

Photooxidation of Ferrocene in Halocarbon Solvents

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The photooxidation of ferrocene in CCl_4 -ethanol and CHCl_3 -ethanol solutions has been investigated at several wavelengths of irradiation in the range 313-472 nm. No photoreaction was detected when the irradiation was carried out in the intramolecular ferrocene band with maximum at 440 nm. Irradiation in the spectral region where the ferrocene-to-halocarbon solvent charge transfer bands overlap the intramolecular ferrocene bands caused the oxidation of ferrocene to ferricenium cation. In this spectral region, only the light intensity absorbed by the charge-transfer-to-solvent band was active. The photooxidation reaction was found to involve a primary photochemical process and a secondary thermal reaction, both producing the ferricenium cation. The primary photochemical process was the dissociation of the charge-transfer-to-solvent excited state into a ferricenium cation, a chloride ion, and a radical (CCl_3 or CHCl_2 in the case of CCl_4 and CHCl_3 , respectively). In both acceptor solvents the primary photoprocess occurred with unitary efficiency with respect to the light absorbed by the charge-transfer-to-solvent band. The secondary thermal oxidation of ferrocene was initiated by the radical species produced in the primary photoprocess. The efficiency of the secondary oxidation depended on concentrations of ferrocene, dissolved oxygen and radical scavengers.

Introduction

The chemical and spectroscopic properties of ferrocene have been extensively investigated.^{1,2} By contrast, only scattered and qualitative information is available on the photochemical behavior of ferrocene.^{3,4} The formation of cyclopentadienyl radicals has been reported to occur during the flash photolysis of ferrocene vapor.⁵ In solvents such as hydrocarbons or alcohols, in which the electronic spectrum of ferrocene does not undergo significant solvent effects, ferrocene shows a remarkable stability to visible and ultraviolet irradiation.^{3,6} In these solvents the photosensitivity appears to be markedly enhanced by substitution in the cyclopentadienyl rings.^{6,7}

In 1957, Brand and Snedden⁸ demonstrated that the spectrum of ferrocene in halogen-containing solvents had an additional intense band in the range 300-400 nm which was the result of ferrocene-to-solvent charge transfer transitions. They also observed that in these solvents ultraviolet irradiation caused the decomposition of ferrocene via a primary photooxidation process. Since then, a number of studies have been carried out on the photooxidation of ferrocene in various organic halides.³ In most cases, a solid product was obtained, which has been formulated as ferricenium tetrahaloferrate $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeX}_4$.

Apparently, however, most of these studies were qualitative in character, so that they did not permit the making of a clear distinction between primary photochemical, secondary thermal, and secondary photochemical processes.

In this article, we wish to report the results of an investigation on the photooxidation of ferrocene in chloroform and carbon tetrachloride.

Experimental Section

Materials. Reagent grade ferrocene (BDH Chemicals, Poole, England) was twice recrystallized from methanol. Reagent grade acrylamide monomer (BDH Chemicals Poole, England) was used without further purification. All of the solvents used were of spectroscopic grade.

Solid ferricenium tetrachloroferrate, $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$, was prepared from ferrocene and ferric chloride.⁹ A concentrated ethanolic solution of ferric chloride was added to a concentrated solution of ferrocene in carbon tetrachloride. The blue precipitate was filtered and washed several times with ethyl ether. The solid was soluble in water and ethanol, yielding blue and green solutions, respectively. In the aqueous solutions of $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$ the ferricenium cation was only stable at pH values lower than 3. In acid (pH 1) aqueous solutions of $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$, Fe^{3+} ions could be detected with thiocyanate.

(1) M. Rosenblum, « Chemistry of the Iron Group Metallocenes », Interscience Publishers, New York, N. Y., (1965).

(2) A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967).

(3) E. Koerner von Gustorf and F. W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 366 (1969).

(4) V. Balzani and V. Carassiti, « Photochemistry of Coordination Compounds » Academic Press, London (1970).

(5) B. A. Thrush, *Nature*, **178**, 155 (1956).

(6) A. M. Tarr and D. M. Wiles, *Can. J. Chem.*, **46**, 2725 (1968).

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(8) J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, **53**, 894 (1957).

(9) A. N. Nesmeyanov, E. G. Perevalova and L. P. Jurjeva, *Chem. Ber.*, **93**, 2729 (1960).

Solutions of ferricenium chloride were obtained from acid (pH 1) aqueous solutions of $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$ by precipitation of the Fe^{3+} ions with KH_2PO_4 . That the precipitation was quantitative and only involved the iron contained in the FeCl_4^- anion was proved by the negative thiocyanate test and by the constancy of the characteristic ferricenium absorption (see Results). The acid aqueous solutions of ferricenium chloride were stable for a period of several days. When these solutions were neutralized, a rapid decomposition of the ferricenium cation occurred, as shown by a change in color from blue to green and by the evident formation of free Fe^{3+} .

Solid ferricenium tetraphenylborate was prepared by precipitation of the ferricenium cation with sodium tetraphenylborate from acid aqueous solutions of $[\text{Fe}(\text{C}_5\text{H}_5)_2]\text{FeCl}_4$. The freshly prepared solid readily dissolved in acid ethanol, while moderate heating was required for the dissolution of the dry salt.

Apparatus. The same apparatus as previously described¹⁰⁻¹² was used to obtain radiations of 313, 334, 365, 404, and 472 nm, except for the use of Ealing-TFP interference filters at 334 and 365 nm. The irradiations were performed using 1 cm spectrophotometer cells filled with 3 ml of solution and housed in suitable cell holders thermostated at 25°. During the irradiation, the solutions were stirred by bubbling pure nitrogen from a glass capillary. The incident light intensity was measured by means of the ferric oxalate actinometer¹³ and it was of the order of 10^{-7} einstein/minute at each one of the wavelengths of irradiation. Absorption spectra were recorded with an Optica CF4NI spectrophotometer.

Procedures. Solutions containing 7.5×10^{-3} M ferrocene were used in the bulk of the quantitative photochemical experiments. The photoreaction was followed (see Results) measuring the increase in absorbance at 617 nm. In all the experiments, the irradiation was only carried out until a small percentage ($\leq 5\%$) of the initial ferrocene concentration was consumed. Since in these conditions the photoreaction appreciably followed zero-order kinetics (see Results), the quantum yields could be easily calculated on the basis of the initial rate of light absorption. Where necessary, allowance was made for incomplete light absorption (note that the absorbance of the irradiated solutions depended on both the wavelength of irradiation and the solvent). In most of the photochemical experiments, the solutions were preliminarily deoxygenated by saturation with pure nitrogen. For the experiments in the presence of acrylamide, which were also carried out on such deaerated solutions, the photooxidation was followed in the usual way and the formation of the acrylamide polymer was looked for by diluting the irradiated solutions with an excess (10:1 in volume) of methanol.

(10) V. Balzani, V. Carassiti, L. Moggi and F. Scandola, *Inorg. Chem.*, **4**, 1243 (1965).

(11) F. Scandola, O. Traverso and V. Carassiti, *Mol. Photochem.*, **1**, 11 (1969).

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(13) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1959).

Results

Electronic Spectra. The spectra of ferrocene in pure ethanol, pure halocarbon solvent and in several CCl_4 -ethanol and CHCl_3 -ethanol solvent mixtures are shown in Figures 1 and 2. The spectra in the pure halocarbon solvents agree with those reported by Brand and Snedden.⁸ The increase in the charge-transfer-to-solvent absorption with increasing acceptor solvent concentration may be quantitatively accounted for by the following equation¹⁴

$$\frac{1}{\epsilon - \epsilon_{\text{Fn}}} = \frac{1}{\epsilon_c - \epsilon_{\text{Fn}}} + \frac{1}{(\epsilon_c - \epsilon_{\text{Fn}})K} \cdot \frac{1}{[A]} \quad (1)$$

where ϵ is the apparent molar absorptivity (*i.e.*, that based on the total concentration of ferrocene), ϵ_{Fn} is the molar absorptivity of ferrocene in ethanol, ϵ_c is the molar absorptivity of the ferrocene-halocarbon solvent complex, K is the association constant of the complex, and $[A]$ is the mole fraction concentration of the halocarbon solvent.¹⁵ In the case of CCl_4 , good linear plots of $1/(\epsilon - \epsilon_{\text{Fn}})$ vs. $1/[A]$ were obtained for several wavelengths from 290 to 315 nm. The mean value for the association constant was $K = 1.5 \pm 0.2$ mole fraction⁻¹.¹⁶ In the case of CHCl_3 , no calculation was attempted due to the smallness of the spectral variations.

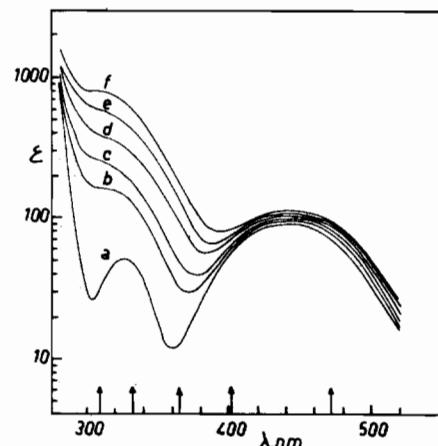


Figure 1. Spectra of ferrocene in CCl_4 -ethanol solvent mixtures: a) pure ethanol, b) 15% CCl_4 , c) 25% CCl_4 , d) 50% CCl_4 , e) 75% CCl_4 , f) pure CCl_4 .

(14) J. A. Ketelaar, C. van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. Trav. Chim.*, **71**, 1104 (1952).

(15) As Brand and Snedden pointed out,⁸ Eq. 1 may be obtained either assuming that the absorption band results from a charge transfer within a thermodynamically stable donor-acceptor complex, or by considering that there is a « contact charge transfer » between ferrocene and the solvent (in this case the apparent association constant K should have the meaning of a probability factor). Although no decision can be made on the basis of the spectral data alone, we shall hereafter assume, for the sake of simplicity, that a stable complex is formed. This assumption is not essential for the interpretation of the photochemical results.

(16) Using cyclohexane as the inactive solvent, Brand and Snedden obtained a value of 0.11 mole fraction⁻¹ for the apparent association constant of ferrocene in CCl_4 . It should be noted that these two values cannot be directly compared since they have been obtained with different inactive solvents and the mole fraction concentration of the active solvent is dependent on the molar volume of the inactive solvent (in some instances, such comparisons have nevertheless been made¹⁷). Comparable values may be obtained by converting the above values to units of mole⁻¹ by means of the appropriate relation.¹⁸ The resulting values are 0.24 mole⁻¹ (Brand and Snedden) and 0.41 mole⁻¹ (this work).

The spectrum of ferricenium tetraphenylborate in ethanolic solutions containing 1 M HClO₄ is shown in Figure 3. No significant change in the spectrum was observed when the solvent was changed from ethanol to 50% ethanol-CCl₄ or 50% ethanol-CHCl₃. The spectrum of ferricenium chloride in 1 M aqueous HClO₄ is identical to that of Figure 3.¹⁹

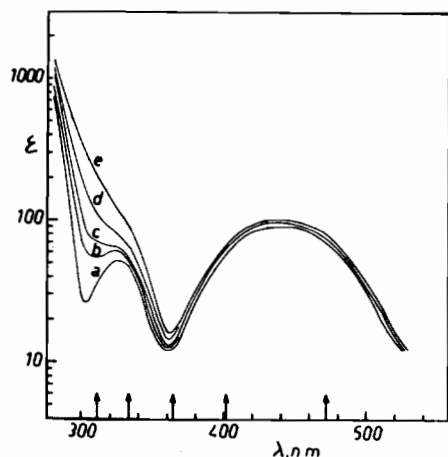


Figure 2. Spectra of ferrocene in CHCl₃-ethanol solvent mixtures: a) pure ethanol, b) 15% CHCl₃, c) 25% CHCl₃, d) 50% CHCl₃, e) pure CHCl₃.

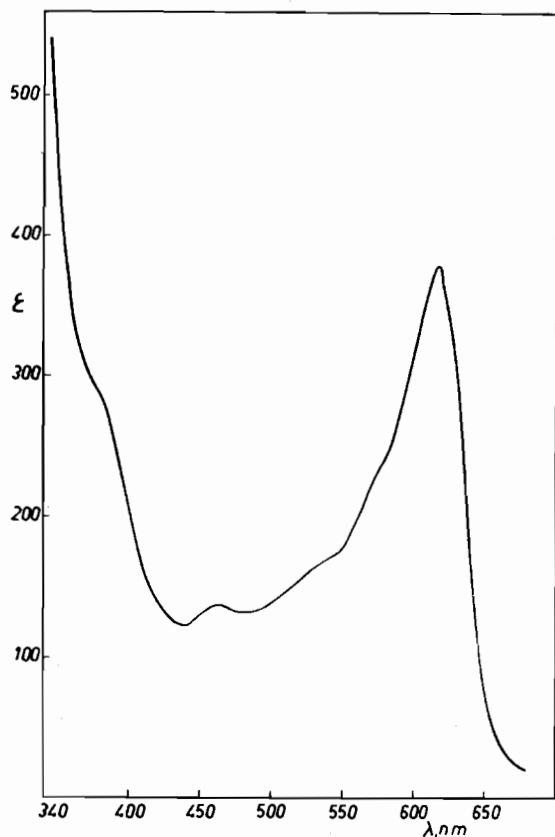


Figure 3. Spectrum of ferricenium tetraphenylborate in ethanol solutions containing 1 M HClO₄.

Photochemical Behavior. Solutions of ferrocene in CCl₄ or CHCl₃ were stable in the dark for long periods. When the solutions were irradiated with ultraviolet light, the formation of a dark precipitate was observed. In agreement with previous observations,⁸ an increase in absorbance with maximum at 617 nm could be observed after very short irradiation periods. This spectral behavior is indicative of the formation of ferricenium cation (Figure 3). Unfortunately, the slight solubility of the cationic product in the pure halocarbon solvents caused an almost immediate clouding of the irradiated solutions, thus preventing any quantitative determination of the ferricenium concentration.

In order to improve the solubility of the cationic product, ethanol-CCl₄ or ethanol-CHCl₃ binary mixtures were used as solvent. It was found that, if the binary solvent contained more than about 40% ethanol, the kinetics of the photochemical formation of ferricenium could be satisfactorily followed. For short irradiation periods (of the order of a few minutes), good zero order plots of ferricenium concentrations vs. irradiation time were obtained. Under these conditions, Cl⁻ ions were formed, but no Fe³⁺ could be detected in the irradiated solutions. For longer irradiation periods, some decomposition of the ferricenium product occurred, causing first the departure from the zero order kinetics and then, the clouding of the irradiated solutions. The quantum yields of the photooxidation reaction were calculated from the slope of the initial zero order plots.²⁰ Analytical tests²¹ performed on the irradiated solutions failed to give any evidence for the formation of phosgene (which was claimed to be one of the products of the photoreaction in CCl₄⁸).

Quantitative experiments were carried out on solutions of ferrocene in 15%, 25%, and 50% halocarbon solvent-ethanol mixtures. Several different wavelengths of irradiation in the range 313-472 nm were used (irradiation was not performed at 254 nm because the light of this wavelength is strongly absorbed by the halocarbon solvents). The quantum yield values, Φ , for the photooxidation of deoxygenated 7.5 × 10⁻³ M solutions of ferrocene are collected in Table I. An increase in the ferrocene concentration brought about a pronounced increase in the quantum yield of photooxidation, as shown by Figures 4 and 5. Aeration of the solutions was also found to cause an increase in the quantum yield values; this effect was almost negligible at low ferrocene concentrations but it became evident at high concentrations (Figures 4 and 5).

Experiments were also performed in the presence of acrylamide monomer. It was found that the pho-

(19) The previously reported spectrum of ferricenium tetrafluoborate in aqueous solution¹ is similar to that of Figure 3, except for being somewhat lower in the 617 nm band and more intense in the 350-500 nm region. This spectral difference is similar to the spectral variations which can be observed in the very initial stages of the decomposition of the ferricenium cation in neutral solutions.

(20) The reliability of such a procedure was checked by performing some experiments in halocarbon-ethanol solutions containing 10⁻¹ M HClO₄. Since in acid medium the ferricenium cation is relatively stable, the zero order kinetics was obeyed for longer irradiation times. The slopes of the zero order plots, however, were identical to those obtained in neutral solutions. Acid solutions were not used in the bulk of the experiments because of the occurrence of a slow thermal oxidation of ferrocene.

(21) F. Feigl, « Spot Tests in Organic Analysis », Elsevier Publishing Company, 1960, p. 449.

(17) R. E. Merrifield and W. D. Phillips, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).

(18) N. Ogimachi, L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, **77**, 4202 (1955).

Table I. Quantum yields of formation of the ferricenium cation in ethanol-halocarbon solvent binary mixtures^a

Solvent	Wavelength of irradiation, nm									
	313		334		365		404		472	
	Φ	Φ_p^b	Φ	Φ_p^b	Φ	Φ_p^b	Φ	Φ_p^b	Φ	Φ_p^b
15% CCl ₄	1.2	0.89	1.1	0.86	0.83	0.69	0.06	0.04	$\leq 10^{-4}$	$\leq 10^{-4}$
25% CCl ₄	1.5	0.89	1.2	0.89	1.1	0.81	0.16	0.11	$\leq 10^{-4}$	$\leq 10^{-4}$
50% CCl ₄	1.8	0.92	1.3	0.95	1.2	0.91	0.22	0.15	$\leq 10^{-4}$	$\leq 10^{-4}$
15% CHCl ₃	0.47	0.40	0.27	0.19	0.03	0.02	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$
25% CHCl ₃	0.71	0.56	0.49	0.36	0.06	0.04	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$
50% CHCl ₃	1.0	0.89	0.71	0.51	0.11	0.10	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$	$\leq 10^{-4}$

^a Ferrocene concentration: $7.5 \times 10^{-3} M$; deoxygenated solutions. ^b Quantum yield values in the presence of $7 \times 10^{-2} M$ acrylamide monomer (primary quantum yields, see Discussion).

tochemical formation of ferricenium was accompanied by the polymerization of acrylamide. The quantum yields of formation of the ferricenium cation were lower than the corresponding values in the absence of acrylamide. The effect of the acrylamide concentration on the quantum yield of photooxidation is shown in Figure 6. As it can be seen, the quantum yield tends towards a lower limit value which is practically reached for acrylamide concentrations higher than $5 \times 10^{-2} M$. The quantum yields, Φ_p ,

for the photooxidation of $7.5 \times 10^{-3} M$ ferrocene in the presence of $7 \times 10^{-2} M$ acrylamide are reported in Table I.

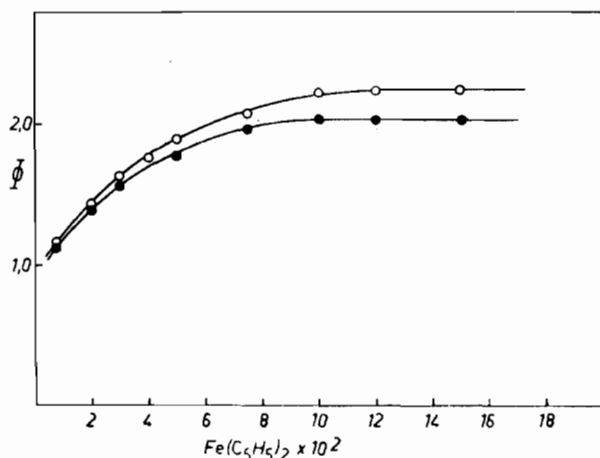


Figure 4. Effect of the ferrocene concentration on the quantum yield of photooxidation. Solvent: 25% CCl₄-ethanol; wavelength of irradiation: 334 nm; ● deoxygenated solution, ○ aerated solution.

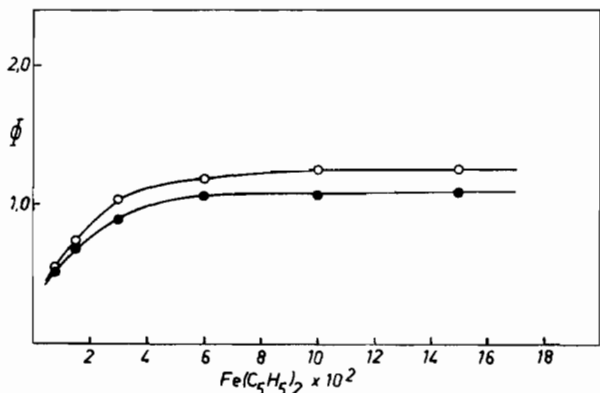


Figure 5. Effect of the ferrocene concentration on the quantum yield of photooxidation: ● deoxygenated solution, ○ aerated solution. Solvent: 25% CHCl₃-ethanol; wavelength of irradiation: 334 nm.

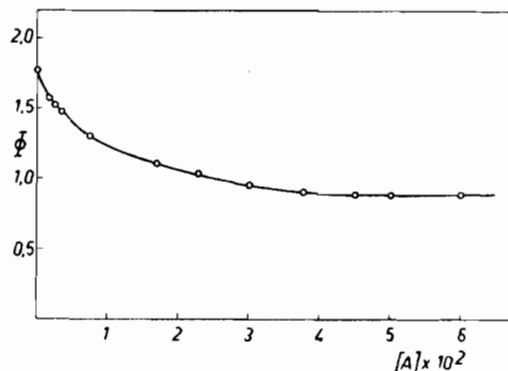


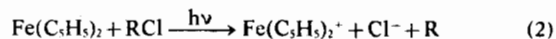
Figure 6. Effect of the acrylamide monomer concentration on the quantum yield of photooxidation. Solvent: 50% CCl₄-ethanol; wavelength of irradiation 313 nm, deoxygenated solution.

Discussion

Brand and Snedden⁸ first observed the initial increase in absorbance at 617 nm during the photodecomposition of ferrocene in CCl₄. They suggested that the primary step of the photodecomposition was a dissociative charge transfer from ferrocene to the halocarbon solvent, yielding a ferricenium ion, a chloride ion and a trichloromethyl radical.

In our experimental conditions, ferricenium is formed by zero order kinetics and no tetrachloroferrate is formed (as shown by the negative tests for Fe³⁺ in the irradiated solutions).

On the basis of these results, one could argue that only the following primary photochemical process occurs:



However, other experimental results clearly show that the mechanism is more complicated than that. In particular, the higher than unity values of the quantum yields of ferricenium production, Φ , and the general increase in the quantum yields with increasing ferrocene concentration (Table I and Figures 4 and 5) indicated that, in addition to the primary photochemical process shown in Eq. 2, some secondary thermal processes must take place which also cause

the oxidation of ferrocene to ferricenium cation. In view of the observed zero-order kinetics of the overall photoreaction, these secondary oxidation processes must be much faster than the primary photoprocess. Thus, these secondary reactions must be different from those relatively slow processes (not observed in our conditions) which eventually cause the formation of tetrachloroferrate ion.³

According to Eq. 2, highly reactive R· radicals (CCl₃ in the case of CCl₄, and CHCl₂ in the case of CHCl₃) are formed in the primary photochemical process. The effect of acrylamide on the photochemical reaction clearly shows that these radical species are responsible for the secondary oxidation of ferrocene. In fact, the capture of the R· radicals by acrylamide (which is the cause of the observed polymerization) brings about a considerable decrease in the quantum yields of photooxidation (Table I and Figure 6). As shown in Figure 6, the quantum yield of photooxidation tends towards a lower limit value with increasing acrylamide concentration. Such lower limit values, Φ_p , (Table I) can be taken as a measure of the quantum yield of the primary photooxidation process.

Primary photochemical process. As to the nature of the primary photochemical process which causes the photooxidation of ferrocene, Brand and Snedden⁸ proposed a dissociative charge transfer from ferrocene to the halocarbon solvent. It should be noted, however, that a photoelectron production followed by dissociative capture of the ejected electron by the halocarbon solvent would give rise to the same photoproducts as the charge-transfer-to-solvent process. Clearly, the main difference between these two mechanisms lies in the nature of the excited states which are thought to be responsible for the photooxidation: according to Brand and Snedden, only the intermolecular ferrocene-to-solvent charge transfer excited states are active, while according to the photoelectron production mechanism some intramolecular excited states of ferrocene may also be involved.²² The lack of ferrocene photooxidation in spectrally « inactive » solvents cannot be taken as a proof of the charge transfer to solvent mechanism, since the photoelectron ejection could be reversible in these solvents. Our experimental results, however, clearly show that the primary photooxidation is the result of the dissociation of ferrocene-to-halocarbon solvent charge transfer excited states, as originally suggested by Brand and Snedden. In fact, the results indicate that, even in spectrally « active » solvents, the intramolecular excitation of ferrocene is completely inefficient.

The inactivity of the intramolecular excitation is evident (Table I) for those wavelengths of irradiation which correspond to the unperturbed ferrocene band with maximum at 440 nm. In the region of overlap-

ping charge-transfer-to-solvent and intramolecular bands, the inactivity of the intramolecular excitation may be checked by quantitative means. In this region, both Φ and Φ_p increase with increasing concentration of the halocarbon solvent in the solvent mixture (Table I). In order to find out whether this increase can be accounted for by the increase in the intensity of the charge-transfer-to-solvent bands relative to the underlying ferrocene bands, the quantum yields Φ and Φ_p of Table I may be corrected so as to be only based on the light intensity absorbed by the intermolecular charge transfer bands. This may be accomplished by dividing the quantum yield values by $(\epsilon - \epsilon_{Fn})/\epsilon$, where ϵ is the apparent extinction coefficient of ferrocene at the wavelength of irradiation in the particular solvent mixture used and ϵ_{Fn} is the corresponding molar extinction coefficient in inactive solvents. The corrected quantum yield values, Φ' and Φ_p' , are reported in Table II. The reasonable constancy of the corrected quantum yields as a function of the halocarbon content of the solvent mixture confirms that the excitation in the intramolecular ferrocene band at 325 nm is inactive.

It should be remarked that the experimental quantum yield values, Φ and Φ_p , are profoundly affected (especially in CHCl₃) by the inner filter effect of the intramolecular ferrocene bands. It may be noticed, for instance, that while the apparent (uncorrected) quantum yields generally decrease with increasing wavelength of irradiation (Table I), the corrected values are reasonably constant throughout the whole charge transfer bands (Table II). Also, the difference between the uncorrected quantum yields in CCl₄ and in CHCl₃ is seen to be mainly a matter of light absorption (at least in the experimental conditions of Tables I and II).

The values of the true (corrected) primary quantum yield, Φ_p' , are of particular interest. Table II shows that, with both acceptor solvents, the mean value of Φ_p' is essentially one. On the basis of a thermodynamic cycle, Brand and Snedden⁸ estimated that the « vertical » ferrocene-to-CCl₄ charge transfer excited state (*i.e.*, the high vibrational level of the excited state which corresponds to the energy of the charge-transfer-to-solvent band maximum) must have an excess energy of about 1 eV relative to the equilibrium state of the primary photoproducts. This means that the dissociation products are likely to diffuse apart with a considerable kinetic energy after the excitation. The photochemical results clearly show that, for both ferrocene-to-CCl₄ and ferrocene-to-CHCl₃ charge transfer excited states, the dissociation products have enough kinetic energy to escape from the solvent cage before undergoing any recombination process. The results show that cage recombination is unimportant even when the dissociation starts from the lowest spectroscopically accessible levels of the charge transfer excited states.

Secondary processes. The details of the secondary oxidation induced by the R· radicals are not easily definable. In principle, the R· radicals could act in two different ways: (i) they could directly oxidize ferrocene, or (ii) they could react with molecular oxygen to give intermediate species capable of oxi-

(22) In the field of coordination compounds, photoelectron production has been observed in a number of cases.²³ In most cases, an excitation leading to an increase in the electronic charge towards the periphery of the complex seems to be necessary in order to obtain the photoelectron ejection.²⁴ In the case of ferrocene, this condition is met since all of the intramolecular absorption bands have some metal-to-ring charge transfer character.^{1,25}

(23) W. L. Waltz and A. W. Adamson, *J. Phys. Chem.*, **73**, 4250 (1969).

(24) Ref. 4, p. 378

(25) G. B. Zaslavskaya, B. M. Yavorskii, N. S. Kochetkova and N. P. Gambaryan, *Doklady Akad. Nauk SSSR*, **179**, 589 (1968).

Table II. Quantum yields of formation of the ferricenium cation calculated on the basis of the fraction of light absorbed by the intermolecular charge transfer band ^a

Solvent	Wavelength of irradiation, nm									
	313		334		365		404		472	
	Φ'	$\Phi_p'^d$	Φ'	$\Phi_p'^d$	Φ'	$\Phi_p'^d$	Φ'	$\Phi_p'^d$	Φ'	$\Phi_p'^d$
15% CCl ₄	1.5	1.1	1.4	1.1	1.4	1.1	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
25% CCl ₄	1.8	1.1	1.5	1.1	1.6	1.1	1.1 ^c	0.78 ^c	<i>b</i>	<i>b</i>
50% CCl ₄	1.9	1.0	1.4	1.1	1.5	1.1	1.2 ^c	0.80 ^c	<i>b</i>	<i>b</i>
15% CHCl ₃	1.5	1.2	1.3	0.94	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
25% CHCl ₃	1.7	1.2	1.5	1.1	1.2 ^c	0.78 ^c	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
50% CHCl ₃	1.6	1.3	1.6	1.1	1.1 ^c	0.85 ^c	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

^a Ferrocene concentration: $7.5 \times 10^{-3} M$; deoxygenated solutions. ^b In these experimental conditions, the fraction of light absorbed by the intermolecular charge transfer band is almost negligible. ^c Owing to the small amount of charge transfer absorption, these values are affected by a considerable experimental error. ^d Quantum yield values in the presence of $7.5 \times 10^{-2} M$ acrylamide monomer (« corrected » primary quantum yields, see Discussion).

dizing ferrocene. Processes of the first kind are known to occur when ferrocene is oxidized during the γ radiolysis of CCl₄^{26,27} (among the radicals formed in this case, Cl \cdot is certainly a very effective one, but oxidation by other radical species, such as CCl₃ \cdot , is also likely to occur²⁷). On the other hand, the formation of peroxy intermediates has been claimed to occur in the γ radiolysis of oxygenated CHCl₃.²⁸ The experimental results show that the secondary oxidation of ferrocene occurs with high efficiency in both aerated and deaerated solutions (Figures 4 and 5).

(26) E. Koerner von Gustorf, M. J. Jun, H. Köller, and G.O. Schenck, *Ind. Uses of Large Radiation Sources, Proc. Conf., Salzburg (Austria), 2, 73 (1963)*, Internat. At. En. Agency, Vienna, 1963.

(27) E. Collinson, F. S. Dainton and H. Gillis, *J. Phys. Chem.* 65, 695 (1961).

(28) J. W. Schulte, J. F. Suttle and R. Wilhelm, *J. Amer. Chem. Soc.*, 75, 2222 (1953).

This indicates that mechanism (i) is operative. However, the small increase in the quantum yields of aerated vs. deaerated solutions clearly indicates that mechanism (ii) also gives some contribution to the overall secondary oxidation. (It is worthwhile noting that the observed increase requires that the intermediate of mechanism (ii) be a more efficient oxidizing species than the radical itself). Finally, it may be noticed that, at high ferrocene concentrations, quantum yield values higher than two are obtained (see Figure 4). The implication is that the secondary oxidation must actually involve several consecutive steps.

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