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Voltammetric Behaviour of Technetium^{99} Complexes with π-acceptor Ligands in Aprotic Medium. III. Oxidation of Technetium(I) Complexes with Phosphine and Carbon Monoxide Ligands

U. MAZZI, E. RONCARI

Laboratorio di Chimica e Tecnologia dei Radioelementi, CNR, Corso Stati Uniti, 35100 Padua, Italy

R. SEEBER and G. A. MAZZOCCHIN

Istituto di Chimica Generale dell'Universitá di Siena, Pian dei Mantellini 44, 53100 Siena, Italy

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The anodic behaviour of $TcCl(CO)_2(PMe_2Ph)_3$ *and* $TcCl(CO)_3(PMe_2Ph)_2$ *complexes has been studied in acetonitrile solvent. Both the complexes undergo an overall two-electron oxidation process with the formation of Tc(III) species; the electrode mechanism leading to their formation has been studied. In particular the* $[TcCl(CO)(MeCN)_2(PMe_2Ph)_3][ClO_4]_2$ *compound has been isolated and characterized.*

Introduction

In recent years the chemistry of technetium has developed from nuclear and inorganic viewpoint. However the latter aspect has been less considered and, in particular, little work dealing with technetium complexes in low oxidation state has been carried out. Some technetium^{99} complexes with carbon monoxide and phosphine ligands have recently been prepared and characterized [1–3]. Their electrochemical behaviour is of interest in obtaining useful information about the redox properties of coordination compounds with technetium in low oxidation states.

Voltammetric techniques are well suited for investigating these complexes in that they allow the elucidating of the electrode mechanisms and checking of the feasibility of synthesizing new species which are difficult to prepare via conventional methods.

This paper deals with the electrode oxidation of $TcCl(CO)_2(PMe_2Ph)_3$ and $TcCl(CO)_3(PMe_2Ph)_2$ complexes in acetonitrile solvent and is a part of our study on the electrochemical behaviour of technetium^{99} complexes with π-acceptor ligands in aprotic medium. Part I [4] and II [5] reported the redox behaviour of phosphine technetium(III) and technetium(IV) complexes.

Experimental

Chemicals, apparati and methods have already been reported [4]. All potential values are referred to an aqueous S.C.E.; the electroanalytical tests were carried out at 20 °C. The complexes $TcCl(CO)_2(PMe_2Ph)_3$ and $TcCl(CO)_3(PMe_2Ph)_2$ were prepared according to ref. [1]. Magnetic susceptibilities in MeCN or $MeNO_2$ solutions were measured by Evans' method [6] and corrected for diamagnetism of the ligands [7]. ^1H NMR spectra were recorded on a Varian T60 instrument with TMS as internal standard. Conductivity measurements were carried out on an Amel mod. 131 conductometer on 10^{-3} M MeCN solutions at 20 °C ± 0.1. The analysis of chlorine was performed by two methods: (i) by decomposition of the compound with hydrogen peroxide and subsequent titration of the chloride anion with a standard $AgNO_3$ solution and potentiometric determination of the end point; in this case the perchlorate anion remains unchanged and is not determined; (ii) by decomposing the complexes with Schoeniger's method and finally determining the total halogen amount with the same method described above.

Technetium^{99} was determined by a method described elsewhere [8]; for the microdetermination of phosphorus we have used the method of Puschel *et al.* [9] corrected as suggested by Nuti *et al.* [10].

Results and Discussion

$TcCl(CO)_2(PMe_2Ph)_3$

Figure 1 shows a cyclic voltammogram recorded with a platinum electrode on a 3.1×10^{-3} M $TcCl(CO)_2(PMe_2Ph)_3$, 0.1 M $NaClO_4$, MeCN solution, by scanning the potential initially in anodic direction.

In the forward scan two rather close peaks are noted; the E_p values are +0.83 and +1.02 V respectively; a cathodic peak associated with the two anodic ones is recorded (E_p = +0.74 V).

As shown in the figure, by switching the potential scan direction just after traversing the first anodic peak (A) the i_p value of the cathodic one (C) results

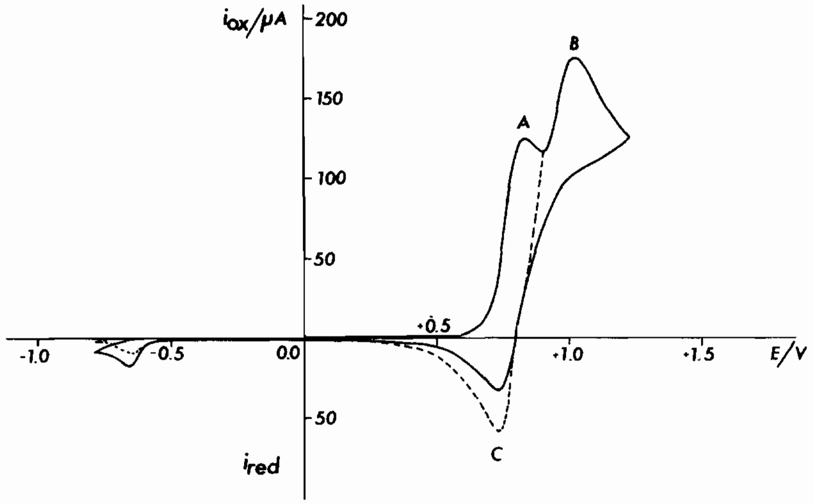

Fig. 1. Cyclic voltammetric curves recorded on a 3.1 × 10^{-3} *M* $TcCl(CO)_2(PMe_2Ph)_3$, 0.1 *M* $NaClO_4$, MeCN soln.; potential scan initially anodic in direction. Pt working microelectrode. Scan rate 0.2 V s^{-1}.

higher than that recorded after traversing also the second anodic peak (B); still smaller $(i_p)_C$ values were obtained if the electrode potential was stopped for few seconds beyond peak A or peak B. Furthermore, in the reverse scan a second cathodic peak, small in height, with an E_p value of –0.65 V, was also recorded; this peak increased in correspondence to the decrease of peak C.

Cyclic voltammetric tests carried out at different potential scan rates revealed that both $(i_p)_B/(i_p)_A$ and $(i_p)_C/(i_p)_A$ increased at increasing potential sweep rate.

It must be noted that the voltammetric picture was not found to be perfectly reproducible, mainly as regards position and height of peak B, depending on the state of the electrode surface, suggesting the absorption phenomena are operative to some extent. Consequently, the obtained voltammetric data have to be considered only from a qualitative point of view.

Controlled potential coulometric experiments carried out in correspondence to the foot of peak A led to a consumption of two mol of electrons per mol of electrolyzed compound. Cyclic voltammograms recorded on the electrolyzed solutions revealed the disappearance of both peaks A and B; furthermore no species oxidizable in the available potential range was present in the solution. On the other hand a reducible species gave rise to a peak with E_p equal to –0.65 V, the same value found for the more cathodic peak associated to the anodic ones recorded on the starting solutions. This response appeared typical for an irreversible electrode process.

Coulometric tests performed on the starting solution, directly at potential values more anodic than $(E_p)_B$ again revealed the occurrence of an overall two-electron oxidation process; moreover, cyclic voltammetric tests on the electrolyzed solutions showed a picture very similar to that previously described.

The determinations performed on solutions exhaustively electrolyzed at the two different potentials confirmed that in both cases the same technetium(III) complex was formed.

The electrolyzed light yellow solution was dried under vacuum and then washed with water. The pale yellow powder obtained was washed with a small amount of ethanol and dried with diethyl ether[a].

The potentiometric titration of the chlorine directly bonded to the technetium atom led to a ratio Cl/Tc = 1:1, while a ratio 3:1 was found when the overall chlorine amount present in the compound was measured. The quantitative determination of phosphorus allowed to conclude that the ratio 3:1 between phosphine groups and central technetium metal was retained also in the oxidation product.

I.R. spectra of the recovered compound proved the presence of perchlorate ions (broad absorption band at 1090 cm^{-1} and narrow band at 630 cm^{-1}); moreover the presence of both CO (ν(CO) = 1947 cm^{-1}) and MeCN (ν(CN) = 2284 cm^{-1}) molecules coordinated to the metal center was checked. Finally the whole set of absorption bands due to the dimethylphenylphosphine groups, was detectable. Magnetic susceptivity measurements revealed that the formed complex is diamagnetic both in MeCN and in $MeNO_2$ solutions. Diamagnetism is consistent, for a d^4 electronic configuration, with an epta-coordinaton around the metal. In fact the molecular-orbital energy level for the only possible D_{5h} or C_{3v} seven-

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[a] This compound is explosive on continuous rubbing.

coordinate geometries, show a degenerate pair of low-lying levels [3] in which the four electrons settle with coupling.

All the elemental analysis data ($Cl_{coord}\%$ = 4.12(4.13), $Cl_{tot}\%$ = 12.80(12.40), Tc% = 12.02 (11.53) and P% = 10.70(10.83)) relative to the oxidation product of $TcCl(CO)_2(PMe_2Ph)_3$ are consistent with the formula $[TcCl(CO)(MeCN)_2(PMe_2Ph)_3][ClO_4]_2$.

The molar conductivity in 10^{-3} *M* MeCN solution, equal to 230 cm^2 ohm^{-1} mol^{-1}, fell in the range typical for a 1:2 electrolyte type in the same solvent (230–300 cm^2 ohm^{-1} mol^{-1}).

^1H NMR spectrum in saturated CD_3NO_2 solution showed a very narrow doublet at δ = 2.74 ppm (J = 1.5 Hz), a group of two nearly superimposed doublets at δ = 1.84 ppm (J = 9.6 Hz) and at δ = 1.78 ppm (J = 6.5 Hz) and, in the phenyl proton region, a multiplet at δ = 7.77 ppm. The area integrations of the three groups of peaks gave 2:6:5 relative ratios.

The first split peak is attributable to the CH_3-protons of the two *quasi* equivalent acetonitrile ligands; the chemical shift values fall at lower field than the free ligand (δ = 1.96 ppm) showing that the coordination involves a moving of electrons towards the C≡N group. This conclusion is supported by I.R. results; in fact a shift to higher frequencies of ν(C≡N) stretching vibration in respect to the free ligand (2284 *vs.* 2245 cm^{-1}) has been observed. The doublets at 1.84 and 1.78 ppm could not be integrated separately, since they overlapped each other leading to three peaks with areas in 1:2:3 ratios. These signals are attributable to the methyl protons of the three dimethylphenylphosphine ligands, one being in a non equivalent position in respect to the other two, split by coupling with the phosphorus atom.

From the ^1H NMR results a possible configuration of the compound is reported in Fig. 2.

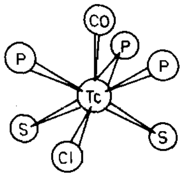


Fig. 2. Probable configuration of $[TcCl(CO)(MeCN)_2(PMe_2Ph)_3][ClO_4]_2$.

A similar structure is not unusual for technetium compound; in fact also the X-ray structure determination of the $TcCl_3(CO)(PMe_2Ph)_3$ complex [3] shows the CO group to be surrounded by three phosphine ligands. On the other hand just the $TcCl_3(CO)(PMe_2Ph)_3$ compound was obtained when $[TcCl(CO)(MeCN)_2(PMe_2Ph)_3][ClO_4]_2$ was treated with $AsPh_4Cl$ in ethanol or acetonitrile.

The oxidation pathway leading to the final oxidation product seems to be rather complicated. However, even if a single mechanism cannot be proposed, the results can be discussed.

Recalling that peak B is no more detectable in the voltammograms recorded on solutions exhaustively electrolyzed at peak A, that the number of electrons involved in the oxidation process at potentials corresponding either to peak A or to peak B is the same, and that identical is the recovered electrolysis product, and finally that the ratio $(i_p)_B/(i_p)_A$ increases on increasing the potential sweep rate, we can conclude that the peak B is attributable to the oxidation of an intermediate species of the overall process occurring at peak A. This intermediate species has to be oxidized at peak B and reduced at peak C, since the latter peak results lower in height if the potential scan is reversed beyond peak B. However, since peak C is in any case well detectable it must be assumed that the oxidation process occurring at peak B does not involve the whole amount of this intermediate species. A similar hypothesis is consistent with an anodic oxidation leading to a species adsorbed on the electrode surface; since poisoning of the electrode surface is often coupled to adsorption phenomena, this explanation accounts for the poor reproducibility of the response, depending on the state of the electrode surface.

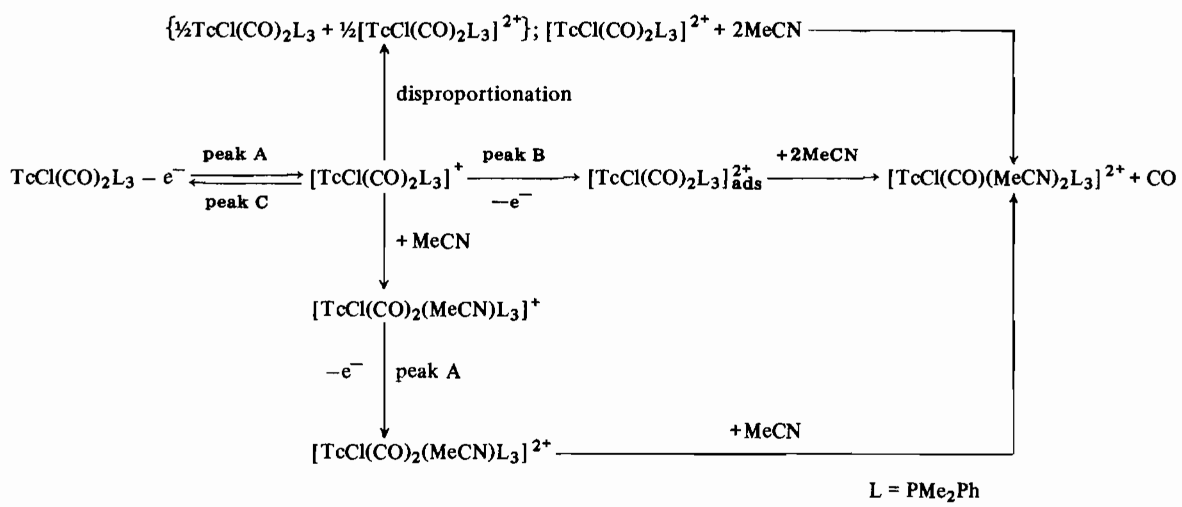
Moreover, on the basis of the stoichiometry of the recovered product, it must be considered also the occurrence of chemical reactions involving the release of a CO molecule and the addition of two solvent molecules. The mechanism reported below, with two pathways both in agreement with the obtained results, can be hence proposed.

It can be noted that in both possible oxidation pathways, at peak A an e.c.e. type mechanism is operative; in the one the chemical reaction is a disproportionation of the Tc(II) species, while in the other a simple first order chemical reaction is interposed between two charge transfer steps. Unfortunately, the poor reproducibility of the response and the closeness of the two anodic peaks prevented the feasibility of accurate voltammetric and chronoamperometric measurements on the process occurring at peak A, to ascertain the order of chemical reaction coupled to the charge transfer, and hence to decide either the outlined mechanims simultaneously occur or only one is operative.

$TcCl(CO)_3(PMe_2Ph)_2$

Figure 3 shows the cyclic voltammetric behaviour exhibited at a platinum electrode by a 3.4 × 10^{-3} *M* $TcCl(CO)_3(PMe_2Ph)_2$, 0.1 *M* $NaClO_4$, MeCN solution, with the initial potential scan anodic in direction, at a sweep rate of 0.2 V s^{-1}.

Two anodic peaks (D and E) are recorded; to the first one a cathodic peak (F) is associated. The



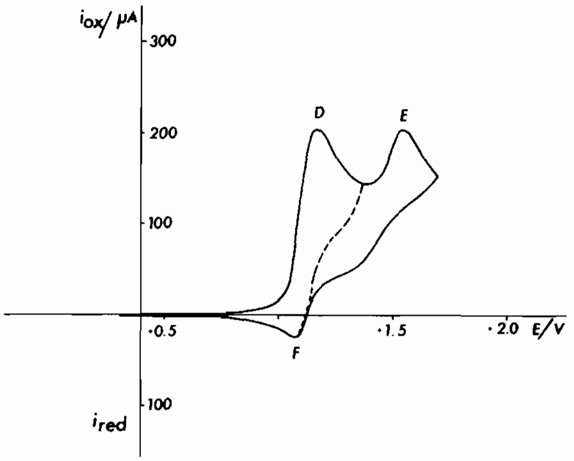


Fig. 3. Cyclic voltammetric curves recorded on a 3.4×10^{-3} *M* $TcCl(CO)_3(PMe_2Ph)_2$, 0.1 *M* $NaClO_4$, MeCN soln. Pt working microelectrode. Scan rate 0.2 Vs^{-1}.

relative E_p values resulted +1.17, +1.54 and +1.08 V, respectively.

The height of the cathodic peak F resulted independent of the switching potential, *i.e.* it remained unchanged if the potential scan was reversed after traversing peak D alone or both peaks D and E. The runs performed at different scan rates showed a decrease of the ratio $(i_p)_D/v^{1/2}$ and a corresponding increase of $(i_p)_F/(i_p)_D$ at increasing potential scan rate.

Coulometric tests carried out at potential values corresponding either to the foot or to the maximum of peak D led in any case to a consumption of two mol of electrons per mole of starting compound.

Voltammetric tests recorded on the electrolyzed solutions revealed that peak E was still present, together with a broad reduction peak (E_p = −0.75 V). When these solutions were further electrolyzed in correspondence to peak E a third electron was spent. Accordingly, three electrons per molecule were used if the starting solution was directly electrolyzed in correspondence to peak E.

The recovery of the products present in the solutions electrolyzed at peaks D and E gave rise in both cases to a yellow oil from which no solid product could be isolated. Preliminary results on the electroxidation of the analogous Re(I) compound, $ReCl(CO)_3(PMe_2Ph)_2$, [11] show that the oxidation product is the $ReCl_3(CO)_2(PMe_2Ph)_2$ complex. By analogy a similar compound can be hypothesized for the technetium derivative formed by electrolysis at peak D; however, it can be remarked that this technetium compound was not obtained also by following the chemical method already reported in literature for the rhenium one [12].

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