

Kinetics of the Electron Transfer Reaction in Tetracyanoquinodimethan Solutions Studied by Electron Spin Resonance

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Abstract: The electron exchange reaction between TCNQ molecules and TCNQ⁻ radical ions in dilute solutions of acetonitrile, acetone, tetrahydrofuran, and dimethyl sulfoxide has been studied by the esr line-broadening technique. The reaction was found to be of first order with respect to TCNQ and TCNQ⁻, with rate constants at 22° of 3.9×10^9 , 3.2×10^9 , 1.6×10^9 , and $0.83 \times 10^9 M^{-1} \text{ sec}^{-1}$ in the four solvents, respectively. The activation energies were determined in acetonitrile and tetrahydrofuran yielding 2.2 and 1.4 kcal mol⁻¹. The relative rates are roughly inversely proportional to the solvent viscosities and the rates are of the order expected from Smoluchowski's equation for the rate of encounter between molecules. It is concluded that the reaction is diffusion controlled in all the solvents studied.

The synthesis of tetracyanoquinodimethan (TCNQ) and its salts was first reported in 1962 by a group of Du Pont researchers.^{1,2} TCNQ salts, in particular of the complex type $M^{n+}(\text{TCNQ})_{n+m}$, reveal many unusual and interesting physical properties and recently have even been claimed to exhibit superconductivity.³ Paramagnetic studies of complex TCNQ salts show typical triplet type esr spectra, due to exchange interactions between the unpaired electrons.⁴ Dilute solutions of simple salts give esr spectra typical of isolated molecules with sharp hyperfine structure.⁵ In solutions containing both TCNQ and a TCNQ salt there is fast electron exchange between the radical ions which results in line broadening of the esr spectrum. This observation was used² to obtain a rough estimate of $k \simeq 10^9 M^{-1} \text{ sec}^{-1}$ for the rate constant of the reaction



In the present paper we report a kinetic study of this reaction in solutions containing TCNQ and LiTCNQ in a number of organic solvents and over a wide range of temperatures. The study is based on a detailed line-shape analysis of the esr spectrum of the TCNQ ion radical. Similar studies of electron exchange between π radicals in solutions were reported for a number of other aromatic systems.⁶ Analysis of the present results strongly suggests that the exchange process (eq 1) is diffusion controlled in all the solvents studied.

Experimental Section

Material. TCNQ was synthesized from 1,4-cyclohexadione and malonitrile according to the procedure of Acker and Hertler.¹ A few samples were also prepared from commercial material (Eastman Kodak). The compound was purified by sublimation at 200° under reduced pressure. LiTCNQ was prepared by reacting TCNQ and LiI according to the procedure of Melby, *et al.*²

(1) D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, **84**, 3370 (1962).

(2) L. R. Melby, R. J. Harder, W. R. Hertler, J. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3374 (1962).

(3) L. B. Coleman, M. J. Cohen, D. J. Landman, F. G. Yamagaishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).

(4) D. B. Chesnut and P. Arthur, Jr., *J. Chem. Phys.*, **36**, 2969 (1962).

(5) M. T. Jones and W. R. Hertler, *J. Amer. Chem. Soc.*, **86**, 1881 (1964).

(6) M. T. Jones and S. I. Weissman, *J. Amer. Chem. Soc.*, **84**, 4269 (1962).

The solvents were spectroscopic grade and were carefully dried by distillation over hygroscopic materials: acetonitrile, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO), were distilled several times over P₂O₅. Acetone was equilibrated and then distilled from molecular sieves.

Preparation of Solution. The solutions were prepared in a vacuum system in order to prevent decomposition of the TCNQ salt by oxygen or moisture. Small amounts of TCNQ and LiTCNQ were weighed, using a microbalance, into quartz capillaries and placed into a glass bulb equipped with a 2 mm i.d. quartz side arm. The bulb was attached to the vacuum system and evacuated, and then a predetermined amount of solvent was transferred into the bulb. After the TCNQ and LiTCNQ were dissolved, part of the solution was transferred to the side arm and the latter sealed off for esr measurements.

Esr Measurements. Spectra were recorded on a Varian E-12 X-band spectrometer using 100-kHz modulation. Care was taken to work at low microwave power and low modulation amplitudes to avoid line broadening. The temperature of the sample was controlled, using the variable temperature V-257 accessory, and monitored, using a thermocouple placed next to the capillary.

Rate Determination. The mean lifetime, τ , of the TCNQ⁻ radical ion between successive exchanges of the unpaired electron was determined by comparing the experimental results with computer simulated spectra. The line shape function of a magnetic resonance absorption spectrum, $I(\omega, \tau)$ in the presence of an exchange process, characterized by a specific half-time τ is given by

$$I(\omega, \tau) = \text{Re}\{\mathbf{P}\mathbf{A}^{-1}\mathbf{1}\} \quad (2)$$

where \mathbf{P} is a vector with components proportional to the relative intensities, p_i , of the various hyperfine lines in the spectrum, $\mathbf{1}$ is the unit vector, and \mathbf{A} is a matrix whose elements in the present case can be written as follows

$$A_{ii} = i(\omega_i - \omega) - \frac{1}{T_2} - \frac{1}{\tau} (1 - p_i) \quad (3a)$$

$$A_{ij} = \frac{1}{\tau} p_j \quad (\text{for } i \neq j) \quad (3b)$$

In these equations ω_i is the frequency of the i th hyperfine component and $1/T_2$ the natural half-width assumed to be the same for all lines. For the practical computation of the spectrum it is convenient to transform eq 2 into the form⁷

$$I(\omega, \tau) = \text{Re} \sum_{im} \frac{S_{ii}(S^{-1})_{im}}{-i\omega + \lambda_i} \quad (4)$$

where S_{rs} are elements of the matrix \mathbf{S} that diagonalizes \mathbf{A} and $(-i\omega + \lambda_i)$ are the eigenvalues. Finally, the derivative spectrum

(7) R. G. Gordon and R. P. McGinnis, *J. Chem. Phys.*, **49**, 2455 (1968).

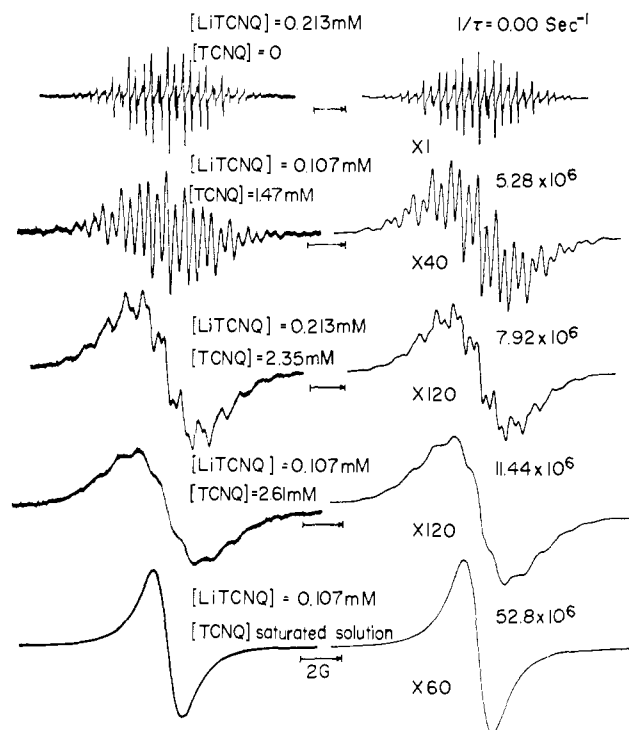


Figure 1. Electron spin resonance spectra of the TCNQ^- radical ion for various values of electron exchange rate. In the right column are simulated spectra calculated with $A_N = 1.00$ G, $A_H = 1.45$ G, $1/T_2 = 0.055$ G, and $1/\tau$ values as indicated in the figure. The relative expansion of the vertical scale is indicated to the left of each spectrum. In the left column are shown experimental spectra for acetonitrile solutions at 22° with the compositions as indicated in the figure.

is obtained by differentiating eq 4 with respect to ω

$$\frac{dI(\omega, \tau)}{d\omega} = \text{Im} \sum_{im} p_i \frac{S_{it}(S^{-1})_{tm}}{(-i\omega + \lambda_i)^2} \quad (5)$$

Examples of calculated spectra are shown in the right column of Figure 1 for various values of τ . In the quantitative comparison of these results with the experimental spectra, certain features, such as the initial broadening, relative peak intensities, and peak separations were used.

A different method of solving eq 2, which does not require matrix diagonalization, was suggested by Norris.⁸

Results and Discussion

The esr spectrum of a solution of LiTCNQ in acetonitrile (without TCNQ) is shown in the upper left-hand side of Figure 1. There are 45 lines and the spectrum can be interpreted in terms of four equivalent nitrogen nuclei ($I_N = 1$) and four equivalent protons ($I_H = 1/2$) with the following hyperfine interaction constants: $A_N = 1.00$ G and $A_H = 1.45$ G. The half-width, $1/T_2$, is 55 mG and probably includes a significant contribution due to the magnetic field inhomogeneity. In addition weak lines due to ^{13}C satellites were also observed at high gain. The results are very similar to those reported previously by Jones and Hertler.⁵ No measurable solvent effect on the magnetic parameters was detected in the four solvents used.

As TCNQ is added to the solution in successively increasing amounts, the spectrum broadens and eventually coalesces into a single line (see left column in Figure 1). Clearly, the addition of TCNQ shortens the

(8) J. R. Norris, Jr., *Chem. Phys. Lett.*, **1**, 333 (1967).

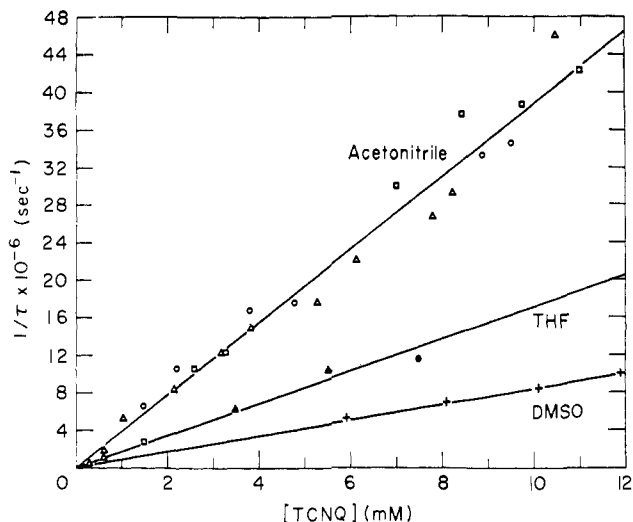


Figure 2. Reciprocal mean lifetime $1/\tau$ for TCNQ^- vs. the concentration of TCNQ in acetonitrile, THF, and DMSO at 22° . The various symbols for a given solvent correspond to different concentrations of LiTCNQ, ranging from 0.052 to 0.237 mM.

electron residence time on the TCNQ^- ions. To obtain values for $1/\tau$, the experimental spectra were compared with computer simulated spectra calculated over a wide range of exchange rates. The calculated spectra that best fit those shown in the left column of Figure 1 are shown in the right column of the figure.

The most extensive kinetic measurements were made in acetonitrile. In this solvent, measurements were made with LiTCNQ concentrations between 0.052 and 0.237 mM and TCNQ in concentrations ranging up to 11.2 mM. The results for $1/\tau$ at 22° are plotted vs. the concentration of TCNQ in Figure 2. Similar measurements, though not as extensive, were performed with other solvents. The results are also shown in Figure 2 (except for acetone, since the experimental points in this solvent interfere with those of acetonitrile).

The linear dependence of $1/\tau$ on the TCNQ concentration and its independence of the LiTCNQ concentration is quite evident and is consistent with eq 1 if we assume complete dissociation of the LiTCNQ salts into its constituting ions. This is a very plausible assumption for these dilute solutions. It is further supported by the lack of lithium hyperfine structure in the spectra, which would be expected if ion pairing took place. In fact, no line broadening was observed at all in the LiTCNQ solutions (not containing TCNQ) over the whole temperature range (-50 to 30°) studied. The results of Figure 2 thus fit the rate law

$$\frac{1}{\tau} = \frac{1}{[\text{TCNQ}^-]} \frac{d[\text{TCNQ}^-]}{dt} = k[\text{TCNQ}] \quad (6)$$

as expected from eq 1. Rate constants calculated from the slopes of Figure 2 are summarized in Table I.

Table I. Kinetic Parameters for the Electron Exchange Reaction (eq 1) in the Various Solvents Studied

Solvent	$k(22^\circ), 10^9$ $M^{-1} \text{sec}^{-1}$	$\Delta E, \text{kcal}$ mol^{-1}	$\eta^{-1}(22^\circ), \text{P}^{-1}$
Acetonitrile	3.9	2.2	290
Acetone	3.2		310
THF	1.6	1.4	180
DMSO	0.83		50

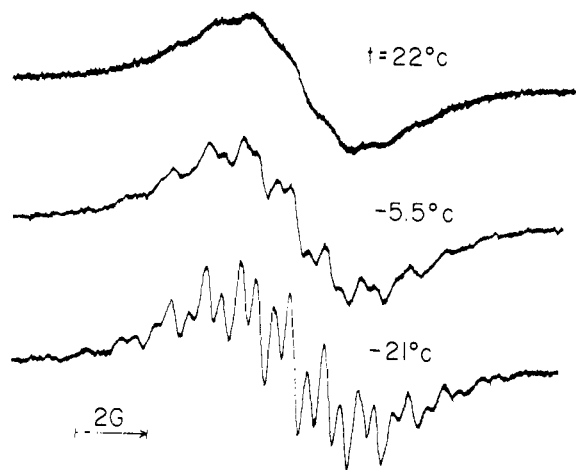


Figure 3. Experimental esr spectra of an acetonitrile solution containing 3.21 mM TCNQ and 0.213 mM LiTCNQ at various temperatures.

The temperature dependence of the reaction was studied in acetonitrile and THF in a number of solutions containing both TCNQ and LiTCNQ. Examples of spectra are shown in Figure 3 and some representative Arrhenius plots are shown in Figure 4. The calculated activation energies are given in Table I.

The results strongly suggest that the electron transfer reaction in the solvents studied is diffusion controlled. Referring to Table I it may be seen that the rate constants (at room temperature) in the various solutions are very nearly proportional to the inverse viscosities (η^{-1}) of the corresponding solvents as would be expected for a diffusion-controlled reaction. Even more instructive is the comparison of the actual magnitudes of the k 's with values calculated on the assumption of a diffusion-controlled reaction. The Smoluchowski equation gives for the encounter rate⁹

$$k_s = \frac{4\pi(D_{\text{TCNQ}} + D_{\text{LiTCNQ}})aN}{1000} \quad (7)$$

where the D 's are diffusion coefficients, a is the reaction

(9) H. Eyring and E. M. Eyring, "Modern Chemical Kinetics," Reinhold, New York, N. Y., 1963, Chapter 6.

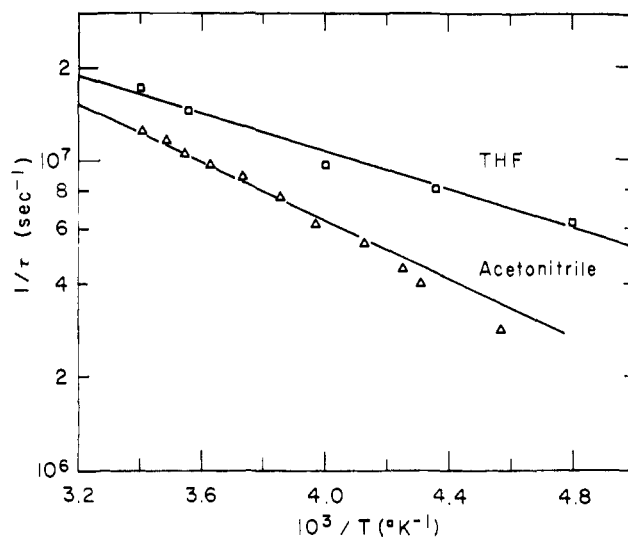


Figure 4. Arrhenius plots for the electron exchange reactions in THF and acetonitrile solutions. Both solutions contain 0.213 mM LiTCNQ. The concentration of TCNQ is 13.3 mM for the THF solution and 3.21 mM for acetonitrile.

distance, and N is Avogadro's number. Taking for both molecules $D = 2.5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ (the diffusion coefficient in acetonitrile of naphthalene¹⁰ which is similar in size to that of TCNQ) and $a = 5 \text{ \AA}$ (estimated from molecular models), one obtains $k_s = 19 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. In order to compare this value with the observed rate constant it must be multiplied by (i) a factor $1/2$ which is the probability that an encounter results in an electron transfer and (ii) a steric factor. This latter parameter is difficult to estimate since it depends on the shape of the encounter complex which is not known. From the experimental result this factor is calculated to be 0.4, certainly within the right order of magnitude. The approximate nature of this calculation precludes an accurate determination of the steric factor, but the good agreement with Smoluchowski's equation indicates quite clearly that the reaction is diffusion controlled.

(10) T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Amer. Chem. Soc.*, **87**, 121 (1965).