[Ru^{III}(dAdtc)_3]^°$ species is ∼ − 0·950 volt and the half-wave potential of free $dAdtc^-$ anion is approximately equal to − 0·840 volt. If there is any dissociation of the ruthenium(II) species as per step (C_1), then $dAdtc^-$ anions will be released at potentials more negative than the potential at which the $[Ru^{III}(dAdtc)_3]^°$ species begin to be reduced (i.e. ∼ −0·90 volt)[3].

Therefore, between -0.90 volt and the potential at which mercury (O) is no longer oxidised in the presence of Et_2dtc^-, i.e. ~ 1.1 volt, mercury (O) will oxidise as per step $(\overleftarrow{E})$ and anodic current will flow. In these circumstances, the nett current flowing in this voltage range will be the difference between the reduction current from step $(\overrightarrow{E})$ and the oxidation current from step $(\overleftarrow{E})$. At potentials more negative than about ~ 1.1 volt, the oxidation of Hg (O) ceases, and the limiting current of the experimental wave reverts to the diffusion current for step $(\overrightarrow{E})$.

Cyclic voltammetry was carried out on a solution of $Ru(Et_2dtc)_3$ after exhaustive reduction for 6 hr without exposing the solution to the atmosphere. The potential of the h.m.d.e. was cycled anodic to cathodic between 0.00 and -2.10 volt at 0.01 V/s. From measurements of the peak current obtained at -0.840 volt, which corresponds to that for the oxidation of mercury in DMSO in the presence of $NaEt_2dtc$, it was confirmed that, during the reduction of Ru $(Et_2dtc)_3$, free ligand is released into solution. Further, from measurement of peak currents of solutions of the complex of known concentration at the same scan rate and comparison with the peak current for the oxidation of mercury in solutions of known concentration of $NaEt_2dtc$, it was confirmed that not all of the complexed ligand is released into solution.

Cyclic voltammograms at a platinum and gold electrodes produced results consistent with those obtained from other techniques. In the absence of oxygen a wave characteristic of reaction $(\overrightarrow{E})$ was seen. The reduction step remained reversible, as shown by the constancy of the peak potential over a range of scan rates and by the direct proportionality between the peak height and the square root of the scan rate. It was also observed that at very low scan rates, after the anodic peak of the electron transfer, a small peak was also obtained at -0.63 volt due to release of $dAdtc^-$. The fact that no wave corresponding to the oxidation step $\overleftarrow{E}$ was obtained in the absence of mercury further verifies the proposed mechanism.
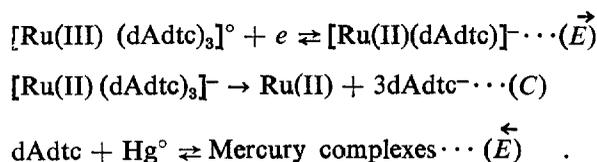
3.4. *Controlled-potential coulometry*

Constant potential coulometry was carried out on 25 ml solutions of $Ru(Et_2dtc)_3$ and $Ru(nPr_2dtc)_3$ at a potential on the plateau of wave I $(-1.209$ volt). Background charge from the supporting electrolyte solvent system was found to be very small, but was subtracted from total charge flowing. The integral values of n (i.e., $n = 1$) obtained from coulometry also suggest that there is no catalytic chemical reaction associated with wave I. It was also observed that in the current time traces obtained in the coulometric studies, the current approaches a zero value in a very short interval of time and the colour of the solution changed from dark brown to colourless.

3.5. *Half-wave potentials and $E°$ [Ru(III)/Ru(II)]*

If the rate constant k_f in the reaction $[Ru(II) (dAdtc)_3]^- \rightleftarrows Ru(II) + 3\,dAdtc^-$ is of comparable magnitude to k_b and, if both are fast enough to ensure that equilibrium conditions apply, then $E_{1/2}$ values will vary with the concentration of the ligand (as the concentration of $[Ru(II) (dAdtc)_3]^-$ will depend on the concentration of the ligand anion). To test the influence of this reaction on $E_{1/2}$ (or E_p),

A.C. and cyclic voltammetric studies were carried out using platinum and gold electrodes (the d.m.e. was not used to eliminate processes which are associated with the oxidation of mercury, i.e. ($\overleftarrow{E}$) steps). Under these circumstances, the electrode mechanism was reduced to an $\overrightarrow{EC}$ process, or simply an $\overrightarrow{E}$ step, when k_f is very small (i.e., step (2) $[\text{Ru(II)}(\text{dAdtc})_3]^- \rightarrow \text{Ru(II)} + 3\,\text{dAdtc}^-$ is negligible). The A.C. peak potential of step ($\overrightarrow{E}$) was measured as a function of ligand concentration, by addition of varying amounts of free ligand to the test solutions. It was found to be completely independent of concentration for all the ruthenium complexes. In cases, therefore, where small dissociation of the ruthenium(II) species occurs, it would appear that step (2) is not an equilibrium reaction and the complete electrode process may be written more precisely as:

$$[\text{Ru(III)} \ (\text{dAdtc})_3]^\circ + e \rightleftarrows [\text{Ru(II)}(\text{dAdtc})]^- \cdots (\overrightarrow{E})$$

$$[\text{Ru(II)} \ (\text{dAdtc})_3]^- \rightarrow \text{Ru(II)} + 3\text{dAdtc}^- \cdots (C)$$

$$\text{dAdtc} + \text{Hg}^\circ \rightleftarrows \text{Mercury complexes} \cdots (\overleftarrow{E}) \quad .$$

However, where dissociation is well-marked, the concentration of the $[\text{Ru(II)} (\text{dAdtc})_3]^-$ species will be lowered and the measured half-wave or peak potential will no longer be exactly equivalent to $(E^\circ \ (\text{Ru(III)}/\text{Ru(II)}))$. In most cases, although dissociation occurs, the effect on the reversible $E_{1/2}$ value is considered to be slight. As a consequence, measured half-wave potentials can be used for the purpose of qualitative comparison between the various ruthenium complexes.

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