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# Cyclic Voltammetry in Trifluoromethanesulfonic Acid: Facile Electrochemistry up to +3 V

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## Abstract

A 0.1 M solution of sodium trifluoromethanesulfonate in neat trifluoromethanesulfonic (triflic) acid is used as solvent in cyclic voltammetry. Working, counter and quasi-reference electrodes consist of glassy carbon, platinum and silver wire, respectively. Reversible voltammograms between +0.4 and +3 V versus NHE are recorded at 0 °C with scan rates around 100 mV $s^{-1}$ and are calibrated against $Ru(bpy)_3^{3+/2+}$. Redox processes for a series of coordination compounds involving high oxidation states are studied without complicating chemical reactions.

## Introduction

The feasibility for measuring reduction potentials of high oxidation states in transition metal complexes is limited by the working range of solvents and by the solubility of usually quite highly charged species. For the most important solvent, water, the accessible electrochemical window closes at about 1.5 V versus NHE, depending on the specific electrode material. A considerable extension to more positive potentials is offered by acetonitrile. The good ligating property of this solvent, however, limits its range of application. For electrochemical studies of a variety of organometallic and organic compounds trifluoroacetic acid proved to be a convenient solvent for measurements up to 2.5 V [1]. We expect trifluoromethanesulfonic acid (triflic acid, HTFL) to belong to the same solvent category. The use of triflic acid in synthetic coordination chemistry has recently been reviewed [2]. To our knowledge HTFL has been used only occasionally for studying the electrochemical behavior of organic compounds [3].

HTFL and its anion have excellent thermal stability and do not provide a source for fluoride ions even in the presence of strong nucleophiles. Pure HTFL is a clear colorless liquid fuming in moist air. The following data are reported for boiling point, density, viscosity and electrical conductivity: 162 °C, 1.698 g $cm^{-3}$, 2.87 cP, and $2 \times 10^{-4} \Omega^{-1} cm^{-1}$, respectively [4]. In order to test the use of HTFL as a solvent in electrochemical studies we applied cyclic voltammetry to a selection of coordination compounds, primarily ruthenium complexes.

## Experimental

A standard three-electrode arrangement was used for performing cyclic voltammetry. Working and counter electrodes were glassy carbon and Pt wire, respectively. The quasi-reference electrode (QRE) consisted of a Ag wire. Before each run glassy carbon was polished and Pt and Ag electrodes were treated with nitric acid, thoroughly washed with distilled water and dried. Scan rates (Metrohm 612, 626) varied between 50 and 100 mV $s^{-1}$. Since distillation did not show any effects on the results, anhydrous HTFL (Fluka) was used without further purification. NaTFL served as supporting electrolyte (0.1 M). The concentration of the electroactive species was in the order of $10^{-3}$ M. All the measurements were carried out at 0 °C (ice/water bath) in about 5 ml Ar saturated solution, gently blanketing with dry Ar. Although under these conditions no

TABLE 1. $M(bpy)_3^{3+/2+}$ potentials as calibration points for the Ag quasi-reference electrode in triflic acid

| M | $E$ ($M(bpy)_3^{3+/2+}$) (V) | | $E$ ($Ag^+/Ag$) (V) | $\Delta^a$ |
|---|---|---|---|---|
| | vs. NHE; $H_2O$ | vs. Ag; HTFL | in HTFL | (mV) |
| Fe | $1.05^b$ | 0.135 | 0.915 | 70 |
| Ru | $1.26^c$ | 0.32 | 0.94 | 65 |
| Os | $0.858^d$ | −0.117 | 0.975 | 125 |

[a] Difference between cathodic and anodic peak potentials. [b] Ref. 6. [c] Ref. 5. [d] Ref. 7.

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TABLE 2. Reduction potentials (V) in triflic acid, $CF_3SO_3H$[a]

| Redox couple | $E$ |  | Δ[b] (mV) |
|---|---|---|---|
|  | vs. Ag QRE | vs. NHE |  |
| $Ru(phen)_3^{3+/2+}$ | 0.32 | 1.26 | 90 |
| *cis*$[Ru(NH_3)_4Cl_2]^{2+/+}$ | 1.22 | 2.16 | 85 |
| $Ru(NCCH_3)_6^{3+/2+}$ [c] | 1.11 | 2.05 | 80 |
| $[Ru_3O(CH_3COO)_6py_3]^{3+/2+/+}$ [d] | 0.33; 1.11 | 1.27; 2.05 | 90, 80 |
| $[Ru(NH_3)_5Cl]^{3+/2+}$ | 1.26 | 2.2 | 80 |
| $Ru(capten)^{3+/2+}$ [e] | 0.24 | 1.18 | 70 |
| $Ru(\eta^6\text{-}C_6Me_6)(NCCH_3)_3^{3+/2+}$ [f] | 1.49 | 2.43 | 100 |
| $Ru(\eta^6\text{-}C_6H_6)(S(CH_3)_2)_3^{3+/2+}$ [f] | 1.51 | 2.45 | 95 |
| $Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^{2+/+}$ [g] | 1.51 | 2.45 | 170 |
| $Os(bpy)_3^{4+/3+}$ [h] | 1.65 | 2.59 | 165 |
| $Ni(capten)^{3+/2+}$ [e] | 0.21 | 1.15 | 150 |
| $Cr(CO)_6^{+/0}$ [i] | 0.36 | 1.3 | 140 |

[a] Electrolyte: HTFL + 0.1 M NaTFL. [b] Difference between cathodic and anodic peak potentials. [c] Ref. 8. [d] Ref. 9. [e] See footnote p. 67 and ref. 10. [f] Ref. 11. [g] Ref. 12. [h] 2.7 V in liquid $SO_2$; ref. 13. [i] Ref. 1(b); 1.09 V vs. SCE in $CF_3COOH$.

particular problems owing to aggressive fumes were encountered we recommend that all experiments are carried out in a well-ventilated hood. The reduction potential of 1.26 V for the $Ru(bpy)_3^{3+/2+}$ couple [5] was employed as a point of reference. The potentials given in this paper are calculated as the arithmetic mean of anodic and cathodic peak and are on the NHE scale assuming a similar temperature dependence for all the reduction potentials.

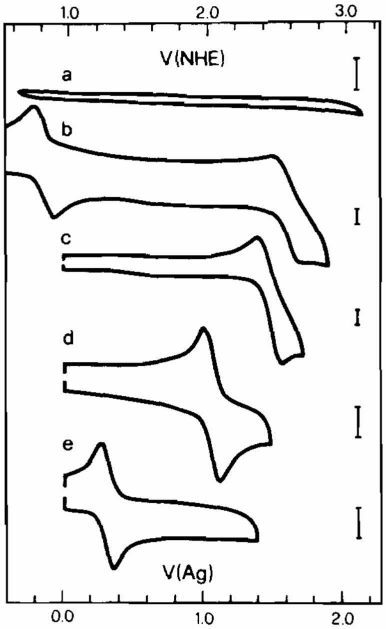

Fig. 1. Cyclic voltammograms recorded in triflic acid containing 0.1 M sodium triflate: a, HTFL/NaTFL; b, $Os(bpy)_3^{4+/3+/2+}$; c, $Ru(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5H_5)^{2+/+}$; d, $Ru(NCCH_3)_6^{3+/2+}$; e, $Ru(bpy)_3^{3+/2+}$. The bars indicate a current of 10 μA.

## Results

A flat signal-free baseline is recorded for the HTFL/NaTFL electrolyte from −0.4 to +2.5 V against the Ag QRE. The accessible electrochemical window extends thus from +0.4 to +3.3 V versus NHE. The study of the reduction potentials for a variety of Ru compounds justifies the calibration of our measurements with the value for the $Ru(bpy)_3^{3+/2+}$ couple to produce a consistent set of data. This arbitrarily chosen reference allows an operational scaling of data measured under distinctively different conditions. The reduction potentials of the $M(bpy)_3^{3+/2+}$ couples of the iron trian (Table 1) are given as an illustration. The $Ag^+/Ag$ QRE potential derived from this reference points is 0.95 V in HTFL.

Compounds listed in Table 2 show reversible or quasi-reversible electrochemical behavior on the cyclic voltammetry time scale. The anodic to cathodic peak separation is generally in the order of 70 to 100 mV. This peak to peak difference is increased to about 200 mV when measurements are made without the supporting electrolyte NaTFL. A selection of voltammograms is displayed in Fig. 1. Irreversible redox characteristics are observed for $Ru(\eta^6\text{-}C_6H_6)(NCCH_3)_3^{2+}$, *trans*-$[Co(en)_2Cl_2]^+$ and *p*-toluenesulfonic acid. The waves attributed to the oxidation step for these three compounds occur at 3.02, 2.97 and 2.80 V, respectively. Whereas the redox reactions are assumed to be accompanied by ligand exchange processes for the two complex ions, the cation of the aromatic sulfonic acid may not be long lived enough on the timescale of our experiments. Similarly, ruthenocene presents voltammograms with irreversible characteristics, oxidative peaks only at 2.56 and 2.86 V. Further studies are required to attribute these signals to one or two electron processes and to relate them to electrochemical studies in other solvents [14]. No signals could be detected for $[Ru(\eta^6\text{-}C_6Me_6)_2]^{2+}$, $[Ru(\eta^5\text{-}C_5H_5)(NCCH_3)_3]^+$ and the Co(III) amine complexes with en, tmen, sar and sep*.

## Discussion

Our experiments demonstrate that triflic acid can successfully be used as a solvent for scanning cyclic voltammograms using conventional electrochemical equipment. Anhydrous HTFL is a good solvent for a wide variety of coordination and organometallic compounds. Its employment in electrochemical studies leads to an expansion of the useful potential range up to +3.3 V. Ruthenium complexes with nitrogen donors or organic $\pi$-acids show reversible or quasi-reversible behavior. For rather labile complex ions ligand exchange may compete with the redox process and thus produce irreversible voltammograms although the triflate anion generally shows poor donor properties [2]. Analogous difficulties may arise when ligands are easily protonated. However, the oxocentered acetato complex of Ru (Table 2) showed no indication of such ligand reactions within the time limits of the experiment.

Some difficulties arise for the adjustment of the reduction potentials measured in HTFL to the standard NHE scale. The adoption of the same value for the $Ag^+/Ag$ potential in both media, aqueous solution and the chemically quite different triflic acid, obviously is questionable. We instead use the reduction potential of a standard redox couple to match potentials determined in different solvents. Solvation effects are assumed to be less dramatic for coordination compounds with rather bulky ligands, such as $Ru(bpy)_3{}^{n+}$, than for a situation where the solvent molecules enter the inner coordination shell, as for the $Ag^+/Ag$ couple. This calibration procedure based on an internal standard provides a consistent set of data.

Reduction potentials $Ru^{3+/2+}$ for complex ions with a $N_6$ core span a range of about 1.2 V with 0.05 V for $Ru(NH_3)_6{}^{3+/2+}$ and 1.26 V for $Ru(bpy)_3{}^{3+/2+}$ at the two limits for conventional solvents. A remarkably high positive value of 2.05 V is obtained for the $Ru(NCCH_3)_6{}^{3+/2+}$ couple. This extraordinary stabilization of Ru(II) by $NCCH_3$ is matched by its extreme substitution inertness, $k$ for ligand exchange being $8.9 \times 10^{-11}$ $s^{-1}$ [8]. Other $\pi$-acids such as $C_5H_5{}^-$ or $C_6H_6$ show the same stabilizing influence on the low-spin $d^6$ configuration of Ru(II) [4]. Thus oxidation of organoruthenium(II) compounds with aromatic ligands is observed only at very positive potentials between 2.1 and 2.5 V.

## Conclusions

We have demonstrated that triflic acid is a very useful solvent for electrochemical studies, particularly in the positive potential range up to +3.3 V. We emphasize the simplicity of the experimental arrangement compared with other solvents, such as liquid $SO_2$, neither extensive solvent purification nor cryostatic equipment being required. Moreover, owing to its intrinsic nature as a strong acid, triflic acid suppresses deprotonation reactions occurring in other media when coordination compounds of high metal oxidation states are generated. This deprotonation process generally triggers a sequence of reactions, e.g. disproportionation, destroying thus the electrochemical reversibility. This aspect is most clearly illustrated by the Ru capten$^{3+/2+}$ couple (see footnote and ref. 10). In aqueous solution the oxidized Ru(III) complex is immediately deprotonated and undergoes ligand dehydrogenation. Hence cyclic voltammetry is not reversible, even in 4 M triflic acid. Barely reversible voltammograms can be recorded in dry acetonitrile at −26 °C with a scan rate of 10 V $s^{-1}$ [10]. Reversible voltammograms are obtained in neat triflic acid without difficulty. In combination with an appropriate selection for internal reference electrochemical studies in triflic acid offer a convenient and facile way to investigate a variety of materials extending to unusually high oxidation states which are unstable in conventional media.

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*en = 1,2-diaminoethane; tmen = 2,3-diamino-2,3-dimethylbutane; sar = 3,6,10,13,16 19-hexaazabicyclo[6.6.6]eicosane; sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; capten = 1-methyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]-eicosane.

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