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Dimerization and Electronic Absorption Spectra of Tetracyanoethylene Anion in Solution and in Solid

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The 2-methyltetrahydrofuran solutions of several alkali tetracyanoethylenides (M^+, $TCNE^-$, where M=Na, K, Rb, and Cs) show strong visible absorption spectra at low temperature which might be considered to be charge-transfer bands between two TCNE anions. Temperature dependence of the electronic absorption and ESR spectra of $TCNE^-$ in solution yields the monomer-dimer equilibrium of the TCNE anion. The heat of dimer formation of the anion was found to decrease in the order $Na^+ > K^+ > Rb^+ > Cs^+$ with the size of the counter ions. The heat of dimer formation in $Na^+(TCNE)^-$ also depends considerably on the solvent system. The absorption spectra of the solid TCNE anions were found to resemble the spectrum of the TCNE anion dimer $(TCNE^-)_2$ in solution to a great extent. A comparison of the electronic absorption and ESR spectra of $M^+(TCNE)^-$ in solution and in solid demonstrates that the solid $TCNE^-$ is almost diamagnetic, and the anion dimer can be the unit of structure in the solid salts.

Numerous studies were carried out on the electronic and magnetic properties of radical dimer $(TCNQ^-)_2$ and dimer radical $(TCNQ)_2^-$ of 7,7,8,8-tetracyanoquinodimethane anion $(TCNQ)^-$ in solution[1] and in solid[2-4]. However, few spectroscopic studies of the TCNE anion dimer have been reported since the first preparation of the solid TCNE anion by Webster *et al.*[5] Phillips and Powell[6] suggested complex formation taking place between the TCNE anion and its parent molecule $(TCNE)_2^-$ on the basis of the reversible color change of the THF solution with decreasing temperature. In a previous paper,[7] the present author erroneously proposed the formation of the dimer radical in the MTHF solution at low temperature by means of electronic absorption spectroscopy for which a MTHF solution of TCNE anion containing neutral TCNE was used. Subsequently, the author came to observe the electronic absorption spectra of the solid TCNE anion, ($M^+(TCNE)^-$, M=Na, K, Rb, and Cs), which were very similar to the low temperature spectra of the MTHF solution of $TCNE^-$. Recently, Chang[8] has proposed the formation of the TCNE anion dimer in MTHF by ESR spectroscopy.

The author investigated the solid TCNE anion, and reinvestigated the anion in solution by both optical and ESR spectroscopies. The results indicate the formation of the radical dimer in solution at a low temperature, and suggest that the dimer of $TCNE^-$ can be the unit of structure in solid $M^+(TCNE)^-$. The heat of dimer formation of $TCNE^-$ depends largely on the counter cation (Na^+, K^+, Rb^+, and Cs^+) and also on the solvent composition. The electronic absorption spectra of $TCNE^-$ and $(TCNE^-)_2$ were discussed.

Experimental

Preparation and Materials. To a degassed acetonitrile solution (~8 m*l*) of TCNE (~0.3 g) was added NaCN or KCN (~1.5 g) in a sealed vessel. The dark brown reaction solution was stirred on a magnetic stirrer at 5°C for 3—4 days. The reaction mixture was filtered through a glass filter, and the solvent (CH_3CN) was removed by vacuum evaporation. The solid residue was washed two or three times with THF (~5 m*l*). Dark brown or black solid $Na^+(TCNE)^-$ or $K^+(TCNE)^-$ was obtained. Each procedure was performed in a sealed glass vessel in a vacuum.

$Rb^+(TCNE)^-$ and $Cs^+(TCNE)^-$ were prepared by the same procedures as for $Na^+(TCNE)^-$ from RbI and CsI, respectively. The compositions of the solid salts were confirmed by the elementary analysis of carbon and nitrogen.

$M^+(TCNE)^-$ film was prepared in a quartz optical cell (1 mm or 1 cm) by vacuum evaporation of the solvent from the CH_3CN solution of the salt. Reddish blue or purple film was obtained.

Purification of the solvent was carried out in the same manner as described previously.[7]

Measurements. Electronic absorption spectra were determined with a Cary recording spectrophotometer Model 11. However, spectroscopic study of the monomer-dimer equilibrium was made on a Beckman DK-2U spectrophotometer.[7] All the ESR measurements were made on a JEOLCO P-10 ESR spectrometer (100 kc modulation) with a variable temperature equipment.

Results and Discussion

Electronic Absorption Spectra and ESR in Solid TCNE Anion. Since Webster *et al.*[5] reported the solid formation of metal tetracyanoethylenides from an acetonitrile solution of TCNE and metal iodide or cyanide, few spectroscopic studies of the solid TCNE anion have been reported. This seems to be due to the fact that the preparation of solid $M^+(TCNE)^-$ is more difficult than that of the 7,7,8,8-tetracyanoquinodimethane anion or Würster's salt. In this work, electronic absorption spectra of the pure samples of $M^+(TCNE)^-$ were determined in film and in KBr pellet. The spectra of the solid salts in KBr pellets, shown in Fig. 1, are almost unaltered by changing

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[1] R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

[2] D. B. Chesnut, H. Foster, and W. D. Phillips, *ibid.*, **34**, 684 (1961).

[3] D. B. Chesnut and W. D. Phillips, *ibid.*, **35**, 1002 (1961).

[4] R. G. Kepler, *ibid.*, **39**, 3528 (1963).

[5] O. W. Webster, W. Mahler, and R. E. Benson, *J. Amer. Chem. Soc.*, **84**, 3678 (1962); *J. Org. Chem.*, **25**, 1470 (1960).

[6] W. D. Phillips and J. C. Powell, *J. Chem. Phys.*, **33**, 626 (1960).

[7] M. Itoh, *J. Amer. Chem. Soc.*, **92**, 886 (1970).

[8] R. Chang, *J. Phys. Chem.*, **74**, 2029 (1970).

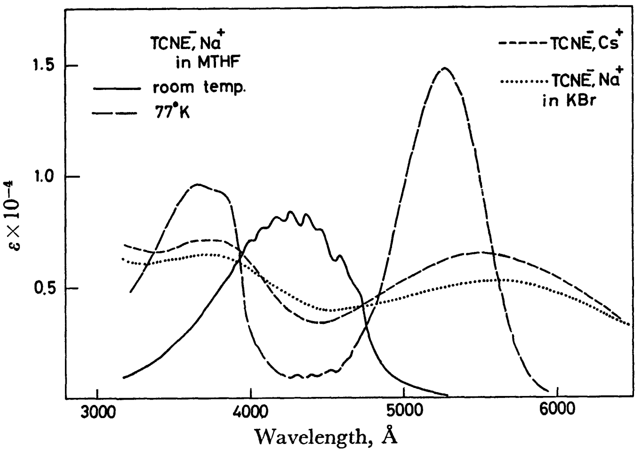

Fig. 1. Electronic absorption spectra of the solid TCNE anions in KBr pellets, and of the MTHF solution of Na$^+$ (TCNE)$^-$ at room temperature and at liquid nitrogen temperature. The ordinate for the spectra of the solid salts is in an arbitary scale.

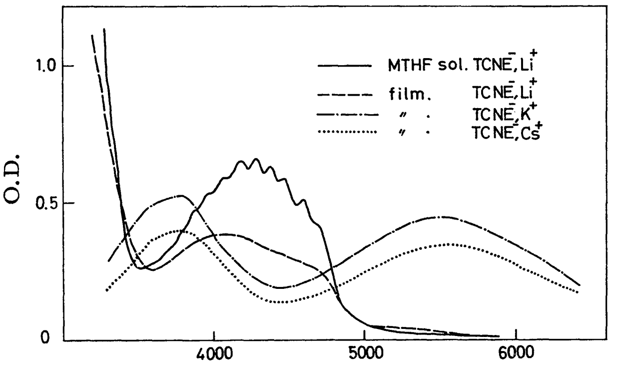

Fig. 2. Electronic absorption spectra of M$^+$ (TCNE)$^-$ (M= Li, K, and Cs) in films at room temperature, and of the MTHF solution of Li$^+$ (TCNE)$^-$ at room temperature.

M$^+$. It is noteworthy that these spectra of solid M$^+$(TCNE)$^-$ are differ remarkably from those in solution at room temperature, but are similar to the low temperature spectra (77°K) of the anion in MTHF.

Chesnut and Phillips$^{3)}$ explained the temperature dependence of ESR intensity of the solid Na$^+$(TCNE)$^-$ by a singlet-triplet model with J=0.26 eV. The apparent relative concentration of paramagnetic species in the solid M$^+$(TCNE)$^-$ (Na$^+$, K$^+$, Rb$^+$, and Cs$^+$) were determined to be only 0.1—0.01 mol%. In powdered sample of the solid M$^+$(TCNE)$^-$, apparent relative concentration of paramagnetic species showed a slight change with temperature (123—380°K). It seems that this paramagnetic species in the salt is impurity or one with defect in solid.

The absorption spectrum of Li$^+$(TCNE)$^-$ in film, shown in Fig. 2, was determined to be similar to that in solution at room temperature. No significant temperature dependences were observed with the ESR and absorption spectra in the MTHF solution of Li$^+$-(TCNE)$^-$. Thus Li$^+$(TCNE)$^-$ is considered to be monomeric both in solid and in solution even at a low temperature. Repeated attempts of preparation and isolation of the solid Li$^+$(TCNE)$^-$ failed.

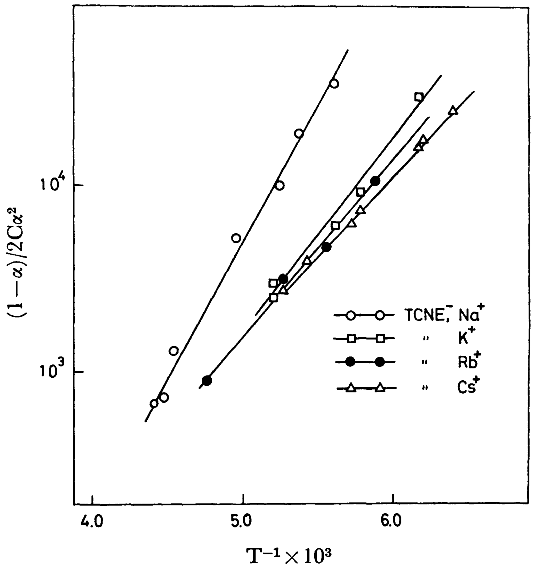

Fig. 3. Plots of log $(1-\alpha)/2C\alpha^2$ against 1/T in the MTHF solutions of M$^+$ (TCNE)$^-$.

Monomer-Dimer Equilibrium Determined by ESR. A procedure similar to that for the investigation of the dimerization of Würster's cation by Kawamori *et al.*$^{9)}$ was applied to the temperature dependence of ESR signal strength in the MTHF solution of M$^+$(TCNE)$^-$. Monomer-dimer equilibrium constant $K=K_0\exp(-\Delta H/RT)=(1-\alpha)/2C\alpha^2$, where C is the concentration of the TCNE anion and α is the fractional concentration of the monomer at a certain temperature, which is given by IT/C; I is the relative ESR intensity. Figure 3 shows the plots of log $(1-\alpha)/2C\alpha^2$ against $1/T$ in the MTHF solutions of the Na, K, Rb, and Cs salts. The slope of the straight line which suggests the dimerization of TCNE$^-$ gave the heat of dimer formation. The results are summarized in Table 1.

Table 1. Heat of dimer formation of M$^+$(TCNE)$^-$

M$^+$	Na$^+$	K$^+$	Rb$^+$	Cs$^+$
$-\Delta H$, kcal	7.1	4.8	4.3	4.0

Values of $-\Delta H$ (l/mol) depend considerably on the counter ion in the order Na$^+$>K$^+$>Rb$^+$>Cs$^+$. The value of $-\Delta H$ obtained in Na$^+$(TCNE)$^-$ (7.1 kcal) agrees well with that obtained by Chang (8 kcal), and is comparable to the value (10 kcal) obtained by Boyd and Phillips for the dimerization of TCNQ$^-$ in an aqueous solution. If the difference of solvent system in the formation of (TCNE$^-$)$_2$ and (TCNQ$^-$)$_2$ is taken into account, $-\Delta H$ might be smaller in the former.

Reinvestigation of the Monomer-Dimer Equilibrium by Electronic Absorption Spectra. The absorption spectra of the MTHF solution of Na$^+$(TCNE)$^-$ (analytically pure) were determined at room temperature and at 77°K, as shown in Fig. 1. A strong absorption band at 5400 Å region was tentatively assigned to be a charge-transfer band between two TCNE anions. This

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9) A. Kawamori, A. Honda, K. Suzuki, and Y. Ooshika, *J. Chem. Phys.* **44**, 4363 (1966).

absorption at low temperature was confirmed to be independent of the neutral TCNE by the addition of TCNE to the solution of anion. The previous results[7] were reinvestigated by assuming the monomer-dimer equilibrium of $TCNE^-$ at low temperature. Itoh and Nagakura[10] demonstrated the dimerization of the substituted pyridinyl radicals by means of the equation $\log K = \log \varepsilon \cdot \varepsilon_d / 2a(\varepsilon_d - \varepsilon)^2$, where K is equilibrium constant of dimerization and a is stoichiometric concentration of the monomer; a was determined from optical absorbance at 4500 Å of the MTHF solution of $M^+(TCNE)^-$ at room temperature, assuming the TCNE anion to be entirely monomer at room temperature. The values, ε and ε_d are apparent absorption coefficient and molar absorption coefficient of the absorption maxima at 5400 Å at various temperatures, respectively. The absorption of monomer at 5400 Å region was neglected. If $TCNE^-$ in a considerably concentrated solution of MTHF is assumed to be in the dimer form $(TCNE^-)_2$ at 77°K (see Fig. 1), ε_d is evaluated to be 15,000 at 77°K. However, while the oscillator strength (f-value) of the absorption band of the dimer was assumed to be independent of temperature, ε_d at absorption maxima gradually increased but a half-width decreased with decreasing temperature, as shown in Fig. 4.

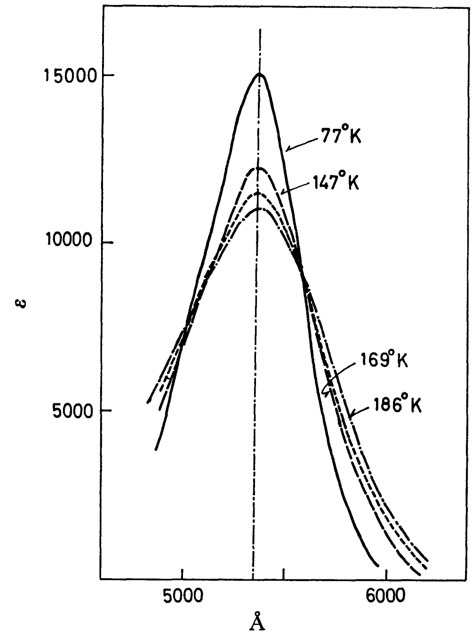

Fig. 4. Temperature dependence of the molar absorption coefficient, ε_d, of the charge-transfer band in $(TCNE^-)_2$, determination of which was made as follows. The molar absorption coefficient (ε_{d77}) and intensity (I_{77}) at 77°K were evaluated by assuming that Na^+ $(TCNE)^-$ in a highly concentrated solution (MTHF) was entirely dimeric at 77°K. The absorption spectra of the MTHF solution of the salts were measured at several temperatures. Apparent absorbance (ε_d') and intensity (I') of the charge-transfer band were determined at a certain temperature. The molar absorption coefficient (ε_d) at a certain temperature was obtained by the equation $\varepsilon_d = \varepsilon_d' \cdot I_{77}/I'$, where the integrated intensity ($I \propto f$-value) of charge-transfer band was assumed to be independent of temperature.

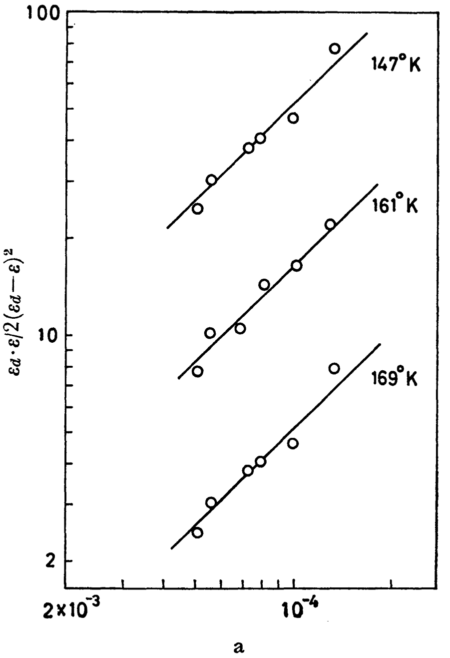

Fig. 5. Plots of $\log \varepsilon \cdot \varepsilon_d / 2$ $(\varepsilon_d - \varepsilon)^2$ against $1/T$ in the MTHF solution of Na^+ $(TCNE)^-$ at various temperatures.

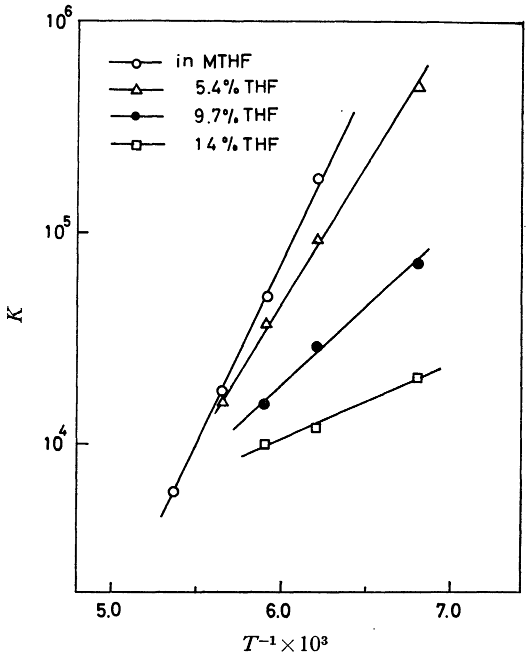

Fig. 6. Temperature dependence of the monomer-dimer equilibrium constant K in MTHF and THF-MTHF mixed systems.

Using ε_d obtained at several temperatures, straight lines close to a slope were obtained in the plots, $\log \varepsilon \cdot \varepsilon_d / 2(\varepsilon_d - \varepsilon)^2$ against $\log a$, as shown in Fig. 5. The slope$=1$ suggests the monomer-dimer equilibrium of $TCNE^-$ at various temperatures. Equilibrium constant K (l/mol) at several temperatures was obtained by a least-squares fit. Figure 6 shows temperature dependence of K in the MTHF and MTHF-THF mixed systems. Heats of dimer formation for $Na^+(TCNE)^-$ were obtained from slopes of the straight lines of each solvent system. The results are sum-

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10) M. Itoh and S. Nagakura, *J. Amer. Chem. Soc.*, **89**, 3959 (1967).

marized in Table 2. As for Na$^+$(TCNE)$^-$ in MTHF, the value of $-\Delta H$ obtained by absorption spectroscopy was in good agreement with that obtained by ESR, as shown in Tables 1 and 2. However, the values of K corresponding to log $(1-\alpha)/2C\alpha^2$ in Fig. 3 show considerable deviation from those of absorption spectra. Although $-\Delta H$ obtained by ESR might be fairly accurate, the values of K by ESR seem to be much less accurate than those by absorption spectra. The value, $-\Delta H$ in Na$^+$(TCNE)$^-$ is largely dependent upon the solvent system (Table 2). When MTHF was mixed with a small amount of THF which is more polar than MTHF, $-\Delta H$ decreased remarkably while the entropy change increased. The decrease in $-\Delta H$ and the increase in ΔS (from large minus to plus) with increasing solvent polarity were observed in the dimer formation of the ketyl radicals reported by Hirota and Weissman.[11] These results seem to be attributed to the greater solvation in monomer than in dimer.

TABLE 2. THERMODYNAMIC DATA FOR THE FORMATION OF $(Na^+)_2$ $(TCNE^-)_2$ BY MEANS OF ELECTRONIC ABSORPTION SPECTROSCOPY

Solvent	MTHF	5.4% THF	9.6% THF	14.5% THF
K, mol^{-1} (169°K)	5.0×10^4	3.6×10^4	1.5×10^4	1.0×10^4
$-\Delta H$, kcal	7.6	5.7	3.4	1.8
ΔS, eu	−11.8	−6.5	−0.5	3.7

Electronic Absorption Spectra of Monomer and Dimer of TCNE$^-$. The MTHF solution of TCNE$^-$ shows a broad absorption spectrum with a vibrational structure at 3600—4700 Å region. From the shape of absorption, it seems that the absorption spectrum of TCNE$^-$ at 3600—4700 Å region consists of two electronic transitions. This is supported by an open shell SCF MO calculation of TCNE$^-$. The observed and calculated data are summarized in Table 3.

TABLE 3. OBSERVED AND CALCULATED ELECTRONIC TRANSITION ENERGIES AND OSCILLATOR STRENGTHS (f-values)

Obsd		Calcd	
E(eV)	f	E(eV)	f
2.7 2.8	0.21	2.2 2.4	0.11 0.08
—	—	3.4	0.42

From the experimental results of TCNE$^-$ both in solution and in solid, it is clearly seen that the strong absorption spectrum at 5300—5500 Å region and another absorption at 3500—4000 Å region are attributed to the dimer. From the standpoint of charge-transfer interaction in the radical dimer, the visible absorption at ~5400 Å observed for the TCNE anion dimer can be interpreted to be the charge-transfer band between two TCNE$^-$ and the shorter wavelength absorption with two maxima is ascribed to the shifted local excitations.

The electronic absorption spectra of the solid M$^+$(TCNE)$^-$ were found to greatly resemble the spectra of the dimer in solution. The magnetic and optical properties of the solid salt suggest that the TCNE radical dimer is the unit of structure in the solid state where the spin exchange interaction in the dimer is extremely great in a considerably wide range of temperature (123—380°K) in comparison with those of Würster's salt,[12–14] ethylphenazyl[15] and other radical salts.[3,4,16]

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11) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.* **89**, 2538 (1964).

12) D. D. Thomas, H. Keller, and H. M. McConnell, *J. Chem. Phys.*, **39**, 2321 (1963).

13) T. Sakata and S. Nagakura, This Bulletin, **43**, 2414 (1970).

14) See references cited in 12.

15) T. Sakata and S. Nagakura, This Bulletin, **42**, 1497 (1969).

16) Y. Sato, M. Kinoshita, M. Sano, and H. Akamatu, *ibid.*, **42**, 3051 (1969); *ibid.*, **42**, 548 (1969).