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Effect of Cesium Counterion on the ESR Spectrum of Tetracyanoethylene Anion Radicals

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Evidence was obtained by ESR for the ion-pair formation between the tetracyanoethylene anion radical and the cesium counterion in tetrahydrofuran. The hyperfine lines of the ESR spectrum of cesium tetracyanoethylenide were exceptionally broad at high salt concentrations in tetrahydrofuran, while they were remarkably narrowed by the addition of a small amount of DMF or triglyme (cation-solvating agents) or by replacing the counterion with the tetra-*n*-butylammonium ion. This indicates that the broad linewidth is due to the unresolved hyperfine splitting of the cesium counterion. In addition, the concentration dependence of the ESR spectrum indicates that the line broadening is to be interpreted not only in terms of the Heisenberg spin exchange, but also in terms of the equilibrium between the ion-pair and the free ion. The cesium hyperfine coupling constant was estimated by simulating the line shape to be 40 m Gauss in the ion-pair state between the tetracyanoethylene anion radical and the cesium ion in the tetrahydrofuran solution.

Since the first observation of the electron spin resonance (ESR) spectrum of the tetracyanoethylene (TCNE) anion radical by Weissman *et al.* in 1960,[1] this anion radical has been known to be very stable in many solutions at room temperature and has been known to give a simple well-resolved ESR spectrum with a hyperfine structure due to the four equivalent ^{14}N nuclei. Several workers have studied the variety of metal tetracyanoethylenide systems by ESR, but have failed to observe any metal hyperfine splittings.[1-4] Furthermore, the electronic spectra of these systems were found to depend neither on the solvent nor on the metal cation.[5]

Recently, we studied the electron-transfer reaction of the TCNE anion in ethereal solvents and found that the observed kinetical behavior could be interpreted in terms of the electrostatic interactions between anions and counterions, and also that the line shape of the ESR spectrum of cesium tetracyanoethylenide became wide and distorted as the concentration of TCNE anion increased.[6] The previous investigation will be extended here to a study of the shape of the ESR spectrum of cesium tetracyanoethylenide in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) in more detail. Our new evidence for the ion-pair formation of the TCNE anion will be reported in the present paper.

Experimental

Materials. The cesium tetracyanoethylenide ($TCNE^-Cs^+$) was synthesized as follows.[7] TCNE of a guaranteed reagent grade (Tokyo Kasei Kogyo Co., Ltd.) was purified by repeated sublimations *in vacuo*. Cesium iodide of a guaranteed reagent grade (Wako Pure Chemical Ind., Ltd.) was dried *in vacuo* at 100 °C for 24 hr. The TCNE and cesium iodide were dissolved into acetonitrile *in vacuo*, and the mixture was stirred by a magnetic stirrer for 48 hr at 0 °C. The solution was filtered *in vacuo* and condensed by evaporating the solvent. After the solution had then stood overnight, a reddish-brown solid, $TCNE^-Cs^+$, crystallized; this was washed with acetonitrile and dried. The crystalline $TCNE^-Cs^+$ was stable at room temperature in a glass ampoule for more than one year. The purity of the sample, as determined by elementary analysis, was approximately 92%.

The THF and DME were carefully purified and dried as has been described previously.[6] The trimethylene glycol dimethylether (triglyme) and *N,N*-dimethylformamide (DMF) were distilled over calcium hydride at reduced pressure. The tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) was synthesized and purified as has been described previously.[6]

Sample Preparation and Measurements. The sample solution was prepared by dissolving crystalline $TCNE^-Cs^+$ into the respective solvent *in vacuo* and was sealed into a ESR sample tube made of Pyrex glass. Triglyme or DMF was added to the sample solution, if needed, through a break seal.

The concentration of $TCNE^-Cs^+$ was determined from the absorption maximum at 420 nm ($\varepsilon = 7100\ cm^{-1} \cdot l \cdot mol^{-1}$)[7] in the visible spectra.

All the ESR spectra were taken with a JES-NE-2X spectrometer equipped with 100 kHz filed modulation and a variable-temperature control unit.

Results and Discussion

Effect of Additives. The ESR spectrum of the TCNE anion consists of 11 lines with a separation of 1.65 Gauss, as has been reported by Weissman *et al.*[1] Most of the alkali metal (Li^+, Na^+, K^+) salts and tetra-*n*-butylammonium(Bu_4N^+) salt give ESR spectra consisting of sharp hyperfine lines, though their width increases slightly with an increase in the salt concentration. In contrast, it was found for cesium salt that the width of the hyperfine lines increased remarkably with an increase in the concentration. Figure 1 shows a representative spectrum with broad hyperfine lines at a high concentration of cesium salt. It was also found that the line shape deviated more and more

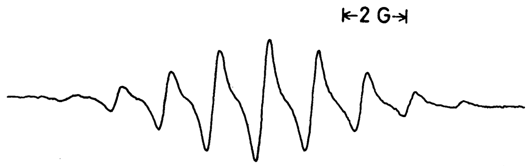

Fig. 1. ESR spectrum of 3.0×10^{-4} M $TCNE^-Cs^+$ in THF at 25 °C.

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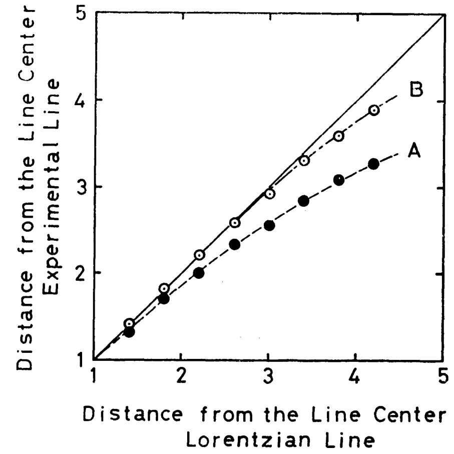

Fig. 2. Line shapes of the $\bar{M}=0$ lines in the first-derivative ESR spectra of TCNE$^-$Cs$^+$ at 25 °C. The distance in units of half the peak-to-peak width of the experimental line is plotted against the distance at which a Lorentzian line has the same relative amplitude: A, 4.2×10^{-4} M TCNE$^-$Cs$^+$ in THF; B, 4.6×10^{-4} M TCNE$^-$Cs$^+$ in THF–triglyme (2.8 mole%) mixture; solid line, a Lorentzian shape.

from a Lorentzian shape as the concentration increased. Figure 2(A) shows the deviation of the ESR spectral shape for the central hyperfine line observed at the 4.2×10^{-4} M TCNE$^-$, Cs$^+$ solution in THF from the ideal Lorentzian shape. The experimentally-observed first-derivative line shape is compared with the first-derivative line shape of a Lorentzian line having the same peak-to-peak amplitude and width as the experimental line. The distance in units of half the peak-to-peak width of the experimental line from the line center at several amplitudes is plotted against the corresponding value for the pure Lorentzian line. The solid line indicates the relation expected for a pure Lorentzian line shape. It is evident that the observed shape falls off at the tail much more rapidly than a Lorentzian shape. It has been reported that potassium tetracyanoethylenide gave a Lorentzian shape even at concentrations as high as 7×10^{-4} M.[4)]

To study the effect of solvation on the ESR spectrum of the TCNE$^-$Cs$^+$–THF system, DMF and triglyme were used as cation-solvating agents. Figure 3 shows the change in the ESR linewidth for the 3×10^{-4} M of TCNE$^-$ caused by the added DMF. The linewidth is considerably reduced by the presence of a small amount of DMF. With the increasing amount of DMF, the linewidth seems to decrease beyond the limit of measurement (—25 m Gauss). The linewidth is also reduced by the addition of triglyme. The results at several temperatures are shown in Fig. 4.

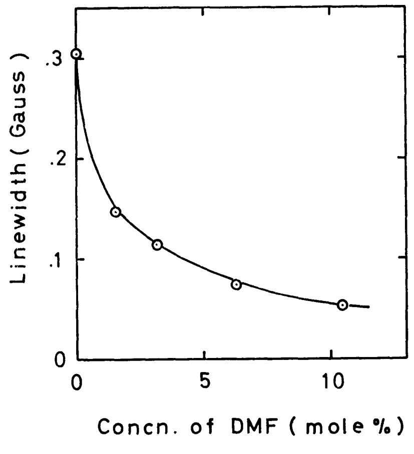

Fig. 3. Change of ESR linewidth ($\bar{M}=0$) of 3.0×10^{-4} M TCNE$^-$Cs$^+$ upon addition of DMF into THF solution at 25 °C.

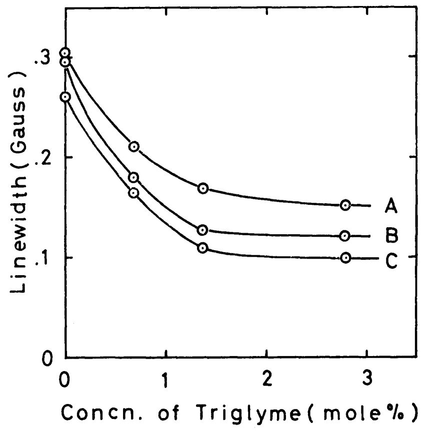

Fig. 4. Change of ESR linewidth ($\bar{M}=0$) of 3.0×10^{-4}M TCNE$^-$Cs$^+$ upon addition of triglyme into THF solution at various temperatures: A, 25 °C; B, 0 °C; C, −30 °C.

Because both additives are known to solvate preferentially the cesium ion,[8,9)] the observed change of the linewidth may be interpreted by Process (1) or (2);

$$\mathrm{TCNE^-Cs^+} + n\mathrm{DMF} \longrightarrow \mathrm{TCNE^-Cs^+(DMF)}_n \qquad (1)$$

$$\mathrm{TCNE^-Cs^+} + n\mathrm{Triglyme} \longrightarrow \mathrm{TCNE^-Cs^+(Triglyme)}_n \qquad (2)$$

Here, TCNE$^-$Cs$^+$ and TCNE$^-$Cs$^+$(additive)$_n$ denote the ion-pair and the solvent-separated ion-pair respectively. Thus, the effect of cation-solvating agents strongly suggests that the abnormally broad ESR spectrum is to be attributed to unresolved cesium hyperfine splitting.

The linewidth tends to reach a plateau at high concentrations of triglyme (>2—3 mol%). The plateau value is thought to be the linewidth of the cesium-free TCNE anion at this radical concentration. On the other hand, there is no such trend for DMF, and the linewidth seems to decrease continuously. Because DMF is known to solvate not only cations but also anions, the narrower linewidth at high concentrations of DMF may be due to the coordination of DMF molecules to the TCNE anion.

Figure 5 shows the change in the linewidth of the 3.0×10^{-4} M TCNE$^-$Cs$^+$ sample caused by the addition of Bu$_4$NClO$_4$ salt. The linewidth is rapidly reduced at first and then gradually by the addition of Bu$_4$NClO$_4$. It is known that the alkali metal hyperfine splitting in the ESR spectrum of the alkali metal anthracenide–THF system disappears upon the addition of this salt, which has been interpreted in terms of the

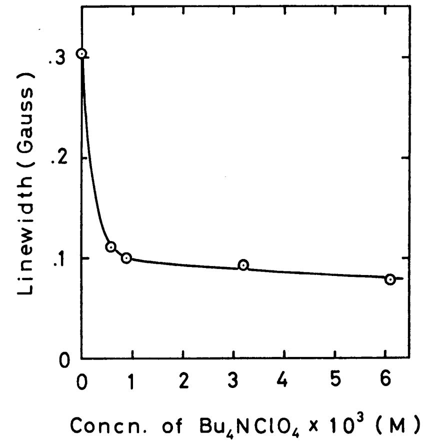

Fig. 5. Change of ESR linewidth ($\bar{M}=0$) of 3.0×10^{-4}M TCNE$^-$Cs$^+$ upon addition of tetra-*n*-butylammonium perchlorate into THF solution at 25 °C.

replacement of counterion.[10] The analogous replacement of the counterion is responsible, in this case, for the narrowing of the linewidth, as;

$$\text{TCNE}^-\text{Cs}^+ + \text{Bu}_4\text{N}^+ \longrightarrow \text{TCNE}^-\text{Bu}_4\text{N}^+ + \text{Cs}^+. \quad (3)$$

Concentration Dependence. Figure 6 shows the relation between the radical concentration and the ESR linewidth of TCNE$^-$Cs$^+$ in three different solvents; THF, DME, and THF containing 2.8 mol% of triglyme. In THF, the linewidth increases rapidly with an increase in the radical concentration up to 3×10^{-4} M and then the rate of increase is lowered. The linewidth in DME and the THF–triglyme mixture is dependent rather slightly on the radical concentration. Especially in the THF–triglyme mixture, only a small dependence was observed. The intercepts of these three curves at zero concentration were coincident with each other within the limits of experimental error.

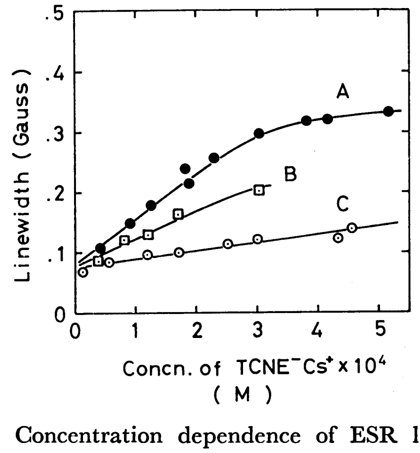

Fig. 6. Concentration dependence of ESR linewidth ($\bar{M}=0$) of TCNE$^-$Cs$^+$ in various solvents at 0 °C: A, THF; B, DME; C, THF–triglyme (2.8 mol%) mixture.

One of the possible mechanisms is the Heisenberg spin exchange between the anion radicals, which results in an increase in the linewidth with an increase in the concentration. It is well established that the effects of the Heisenberg spin exchange on the ESR spectra are identical with those of the diffusion-controlled or nearly diffusion-controlled chemical exchange.[4,11,12] In the slow exchange limit, the second-order rate constant of the spin exchange, k, is expressed for a Lorentzian line as:

$$k = \frac{\sqrt{3}}{2} f_{\bar{M}} |\gamma_e| \Delta H_{\bar{M}}/C, \quad (4)$$

where γ_e is the gyromagnetic ratio; $\Delta H_{\bar{M}}$ is the increase in linewidth due to the spin exchange; C, the concentration of paramagnetic entities in question, and $f_{\bar{M}}$, the statistical factor for the transition of the spectral index number, $\bar{M}$ ($f_0=1.306$ for the TCNE anion).[4] Assuming that the observed ESR broadening is attributable to the Heisenberg spin exchange, the second-order rate constant can be evaluated from Fig. 6 and Eq. (4). Table 1 summarizes the values calculated from the slopes of the lines in Fig. 6. Since the plots for the THF as solvent are not linear over the entire concentration range examined, the rate constant was evaluated from the slope of the line (A) in the low-concentration range (0—2×10^{-4} M).

Table 1. Spin-exchange rate constants k at 0 °C

Solvent	k(M$^{-1}\cdot$s^{-1}) Experimental	Theoretical
THF	1.48×10^{10}	5.0×10^9
DME	8.9×10^9	4.9×10^9
THF–triglyme (2.8 mol%) mixture	2.7×10^9	5.0×10^9

Table 1 also includes the rate constants estimated from the simple Brownian diffusion model, in which the mean time, τ, between successive bimolecular encounters of radicals is represented by the following equation:[4]

$$\tau^{-1} = 4\pi dD\Pi \quad (5)$$

where Π refers the density of the radicals and where D is the diffusion coefficient in a Stokes-Einstein model:

$$D = kT/6\pi a\eta \quad (6)$$

determined by the molecular radius, a, the solvent viscosity, η, and the interaction distance for exchange, d (here it was assumed to be $2a$).[4] For the sake of simplicity, the effect of the charge was neglected in deriving Eq. (5). With the effect of the charge involved, the rate constant would be smaller than those given in Table 1. The viscosity of THF–triglyme was assumed to be the same as that of pure THF.

The k value derived from the observed linewidths in THF is much larger than that to be expected from the diffusion model. This leads to the recognition that the line broadening (Line A in Fig. 6) can not be explained solely by the spin-exchange mechanism. This fact, together with the effects of additives, may indicate that the strong dependence of the linewidth on the radical concentration in THF is, to a large extent, due to the ion-pair formation between the THF anion and the cesium ion. The equilibrium between the ion-pair and the free ion:

$$\text{TCNE}^-\text{Cs}^+ \rightleftharpoons \text{TCNE}^- + \text{Cs}^+, \quad (7)$$

shifts to the left-hand side, and the fraction of the ion-pair increases, when the radical concentration increases, resulting in a broadening of the ESR linewidth. The break of Line (A) at 3×10^{-4} M may be interpreted in terms of the complete ion-pair formation at this concentration.

As is shown in Fig. 6 and Table 1, the linewidth increases more slowly and the observed k is rather close to the expected k in DME than in THF. This is attributable to the high solvation of the cesium ion in DME,[13] which results in the formation of a solvent-separated ion-pair and/or increase in the free-ion fraction and, therefore, less effect of the cesium counterion on the ESR linewidth.

In the THF–triglyme mixture, the observed k is in agreement with the expected one. A more excellent agreement can be obtained if the effect of the charge and the increment in the viscosity arising from the addition of triglyme are taken into account. The activation energy evaluated from the Arrhenius plot of the observed k was found to be 3 kcal·mol^{-1}. This value is comparable with that of the diffusion-controlled chemical reaction in THF. Furthermore, the observed k agrees with that for the potassium tetracyanoethylenide–DME system reported by Freed *et al.*[4] In addition, the hyperfine lines were found to have a Lorentzian shape in this solvent within the limits of experimental error, as is shown in Fig. 2(B). These observations indicate that there is no broadening effect of the cesium ion in the THF–triglyme mixture and that the Heisenberg spin exchange solely determines the ESR linewidth in this system.

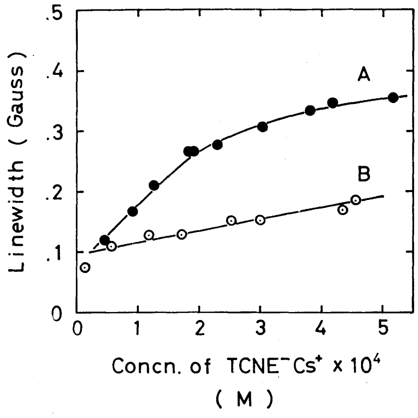

Fig. 7. Concentration dependence of ESR linewidth ($\bar{M}=0$) of TCNE$^-$Cs$^+$ in various solvents at 25 °C: A, THF; B, THF–triglyme (2.8 mol%) mixture.

Figure 7 shows the concentration dependence of the linewidth at 25 °C in THF and THF–triglyme. In comparison with the results obtained at 0 °C (Fig. 6), the break of the curve for the THF shifts toward a lower concentration. This can reasonably be interpreted in terms of the quilibrium (7). Because the dissociation reaction of the ion-pair is exothermic in a liquid, as has been suggested by Denison and Ramsay[14] and Szwarc *et al.*,[13,15] the equilibrium (7) will be shifted to the left-hand side by raising temperature. Therefore, the higher the temperature, the more readily is the ultimate formation of the ion-pair reached. Figure 7 shows the same slope for both THF and THF–triglyme, after the ultimate formation of ion-pair is reached in the former solvent. This suggests that only the Heisenberg spin exchange contributes to the ESR line-broadening in this concentration range in THF, as is the case over the entire concentration range in the THF–triglyme mixture.

Simulation of ESR Spectra. Although the behavior of the spectra indicated ion-pair formation in the TCNE$^-$Cs$^+$–THF system, as has been mentioned above, the hyperfine splitting due to the cesium ion was too small to be resolved experimentally.

Therefore, the hyperfine coupling constant was estimated by comparing the observed spectra with the simulated ones. The simulated spectra were synthesized by means of digital computer (Hokkaido University Computing Center) under the following assumptions: (1) the life-time of the cation-anion pair is long enough compared with the inverse of the cesium hyperfine splitting; (2) each of the 11 lines of the spectrum of the TCNE anion (see Fig. 1) consists of equally-spaced Lorentzian component lines due to $I=7/2$ for the cesium nuclei, and (3) the contribution from the natural abundance of ^{13}C can be ignored. Then, the first-derivative line shape was simulated for an observed line; the $\Delta H_{\mathrm{obs}}/\Delta H_{\mathrm{L}}$ ratio is numerically related to the $a_{\mathrm{Cs}}/\Delta H_{\mathrm{L}}$ ratio. Here, ΔH_{obs} is the observed peak-to-peak linewidth; ΔH_{L}, the peak-to-peak linewidth for the first-derivative of the component Lorentzian line, and a_{Cs}, the hyperfine coupling constant of the cesium ion. This treatment is essentially the same as that used for the ion-pair with a sodium counterion by Jones *et al.*[16] The ΔH_{obs} increases with the increasing $a_{\mathrm{Cs}}/\Delta H_{\mathrm{L}}$ ratio. When the value of $a_{\mathrm{Cs}}/\Delta H_{\mathrm{L}}$ reaches 0.8, the individual component lines begin to become resolved.

If the value of ΔH_{L} is known, a_{Cs} can be derived from the observed linewidth of the TCNE$^-$Cs$^+$–THF system (ΔH_{obs}) at concentrations high enough for all the anions to form ion-pairs with cesium ion. We presumed that the linewidth observed in the THF–triglyme mixture (Line B in Fig. 7) is identical with the ΔH_{L} in THF at the same concentration and temperature, because the anion is free from the counterion in the mixture solvent. Thus, the cesium hyperfine coupling constant, a_{Cs}, in THF at 25 °C is determined to be 40 m Gauss from the Line A in Fig. 7 at concentrations higher than 3×10^{-4} M.

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