# Ionic Photodissociation of Some Weak Charge Transfer Complexes of Tetracyanoethylene with n-Type Donor Molecules

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During the last few years, several reports have appeared on ionic dissociation by photo-excitation of weak charge transfer (CT) complexes.[1–6] Potashnik *et al.*[4] and Masuhara *et al.*[5] studied spectroscopically the mechanisms of the ionic photo-dissociation process of some weak CT complexes composed of $\pi$-type donors and acceptors. We here report on preliminary results of the steady-state UV photolysis and flash photolysis of several weak CT complexes of tetracyanoethylene (TCNE) with tetrahydrofuran (THF), dioxane, acetonitrile, benzene and hexamethylbenzene. It is known that TCNE forms CT complexes with ether,[7] THF,[8] and dioxane[8] as n-type donors in nonpolar solvents at room temperature. We recently found that a weak CT complex is formed between donor acetonitrile and acceptor TCNE with an equilibrium constant of 1.86 *l*/mol at 25°C.[6]

Table 1. Wavelengths of the CT-band maxima (in nm units) of several TCNE complexes

| Electron Donor | at 25°C | | | at 77°K | |
|---|---|---|---|---|---|
| ether | 335[a] | 335[b] | 335[d] | 320[a] | 320[b] |
| THF | 320[a] | | 318[e] | 295[a] | |
| dioxane | 345[a] | | 350[e] | 325[a] | |
| acetonitrile | 360[a] | | | 325[a] | |
| benzene | | 380[c] | 384[f] | | 380[c] |
| hexamethylbenzene | | 525[c] | 545[f] | 528 and 562[c] | |

a) The donor was used as a solvent. b) In ether-isopentane (1:1 and 1:2). c) In methylcyclohexane-isopentane (1:2). d) In ether (Ref. 7). e) In chloroform (Ref. 8). f) In dichloromethane (Ref. 7).

Ether, THF, dioxane, and acetonitrile were used as rigid solvents at 77°K. Since these rigid matrices are somewhat opaque, we used a 0.1-cm quartz cell capable of measuring absorption spectra with a Cary spectrophotometer, Model 15. Low-temperature photolyses of the rigid solutions were carried out with a high-pressure mercury lamp through Toshiba filter glasses UV-31 and -35 with which lights of wavelength shorter than 310 and 350 nm, respectively, are cut off. When ether, THF, dioxane, and acetonitrile were used as donor molecules, the CT bands are significantly enhanced and shifted to a shorter wavelength by freezing the solutions, as shown in Table 1. For the TCNE complexes with benzene and hexamethylbenzene, however, no such blue shifts were observed by freezing the solutions. The observed remarkable blue shifts seem to be a characteristic of the n-type CT complexes. The large blue shift (3000 cm$^{-1}$) observed for the CT band of the TCNE-acetonitrile system suggests that acetonitrile molecule acts as an n-type donor for TCNE.

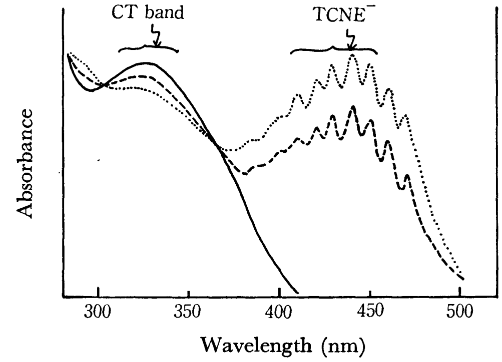

Fig. 1. Electronic absorption spectra showing the formation of TCNE$^-$ by excitation of the CT band of the TCNE-dioxane complex in a dioxane rigid matrix at 77°K. Curve (——): before irradiation, and curves (······) and (------): after irradiation through UV-31 and -35 respectively.

When a dioxane rigid matrix containing TCNE ($10^{-3}$M) was irradiated at 77°K by exciting the CT band of the TCNE-dioxane complex, the rigid matrix turned yellow, showing a new broad absorption band with vibrational structure exactly the same as that reported for the TCNE anion (TCNE$^-$), as shown in Fig. 1.

The same stable TCNE$^-$ species can be produced by the CT-band excitation in the cases of ether, THF and acetonitrile matrices at 77°K. We thus conclude that the ionic photodissociation takes place in the excited states of these complexes. It should be mentioned that in the case of the TCNE complexes with benzene and with hexamethylbenzene, no stable TCNE$^-$ species was formed by exciting their CTbands in a methylcyclohexane-isopentane matrix at 77°K.

Further photolytical experiments were performed with deaerated solutions containing TCNE ($10^{-4}$M) and one of the donors (about 1 M) in dichloromethane by means of the flash spectroscopic technique. As a result, the transient TCNE$^-$ absorption spectrum was observed within 50 $\mu$sec in all the cases.[9] It should be mentioned that either in the absence of these donors or in the presence of oxygen no transient absorptions were detected.

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