

## *In situ* low temperature dynamic electrochemistry and EPR spectroelectrochemistry of coordination compounds

### Part I. The construction of EPR microspectroelectrochemical cryostat equipped with non-aqueous reference half-cell with liquid junction and its utilization to characterization of the unstable, paramagnetic $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$ complex cation ¶

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#### Abstract

The construction of the EPR microspectroelectrochemical cryostat equipped with non-aqueous reference half-cell with liquid junction is described. The electrochemically generated, chemically unstable, paramagnetic  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation was *in situ* detected and characterized by EPR spectroscopy.

*Keywords:* EPR microspectroelectrochemical cryostat construction; Non-aqueous reference half-cell with liquid junction; *In situ* low temperature dynamic electrochemistry and EPR spectroelectrochemistry; Oxo-rhenium(V)/oxo-rhenium(VI) couple

#### 1. Introduction

Many different types of the electrochemical cells for EPR detection of electrochemically generated redox species have been described [1-7]. Application of the stable and accurate reference electrode is in such constructions of basic importance for the reliability and comparability of the results (obtained in various laboratories for both, the given compound and different compounds between one another) especially in high resistance, non-aqueous media at low temperatures. Most often to high purity and dry solvent the 'aqueous' reference electrode is introduced with one or two fritted glass (at the end of R.E. and of the intermediate salt bridge). Such a procedure causes the inevitable leakage of  $\text{H}_2\text{O}$ ,  $\text{Cl}^-$  or  $\text{Ag}^+$  to a sample solution even if the salt bridge is used. Every frit increases the IR drop of the electrochemical cell. In consequence, it could result in the apparent irreversibility of the electrode process, or in the limiting case, in the complete change of the electrode reaction mechanism. Such problems become particularly significant when the volume of a sample solution has to be possibly small. Basing on our potentiometric [8] and voltammetric studies [9,10] we have found that such conditions can be satisfied by Kawai's type reference half-cell with J-shaped liquid

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junction [11], after its slight modification and adaptation for non-aqueous, high resistive media, and miniaturization for *in situ* EPR-spectroelectrochemical studies with a small volume of the sample solution *ca.* 0.15 mL. In the present paper the construction of the microspectroelectrochemical cryostat equipped with non-aqueous reference half-cell with liquid junction, for simultaneous cyclic voltammetric and EPR detection of the electrochemically generated coordination compounds, is described. Using this cryostat, the chemically unstable, paramagnetic  $[O=Re(OEt)Cl_2(py)_2]^+$  complex cation (which is the product of low temperature (-61°C) electrooxidation of  $ReOCl_2(OEt)(py)_2$  starting complex) was *in situ* detected (at -196°C) and characterized by EPR spectroscopy.

## 2. Experimental

### 2.1. Instrumentation

**Electrochemistry.** 2.1.1. Preliminary cyclic voltammetry (CV) measurements were carried out (at 25°C) on a Laboratorni Pristroje Polarographic Analyzer (PA3 and PA4) and an XY recorder (types 4103 4105) or were displayed on the monitor screen using a measuring system consisting of a potentiostat (PA3 and PA4) connected to an IBM PC computer via an Ambex (Poland) AC module, type LC-20. The I-E data were elaborated using a program written in our laboratory. In this case the CV cell was a closed jacketed vessel (with thermostated water flow, 25°C) which was provided with a planar platinum working electrode (2mm disk diameter), Luggin capillary, the salt bridge (0.1 M  $Bu_4NPF_6 - CH_2Cl_2$  solution) with a fine porosity frit, reference ( $Hg_2Cl_2/Hg$ , satd.  $NaCl_{aq}$ ) electrode, Pt spiral auxiliary electrode, a side arm for introducing (under argon pressure) deoxygenated test solution, and a glass tube for argon inlet and outlet [12, 13]. 2.1.2. The final CV curves were digitally collected using a PAR 273A potentiostat/galvanostat associated with an IBM PS/2 computer. In the final CV measurements the electrochemical cryostat for 15 mL of sample solution (described previously [10]), and microspectroelectrochemical cryostat (0.15÷0.2 mL of sample) presented here (Figure 1) were used. Both cryostats were equipped with the slightly modified, non-aqueous ( $Ag/AgCl/satd. LiCl$ , 0.1 M TBAP in  $CH_2Cl_2$ ), Kawai's type [11] reference half-cell with liquid junction between the salt bridge solution (0.1 M TBAP in  $CH_2Cl_2$ ) and the sample solution ( $\sim 0.001 M \div \sim 0.01 M ReOCl_2(OEt)(py)_2$ , 0.1 M TBAP in  $CH_2Cl_2$ ). 2.1.3. The controlled potential coulometric measurements were carried out with a Radelkis OH 404 A potentiostat connected with an OH 404 C digital integrator. The coulometric cells (1÷0.5 mL) were provided with a platinum minigrid (Pt-Ir10%, 225 mesh) working and auxiliary electrodes, and a reference electrode (SCE) with a micro-salt bridge (J-shaped Luggin capillary). The cathodic and anodic compartments of the coulometric cells were separated by a fine porosity frit and both provided with a glass tube for argon inlet and outlet and a side arm for introducing (under argon pressure) deoxygenated test solution or supporting electrolyte solution, respectively. 2.1.4. The potentiometric measurements of the electrode potential of the Kawai's type reference half-cell were performed (in 0.1 M TBAP/ $CH_2Cl_2$  test solution) versus saturated ( $NaCl_{aq}$ ) calomel electrode with salt bridge (0.1 M TBAP in  $CH_2Cl_2$ ) using an Orion Research Digital Ionanalyser (Model 701A). The temperature was maintained at  $25 \pm 0.1^\circ C$ .

All electrochemical cells were deaerated by passing a stream of argon (20 min) prior to introducing (by the argon pressure) the deoxygenated test solutions. During all measurements, argon (99.995%) was passed over the test or supporting electrolyte solution.

**2.2. Electron paramagnetic resonance.** The EPR spectra were recorded on Radiopan (Poland) spectrometer.

**2.3. Synthesis.** All preparations were performed (by one of us - W.K.R.) under dinitrogen atmosphere (free of moisture and oxygen) by using Schlenk techniques. Previously described  $ReOCl_2(OEt)(py)_2$  [14] was obtained here by alternative procedure. A mixture of 0.33 g (0.5 mmol)  $ReOCl_3(SMe_2)(OPPh_3)$  (*cf.* Ref. 15) in absolute ethanol (15 ml) containing 0.8 ml (10 mmol) pyridyne was stirred at 50-60°C for 2 hours. The blue-violet solid was filtered and recrystallized from  $CH_2Cl_2/EtOH$  solution as the blue plates. Yield 70%.

## 3. Results and discussion

### 3.1. The variable temperature microspectroelectrochemical cryostat equipped with non-aqueous reference half-cell with liquid junction for *in situ* EPR detection of the electrochemically generated paramagnetic species

The present EPR microspectroelectrochemical cryostat was constructed on the basis of the following idea: a simultaneous *in situ* cyclic voltammetric and electron paramagnetic resonance studies in 0.1 M TBAP/ $CH_2Cl_2$  supporting electrolyte should be possible including low temperature range, and the reference electrode potential should be stable and accurate (close to that attainable in potentiometry).

The apparatus shown in Fig. 1 consists of three parts, A, B, C. A is the quartz tube - CV/EPR measuring cell. B is the Kawai's type non-aqueous reference half-cell with liquid junction (reference electrode- salt bridge solution; salt bridge- sample solution):  $Ag|AgCl|reference\ electrode\ solution||salt\ bridge\ solution||sample\ solution|Pt(working\ electrode)$ ; where: reference electrode solution (in B2 compartment): 0.1 M TBAP, satd.  $LiCl$  in  $CH_2Cl_2$ ; salt bridge solution (in B1 compartment): 0.1 M TBAP in  $CH_2Cl_2$ ; sample solution (in A1 compartment): 0.001÷0.01 M complex compound under study, 0.1 M TBAP in  $CH_2Cl_2$ .

C is the quartz Dewar. The quality of quartz (part A, B, C, b, d and f) was carefully checked by the separate EPR measurements (prior to the final set-up).

The non-aqueous reference half-cell with liquid junction used here (B) was checked daily against the calomel reference electrode ( $Hg/Hg_2Cl_2/satd. NaCl$  in water) immersed in the salt bridge (filled with 0.1 M TBAP in  $CH_2Cl_2$ ) which was equipped with a fine porosity frit. The difference between those two reference half-cell ( $\Delta E = E_{Kawai's\ type} - E_{SCE}$ ) was about 2mV. Moreover, the above mentioned potentiometric measurements revealed the sufficient stability of the Kawai's type reference half-cells used, because after test measurements lasting 12 hours, the difference between two reference half-cell potentials was 1.7 mV ( $Ag/AgCl$  in  $CH_2Cl_2$ ); In acetonitrile as a solvent the stability of the Kawai's type reference half-cell ( $Ag/Ag^+$ ) was better (0.2 mV, *cf.* Ref. 9). Using the presented here microspectroelectrochemical cryostat equipped with the Kawai's type reference half-cell ( $Ag/AgCl$ ), the formal potential for ferrocene in  $CH_2Cl_2$  containing 0.1 M TBAP was evaluated from CV measurements:  $E^0 = (E_{pc} + E_{pa})/2 = 346\ mV$ ;  $\Delta E_p = 85\ mV$  (at -61°C and at scan rate of  $200\ mV\ s^{-1}$ ).

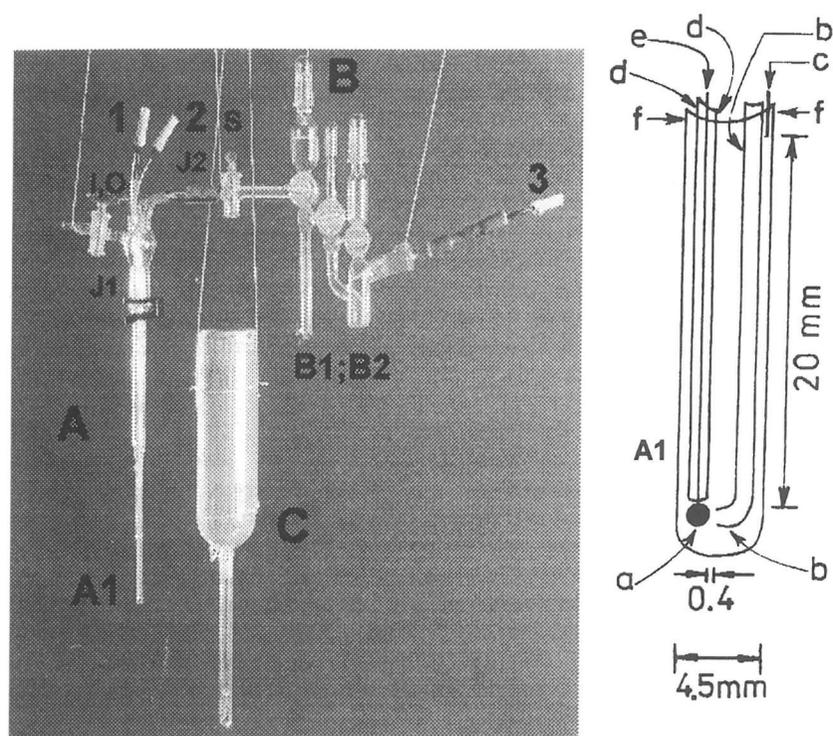


Fig. 1. Variable temperature EPR microspectroelectrochemical cryostat equipped with non-aqueous reference half-cell with liquid junction. *Left figure.* Photograph illustrating the structure of the microspectroelectrochemical cryostat for simultaneous *in situ* CV - EPR measurements: A - quartz tube (outer diameter: bottom 4.5 mm, top 10 mm); A1 - bottom part of A (see right figure); B - non-aqueous reference half-cell (pyrex); B1 - salt bridge compartment; B2 - reference electrode compartment; C - quartz Dewar; I -, O - flushing valves (argon inlet (I) and outlet (O)); J1, J2 - joints (J1: male-quartz, female-pyrex; J2: male-, female-pyrex); S - stopcock ; 1-, 2-, 3 - microjacks (for connection of working electrode (1), auxiliary electrode (2), reference half-cell (3) to the potentiostat/coulometer). *Right figure.* Cross-sections of A1 (4.5 mm x 20 mm). a - platinum (drop) working electrode ( $\phi \cong 1.5$  mm); b - quartz Luggin capillary (filled with salt bridge solution) which is J-type end of the reference half-cell (B); c- platinum wire auxiliary electrode ( $\phi = 0.1$  mm); d - thin-walled quartz capillary (isolation tube); e - platinum wire ( $\phi = 0.05$  mm); f - walls of the EPR quartz tube.

### 3.2. Dynamic electrochemistry of $\text{ReOCl}_2(\text{OEt})(\text{py})_2$ at 25°C

The  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  complex was found to produce well-shaped cyclic voltammograms at the Pt-working electrode. At room temperatures two peaks were observed in  $\text{CH}_2\text{Cl}_2$  solution containing 0.1 M tetrabutylammonium supporting

electrolyte salts (TBAX,  $\text{X} = \text{PF}_6^-$ ,  $\text{ClO}_4^-$ ). The representative parts of the CV data are summarized in Table 1 and 2.

TABLE 1 Cyclic voltammetric data for  $9.65 \times 10^{-4}$  M  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  oxidation in 0.1 M  $\text{Bu}_4\text{NPF}_6 - \text{CH}_2\text{Cl}_2$  solution at the Pt-planar (2mm disk diameter) electrode at 25°C.

$E_{pc}/\text{mV}$	$E_{pa} - E_{pc}/\text{mV}$	Scan rate/ $\text{mV s}^{-1}$	$E^{o'}$	$I_{pa}/I_{pc}$
1212.5	77.5	200	1251	1
1215	70	100	1250	1
1220	65	50	1252	1
1220	65	20	1252	1

TABLE 2 Cyclic voltammetric data for  $9.65 \times 10^{-4}$  M  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  reduction in 0.1 M  $\text{Bu}_4\text{NPF}_6 - \text{CH}_2\text{Cl}_2$  solution at the Pt-planar (2mm disk diameter) electrode at 25°C.

$E_{pc}/\text{mV}$	$E_{pc/2} - E_{pc}/\text{mV}$	Scan rate/ $\text{mV s}^{-1}$
-1430	85	500
-1415	75	200
-1405	65	100
-1390	70	50
-1370	65	20
-1365	60	10

For the peak observed at  $\sim 1.2$  V the ratio of the anodic to the cathodic peak current,  $I_{pa}/I_{pc}$ , was close to unity, and the values of  $I_p V^{-1/2}$  were constant, indicating the absence of coupled chemical reactions and diffusion control of the electrode process. The analysis of peak separation led to the conclusion that  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  undergoes totally reversible oxidation (Table 1), and the product of its one electron oxidation,  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation, is stable on the voltammetric time scale. However,  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation is unstable at room temperatures on the bulk electrolysis time scale (even for 1÷0.5 mL sample solution, the coulometrically measured charge increases monotonically and the starting solution continuous change of the colour (from blue to brown) is observed).

For the peak *ca.* at -1.4 V only the forward (cathodic) wave is detected. The  $E_{pc}$  value shifts linearly towards more negative potentials with the scan rate increase, while the  $E_{pc/2} - E_{pc}$  value remains practically constant (Table 2). Therefore, this peak could be assigned to the reduction of  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  starting complex to  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^-$  complex anion followed by the decomposition of the latter (oxo  $\text{Re(IV)}$ ) species.

The CV results presented here are in agreement with the literature data obtained at room temperatures for related systems containing the  $[\text{O}=\text{Re}(\text{OEt})]$  core [16].

### 3.3. *In situ* low temperature dynamic electrochemistry and EPR spectro-electrochemistry of $\text{ReOCl}_2(\text{OEt})(\text{py})_2$

Figure 2 shows the representative part of careful CV and EPR results *in situ* obtained, in the microspectroelectrochemical cryostat (presented here in Fig. 1), over the temperature range +25 to -61°C.

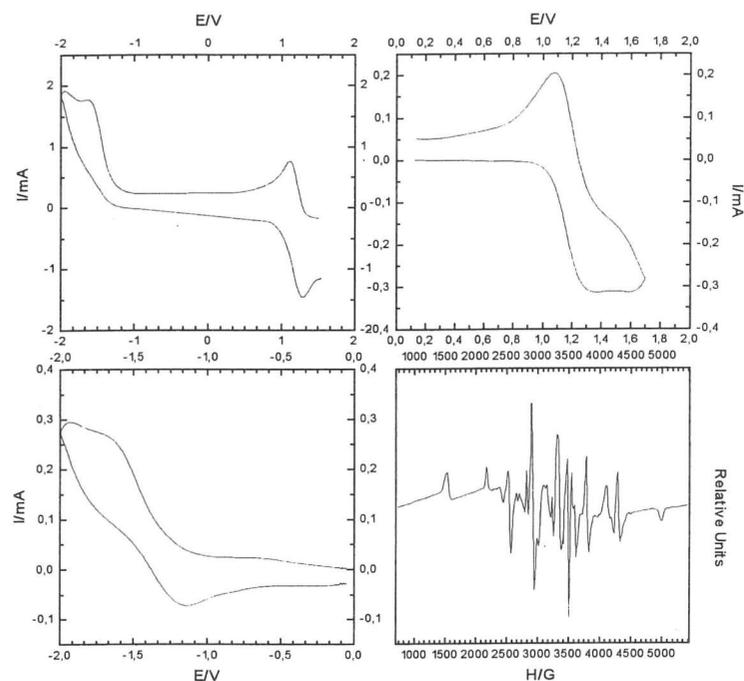


Fig. 2. *In situ* cyclic voltammetry and EPR-spectroelectrochemistry of  $1.81 \times 10^{-2}$  M  $\text{ReOCl}_2(\text{OEt})(\text{py})_2$  in  $\text{CH}_2\text{Cl}_2$  containing of 0.1 M TBAP, scan rate =  $1 \text{ V}\cdot\text{s}^{-1}$ . Measurements performed in the variable temperature EPR-microspectroelectrochemical criostat presented in Fig. 1. *Upper-left*: Cyclic voltammogram at 25°C. *Upper-right*: Low temperature CV (only oxidation wave is recorded) at -61°C. *Lower-right*: Low temperature CV (only reduction wave is recorded) at -61°C. *Lower-left*: EPR spectrum of  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation electrogenerated at +1550 mV and at -61°C, and recorded as a frozen solution in liquid nitrogen (-196°C); after 30 seconds electrolysis time instead of cold  $\text{N}_2$  stream (-61°C) the liquid nitrogen was immediately added to Dewar (see Fig 1). The CV curves were collected without IR compensation.

The oxidation process (*ca.* at 1.2 V) is electrochemically and chemically reversible both at 25°C and at low temperature (-61°C and at scan rate of  $1 \text{ V s}^{-1}$ , (Fig. 2)).

In contrast, the electrode reduction product (*ca.* at -1.5 V), which undergoes decomposition at 25°C, is fairly stable at -61°C, although the electron transfer reaction becomes quasireversible at low temperature (Fig. 2).

The  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation (*in situ* electrogenerated at -61°C) with its  $d^1$  configuration exhibits a typical EPR appearance in frozen  $\text{CH}_2\text{Cl}_2$  solution (Fig 2), similar to that reported for the related, chemically stable, oxo Re(VI) inorganic systems [17-24]. The following EPR parameters for  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation (rose coloured) in frozen  $\text{CH}_2\text{Cl}_2$  solution containing 0.1 M TBAP were calculated:  $A_{\parallel} = 620 \times 10^{-4} \text{ cm}^{-1}$ ,  $g_{\parallel} = 1.990$ ,  $A_{\perp} = 332 \times 10^{-4} \text{ cm}^{-1}$ ,  $g_{\perp} = 1.915$  (according to the second order of the perturbation theory and Breit-Rabi corrections [25]).

An attempt was also made at EPR detection of  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^-$  complex anion ( $d^3$ , yellow), but from our EPR measurements the existence of the oxo Re(IV) species could not be confirmed on the spectroelectrochemical time scale applied (30 s). However, on the CV time scale the existence of the forward (cathodic) and the coupled, backward (anodic) peak is observed at low temperature (-61°C). Therefore, the possible formation of  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^-$  complex anion is supported only by low temperature CV result presented here. It should be noted, that the Re(IV) EPR spectra [26-28] are even less common in literature than those for Re(VI) [17-24].

The present data allow: (i) qualitative recognition of the  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2] - e \leftrightarrow [\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$ , and  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2] + e \leftrightarrow [\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^-$  electrode reaction mechanism, (ii) qualitative description of the EPR spectrum for the chemically unstable  $[\text{O}=\text{Re}(\text{OEt})\text{Cl}_2(\text{py})_2]^+$  complex cation. However, for the estimation of electrode and chemical kinetic parameters for the electrochemically generated species further spectroelectrochemical investigations would naturally be required.

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## CATHODIC STRIPPING VOLTAMMETRY AND SENSORS : SULFONAMIDES AND THIOLS ¶

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### Introduction

Disposable sensor devices, such as those for glucose, use enzyme reactions in order to reach high sensitivities and low detection limits. The cathodic stripping voltammetric methods being developed in our laboratory are, in part, designed to be adapted for use in capillary-fill or similar disposable sensor devices [1,2]. If accumulation could be effected in a sensor device incorporating adequate convective mass transport this should allow uncatalysed reactions to reach sufficiently low detection limits for the purposes of trace analysis.

The first reported work on cathodic stripping voltammetry from our laboratory was carried out by A.A. Barros on synthetic food colouring matters [3] under an initial collaboration with Professor J.O. Cabral in Porto. New collaborative studies have started on the CSV and reduction mechanisms of nitroprusside with Professor J. Simao in Aveiro. Fogg made Ph.D. studies of the Boedeker reaction (nitroprusside + sulfite) [4-7], the main finding being the important visible role played by ion pairing by alkali metal ions on this equilibrium. A preliminary paper was published on the CSV of nitroprusside in 1994 [8]. Preliminary work on the new studies in Aveiro are reported elsewhere in this journal.

Fogg has attempted recently to document systematically and fully the different methods that can be used to accumulate determinands in stripping voltammetry (SV) and the combinations of accumulation and stripping methods that can be used [9]. A preliminary paper has been published also on the nomenclature of SV and on a proposed acronym system [10]. This work is being undertaken towards the production of an IUPAC publication. In considering a general nomenclature some more recent and less well known

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