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A Kinetic Study of the Photolysis of Ethylferrocene in Chloroform

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The photooxidation of ethylferrocene to ethylferricinium ion and tetrachloroferrate in $CHCl_3$ under 254 nm irradiation proceeds through light absorption by both ethylferrocene and chloroform. The products remain in solution at concentrations below 10^{-3} M. The fraction occurring through a solvent-initiated pathway increases during the course of the reaction. A secondary thermal reaction is responsible for generating tetrachloroferrate from ethylferricinium ion. The rate of the reaction increases during the early stages, and the data throughout the course of the reaction are consistent with the rate law $(af_S + bf_R)/(1 + c[R]/[P] - d[R]/[Cl^-])$, where [R] and [P] are the concentrations of ethylferrocene and ethylferricinium ion, respectively, and f_S and f_R are the fractions of light absorbed by the solvent and ethylferrocene, respectively.

INTRODUCTION

Recent experiments have shown that in some photoreactions of metal complexes in halogenated solvents the solvent is the photoactive species rather than the metal complex [1–3]. In chloroform this can occur even under 313 nm irradiation where $CHCl_3$ absorbs only a small fraction of the incident radiation [1]. Examples of solvent-initiated photosubstitution and photooxidation reactions have been observed, with products that are indistinguishable from those expected from metal-initiated reactions. Careful kinetic studies are required to determine whether the rate of reaction depends on the fraction of light absorbed by the metal complex or the bulk solvent.

One of the characteristics of a solvent-initiated reaction is that the apparent quantum yield, calculated with reference to the light absorbed by the metal complex, increases with decreasing wavelength, and is zero outside the range in which the solvent absorbs light. When such behavior presents itself, an alternative sometimes invoked is that a charge transfer to solvent (CTTS) band[4] is responsible for the photochemistry, which causes the wavelength dependence of the quantum yield. Such a mechanism is still metal-initiated.

A particularly well-substantiated example of a photoreaction initiated through a CTTS transition is the photooxidation of ferrocene to ferricinium

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tetrachloroferrate in chlorinated hydrocarbon solvents [5–10]. In CCl_4/ethanol and $CHCl_3$/ethanol solvents, Traverso and Scandola found the quantum yield, from initial rate data, to be constant at different wavelengths when referred only to the fraction of light absorbed by the CTTS band [7]. Consequently, the metal complex was the photoactive species. The mixed solvent was used because the product precipitated from solution in neat haloalkane solvents.

Akiyama *et al.* also studied the photochemistry of ferrocene in haloalkane/ethanol solvents, and found little or no [Fe(cp)$_2$][FeCl$_4$] (Hcp = cyclopentadiene). Instead, aldehyde, ester, or ether ring substitution products were obtained, depending on the solvent [9,10]. The two very different results from the two laboratories is somewhat puzzling, since there was little difference in the irradiation conditions reported. Akiyama *et al.* used a 1:1 ratio of haloalkane to ethanol. Traverso and Scandola used several different ratios, including 1:1, and the same haloalkanes were used. Akiyama *et al.* did use a ferrocene concentration about seven times greater than the highest concentration employed by Traverso and Scandola.

We wished to explore the possibility that under some conditions there might be a solvent-initiated process that could lead to the same [Fe(cp)$_2$][FeCl$_4$] product observed in halogenated hydrocarbons and, at least under Traverso and Scandola's conditions, in haloalkane mixed solvents. We chose ethylferrocene rather than simple ferrocene, because the product was soluble to some extent in chloroform, and therefore kinetic studies could be done in the pure solvent, without the potential complications of ring substitution products.

The key distinction to make is whether the rate of reaction is proportional to the fraction of light absorbed by the reactant metal complex, f_R, or the fraction of light absorbed by the solvent, f_S, either possibly raised to some power. In a solution containing a reactant, R, and a product, P, these

may be expressed as

$$f_R = \left\{1 - 10^{-(\varepsilon_R[R]+\varepsilon_P[P]+A_S)}\right\} \frac{\varepsilon_R[R]}{\varepsilon_R[R] + \varepsilon_P[P] + A_S},$$
(1)

$$f_S = \left\{1 - 10^{-(\varepsilon_R[R]+\varepsilon_P[P]+A_S)}\right\} \frac{A_S}{\varepsilon_R[R] + \varepsilon_P[P] + A_S},$$
(2)

where A_S is the absorbance of the solvent and ε_R and ε_P are the extinction coefficients of reactant and product, all at the irradiation wavelength.

We also wished to test the conclusion by Traverso *et al.* that [FeCl$_4$]$^-$ is formed through the reaction of $^\bullet CCl_3$ with [Fe(cp)$_2$]$^+$ [8]. They based this conclusion on the ability of acrylamide, a radical scavenger, to suppress the formation of the tetrachloroferrate ion, leaving chloride as the counterion for the ferricinium ion [8].

EXPERIMENTAL

Ethylferrocene, Fe(C$_5$H$_5$)(C$_5$H$_4$C$_2$H$_5$), FeCl$_2$, FeCl$_3$, and CHCl$_3$ were used as supplied by Aldrich Chemical Co. Chloroform was HPLC grade, stabilized with ethanol. Electronic spectra were measured on a Hewlett Packard Model 8453 diode array spectrometer. The initial concentration of ethylferrocene in CHCl$_3$ solution was determined from the extinction coefficient at 254 nm, 4.28 $(\pm 0.10) \times 10^3\,M^{-1}\,cm^{-1}$ from a Beer's Law plot. The spectrum of the final product was determined following exhaustive irradiation. The growth of ethylferricinium ion could be followed by the rapid increase in absorbance at 254 nm, while the growth of the tetrachloroferrate ion could be seen through the appearance of a peak at 365 nm. [FeCl$_4$]$^-$ has an equally intense peak at 316 nm, which, however, appears as a shoulder on the growing ferricinium band. FeCl$_3$, which has a peak at 340 nm, was not detectable at any stage of the reaction.

The concentrations of all three species were calculated from extinction coefficients at 254 nm (ethylferricinium ion, 2.13 (± 0.10) $\times$ $10^4 M^{-1} cm^{-1}$) and 365 nm (tetrachloroferrate, 7.22 (± 0.32) $\times 10^3$; ethylferrocene, 65 (± 2) M^{-1} cm^{-1}). The photolysis of chloroform yields products that absorb at 254 nm [1], so there is some error associated with the determination of concentrations at that wavelength, but the high extinction coefficient of ethylferricinium ion should make those errors small.

Samples were dissolved in $CHCl_3$ in a quartz cuvette, deoxygenated by bubbling N_2 through the cell for three minutes, and irradiated at 254 nm with a 100 W mercury lamp in an Oriel Q housing, passed through an Oriel 0.125 m monochromator, with slit widths between 0.5 and 2.5 mm. Initial concentrations were $8 \times 10^{-4} M$ or less, to avoid precipitation of the product. Light intensities were measured in triplicate by ferrioxalate actinometry [11,12]. Initial rates were determined by fitting the change in concentration with time at the beginning of the reaction to a quadratic equation, taking the coefficient of the linear term as the initial rate. Reaction rates during the course of a reaction were estimated as $-\Delta[R]/\Delta t$, where [R] is the concentration of reactant, for a sequence of overlapping time intervals, and assigned to the average reaction time and average concentrations of reactant and products for that interval.

RESULTS

Figure 1 shows a typical concentration profile for $[Fe(cp)_2]$, $[Fe(cp)_2]^+$, and $[FeCl_4]^-$ with irradiation time (cp will be used for both $C_5H_5^-$ and $C_5H_4C_2H_5^-$). The two products were formed almost in parallel, $[FeCl_4]^-$ lagging $[Fe(cp)_2]^+$ only slightly. This rules out the possibility that tetrachloroferrate is formed through secondary photolysis from $[Fe(cp)_2]^+$. Photolyses were characterized by a rate that increased with time at the beginning, but later decelerated.
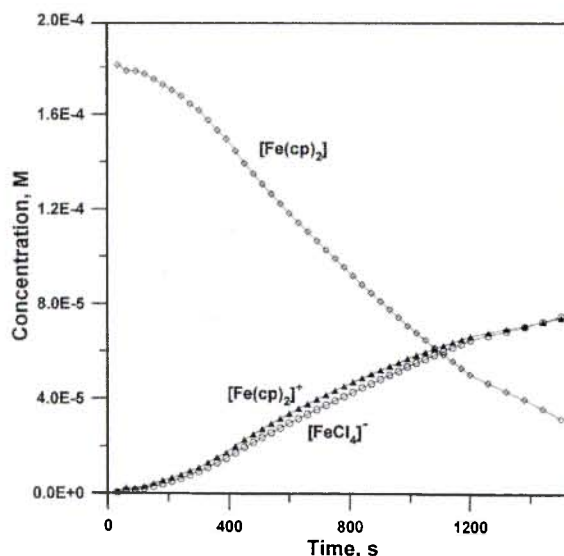

FIGURE 1 Concentration profile during the course of the photooxidation of ethylferrocene in $CHCl_3$ under 254 nm irradiation.

Initial rates, $-d[R]/dt$, at one concentration of $[Fe(cp)_2]$ were measured as a function of the incident light intensity, I_0. The results, in Figure 2, show a linear relationship, implying a linear dependence of the rate on the fraction of light absorbed, whether f_R or f_S.

Initial rates, $-d[R]/dt$, at constant light intensity were measured at several concentrations of $[Fe(cp)_2]$. These rates were plotted against f_R, f_S and several functions in which these were multiplied by the reactant concentration to some power. Though far from good, the best linear fit to the data occurred with f_R alone, shown in Figure 3 [13]. If the reaction were completely metal-initiated, this line should pass through the origin. A best-fit straight line yields an intercept of 9(± 2) $\times 10^{-8} M s^{-1}$. The positive intercept implies that another pathway depletes the reactant when its concentration is low. The scatter is high partly because of the imprecision in rates derived from small differences in concentrations, and partly because there are species present other than ferrocene and ferrocinium ion that absorb in the region observed (some of these are $CHCl_3$
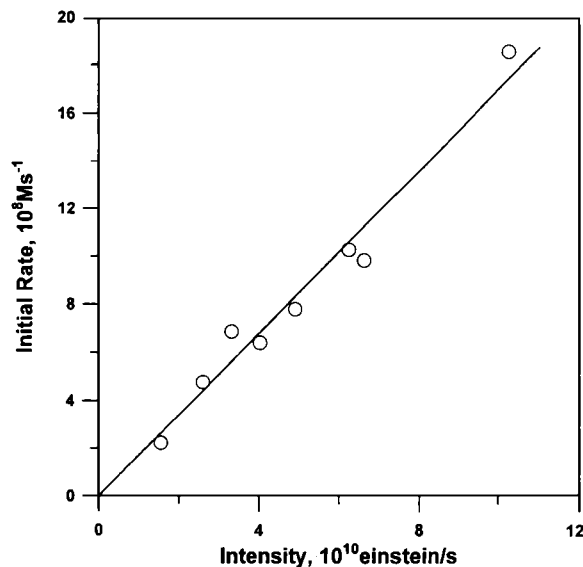
FIGURE 2   Initial rate, $-d[R]/dt$, for the photooxidation of ethylferrocene in $CHCl_3$ at 254 nm as a function of incident light intensity. $[R]_0 = 7.4 \times 10^{-4}$ M. The slope of the best fit straight line through the origin ($R^2 = 0.84$) is 170 M/einstein, equivalent to a quantum yield of 0.54 mol/einstein based only on the light absorbed by ethylferrocene.
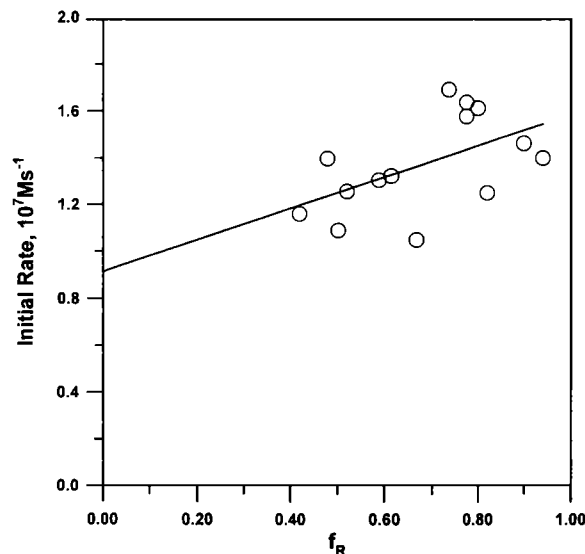

FIGURE 3   Initial rate, $-d[R]/dt$, for the photooxidation of ethylferrocene in $CHCl_3$ at 254 nm as a function of f_R, the fraction of incident light absorbed by ethylferrocene. $I_0 = 8 \times 10^{-10}$ einstein/s. R^2 for the best-fit straight line is 0.29.

photolysis products), but also because an f_R dependence is not a sufficient rate law by itself, as the next graph should make clear. If the second pathway is solvent-initiated, the overall rate may be expressed as

$$-\frac{d[R]}{dt} = af_R + bf_S. \qquad (3)$$

This suggests that a plot of $-(\Delta[R]/\Delta t)/f_S$ vs. f_R/f_S would be linear, and better than a plot of rate vs. f_R alone. This plot is shown in Figure 4, and is in fact better ($R^2 = 0.89$ compared to 0.29 for the plot in Figure 3). The scatter is considerably reduced. The slope (a in Equation (3)), 1.27($\pm$ 0.13) $\times 10^{-7}$ M s^{-1}, and the intercept (b), 1.17($\pm$ 0.25) $\times 10^{-6}$ M s^{-1}, allow us to compare the efficiencies of the metal-initiated and solvent-initiated pathways, respectively, at the outset of the reaction. For example, at a starting concentration of 1.8 $\times 10^{-4}$ M ethylferrocene, $f_R = 0.52$ and $f_S = 0.054$ at 254 nm. Under these conditions,
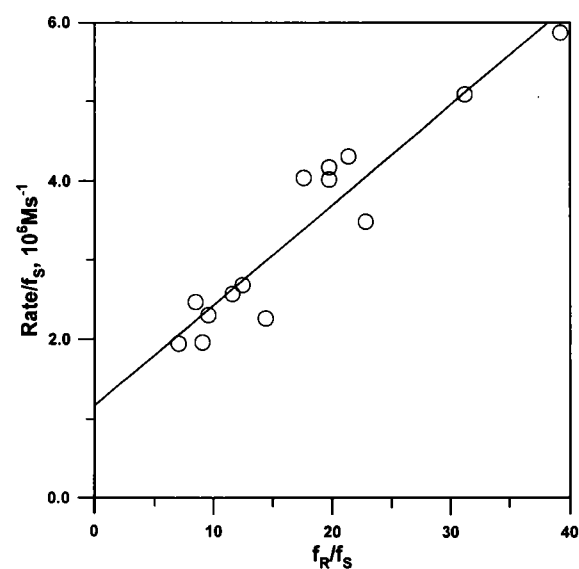

FIGURE 4   Plot of rate/f_S vs. f_R/f_S, demonstrating the dependence of the initial rate for the photooxidation of ethylferrocene in $CHCl_3$ at 254 nm on both f_R and f_S. R^2 for the best-fit straight line is 0.89. $I_0 = 8 \times 10^{-10}$ einstein/s.

50% of the reaction should occur through the solvent-initiated pathway.

Similar plots were constructed based on rates determined throughout the course of reactions carried out to about 75% completion. Plots of rates early in the reaction against the same functions yielded results very similar to those obtained for initial rates, that is, the rate could still be represented well as $af_R + bf_S$. Plots of $-(\Delta[R]/\Delta t)$ vs. f_R or $-(\Delta[R]/\Delta t)/f_S$ vs. f_R/f_S for rates later in the reaction were not linear, and points from runs at different starting concentrations clustered in different areas of the graph, regardless of the values of f_R and f_S. Plots of rate against any of the other simple functions of f_R, f_S, and [R] were worse.

DISCUSSION

Brand and Snedden [6], Traverso and Scandola [7,8] and Akiyama et al. [9,10] agree that the primary photochemical step involves an electron transfer from ferrocene (in a CTTS excited state) to the solvent. For chloroform this would take the form:
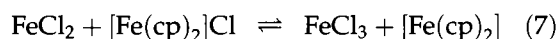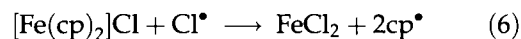
$$Fe(cp)_2 \bullet CHCl_3 \xrightarrow{h\nu} Fe(cp)_2^+ +\bullet CHCl_2 + Cl^- \tag{4}$$
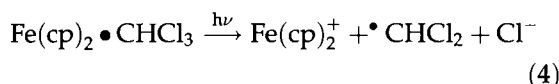
By hydrogen abstraction, $\bullet CHCl_2$ radicals will be transformed to $\bullet CCl_3$. The existence of a solvent-initiated pathway makes it likely that ferricinium ions can also be formed through a direct reaction with trichloromethyl radicals:

$$[Fe(cp)_2] +\bullet CCl_3 \longrightarrow [Fe(cp)_2]^+ + Cl^- + :CCl_2 \tag{5}$$
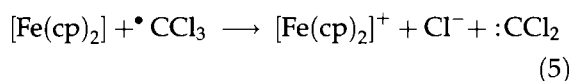
Koerner von Gustorf et al. suggested a similar step, with $Cl^\bullet$ instead of $\bullet CCl_3$, to explain the oxidation of ferrocene in CCl_4 under X-ray irradiation [5].

Traverso et al. [8] proposed that $FeCl_3$ is formed through repeated attack by $\bullet CCl_3$ radicals on the ferricinium cation, while Koerner von Gustorf et al. [5] suggested that radical attack leads first
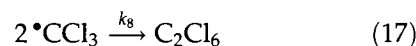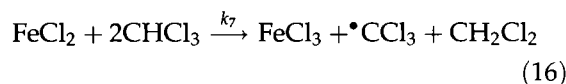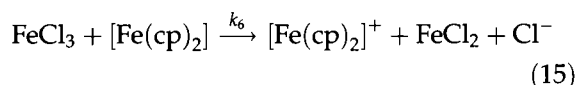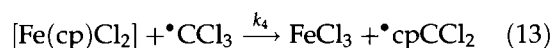
to $FeCl_2$ as in Equation (6), which is oxidized to $FeCl_3$ by another ferricinium ion.

$$[Fe(cp)_2]Cl + Cl^\bullet \longrightarrow FeCl_2 + 2cp^\bullet \tag{6}$$

$$FeCl_2 + [Fe(cp)_2]Cl \rightleftharpoons FeCl_3 + [Fe(cp)_2] \tag{7}$$

In either case, $FeCl_3$ would combine with $[Fe(cp)_2]Cl$ to yield the tetrachloroferrate salt.

The equilibrium proposed by Koerner von Gustorf et al. must lie very far toward the ferricinium side, because anhydrous $FeCl_3$ and $[Fe(cp)_2]$ react almost instantaneously in chloroform to yield $[Fe(cp)_2]^+$ and $[FeCl_4]^-$. When anhydrous $FeCl_2$ is dissolved in chloroform, it is very rapidly converted to $FeCl_3$, implying a direct reduction of chloroform.
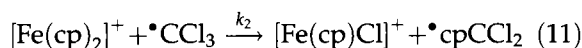
These considerations led to the following proposed mechanism, in which the hydrogen abstraction by $Cl^\bullet$ and $\bullet CHCl_2$ have been included with the processes that generate them:

$$[Fe(cp)_2] + 2CHCl_3 \xrightarrow{h\nu} [Fe(cp)_2]^+ +\bullet CCl_3 + CH_2Cl_2 + Cl^- \tag{8}$$

$$3CHCl_3 \xrightarrow{h\nu} 2\bullet CCl_3 + CH_2Cl_2 + HCl \tag{9}$$

$$[Fe(cp)_2] +\bullet CCl_3 \xrightarrow{k_1} [Fe(cp)_2]^+ + :CCl_2 + Cl^- \tag{10}$$

$$[Fe(cp)_2]^+ +\bullet CCl_3 \xrightarrow{k_2} [Fe(cp)Cl]^+ +\bullet cpCCl_2 \tag{11}$$

$$[Fe(cp)Cl]^+ + Cl^- \xrightarrow{k_3} [Fe(cp)Cl_2] \tag{12}$$

$$[Fe(cp)Cl_2] +\bullet CCl_3 \xrightarrow{k_4} FeCl_3 +\bullet cpCCl_2 \tag{13}$$

$$FeCl_3 + Cl^- \xrightarrow{k_5} [FeCl_4]^- \tag{14}$$

$$FeCl_3 + [Fe(cp)_2] \xrightarrow{k_6} [Fe(cp)_2]^+ + FeCl_2 + Cl^- \tag{15}$$

$$FeCl_2 + 2CHCl_3 \xrightarrow{k_7} FeCl_3 +\bullet CCl_3 + CH_2Cl_2 \tag{16}$$

$$2\bullet CCl_3 \xrightarrow{k_8} C_2Cl_6 \tag{17}$$
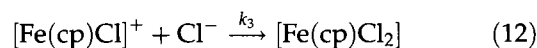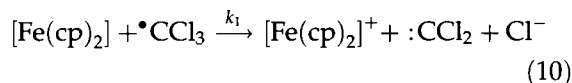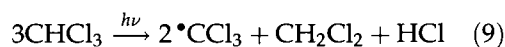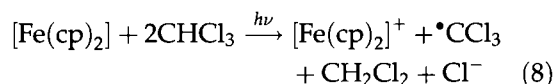
The rates for Equations (8) and (9) can be expressed as $I_0 f_R \phi_R / V$ and $I_0 f_S \phi_S / V$, respectively, where ϕ_R and ϕ_S are the quantum yields for the respective steps. If Equation (17), the bimolecular

termination of $^\bullet CCl_3$, were rapid compared to Equations (10), (11) and (13), it would lead to a square root dependence of the rate on I_0. Because of the observed dependence of the initial rate of reaction on I_0 rather than $I_0^{1/2}$, we have ignored Equation (17) in the derivation of the rate expression, even though conditions later in the reaction may differ significantly from initial conditions.

Equations (11)–(13) suggest a sequence of steps by which $FeCl_3$ may be generated from ethylferricinium ions. There are, of course, other possibilities, but kinetically they will be equivalent as long as two $^\bullet CCl_3$ radicals are consumed along with a chloride ion. The latter is required for charge balance, while the former condition is maintained as long as none of the chlorination steps occur through direct reaction with chloroform. In that case a trichloromethyl radical would be generated rather than consumed.

Steady state conditions were assumed for $^\bullet CCl_3$, $[Fe(cp)Cl]^+$, $[Fe(cp)Cl_2]$, $FeCl_3$, and $FeCl_2$. A steady state for Cl^- would be inappropriate, because even though $[Fe(cp)_2]^+$ and $[FeCl_4]^-$ are formed nearly in parallel, the difference, which by charge balance is equal to the chloride ion concentration, is significant. Figure 5 shows the chloride ion concentration during the course of one photolysis, and similar behavior was observed in all cases.

Application of the steady state equations leads to Equation (18) for the concentration of $^\bullet CCl_3$:

$$[CCl_3] = \frac{2(I_0 f_S \phi_S/V) + (I_0 f_R \phi_R/V)}{k_1[R] + k_2[P] - (k_2 k_6[P][R])/(k_5[Cl^-])}. \quad (18)$$

In Equation (18), [P] is the concentration of $[Fe(cp)_2]^+$, and $[Cl^-] = [Fe(cp)_2^+] - [FeCl_4^-]$. Taking the rate of reaction as the rate of formation of $[FeCl_4]^-$, the rate law becomes

$$\frac{d[FeCl_4^-]}{dt} = k_2[P][CCl_3]$$

$$= \frac{2(I_0 f_S \phi_S/V) + (I_0 f_R \phi_R/V)}{1 + (k_1[R]/k_2[P]) - (k_6[R]/k_5[Cl^-])}. \quad (19)$$
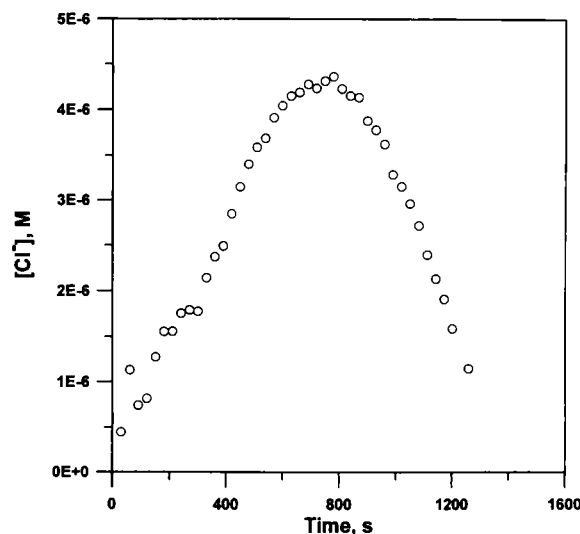

FIGURE 5 Chloride ion concentration, as the difference between the concentrations of ethylferricinium and tetrachloroferrate ions, during the course of the photooxidation of ethylferrocene in $CHCl_3$ at 254 nm.

This suggests that a plot of reaction rates during the course of the reaction against the function

$$\frac{f_S + a f_R}{1 + b([R]/[P]) - c([R]/[Cl^-])} \quad (20)$$

will be linear and pass through the origin for some set of values a, b and c. Optimization of the coefficients for maximum R^2 led to the graph shown in Figure 6 for the values $a = 0.44$, $b = 0.079$ and $c = 0.0017$. The problem with scatter is even greater than with initial rates, because each point represents the small difference between much larger concentrations. Nevertheless, the linear behavior is evident.

It should be noted that Equations (8)–(17) represent less a complete mechanism for the photooxidation of ferrocene than a list of known or probable processes, excepting Equations (11) and (13), in which the nature of the cyclopentadiene product is unclear. Nevertheless, the rate law derived from these steps is consistent with the experimental data. Other steps may occur which lead to equations that fit equally well.
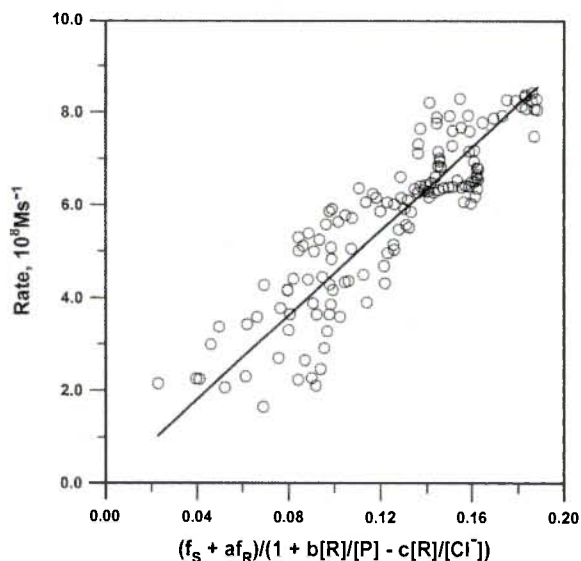
FIGURE 6 Dependence of the rate of ethylferrocene photooxidation, $-\Delta[R]/\Delta t$, throughout the course of several reactions on the function $(f_S + af_R)/(1 + b[R]/[P] - c[R]/[Cl^-])$, for $a = 0.44$, $b = 0.079$, and $c = 0.0017$. R^2 for the straight line through the origin is 0.78.

If Equation (9) is a reasonable representation of events, and Figure 6 makes it appear so, it sheds some light on the concentration profile in Figure 1. The initial reaction rates reflect only the primary steps, Equations (8)–(10), and hence depend only on f_R and f_S. Early in the reaction steady states are established for $FeCl_3$ and $FeCl_2$, and the net rates of formation of $[Fe(cp)_2]^+$ and $[FeCl_4]^-$ become nearly equal. The rate of formation of $[FeCl_4]^-$ increases as $[Fe(cp)_2]^+$ is formed and undergoes attack by $^\bullet CCl_3$ as in Equation (10). The rate of disappearance of ethylferrocene is also increased because the $FeCl_3$ formed in the secondary reaction can cause further thermal oxidation. As the second term in the denominator of Equation (19) decreases, the rate increases because of the increase in the concentration of ethylferricinium ion (P), enhancing the secondary reaction, Equation (11). The concentration of trichloromethyl radicals appears to fall slowly during the reaction, given the coefficients used in Figure 6. At approximately the time when the second term in the denominator approaches a value of

one, the decrease in the fraction of light absorbed by ethylferrocene and by the solvent is more rapid than the decrease in the denominator of Equation (19), and the reaction decelerates.

From the coefficients used for Figure 6, the third term, arising from the generation of $^\bullet CCl_3$ radicals when $FeCl_3$ oxidizes ferrocene, contributes less than 20% to the denominator throughout the reaction. The ratio $[R]/[Cl^-]$ decreases through most of the reaction. However, towards the end the concentration of chloride ion declines faster than does the concentration of ethylferrocene. The third term begins to grow, slowing the deceleration of the reaction.

The coefficients for f_R and f_S determined from Figure 6 differ somewhat from those determined from initial rates, which would correspond to $a = 0.11$ in Equation (20). The value of 0.44 for a from Figure 6 would imply that for $1.8 \times 10^{-4} M$ ethylferrocene, 20% of the initial reaction occurs through the solvent-initiated pathway, compared to the 50% estimated from initial rates. Errors from the initial rate measurements are probably smaller, and are easier to estimate. Whatever the initial percentage occurring through the solvent-initiated pathway, it must increase during the course of the reaction as f_R decreases relative to f_S. Using the estimate of $a = 0.11$ from initial rates, by the time two-thirds of an initially $1.8 \times 10^{-4} M$ solution of ethylferrocene has reacted, 75% of the reaction is solvent-initiated.

CONCLUSIONS

The results presented here confirm the basic framework for the photooxidation outlined by Traverso et al. [8], who posited that tetrachloroferrate was generated through successive attacks by $^\bullet CCl_3$ radicals on the ferricinium ion produced photochemically. The ability of $FeCl_3$ to oxidize ethylferrocene, and the $FeCl_2$ produced to regenerate $FeCl_3$, provide conditions under which the rates of formation of $[Fe(cp)_2]^+$ and $[FeCl_4]^-$ are equalized and the overall rate increases with time during the early stages of the reaction.

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[13] The function $f_S[R]$ has the same functional form as f_R and is indistinguishable at a single irradiation wavelength. However, the known dependence on f_R in haloalkane/ethanol solution at higher irradiation wavelengths, makes it very unlikely that $f_S[R]$ is the proper rate function.