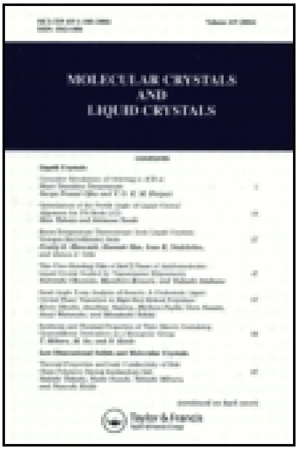

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The Influence of Water and Oxygen on Stability of TCNQ Solution in Acetonitrile

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THE INFLUENCE OF WATER AND OXYGEN ON STABILITY OF TCNQ SOLUTION IN ACETONITRILE

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Abstract UV-VIS absorption spectra of $TCNQ^o$ in acetonitrile solution in the presence of water have been studied. For the H_2O content greater than 5 v.p.c. rapid decay of 395 nm - $TCNQ^o$ absorption band was observed. Simultaneous formation of absorption bands typical for $TCNQ^{\tau}$ and DCTC was found as well as the band characteristic for final product of hydrolisis of TCNQ. Possible mechanism of occuring reactions is proposed.

INTRODUCTION

Our interest in the chemical behaviour of TCNQ compounds arose from systematic investigations of ion-selective electrodes, prepared on the basis of these compounds[1,2]. Due to particular physical properties of complexes, simple and complex salts of TCNQ, they have been the subject of interest for many years. Very early investigations show a "sample dependence" of such properties as electrical conductivity, thermoelectric power and so on.

In the literature there are various explanations of these phenomena: either changes in the local stoichiometry of the crystal[3] or disorder in the donor stacks[4] is suggested. On the other hand, it is well known that even a very small amount of water and/or oxygen in the reaction mixture during the preparation of salts gives rise to obtaining of crystals with irreproducible physical properties.

RESULTS AND DISCUSSION

The authors have established that TCNQ and its salts hydrolise in the presence of water and O_2 both in the solution and in the solid state[5,6]. In this work we have studied the stability of $TCNQ^o$ solutions in CH_3CN, using UV-VIS absorption spectroscopy as an analytical method. A special attention was paid to the absorption band of $TCNQ^o$ at 395 nm, the bands at 424 nm, 743 nm and 842 nm of $TCNQ^{\bar{•}}$, as well as the 480 nm band of dicyanotolluilocyanide (DCTC) and the 340 nm band of the final product of hydrolysis of TCNQ (FPH).

Solutions containing less than 5 v.p.c. of H_2O in acenonitrile were very stable: neither any change in the absorption at 395 nm was observed nor the formation of any other absorption bands for at least 10 hours. On the other hand, for the H_2O content greater than 5 v.p.c. - in the presence of oxygen, or 10 v.p.c. - without oxygen, a rapid decay of the 395 nm band $k^I = 1.8 \cdot 10^{-3}\ s^{-1}$ is observed (see figure 1). Simultaneously the DCTC band at 480 nm and the FPH band at 340 nm are formed, and the time dependence of the intensity of bands proves that the formed DCTC is an intermediate for the formation of FPH. The rate of these reactions increase significantly on adding a base e.g. LiOH due to a possible nucleofilic attack of OH^- at TCNQ. Parameters of the kinetics of these reactions are in elaboration.

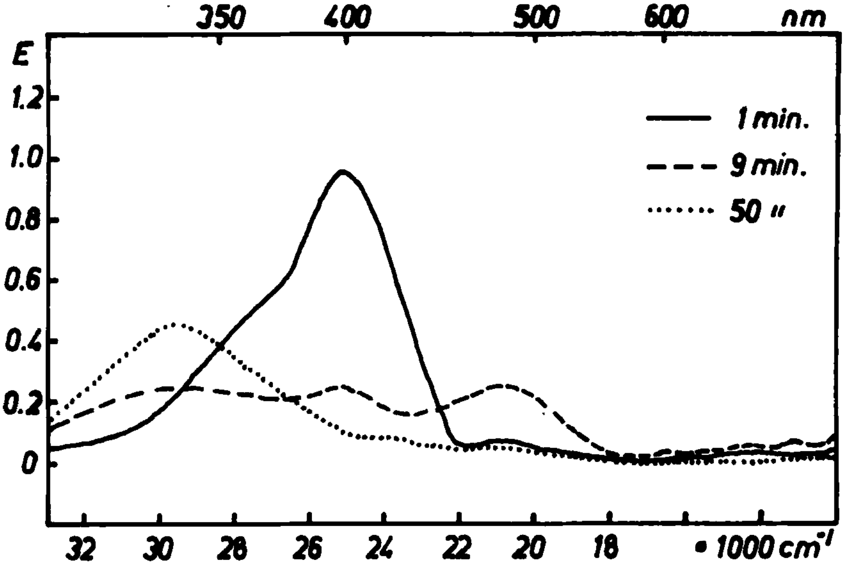
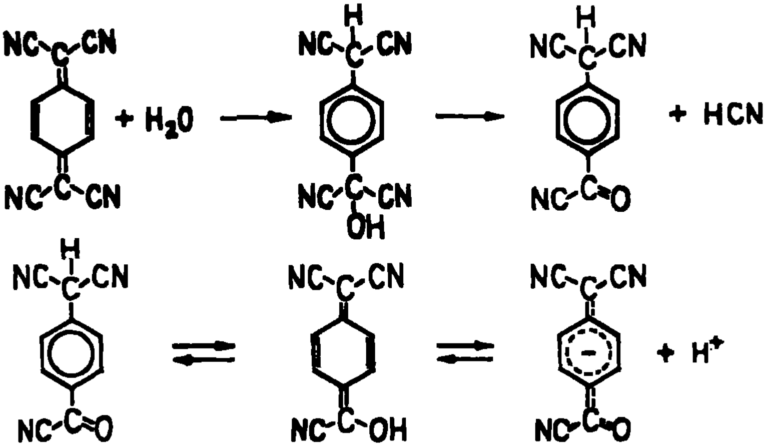


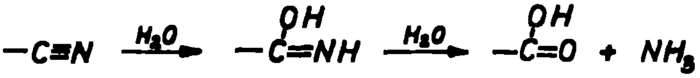
FIGURE 1 Time dependence of absorption spectra of TCNQ^0 in CH_3CN. $c_o = 1.94\cdot10^{-5}M$, O_2, 11.9 v.p.c. H_2O, l = 1 cm

Usually, it is possible to observe a simultaneous formation of TCNQ$^{\bar{\cdot}}$ absorption bands at 424 nm, 743 nm and 842 nm, however, low intensity of these bands suggests that the concentration of TCNQ$^{\bar{\cdot}}$ is less than 10 pc of the initial TCNQ^0 concentration.

After a sufficiently long time not only the TCNQ^0 band but both DCTC and TCNQ$^{\bar{\cdot}}$ absorption bands dissapear and the FPH band reaches its maximum intensity, which means that the reaction of hydrolysis of TCNQ is completed.



(1)



$$-C{\equiv}N \xrightarrow{H_2O} -\overset{OH}{\overset{|}{C}}{=}NH \xrightarrow{H_2O} -\overset{OH}{\overset{|}{C}}{=}O + NH_3 \qquad (2)$$

$$={\overset{|}{C}}-CN \xrightarrow{H_2O} ={\overset{|}{C}}-OH + HCN \qquad (3)$$

$$CH_3CN + 2\,H_2O \xrightarrow{OH^-/H^+} CH_3COO^- + NH_4^+ \qquad (4)$$

$$2\,CH_3CN \xrightarrow{OH^-/H^+} CH_3CNH^+ + CH_2CN^- \qquad (5)$$

CONCLUSIONS

- formation of DCTC is possible under conditions usually applied for the synthesis of TCNQ salts (reaction 1).

- the possible hydrolysis of CN groups of TCNQ leads to the formation of various carboxylic acids, denoted here FPH (reactions 2 & 3).
- acetonitrile itself can hydrolyse (reaction 4) and dissociate (reaction 5) forming ionic products.
- due to the presence of all the species mentioned above in the reaction mixture one can expect numerous compounds like: NH_4·TCNQ, CH_4CN·TCNQ, NH_4·FPH, CH_4CN·FPH, K·FPH, K·DCTC, to coprecipitate during the crystallization of TCNQ salts. The inclusion of these compounds in the crystals of TCNQ salts may be a reason of sample dependent properties of these crystals.

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