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SOME MECHANISTIC ASPECTS IN THE FORMATION OF TETRATHIAFULVALENIUM SALTS

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Abstract The anodic oxidation of TTF in the presence of SCN ions has been studied by several electrochemical technics. Two different mixed-valence salts TTF $(SCN)_{0.59}$ and TTF $(SCN)_{0.64}$ have been isolated.

INTRODUCTION

Much interest has been focussed these last years on the synthesis and physical properties of TTF mixed-valence salts TTFX $_{\rm n}$ (0<n<1) because of their high conductivity. In the case of X \blacksquare SCN different phases have been isolated which composition varies from TTF(SCN) $_{0.45}^{1}$ to TTF(SCN) $_{0.70}^{2-3}$. We have studied the anodic oxidation of TTF in the presence of thiocyanate ions in order to precise the composition of the different phases formed during the electrochemical reactions and their mechanism of formation.

ANODIC OXIDATION OF TTF IN ACETONITRILE OR AQUEOUS MEDIUM

In the presence of 10^{-1}M tetrabutylammonium perchlorate $(\text{NBu}_4\text{ClO}_4)$ as supporting electrolyte, the voltammogram of an acetonitrile solution of ITF shows at a rotating platinum electrode, two reversible one-electron waves corresponding to the successive formation of ITF $^{\bullet+}$ and ITF $^{2+}$ (Fig. 1b). When SCN is added, the formation of a solid deposit can be observed at the anode for E \geqslant 0.30 V. The enhancement of the limiting current (Fig. 1c) indicates the formation of a conducting species.

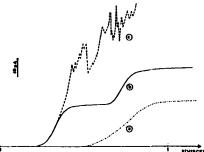


FIGURE 1: i-E curve at a rotating platinum electrode of acetonitrile solutions $(10^{-1}\text{M NBu}_4\text{ClO}_4)$. (b) TTF 3×10^{-3} M; (c) TTF 3×10^{-3} M + 5CN^{-3} 3×10^{-3} M; (a) 5CN^{-3} 3×10^{-3} M.

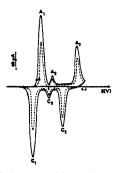


FIGURE 2: cyclic voltammogram at a carbon paste electrode; aqueous 1M KSCN; $v = 2.5 \times 10^{-5}$ $v.s^{-1}$.

Controlled-potential and controlled-current electrolyses of $3 \times 10^{-3} \, \mathrm{M}$ TTF solutions have been performed in the presence of $10^{-1} \, \mathrm{M}$ NBu₄SCN. For low applied voltage (0.30 V) one phase is isolated: TTF (SCN)_{0.59}. The solid consists of black-bright needles 10 mm long. For higher applied voltage, or at constant current (20 $\mu \mathrm{A}$), there is formation of a mixture of two phases: TTF(SCN)_{0.59} and TTF(SCN)_{0.64} (black powder).

1.57 mg

The anodic oxidation of solid TTF has also been studied by means of a carbon paste electrode $\frac{4}{4}$. The curve obtained in an aqueous medium containing SCN ions is characterized by three anodic peaks (A₁, A₂, A₃) which areas correspond respectively to the exchange of 0.59, 0.05 and 0.36 electron per TTF molecule (Fig. 2), indicating the formation of the two mixed-valence salts: TTF(SCN)_{0.59} and TTF(SCN)_{0.64} (Fig. 2). Taking in account the reversibility of the electrochemical reactions, the overall process can be summarized by the following scheme:

ITF
$$\frac{A_1}{C_1}$$
 ITF(SCN)_{0.59} $\frac{A_2}{C_2}$ ITF SCN_{0.64}

VOLTAMMETRIC INVESTIGATION OF THE ELECTRODE PROCESS

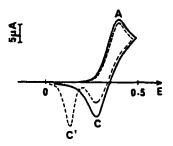
The shape of the cyclic voltammogram of acetonitrile solutions of TTF depends on the potential scan rate (v), thiocyanate and TTF concentrations (|SCNT|, |TTF|). For low values of |SCNT| and |TTF| and $v = 10^{-1} \text{V.s}^{-1}$; the curve shows one anodic peak (A) and one cathodic peak (C) corresponding to the reversible reaction : ITF TTF $^{++}$ + e $^{-}$ (1); the ratio $i_{pC,o}/i_{pA,o}$ = 1 (Fig. 3a). For high values of $|SCN^-|$ or |TTF|, this electron transfer is followed by a chemical reaction which affects the limiting currents : i_{pl}/i_{pl} decreases, and a second cathodic peak (C') appears (Fig. 3b). The variation of the ratio of the limiting peak current $\boldsymbol{i}_{\text{pA}}$ to the diffusion-controlled current $i_{pA,o}$ (obtained in the absence of coupled chemical reaction) with | TTF | is shown on Figure 4. For $|\text{TIF}| \le 2 \times 10^{-3} \text{ M}, i_{pA}/i_{pA,o} = 1 \text{ only reaction (1) occurs. For } 2 \times 10^{-3} \text{ M} < |\text{TIF}| < 8 \times 10^{-3} \text{ M}, i_{pA}/i_{pA,o} \text{ decreases due to the existential of the existential occurs.}$ ce of the chemical reaction which involves the species ITF, ITF ** and SCN $^{-}$. For |TTF| \geqslant 8×10^{-3} M $~\mathrm{i}_{pA}/\mathrm{i}_{pA,o}$ tends towards a limiting value. The presence of crystals is then observed at the electrode, indicating that the chemical reaction is fast. The following reactions occur:

$$(1-n)\mathsf{TIF} + n \mathsf{TIF}^{\bullet +} + n \mathsf{SCN}^{-} \to \mathsf{TIF}(\mathsf{SCN})_{n}$$
 (2)

the value of the number of electron (n) exchanged during the overall process :

$$IIF + n SCN \rightarrow IIF(SCN)_n + ne^-$$
 (3)

which can be deduced from the value of $i_{pA}/i_{pA,o}$ is found close to 0.6.



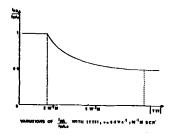


FIGURE 3 : cyclic voltammogram of FIGURE 4 : Variation of $i_{pA}/$ TIF in acetonitrile (10^{-1} M $i_{pA,o}$ with the TIF concentra-NBu₄ClO₄) v = 10^{-1} V.s⁻¹; a: — tion; v = 0.5V.s⁻¹; 10^{-1} M |SCN $^{-1}$ = 10^{-3} M; b: --- |SCN $^{-1}$ = NBu₄SCN 3×10^{-3} M

This value can be compared to the composition of the first mixedvalence salt isolated by electrocrystallization : $IIF(SCN)_{0.59}$.

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