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Voltammetric Behaviour of Technetium^{99} Complexes with π-Acceptor Ligands in Aprotic Medium. I. Oxidation of $TcCl_3(PMe_2Ph)_3$

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The use of the electroanalytical techniques to study the oxidation of the technetium(III) phosphine complex $TcCl_3(PMe_2Ph)_3$ in acetonitrile medium evidentiated the feasibility of the obtainement of two distinct oxidation products, $TcCl_4(PMe_2Ph)_2$ and $[TcCl_2(PMe_2Ph)_3(MeCN)]^+ ClO_4^-$, depending on the nature of the supporting electrolyte. The latter compound has been also chemically prepared and characterized. Furthermore the formation, as primary electrode product, of a relatively long lived intermediate compound, $[TcCl_3(PMe_2Ph)_3]^+ ClO_4^-$, has been observed. The electrode oxidation processes have been also studied.

Introduction

In recent years phosphine complexes of technetium^{99} have been synthesized [1–5]; phosphine ligands stabilize the technetium complexes with the metal ion in a low oxidation state (+4, +3, +2). In fact complexes of the type TcX_4L_2 and TcX_3L_3 (X = Cl, Br and L = PR_2Ph, $PRPh_2$, PPh_3 with R = Me and Et) have been easily prepared varying the ratio between the technetium and the phosphine ligand amounts [4]. More recently [6] X-ray analyses have been carried out on the complex $TcCl_3(PMe_2Ph)_3$, elucidating its structure and forecasting its reactivity.

As no electrochemical study on technetium complexes with π-acceptor ligands has been reported until now, the aim of this series of investigations is to apply electroanalytical techniques to this class of compounds, in order to study the redox behaviour, to evidentiate unusual oxidation states, the existence of equilibria in solution and to ascertain the possibility of preparative electrochemical methods.

The present paper reports the results obtained in the study of the electrode oxidation of $TcCl_3(PMe_2Ph)_3$ in acetonitrile solvent. For this purpose cyclic voltammetry, chronoamperometry and controlled potential coulometry were the main techniques employed.

Experimental

Chemicals and Reagents

The technetium complexes $TcCl_3(PMe_2Ph)_3$ and $TcCl_4(PMe_2Ph)_2$ were prepared according to the methods suggested in ref. 4. All other chemicals were of reagent grade purity. Reagent grade acetonitrile (C. Erba) was purified by repeated distillation on phosphorus pentoxide and stored on molecular sieves (3Å).

The supporting electrolytes were anhydrous sodium perchlorate, tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium tetrafluoroborate (TBATFB), prepared by neutralizing perchloric acid with sodium carbonate, perchloric acid and hydrogen tetrafluoroborate with tetrabutylammonium hydroxide, respectively. The salts were recrystallized from methanol and dried in a vacuum oven.

Apparatus and Methods

The coulometric experiments were carried out in a H shaped cell with anodic and cathodic compartments separated by a sintered glass disk. The polarizing unit was an Amel potentiostat Mod. 557 with an associated Amel integrator Mod. 558.

The apparatus employed in the cyclic voltammetric experiments and in the chronoamperometric ones has been already described [7]; in these tests a cell of suitable geometry was used [8].

Platinum working electrodes were always used (Pt sphere stationary microelectrode in the voltammetric and chronoamperometric tests, Pt gauze in the controlled potential electrolyses).

The reference electrode was an aqueous S.C.E., to which all the potential values are referred. All the electroanalytical tests were carried out at 20 °C.

I.R. spectra were recorded with a Perkin Elmer Mod. 577 spectrophotometer.

In the electrolyses carried out with the aim to recover the products $NaClO_4$ was employed as supporting electrolyte; in fact it is slightly soluble in chloroform, in which solvent the complexes exhibit a high solubility. After completion of the electrolyses, MeCN solvent was removed by evaporation under vacuum and the residual solid was shaken with a small amount of chloroform; after filtration the solution was further evaporated and the residua washed with ethanol giving small crystals of the complexes.

The quantitative analysis of the chlorine bonded to the central technetium metal was carried out by potentiometric titration with a standard $AgNO_3$ solution. For this purpose the technetium complexes were preliminarily converted to pertechnetate ion by reacting with hydrogen peroxide.

The compound $[TcCl_2(PMe_2Ph)_3(MeCN)]^+ClO_4^-$ has been chemically prepared by reacting the $TcCl_3(PMe_2Ph)_3$ complex with a stoichiometric amount of $AgClO_4$ in MeCN solution; the precipitation of the sparingly soluble AgCl forced the equilibrium to the quantitative formation of the desired ionic technetium compound. The complex was recovered, after filtration of AgCl, by evaporation under vacuum of the solvent and by washing the residuum with small amounts of ethanol. The recrystallization was carried out by slow evaporation of an ethanol–acetonitrile solution.

Results

Fig. 1 shows the cyclic voltammetric picture exhibited by a $2.1 \times 10^{-3}M$ $TcCl_3(PMe_2Ph)_3$, $0.1M$ TBAP, MeCN solution; the potential was initially scanned in the anodic direction; no difference could be noted when $NaClO_4$ or TBATFB were used as supporting electrolytes.

As can be observed, the examined compound undergoes an oxidation process (peak A) with an E_p value of +0.86 V; by reversing the potential scan an associated cathodic response appears (peak B). The $(E_p)_a - (E_p)_c$ value relative to this catho–anodic system is equal to 75 mV; the $(E_p)_a - (E_{p/2})_a$ value is equal to 70 mV.

Cyclic voltammetric tests carried out at different potential scan rates led to a plot of $(i_p)_a$ *vs.* $v^{1/2}$ showing a linear trend, so indicating a diffusive character for the anodic process; moreover the $(E_p)_a$ value remained unchanged at the different scan rates and the $(i_p)_c/(i_p)_a$ ratio resulted always equal to one.

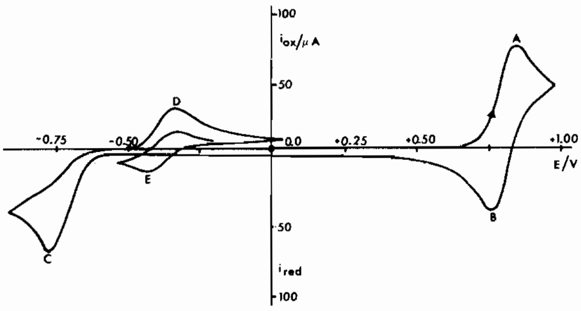

Figure 1. Cyclic voltammetric curve recorded with a platinum microelectrode: $2.1 \times 10^{-3}M$ $TcCl_3(PMe_2Ph)_3$, 0.1 TBAP, MeCN soln. Scan rate 0.2 V s^{-1}; ● starting potential, anodic scan.

Chronoamperometric experiments confirmed the diffusive control of the anodic process.

The more cathodic peak (C) shown in Fig. 1 could be observed also by scanning the potential in the cathodic direction starting from an initial value of 0.0 V; it must be hence attributed to the reduction of the studied compound and cannot be associated to species produced in correspondence to peak A.

Controlled potential coulometric experiments carried out at potential values corresponding to peak A indicated that one mol of electrons per mol of technetium complex is involved in the overall oxidation process.

In the presence of $NaClO_4$ as supporting electrolyte the solution, bright yellow in colour at the start of the electrolysis, became initially green, but changed progressively to a brick-red colour; at the same time a white precipitate, identified as NaCl, appeared. The quantitative analysis revealed that the number of mol of the precipitated chloride was equal to that of initial technetium complex (and to the number of Faradays spent). The potentiometric determination of the chlorine bonded to the technetium in the recovered oxidation product indicated that only two chlorine atoms per technetium atom were still present. I.R. spectra performed on this technetium compound allowed to evidentiate also the presence of ClO_4^- ions, as demonstrated by the appearance of two bands at 1090 and 631 cm^{-1} and of MeCN (C≡N stretching, weak and sharp band at 2290 cm^{-1}).

When the electrolyses were performed by using TBAP or TBATFB as supporting electrolytes, no precipitate appeared and the initially green solution became orange in colour.

When the electrolyses were performed in presence of large amounts of tetrabutylammonium chloride the solution remained bright green in colour.

Cyclic voltammetric tests carried out on the electrolyzed solutions showed, as reported in Figs. 2, three different pictures, depending on the type of the employed electrolyte.

When $NaClO_4$ was used two cathodic peaks could be noted (Fig. 2a); the first, rounded and poorly defined, located at about −0.15 V, appeared as a shoulder of a more developed peak with $(E_p)_c$ value of −0.4 V; an anodic response ($(E_p)_a$ = −0.3 V) was associated to this last peak.

When TBAP was used as supporting electrolyte a voltammetric curve like that reported in Fig. 2b was recorded: together with the above reported responses, a catho–anodic system with $(E_p)_c$ = −0.025 V and $(E_p)_a$ = 0.05 V appeared.

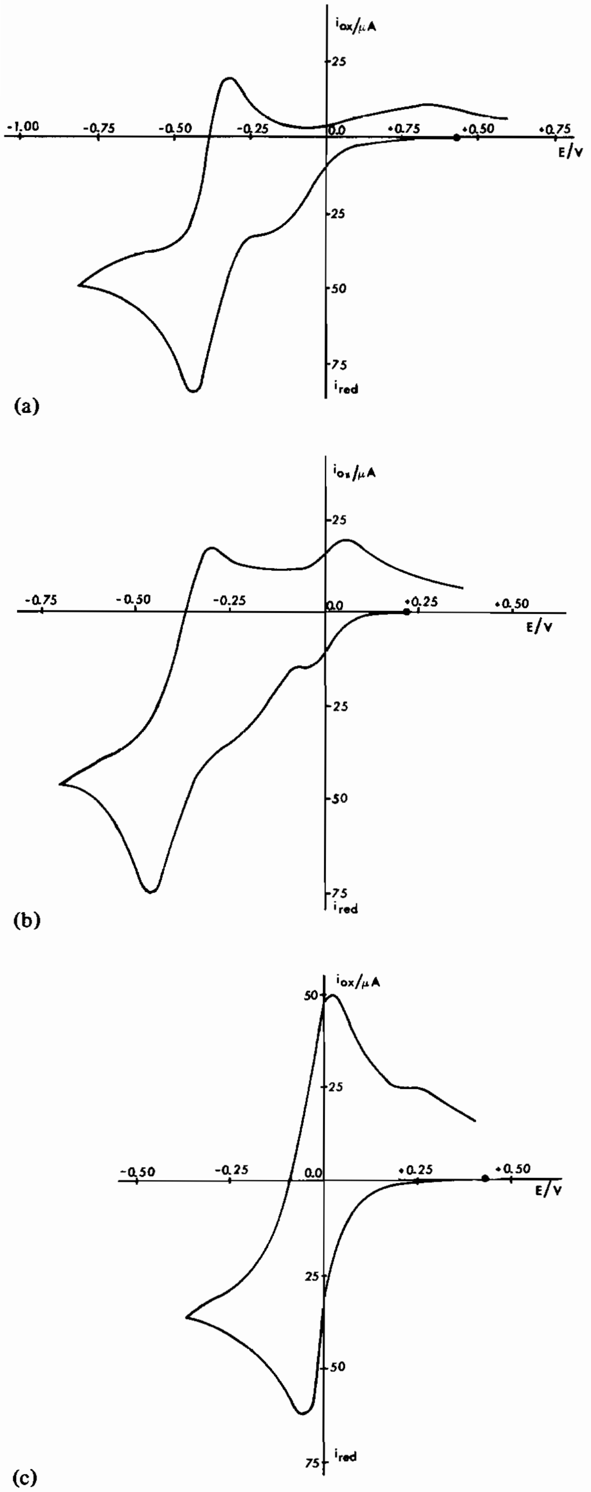

Figure 2. Cyclic voltammetric curves recorded on TcCl$_3$(PMe$_2$Ph)$_3$ solutions electrolyzed at +1.00 V in presence of: a) 0.1*M* NaClO$_4$ supporting electrolyte; b) 0.1*M* TBAP supporting electrolyte; c) 0.1*M* TBAP supporting electrolyte, 5 × 10^{-2}*M* tetrabutylammonium chloride. Platinum working microelectrode; scan rate 0.2 V s^{-1}, ● starting potential, cathodic scan.

Fig. 2c shows that in presence of tetrabutylammonium chloride the compound responsible of the last cited cathodic peak is the main oxidation product.

It must be also noted that the solutions resulting from the anodic oxidation carried out in presence of NaClO$_4$, TBAP or TBATFB, but in absence of chloride ions, were acidic; the most marked acid character was exhibited by the solutions electrolyzed in presence of NaClO$_4$.

The above cited cathodic peak with $(E_p)_c$ = –0.025 V has to be attributed to the reduction of TcCl$_4$(PMe$_2$Ph)$_2$, as checked by us by comparison with the voltammetric behaviour of authentic samples. The intermediate broad peak in Fig. 2b, coincident with the less cathodic one in Fig. 2a, is due to the reduction of free H$^+$ ions, as checked by adding anhydrous HClO$_4$ in MeCN [9]. The more cathodic peak in Fig. 2a and 2b is attributable to the reduction of the species [TcCl$_2$(PMe$_2$Ph)$_3$(MeCN)]$^+$-ClO$_4^-$, as demonstrated by the voltammetric behaviour of this compound, chemically prepared (see Experimental). In this connection it can be noted that MeCN solutions of TcCl$_4$(PMe$_2$Ph)$_2$ appear green in colour, while MeCN solutions of [TcCl$_2$(PMe$_2$Ph)$_3$-(MeCN)]$^+$ClO$_4^-$ are red in colour.

When NaClO$_4$ supporting electrolyte was used, coulometric tests carried out by reducing at a potential value of –0.6 V previously oxidized solutions of TcCl$_3$(PMe$_2$Ph)$_3$ required two mol of electrons per mol of electrolyzed technetium(III) complex. At the end of these reductions the solutions were no more acidic in character.

Controlled potential coulometric reductions carried out at –0.6 V on MeCN solutions of [TcCl$_2$-(PMe$_2$Ph)$_3$(MeCN)]$^+$ClO$_4^-$ chemically prepared indicated that one mol of electrons per mol of compound was used.

Discussion

The voltammetric data relative to the catho–anodic system A/B in Fig. 1, together with the coulometric results (n_e = 1), indicate the quasi-reversible character of the electrode process.

On this basis it is possible to state that the electrode reaction is the following:

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

However the complete absence of peak B in the voltammograms recorded at the end of the electrolyses, together with the appearance of the set of cathodic peaks reported in Figs. 2, undetectable in the cyclic voltammograms recorded on the starting solutions, suggest that the electrogenerated technetium(IV) complex must undergo a chemical reaction following the charge transfer step 1.

The constant value of the ratios $(i_p)_c/(i_p)_a$ and $(i_p)_a/v^{1/2}$ calculated at different potential scan rates, together with the absence of any cathodic shift in $(E_p)_a$ values at increasing scan rate, indicate that the arising chemical complications must be slow enough not to occur significatively in the time required by a voltammetric scan (also at the lowest scan rates).

The recovery of two different products and the appearance of different voltammetric pictures depending on the nature of the supporting electrolyte forced us to hypothesize two different ways for the decay of the primary electrode product $[TcCl_3(PMe_2Ph)_3]^+ClO_4^-$. The voltammetric responses reported in Figs. 2 and the quantitative determination of the chlorine indicate that the occurrence of the different pathways depends on the presence either of Na^+ or of Cl^- ions in the electrolyzed solution.

When Na^+ ions, coming from $NaClO_4$ supporting electrolyte, were present the recovered product was a technetium(III) compound. It is well known that water is always present in the nominally anhydrous MeCN; the acidic character of the electrolysed solution indicates that water acts as a reducing agent in respect to the electrogenerated technetium(IV) complex, according to the following reaction:

$$2[TcCl_3(PMe_2Ph)_3]^+ClO_4^- + H_2O + 2Na^+ + MeCN \longrightarrow 2[TcCl_2(PMe_2Ph)_3(MeCN)]^+ClO_4^- + 2H^+ + \tfrac{1}{2}O_2 + 2NaCl\downarrow \qquad (2)$$

The formula of the technetium compound resulting from this reaction agrees well with the data of the performed analyses, which indicated its ionic character (ClO_4^- ions from I.R. spectra) and the presence in the molecule of two chlorine atoms and of MeCN. A further proof was achieved by comparing the voltammetric reduction peak exhibited by this product with that of an authentic sample chemically prepared.

The coulometric data obtained by reducing previously oxidized solutions confirmed the occurrence of the above reported reaction 2. In fact its stoichiometry provides for the formation of one mol of $[TcCl_2(PMe_2Ph)_3(MeCN)]^+ClO_4^-$ and one mol of H^+ ions per mol of initial complex; both H^+ and the technetium(III) ionic compound undergo an one-electron reduction process.

As a further check of the nature of the main oxidation product obtained in presence of $NaClO_4$, it must be noted that voltammetric tests carried out on the anodically electrolyzed solutions by scanning the potential in the anodic direction evidentiated a broad oxidation peak at about +1.6 V with an associated cathodic peak at about +1.0 V; both these peaks were exhibited also by solutions of $[TcCl_2(PMe_2Ph)_3(MeCN)]^+ClO_4^-$, chemically prepared.

The alternative decay reaction of $[TcCl_3(PMe_2Ph)_3]^+ClO_4^-$, operative in presence of TBAP or of TBATFB as supporting electrolytes forecasts the formation of the uncharged technetium(IV) compounds, according to:

$$[TcCl_3(PMe_2Ph)_3]^+ClO_4^- + Cl^- \longrightarrow TcCl_4(PMe_2Ph)_2 + PMe_2Ph + ClO_4^- \qquad (3)$$

The required chloride ions are supplied, in this case, by a side reaction involving the decay of the primary electrode product, similar to reaction 2; however, the absence of Na^+ ions allows in this case the Cl^- ions to be available for the occurrence of reaction 3.

In conclusion the reported reactions 2 and 3 following the charge transfer step account well for the effect of the presence in solution of $NaClO_4$ or of tetrabutylammonium chloride. In fact sodium ions precipitate almost quantitatively the chloride ions produced in reaction 2, making negligible the amount of the species $TcCl_4(PMe_2Ph)_2$ produced *via* reaction 3; the main oxidation product is hence $[TcCl_2(PMe_2Ph)_3(MeCN)]^+ClO_4^-$. On the contrary, when chloride ions are present, the occurrence of reaction 3 is favoured in respect to reaction 2, leading to $TcCl_4(PMe_2Ph)_2$ as the main product.

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