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Formation Constants of Radical-Ion Pairs and Charge-Transfer Complexes of Tetracyanoethylene with Group 8 Metallocenes

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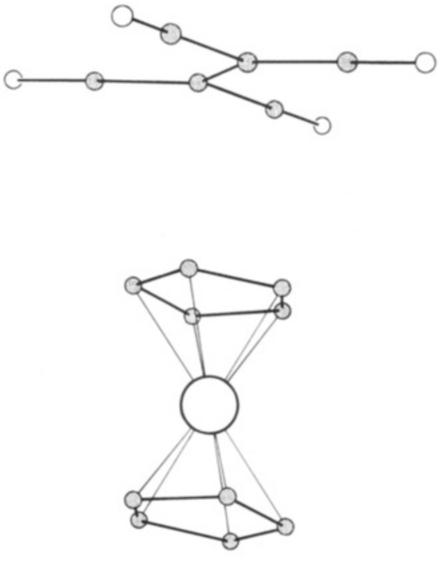
Formation constants K_i of radical-ion pairs and K_c of charge-transfer (CT) complexes of tetracyanoethylene (**T**) with ferrocene and ruthenocene and some of their alkyl derivatives in dichloromethane (DCM) are presented. The spectra of some alkylmetallocene/**T**/DCM systems simultaneously exhibit CT bands for the feeble π-covalent complex and bands for the radical-ion pairs which follow electron transfer. K_i and K_c are calculated using a modified form of the Benesi−Hildebrand equation which includes the parameter $\varrho = [\mathbf{D}^+\mathbf{T}^-]/[\mathbf{D} - \mathbf{T}]$. Correlation of $\lambda_{\max}$ values for CT bands in the spectra of metallocene/**T**/DCM systems with ionization energies derived from the photoelectron spectra of the metallocenes indicates that the bands are due to electronic transitions from the e_{2g} and e_{1u} orbitals of the metallocene to the LUMO of the complex. Values of λ_{CT} and K_i tend to increase with alkyl substitution on the metallocene ring. Ruthenocene with IE = 7.45 eV forms only the π-covalent complex with **T** in DCM, whereas decamethylferrocene with an IE of 5.88 eV forms only radical-ion pairs. The spectra of DCM solutions consisting of **T** with alkylmetallocenes having intermediate IE values exhibit bands for both the π-complex and radical-ion pair simultaneously.

Introduction

Renewed interest in the reactions of metallocenes with strong π-electron acceptors such as tetracyanoethylene (**T**) has been prompted by the work of Miller et al.[1] who showed that the crystalline radical-ion salt, $[\mathrm{Fe(C_5Me_5)_2}^{\bullet+}][\mathrm{C_2(CN)_4}^{\bullet-}]$, exhibits ferromagnetism. The first studies of such systems were conducted by Webster et al.[2] who reported that the reaction of ferrocene (**F**) and tetracyanoethylene produced a green salt with the formula $\mathbf{F}^+\mathbf{T}^-$. Rosenblum et al.[3] reported that a solution of **F** and **T** in cyclohexane contains a weak π-complex, **F**−**T** (structure 1)



that exhibits CT bands in the near-infrared region. In this study we show that solutions in some Group 8 metallocenes with **T** in dichloromethane (DCM) contain appreciable quantities of both the neutral complex and the radical-ion pair in equilibrium.

The interaction of an electron donor molecule, **D**, with the electron acceptor tetracyanoethylene, **T**, in a weakly polar, nonionizing solvent, such as DCM, often leads to the formation of an electron donor−acceptor (EDA) complex **D**−**T** in rapid equilibrium with the free molecules (process 1). In the presence of radiation of appropriate energy, an electron is promoted from the HOMO to the LUMO of the complex (process 2) leading to the reversible formation of a radical-ion pair, $\mathbf{D}^{\bullet+}\mathbf{T}^{\bullet-}$.

$$\mathbf{D} + \mathbf{T} \underset{1}{\rightleftarrows} \mathbf{D}{-}\mathbf{T} \overset{h\nu}{\underset{2}{\rightleftarrows}} \mathbf{D}^+\mathbf{T}^- \underset{3}{\rightleftarrows} \mathbf{D}^+ + \mathbf{T}^-$$

Although the radiation absorbed in process 2 is observed as a prominent charge-transfer (CT) band, very few **D**/**T**/DCM systems show evidence for the presence of $\mathbf{T}^-$ in spite of its high molar absorbance ($\epsilon_{\max}$ 7100 L/mol-cm) and a spectrum with distinctive fine-structure from 350 to 500 nm[2]. Liptay et al.[4] characterized systems with *N,N,N′,N′*-tetramethyl-1,4-phenylenediamine and **T** in various solvents. They reported that the tendency toward ion pair formation increases with the dielectric constant of the solvent, being nil for ethyl ether (4.33), intermediate for tetrahydrofuran (7.5), and complete for acetonitrile (37.5). They further showed that the equilibrium constants for the dissociation of the short-lived ion pair to the solvated ions, process 3, are extremely small ($K_d \approx 10^{-5}$) in solvents with intermediate dielectric constants. Therefore, an EDA system in a solvent such as DCM is essentially described by three equilibrium expressions.

$$\mathbf{D} + \mathbf{T} \rightleftarrows \mathbf{D}{-}\mathbf{T} \qquad K_c = [\mathbf{D}{-}\mathbf{T}]/[\mathbf{D}][\mathbf{T}] \qquad (1)$$

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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$$\mathbf{D{-}T} \rightleftarrows \mathbf{D^+T^-} \qquad \varrho = [\mathbf{D^+T^-}]/[\mathbf{D{-}T}] \qquad (2)$$

$$\mathbf{D} + \mathbf{T} \rightleftarrows \mathbf{D^+T^-} \qquad K_i = \varrho K_c = [\mathbf{D^+T^-}]/[\mathbf{D}][\mathbf{T}] \qquad (3)$$

We place EDA systems in DCM into one of three categories depending on the appearance of their spectra.

Type A. In this class only CT bands are observed in the spectrum of the system, indicating that the radical-ion pair is a short-lived species in such low concentration that the spectra of the ions are not observed. Even though K_c seldom exceeds a values of 2 L/mol, $K_c \gg K_i$. Kochi et al.[5] have directly verified the presence of transient radical ions in several type−A systems by irradiating the EDA complex with a laser beam tuned to the CT wavelength and observing the ion spectra by means of time-resolved picosecond spectroscopy.

Type B. In this class the band systems of $\mathbf{T}^-$ and $\mathbf{D}^+$ alone appear in the spectra and the CT bands are not observed at all. Here the EDA complex is a transitory intermediate which transforms spontaneously and irreversibly into the more stable radical-ion pair and $K_c \ll K_i$.

Type AB. These systems exhibit both CT and radical-ion bands simultaneously. Here the molar concentrations of the complex and ion pair are of the same order of magnitude and $K_i \approx K_c$.

In a series of EDA systems containing a common acceptor and solvent, the outcome of a CT interaction depends primarily on the vertical ionization energy, I_D of the donor. For donor/**T**/DCM systems the absorbance maximum of the CT band, λ_{CT} (nm), is related to the corresponding I_D (eV), by the empirical equation[6]

$$\lambda_{CT} = 1240/(0.81 I_D - 4.28) \qquad (4)$$

where I_D values are taken from the photoelectron spectra of the donor molecules. Equation 4 is used to specify the donor orbitals which give rise to the bands observed in the CT spectra.

The formation constants, K_C, for type A systems are usually calculated with the familiar Benesi−Hildebrand equation or its Scott variant.[7]

$$C_D C_T/A = 1/\epsilon K_c + (1/\epsilon) C_D \qquad (5)$$

This equation is valid only when the assumptions that $C_D \gg C_T \gg [\mathbf{D{-}T}] \gg [\mathbf{D^+T^-}]$ are satisfied. (Note: C_D and C_T are interchanged when $C_T \gg C_D$.) Equation 5 is a linear expression of the type

$$y = b + mx$$

where K_C and ϵ are evaluated by setting the slope m equal to $1/\epsilon$ and the intercept b equal to $1/\epsilon K_c$.

However, for type AB systems $[\mathbf{D{-}T}]$ and $[\mathbf{D^+T^-}]$ are of the same order of magnitude; consequently, eq 5 is not valid for these systems. The equilibrium concentrations of donor and acceptor are given by eqs 6 and 7.

$$[\mathbf{D}] = C_D - [\mathbf{D{-}T}] - [\mathbf{D^+T^-}] \qquad (6)$$

$$[\mathbf{T}] = C_T - [\mathbf{D{-}T}] - [\mathbf{D^+T^-}] \qquad (7)$$

A suitable expression is derived by substituting eqs 6 and 7 into eq 1 to yield eq 8.

$$K_c = [\mathbf{D{-}T}]/[C_D - [\mathbf{D{-}T}] - [\mathbf{D^+T^-}]][C_T - [\mathbf{D{-}T}] - [\mathbf{D^+T^-}]] \qquad (8)$$

Reorganization of eq 8 yields a nine-term expression which reduces to the linear eq 9 on using the assumptions $C_D \gg C_T \gg [[\mathbf{D{-}T}] + [\mathbf{D^+T^-}]]$ to omit negligible terms.

$$C_D C_T/A = 1/\epsilon K_c + [(1 + \varrho)/\epsilon] C_D \qquad (9)$$

Here $\varrho = [\mathbf{D^+T^-}]/[\mathbf{DT}]$, the slope $m = (1 + \varrho)/\epsilon$, and the intercept $b = 1/\epsilon K_c$. ϵ and K_c can be evaluated only if ϱ is known. A procedure for determining ϱ is proposed in a later section. Note that eq 9 reduces to eq 5 as ϱ tends toward zero and that K_c decreases with increasing ϱ. Eq 9 is valid for EDA systems in which the value of ϱ is in the range 0−2.

Our specific objectives in this investigation are to determine (1) values of K_c, K_i, and ϱ and spectral characteristics of complexes of Group 8 metallocenes with **T**, (2) the effects of varying both metals and ring substituents on the CT energies of these complexes, (3) the specific donor orbitals which are involved in complex formation, and (4) the correlation between the ionization energies of the metallocenes with their mode of interaction with **T**.

Experimental Section

Reagents. Solvents and reagents are the purest grades available from the following chemical suppliers: Aldrich, Fisher, and Strem. Purities were determined using a Hewlett-Packard HP5980SA capillary column gas chromatograph. **T** was recrystallized twice from chlorobenzene and sublimed twice in vacuo. Spectrograde DCM was used without further purification.

Spectral Analysis and Association Constants. Experimental procedures, data collection and processing, and judgmental criteria are described in a previous publication.[8] Spectra of complexes were recorded with either a Beckman ACTA-CIII or UV−vis−NIR Shimadzu UV3101PC. In systems where air-sensitive metallocenes and complexes were studied, stock solutions were prepared in an atmosphere of dry nitrogen and the spectra of selected mixtures were run immediately after mixing to ensure that equilibria were not disturbed by adventitious reactions. Acquisition of reliable formation constants and spectral characteristics was regarded as evidence that the systems were not being affected by air or light during the spectral runs.

Results and Discussion

The characteristics of **T** complexes of metallocenes are summarized in Table 1. Donors are coded for reference in the text according to the alphanumeric characters shown in column 1. The CT spectra of the simple complexes usually exhibit one or two broad unstructured bands; their λ_{max} values are designated λ_1 and λ_2 and inserted in columns 3 and 4. However, solutions of these complexes may contain unreacted donor as well as appreciable amounts of the radical-ions which exhibit their own characteristic spectra (Table 2). Absorbance maxima for radical-ions, λ_{ion}, appear in column 5. Values of band height at half-width, $\Delta\nu_{1/2}$, for λ_1 appear in column 6. Ratios of the molarities of stock solutions of

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Table 1. Complexes of Tetracyanoethylene with Group 8 Metallocenes in Dichloromethane at 22 °C

code	donor compd	λ_1, nm	λ_2, nm	λ_{ion}, nm	$\Delta\nu_4$, cm^{-1}	ϵ_1, L/mol−cm	K_c, L/mol	K_i, L/mol	ϱ	C_D/C_T	% *s*
F	ferrocene	1090	*410*	425	6000	840 ± 130	0.35 ± 0.05	0.01	0.04	1/10	7−14
	ferrocene[a,b]	1075, 900				465	2.5				
	ferrocene[a,c]	1000					1.95				
MF	methylferrocene[a,b]	1125, 975									
EF	ethylferrocene	1173	*450*	430	5700	290 ± 60	1.32 ± 0.28	0.36	0.27	1/8	5−10
BF	*n*-butylferrocene	1210	<*430*	425	6000	680 ± 40	0.52 ± 0.06	0.37	0.71	1/8	13−26
PF	phenylferrocene[a,b]	950									
11MF	1,1′-dimethylferrocene	1280	<*430*	425		830 ± 80	0.54 ± 0.06	0.44	0.81	1/4	12−24
	1,1′-dimethylferrocene[a,b]	1225, 1050									
	1,1′-dimethylferrocene[a,c]	1025					3.33				
DMF	decamethylferrocene			775, 427							
R	ruthenocene	715	425		6000	215 ± 19	0.96 ± 0.09			10	7−15
DMR	decamethylruthenocene[d]	>1000	702	425	5200	2300 ± 500	1.78 ± 0.38	0.45	0.26	10	5−13

[a] Cyclohexane solvent. [b] Reference 3. [c] Adman, E.; Rosenblum, M.; Sullivan, S.; Margulis, T. N. *J. Am. Chem. Soc.* **1967**, *89*, 4540−4542. [d] System reacts irreversibly.

Table 2. Spectral Characteristics of Selected Molecules and Ions in the UV−vis Region

species	solvent	λ_{max}, nm	ϵ_{max}, L/mol-cm	$\Delta\nu_{1/2}$, cm^{-1}	ref
F	DCM	442	101	5100	*a*
F$^+$	aq	619	360		*b*
EF	DCM	440	124	5300	*a*
BF	DCM	440	116	4400	*a*
BF$^+$	aq	625	330		*c*
11MF	DCM	439	92	5000	*a*
11MF$^+$	DCM	660			*a*
11MF$^+$	*d*	650	332		*e*
DMF	DCM	420	129	5000	*a*
DMF$^+$	DCM	775	579		*a*
R	*f*	323	200		*c*
T$^-$	MeCN	425	7100		*a*

[a] This work. [b] Reference 10. [c] Reference 13. [d] Isopentane. [e] P-ladziewicz, J. R. Ph.D. Dissertation, Iowa State University, 1971. [f] 1:1 v/v water−ethanol.

the donor, C_D, and of **T**, C_T, are given in column 11. The stock solutions are normally mixed in ratios ranging from 9:1 to 4:6 in order to produce a series of solutions where one reagent is present in large excess over the other. The saturation fraction, *s*, of a complex is the sum of the equilibrium molar concentrations of the complex and radical-ion pair divided by the concentration of the limiting reactant. The range of % *s* for the various solutions is given in column 10.

1. Ferrocenes. The ferrocenes have strong absorbance bands in the 350−500 nm region which overlap the **T**$^-$ band and the λ_2 band of the CT complexes. Consequently, evaluation of ϵ, K_c, and K_i involve data from two sets of solutions, one having excess donor and the other excess **T**.

a. Ferrocene. The spectral scan of a solution of 0.2250 M **F** and 0.0100 M **T** in DCM from 300 to 1600 nm (Figure 1) consists of a broad band with λ_1 1090 nm ($\Delta\nu_{1/2}$ 6000 cm^{-1}), a very weak absorbance at λ 620 nm, and a sharp cutoff which runs off-scale at 550 nm. Analysis of the 1090-nm band of a series of eight solutions, set 1, using eq 5 yields values of slope m = 0.001 24 and intercept b = 0.003 45 for the complex **F−T**.

Details of the intense band at λ < 550 nm (Figure 2) are brought out by scanning set 2, prepared by mixing 0.007 80 M **F** with 0.080 00 M **T**. The spectrum of the 1:1 mixture consists of a symmetrical band with λ_{max} 425 nm ($\Delta\nu_{1/2}$ 5700 cm^{-1}) which exhibits several barely perceptible irregularities coinciding with the peaks observed in the fine structure of the **T**$^-$ spectrum[2] at 427, 437, 447, and 460 nm. Digital subtraction of the spectrum of 0.0039 M **F** (λ_{max} 442 nm, $\Delta\nu_{1/2}$ 5100 cm^{-1}) from the overall band yields a residual band (λ_{max} 410 nm, $\Delta\nu_{1/2}$ 6400 cm^{-1}) which appears as the λ_2 band of **F−T** showing a slight irregularity due to a trace of **T**$^-$. Analysis of the solutions of set 2 using eq 5 yields a looping curve rather than a straight line. This pronounced deviation from linearity is probably due to the presence of small amounts of **T**$^-$ in the solution. Analysis of the spectra of set 1 following the procedure described for **EF/T/DCM** (vide infra) yields mean values of 0.015 L/mol (SD 0.001) for K_i and 0.35 L/mol (SD 0.01) for K_c. The calculated value of ϱ is 0.043. For the 1:1 mixture of stock solutions, [$\mathbf{F^+T^-}$] = 0.2 × 10^{-5} M and [**F−T**] = 5.4 × 10^{-5} M. From eq 9, $\epsilon_1 = (1 + 0.043)/0.00124$ = 840 L/mol-cm. The ratio of absorbance values for the λ_2 and λ_1 bands, 0.293/0.046 = 6.4, gives the ratio of molar absorbancies ϵ_2/ϵ_1. Therefore ϵ_2 = 5400 L/mol-cm.

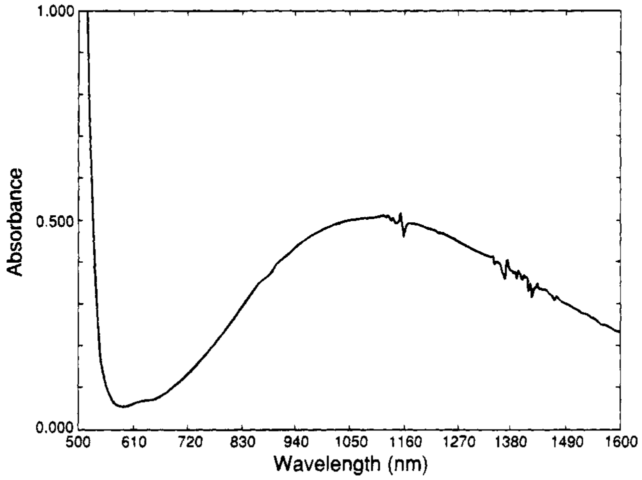


Figure 1. Vis−NIR spectrum of ferrocene−TCNE.

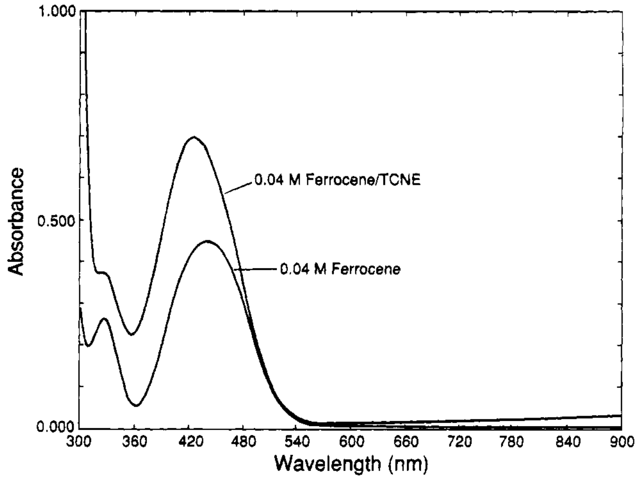


Figure 2. UV−vis spectra of ferrocene and ferrocene−TCNE.

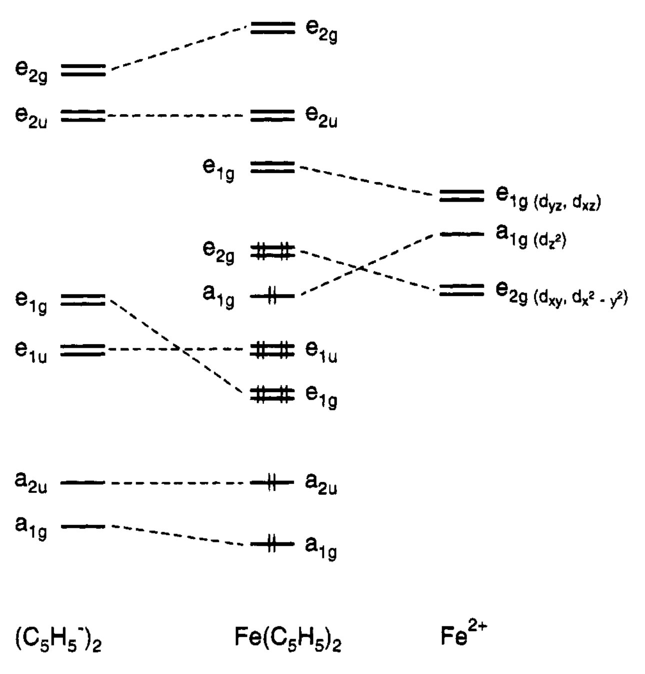
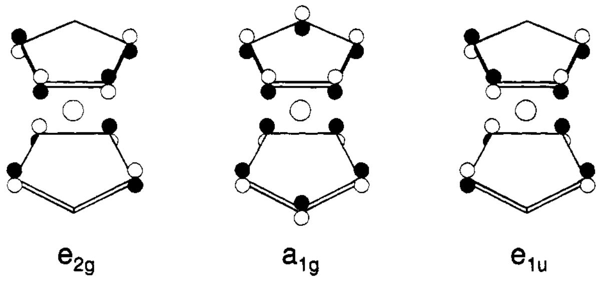


Figure 3. Molecular orbital diagram for ferrocene in the D_{5d} configuration.

In order to confirm the assignment of the bands in the optical spectrum we refer to the paper of Evans et al.[9] on the PE spectrum of **F**. They report ionization values of I_1 6.88, I_2 7.23, and I_3 8.72 eV for **F** which are assigned to the removal of electrons from the three HOMO's π_1 (e_{2g}), π_2 (a_{1g}), and π_3 (e_{1u}) (Figure 3 and strcuture 2).



Orbitals π_1 and π_3 with nodes perpendicular to the planes of the Cp rings have the appropriate symmetry for overlap with the π^* orbital of **T**. π_2 having no nodes perpendicular to the rings and being essentially localized on the Fe atom cannot interact effectively with **T**. Consequently, only two CT bands are expected to appear in the spectrum of the **F/T/DCM** system.

When the I_D values of **F** are substituted into eq 4 they yield λ_{CT} values of 959, 787, and 446 nm for **F−T**. Therefore, the spectrum should exhibit one CT band at about 900−1050 nm and another at about 400−500 nm; no band is anticipated in the vicinity of 800 nm. The first and third of the predicted λ_{CT} values correlate well with the observed bands at 1090 and 410 nm, whereas no band corresponding to the second value appears at all. We conclude that the 1090-nm band in Figure 1 is a CT absorbance which arises from an electron transfer from the HOMO of the complex corresponding to the π_1 (e_{2g}) orbital of **F** to the LUMO of **F−T**; the 410-nm band in Figure 2 is due in part to a similar CT interaction involving a $\pi^* \leftarrow \pi_3(e_{1u})$ transition in **F−T**.

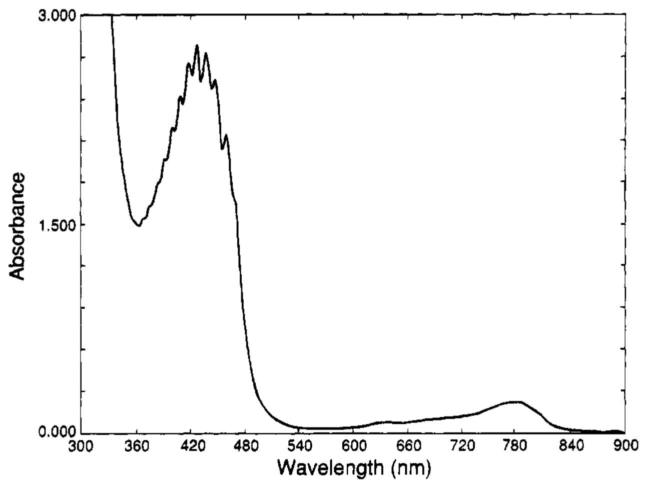


Figure 4. Spectrum of decamethylferricenium$^+$TCNE$^-$.

The minor features of the spectra, namely the weak absorbance at 620 nm in Figure 1 and the irregularities at 400−460 nm in Figure 2, are attributed to trace amounts of $\mathbf{F^+T^-}$ in solution. The 620-nm absorbance coincides with the 619 nm band (ϵ 360 L/mol-cm) for $\mathbf{F^+}$ reported by Wilkinson et al.[10] The undulations correspond to an attribute of $\mathbf{T^-}$ reported by Webster et al.[2] who found that the spectrum of a solution of $\mathrm{K^+}\mathbf{T^-}$ in MeCN contains 12 vibrational maxima in the region 360−470 nm (λ_{max} 425 and 435 nm, ϵ 7100 L/mol-cm) at intervals of 530 cm^{-1} (see Figure 4).

In summary, the **F/T/DCM** system exhibits CT bands at 1090 and 410 nm; the 425 nm band in the spectra of set 2 is a combination of absorbancies due primarily to **F**, plus small amounts of **F−T** and $\mathbf{T^-}$; the weak band at 620 nm is due to a small quantity of $\mathbf{F^+}$. The small value of ϱ indicates that the **F/T/DCM** system is a borderline type A/type AB case.

b. Decamethylferrocene. The spectrum of **DMF** in DCM consists of a smooth band with λ_{max} 420 nm, $\Delta\nu_{1/2}$ 5020 cm^{-1}, and ϵ 129 L/mol-cm. The spectrum of a solution of 2.4×10^{-4} M **DMF** and **T** in DCM (Figure 4) consists of two highly structured groups of bands. The group at λ 600−850 nm with λ_{max} 775 nm is identical to that of $\mathbf{DMF^+}$ as described by Gale et al.[11] A plot of A_{775} versus $C_{\mathbf{DMF}}$ for a series of solutions in which **DMF** is the limiting reagent yields a straight line (correlation coefficient $r = 1.000$) with slope ϵ 579 L/mol-cm showing that the **DMF** is quantitatively ionized.

The group at 350−500 nm is identical to the distinctive spectrum of $\mathbf{T^-}$. A plot of A_{427} versus $C_{\mathbf{T}}$ for a series of solutions where **T** is the limiting reagent is also linear ($r = 0.999$) with slope ϵ 7160 L/mol-cm. This indicates that the 427 nm band is due to $\mathbf{T^-}$ and that **T** is also quantitatively ionized. In a study of a series of **DMF/T/DCM** solutions of varying concentration, the ratio of absorbancies, A_{427}/A_{775}, is constant, confirming the presence of $\mathbf{DMF^+}$ and $\mathbf{T^-}$ in equimolar amounts as the radical-ion pair.

Cauletti et al.[12] reported I_D values of 5.88, 6.28, 7.31, and 8.08 eV for **DMF** which correspond to λ_{CT} values of 2570, 1540, 756, and 546 nm for **DMF−T**. Since no CT bands whatsoever are observed in the region 300−2500

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(9) Evans, S.; Green, M. L. H.; Jewitt, B.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1847−1865.

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(12) Cauletti, C.; Green, J. C.; Kelly, R. M.; Powell, P.; Van Tilborg, J. *J. Electron Spectrosc.* **1980**, *19*, 327−353.

nm for **DMF/T**/DCM systems we conclude that the spectral bands are due solely to $\mathbf{DMF^+T^-}$ in solution and that **DMF** and **T** form a type B system in DCM.

c. Ethylferrocene. The spectrum of the **EF/T**/DCM system exhibits both a smooth CT band in the NIR region as well as a second band in the UV−vis region with the fine structure of $\mathbf{T^-}$ indicating that this system belongs to the type AB category. In order to characterize this system it is necessary to examine the regions from 900 to 1200 nm and 400 to 500 nm where λ_1 and λ_2 are expected. The analysis of this system is complicated by the fact that high concentrations of reagents are required to display the CT bands adequately. The intense band of **EF** in the region 300−500 nm (λ_{max} 439 nm, ϵ_{440} 124 L/mol-cm, and $\Delta\nu_{1/2}$ 5270 cm^{-1}) precludes the complete analysis of the spectra for systems containing excess **EF**. On the other hand, the low solubility of **T** (~0.09 M in DCM) limits the study of systems with excess **T** because of the poor delineation of the CT bands. Consequently, we used two sets of solutions, set 1 with excess **EF** to analyze the NIR region and set 2 with excess **T** to analyze the UV-Vis region.

The spectra of set 1, prepared by mixing accurately measured amounts of stock solutions of 0.1772 M **EF** and 0.0240 M **T**, exhibit a CT band with λ_1 1173 nm which appears in the region expected for a $\pi^* \leftarrow \pi_1$ transition. Analysis of this band using eq 9 yields values for the slope $m = 0.004\,42$ and intercept $b = 0.002\,63$. Since this is a type-AB system the calculation of ϵ and K_c requires knowledge of ϱ which is determined in conjunction with data from set 2.

The spectra of set 2 solutions, prepared by mixing 0.0100 M **EF** and 0.0787 M **T**, feature a band at 430 nm which exhibits the wavy appearance of the $\mathbf{T^-}$ spectrum overlaying the band of **EF**, **T**, $\mathbf{T^-}$, and λ_2 of **EF−T**. The total absorbance of any of these solutions at 430 nm in a 1.00 cm cell is given by eq 10.

$$A = \epsilon_{\mathbf{EF}}[\mathbf{EF}] + \epsilon_{\mathbf{T}}[\mathbf{T}] + \epsilon_2[\mathbf{EF{-}T}] + (\epsilon_{\mathbf{ET^+}} + \epsilon_{\mathbf{T^-}})[\mathbf{EF^+T^-}] \quad (10)$$

There are three terms in eq 10 which cannot be measured independently from spectra taken at 400−500 nm, namely ϵ_2, [**EF−T**], and $[\mathbf{EF^+T^-}]$. A sample calculation using data from the 1:1 mixture of the stock solutions at λ_{430} illustrates the method used to determine these unknown terms. We assume the following: (1) $[[\mathbf{EF{-}T}] + [\mathbf{EF^+T^-}]] < 10^{-1}C_{\mathbf{EF}}$. I.e., the concentrations of the products are negligible compared to the initial amounts of reactants in the mixture. It follows, in the first approximation, that $[\mathbf{EF}] \approx C_{\mathbf{EF}} = 0.0050$ M and $[\mathbf{T}] \approx C_{\mathbf{T}} = 0.0393$ M. (2) $\varrho \approx 1$; therefore, $[\mathbf{EF{-}T}] \approx [\mathbf{EF^+T^-}]$, and from eq 9, $K_c \approx 0.8$ L/mol and $\epsilon_1 \approx 450$ L/mol-cm. (3) $\epsilon_2 \approx \epsilon_1 \approx 450$ L/mol-cm for **EF−T**. Therefore, the absorbance of **EF−T** at 430 nm is about 0.05. (4) The radical-ion pair $\mathbf{EF^+T^-}$ exhibits the individual spectra of its constituent ions. At 430 nm, $\epsilon_{\mathbf{T^-}}$ is 7160 L/mol-cm and $\epsilon_{\mathbf{EF^+}}$ is nil.

It follows from eqs 3 and 10 that

$$\begin{aligned} K_i &= [\mathbf{EF^+T^-}]/[\mathbf{EF}][\mathbf{T}] = A_{\mathbf{T^-}}/\epsilon_{\mathbf{T^-}}C_{\mathbf{EF}}C_{\mathbf{T}} \\ &= [A - \epsilon_{\mathbf{EF}}C_{\mathbf{EF}} - \epsilon_{\mathbf{T}}C_{\mathbf{T}} - \epsilon_2[\mathbf{EF{-}T}]]/\epsilon_{\mathbf{T^-}}C_{\mathbf{EF}}C_{\mathbf{T}} \end{aligned} \quad (11)$$

Substituting numerical values into eq 11 we obtain

$$\begin{aligned} K_i &= 1.047 - (111)(0.0050) - (0.1)(0.0393) - 0.05/[(7160)(0.0050)(0.0393)] \\ &= 0.31 \text{ L/mol} \end{aligned}$$

Recalculation of K_i by successive approximations (see Appendix) yields a series of values which converge to 0.35 L/mol after three iterations. Corresponding values of $\varrho = 0.25$, $K_c = 1.33$ L/mol, and $\epsilon_1 = 267$ L/mol-cm are obtained using eqs 2, 3, and 8. Additional calculations show that

$$[\mathbf{EF^+T^-}] = A_{\mathbf{T^-}}/\epsilon_{\mathbf{T^-}}b = 0.45/[(7160)(1.000)] = 6.3 \times 10^{-5} \text{ mol/L}$$

and

$$[\mathbf{EF{-}T}] = [\mathbf{EF^+T^-}]/\varrho = (6.3 \times 10^{-5})/0.26 = 24.2 \times 10^{-5} \text{ mol/L}$$

Since the sum of these concentrations is less than $10^{-1}C_{\mathbf{EF}}$, assumption (1) is verified.

The validity of the procedure is supported by the consistency of the results for the remaining seven mixtures of set 2 which yield mean values of $K_i = 0.36$ L/mol (SD 0.01), $K_c = 1.32$ L/mol (SD 0.01), $\varrho = 0.36/1.32$ or 0.27, and $\epsilon_1 = (1 + \varrho)/m = 1.27/0.00442 = 290$ L/mol-cm. Finally, the ratio of CT absorbancies at λ_1 and λ_2, 0.065/0.076, yields the values $\epsilon_2/\epsilon_1 = 0.86$ and $\epsilon_2 = 250$ L/mol-cm.

The λ_1 value of **EF-T** at 1173 nm is 87 nm higher than that of **F−T** (1090 nm) indicating that the ethyl substituent increases the energy of the π_1 orbital through induction. This effect increases λ_1, K_i, and K_c relative to **F−T** and results in the formation of easily perceptible amounts of $\mathbf{EF^+T^-}$. Although the value of λ_2 cannot be determined accurately it is probably in the range 410−430 nm.

d. *n*-Butylferrocene. The **BF/T**/DCM system bears a strong resemblance to the **EF/T**/DCM system and is treated in the same manner. The spectra of a series of solutions, set 1, prepared by mixing stock solutions of 0.4500 M **BF** and 0.0200 M **T**, exhibit a major band with λ_1 1210 and a very weak band at 656 nm. A strong band runs off-scale at 500 nm. The 1210-nm band is a typical CT absorbance and appears in the region expected for a $\pi^* \leftarrow \pi_1$ transition. Analysis of this band yields values of slope $m = 0.002\,52$ and intercept $b = 0.002\,86$. The 656 nm band indicates the presence of $\mathbf{BF^+}$ since this value corresponds to λ_{max} 625 nm (ϵ 330 L/mol-cm) reported by Sohn et al.[13] for aqueous $\mathbf{BF^+}\mathrm{PF_6}^-$.

Solution set 2, prepared by mixing stock solutions of 0.0100 M **BF** and 0.0784 M **T**, exhibits a 428 nm band displaying the wavy structure characteristic of $\mathbf{T^-}$ superimposed on the band of **BF** at 440 nm (ϵ 116 L/mol-cm, $\Delta\nu_{1/2}$ 4400 cm^{-1}). A CT band is also expected for this region. Therefore, the 428 nm band is a composite of three overlapping bands consisting of the **BF** absorbance band, a CT band arising from a $\pi^* \leftarrow \pi_3$ transition in **BF−T**, and the fine-structured $\mathbf{T^-}$ band. Analysis of the spectra of these eight solutions following the procedure described above yields mean values of 0.37 L/mol (SD 0.02) for K_i and 0.52 L/mol (SD 0.02) for K_c. The

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[13] Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603−3612.

calculated value of ϱ is 0.71. For the 1:1 mixture of stock solutions, [**BF**$^+$**T**$^-$] = 3.2×10^{-5} M and [**BF−T**] = 4.8×10^{-5} M.

e. 1,1′-Dimethylferrocene. The spectrum of a freshly prepared 1:1 mixture of 0.3397 M **11MF** and 0.0140 M **T** exhibits a broad band at λ_1 1280 nm, a weak band at 660 nm, and a strong band which runs off-scale at 500 nm. On standing for several minutes a secondary reaction occurs which is manifested by a decrease in the 1280-nm band and the appearance of a new band at 900 nm and a steep shoulder at 700 nm. Scott analysis of the 1280 nm band for a series of fresh mixtures, set 1, prepared from these stock solutions yields a linear plot (r = 0.990) with slope m = 0.002 19 and intercept b = 0.002 23.

The spectra of a series of six mixtures, set 2, prepared from stock solutions of 0.001 92 M **11MF** and 0.079 34 M **T** each exhibit a highly structured band with λ_{max} 428 nm and $\Delta\nu_{1/2}$ 5800 cm^{-1}. The pronounced fine structure in the 428 nm band indicates that this system contains substantial amounts of **T**$^-$. Calculations using the iteration procedure yield mean values of K_i 0.44 L/mol (SD 0.06), K_c 0.54 L/mol-cm (SD 0.06), and ϱ 0.81 with the assumption that $\epsilon_2/\epsilon_1 = 12$. The use of lower values of this ratio in the iteration procedure did not generate stable values of K_c.

Evans[9] reported I_D values of 6.72, 7.06, and 8.53 eV for **11MF** which correspond to λ_{CT} values of 1066, 862, and 472 nm for **11MF−T** indicating that the 1280 nm band arises from a $\pi^* \leftarrow \pi_1$ transition. The weak 660 nm band corresponds to the band for **11MF**$^+$ reported by Prins[14] at 645 nm with ϵ 290 L/mol-cm.

2. Ruthenocenes and Osmocenes. The ruthenocenes and osmocenes are pale-yellow or colorless making most of the visible region free of spectral interferences from the reactants in these studies.

a. Ruthenocene. A solution of DCM which is 0.0402 M in both **R** and **T** has an olive green color; its spectrum exhibits a smooth flat band λ_1 725 nm and a second smooth band λ_2 435 nm abutting the sharp cuttoff for **R** at 400 nm. In order to bring the λ_1 band into greater prominence we prepared a 1:1 mixture of 0.2006 M **R** and 0.0206 M **T** in DCM. The spectrum of this system exhibits a smooth symmetrical band with λ_1 725 nm ($\Delta\nu_{1/2}$ 6000 cm^{-1}); analysis of the 725-nm band using eq 5 yields ϵ 215 L/mol-cm and K_c 0.96 L/mol for **R−T**.

Sostero et al.[15] prepared **R−T** by photolysis of mixtures of **R** and **T** in cyclohexane. They reported λ_{CT} values of 791 and 710 nm for **R−T** (ϵ_{max} 400 L/mol-cm) which they attributed to transitions from the a_1 and e_2 orbitals of **R**. Evans et al.[9] assigned the ionization bands at 7.45, *7.63 sh*, and 8.53 eV in the PE spectrum of **R** to the $\pi_1(e_{2g})$, $\pi_2(a_{1g})$, and $\pi_3(e_{1u})$ orbitals. These values correspond to λ_{CT} values of 707, *653*, and 476 nm. By analogy with our results on the ferrocenes we expect CT bands at λ 710 and 475 nm arising from the π_1 and π_3 orbitals but no CT band near 650 nm. The narrow bandwidth of λ_1 indicates that it arises from a single CT transition at 710 nm. The predicted wavelengths agree well with our observations. The absence of fine structure in the spectra precludes the presence of **R**$^+$**T**$^-$ in detectable quantities in DCM systems indicating that this is a type-A system.

b. Decamethylruthenocene. DMR and **T** react slowly and irreversibly in DCM at 22 °C. Fresh mixtures of 0.0082 M **DMR** and 0.0799 M **T** however, exhibit a smooth CT band (Figure 5) with λ_1 702 ($\Delta\nu_{1/2}$ 5200 cm^{-1}), a highly-structured band with λ_{max} 428 nm, and a broad, flat absorbance at $\lambda > 1000$ nm. Analysis of the 702 nm band yields values of slope $m = 5.49 \times 10^{-4}$ and intercept $b = 2.45 \times 10^{-4}$ indicating that it is a CT band for **DMR-T**.

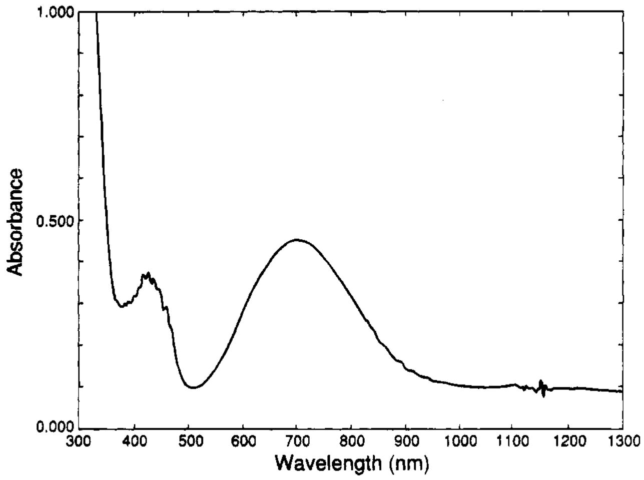

Figure 5. Spectrum of decamethylruthenocene/TCNE.

The 428-nm band strongly resembles the spectrum of **T**$^-$ indicating the presence of **DMR**$^+$**T**$^-$. Since this band has a lower absorbance than that of the 702-nm band it appears that a second CT band of **DMR-T** does not contribute significantly to it. This means that $\epsilon_2/\epsilon_1 < 0.1$ and that the 428-nm band is essentially a pure **T**$^-$ band. Therefore, the determination of K_i, K_c, and ϱ requires the analysis of the spectra of only one set of solutions. When values of K_i 0.45 L/mol (SD 0.03), K_c 1.78 L/mol (SD 0.04), and ϱ 0.25 are obtained using the iteration procedure described above.

O'Hare et al.[16] reported I_D values of *6.74*, *6.74*, 7.34, and 8.95 eV for the $\pi_1(e_{2g})$, $\pi_2(a_{1g})$, $\pi_3(e_{1u})$, and $\pi_4(e_{1g})$ orbitals of **DMR** which correspond to λ_{CT} values of 1050, 745, and 418 nm. All of these calculated values correspond to the absorbance bands found in the spectrum.

c. Osmocene and Decamethylosmocene. Both **O** and **DMO** react rapidly and irreversibly with **T** in DCM to yield gray-blue and brown solids, respectively. No evidence of CT interactions were observed in these systems.

Summary and Conclusions

The spectra of DCM solutions of **T** with some ferrocenes and ruthenocenes exhibit spectra containing both CT bands for the EDA complex and radical-ion pair bands. A modification of the Benesi−Hildebrand equation, incorporating the ion-pair/complex ratio ϱ and an approximation procedure, are used to calculate the equilibrium constants and molar absorbancies. Specific conclusions follow.

(1) Spectra of the **F/T/DCM** and **R/T/DCM** systems exhibit prominent CT bands due to transitions from the $\pi_1(e_{2g})$ and $\pi_3(e_{1u})$ orbitals to the π^* orbital in their EDA complexes. **R/T/DCM** is a type-A system, whereas **F/T/DCM** is a borderline type-A/type-AB system since evidence for trace amounts of **F**$^+$**T**$^-$ is found in its spectra.

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[14] Prins, R. J. *J. Chem. Soc., Chem. Commun.* **1970**, 280–281.

[15] Sostero, S.; Duatti, A.; Zanella, P.; Traverso, O. *J. Organomet. Chem.* **1978**, *157*, 437–443.

[16] O'Hare, D.; Green, J. C.; Chadwick, T. P.; Miller, J. S. *Organometallics* **1988**, *7*, 1335–1342.

(2) Solutions of **EF**, **BF**, **11MF**, and **DMR** with **T** in DCM form type-AB systems; both ϱ and λ_1 increase with the degree of alkyl substitution on the metallocene ring. The **DMR**–**T** system is relatively simple to analyze because there are no adventitious absorbancies in 400–500 nm region that overlap the $\mathbf{T}^-$ bands.

(3) The **DMF/T/DCM** system exhibits only the spectra of the radical ions indicating that it belongs to the type-B category.

(4) The degree of radical-ion pair formation in the metallocene/T/DCM systems is strongly linked with the I_D value of the metallocene. When $I_D > 7$ eV, $\varrho < 0.01$; when $I_D < 6.5$ eV, $\varrho > 1$. When I_D is 6.5–7.0 eV, ϱ has a value of 0.01–1.

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Appendix. Evaluation of Formation Constants for Type-AB Donor/TCNE Systems by the Method of Successive Approximations

Spectra of type-AB systems are distinguished by the appearance of two CT bands, λ_1 (900–1300 nm) and λ_2 (350–500 nm), and of the distinctive highly structured bands of the radical-ion pairs. The spectra are often complicated by the presence of a strong band of the metallocene itself. A preliminary visual inspection of the spectra is necessary to estimate two critical parameters, (1) the relative concentrations of the complex and ion-pair used to establish a provisional value of ϱ and (2) the relative absorbancies of λ_1 and λ_2 used to establish a provisional value of ϵ_2/ϵ_1 or q. The value of ϱ can be estimated from the depth of the indentations on the band at 350–500 nm; deep equally-spaced indentations signify $\varrho > 1$, whereas slight or imperceptible indentations signify $\varrho < 0.1$. The value of q is gauged by comparing the absorbance values of the NIR and UV–vis bands; if the NIR band is substantially higher, then q is probably less than 1 and vice versa. When these initial approximations are reliable the iteration procedure described below yields invariable and reasonable values of equilibrium constants and molar absorbancies. If persistently variable or unrealistic values are generated by the iteration procedure the parameter q may be adjusted accordingly.

One of two situations may arise in type-AB EDA systems. In the first instance the maxima of the major band systems fall in a range of 0.1–1.0 absorbance units. Data from region 1, which usually contains only the λ_1 band, are used to determine the intercept b and slope m of the linear equation

$$C_\mathbf{D}C_\mathbf{T}/A_1 = 1/\epsilon_1 K_{c1} + [(1+\varrho)/\epsilon_1]C_\mathbf{D} \qquad \text{(A1)}$$

and to evaluate ϵ_1 and K_{c1}. The numerical subscripts in eq A1 indicate the values relate to the λ_1 band. Data from region 2 (300–500 nm) are used to evaluate ϵ_2, K_{i2}, and ϱ by means of eq A2

$$K_{i2} = [A_2 - \epsilon_\mathbf{D}C_\mathbf{D} - \epsilon_\mathbf{T}C_\mathbf{T} - \epsilon_2[\mathbf{D{-}T}]]/\epsilon_{\mathbf{T}^-}C_\mathbf{D}C_\mathbf{T} \qquad \text{(A2)}$$

in combination with the approximation method described below.

In the second instance the maxima for CT and radical-ion pair spectra do not appear in the appropriate absorbance range in same plot, and the donor band interferes strongly in region 2. Then it is necessary to prepare two sets of solutions, set 1 with excess **D** (depicting region 1) and set 2 with excess **T** (depicting region 2). Data from set 1 are used to determine ϵ_1 and K_{c1}; data from set 2 are used to determine ϵ_2, ϱ, and K_{i2} as before.

Proceed with the calculations using the following iteration procedure.

1. After a careful examination of the spectrum, enter the experimental data and constants for the appropriate wavelength near λ_2 and the estimated parameters into a computer or calculator. These include the invariant values for $C_\mathbf{D}$, $C_\mathbf{T}$, A_2, $\epsilon_\mathbf{D}$, $\epsilon_\mathbf{T}$, $\epsilon_{\mathbf{T}^-}$, and (m/b), as well as the parameters q and ϱ.
2. Determine the absorbance of the radical-ion, $A_{\mathbf{T}^-}$, assuming that $[\mathbf{D}] \approx C_\mathbf{D}$ and $[\mathbf{T}] \approx C_\mathbf{T}$. Assign a provisional value to $A_\mathbf{DT}$.

$$A_{\mathbf{T}^-} = A_2 - \epsilon_\mathbf{D}C_\mathbf{D} - \epsilon_\mathbf{T}C_\mathbf{T} - A_\mathbf{DT}$$

3. $[\mathbf{D}^+\mathbf{T}^-] = A_{\mathbf{T}^-}/\epsilon_{\mathbf{T}^-}$
4. $K_{i2} = [\mathbf{D}^+\mathbf{T}^-]/C_\mathbf{D}C_\mathbf{T}$
5. $K_{c1} = (m/b)/(1+\varrho)$
6. Calculate a defined approximation of ϱ.

$$\varrho' = K_{i2}/K_{c1}$$

The values of singly-primed terms from this point forward are second approximations.

7. $[\mathbf{DT}] = [\mathbf{D}^+\mathbf{T}^-]/\varrho'$
8. Calculate K_{c2} using approximate values of $[\mathbf{D}]$ and $[\mathbf{T}]$.

$$\begin{aligned} K_{c2} &= [\mathbf{DT}]/[\mathbf{D}][\mathbf{T}] \\ &= [\mathbf{DT}]/[C_\mathbf{D} - [\mathbf{DT}] - [\mathbf{D}^+\mathbf{T}^-]][C_\mathbf{T} - [\mathbf{DT}] - [\mathbf{D}^+\mathbf{T}^-]] \end{aligned}$$

9. Since there is only one value of K_c for this system, set K_{c2} equal to K_{c1} and calculate a provisional value of ϵ_2.

$$\epsilon_2 = q\epsilon_1 = q/bK_{c2}$$

10. $A_\mathbf{DT}' = \epsilon_2[\mathbf{DT}]$
11. Calculate $A_{\mathbf{T}^-}$ using approximate equilibrium concentrations.

$$A_{\mathbf{T}^-}' = A_2 - \epsilon_\mathbf{D}[\mathbf{D}] - \epsilon_\mathbf{T}[\mathbf{T}] - A_\mathbf{DT}'$$

12. $[\mathbf{D}^+\mathbf{T}^-]' = A_{\mathbf{T}^-}'/\epsilon_{\mathbf{T}^-}$
13. $K_{i2}' = [\mathbf{D}^+\mathbf{T}^-]'/[\mathbf{D}][\mathbf{T}]$
14. At this point iterate steps 5–13 several times until ϱ approaches a constant value. If ϱ persistently increases with each iteraction, increase the value of q and begin again. If ϱ approaches an unreasonably small value, decrease q and resume the calculations.