

Methanolysis of 7,7,8,8-Tetracyanoquinodimethane: A Consequence of an Initial Charge Transfer Complexation

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7,7,8,8-Tetracyanoquinodimethane (TCNQ) has several π -bonds and four nitrogen atoms having four unshared electron pairs. This unique structure enhances TCNQ to perform intramolecular charge transfer (CT) transitions within its molecular moiety and/or intermolecular CT interactions with different species having electron-donor properties. The electron affinity¹ of TCNQ is 2.8 eV which permits it to be one of the well known π -acceptors.²⁻⁴ In addition, TCNQ-based charge transfer salts are well known too.^{5,6} Thus, through the interaction of TCNQ with electron donors it should be considered the simultaneous competing transitions between the intra-transitions (within TCNQ molecule) and the inter-transitions from the donors toward TCNQ. On the other hand, due to the unshared electron pairs on the oxygen atom, MeOH has been used as *n*-donor in several CT interactions.^{2,7-9} Thus, the thing is, on considering a CT interaction between an electron donor and TCNQ (as an electron acceptor) in the presence of MeOH as a medium (solvent) for this interaction, an additional factor should be considered too: the probable occurrence of an addition reaction of MeOH molecule to TCNQ molecule in a nucleophilic attack (as a result of a probable MeOH/TCNQ CT interaction) in competition with the main electron donor/TCNQ CT interaction. In turn, it is worthwhile to investigate the absorption spectral behavior of the sole MeOH/TCNQ interaction especially from the kinetic standpoint of view. For this purpose this piece of work has been devoted.

Experimental Section

Materials and Solutions. 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was purchased from Aldrich-Sigma Chemical Co.. The solvents, methanol (MeOH), ethylene chloride and methylene chloride, were of pure spectral grade (E. Merck Co.).

Physical Measurements. The electronic absorption spectra were recorded on a Perkin-Elmer Lambda 40 spectrophotometer equipped with a Julabo FP 40 thermostat (± 0.1 °C) using 1.0 cm matched quartz cells.

Results and Discussion

Electronic Absorption Spectra of TCNQ in Pure Organic Non Polar Solvents. Electronic absorption spectra in the

wavelength range of 250-850 nm were recorded for the ethylene chloride solution of TCNQ at 25 °C, cf. Figure 1. Two main spectral bands have been observed at 373 and 401 nm. These two bands have been observed too at the same bands positions in the spectra of TCNQ solution in methylene chloride at 25 °C, cf. Figure 1.

Due to TCNQ has π - π^* and n - π^* intramolecular transitions, one can assign the band located at 373 nm, which has the shorter wavelength and higher energy, to the n - π^* intramolecular transition(s) (within TCNQ molecule) from the nitrogen atoms to the LUMO of the C=C (exocyclic) π -bonds, meanwhile the other band located at 401 nm, which has the higher wavelength and lower energy, can be assigned to the π - π^* intramolecular transition(s).

It is worthy to illustrate that the absorption spectra of the TCNQ solution either in ethylene chloride or in methylene chloride are time independent, whereas, on elapsing time (~30 min) no appreciable change has been observed neither in the intensities of the bands nor their positions.

Electronic Absorption Spectra of TCNQ in Pure Methanol. On using methanol, as a solvent, a different spectral behavior has been noticed. The absorption spectra of the MeOH/TCNQ system have also shown two absorption spectral bands located at 373 and 394 nm. These two bands are the same bands which have been previously seen in the spectra of TCNQ in either methylene chloride or ethylene chloride, but with a little bathochromic shift as a result of

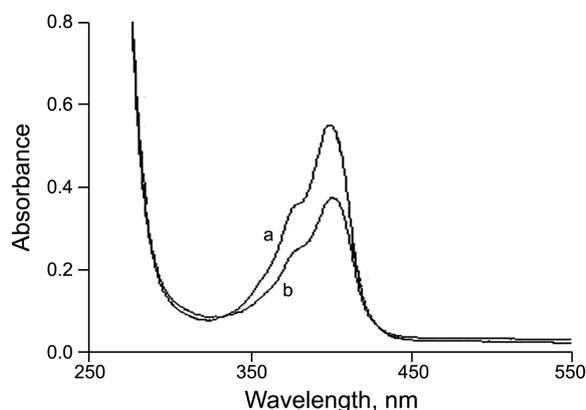


Figure 1. Electronic absorption spectra of TCNQ solutions at 25 °C. ([TCNQ] = 5.0×10^{-5} mol dm⁻³; (a) = in C₂H₄Cl₂; (b) = in CH₂Cl₂).

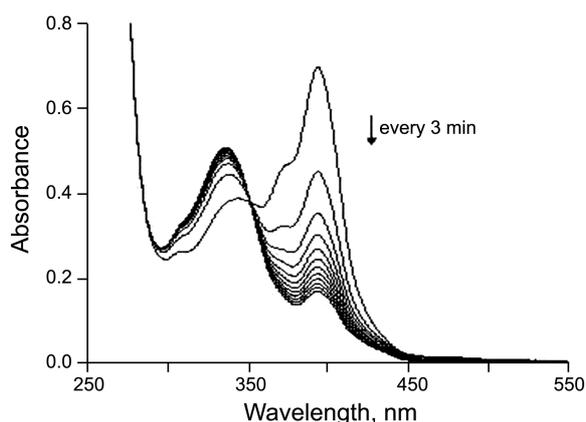
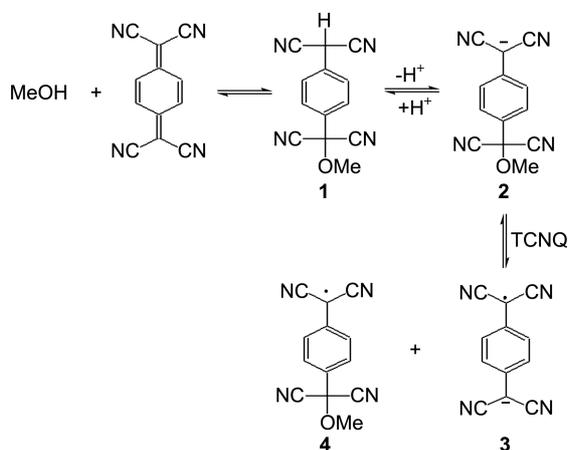


Figure 2. Electronic absorption spectra of MeOH solutions of TCNQ at 25 °C. ([TCNQ] = 4.0×10^{-6} mol dm⁻³).

changing solvent polarity.

However, on elapsing of time, the spectra of the MeOH/TCNQ system have gained an interesting observation. Thus, on elapsing of time, the intensities of each of these two bands of the MeOH/TCNQ system (located at 373 and 394 nm) are gradually decreasing meanwhile a new band appears at 336 nm accompanying with a simultaneous increasing in its intensity, cf. Figure 2. After a period of 33 min, the previously observed spectral band of the shorter wavelength (at 373 nm) has been vanished, whereas the new band which is located at 336 nm has reached its maximum intensity.

Tanemura *et al.*¹⁰ have previously reported the following Scheme 1 as a representative mechanism of the methanolysis of TCNQ. They¹⁰ have illustrated that the interaction of TCNQ with MeOH has proceeded in several steps. A nucleophilic attack of MeOH to TCNQ is the first step in their interaction which yields α -methoxy-*p*-phenylenedimalononitrile (adduct **1**), whereas confirmation of the adduct **1** has been attained¹⁰ by elemental analysis, FT-IR, electronic absorption spectra and ¹H NMR spectra. The adduct **1** is then deprotonated to the corresponding anion radical **2**, meanwhile, this anion radical **2** reacts with another molecule of TCNQ to afford the final anion radicals **3** and **4**. This



Scheme 1

reaction mechanism is a reasonable one and it has been illustrated.

In turn, herein, the new absorption spectral band which was appearing at 336 nm for the MeOH/TCNQ system might be assigned for a new intramolecular transition within the adduct **1**, meanwhile the gradual increasing in the intensity of this absorption spectral band by elapsing of time could be referred to the slow formation of the adduct **1**.

Further, formation of adduct **1** (cf. Scheme 1) means that a cleavage of the two exocyclic C=C bonds has been occurred whereas these C=C π -bonds and their LUMO have no longer present. This leads to stop the $n\text{-}\pi^*$ intramolecular transition from the nitrogen atoms and, in turn, disappearing of the spectral band located at 373 nm by elapsing of time. Indeed, this confirms the aforementioned assignment for the spectral bands; *i.e.* the band located at 373 nm belongs to the $n\text{-}\pi^*$ intramolecular transition(s) from the nitrogen atoms to the LUMO of the C=C (exocyclic) π -bonds, meanwhile the other band located at 401 nm belongs to the $\pi\text{-}\pi^*$ transition(s) within the TCNQ moiety. Thus vanishing of the absorption spectral band (at 373 nm), which is characteristic to the $n\text{-}\pi^*$ transitions, during the nucleophilic attack of MeOH to TCNQ might be understandable in the view of the cleavage of the π -bonds of the two exocyclic C=C to the corresponding sigma bonds. Meanwhile, the new band located at 336 nm which is gradually increasing in its intensity during this nucleophilic addition of MeOH to TCNQ is assigned as an intramolecular transition within the adduct **1**.

It is worthy to mention that appearing of an isosbestic point (at 350 nm) in the absorption spectra of the MeOH/TCNQ solution (cf. Fig. 2) provides an evidence¹¹ for the occurrence of only two species in the solution under spectral measurements, *i.e.* absence of a reaction intermediate. Thus, the two species present in the solution are the starting TCNQ molecule and the adduct **1** resulted from the addition of the MeOH molecule to the TCNQ molecule, cf. Scheme 1.

However, in addition to the aforementioned reaction mechanism which have been presented by Tanemura *et al.*¹⁰ for the methanolysis of TCNQ, we believe that an initial formation of a charge-transfer complex (CT) between the MeOH and TCNQ has occurred prior the nucleophilic addition of the MeOH to the TCNQ molecule. MeOH is an electron donor^{2,7-9} and TCNQ is a well known π -acceptor²⁻⁶ having 2.8 eV electron affinity.¹ This means that formation of a MeOH-TCNQ CT complex might probably occur at least initially when the two species (MeOH and TCNQ) undergo interaction. However, failure of observing the, expected, CT absorption band(s) for this MeOH-TCNQ interaction in solutions might be due to either the perturbation of this (expected) CT band with the absorptions of the free donor and/or the free acceptor or the CT complexation occurs in a very fast step that it can not be observed in the absorption spectra.

Kinetic Study of the Methanolysis of TCNQ. In order to obtain information about the kinetics and mechanism of the methanolysis of TCNQ, the electronic spectra of the TCNQ solution in MeOH ([TCNQ] = 4.0×10^{-6} M, *i.e.* [MeOH]

>>> [TCNQ]) were measured as a function of time, cf. Figure 2. Increasing of the intensity of the spectral band located at 336 nm, which is characteristic to the new adduct **1**, by elapsing of time, has been used to determine the kinetics of the MeOH/TCNQ interaction; methanolysis of TCNQ.

Methanolysis of TCNQ can be simply represented by the equation:



The experimental rate law for formation of the adduct **1** may be given as:

$$\frac{d[\text{adduct}]}{dt} = k[\text{MeOH}][\text{TCNQ}]$$

The rate of this reaction is a pseudo first-order of TCNQ because MeOH is used in a very large amount (concentration); [MeOH] >>> [TCNQ], and the reaction is then dependent mainly on the concentration of TCNQ. Moreover, existence of an isosbestic point (at 350 nm) in the absorption spectra of MeOH/TCNQ system implies¹² the absence of appreciable amounts of reaction intermediates, *i.e.* this supports formation of the adduct **1** directly in one step.

The first order rate constant, k , for the methanolysis of TCNQ has been evaluated by employing the equation,^{11,12}

$$t = \frac{2.303}{k} \log \frac{D_x - D_0}{D_x - D_t}$$

at the $\lambda_{\text{max}} = 336$ nm which is characteristic to adduct **1**. Here, D_0 , D_t and D_x are the absorbances at times 0, t and x , respectively. The rate data were recorded for the first ~30

min. The rate constant, k , of the methanolysis of TCNQ was found to be $51.24 \times 10^{-2} \text{ dm}^{-3} \text{ mol}^{-1} \text{ min}^{-1}$, which is a quite large.

Conclusion

Methanolysis of TCNQ is a nucleophilic attack of MeOH to TCNQ after an initial formation of the MeOH-TCNQ CT complex. This methanolysis is a pseudo first order and its reaction rate constant is of a quite large value.

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