NOTE

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Electron Transfer Between Tetracyanoethylene and Its Anion Radical

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The rate of homogeneous electron transfer reactions between an organic anion radical and its neutral molecule is usually close to the diffusion-controlled limit; however, such fast reactions can be conveniently studied by the electron spin resonance (ESR) technique.[1] It is now well known that many anion radicals can exist in thermodynamically distinct species called contact ion-pairs, solvent separated ion-pairs, and free ions.[2] For a given radical, the relative concentrations of these species depend on the nature of the metal cation, solvent, and temperature. In solvents of high dielectric constants such as dimethylformamide and hexamethylphosphoramide, these radicals are assumed to be in the free ion form[3] whereas in solvents of low dielectric constants such as 1,2-dimethoxyethane or tetrahydrofuran (THF) they are believed to be predominantly contact ion-pairs.[2] Although a detailed knowledge of the structure of such ion-pairs is often difficult to obtain, their reactivities can be readily compared from the rate measurements on the electron transfer reactions. For example, the second-order rate constants for the transfer reactions between naphthalene and its anion radical in THF with potassium and sodium as counter ions differ by at least a factor of three.[4,5] Presumably, as a result of the proximity of the metal cation in the ion-pair, a sandwich-type of collision complex is formed with the metal ion between two naphthalene molecules.[6] Thus we would expect that the size and charge distribution of the metal ion to have an important influence on the rate of transfer.

We report here the rate measurements on the electron transfer reactions between tetracyanoethylene (TCNE) and its anion radical ($TCNE^-$)

$$TCNE^- + TCNE \rightleftharpoons TCNE + TCNE^-$$

in THF with alkali metals as the counter ion and present indirect evidence on the structure of ion-pair in solution. Table 1 summarizes the second-order rate constants together with the corresponding energies of activation. All the rates were measured in the so-called slow-limit.[1] The most surprising result from Table 1 is that all the rate constants are essentially the same. This implies that the reactivity of the TCNE anion radical is independent of the nature of its counter ion and hence the radical is probably in the free ion form. This is not in accordance with the low dielectric constant of THF (7.4)[7] and the fact that the cyanide functional groups are expected to tightly bind the metal ions. Furthermore, the rate constants here are about an order of magnitude smaller than those for aromatic hydrocarbon free ions. However, the results are at least consistent with the fact that no metal splittings are observed except perhaps in the case of cesium where the ESR lines are somewhat distorted at room temperature, suggesting that there might be a small, unresolved hyperfine interaction due to the cesium nucleus. Linear Arrhenius plots were obtained for all the systems from 20 °C to −60 °C. This suggests that over this temperature range there is only one type of radical anion present and its structure (with the metal ion) is insensitive to the change in dielectric constant of the solvent.

TABLE 1. SECOND-ORDER RATE CONSTANTS FOR ELECTRON TRANSFER IN THE $TCNE–TCNE^-$ SYSTEM IN THF AT 25 °C

Metal ion	$k\times 10^{-8}$ (M^{-1} sec^{-1})	Activation energy (kcal mol^{-1})
Li	1.8±0.2	2.8±0.2
Na	1.7±0.2	3.1±0.2
K	1.9±0.3	3.1±0.2
Rb	1.8±0.2	2.8±0.2
Cs	2.0±0.4	2.6±0.5

a) Values obtained over the temperature range of 20 °C to −60 °C.

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