Voltammetric Behaviour of Technetium[99] Complexes with π-Acceptor Ligands in Aprotic Medium. II. Reduction of TcCl₃(PMe₂Ph)₃ and of TcCl₄(PMe₂Ph)₂

G. A. MAZZOCCHIN, R. SEEBER

Istituto di Chimica Generale, Università di Siena, Pian dei Mantellini, 44, 53100 Siena, Italy

U. MAZZI, E. RONCARI

Laboratorio di Chimica e Tecnologia dei Radioelementi, C.N.R., Corso Stati Uniti, 35100 Padova, Italy

Received September 15, 1977

The electrode reduction of the technetium[99] phosphine complexes TcCl₃(PMe₂Ph)₃ and TcCl₄-(PMe₂Ph)₂ has been studied in acetonitrile solvent by electroanalytical techniques. The electrode processes, as well as the involved chemical equilibria, have been studied.

Technetium(II) and technetium(I) phosphine complexes have been obtained by reducing TcCl₃(PMe₂-Ph)₃ at different potential values. The voltammetric behaviour of these compounds of technetium in low oxidation states has been also reported. TcCl₄-(PMe₂Ph)₂ undergoes an one-electron reduction giving rise to TcCl₃(PMe₂Ph)₃ as the main product.

Introduction

In recent years the synthesis and the characterization of technetium[99] complexes [1–5] constituted an active field of research.

As part of our systematic study dealing with the electrochemical behaviour of technetium complexes with π-acceptor ligands in aprotic medium part I [6] refers on the anodic behaviour of TcCl₃(PMe₂Ph)₃ and the present paper reports an electroanalytical study on the electrode reduction processes of TcCl₃-(PMe₂Ph)₃ and of TcCl₄(PMe₂Ph)₂.

The aim of this work was to evidentiate the formation of technetium complexes in low oxidation states, to study the involved equilibria in aprotic solvent and to define the mechanisms of the electrode processes.

Experimental

All chemicals and reagents were prepared as described in part I of this series. The complexes TcCl₃(PMe₂Ph)₃ and TcCl₄(PMe₂Ph)₂ were prepared as described in ref. 4. The apparatus employed in voltammetric, chronoamperometric and coulometric experiments, as well as the experimental conditions

and the followed procedures, were already described [6]. Also in the present study platinum electrodes were employed.

Results

Reduction of TcCl₃(PMe₂Ph)₃

In Fig. 1 a typical cyclic voltammetric curve recorded at a Pt microelectrode on a $3.2 \times 10^{-3} M$ TcCl₃(PMe₂Ph)₃, $0.1 M$ TBAP, MeCN solution, is reported.
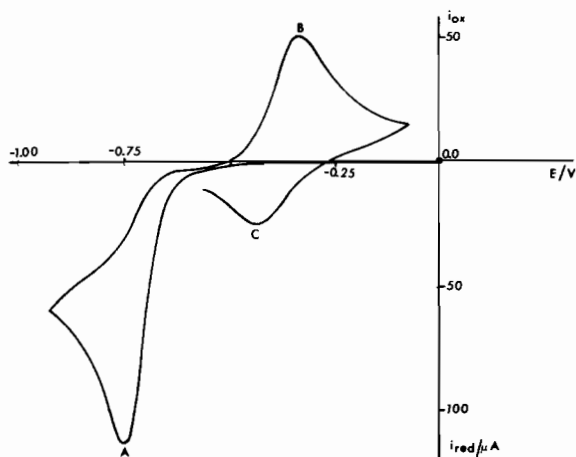

Figure 1. Cyclic voltammetric curve recorded on a $3.2 \times 10^{-3} M$ TcCl₃(PMe₂Ph)₃, $0.1 M$ TBAP, MeCN soln.; Pt working microelectrode. Scan rate 0.2 V s⁻¹; ● starting potential.

A cathodic peak (A) located at −0.75 V appears. The relative $E_{p/2} - E_p$ value is equal to 60 mV, as required for a one-electron reversible process; however no reversible associated anodic response can be noted, even at a scan rate of 2.0 V s⁻¹. By reversing the potential scan an anodic peak (B) located at −0.33 V arises; to this anodic peak a cathodic one (C) is associated. Except for a low anodic peak at about

+0.32 V, no other anodic response related to peak A could be seen. At about + 0.85 V the oxidation of the starting compound occurs [6].

Linear sweep voltammetric tests carried out at different potential scan rates indicated that the ratio $i_p/v^{1/2}$ relative to peak A slightly decreased at increasing scan rate. Moreover, the E_p value shifted towards more negative potential values to an extent of about 30 mV by a tenfold increase in scan rate. Chronoamperometric experiments carried out by polarizing the working electrode at −1.20 V gave $i_t \cdot t^{1/2}$ values slightly increasing at increasing t.

Cyclic voltammetric tests performed at different scan rates showed that the ratio between the i_p values relative to peaks B and A increased at increasing scan rate, tending to one at the highest tested scan rates.

The height of peak A in Fig. 1 resulted equal to that of the oxidation peak of $TcCl_3(PMe_2Ph)_3$, recorded on the same solution. However, controlled potential coulometric experiments carried out at a potential value of −1.20 V led to a consumption of two mol of electrons per mol of the starting compound.

When $NaClO_4$ was used as supporting electrolyte, during the exhaustive electrolyses two mol of the sparingly soluble NaCl per mol of $TcCl_3(PMe_2Ph)_3$ precipitated.
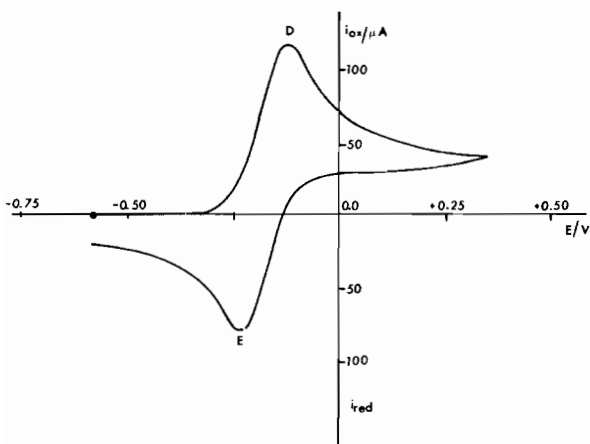

Figure 2. Cyclic voltammetric curve recorded on a $TcCl_3$-$(PMe_2Ph)_3$ solution, previously electrolyzed at −1.2 V. Experimental conditions as in Figure 1; ● starting potential.

Cyclic voltammetric tests performed at the end of these electrolyses gave the voltammetric picture reported in Fig. 2: a quasi-reversible catho–anodic system appears, with $(E_p)_a$ = −0.12 V and $(E_p)_c$ = −0.24 V.

The checked diffuse character of the oxidation process occurring at peak D allowed to compare its height with that relative to the oxidation of the starting compound: the i_p values resulted very similar.

When the coulometric experiments were performed by polarizing the working platinum gauze at a potential value (−0.70 V) corresponding to the initial portion of peak A, only one mol of electrons per mol of starting compound was used when the current flowing through the electrode fell to a very low value (about 5% if referred to the starting one). In this case one mol of NaCl per mol of electrolyzed $TcCl_3(PMe_2-Ph)_3$ was recovered at the end of the electrolyses carried out in the presence of Na^+ ions.
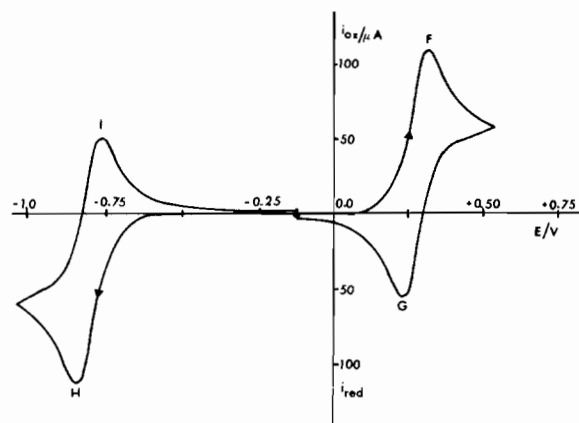

Figure 3. Cyclic voltammetric curve recorded on a $TcCl_3$-$(PMe_2Ph)_3$ solution, previously electrolyzed at −0.7 V. Experimental conditions as in Figure 1; ● starting potential.

Fig. 3 shows the voltammetric picture exhibited by this latter electrolyzed solution. As can be noted, two quasi-reversible catho–anodic systems are evidentiated; to the reduction peak H, diffusive in character, with an E_p value of −0.86 V, the anodic response I was associated; to the oxidation peak F, again diffusion-controlled, with an E_p value of + 0.32 V, the cathodic response G was related. Also peaks H and F exhibited an i_p value equal to that of the peak relative to the oxidation of the starting compound.

When this solution was further reduced at a potential value of −1.20 V one mol of electrons per mol of starting compound was again used, and one mol of NaCl per Faradays spent precipitated in presence of $NaClO_4$ supporting electrolyte.

The cyclic voltammogram recorded on the exhaustively electrolyzed solution perfectly resembled the curve reported in Fig. 2.

Reduction of $TcCl_4(PMe_2Ph)_2$

The technetium(IV) complex $TcCl_4(PMe_2Ph)_2$ undergoes a quasi reversible, diffusion-controlled, reduction process; a typical cyclic voltammetric curve is shown in Fig. 4.

The ratio $(i_p)_a/(i_p)_c$ slowly decreased from unity at potential scan rates lower than 0.2 V s^{-1} reaching a value of 0.8 at 0.02 V s^{-1}.
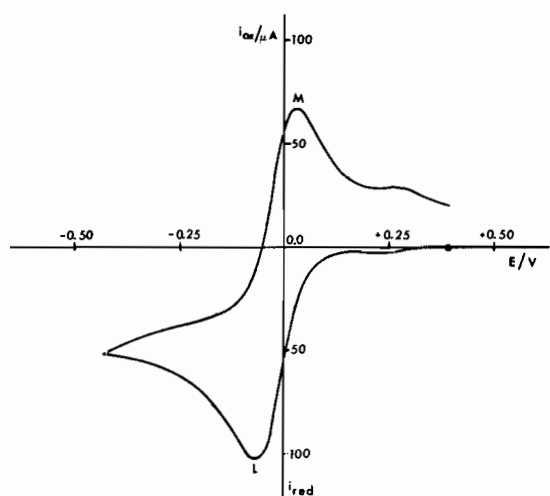
Figure 4. Cyclic voltammetric curve recorded on a 2.95 × $10^{-3}M$ $TcCl_4(PMe_2Ph)_2$, 0.1M TBAP, MeCN soln.; Pt working microelectrode. Scan rate 0.2 V s^{-1}; ● starting potential.

Controlled potential coulometric tests carried out at a working potential of −0.3 V indicated that a one-electron reduction process is involved. In presence of Na$^+$ ions one mol of NaCl per Faradays spent precipitated during the electrolyses.

Cyclic voltammetric curves recorded at the end of these electrolyses showed an overall picture similar to that reported in Fig. 1; in good agreement with these findings, the recovery of the reduction product after the end of these electrolyses led to a crystalline yellow product, which has been identified as $TcCl_3$-$(PMe_2Ph)_3$.

The electrolyzed solution, initially yellow in colour, slowly darkened. The amount of $TcCl_3(PMe_2$-$Ph)_3$, as evaluated by linear sweep voltammetry, increased with time; the height of the reduction peak was however always lower than that of the reduction of the starting $TcCl_4(PMe_2Ph)_2$ compound.
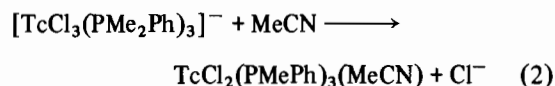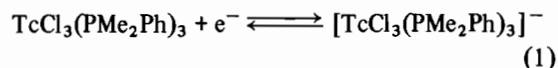
Discussion

Reduction of $TcCl_3(PMe_2Ph)_3$

The results of the cyclic voltammetric tests suggest that the product of the electrode reduction occurring at peak A in Fig. 1 must undergo a fast chemical reaction; in fact, the peak potential shifts towards more negative values at increasing scan rate and no reversible associated peak is present, in spite of the shape ($E_{p/2}$ − E_p value) of the reduction peak, which indicates the reversible character of the charge transfer step.

The catho—anodic system C/B is located at potential values coincident with those of the redox couple $[TcCl_2(PMe_2Ph)_3(MeCN)]^+$/$TcCl_2(PMe_2Ph)_3$-$(MeCN)$ [6]; in view of these findings the chemical reaction following the charge transfer step had to be the release of a chloride ion which is substituted by a solvent molecule. Hence the reduction mechanism occurring at peak A must be the following:

$$TcCl_3(PMe_2Ph)_3 + e^- \rightleftharpoons [TcCl_3(PMe_2Ph)_3]^- \quad (1)$$

$$[TcCl_3(PMe_2Ph)_3]^- + MeCN \longrightarrow$$
$$TcCl_2(PMePh)_3(MeCN) + Cl^- \quad (2)$$

The trend of the ratio between the peak current of the two associated peaks B and A, decreasing at decreasing potential scan rate, indicates that the product of chemical reaction 2, which is oxidized at peak B, must undergo in its turn a further slow chemical reaction. Hence, reaction 2 cannot be the only chemical complication, as also revealed from voltammetric, chronoamperometric and, mainly, coulometric results, which indicated the occurrence of an e.c.e. type mechanism leading to an overall two-electron reduction process at potential values corresponding to peak A. In this connection it must be noted that the species $TcCl_2(PMe_2Ph)_3(MeCN)$ cannot be responsible for the second charge transfer step because the chemical reaction 2 must be very fast, as demonstrated by the absence of any reversible anodic peak associated to peak A; by consequence the height of peak A had to be in this hypothesis noticeably higher.

The analyses performed on the NaCl precipitated during the electrolyses carried out at a potential value of −1.2 V indicated that the final reduction product should be $TcCl(PMe_2Ph)_3(MeCN)_2$. The voltammetric curve recorded at the end of these electrolyses, reported in Fig. 2, indicates the potential values at which this species is oxidizable.

The overall reduction process occurring at −1.2 V can be hence summarized as follows:

$$TcCl_3(PMe_2Ph)_3 + 2MeCN + 2e^- \longrightarrow$$
$$TcCl(PMe_2Ph)_3(MeCN)_2 + 2Cl^- \quad (3)$$
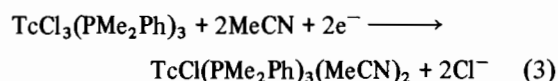
To ascertain if the second charge transfer step occurs at less or more cathodic potential values than the first one, controlled potential coulometric experiments were performed on the initial portion of peak A. Both the coulometric results (n_e = 1) and the voltammetric curves recorded at the end of these electrolyses (Fig. 3) indicate that the above cited second charge transfer step occurs at potential values slightly cathodic (peak H, E_p = −0.86 V) in respect to the first one.

The coulometric results of the electrolyses carried out on these solutions at a working potential of −1.2 V, together with the resulting voltammetric picture, confirm again the sequence of the reduction potentials in the e.c.e. type mechanism.

It can be concluded that the same slow chemical reaction is responsible both for the trend of the ratio $(i_p)_B/(i_p)_A$ at different scan rates, as it involves the species oxidizable at peak B, and for the formation of a compound which is reducible at peak H and oxidizable at peak F (Fig. 3). This species must be undoubtedly a technetium(II) complex, resulting from a one-electron reduction of the technetium(III) compound and leading in its turn, *via* a one-electron reduction, to a technetium(I) species.

The slow chemical reaction following the fast reaction 2 and interposed between the two charge transfer steps should be hence:
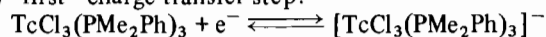
$$TcCl_2(PMe_2Ph)_3(MeCN) + MeCN \longrightarrow$$
$$TcCl_2(PMe_2Ph)_3(MeCN)_2 \quad (4)$$
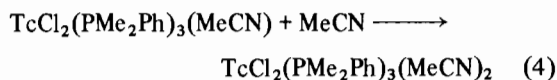
This reaction involves the formation of an eptacoordinated technetium(II) complex; this coordination number has been already reported for technetium(III) compounds [7, 8] but not for technetium(II) ones.

An alternative chemical reaction involving $TcCl_2$-$(PMe_2Ph)_3(MeCN)$ and generating a technetium(II) complex responsible for the redox systems involved in the voltammetric peaks F–G and H–I could be the release of a phosphine group; however, no experimental evidence has been gained for the presence of free phosphine molecules in the solution electrolyzed at -0.7 V, as checked by us by comparing the voltammetric behaviour of PMe_2Ph in acetonitrile medium.
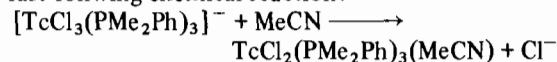
In conclusion the mechanisms involved in the processes arising from the reduction of $TcCl_3(PMe_2$-$Ph)_3$ are the following:
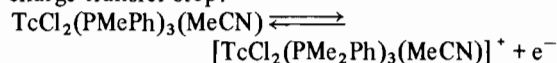
Peak A:
1) "first" charge transfer step:
$$TcCl_3(PMe_2Ph)_3 + e^- \rightleftharpoons [TcCl_3(PMe_2Ph)_3]^-$$
2) fast follwing chemical reaction:
$$[TcCl_3(PMe_2Ph)_3]^- + MeCN \longrightarrow$$
$$TcCl_2(PMe_2Ph)_3(MeCN) + Cl^-$$

Peaks B–C:
3) charge transfer step:
$$TcCl_2(PMePh)_3(MeCN) \rightleftharpoons$$
$$[TcCl_2(PMe_2Ph)_3(MeCN)]^+ + e^-$$
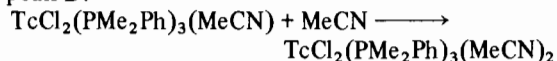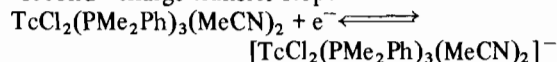4) slow chemical reaction, following the reaction 2, preceding the "second" charge transfer step 5 and lowering the concentration of the species oxidizable at peak B:
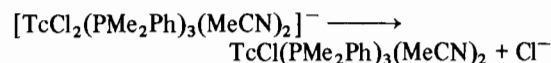$$TcCl_2(PMe_2Ph)_3(MeCN) + MeCN \longrightarrow$$
$$TcCl_2(PMe_2Ph)_3(MeCN)_2$$

Peaks H–I:
5) "second" charge transfer step:
$$TcCl_2(PMe_2Ph)_3(MeCN)_2 + e^- \rightleftharpoons$$
$$[TcCl_2(PMe_2Ph)_3(MeCN)_2]^-$$
6) slow chemical reaction, following the reduction step 5:

$$[TcCl_2(PMe_2Ph)_3(MeCN)_2]^- \longrightarrow$$
$$TcCl(PMe_2Ph)_3(MeCN)_2 + Cl^-$$

Peaks F–G:
7) charge transfer step:
$$TcCl_2(PMe_2Ph)_3(MeCN)_2 \rightleftharpoons$$
$$[TcCl_2(PMe_2Ph)_3(MeCN)_2]^+ + e^-$$
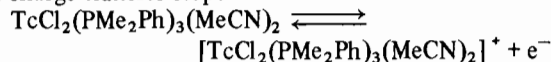
Peaks D–E:
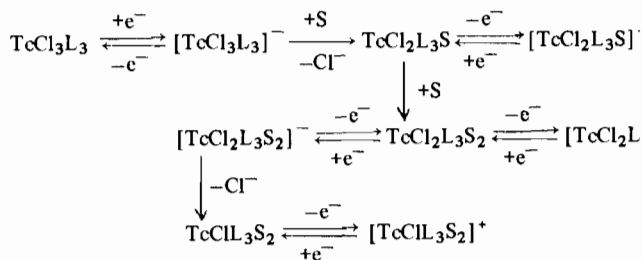8) charge transfer step:
$$TcCl(PMe_2Ph)_3(MeCN)_2 \rightleftharpoons$$
$$[TcCl(PMe_2Ph)_3(MeCN)_2]^+ + e^-$$
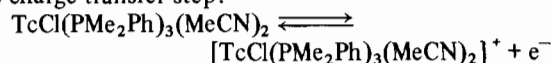
Scheme I summarizes the electrochemical processes together with the equilibria involved in the reduction of $TcCl_3(PMe_2Ph)_3$, acetonitrile solution:

SCHEME I

(L = PMe_2Ph; S = MeCN)

Reduction of TcCl₄(PMe₂Ph)₂

The trend of the $(i_p)_a/(i_p)_c$ ratio as a function of the scan rate allowed to take into account the hypothesis of the occurrence of a slow chemical reaction following the quasi reversible charge transfer step; the quantitative analysis of the precipitated NaCl confirmed this hypothesis.

The reduction mechanism could be hence written as:

$$TcCl_4(PMe_2Ph)_2 + e^- \rightleftharpoons [TcCl_4(PMe_2Ph)_2]^-$$

$$[TcCl_4(PMe_2Ph)_2]^- + MeCN \longrightarrow$$
$$TcCl_3(PMe_2Ph)_2(MeCN) + Cl^-$$
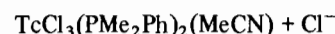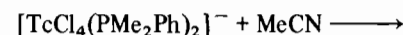
The absence of the third phosphine group in the above resulting technetium(III) compound accounts for its low stability in respect to $TcCl_3(PMe_2Ph)_3$. $TcCl_3(PMe_2Ph)_2(MeCN)$ should hence release a solvent molecule and withdraw a phosphine ligand from another $TcCl_3(PMe_2Ph)_2(MeCN)$ molecule, *via* a slow chemical reaction leading to unidentified products. The occurrence of this slow chemical decomposition is supported also by the voltammetric data obtained at the end of the exhaustive electrolyses, showing the peak relative to the reduction of $TcCl_3(PMe_2Ph)_3$ to be lower than that relative to the reduction of the starting technetium(IV) compound.

Acknowledgements

References

1 J. E. Fergusson and J. H. Hickford, *J. Inorg. Nucl. Chem.*, *28*, 2293 (1966).
2 J. E. Fergusson and J. H. Hickford, *Aust. J. Chem.*, *23*, 453 (1970).
3 U. Mazzi, D. A. Clemente, G. Bandoli, L. Magon and A. A. Orio, *Inorg. Chem.*, *16*, 1042 (1977).
4 U. Mazzi, G. De Paoli, P. Di Bernardo and L. Magon, *J. Inorg. Nucl. Chem.*, *38*, 721 (1976).
5 U. Mazzi, G. De Paoli and O. Traverso, *J. Inorg. Nucl. Chem.*, *39*, 1090 (1977).
6 G. A. Mazzocchin, R. Seeber, U. Mazzi and E. Roncari, *Inorg. Chim. Acta*, preceding paper.
7 D. A. Clemente, G. Bandoli and U. Mazzi, *J. Chem. Soc. Dalton*, in press.
8 U. Mazzi, A. Bismondo, N. Kotsev and D. A. Clemente, *J. Organomet. Chem.*, *135*, 177 (1977).