Naphthalene Sensitization of the Charge Transfer Photochemistry of the Ferrocene-Chloroform System

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The photooxidation of ferrocene in 50% chloroform-ethanol solution has been sensitized by naphthalene. The experimental results suggest that the sensitization occurs by means of an energy transfer process from naphthalene to the ferrocene-chloroform complex producing charge transfer excited states of the latter. The sensitization process is found to be accompained by quenching of the naphthalene fluorescence. Since the Stern-Volmer constants for fluorescence quenching and photosensitization coincide, it is concluded that the energy transfer process responsible for the sensitization is of the singlet-singlet type. As expected on the basis of the proposed sensitization mechanism, the limit value of the sensitization quantum yield is one.

Introduction

In spite of the extensive data available on many aspects of molecular charge transfer complexes,[1] the chemical consequences of light absorption within intermolecular charge transfer bands have only recently gained some attention.[2-5] In the most recent studies, care has been taken to discriminate between intramolecular excitation of the component molecules and excitation of the intermolecular charge transfer transitions of the complex.[4,5] In many cases,[2,3] the use of flash techniques has proven useful in order to detect the transient primary photoproducts of the charge transfer excitation. Recently, triplet states of charge transfer character have been detected by both luminescence[6] and magnetic resonance techiques.[7] In one case, combined flash absorption and emission measurements have shown that the primary photoproducts of the charge transfer excitation are formed by spontaneous ionization of a triplet charge transfer state.[3] So far, sensitization techniques have not been used in the study of the charge transfer photochemistry of

molecular complexes.

Several years ago, Brand and Snedden[6] showed that the spectrum of ferrocene in halocarbon solvents exibits a charachteristic absorption band in the near ultraviolet region which corresponds to ferrocene-to-solvent charge transfer transitions. We have recently investigated the photochemistry of ferrocene in CCl_4-ethanol and $CHCl_3$-ethanol solvent mixtures.[9] It was found that ferrocene-to-halocarbon solvent charge transfer excitation caused the oxidation of ferrocene to ferricenium cation, while the intramolecular excitation of ferrocene was absolutely inefficient. The overall photooxidation reaction was found to consist in a primary dissociative charge transfer within the ferrocene-halocarbon solvent complex

$$Fe(C_5H_5)_2 \cdot RX \xrightarrow{\quad h\nu \quad} Fe(C_5H_5)_2^+ + X^- + R\cdot,$$
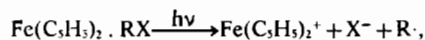
followed by a secondary oxidation of ferrocene to ferricenium induced by the solvent radicals. Since the ferricenium cation produced in the primary process was quite inert in the experimental condition used, the photooxidation quantum yields obtained in the presence of high concentrations of radical scavengers could be taken as a measure of the primary quantum yields. The primary quantum yield based on the intensity of charge transfer light absorption was always 1, indicating that primary recombination after the dissociative charge transfer was negligible.

In the present paper, we report the results of an investigation on the naphthalene sensitization of the charge transfer photochemistry of the ferrocene-chloroform system.

Experimental Section

Materials. Naphthalene "suitable for sensitizer use" was purchased from the Baker Chemical Co. and used without further purification. Reagent grade ferrocene (BDH Chemicals, Poole, England) was twice recrystallized from methanol. The reagent grade acrylamide monomer (BDH Chemicals, Poole, England) was recrystallized from chloroform. All the solvents

(1) a) S. P. Mc Glynn, *Chem. Rev.*, 58, 1113 (1958). b) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.* 13, 107 (1962).
(2) A. M. Halpern and K. Weiss, *J. Phys. Chem.* 72, 3863 (1968).
(3) R. Potashnik, C. R. Goldschmidt and M. Ottolenghi, *J. Phys. Chem.* 73, 3170 (1969).
(4) A. Levy, D. Meyerstein and M. Ottolenghi, *J. Amer. Chem. Soc.*, 92, 418 (1970).
(5) A. Levy, D. Meyerstein and M. Ottolenghi, *J. Phys. Chem.* 75, 3350 (1971).
(6) S. Iwata, J. Tanaka, and S. Nagakura, *J. Chem. Phys.*, 47, 2203 (1967).
(7) H. Hayashi and S. Nagakura, *Mol. Phys.* 13, 489 (1967).

(8) J. C. D. Brand and Snedden, *Trans. Faraday Soc.*, 53, 894 (1957).
(9) O. Traverso and F. Scandola, *Inorg. Chim. Acta*, 4, 493 (1970).

used were of spectroscopic grade.

Apparatus. The 313-nm light used in the sensitization experiments was obtained from a medium pressure mercury vapor lamp (Hanau Q400) by means of an interference filter (Ealing TFP; λ_{max}, 313-nm; T_{max}, 20%; halfwidth, 10 nm). The light was focused on a cell holder containing a 1 cm spectrophotometer cell filled with 3 ml of solution. During the irradiation, the solutions were thermostated at 25° and stirred by bubbling pure nitrogen from a glass capillary. The incident light intensity was measured by means of the ferric oxalate actinometer.[10] Spectrophotometric measurements were performed with an Optica CF4 NI spectrophotometer. Luminescence measurements were performed with a CGA DC 3000/I spectrofluorimeter, adapted to allow frontal illumination of the sample solution.

Procedures. The solvent used was a 50% mixture of chloroform and ethanol. The sensitization experiments were performed by irradiating the sample solution with 313 nm light and measuring the 617 nm absorbance as a function of the irradiation time. In several experiments, most of the dissolved oxygen was removed from the solution prior to the irradiation by saturation with pure nitrogen. These nitrogen saturated solutions are thereafter referred to as "deaerated solutions". During the irradiation, the deaerated or aerated solutions were stirred by a stream of nitrogen or air, respectively. Deaerated solutions were used in the experiments carried out in the presence of acrylamide. In these experiments, the polymerization process was looked for by diluting the irradiated solution with excess methanol (10:1 in volume). When polymerization occurred, the formation of a voluminous white precipitate was observed. The experiments on the quenching of the naphthalene fluorescence were performed at the same wavelength of irradiation and in the same concentration conditions as the sensitization experiments. Due to the very high absorbance of the solutions at the wavelength of irradiation, the method of frontal illumination[11] was preferred to the right-angle one.

Results

The spectra of naphthalene and ferrocene in 50% chloroform-ethanol solution are shown in Figure 1, together with the spectrum of ferrocene in pure ethanol.

Irradiation of deaerated solutions of naphthalene in 50% chloroform-ethanol with 313 nm light did not cause any appreciable decomposition. If the irradiation of naphthalene was performed in the presence of $5 \times 10^{-2}M$ acrylamide monomer, no polymerization of acrylamide was observed.

Sensitization experiments were performed using 50% chloroform ethanol solutions containing 0.187 M

(10) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, *A235*, 518 (1956).
(11) C. A. Parker, « Photoluminescence of Solutions », Elsevier, Amsterdam, (1968).

naphthalene and $10^{-3}-5 \times 10^{-3}M$ ferrocene. In these conditions, the light absorption by ferrocene was absolutely negligible (less than 1% of the total absorbed light intensity). When such solutions were irradiated with 313 nm light, an increase in absorbance with maximum at 617 nm was observed, indicating the occurence of an efficient oxidation of ferrocene to ferricenium cation. Analytical tests performed on the irradiated solutions indicated that formation of Cl^- ions accompanied that of the ferricicenium cation.
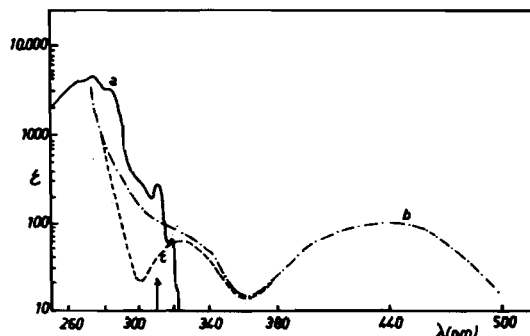

Figure 1. Absorption spectra of: (a) naphthalene in 50% Chloroform-ethanol; (b) Ferrocene in 50% Chloroform-ethanol; (c) Ferrocene in ethanol. The arrow indicates the wavelength of irradiation used (313 nm).

If the irradiation was limited so that only a small percentage of the initial ferrocene concentration was oxidized, the ferricenium ion formation obeyed a zero-order kinetics, and the apparent quantum yield (*i.e.* that based on the light intensity absorbed by naphthalene) could be easily calculated. In deaerated solutions the apparent quantum yields increased with increasing ferrocene concentration (Figure 2, curve A).

Sensitization experiments performed on aerated solutions gave results similar to those obtained for the corresponding deaerated experiments, but with considerably lower apparent quantum yields (Figure 2, curve C).
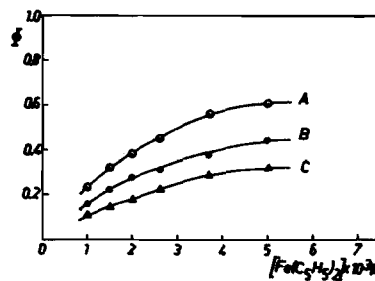

Figure 2. Dependence of the apparent quantum yield of the sensitized photooxidation on the ferrocene concentration: (A) deaerated solution; (B) deaerated solution containing $5 \times 10^{-2}M$ acrylamide; (C) aerated solution.

Photosensitization experiments were also performed with deaerated solutions in the presence of $5 \times 10^{-2}M$ acrylamide monomer. In these conditions, photosen-

sitized oxidation of ferrocene was again observed. The apparent quantum yield, however, was lower than the corresponding one obtained in the absence of acrylamide (Figure 2, curve B). An efficient polymerization of the acrylamide was observed to accompany the photosensitized oxidation of ferrocene.

Sensitization experiments performed in pure ethanol or in pure cyclohexane failed to give any evidence for photooxidation of ferrocene.

Experiments were also performed to investigate the effect of ferrocene on the naphthalene fluorescence. These measurements were carried out in the same concentration conditions as the sensitization experiments. An evident quenching effect of ferrocene on the naphthalene fluorescence was observed. The results obtained in deaerated solutions are shown in the Stern-Volmer plot of Figure 3. The slope of this plot gives a quenching constant for ferrocene of 200 liter mole^{-1}. Addition of $5\times10^{-2}M$ acrylamide did not quench the emission of 50% chloroform-ethanol solutions of naphthalene.
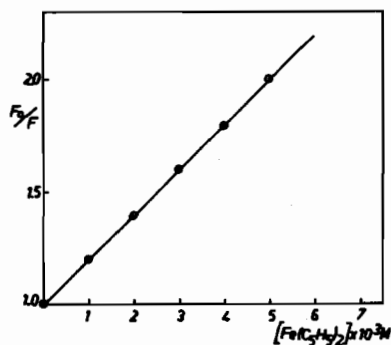

Figure 3. Stern-Volmer plot of the quenching of the naphthalene fluorescence by ferrocene in 50% chloroform-ethanol solution.

Discussion

The experimental results clearly show that in 50% chloroform-ethanol solutions light absorption by naphthalene causes the oxidation of ferrocene. Now, the question arises as to the role (chemical or physical) played by naphthalene in the sensitization process. In principle, the most plausible sensitization mechanisms seem to be:

(i) direct reaction (electron transfer) between the photoexcited naphthalene and ferrocene;

(ii) reaction between the excited naphthalene and chloroform to give radical species capable of oxidizing ferrocene;[12]

(iii) energy transfer from naphthalene leading to the population of charge transfer states of the ferrocene-chloroform system.

Pertinent experimental results are: 1) the formation of Cl$^-$ ions accompanying the sensitized photooxidation, 2) the lack of any photooxidation observed in

spectrally inactive solvents, 3) the lack of radical formation observed by irradiating naphthalene in the absence of ferrocene, 4) the behavior of acrylamide and its effect on the photosensitized oxidation of ferrocene. Results 1, 2, and 4 contrast with mechanism (i). Results 3 and 4 (note that the effect of acrylamide is only one of partial reduction of the sensitization quantum yields) make mechanism (ii) unlikely. By contrast, all the above results agree with hypothesis (iii). More generally, it may be observed that the experimental features of the naphthalene photosensitized oxidation of ferrocene are essentially identical (with the exception of the oxygen influence, see below) to those of the direct photooxidation reaction.[9] This is entirely consistent with a mechanism which assigns to naphthalene the role of a genuine sensitizer of the charge transfer photochemistry of the ferrocene-chloroform system.

According to this mechanism, a charge transfer state of the ferrocene-chloroform system is to be reached following the energy transfer process from naphthalene. In principle, the excited charge transfer state could be reached either directly in the energy transfer process or indirectly from an intramolecular excited state of ferrocene, first populated by the energy transfer process. The first hypothesis seems to be by far the more probable one. In fact, the direct photooxidation results showed that conversions from intramolecular excited states of ferrocene to charge transfer states of the ferrocene-halocarbon solvent complex are completely inefficient.

As to the multiplicity of the excited state of naphalene responsible for the energy transfer, two possibilities may be considered. Generally speaking, sensitization in fluid solution is most often achieved by means of triplet-triplet energy transfer processes. With acceptor concentrations of the order of $10^{-2} M$, however, donors with relatively long lived singlets can also give rise to energy transfer processes of the singlet-singlet type. In our case, the singlet-singlet transfer is energetically allowed, since the intermolecular charge transfer absorption of the ferrocene-chloroform complex (compare curves a and b in Figure 1) extends down to about 370 nm,[9] i.e., to a considerably lower energy than the origin of the naphthalene absorption. As far as the energetics of a hypothetical triplet-triplet transfer is concerned, nothing can be definitely said since he energy of the triplet charge transfer state is not known; actually, it seems unlikely that the singlet-triplet separation for the charge transfer states is so great that the transfer from the triplet naphthalene (E = 62 kcal) becomes exothermic.
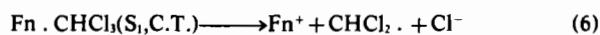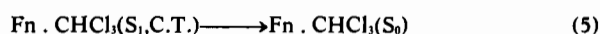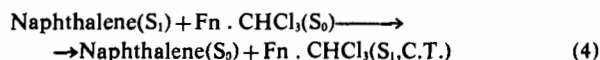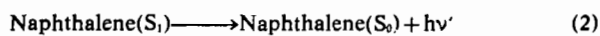
From an experimental point of view, the observed fluorescence quenching strongly suggests that the sensitization occurs by means of a singlet-singlet energy transfer process. It may be pointed out that the observed value of the fluorescence quenching constant (200 liter mole^{-1}) is similar to that obtained by Dubois and Stevens for the collisional singlet-singlet energy transfer from naphthalene to biacetyl in hexane solution.[13] The evident decrease in the sensitization

(12) Evidence for oxidation of ferrocene by radical species produced by halocarbon solvents has been obtained in the study of direct photoreaction[9].

(13) J. T. Dubois and B. Stevens, in « Luminescence of Organic and Inorganic Materials » (H. P. Kallmann and G. M. Spruch, eds., Wiley, New York, N. Y., 1962).

quantum yields brought about by the presence of oxygen is consistent with the known quenching ability of oxygen towards the naphthalene singlets.[14,15]

Thus, we conclude that the most probable mechanism is one of singlet-singlet energy transfer, which may be schematized as follows:

$$\text{Naphthalene}(S_0) \xrightarrow{h\nu} \text{Naphthalene}(S_1) \qquad (1)$$

$$\text{Naphthalene}(S_1) \longrightarrow \text{Naphthalene}(S_0) + h\nu' \qquad (2)$$

$$\text{Naphthalene}(S_1) \longrightarrow \text{Naphthalene}(S_0) \qquad (3)$$

$$\text{Naphthalene}(S_1) + \text{Fn} . \text{CHCl}_3(S_0) \longrightarrow$$
$$\longrightarrow \text{Naphthalene}(S_0) + \text{Fn} . \text{CHCl}_3(S_1, C.T.) \qquad (4)$$

$$\text{Fn} . \text{CHCl}_3(S_1, C.T.) \longrightarrow \text{Fn} . \text{CHCl}_3(S_0) \qquad (5)$$

$$\text{Fn} . \text{CHCl}_3(S_1, C.T.) \longrightarrow \text{Fn}^+ + \text{CHCl}_2 . + \text{Cl}^- \qquad (6)$$

$$\text{CHCl}_2 . + \text{Fn} \longrightarrow \text{Fn}^+ + \text{Products} \qquad (7)$$

where $\text{Fn} = \text{Fe}(C_5H_5)_2$, $\text{Fn}^+ = \text{Fe}(C_5H_5)_2{}^+$.

The direct photooxidation study has shown that the presence of $5 \times 10^{-2} M$ acrylamide is sufficient to quench completely the secondary oxidation of ferrocene initiated by the CHCl_2 radicals. Therefore, in these conditions, process (7) is unimportant, and the, concentration dependence of the observed photooxidation quantum yields is of the simple form:

$$\Phi = \frac{k_4[\text{Fn} . \text{CHCl}_3]}{k_2 + k_3 + k_4[\text{Fn} . \text{CHCl}_3]} \cdot \frac{k_6}{k_5 + k_6} \qquad (8)$$

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{lim}}} \left(1 + \frac{1}{K_s \text{Fn} . \text{CHCl}_3}\right) \qquad (9)$$

where $\Phi_{\text{lim}} = \dfrac{k_6}{k_5 + k_6}$ and $K_s = \dfrac{k_4}{k_2 + k_3} = k_4 \tau_D$.

A plot of the reciprocal quantum yields obtained in the presence of $5 \times 10^{-2} M$ acrylamide vs. the reciprocal ferrocene concentration is shown in Figure 4. The linearity is satisfactory.[16] The ratio of intercept to slope gives a sensitization constant, K_s, of 180

liter mole^{-1}. This may be compared with the Stern-Volmer constant of 200 liter mole^{-1} obtained from the naphthalene fluorescence quenching. The agreement between these two values lends definite support to the hypothesis of a singlet sensitization mechanism. Since the same singlet charge transfer state is reached by either direct or sensitized photooxidation, no differences are to be expected in the two cases even from a quantitative point of view. Actually, the limit primary quantum yield of the sensitized reaction is appreciably 1 (Figure 4), i.e., it coincides with that of the direct photooxidation.
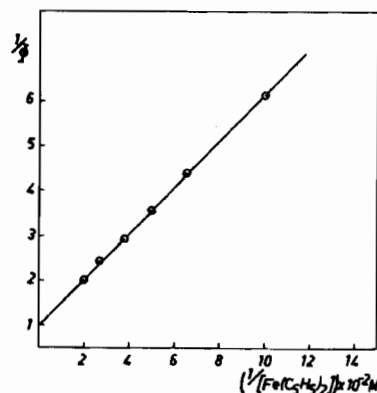

Figure 4. Plot of the apparent sensitization quantum yields obtained in deaerated solution according to Eq. 9.

Finally, it may be pointed out that both the unit value for the limit sensitization quantum yield and the observed coincidence of the sensitization and quenching constants suggests that energy transfer from singlet naphthalene to unreactive intramolecular singlet excited states of ferrocene is relatively inefficient in our conditions. Tentatively, this effect could be ascribed to steric factors that could make the overlap with naphthalene more favorable for intermolecular charge-transfer-to-solvent states than for intramolecular excited states of ferrocene.

(14) I. B. Berlman and T. A. Walter, *J. Chem. Phys.,* 37, 1888 (1962).
(15) The direct photoxidation results[9] have shown that the photooxidation of ferrocene in chloroform is itself oxygen dependent. For ferrocene concentrations of the order of those used in the present work, however, such an oxygen effect is small enough (see Figure 5 of ref. 9) to be safely overlooked in this discussion.

(16) It may be noticed that the concentration of the Fn.CHCl$_3$ complex is a constant fraction of the total ferrocene concentration. Thus, the same Stern-Volmer type of concentration dependence is to be expected either using the total ferrocene concentration or the Fn.CHCl$_3$ complex. It is understood that the true sensitization constant may be larger than the K_s value obtained from Figure 4 by an amount depending on the magnitude of the association constant for the ferrocene-chloroform system.