ELECTRON TRANSFER PROCESSES IN THE PHOTOLYSIS OF FERROCENE IN SOLUTION

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Summary

When ferrocene in ethanol or in cyclohexane and in the presence of N_2O is irradiated with 253.7 nm radiation, a yield of N_2 is obtained which is a continually increasing function of N_2O concentration. At wavelengths $\geqslant$ 313 nm, no N_2 is formed. In ethanol, changes in the electronic spectrum are clearly observable after prolonged irradiation with 253.7 nm radiation with N_2O present. Alkyl substituents cause the N_2 yields to increase and their effect appears to run in parallel to their influence on the half-wave potential.

For ferrocene and all substituted compounds used, the N_2 yields are shown to be consistent with a mechanism involving electron transfer to N_2O from a photoexcited species in competition with its spontaneous deactivation. In all cases the quantum yield of this photoexcited species is found to be significantly less than unity, so it is deduced that it is not the primary photoexcited state.

Introduction

The photochemical behaviour of metallocenes has been dealt with in two recent reviews [1, 2] and is the subject of an increasing number of experimental studies. Whereas in the flash photolysis of ferrocene vapour, Thrush [3] detected the cyclopentadienyl radical, formed presumably by the destruction of the molecule, ferrocene appears to be photochemically stable in many solvents. Tarr and Wiles [4] observed no decomposition in de-aerated solutions in decalin or in 1-propanol and von Gustorf and Grevels [2] report similar negative results of Köller [5] in the solvents cyclohexene, acetone and 2-propanol. However, the type of mercury lamp and the photolysis arrangements used by Tarr and Wiles [4] were such that negligible radiation of wavelength less than 290 nm could be absorbed. It was also found [4] that substituents such as benzoyl render the molecule less photostable, but since a range of exciting wavelengths was used, it is not clear whether

this results from changes in the absorptions or from substituent effects on the behaviour of an excited state.

The absorption spectrum of ferrocene in hydroxylic or hydrocarbon solvents consists of three main bands, with peaks at 440, 325 and < 220 nm, where only the last mentioned is a strong absorption. Detailed spectroscopic investigations [6, 7], which reveal at least 11 distinct electronic bands, agree in assigning the 440 nm peak to a forbiden $d-d$ transition, the 325 nm peak to a forbidden transition, probably of an intramolecular charge transfer type and the bands below 290 nm to other intramolecular charge transfer transitions, probably metal to ring. Since in some of the studies in solution these bands were not excited, it is conceivable that the apparent differences in photolytic behaviour are more a function of wavelength than of phase.

In halogenated solvents such a CCl_4 or $CHCl_3$, ferrocene shows an additional band at 307 nm, which Brand and Snedden [8] assigned to a dissociative intermolecular charge transfer:

$$Fn + RX \xrightarrow{h\nu} Fn^+ + X^- + R$$
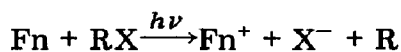
where Fn represents the ferrocene molecule. This assignment readily explains the marked instability of ferrocene in such solvents except in darkness. Traverso and Scandola [9] have studied the photochemistry of solutions of ferrocene plus CCl_4 (or $CHCl_3$) in ethanol and estimate that, at wavelengths of 313 to 404 nm, the observed yield of ferricenium ion corresponds to a quantum yield of about unity on the basis of light absorbed within this intermolecular CT band. More recent studies [10] suggest that in this system ferricenium ions can also be produced by irradiation with shorter wavelengths, not absorbed within this CT band.

It was desired to check the effect on ferrocene in solution of lower wavelength ultra-violet light, corresponding to the main absorption band, and also to clarify why substituents should render the molecule more light-sensitive. Since ferrocene has a low ionization potential, recently determined [11] as 6.88 eV, and is easily oxidized chemically to ferricenium ion, the photoionization of ferrocene in inert solvents would appear to be feasible and so the possibility of the production of solvated electrons was specially investigated, using N_2O which is a convenient scavenger for solvated electrons and the yield of N_2 produced enables quantum yields to be readily measured:

$$e_{sol}^- + N_2O \rightarrow N_2 + O^- \tag{1}$$
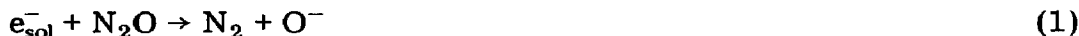
Experimental

Materials

Nitrous oxide (B.O.C. anaesthetic grade) was purified by repeated trap-to-trap distillation, retaining the middle fraction and was degassed at

−196 °C immediately before use. Ferrocene (Koch-Light laboratory grade) was purified by recrystallization from methanol and by twice subliming under vacuum. The substituted ferrocenes, provided by Dr. W. E. Watts of this department, were also sublimed under vacuum. Analar grade ethanol was used without further purification. Cyclohexane (B.D.H. laboratory grade) was stirred with HNO_3/H_2SO_4 nitrating mixture, washed with NaOH solution, then with water, dried with $CaCl_2$ and then by refluxing with sodium, and finally fractionally distilled. Other chemicals used were of Analar grade.

Photolysis procedure

The quartz photolysis cells were similar to those described by Cook and Logan [12] and cells and all apparatus used in preparing solutions were cleaned by the procedure described there.

Solutions of a ferrocene compound were freshly made up for each experiment, degassed by six cycles of freeze−pump−thaw and, if desired, equilibrated with N_2O at a known pressure at 25 °C. During irradiation the cell was thermostated at 25 °C and subsequently the permanent gases were collected and measured. Irradiation times were chosen so that gas yields were approximately 0.5 μmol. Mass spectrometric analysis revealed that only N_2 was present.

The irradiation with 253.7 nm radiation was performed using an Engelhard Hanovia low pressure mercury lamp, with the 184.9 nm line removed by a water filter. The dose rate at the exciting wavelength was measured on each occasion by ferrioxalate actinometry [13], as previously described [12]. Light of 313 and 325 nm wavelength was isolated from the output of a Bausch and Lomb super pressure mercury arc lamp (200 W) using a Bausch and Lomb grating monochromator, and dose rates were also measured by ferrioxalate actinometry.

In calculating N_2O concentration, the solubilities were taken as 1.51×10^{-4} M Torr^{-1} for ethanol [14], interpolating the data given, and 1.37×10^{-4} M Torr^{-1} for cyclohexane [15].

Measurement of half-wave potentials

The half-wave potentials of ferrocene and most of the derivatives were measured by cyclic voltammetry using a Heathkit Polarograph Module, incorporating a saturated calomel reference electrode and a platinum foil working electrode, and an $X-Y$ recorder. Solutions ($\sim 10^{-3}$ M) were made up in 95% aqueous ethanol containing 10^{-1} M $NaClO_4$ and were purged with N_2 before scanning. The curves obtained were reproducible and symmetrical, indicating the reversibility of the redox process.

Where a literature value was available, it agreed with our value within 0.01 V.

Results and Discussion

When solutions of ferrocene, in ethanol or in cyclohexane, and containing N_2O at a known concentration, were illuminated with 253.7 nm radiation at 25 °C, the yield of N_2 was found to be proportional to the number of quanta absorbed. In measuring quantum yields, low concentrations of ferrocene giving an absorbance in a 2 cm cell of about 1.5 were used to obviate skin effects and to minimize the absorption of the longer wavelength mercury lines emitted at low intensities. Quantum yields were calculated on the basis of 253.7 nm light absorbed in the solution.
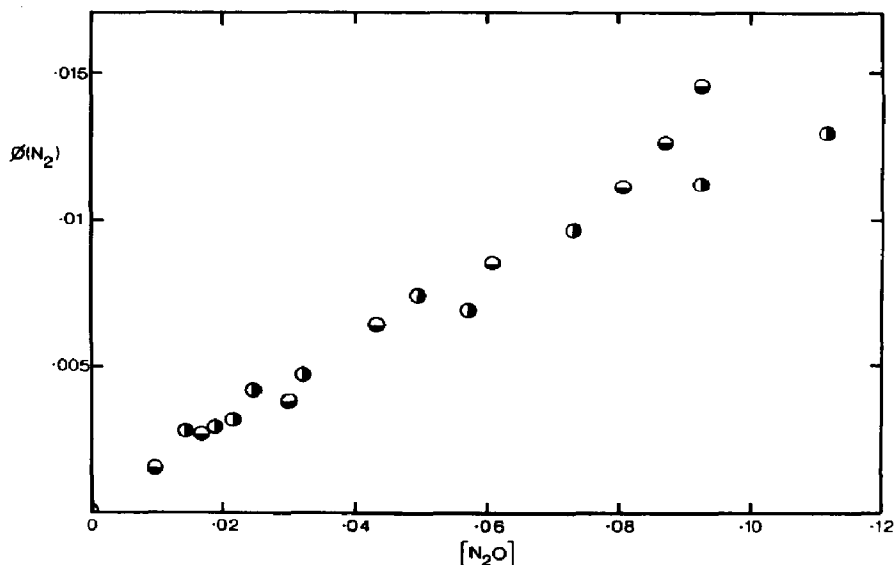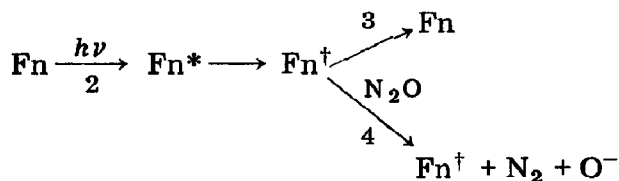

Fig. 1. Dependence of $\Phi(N_2)$ on N_2O concentration in the 253.7 nm photolysis of 4.4 × 10^{-4} M solutions of ferrocene at 25 °C in ethanol (◑) and in cyclohexane (◒).

For both solvents, the quantum yield was found to increase continuously as N_2O concentration was increased, as shown in Fig. 1. This behaviour represents a considerable contrast with that found in the photolysis of halide ions [16 - 18], ferrocyanide ion [19] or phenolate ion [20], where $\Phi(N_2)$ was effectively at a plateau value when N_2O concentration exceeded approximately 5 × 10^{-3} M, and suggests that the solvated electron is not produced in the present system. The hypothesis that it is produced requires that the back-reaction — presumably geminate — and the reaction with solute are on competing terms over a much larger range of concentrations than has been observed previously. In addition, our flash photolysis studies [21] of ferrocene in both solvents showed no transient absorption in the range 575 - 775 nm, so it was concluded that the solvated electron is not produced here and that the N_2 is produced by a reaction other than (1).

An alternative is direct electron transfer from a photoexcited ferrocene state to N_2O, as outlined below:

$$Fn \xrightarrow[2]{h\nu} Fn^* \longrightarrow Fn^\dagger \overset{3}{\underset{4}{\begin{array}{c} \nearrow Fn \\ \searrow N_2O \\ \searrow Fn^\dagger + N_2 + O^- \end{array}}}$$

Thus the quantum yield of N_2 is given by:

$$\Phi(N_2) = \Phi_{Fn\dagger} \frac{k_4[N_2O]}{k_3 + k_4[N_2O]}$$

which leads to the relation:

$$\frac{1}{\Phi(N_2)} = \frac{1}{\Phi_{Fn\dagger}} \left(1 + \frac{k_3}{k_4[N_2O]} \right)$$

The reciprocal plots, for ferrocene in both solvents, are shown in Fig. 2. These are both linear, within the limits of error of the experimental quantum yields ($\pm$ 6%). The intercepts at zero $[N_2O]^{-1}$, = 0,33 ± 6 in ethanol and 6.1 ± 2 in cyclohexane, indicate that $Fn^\dagger$, the photoexcited ferrocene participating in electron transfer to N_2O, has a quantum yield significantly less than unity and thus is not the excited singlet produced directly by optical excitation.

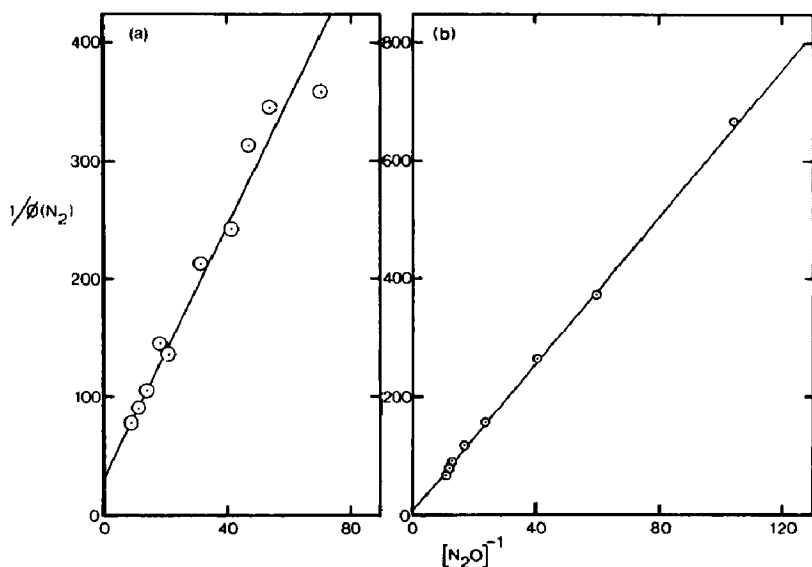Fig. 2. Plots of reciprocal quantum yield of N_2 against reciprocal N_2O concentration for solutions of ferrocene in (a) ethanol and (b) cyclohexane.

Clearly, the above mechanism is not unique in predicting a linear relationship between $\Phi(N_2)^{-1}$ and $[N_2O]^{-1}$, but the simple alternatives appear at odds with other known facts and need not be discussed here.

Other photolysis experiments were carried out at wavelengths of 313 and 325 nm, using ferrocene solutions in ethanol with an absorbance of 1.5

at the wavelength of excitation, and saturated with N_2O at 600 Torr. In neither case was any N_2 production observed and at both wavelengths the quantum yield can be stated to be less than 10^{-4}. Thus, in terms of the proposed mechanism, $Fn^\dagger$ is not produced by excitation in the 325 nm band.

The effects of 253.7 nm radiation on the electronic spectrum of the solutions was monitored. It was found that there was no change in the electronic spectrum of de-aerated ferrocene solutions in cyclohexane or in ethanol when subjected to prolonged irradiation of up to 0.08 Einstein/l. This agrees with and extends the findings of Tarr and Wiles [4]. But in the presence of N_2O, changes were observed, as illustrated in Fig. 3, which demonstrates that in ethanol there appears additional absorption over the whole wavelength range, with a peak in the difference spectrum at about 290 nm.
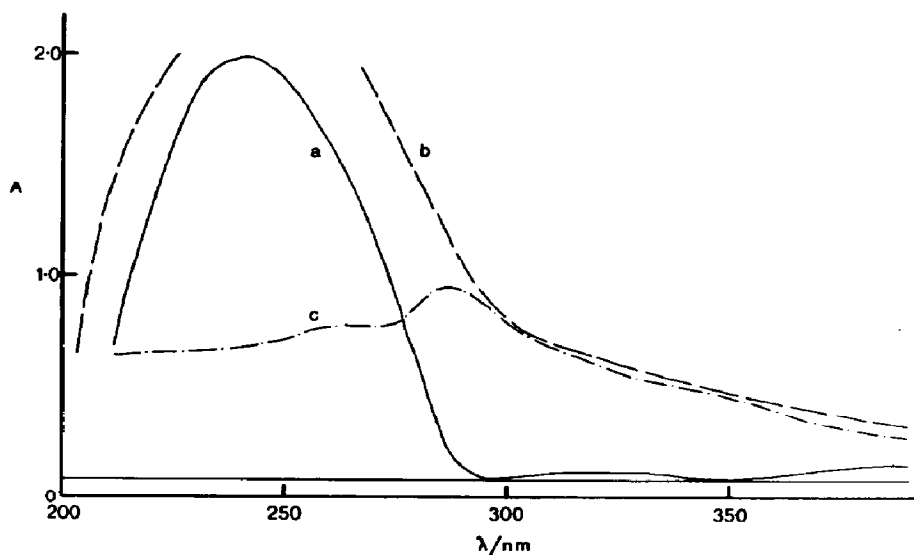

Fig. 3. Spectra of ferrocene solutions in ethanol. (a) Initial spectrum of solution; (b) spectrum after irradiation with 253.7 nm light in presence of N_2O; (c) spectrum of (b) using (a) as reference solution.

However, the actual spectrum of the photolysis products is not easily determined, since the decrease in ferrocene concentration by photolysis is not readily obtained. It was noticed that when the solution was allowed to stand after prolonged irradiation, a dark-brown solid gradually settled out, so some of the decreased transmission is possibly due to suspended particles. Although there is no clear indication of the ferricenium ion, its presence cannot be entirely discounted since its strong peak 253 nm coincides with considerable ferrocene absorption. In any case, the initial formation of the ferricenium ion cannot be ruled out since it would be subsequently subjected to oxidation by O^-.

Additional studies were carried out on several substituted ferrocenes in ethanolic solution, using 253.7 nm light. With N_2O present, quantitative

TABLE 1

Half-wave potentials of ferrocene compounds and data from the 253.7 nm photolysis of these compounds in ethanol at 25 °C with N_2O present

Compound	$\Phi(N_2)$ at $[N_2O] = 0.08\ M$	$E_{1/2}/V$	Source of $E_{1/2}$ value	$\Phi_{Fn\dagger}$	$k_3k_4^{-1}/M$
Acetylferrocene	0.0036	+0.60	22, 23, 24	0.007	0.08
Phenylferrocene	0.0050	+0.37	23, 24	0.024	0.31
Ferrocene	0.0102	+0.34	22	0.031	0.16
Methylferrocene	0.0127	+0.28	23	0.051	0.25
1,1'-Dimethylferrocene	0.0137	+0.24	22	0.056	0.25
1,2-Dimethylferrocene	0.0137	+0.23	this work	0.035	0.13
1,1'-Di-t-butylferrocene	0.0160	+0.26	this work	0.048	0.15

measurements of N_2 yields indicated that in all cases the behaviour was of the same nature as was observed for ferrocene, *viz.* a continual increase in $\Phi(N_2)$ as N_2O concentration was increased. As a measure of the relative yields from each compound under the same conditions, the values of $\Phi(N_2)$ interpolated at 0.08 M N_2O are listed in Table 1. These indicate, in general, that the yield is increased by electron-repelling and reduced by electron-attracting substituents. For two alkyl groups, the effect appears to be cumulative and independent of whether they are on the same or on different rings.

Since this behaviour resembles the substituent effect on the half-wave potential, where these values were known, the half-wave potentials of the remaining compounds were determined. The values for all the compounds used are listed in Table 1, and show that $\Phi(N_2)$ rises as $E_{1/2}$ falls and *vice versa*. A plot of these quantities shows that the points do not all lie on one smooth curve, so that there is not perfect correlation. A distinction may be made between the "transparent" alkyl substituents, which can influence the quantum yield only by electronic effects on the photoexcited species involved, and the chromophores acetyl and phenyl, of which, however, only the latter appears anomalous in respect of the correlation. The di-t-butyl compound also shows slight deviation from the correlation curve. Thus for the ferrocene nucleus there appears to be a close similarity between substituent effects on electron loss from the ground state (measured by $E_{1/2}$) and on electron transfer from a photoexcited state [measured by $\Phi(N_2)$].

For each of these substituted ferrocenes, the reciprocal plots were linear, within the limits of accuracy of the experimental quantum yields as illustrated in Fig. 4. Thus all the data are consistent with the proposed mechanism. In each case, the intercept was substantially greater than unity, indicating that $\Phi_{Fn\dagger} < 1$. Since the experimental quantum yields of N_2 have the same percentage error limits, the best values of slope and intercept for these plots were derived by applying a formula [25] which minimizes *relative* errors in $\Phi(N_2)$ in the same way as the familiar regression formula would min-
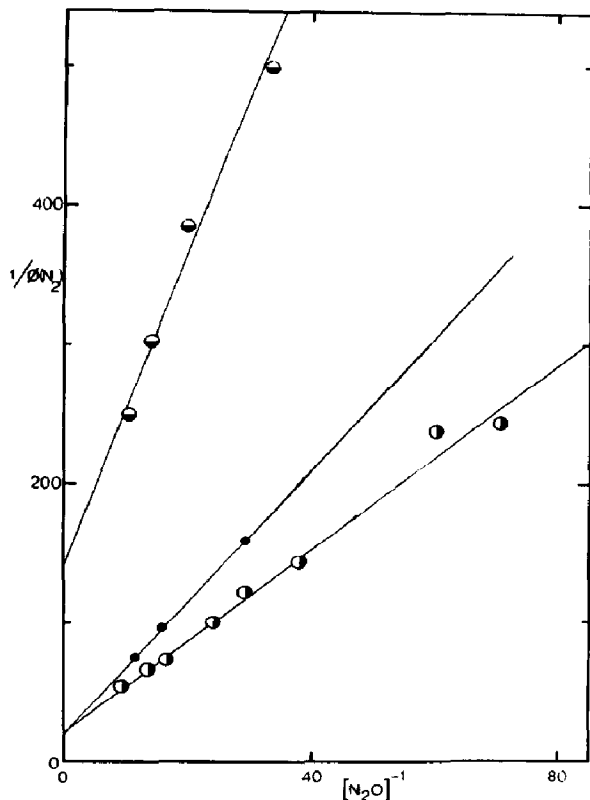
Fig. 4. Plots of reciprocal quantum yield of N_2 against reciprocal N_2O concentration for solutions at 25 °C in ethanol of 1,1'-di-t-butylferrocene (◑), methylferrocene (●) and acetylferrocene (◓).

imize *absolute* errors in $1/\Phi(N_2)$. The values of $\Phi_{Fn\dagger}$ and of k_3/k_4 so obtained are also listed in Table 1. Even for the alkyl compounds, neither appears to be constant. In terms of the proposed mechanism, an alkyl substituent might increase the quantum yield of N_2 obtained from ferrocene (a) by increasing $\Phi_{Fn\dagger}$,(b) by increasing k_4, the rate constant for $Fn^\dagger + N_2O$, or (c) by increasing the lifetime of $Fn^\dagger$, *i.e.* decreasing k_3. The data do not enable us to reach any clear conclusion on this point, though it does appear that in the case of acetyl, $\Phi_{Fn\dagger}$ is substantially less than for other substituents.

From the values of k_3/k_4 we may deduce a minimum value for the lifetime of $Fn^\dagger$. In ethanol, the formula for the rate constant of a diffusion controlled reaction, $k_D = 8\,RT/3000\eta$, gives an upper limit of $6.1 \times 10^9\ M^{-1}\ s^{-1}$ for k_4 and thus for ferrocene we have $\tau = k_3^{-1} \geqslant 1.0 \times 10^{-9}$ s.

Acknowledgements

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