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Oxidation of a Conductive Polymer-TCNQ Salt with Atmospheric Oxygen

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Synopsis. The oxidation reaction of conductive poly-4-vinylpyridinium (P4VP$^+$) tetracyano-*p*-quinodimethanide-(TCNQ$^-$) with oxygen has been studied. The main product of this reaction is found to be α,α-dicyano-*p*-toluoylcyanide. An interesting difference in reactivity was observed between the polymer salt and the ethanol solution of the monomer salt.

In a previous paper,[1] we reported the electronic spectra of the P4VP$^+$TCNQ$^-$ and the complex salt including neutral TCNQ(P4VP$^+$TCNQ$^-$TCNQ$_x$), which form highly conductive films.[2] The conduction mechanism was discussed. The P4VP$^+$TCNQ$^-$ film is green in a vacuum but by the introduction of oxygen, the color changes gradually to light brown and the conductivity descreases. Hatano *et al.* reported the oxidation of the γ-methylpyridinium TCNQ salt in acetonitrile solution by oxygen.[3] Sanada *et al.* reported that the deterioration of TCNQ salts of cationic polymer was caused by oxygen and moisture.[4] However, the mechanism of the oxidation and its product have not been clarified.

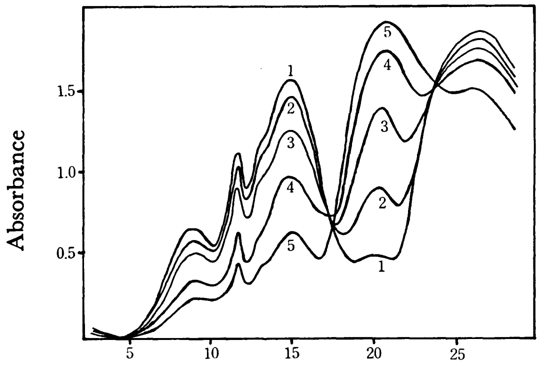


Fig. 1. Electronic absorption spectral change of the polymer film after the introduction of air at 288 K.
1: 2 min, 2: 1 hr 15 min, 3: 3 hr 50 min, 4: 20 hr, 5: 66 hr.

Coherent films of P4VP$^+$TCNQ$^-$ were deposited on quartz plates and kept in a vacuum. The change of absorption spectra after the introduction of oxygen was measured at various temperatures. As shown in Fig. 1, the intensities of the absorption bands attributable to TCNQ monomer at 845 nm, TCNQ$^-$ aggregate at 665 nm, and the charge transfer band between TCNQ$^-$ radicals at 1100 nm decreased with time after the introduction of oxygen, and a new absorption band appeared at 475 nm. Another absorption was found to appear in the infrared region above 1800 nm (Fig. 2), which disappeared with the lapse of time. Since this IR absorption is attributable to a charge resonance band between TCNQ$^-$ and neutral TCNQ, neutral TCNQ is concluded to be one of the products, formed by an electron transfer reaction such as:

$$\mathrm{TCNQ}^- + \mathrm{O_2} \longrightarrow \mathrm{TCNQ} + \mathrm{O_2}^-$$

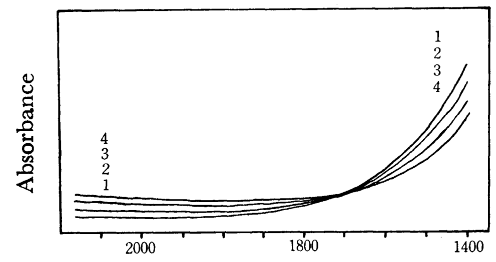


Fig. 2. Infrared absorption spectral change after the introduction of air at 300 K.
1: 0 min, 2: 15 min, 3: 40 min, 4: 90 min.

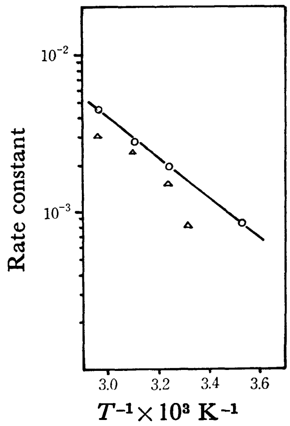
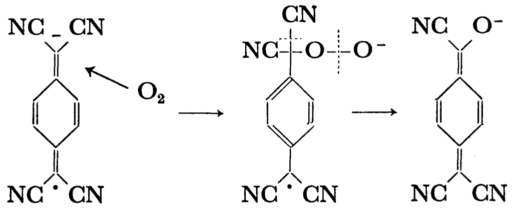


Fig. 3. Logarithmic rate constant plot *versus* inverse absolute temperature, calculated
○: from the change of TCNQ monomer band,
△: from the change of CT absorption band.

The logarithm of the absorbance of TCNQ$^-$ monomer band at 845 nm and that for the charge transfer band between TCNQ$^-$s at 1100 nm of the film under atmosphere of oxygen show a good linear relation with time, showing that the reaction is of the first order as regards the concentration of TCNQ$^-$. The activation energy obtained from the Arrhenius plot of the rate constants obtained from the absorption band is 5.7 kcal/mol. The reaction rate constant calculated from the decay of the monomer band was found to be larger than the one calculated from that of the charge transfer band.

The oxidized polymer film was extracted with ethanol and the extract was separated by thin-layer chromatography using acetone–benzene (1:1). The main orange-colored product was identified to be α,α-dicyano-*p*-toluoylcyanide, because the band shape and peak positions (λ_{max}=476, 276 nm) of the electronic spectrum agreed with those of sodium α,α-dicyano-*p*-toluoylcyanide, synthesized according to the literature.[5] The IR spectra of the main reaction products also show all the strong bands of the synthesized sodium salt (for example, $\nu_{C=O}=1645\ \mathrm{cm}^{-1}$, $\nu_{C\equiv N}=2200$, $2160\ \mathrm{cm}^{-1}$), together with some impurity bands.[6] The R_f value in the thin-layer chromatography of the orange-colored product agreed with that of the sodium α,α-dicyano-*p*-toluoylcyanide. The reaction might proceed as follows,



This deterioration reaction of the polymer TCNQ salt is sensitive to the environment of the anion. *N*-methylpyridinium TCNQ was not deteriorated by oxygen even when it was exposed to air for several weeks.

When the aerated ethanol solution of $\mathrm{Li^+TCNQ^{\overline{\cdot}}}$ was irradiated in the UV region, the color of the solution changed remarkably from green to orange. The resulting photochemical reaction product was found to be also α,α-dicyano-*p*-toluoylcyanide.

It is interesting that the polymer film reacts with oxygen in the dark, while the reaction of $\mathrm{Li^+TCNQ^{\overline{\cdot}}}$ in solution needs UV excitation.

References

1) K. Nakatani, T. Sakata, and H. Tsubomura, This Bulletin, **48**, (2) 657 (1975).

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3) H. Nomori, M. Hatano, and A. Kanbara, *Kogyo Kagaku Zasshi*, **67**, 1608 (1964).

4) K. Sanada, A. Iwasawa, E. Tsuchida, and I. Shinohara, *Nippon Kagaku Kaishi*, **1974**, 961.

5) W. R. Hertler, H. D. Hartzler, D. S. Acker, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3387 (1962).

6) During extraction with ethanol and separation by thin-layer chromatography, a small part of the orange colored product changed into a colorless substance. Consequently, the material used for the IR measurement was considered to contain some impurities.