shorter wavelength Cotton effects exhibited on the one hand by aromatic carboxylic acids having more than one carbon atom interposed between the phenyl and the carboxyl groups or on the other hand by those systems for which it can be reasonably supposed that the interacting carboxyl n–π and the phenyl transitions are juxtaposed. The latter case seems to us to be an intriguing and fruitful area for further investigation.

Formation and Spectrum of Tetracyanoethylene Dimer Anion (TCNE)$_2^-$ [1]

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Abstract: The reversible complex formation of TCNE (tetracyanoethylene) anion radical with its parent molecule in MTHF (methyltetrahydrofuran) or in THF was confirmed spectroscopically at low temperature. The complex, (TCNE)$_2^-$, shows a strong visible absorption band at 5330–5350 Å (ϵ_{max} 15,500). Analysis of the spectra yields an equilibrium constant in MTHF for TCNE$^-$, Na$^+$ + TCNE $\rightleftharpoons$ (TCNE)$_2^-$, Na$^+$ at 161 °K of 1.32 × 10^3 l./mol, $-\Delta H°$ of 1.46 kcal, and $\Delta S°$ of 3.95 eu. Thermodynamic data depend very strongly on the metal cation and also on the solvent composition. Using the equilibrium constant, the spectrum of pure (TCNE)$_2^-$, M$^+$ was obtained. The equilibrium of the complex formation and the absorption spectrum are discussed.

Recently, electronic spectra and structures of the dimers of anion,[3–5] neutral,[6–9] and cation[5,10,11] radicals have been reported in both liquid and solid states. However, only a few spectroscopic studies of complexes (such as the naphthalene dimer cation) between anion or cation radicals and their parent molecules have been reported[12–15] although this kind of complex formation was rather often suggested, and also electron-transfer rates have been determined between anion radical and parent molecule in the liquid state. Among such studies, Ishitani and Nagakura[16] reported the electronic spectrum and structure of paracyclophane monoanion radical as a model for CT (charge-transfer) interaction between benzene anion and neutral molecule. Complex formation of tetracyanoethylene with its anion was first suggested by Phillips and Powell[17] on the basis of the reversible color change of THF (tetrahydrofuran) solution with temperature.

In this paper, the equilibrium of the formation of (TCNE)$_2^-$ from TCNE and TCNE$^-$ was studied for Li, Na, and K salts in MTHF (2-methyltetrahydrofuran), and in mixtures with THF at low temperature. Thermodynamic quantities of the equilibrium are reported. The absorption spectrum of the pure dimer anion, (TCNE)$_2^-$, M$^+$, was obtained from the analysis of this equilibrium.

Experimental Section

A good commercial sample of TCNE was used after sublimation in high vacuum. 2-Methyltetrahydrofuran was distilled over sodium metal after refluxing with sodium metal for 10 hr. The refluxing and distillation were repeated two times. THF was also purified using the same procedures as for MTHF. These solvents were kept with a Na mirror in bottles connected to the vacuum system.

The TCNE anion radical was prepared by reduction with a sodium or potassium mirror for about 5 or 10 sec, respectively. The TCNE anion and TCNE mixed solution was obtained. After that, the tube containing the Na or K mirror was sealed off from the solution tube with the 1-cm optical cell. For TCNE$^-$, Li$^+$, freshly cut lithium metal was used.

Alternatively, TCNE$^-$,Na$^+$ solid was prepared in acetonitrile from NaCN and TCNE *in vacuo* following the method reported by Webster, *et al.*[18] The molar absorption coefficient of the TCNE anion was determined from the solution of the solid salt dissolved in MTHF or THF, and also from the solution made by contacting TCNE with sodium or potassium. The coefficient was also determined by the following electron-transfer reaction from 1-methyl-4-carbomethoxypyridinyl radical[8,19] to TCNE. The absorption spectrum of an MTHF solution of the 1-methyl-4-carbomethoxypyridinyl radical was carefully determined at room temperature. The molar coefficient of the absorption band at 3920 Å of this radical has been reported (ϵ_{max} 4500).[7,19] TCNE was added to the MTHF solution of the pyridinyl radical through a breakable seal. Complete electron transfer from the pyridinyl radical to

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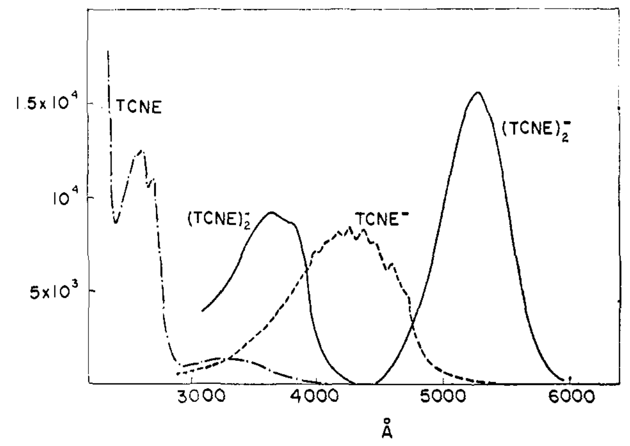

Figure 1. The spectra of TCNE and its anion radical in MTHF, and the spectrum of pure $(TCNE)_2^-$ complex constructed from the equilibrium investigation. The unit of ordinate is ϵ.

TCNE occurred very rapidly to give TCNE anion and pyridinium cation. The absorption spectrum of the pyridinyl radical was completely replaced by that of the TCNE anion in the visible region, and that of the pyridinium cation in the uv region. From this spectrum, the molar absorption coefficient of the TCNE anion was calculated. No interaction between TCNE anion and pyridinium cation was detected in a large temperature range from room temperature to 77°K. The $TCNE^-$ spectra from the Na^+, K^+, and pyridinium salt solutions were substantially identical.

All of the absorption measurements were made on a Beckman DK-2 spectrophotometer. Low-temperature spectra were taken by using a quartz or vicole dewar. Intermediate temperatures (173–123°K) were controlled by a flow of nitrogen gas cooled by liquid N_2.

Results and Discussion

Webster, *et al.*,[18] reported the absorption spectrum of $TCNE^-$, Na^+ prepared from sodium cyanide and TCNE in acetonitrile. In the present paper, the electronic absorption spectrum of the TCNE anion made by conventional sodium metal reduction in MTHF (THF) is shown in Figure 1, together with the spectrum of TCNE itself. The spectrum of TCNE in MTHF or THF is considered as that of a complex with the solvent molecule.[20] The absorption coefficient of the TCNE anion was determined as already described above. The spectrum of the $TCNE^-,Na^+$ solution shows no significant spectral change at low temperature except very much sharpening of vibrational structure.

However, the MTHF solution of $TCNE^-,Na^+$ plus an excess amount of TCNE shows reversibly intense absorption in the 5000–5500-Å region on decreasing the temperature. This can be attributed to $(TCNE)_2^-,Na^+$. The temperature dependence of the intensity of the visible and uv absorption of $TCNE^-,Na^+$ plus TCNE in MTHF is shown in Figure 2, taking into account volume changes with temperature. No absorption in this spectrum at 77°K was observed at longer wavelengths up to 13,000 Å.

Using the intensity of the ~5300-Å band as an index of the amount of $TCNE_2^-$, the equilibrium constant K for the formation of the 1:1 complex was determined from the spectrophotometric analysis by using Scott's equation, $ab/d = 1/K\epsilon + b/\epsilon$. Here a and b are the initial concentrations of $TCNE^-$ and TCNE, d is the measured absorbance at a certain wavelength, and ϵ is the molar absorption coefficient. Absorptions of TCNE and of $TCNE^-,Na^+$ at 5300 Å (λ_{max}) were negligible (see Figure 1), especially since b was greater than a ($b \approx 15a$). The concentration of $TCNE^-,Na^+$, a, was determined from the room-temperature absorbance at 4500 Å of the MTHF solution containing $TCNE^-$, Na^+, and TCNE mentioned above, and the concentration TCNE, b, was determined from the absorbance at 3300 Å of the same solution, because no complex formation occurred at room temperature, as is seen from Figure 2. In this determination of a and b, the absorption of TCNE at 4500 Å and also that of $TCNE^-$ at 3300 Å were taken into account, respectively, as shown in Figure 3.

Figure 4 shows Scott plots for the absorption maximum at 5340 Å of the $TCNE-TCNE^-,Na^+$ system in MTHF at several temperatures. The linearity of this kind of plot may be regarded as evidence for a 1:1 com-

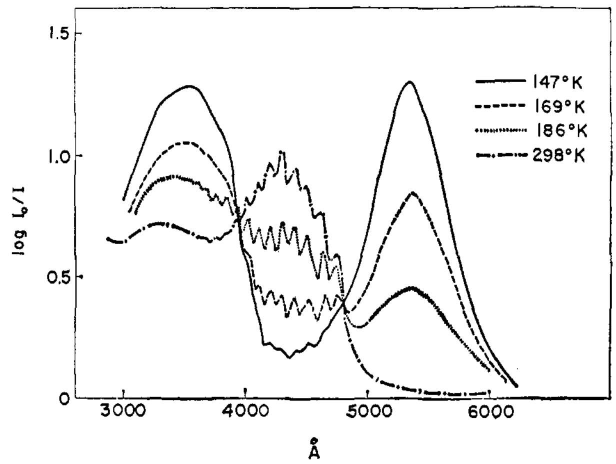

Figure 2. Temperature dependence of absorption spectrum of the $TCNE-TCNE^-$, Na^+ system in MTHF; concentration of TCNE, 4.9×10^{-4}, concentration of $TCNE^-$, Na^+, 0.88×10^{-4}, light pathlength, 1 cm.

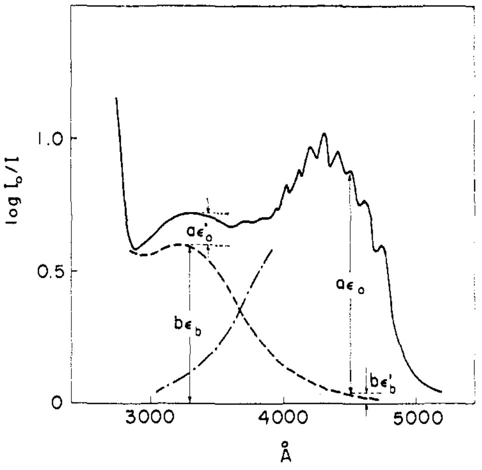

Figure 3. Determination of the concentration of $TCNE^-$ (a) and TCNE (b) from the absorption spectrum. Concentrations, a and b, were determined from the following equations: $d = a\epsilon_a + b\epsilon_b'$ ($\epsilon_a \gg \epsilon_b'$) and $d' = b\epsilon_b + a\epsilon_a'$ ($\epsilon_b \gg \epsilon_a'$) ($b \gg a$), where d and d' are observed absorbances of the solution of the $TCNE-TCNE^-$, Na^+ system at 4500 and 3300 Å, respectively, ϵ_a and ϵ_a' are molar absorption coefficients of $TCNE^-$ at 4500 and 3300 Å, respectively, and ϵ_b' and ϵ_b are molar coefficients of TCNE at 4500 and 3300 Å, respectively, as shown in Figure 3.

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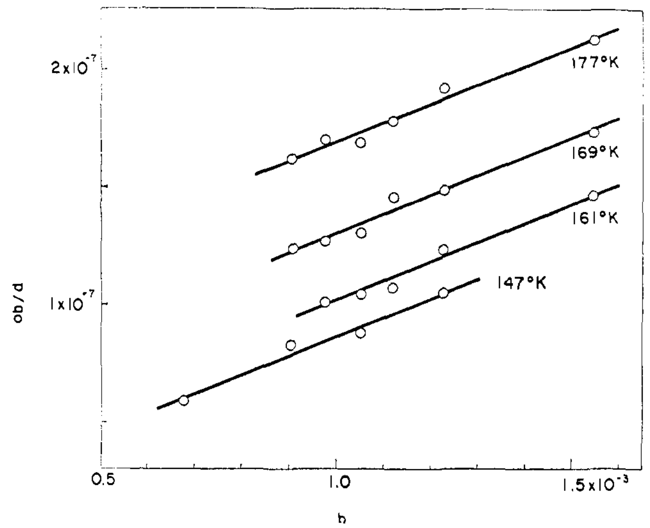

Figure 4. Scott plots for the TCNE–TCNE⁻, Na⁺ system in MTHF at various temperatures.

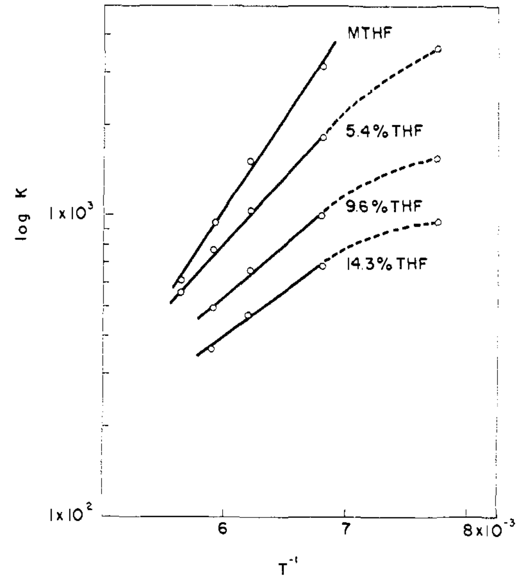

Figure 5. The log of the equilibrium constant for the complex formation of $(TCNE)_2^-$, Na^+ against $1/T$.

plex at the low concentrations used, although a complex with other stoichiometry than 1:1 might be considered at high concentrations. From the Scott plot, the molar absorption coefficient of the 5340-Å band of the complex was calculated by a least-squares fit at each of several temperatures between ~173 and ~123°K. No significant variation in the value of ϵ_{max} was obtained, although one would expect a little increase of ϵ_{max} with decreasing temperature. In this paper, the average value of ϵ_{max} at several temperatures was adopted in order to calculate the equilibrium constant, K, of complex formation.

Alternatively, the spectrum of the $TCNE^-,Na^+$ and TCNE mixed solution ($b \gg a$) in MTHF was taken at room temperature and at 77°K. The value of ϵ_{max} of the complex at 5340 Å was evaluated from these spectra, because at 77°K the TCNE anion may be assumed to be almost completely in the complex form $(TCNE)_2^-$, but completely uncomplexed at room temperature (see Figure 1). The value of ϵ_{max} (15,000) thus obtained at 77°K shows good agreement with the data (15,500) calculated from a Scott plot. This confirms that the $TCNE^-$ really makes a 1:1 complex with its parent molecule within experimental error.

To determine $-\Delta H°$ for the complex, the equilibrium constant was evaluated from each of a series of Scott plots at various temperatures, and log K was plotted against $1/T$ as shown in Figure 5. As seen in Figure 5, the plots of log K against $1/T$ are not straight lines at temperatures below ~140°K. Supposedly, this is because MTHF and also the MTHF–THF mixed system showed gradually increasing viscosity below ~140°K. Constant low viscosity of the solvent within a temperature range is required for this kind of determination. In this paper, the data for less than ~140°K were excluded from the calculation of $-\Delta H°$.

The spectrum of the complex $(TCNE)_2^-,Na^+$ was constructed using the equilibrium constant K and the molar absorption coefficient. The constructed spectrum is shown in Figure 1, together with those of TCNE and $TCNE^-,Na^+$.

The room temperature spectra of $TCNE^-,Li^+$ and $TCNE^-,K^+$ in MTHF were next recorded. In neither case was any significant difference observed in the spectra compared with that of the sodium salt. The low-temperature spectrum of the MTHF solution of $TCNE^-,Li^+$ plus a large excess of TCNE showed no new spectrum attributable to complex formation of $(TCNE)_2^-,Li^+$. On the other hand, the equilibrium constant, K, and absorption coefficient of the visible band of the complex $(TCNE)_2^-,K^+$ were obtained by similar procedures to that of the Na salt. The K obtained for the potassium salt in MTHF is approximately one-tenth of that of the sodium salt, while the absorption maximum and intensity of the ~5340-Å band do not depend on the metal cation within experimental error.

As shown in Figure 5 and Table I, the complex formation of $(TCNE)_2^-,M^+$ also depends very much on the solvent composition. No observable complex formation was found in other solvents including 1,2-dimethoxyethane and acetonitrile, although a color change from yellow to red could be seen from a solidified acetonitrile solution at 77°K. Even in THF at ~170°K, visible spectrum shows only very faint formation of $(TCNE)_2^-,M^+$. Not many solvents could be used for this kind of experiment, because the solvent should be transparent at low temperature, and also dissolve $TCNE^-,M^+$ and the complex. Further, the $TCNE^-$ is unstable in a mixed solvent such as EPA containing ethanol.

Table I. Thermodynamic Data for the Formation of $(TCNE)_2^-$

	$(TCNE)_2^-$, K^+	$(TCNE)_2^-,Na^+$			
Solvent	MTHF	MTHF	5.45% THF	9.6% THF	14.5% THF
ϵ_{max} (5340 Å)	15,800	15,500	16,070	15,400	15,515
K, mol⁻¹ (161°K)	144	1322	971	575	407
$-\Delta H°$, kcal	1.30	1.46	0.85	0.52	0.39
$\Delta S°$, eu	1.78	3.95	8.39	9.39	9.47

The thermodynamic quantities for the complex formation obtained here are summarized in Table I. The heat of formation shows that $(TCNE)_2^-$ is a weaker complex than the anion radical dimers; for example,

$-\Delta H°$ is reported to be ~10 kcal for the dimer of the tetracyanoquinodimethane anion, $(TCNQ)_2{}^{2-}$.[4] However, the formation of $(TCNE)_2{}^-$ reported here may be competing with CT complex formation of TCNE with the solvent molecule. Here $TCNE^-$ and the solvent both are electron donors. The heat of complex formation of TCNE with an ethereal solvent such as THF has been reported to be 1–2 kcal.[19] Although TCNE and its anion are a strong acceptor and donor, respectively, the $-\Delta H°$ obtained here is very similar to that of a weak CT complex. As summarized in Table I, $-\Delta H°$ does not depend very much on the metal cation, while K depends very much as mentioned above. This difference of K is attributed to a change of the entropy terms, as will be mentioned below.

Hogen-Esch and Smid[21] reported the existence of contact and solvent-separated ion pairs in solutions of carbanions and of radical ions, and also reported the effect of a counterion on the absorption spectrum of the metal fluorenide, and on the equilibrium constant between two types of ion pairs, contact and solvent-separated ion pairs. On the other hand, Hirota[22] reported epr studies of the different types of ion pairs in metal–cation naphthalenide and anthracenide in ethereal solvents. The absorption spectra of metal–cation tetracyanoethylenide and its dimer anion neither depend on the solvent (MTHF, THF, and CH_3CN), nor on the metal (Li, Na, and K). From the viewpoint of the ion pairs reported by Hogen-Esch and Smid, and by Hirota, it is likely that both $TCNE^-,M^+$ and $(TCNE)_2{}^-,M^+$ may be solvent-separated or much solvated ion pairs rather than contact pairs in MTHF or THF. On the basis of these assumptions, it is of interest to compare the entropy of formation of $(TCNE)_2{}^-$ with that of radical dimers, and with that of numerous CT complexes with TCNE as acceptor. Boyd and Phillips reported −19.5 eu for dimerization of the 7,7′,8,8′-tetracyanoquinodimethane anion in aqueous solution.[4] Furthermore, numerous papers show considerable entropy loss in formation of the CT complexes of TCNE. It seems that these results mean increased solvation or more ordering of the solvent in the complexes than in the uncomplexed molecules. Hirota and Weissman[3] reported a large *negative* entropy change for *dissociation* of sodium fluorenone anion dimer. According to their argument, the solvation of the Na ion in the ethereal solvent has been considered to be one of the main causes of the large entropy decrease, and the solvation of the Na ion is greatly hindered in the dimer, while in the monomer more space is accessible for the solvent molecule. The considerable *positive* entropy change obtained here in *formation* of $(TCNE)_2{}^-$ means stronger solvation of $TCNE^-,M^+$ in the uncomplexed state. In $(TCNE)_2{}^-,M^+$, the solvation of the metal ion is hindered by the complex anion, and also the complex anion may be much less solvated than $TCNE^-$, because the negative charge is more distributed in the large dimer anion compared with the monomer. In addition to these arguments, partial ordering of the solvent molecule (THF or MTHF) as electron donor[20] by the CT interaction with TCNE could be partly responsible for the entropy change.

As seen in Table I, the equilibrium constant of the $(TCNE)_2{}^-$ complex is much larger in the Na salt than in the K salt. This increase of K is mainly attributed to the increase of the entropy term from the K to the Na salts, which may be ascribed to the size of the counterion. The smaller cation means more solvation by the ethereal solvent, and causes more increase of the entropy.[21] This behavior is similar to that found in the dissociation of metal naphthalenide[23] and of the diamagnetic dimers of ketyls.[3] From these arguments, the entropy of $(TCNE)_2{}^-$ formation seems to increase in the order $K^+ < Na^+ < Li^+$. If $-\Delta H°$ of the $(TCNE)_2{}^-$ complex formation does not depend very much on the counterion, K would be expected to increase in the same order as in the entropy change. Nevertheless, the equilibrium constant of $(TCNE)_2{}^-,Li^+$ complex formation is abnormally too small to be determined. It seems that the structure of the complex from the Li salt might be different from those of the other salts, and therefore the heat of formation might be different.

Table I shows considerable solvent dependence of $-\Delta H°$ and $\Delta S°$. This seems to confirm strong electronic interaction of $TCNE^-,Na^+$ or TCNE with the solvent mentioned above. When MTHF was mixed with a small amount of THF, which is more polar than MTHF, the heat of complex formation decreased, while the entropy change considerably increased. The solvent dependence of $-\Delta H°$ can be well understood from the argument that $(TCNE)_2{}^-$ formation may compete with the formation of the CT complex of TCNE with the solvent molecule. The change of $\Delta S°$ with solvent composition is also explained by the supposition that $TCNE^-,Na^+$ is more solvated than $(TCNE)_2{}^-,Na^+$, as mentioned above.

Lewis and Singer[12] reported the epr spectrum in methylene chloride at −85 to −90° of the naphthalene dimer cation, which was made by oxidation with antimonyl pentachloride. The purple color of the solution was tentatively ascribed to $(C_{10}H_8)_2{}^+$. Recently, Badger, *et al.*,[14] have observed the 9600 cm^{-1} band of $(C_{10}H_8)_2{}^+$ in a methylcyclohexane–isopentane system, generated by γ irradiation at low temperature.

As mentioned above, Ishitani and Nagakura[16] reported a strong absorption band at 13200 cm^{-1} of the paracyclophane monoanion and attributed it to a CT band between two benzene rings on the basis of theoretical considerations. If $(TCNE)_2{}^-$ is assumed to be a sandwich-type complex as proposed for substituted pyridinyl dimers in previous papers[7,8,24] and in other numerous complexes, the charge-resonance band due to the transition between the following two states should be observed in visible or ir regions: $(A^-, B \pm A, B^-)$ I, II, where A^- and B are $TCNE^-$ and TCNE, respectively. However, it seems that the strong band at ~5340 Å of the $(TCNE)_2{}^-$ is too short a wavelength to be assigned to this transition. It is more likely that the visible band of the complex is tentatively ascribed to the transition from I to the lower of the two states III, IV: $(A^{-*},B \pm A,B^{-*})$ III, IV, where A^{-*} and B^{-*} are excited states of $TCNE^-$.

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