Attempted Isolation of the Reaction Intermediate. As we have already mentioned, h^5-$C_5H_5Fe(CO)_2CH_3$ and $Re(CO)_5$-CH_3 rapidly react with SO_2 to give the O-sulfinates which only slowly isomerize to the corresponding S-sulfinates. Therefore, these compounds presented themselves as ideal candidates for isolation and characterization of the intermediate of the insertion reaction. Unfortunately, all attempts at obtaining the O-sulfinates which are free of SO_2 have led to the isolation of the S-sulfinates instead. Removal of the last traces of SO_2 causes rapid linkage isomerization, even at $-30°$. The nature of this stabilization of the O-sulfinates by sulfur dioxide is not clear to us at present.

Conclusions

Sulfur dioxide reacts with transition metal alkyls ([M]-R) of the types h^5-$C_5H_5Fe(CO)_2R$, h^5-$C_5H_5Mo(CO)_3R$, and $M(CO)_5R$ (M = Mn, Re) either in the liquid or in solution to yield SO_2-containing species which differ from the isolable S-sulfinates ([M]-$S(O)_2R$). The ^1H nmr and infrared spectroscopic data, coupled with electrical conductivity measurements, identify these intermediates as either the O-sulfinato ([M]-$OS(O)R$) or the S-alkoxysulfenato ([M]-$S(O)OR$) complexes. The first formulation is supported by the relatively facile replacement of RSO_2^- in the intermediate with I^- to afford the carbonyl iodide ([M]-I). Moreover, the direction of polarization of the M-R and S-O bonds renders much more probable the formation of M-OS(O)R, known to occur with a wide variety of the main-group alkyls,[33] than of the alternative M-S(O)OR. The O-sulfinato intermediates undergo rearrangement in the course of attempts at their isolation to yield the stable S-bonded isomers. This behavior accords with the expected greater stability of the S-sulfinato than the O-sulfinato ligand when present in conjunction with a soft (or class "b") transition metal.

(33) W. Kitching and C. W. Fong, *Organometal. Chem. Rev.*, *Sect. A*, **5**, 281 (1970).

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# Kinetics of the Oxidation of Bis(π-cyclopentadienyldicarbonyliron) by Ru(bipy)₂Cl₂⁺ and by [(π-C₅H₅)Fe(CO)]₄⁺

JAMES N. BRADDOCK and THOMAS J. MEYER*

In acetonitrile bis(π-cyclopentadienyldicarbonyliron) is oxidized by $Ru(bipy)_2Cl_2^+$ (bipy is 2,2'-bipyridine) and by the tetrahedral, metal–metal bonded cluster ion $[(\pi$-$C_5H_5)Fe(CO)]_4^+$ according to the stoichiometry $[(\pi$-$C_5H_5)Fe(CO)_2]_2 + 2Ox + 2CH_3CN \rightarrow 2(\pi$-$C_5H_5)Fe(CO)_2NCCH_3^+ + 2Red$, where Ox is $Ru(bipy)_2Cl_2^+$ or $[(\pi$-$C_5H_5)Fe(CO)]_4^+$ and Red is $Ru(bipy)_2Cl_2$ or $[(\pi$-$C_5H_5)Fe(CO)]_4$. For both reactions the observed rate law is $-d[(\pi$-$C_5H_5)_2Fe_2(CO)_4]/dt = k[(\pi$-$C_5H_5)_2Fe_2(CO)_4][Ox]$. The kinetics of the two reactions were measured using a stopped-flow spectrometer. For $Ru(bipy)_2Cl_2^+$ as the oxidant $k(24°) = (4.24 \pm 0.12) \times 10^4\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = 6.2 \pm 0.5$ kcal/mol, and $\Delta S^{\ddagger}(25°) = -16.6 \pm 1.5$ eu and for $[(\pi$-$C_5H_5)Fe(CO)]_4^+$ as the oxidant $k(25°) = (6.12 \pm 0.21) \times 10^4\ M^{-1}\ sec^{-1}$, $\Delta H^{\ddagger} = 1.8 \pm 0.2$ kcal/mol, and $\Delta S^{\ddagger}(25°) = -31 \pm 3$ eu. The rate constants for both reactions were found to be somewhat sensitive to added electrolyte $((n$-$C_4H_9)_4N^+PF_6^-)$. The kinetic information is discussed in terms of the likely detailed mechanisms of electron transfer and also in terms of the known stereochemical properties of bis(π-cyclopentadienyldicarbonyliron) in solution.
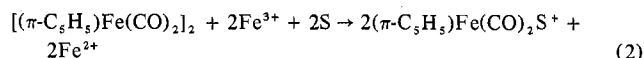
Introduction

A common reaction of structurally simple compounds which contain strong metal–metal bonds is oxidative cleavage with halogens,[1] *e.g.*

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + Br_2 \xrightarrow{CH_2Cl_2} 2(\pi\text{-}C_5H_5)Fe(CO)_2Br \quad (1)$$
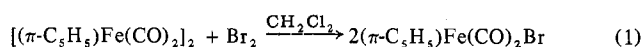
The oxidation–reduction character of such reactions can be seen more clearly by using a metal ion oxidant[2]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2Fe^{3+} + 2S \rightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+ + 2Fe^{2+} \quad (2)$$

$$(S = \text{acetone or acetonitrile})$$

or by carrying out the net oxidation of the metal–metal bond electrochemically[3]

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2S \xrightarrow{-2e^-} 2(\pi\text{-}C_5H_5)Fe(CO)_2S^+ \quad (3)$$

Some rate and mechanistic studies have been reported for reactions in which metal–metal bonds are oxidized by
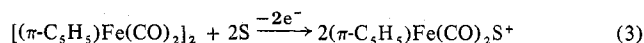
(1) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965.

(2) E. C. Johnson, T. J. Meyer, and N. Winterton, *Inorg. Chem.*, **10**, 1673 (1971).

(3) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, **10**, 1025 (1971).

halogens.[4,5] Also, Espenson[6] and his coworkers have reported electron-transfer rate studies on metal-metal bonded complexes where, in contrast to the $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ system, the metal-metal bonded framework remains intact in more than one molecular oxidation state.

As part of a wider interest in the oxidation-reduction properties of metal-metal bonds,[2,3,7,8] we have begun a series of rate studies on reactions in which metal-metal bonds are oxidized. The redox couples $[(\pi\text{-}C_5H_5)Fe\text{-}(CO)]_4^{+,0}$ [8] and $Ru(bipy)_2Cl_2^{+,0}$ (bipy is 2,2'-bipyridine) appear to be especially suited for such a study because they undergo facile, reversible electron transfer in solution, free of complications arising from secondary reactions following the electron-transfer act. We report here the stoichiometries and the kinetics of the oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ to $(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)^+$ in acetonitrile by $Ru(bipy)_2Cl_2^+$ and by the tetrahedral metal-metal bonded cluster oxidant $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$.

Experimental Section

Materials. Commercial grade acetonitrile (99 mol % pure) was purified by two distillations under nitrogen from sodium carbonate-potassium permanganate and dried over activated alumina. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was prepared by standard techniques,[9] recrystallized three times from hot ethanol-water mixtures, and dried in a vacuum oven for 10 hr at 70°. Bis(*π*-cyclopentadienyldicarbonyliron) was purchased from Alfa Inorganics and purified under nitrogen by successive recrystallizations from benzene-petroleum ether and dichloromethane-pentane. $[(\pi\text{-}C_5H_5)Fe(CO)]_4PF_6$ was prepared as described by Ferguson[8] and purified by recrystallization from a 1:1 (by volume) acetone-carbon tetrachloride solution by slow evaporation under nitrogen. $[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]PF_6$ was prepared and purified as described by Ferguson.[3] $Ru(bipy)_2Cl_2\cdot2H_2O$ was prepared and purified as described by Dwyer[10] and converted into the anhydrous form, $Ru(bipy)_2Cl_2$, by recrystallization from dichloromethane-anhydrous ether followed by careful drying in a stream of dry nitrogen gas.

Preparations. $[Ru(bipy)_2(NCCH_3)Cl]PF_6$ was prepared by refluxing $Ru(bipy)_2Cl_2$ in acetonitrile for ~5 hr. The acetonitrile solution was evaporated to dryness and the residue dissolved in the minimum volume of water. A saturated aqueous solution of ammonium hexafluorophosphate was added and the red-brown solid was collected and recrystallized from dichloromethane-anhydrous ether. $[Ru(bipy)_2Cl_2]PF_6$ (1.0 g) was prepared by passing a stream of chlorine gas through a suspension of $Ru(bipy)_2Cl_2$ in H_2O (50 ml) for 25 min, forming the red solid $[Ru(bipy)_2Cl_2]Cl$. The red solid was collected on a frit and dissolved in 30 ml of hot H_2O. Upon addition of a saturated solution of ammonium hexafluorophosphate to this solution, a red-orange precipitate formed which was recrystallized from acetone-ether giving $[Ru(bipy)_2Cl_2]PF_6$ in 71% yield. *Anal.* Calcd for $RuC_{20}H_{16}N_4Cl_2PF_6$: C, 38.17; H, 2.56; N, 8.90. Found: C, 38.36; H, 2.60; N, 8.90.

Measurements. Ultraviolet-visible spectra were obtained using Cary Model 14, Guilford Model 240, and Unicam Model SP800B spectrophotometers. Infrared spectra were measured in acetonitrile solutions on a Perkin-Elmer 421 spectrophotometer. Quantitative measurements of concentration were carried out using carbonyl bands in the infrared by measuring total peak areas. Calibration curves relating peak areas to concentrations were established for the ν_{CO} bands for a given compound. The concentration of that compound in a given experiment was then calculated by

measuring the area(s) under its ν_{CO} band(s) using the previously determined calibration curve(s).

The stopped-flow spectrometer used for the kinetic studies was similar to that described by Sutin[11] but had certain modifications. The drive system used had all glass stopcocks with Apiezon 100 stopcock grease and silicone O rings (Parker Seal Co.) in both the stop syringe and the 8-jet Teflon mixing chamber. The reservoirs for the reactant solutions were equipped with a gas dispersion tube for degassing purposes, lined with aluminum foil for protection from light, surrounded by a water jacket for constant-temperature control, and positioned above the instrument giving a gravity assist for filling the drive syringes. The solution reservoirs, drive syringes, mixing chamber, and observation tube were thermostated by a model 2074A Forma Scientific refrigerated constant-temperature bath designed to control temperature to ±0.02°. Maximum optical density changes occurred at 344 nm for the disappearance of $(\pi\text{-}C_5H_5)Fe_2(CO)_4$ or, when $Ru(bipy)_2Cl_2^+$ was used as the oxidant, at 553 nm for the appearance of $Ru(bipy)_2Cl_2$.

Both reactions studied, the oxidation of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ by both $Ru(bipy)_2Cl_2$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$, were found to be first order in oxidant and first order in $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$. As shown below the stoichiometry of the reactions is

$$(\pi\text{-}C_5H_5)_2Fe_2(CO)_4 + 2Ox + 2CH_3CN \rightarrow$$
$$2[(\pi\text{-}C_5H_5)Fe(CO)_2(NCCH_3)]^+ + 2Red$$
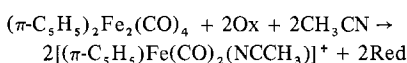
where Ox represents the oxidized form of the redox couple $\{Ru(bipy)_2Cl_2^+$ or $[(\pi\text{-}C_5H_5)Fe(CO)_4)]^+\}$ and Red the reduced form $\{Ru(bipy)_2Cl_2$ or $[(\pi\text{-}C_5H_5)Fe(CO)]_4\}$. The reactions were carried out under second-order conditions. Plots of log $[((b/a) - 2)\cdot(A_m/A) + 2]$ *vs.* time were linear for >90% of the reactions. Calculated rate constants for both reactions were found to be independent of the wavelength used in the kinetic runs.

The stoichiometries of the two reactions were measured spectrophotometrically. A series of experiments was carried out in which $Ru(bipy)_2Cl_2^+$ in the concentration range 10×10^{-4} to 1×10^{-4} *M* was allowed to react with $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ with the ratio of $[Ru(bipy)_2Cl_2^+]/[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4] = 4.0\text{-}0.25$. The $Ru(bipy)_2Cl_2$ produced was determined spectrophotometrically at 553 nm. At this wavelength contributions to the measured absorbance from the other species present were negligible (see Table I). The ratio of $Ru(bipy)_2Cl_2$ produced to $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ initially present in the solution was found to be 2.0 ± 0.1 (average of six determinations). No evidence was found in the spectrophotometric experiments for the presence of $Ru(bipy)_2(NCCH_3)Cl^+$.

The amount of $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ formed was determined quantitatively by measuring the areas of ν_{CO} bands at 2080 and 2035 cm^{-1} and comparing them with previously established calibration curves. In a series of experiments in which the oxidant $\{Ru(bipy)_2Cl_2^+$ or $[(\pi\text{-}C_5H_5Fe(CO)]_4^+\}$ was treated with excess iron dimer, the ratio of $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ produced to oxidant added was found to be 1.85 ± 0.15 (average of five determinations) for $Ru(bipy)_2Cl_2^+$ and 1.83 ± 0.16 (average of five determinations) for $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$. The deviation of these values from the expected value of 2 is partly due to the inherent inaccuracy of the infrared technique. In reactions where $Ru(bipy)_2Cl_2^+$ was the oxidant, no evidence was found in the infrared that $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ was also a product of the reaction.

Results

For the two oxidants $Ru(bipy)_2Cl_2^+$ (bipy is 2,2'-bipyridine) and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$, reduction potentials, measured electrochemically as $E_{1/2}$ values in acetonitrile, are as follows

$$Ru(bipy)_2Cl_2^+ + e^- \rightarrow Ru(bipy)_2Cl_2 \quad \epsilon = 0.296 \ V^{12}$$

$$[(\pi\text{-}C_5H_5)Fe(CO)]_4^+ + e^- \rightarrow [(\pi\text{-}C_5H_5)Fe(CO)]_4 \quad \epsilon = 0.32 \ V^8$$

The values reported are *vs.* the saturated sodium chloride calomel electrode at 22 ± 2° using tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. Since both couples are electrochemically reversible, the $E_{1/2}$ data give a direct measure (except for a usually small diffusion coefficient term) of the relative oxidizing abilities of $Ru(bipy)_2Cl_2^+$ and $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ in this medium.

(4) A. J. Poe, *Proc. Int. Conf. Coord. Chem., 1972*, 14 (1972).

(5) J. P. Candlin and J. Cooper, *J. Organometal. Chem.*, 15, 230 (1968).

(6) J. H. Espenson and D. J. Boone, *Inorg. Chem.*, 7, 636 (1968); N. Cooke, T. Kuwana, and J. H. Espenson, *ibid.*, 10, 1081 (1971); J. H. Espenson and R. J. Kinney, *ibid.*, 10, 376 (1971); J. H. Espenson, *ibid.*, 7, 631 (1968); J. H. Espenson and R. E. McCarley, *J. Amer. Chem. Soc.*, 88, 1063 (1966).

(7) J. A. Ferguson and T. J. Meyer, *Inorg. Chem.*, 11, 631 (1972).

(8) J. A. Ferguson and T. J. Meyer, *J. Amer. Chem. Soc.*, 94, 3409 (1972).
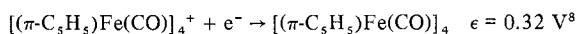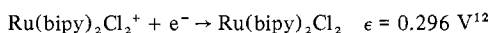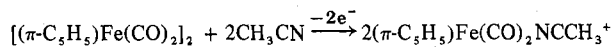
(9) L. Lange and B. Muller, *Ber. Deut. Chem. Ges. B*, 63, 1058 (1930).

(10) F. P. Dwyer, H. A. Goodwin, and E. C. Gyarfas, *Aust. J. Chem.*, 16, 544 (1963).

(11) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

(12) M. Cooke and J. A. Ferguson, unpublished results.

Under essentially the same conditions, the oxidation of [(π-C_5H_5)Fe(CO)_2]_2

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2CH_3CN \xrightarrow{-2e^-} 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$$

occurs at 0.19 V (at a carbon cloth electrode).[3] However, the iron dimer couple is electrochemically irreversible, so that values of ΔG for the oxidation of [(π-C_5H_5)Fe(CO)_2]_2 by either Ru(bipy)_2Cl_2^+ or [(π-C_5H_5)Fe(CO)]_4^+ cannot be calculated from the electrochemical data.

Both [(π-C_5H_5)Fe(CO)]_4^+ and [(π-C_5H_5)Fe(CO)]_4 are stable for days in acetonitrile when protected from light. The two ruthenium complexes, Ru(bipy)_2Cl_2^+ and Ru(bipy)_2Cl_2, are also stable for long periods under the conditions of the kinetics experiments, although a reasonably efficient light-catalyzed path does exist for the reaction

$$Ru(bipy)_2Cl_2 + CH_3CN \xrightarrow{h\nu} Ru(bipy)_2(NCCH_3)Cl^+ + Cl^-$$
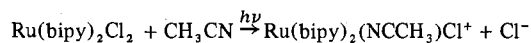
The acetonitrile complex can be prepared by refluxing Ru(bipy)_2Cl_2 in acetonitrile (Experimental Section). The configuration of Ru(bipy)_2Cl_2 is known to be cis[10,13] and Ru(bipy)_2Cl_2^+ is presumably also cis.

Acetonitrile solutions of [(π-C_5H_5)Fe(CO)_2]_2 and of (π-C_5H_5)Fe(CO)_2(NCCH_3)^+ are stable for several hours when protected from light. However, for the kinetic runs, solutions of the iron dimer were protected from both light and air (by working under an atmosphere of nitrogen). The acetonitrile complex is noticeably light sensitive in acetonitrile and care was taken to protect its solutions from light. The ultraviolet–visible spectra of [Ru(bipy)_2Cl_2], [Ru(bipy)_2Cl_2]^+, [Ru(bipy)_2(NCCH_3)Cl]^+, [(π-C_5H_5)Fe(CO)_2]_2, [(π-C_5H_5)Fe(CO)]_4^+, and [(π-C_5H_5)Fe(CO)_2(NCCH_3)]^+ in acetonitrile are summarized in Table I.

Kinetics. The rate law for both of the oxidation–reduction reactions was found to be

$$\frac{-d[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4]}{dt} = k[Ox][(\pi\text{-}C_5H_5)_2Fe_2(CO)_4]$$

where Ox is either Ru(bipy)_2Cl_2^+ or [(π-C_5H_5)Fe(CO)]_4^+. Rate constants for both reactions obtained by stopped-flow kinetic measurements at various temperatures are given in Table II.

The results of individual kinetic runs were very reproducible regardless of whether [(π-C_5H_5)Fe(CO)_2]_2 or the oxidant was in excess. The uncertainties in the k values in Table II represent the average error for from three to seven separate runs with the iron dimer in the concentration range 1.40×10^{-5} to 15.3×10^{-5} M and the oxidant in the concentration range 4.08×10^{-5} to 19.5×10^{-5} M.

An attempt was also made to assess quantitatively the effects of added electrolyte on the observed rate constants. The results of these studies are given in Table III. From the results of Table III it is apparent that the rate constants are somewhat sensitive to added electrolyte. We have also observed that the rates of the reactions can be strongly catalyzed by adding water in sizable amounts. With the low concentrations of the ionic oxidants used in the kinetics experiments and the care that was taken in purifying and storing the acetonitrile, the rate constants given in Table II were measured under conditions where they are relatively insensitive to the total concentration of electrolyte and to trace amounts of water.

Activation parameters are given in Table IV.

(13) J. G. Gibson, R. Laird, and E. D. McKenzie, *J. Chem. Soc. A*, 2089 (1969).

Table I. Ultraviolet–Visible Spectral Data in Acetonitrile

Compound	λ_{max}, nm[a]	
[Ru(bipy)_2Cl_2]	553 (9100)	380 (8850)
	297 (50,000)	243 (21,000)
[Ru(bipy)_2Cl_2]^+		380 (5650)
	310 (22,400)	298 (24,800)
[Ru(bipy)_2(NCCH_3)Cl]^+	480 (6740)	345 (7110)
	292 (50,700)	243 (18,550)
[(π-C_5H_5Fe(CO)_2]_2	500 sh (~580)	405 sh (~1600)
	344 (8000)	
[(π-C_5H_5)Fe(CO)]_4^+	668 (3200)	388 (18,000)
	275 sh (~23,000)	
[(π-C_5H_5)Fe(CO)_2(NCCH_3)]^+		372 (765)
	260 sh (~3080)	

[a] Molar extinction coefficient values (±5%) are given in parentheses; sh is shoulder.

Table II. Rate Constants for the Oxidation of [(π-C_5H_5)Fe(CO)_2]_2 by Ru(bipy)_2Cl_2^+ and [(π-C_5H_5)Fe(CO)]_4^+ in Acetonitrile

Oxidant	T, °C[a]	$10^{-4}k$, M^{-1} sec^{-1}	No. of runs
Ru(bipy)_2Cl_2^+	24.0	4.24 ± 0.12	7
	16.0	3.27 ± 0.10	5
	4.0	1.83 ± 0.03	4
[(π-C_5H_5)Fe(CO)]_4^+	25.0	6.12 ± 0.21	3
	15.0	5.40 ± 0.6	3
	5.0	4.65 ± 0.15	4

[a] ±0.1°.

Table III. Effects of Added Tetra-*n*-butylammonium Hexafluorophosphate on k at 15.0° (±0.1°) in Acetonitrile

Oxidant	$10^{-4}k$,[a] M^{-1} sec^{-1}	[(*n*-C_4H_9)_4N^+PF_6^-], M
Ru(bipy)_2Cl_2^+	3.07 ± 0.10	0.00
	2.64 ± 0.32	0.01
	2.38 ± 0.15	0.10
[(π-C_5H_5)Fe(CO)]_4^+	5.40 ± 0.6	0.00
	4.59 ± 0.31	0.01
	3.79 ± 0.07	0.10

[a] Average of from three to five separate runs.

Table IV. Activation Parameters for the Oxidation of [(π-C_5H_5)Fe(CO)_2]_2 by Ru(bipy)_2Cl_2^+ and by [(π-C_5H_5)Fe(CO)]_4^+

Oxidant	$\Delta G^{\ddagger}(25°)$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}(25°)$, eu
Ru(bipy)_2Cl_2^+	11.1 ± 0.5	6.2 ± 0.5	−16.6 ± 1.5
[(π-C_5H_5)Fe(CO)]_4^+	10.9 ± 1.0	1.8 ± 0.2	−31 ± 3

Discussion

As shown by the stoichiometry experiments the net reactions studied here are

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + 2Ox + 2CH_3CN \rightarrow$$
$$2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ + 2Red \quad (4)$$
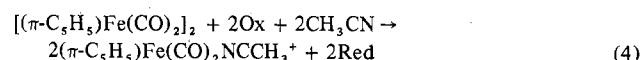
where Ox is Ru(bipy)_2Cl_2^+ or [(π-C_5H_5)Fe(CO)]_4^+ and Red is Ru(bipy)_2Cl_2 or [(π-C_5H_5)Fe(CO)]_4. From the products of reactions like (1)–(4), it is apparent that the metal-metal bond between iron atoms is the ultimate source of electrons in net electron transfer. In the rate-determining step, transfer of a single electron from the iron dimer to the oxidant occurs. The electron is probably removed from the metal-metal bond giving the reactive intermediate [(π-C_5H_5)Fe(CO)_2]_2^+

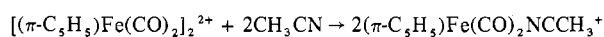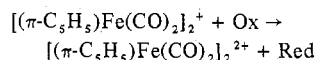$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + Ox \rightarrow [(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+ + Red$$
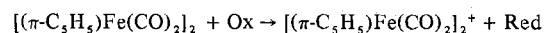
Attempts to observe [(π-C_5H_5)Fe(CO)_2]_2^+ by rapid-scan cyclic voltammetry have been unsuccessful.[3] However, for the related di(tertiary phosphine)-bridged dimers [(π-

$C_5H_5)Fe(CO)]_2(Ph_2P(CH_2)_nPPh_2)$ (Ph is phenyl; $n = 1$-3)[14]
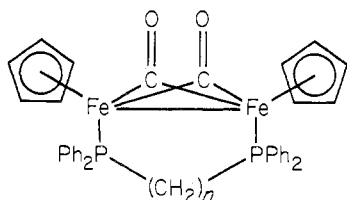
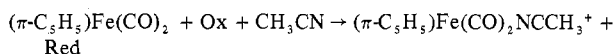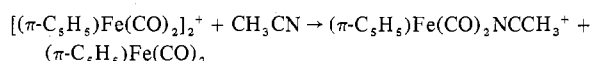the singly oxidized monocations $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2P\text{-}(CH_2)_nPPh_2)^+$ have been characterized and found to undergo reversible chemical and electrochemical electron transfer back to the neutral dimers.[7,15,16]

There are several possible fates for $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+$. It may react with a second molecule of oxidant as an intact unit giving a reactive dication
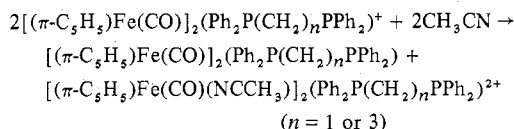
$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+ + Ox \rightarrow$
    $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^{2+} + Red$

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^{2+} + 2CH_3CN \rightarrow 2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$

or by initial dissociation followed by oxidation

$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+ + CH_3CN \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ +$
    $(\pi\text{-}C_5H_5)Fe(CO)_2$

$(\pi\text{-}C_5H_5)Fe(CO)_2 + Ox + CH_3CN \rightarrow (\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+ +$
    Red

or possibly it may give $(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$ directly by disproportionation[17]

$2[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+ + 2CH_3CN \rightarrow [(\pi\text{-}C_5H_5)Fe(CO)_2]_2 +$
    $2(\pi\text{-}C_5H_5)Fe(CO)_2NCCH_3^+$
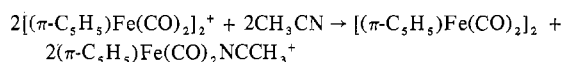
Although we have no direct evidence favoring any of these three possibilities, they are worth mentioning in light of the oxidation-reduction properties of the dimers $[(\pi\text{-}C_5H_5)Fe\text{-}(CO)]_2(Ph_2P(CH_2)_nPPh_2)$. The dication $[(\pi\text{-}C_5H_5)Fe(CO)]_2\text{-}(Ph_2(CH_2)_3PPh_2)^{2+}$ has been observed as a transient by cyclic voltammetry;[16] and the monocations $[(\pi\text{-}C_5H_5)Fe\text{-}(CO)]_2(Ph_2P(CH_2)_nPPh_2)^+$ ($n = 1$ or 3) are known to undergo rapid disproportionation in acetonitrile[16]

$2[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2P(CH_2)_nPPh_2)^+ + 2CH_3CN \rightarrow$
    $[(\pi\text{-}C_5H_5)Fe(CO)]_2(Ph_2P(CH_2)_nPPh_2) +$
    $[(\pi\text{-}C_5H_5)Fe(CO)(NCCH_3)]_2(Ph_2P(CH_2)_nPPh_2)^{2+}$

$(n = 1$ or 3$)$

Electron-transfer reactions involving the cluster couple $[(\pi\text{-}C_5H_5)Fe(CO)]_4^{+,0}$ should be outer sphere and therefore $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ is a useful oxidant for a kinetic study in which attention is to be focused on the electron-transfer act free of possible secondary reactions. For the cluster couple, electrons are gained or lost from extensively delocalized molecular orbitals.[18] In such highly delocalized

(14) R. J. Haines and A. L. Du Preez, *J. Organometal. Chem.*, 21, 181 (1970).

(15) R. J. Haines and A. L. Du Preez, *Inorg. Chem.*, 11, 330 (1972); R. J. Haines, A. L. Du Preez, and G. T. W. Wittmann, *Chem. Commun.*, 611 (1968).

(16) J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 1544 (1971).

(17) If disproportionation is the major path, its rate constant must be at or near the diffusion-controlled limit. The initial oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)]_2$ is rapid (see Table II) and the disproportionation reaction would be second order with respect to the singly oxidized intermediate, $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2^+$. Given the conditions of the experiments in Table II, the steady-state concentration of the intermediate would be necessarily very low ($<10^{-6}$ *M*), the half-time for disproportionation must be less than ~10 msec, and so the rate constant for disproportionation would have to approach the diffusion-controlled limit.

(18) R. Greatrex and N. N. Greenwood, *Discuss. Faraday Soc.*, No. 47, 126 (1969).

systems the contribution to the barrier to electron transfer from inner-sphere reorganization[19] should be very small, explaining in part the low value found for $\Delta H^\ddagger$ (1.8 ± 0.2 kcal/mol) for the oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$.

The $Ru(bipy)_2Cl_2^{+,0}$ couple undergoes facile outer-sphere electron transfer.[20] In addition, the complex $Ru(bipy)_2\text{-}Cl_2^+$ is capable of undergoing inner-sphere reduction by using a coordinated chloride ion as the bridging group as has been found for $Ru(NH_3)_5Cl^{2+}$.[21] Our failure to observe either $Ru(bipy)_2(NCCH_3)Cl^+$ or $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ as products in the oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by $Ru(bipy)_2Cl_2^+$ demonstrates that an inner-sphere mechanism in which a Cl^- group is transferred from the coordination sphere of ruthenium to iron cannot be an important pathway for electron transfer. However, the bound chloride ions may be important in mediating electron transfer between the metal centers. When it is considered that the charge types for the oxidations of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by $Ru(bipy)_2Cl_2^+$ and by $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ are the same, the large differences found in $\Delta S^\ddagger$ for the two reactions (−16.6 and −31 eu, respectively) may reflect a fundamental difference in the detailed mechanisms of electron transfer for the two reactions.

From infrared and ^1H nmr data, bis(π-cyclopentadienyldicarbonyliron) has been shown to exist in two dominant CO bridged forms (cis and trans) in solution and, of lesser importance, an assumed nonbridged form (or forms)[22-24]

cis   nonbridged
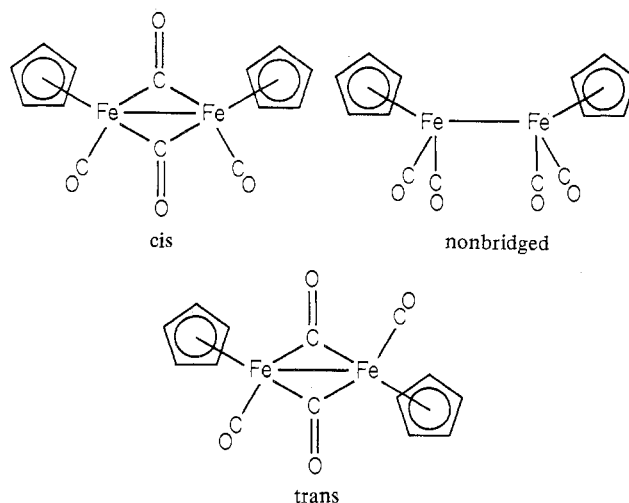
trans

From ν_{CO} infrared spectra the cis isomer of bis(π-cyclopentadienyldicarbonyliron) (ν_{CO} 1992, 1772 cm^{-1}) is in higher concentration in acetonitrile than is the trans isomer (ν_{CO} 1947, 1735 cm^{-1}). The preference for the cis isomer is expected in the polar solvent acetonitrile (ϵ 37.5). Using the results of an infrared analysis by Bullitt, Cotton, and Marks[22] and assuming that extinction coefficients for the CO bands are the same in acetonitrile as in a 3:1 v/v CS_2-$C_6D_5CD_3$ mixture gives $K \approx 0.36$ at 25 ± 2° for the equilibrium

$cis\text{-}(\pi\text{-}C_5H_5)_2Fe_2(CO)_4 \rightleftharpoons trans\text{-}(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$
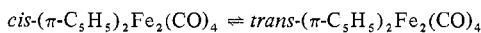
From the approximate nmr rate data obtained by Bullitt,

(19) R. A. Marcus, *Annu. Rev. Phys. Chem.*, 15, 55 (1964).

(20) J. N. Braddock, unpublished results.

(21) J. A. Stritar and H. Taube, *Inorg. Chem.*, 8, 2281 (1969).

(22) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, 11, 671 (1972).

(23) K. Noack, *J. Organometal. Chem.*, 7, 151 (1967).

(24) A. R. Manning, *J. Chem. Soc. A*, 1319 (1968).

Cotton, and Marks, the rates of cis ↔ trans interconversion for the iron dimer are greater than the rates of oxidation of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ by either $Ru(bipy)_2Cl_2^+$ or $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$, even at the lowest temperature used ($4°$) in the electron-transfer rate studies.[25] As a consequence both the cis and trans isomers of the iron dimer may be important in electron transfer, in which case the rate law becomes

$$\frac{-d[(\pi\text{-}C_5H_5)_2Fe_2(CO)_4]_T}{dt} =$$

$$k_{cis}[cis\text{-}(\pi\text{-}C_5H_5)_2Fe_2(CO)_4][Ox] +$$
$$k_{trans}[trans\text{-}(\pi\text{-}C_5H_5)_2Fe_2(CO)_4][Ox]$$

where Ox is either $Ru(bipy)_2Cl_2^+$ or $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ and

$$k_{obsd} = \frac{k_{cis}}{1+K} + \frac{k_{trans}K}{1+K}$$

or since K is relatively small

$$k_{obsd} \approx k_{cis} + k_{trans}K$$

Plots of ln k_{obsd}/T vs. $1/T$ were linear over the temperature ranges studied, which indicates either that a single electron-transfer path, k_{cis} or $k_{trans}K$, is important, or that the net $\Delta H^{\ddagger}$ values for the two paths are very nearly the same.

The measured rate constants, k_{obsd}, and activation parameters (Tables II and IV) may then reflect the reactivities of both the cis and trans isomers and to a certain extent the properties of the cis ⇌ trans equilibrium. For the cis ⇌ trans equilibrium Bullitt, Cotton, and Marks[22] estimated that $\Delta H = 0.9$ kcal/mol and $\Delta S = 3.5$ eu in 3:1 v/v CS_2-$C_6D_5CD_3$. If it is assumed that these data hold, at least approximately, in acetonitrile, any contribution from ΔS for the rapid cis ⇌ trans preequilibrium to the observed $\Delta S^{\ddagger}$ values for electron transfer (−16.6 and −31 eu) is relatively small. However, the observed $\Delta H^{\ddagger}$

values for electron transfer are low, especially for $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ as the oxidant ($\Delta H^{\ddagger} = 1.8 \pm 0.2$ kcal/mol), and if the properties of the preequilibrium are important in the overall mechanism—if electron transfer occurs predominantly *via* the trans isomer—ΔH could represent an appreciable fraction of the observed $\Delta H^{\ddagger}$.

The nonbridged forms of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ are apparently not important kinetically in the oxidation by $[(\pi\text{-}C_5H_5)Fe(CO)]_4^+$ but may be for $Ru(bipy)_2Cl_2^+$. Bullitt, Cotton, and Marks[22] estimated that for the equilibrium

$$cis\text{-}(\pi\text{-}C_5H_5)Fe_2(CO)_4 \rightleftharpoons \text{nonbridged } (\pi\text{-}C_5H_5)_2Fe_2(CO)_4$$
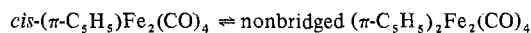
$\Delta H = 4.9 \pm 1$ kcal/mol. If the nonbridged form of the dimer is kinetically important in the oxidation, it is necessary that the observed enthalpy of activation, $\Delta H^{\ddagger}$, be greater than 4.9 kcal/mol—if it is assumed that the enthalpy of activation for the electron-transfer step is positive—but, in fact, $\Delta H^{\ddagger}$ was found to be 1.8 ± 0.2 kcal/mol.

In summary, it appears that both reactions involving $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ occur *via* a rate-determining step in which outer-sphere electron transfer occurs between the metal–metal bond and orbitals on the oxidant giving a singly oxidized, reactive intermediate. An interpretation of the measured kinetic parameters is somewhat complicated by possible contributions from cis, trans, and nonbridging isomers and from the equilibria which interrelate them. Nevertheless, both reactions are rapid, even though outer sphere, which indicates that direct chemical attack on the metal–metal bond, as by a halogen,[26] is not necessary for facile electron transfer.

(25) Bullitt, Cotton, and Marks[22] estimated from their nmr data that for the reaction $cis\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 \rightarrow trans\text{-}[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ $\Delta G^{\ddagger} = 10.4$ kcal/mol at 220°K and that $E_a \approx$ 12–17 kcal/mol in 3:1 v/v CS_2-$C_6D_5CD_3$. Using the higher value for E_a and assuming that E_a is approximately the same in acetonitrile give k(cis → trans) $\approx 5 \times 10^5$ sec^{-1} or $t_{1/2} \approx 10^{-3}$ msec at 277°K (the lowest temperature used in the electron-transfer rate studies). The trans → cis interconversion must also be rapid since at 298°K, for cis ⇌ trans, $K \approx 0.36$ in acetonitrile (*vide supra*). Under all conditions studied here, cis ↔ trans interconversion is more rapid than electron transfer.

(26) R. J. Haines and A. L. du Preez, *J. Chem. Soc. A.*, 2341 (1970).