Counterion Effect in the Electron-Transfer Reactions between a Tetracyanoethylene Radical Anion and Its Neutral Molecule

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The rates of homogeneous electron-transfer reactions between radical anions and neutral molecules were studied in a variety of tetracyanoethylenide systems in order to obtain information concerning the counterion effect on the electron-transfer reactions. The estimated values of the rate constants had the same order of magnitude at room temperature for all the systems, while the activation energies and the preexponential factors were markedly dependent on the natures of the counterions and the solvents. The obtained results are discussed in terms of the forms and structures of the radical anions.

The mechanism of an electron-transfer reaction between an organic radical anion and its neutral molecule is one of the most interesting problems concerning the relationship between the reactivities and the structures of radical ions in solution. Since Ward and Weissman[1] established the method for measuring the rapid rate of electron-transfer reaction by electron spin resonance (ESR), a number of electron-transfer reaction rates have been measured and it has been found that they are essentially dependent on the forms and structures of radical ions in solutions.[2–10]

In the systems where radical anions and their counterions exist in the form of an ion pair, any electron-transfer reaction is thought to be accompanied by a counterion-transfer through the formation of a sandwich structure at the transition state, as has been suggested by Adam *et al.*[2,11] Therefore, it can reasonably be expected that the natures of the counterions and solvent molecules coordinated to the ions profoundly affect the reaction behavior.

As for the radical ions of aromatic hydrocarbons, many authors[7,9,10] have reported in detail on the transfer rates in a number of different ion pairs with various alkali metal ions in various solvents. However, few studies have been made on the systems of *N*-containing radical anions.[5,8,12,16] In this article we will report the results obtained by the ESR technique on the electron-transfer reactions between the tetracyanoethylene radical anion (TCNE$^-$) and neutral tetracyanoethylene (TCNE) in 1,2-dimethoxyethane (DME) and tetrahydrofuran (THF). The effect of different counterions on the reaction rate was studied; the results will be discussed in terms of the ionic forms and structures of the radical ions in solution.

Experimental

Materials. TCNE of a guaranteed Reagent grade was purified by repeated sublimations *in vacuo*. The DME and THF were fractionally distilled over sodium metal, and the middle portions were stored over calcium hydride. They were rigorously dried with sodium mirror or sodium-potassium alloy *in vacuo* and degassed until 10^{-5} Torr before use. The alkali metal tetracyanoethylenides were prepared by reactions between alkali metals and TCNE dissolved in DME or THF. All the operations were carried out on the vacuum line.

The tetra-*n*-butylammonium salt was generated electrochemically in the solvent, using 0.1 M tetra-*n*-butylammonium perchlorate as the supporting electrolyte. Alternatively, the crystalline tetra-*n*-butylammonium tetracyanoethylenide was prepared from tetra-*n*-butylammonium iodide and TCNE[13] and was dissolved in the solvent before use.

Measurements of Reaction Rates. Each radical anion solution for a rate experiment was sealed *in vacuo* into a ESR sample tube made of Pyrex, and then a known amount of TCNE was added through a break seal. The second-order rate constants were evaluated from the linewidth broadening in the ESR spectra produced by the addition of neutral TCNE. All the experiments were carried out at a slow exchange limit.[1] The ESR measurements were made with a JES-NE-2X spectrometer equipped with 100 kc field modulation. The temperature was kept constant within ±1° with a JES-UCD-2X variable-temperature adaptor on the ESR cavity. The temperatures were determined by means of a copper-constantan thermocouple placed just under the sample tube in the cavity.

Results

The obtained ESR spectrum of a dilute solution of TCNE$^-$ was the same as that reported by Phillips *et al.*[12] No alkali metal splitting was observed in the various tetracyanoethylenide systems studied here. The increase in linewidth produced by the addition of neutral TCNE was linearly dependent on the concentration of added TCNE in the range from 1 to 6×10^{-2} M.

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Table 1. Rate constants and activation energies for the electron-transfer reactions between tetracyanoethylene radical anions and their neutral molecules

Solvents	Counterions	Temp, °C	$k\times10^{-8}$ M^{-1} sec^{-1}	E_a[a] kcal mol^{-1}	Log A[a]
DME					
	Li^+	20	1.8	3.8 ± 0.4	11
	Na^+	20	1.7	6.0 ± 0.6	13
	K^+	20	1.5	7.6 ± 0.6	14
	$\mathrm{Bu_4N}^+$	10	1.3	6.5 ± 0.6	14
THF					
	Li^+	20	1.5	2.2 ± 0.4	10
	Na^+	20	1.3	3.6 ± 0.5	11
	K^+	20	1.6	3.2 ± 0.7	11
	$\mathrm{Bu_4N}^{+}$[b]	20	1.9	4.7 ± 0.6	12

a) Determined from the equation $k=A\exp(-E_a/RT)$.
b) Electrochemically prepared radical anion was used.

The estimated values of the rate constants were of the same order of magnitude at room temperature in all the systems, as is shown in Table 1.

The temperature dependence of the rates was investigated in the temperature range from −30° to 20°C. The plots of $\log k$ *vs.* $1/T$ gave almost straight lines, as is shown in Fig. 1. The apparent activation energies, calculated from the Arrhenius plots, are summarized in Table 1, together with the rate constants and the preexponential factors. The activation energies were markedly dependent on the natures of the counterions and the solvents. In DME it was found that the activation energies for alkali metal salts were in the order of $\mathrm{Li}^+<\mathrm{Na}^+<\mathrm{K}^+$, and that of tetra-*n*-butylammonium salt gave a value intermediate between those of sodium and potassium salts. In THF, the evaluated activation energies were rather small in comparison with DME. The values for the alkali metal salts were found to be close to each other. Especially, almost the same value was obtained for the sodium and potassium salts, within the limits of experimental error. The system of tetra-*n*-butylammonium salt showed the largest activation energy in the solvent.

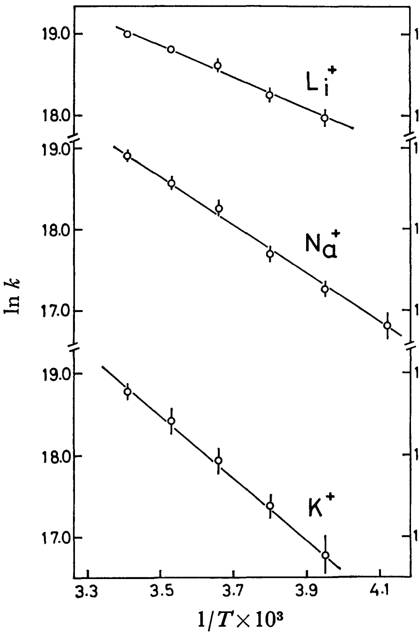

Fig. 1. Temperature dependence of the electron-transfer rates of various alkali metal tetracyanoethylenide systems in DME at the temperature range from −30° to 20°C; upper line: lithium salt; middle line: sodium salt; lower line: potassium salt.

We also studied the cesium tetracyanoethylenide system, but the anomalously large ESR linewidth at higher concentrations of TCNE^- prevented us from obtaining reliable data for this counterion.

Discussion

In order to understand the ionic forms and structures of the radical anions, it is profitable to compare the rate constants and activation energies obtained in this study with those of naphthalenide-naphthalene systems. Hirota *et al.*[9] clearly demonstrated the relationship between the structures of ion pairs and the kinetics of electron-transfer reactions in this system. The rate constants for solvent-separated ion pairs at 25°C were found to be of the order $10^9\mathrm{M}^{-1}\mathrm{sec}^{-1}$, while those for contact ion pairs range from 5×10^6 to $10^8\mathrm{M}^{-1}\mathrm{sec}^{-1}$. The activation energies were 2.9—3.6 kcal/mol for solvent-separated ion pairs and 4—6 kcal for contact ion pairs.

Although it is expected, on the basis of the information described above, that DME-alkali metal tetracyanoethylenide systems involve contact ion-pair structures, no metal splittings and spectral distortions characteristic to contact ion pairs were observed in the ESR spectra of these systems. Consequently, it may be supposed that these systems involve essentially solvent-separated ion pairs. This consideration is in accordance with the fact that small alkali metal ions are well solvated by DME and THF molecules.[14,15] Since normal straight lines are obtained in Arrhenius plots for these systems, we can conclude that essentially only one ionic form is present, at least in this temperature range.[9] This conclusion can be applied to all

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the systems investigated, since similar straight lines are obtained in the remaining systems, also. Accepting the solvent-separated ion-pair model, the order of the activation energies in DME-alkali metal tetracyanoethylenide systems can easily be understood in the following manner. The thickness of the solvation shells around the metal ions is presumed to be in the order of $Li^+>Na^+>K^+$, therefore, the reverse order can be expected in the electrostatic interactions between metal ions and $TCNE^-$.[14] Accordingly, it seems reasonable that the activation energies estimated in this experiment are in the order of $Li^+<Na^+<K^+$, since a higher electrostatic interaction of the ion pair is thought to give a higher activation energy in the electron-transfer reactions.

In THF-alkali metal tetracyanoethylenide systems, the observed values of the rate constants suggest the contact-ion-pair model, whereas the values of the activation energy suggest the solvent-separated ion-pair model. However, the latter structure is more realistic in these systems, because no metal splittings and spectral distortions were observed in the ESR spectra, as in the case of DME. The activation energies for the alkali metal salts are rather small in comparison with those in the DME systems and are close to each other. These results suggest that alkali metal ions paired with $TCNE^-$ are well solvated in THF. In fact, it is reported that sodium ions have a larger solvated radius in THF as compared with DME.[15] A small but not negligible difference in the activation energies between lithium and the other metals can be attributed to the fact that the former ion is more highly solvated than the latter.[14]

In both solvents, tetra-*n*-butylammonium salt gives relatively large activation energies, indicating a strong electrostatic interaction between the alkylammonium ion and the radical anion in spite of its bulkiness. This is because bulky ammonium ions are not coordinated with either DME or THF molecules, as has been suggested by Szwarc *et al.*[15]

The magnitudes of the preexponential factors estimated increase with an increase in the activation energies. This is connected with the fact that nearly the same rate constant is obtained for all the systems. The preexponential factors for the THF systems range from 10^{10} to $10^{12} \mathrm{M}^{-1}\mathrm{sec}^{-1}$. These values are within the limits of those observed in usual liquid-phase reactions. However, rather unexpectedly large preexponential factors are evaluated in all the DME systems except for the lithium salt. It is likely that such large preexponential factors are characteristic of *N*-containing radical anions, because a similar phenomemon has been reported in the potassium 2,2′-bipyridinide system.[16] However, we cannot exclude another possibility that the activation energies are partly contributed by charge-transfer interaction between DME and neutral TCNE. In order to make a conclusive discussion of this problem, more detailed studies should be done in the future.

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