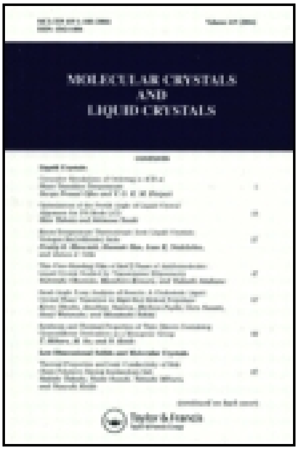

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SOME MECHANISTIC ASPECTS IN THE FORMATION OF TETRATHIAFULVALENIUM SALTS

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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 $TTFX_n$ $(0<n<1)$ because of their high conductivity. In the case of X^- □ 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 (NBu_4ClO_4) as supporting electrolyte, the voltammogram of an acetonitrile solution of TTF shows at a rotating platinum electrode, two reversible one-electron waves corresponding to the successive formation of $TTF^{\bullet +}$ and TTF^{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.

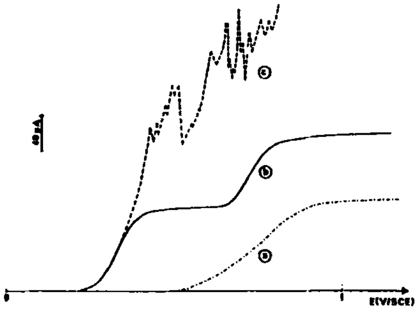

FIGURE 1 : i-E curve at a rotating platinum electrode of acetonitrile solutions (10^{-1}M NBu_4ClO_4). (b) TTF 3×10^{-3} M ; (c) TTF 3×10^{-3} M + SCN^- 3×10^{-3} M ; (a) SCN^- 3×10^{-3} M.

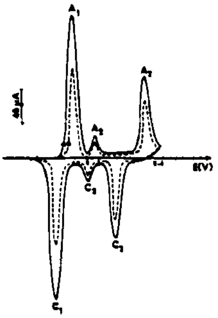

FIGURE 2 : cyclic voltammogram at a carbon paste electrode ; aqueous 1M KSCN ; v = 2.5×10^{-5} $V.s^{-1}$.
(---) TTF 0.64 mg ; (—) TTF 1.57 mg

Controlled-potential and controlled-current electrolyses of 3×10^{-3}M TTF solutions have been performed in the presence of 10^{-1} M NBu_4SCN. 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 µA), there is formation of a mixture of two phases : $TTF(SCN)_{0.59}$ and $TTF(SCN)_{0.64}$ (black powder).

The anodic oxidation of solid TTF has also been studied by means of a carbon paste electrode [4]. The curve obtained in an aqueous medium containing SCN^- ions is characterized by three anodic peaks (A_1, A_2, A_3) 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 :

$$\mathrm{TTF} \underset{C_1}{\overset{A_1}{\rightleftharpoons}} \mathrm{TTF(SCN)_{0.59}} \underset{C_2}{\overset{A_2}{\rightleftharpoons}} \mathrm{TTF\ SCN_{0.64}}$$

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 ($|SCN^-|$, $|TTF|$). For low values of $|SCN^-|$ and $|TTF|$ and $v = 10^{-1} V.s^{-1}$, the curve shows one anodic peak (A) and one cathodic peak (C) corresponding to the reversible reaction : $TTF \rightleftharpoons TTF^{\bullet+} + e^-$ (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_{pC}/i_{pA} decreases, and a second cathodic peak (C') appears (Fig. 3b). The variation of the ratio of the limiting peak current i_{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 $|TTF| \leqslant 2x10^{-3}$ M, $i_{pA}/i_{pA,o} = 1$ only reaction (1) occurs. For $2x10^{-3}$ M < $|TTF|$ < $8x10^{-3}$ M, $i_{pA}/i_{pA,o}$ decreases due to the existence of the chemical reaction which involves the species TTF, $TTF^{\bullet+}$ and SCN^-. For $|TTF| \geqslant 8x10^{-3}$ M $i_{pA}/i_{pA,o}$ 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 :

$$n\ TTF \rightarrow n\ TTF^{\bullet+} + ne^- \qquad (1)$$

$$(1-n)TTF + n\ TTF^{\bullet+} + n\ SCN^- \rightarrow TTF(SCN)_n \qquad (2)$$

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

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

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

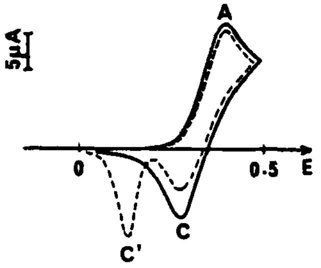

FIGURE 3 : cyclic voltammogram of TTF in acetonitrile (10^{-1} M NBu_4ClO_4) v = 10^{-1} V.s^{-1} ; a : —— $|SCN^-|$ = 10^{-3} M ; b : --- $|SCN^-|$= 3×10^{-3} M

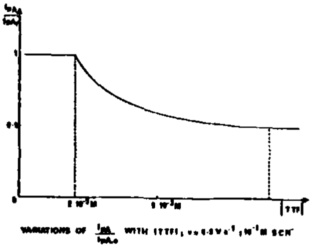

FIGURE 4 : Variation of $i_{pA}/i_{pA,o}$ with the TTF concentration ; v = 0.5V.s^{-1} ; 10^{-1} M NBu_4SCN

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

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