Photochemistry of the Charge-transfer Complex between Ruthenocene and Carbon Tetrachloride

By **Peter Borrell** * and **Eric Henderson**, Department of Chemistry, Keele University, Staffordshire ST5 5BG

The photolysis and naphthalene-photosensitised reaction of the charge-transfer complex between ruthenocene and carbon tetrachloride has been studied in solutions of methanol and carbon tetrachloride. The reaction forms the ruthenocenium cation in the primary process. The overall quantum yield of formation at 313 nm is 0·72, and at 366 nm is 0·52. By studying the partial inhibition of the reaction with $SmCl_3$, oxygen, and acrylamide, it was possible to show that, at 313 nm, ϕ for the decomposition by the singlet state is 0·24 and by the triplet state is 0·40.

The naphthalene-photosensitised reaction proceeds through a triplet state. The reaction is inhibited at higher concentrations by the competitive quenching of the naphthalene singlet state by ruthenocene itself.

The association constant for the complex is 1·80 mol fraction^{-1} (0·012 l mol^{-1}) at 23 °C. A spectrum is recorded for the ruthenocenium cation.

FERROCENE is photostable in hydrogen solutions, but in halocarbons, such as CCl_4, a charge-transfer complex is formed with the solvent, and the complex can be photo-oxidised. The object of this work was to examine the corresponding reactions of ruthenocene. Brand and Sneddon[1] first showed that the prominent new absorption at 307 nm, seen when ferrocene is dissolved in CCl_4, is due to a charge-transfer complex. von Gustorf and his co-workers[2,3] found that in photolysis of the complex, ferrocinium tetrachloroferrate is formed $[Fe(cp)_2][FeCl_4]$ (cp = cyclopentadienyl). Traverso and Scandola[4] estimated the quantum yield for the photo-oxidation to be nearly 1, and they also studied the naphthalene-photosensitised reaction.[5] Akiyami, Sugimori, and Hermann[6,7] examined the photoreaction in mixtures of CCl_4 and ethanol, and suggested a reaction scheme to account for the formation of ethylferrocenecarboxylate in the presence of hydroxylic solvents. The overall processes are similar to those occurring[8] in the γ radiolysis of ferrocene in CCl_4. The partly radical nature of the reaction is shown[9] by the fact that the ferrocene–CCl_4 system can initiate vinyl polymerisation.

Our results indicate that when complications due to the presence of the oxidation state $[Ru(cp)_2Cl]^+$ are removed, ruthenocene is similar to ferrocene in initially forming $[Ru(cp)_2]^+$. However there are differences in the quenching behaviour, particularly with oxygen, between the two compounds and, in contrast to ferrocene, the naphthalene-photosensitised reaction proceeds through a triplet state rather than a singlet state.

EXPERIMENTAL

The photolyses were made in a 1-cm square spectrophotometer cell which was modified to exclude air and to allow the solution to be deaerated and agitated continuously with a fine stream of pure nitrogen.[10] All the analyses were made by spectrophotometry, using a Unicam 800 spectrophotometer. The 313 nm radiation from the medium-pressure mercury lamp was isolated with a Balzer interference filter. Quantum yields were determined with respect to potassium ferrioxalate.[11] The light intensity entering the vessel was *ca.* 6×10^{14} quanta s^{-1}.

Ruthenocene was obtained from Strem Chemicals and used without further purification. The various solvents were all spectroscopic grade reagents.

RESULTS

The Charge-transfer Complex between Ruthenocene and Carbon Tetrachloride.—When carbon tetrachloride is added to a solution of $[Ru(cp)_2]$ in methanol, there is an increase in absorption in the region of 300 nm. The effect is illustrated in Figure 1, and can be attributed to the formation of a complex:

$$[\mathrm{Ru(cp)_2}] + \mathrm{CCl_4} \rightleftharpoons [(\mathrm{cp})_2\mathrm{Ru}{:}\mathrm{CCl_4}] \qquad (1)$$

The change in apparent molar absorptivity for two wavelengths is given in Table 1. Following previous workers[1,4] the equilibrium constant for reaction (1), K_1, can be determined by plotting, for a given wavelength λ, $[\varepsilon(\lambda,A) - \varepsilon(\lambda,R)]^{-1}$ against $(A)^{-1}$, where $\varepsilon(\lambda,A)$ is the apparent molar absorptivity of a solution of $[Ru(cp)_2]$ in a mixture of CCl_4 and CH_3OH, (A) is the mol fraction of CCl_4, and $\varepsilon(\lambda,R)$ is the molar absorptivity of $[Ru(cp)_2]$ in CH_3OH. The intercept/slope of the plot gives K_1, since

$$[\varepsilon(\lambda,A) - \varepsilon(\lambda,R)]^{-1} = [\varepsilon(\lambda,C) - \varepsilon(\lambda,R)]^{-1}[1 + (K_1[A])^{-1}] \qquad \text{(i)}$$

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[1] J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, 1957, **53**, 894.

[2] E. K. von Gustorf, H. Köller, M-J. Jun, and G. O. Schenck, *Chem. Eng. Tech.*, 1963, **35**, 591.

[3] E. K. von Gustorf and F. W. Grevelo, *Fortschr. Chem. Forsch.*, 1969, **13**, 366.

[4] O. Traverso and F. Scandola, *Inorg. Chim. Acta*, 1970, **4**, 493.

[5] O. Traverso, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta*, 1972, **6**, 471.

[6] T. Akiyama, Y. Hoshi, S. Goto, and A. Sugimori, *Bull. Chem. Soc. Japan*, 1973, **46**, 1851.

[7] T. Akiyama, A. Sugimori, and H. Hermann, *Bull. Chem. Soc. Japan*, 1973, **46**, 1855.

[8] R. Blackburn and M. A. Shorthouse, *Radiation Effects*, 1970, **3**, 227.

[9] K. Tsubakiyama and S. Fujisaki, *Polymer Letters*, 1972, **10**, 341.

[10] P. Borrell, J. D. Holmes, and J. Sedlar, *J. Photochem.*, 1973, **1**, 333.

[11] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

where $\varepsilon(\lambda,C)$ is the absorptivity of the complex, which can also be determined from the plot. Plots were made for several wavelengths and the values of K_1 determined for each are shown in Table 2. The mean value obtained, $1{\cdot}80 \pm 0{\cdot}15$ mol fraction^{-1}, is similar to the value of $1{\cdot}5 \pm 0{\cdot}2$ found for the ferrocene complex by Traverso and Scandola[4] who used ethanol rather than methanol as the inactive solvent. If, for direct comparison, the results of each are converted into concentration units, using the equation of Ogimachi, Andrews, and Keefer,[12] the values for the two compounds are $[Ru(cp)_2]$ 0·012 (± 0·001) l mol^{-1} and $[Fe(cp)_2]$ 0·015 l mol^{-1}. The latter value differs from the value quoted in the paper[4] for ferrocene, which was apparently obtained by direct use of the equation in ref. 12 which contains an error.

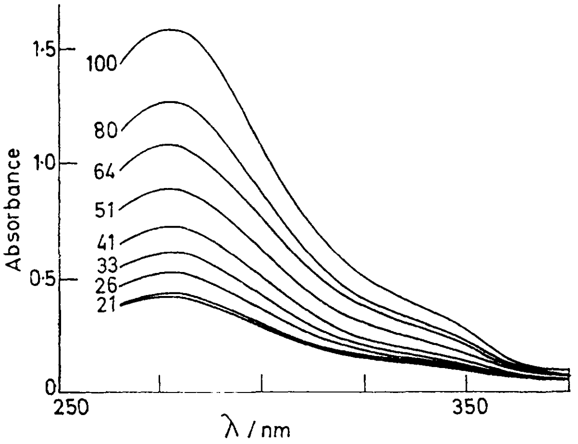

FIGURE 1 Variation of absorption of ruthenocene with solvent composition in mixtures of CCl_4 and CH_3OH. The figures represent the mol fraction percentage CCl_4. Concentration of ruthenocene $8{\cdot}4 \times 10^{-4}$ mol l^{-1}

TABLE 1

Variation of the apparent absorptivity of ruthenocene in mixtures in CCl_4 and CH_3OH (t/°C = 21)

Solvent composition by volume (%)		Molar absorptivity (ε/l mol^{-1} cm^{-1}) 320 nm	278 nm
CH_3OH	100	197	150
CCl_4	20	207	320
CCl_4	25	273	620
CCl_4	50	335	973
CCl_4	75	408	1190
CCl_4	100	680	1460

TABLE 2

Association constant and absorptivities for the complex between ruthenocene and CCl_4 (t/°C = 21)

Wavelength (λ/nm)	Absorptivity (ε/l mol^{-1} cm^{-1})	Association constant determined (in mol fraction^{-1})
300	1040	1·60
295		1·57
290	1390	1·80
285		1·97
280	1580	2·03
	Mean value	1·80 ± 0·15

An attempt was made to determine the enthalpy of reaction (1) by measuring K_1 over a 20 °C temperature range. The variation in absorptivity was very small and we can only conclude that $\Delta H_1 < 7$ kJ mol^{-1}.

Photo-oxidation of $[Ru(cp)_2]$ *in* CCl_4.—Since ionic products were expected from the photolysis, in the first studies, the CCl_4 solution was kept in contact with 0·1M-HCl. The aqueous phase was protected from the light and the photolysis was interrupted from time to time in order to shake the two phases together. As the reaction proceeded, the absorption of the aqueous phase grew, and the spectrum showed the characteristic metallocenium-type absorption with a strong band below 250 nm and a peak at 330 nm (Table 3). Nesmeyanov and his co-workers[13] have shown that Br_2 oxidation of $[Ru(cp)_2]$ in CCl_4 yields the chlorinated ion $[Ru(cp)_2Cl]^+$. We oxidised solutions of $[Ru(cp)_2]$ in CCl_4 with Br_2, HCl (aerated solutions), and I_2 and extracted the aqueous phase. The spectroscopic results are shown in Table 3. With I_2 the spectrum was obscured by the strong absorption of I_3^-, but this was removed by ion exchange with Cl^-.

TABLE 3

Oxidation studies on $[Ru(cp)_2]$ in CCl_4 and its photoproduct

Conditions		U.v. absorption maxima (λ/nm) sh = shoulder		Attribution
Br_2 water, molar ratio Br_2: $[Ru(cp)_2]$ = 2 : 1		360	260sh	$[Ru(cp)_2Cl]^+$
Br_2 water, molar ratio Br_2: $[Ru(cp)_2]$ = 4 : 1		370	265sh	
Br_2 water, excess		370	480	Ru^{3+}
Iodine		370	265sh	$[Ru(cp)_2Cl]^+$
Aerated solution: HCl, 5·5M		360	245sh	$[Ru(cp)_2Cl]$
Photo-oxidation 260 nm in CCl_4 aqueous extract		330	250sh	$[Ru(cp)_2]^+$
Aqueous photoproduct with Br_2 water	small excess	370	265sh	$[Ru(cp)_2Cl]^+$
	large excess	370	480	Ru^{3+}

It can be seen that the photoproduct does not have the same detailed spectrum as the other oxidation products. However if the aqueous photoproduct was treated with bromine water, and the excess of oxidant removed with CCl_4, the photoproduct was converted (Table 3) into the same oxidation product as that obtained by oxidation of $[Ru(cp)_2]$ with bromine water. With an excess of Br_2 the spectrum of Ru^{3+} ions is obtained from all the solutions.

These results are similar to those found in electrochemical oxidation studies[14] where, with a rotating Pt electrode, $[Ru(cp)_2]^+$ is obtained, but with a dropping mercury electrode $[Ru(cp)_2Cl]^+$ is formed. Thus we believe that the photoproduct is $[Ru(cp)_2]^+$.

An attempt was made to identify the other photoproducts by larger scale photolysis followed by mass spectrographic and chemical analysis, but the small amount of product and the ready formation of Ru^{3+} prevented any positive identification.

The Spectrum of $[Ru(cp)_2]^+Cl^-$.—In order to determine the quantum yield of the initial photoreaction, it was necessary to know the absorptivity of ruthenocenium chloride. The chloride was prepared by photochemical oxidation, as

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[12] N. Ogimachi, L. J. Andrews, and R. M. Keefer, *J. Amer. Chem. Soc.*, 1955, **77**, 4202.

[13] A. N. Nesmeyanov, A. K. Lubovich, L. P. Yureva, S. P. Gubin, and E. G. Perevalova, *Izvest. Akad. Nauk. S.S.S.R., Ser. khim.*, 1967, 935.

[14] S. P. Gubin, S. A. Smirnova, L. I. Denisovich, and A. K. Lubovich, *J. Organometallic Chem.*, 1971, **30**, 243.

before, by irradiation of a solution of $[Ru(cp)_2]$ in CCl_4 in contact with 0·1M-HCl. The photolysis was interrupted at 10 min intervals in order to mix the solutions. The fall in $[Ru(cp)_2]$ concentration in CCl_4 was equated to the rise in $[Ru(cp)_2]^+Cl^-$ in 0·1M-HCl. The spectrum determined in this way is shown in Figure 2. The absorptivities (in l mol cm^{-1}) determined at four wavelengths (in nm) are: at 250 (shoulder) 9400 ± 400; at 333 (maximum) 4630 ± 200; at 400 3140 ± 190; and at 440 1790 ± 80. The last two wavelengths were used for estimating the concentrations in the photochemical experiments. The error limits were determined by making several runs, but this type of technique is clearly susceptible to possible systematic errors.

Photolysis at 313 *nm*.—The quantitative experiments were made in mixtures of CCl_4 and CH_3OH (1 : 1 by volume) in which both reactant and product are soluble. The photolyses were followed by observing the increase in absorption at 400 nm. In a 15 min run eight spectra were taken, and in all cases the absorption was found to increase linearly with time. The reactions were not taken beyond 1% conversion since $[Ru(cp)_2]^+$ has a larger absorptivity than $[Ru(cp)_2]$ and would begin to absorb a significant fraction of the light. The quantum yields were determined by comparison with potassium ferrioxalate. In these solutions there is absorption by both $[Ru(cp)_2]$ and by the charge-transfer complex. Since only the charge-transfer complex reacts, the apparent quantum yield, based on the total absorption, is corrected to give a yield based on the absorption of the complex. The absorptivities at 313 nm are: $[Ru(cp)_2]$ in CH_3OH, 197 l mol^{-1} cm^{-1}; $[Ru(cp)_2]$ in 50% CH_3OH–CCl_4 {effective ε including both $[Ru(cp)_2]$ and $[(cp)_2Ru^{\cdot}_{\cdot}CCl_4]$}, 30 l mol^{-1} cm^{-1}, and the correction factor is 1·84. The value of the quantum yield, together with the effect of concentration and aeration of the solutions is shown in Figure 3. Concentration has only a small effect, but aeration reduces the yields considerably. Oxygen was also bubbled through solutions and reduced the yields still more. Following Traverso and Scandola[4] we also added acrylamide to the solutions to inhibit free-radical reactions which might consume the substrate. The effect of these conditions is summarised in Table 4.

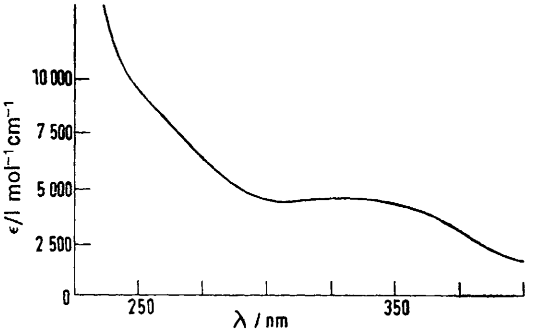

FIGURE 2 Absorptivity of ruthenocenium chloride in 0·1M-HCl. The precision of the values at particular wavelengths is indicated in the text

Similar results were obtained at 366 nm; it was necessary to use a higher concentration of $[Ru(cp)_2]$, and so the photolyses were made in 75 : 25 CCl_4–CH_3OH (by volume) mixtures. As Table 4 shows, the overall quantum yield is lower, but the effect of aeration is similar.

The effect of paramagnetic ions on the photolysis at 313 nm was investigated. We found that Fe^{2+}, Co^{2+}, and Ni^{2+} could not be used because of direct reactions with the ruthenocenium product, forming presumably $[Ru(cp)_2]$. Samarium ions were used and the results are shown in Figure 4; the limiting quantum yield at high concentrations is recorded in Table 4. It can be seen that, as with oxygen, *ca.* two thirds of the photoreaction can be quenched, leaving an unquenchable residual reaction.

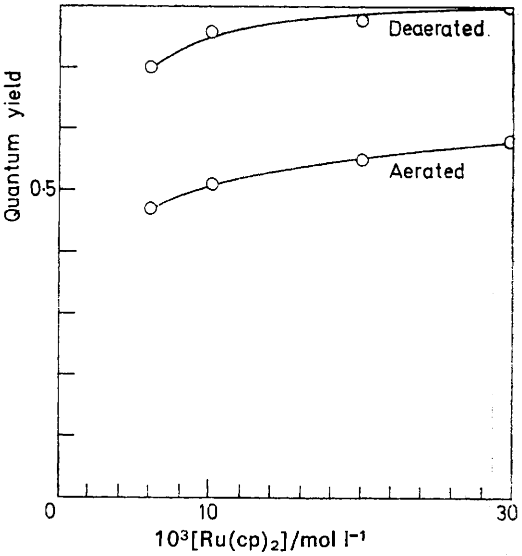

FIGURE 3 Quantum yield for the photo-oxidation of the charge-transfer complex in deaerated and aerated solutions as a function of concentration

TABLE 4

Quantum yields for the photolysis of $[(cp)_2Ru^{\cdot}_{\cdot}CCl_4]$

313 nm : concentration 1·06 × 10^{-3}M in 50% CCl_4 : 50% CH_3OH
366 nm : concentration 4·0 × 10^{-2}M in 75% CCl_4 : 25% CH_3OH

Conditions	Condition of additive (c/mol l^{-1})	$\phi(\lambda =$ 313 nm)	$\phi(\lambda =$ 366 nm)
Deaerated (N_2)		0·76	0·49
+ Acrylamide	5 × 10^{-2}	0·63	
+ Acrylamide	1 × 10^{-1}	0·65	
+ Air	1 atm	0·51	0·33
+ Oxygen	1 atm	0·38	
+ $SmCl_3$	Limiting (see Fig. 4)	0·28	
+ Stilbene	0·05		0·50
+ Biacetyl	1·06 × 10^{-3}	0·76	
+ Biacetyl	5 × 10^{-3}	0·72	
+ Glyoxal	5 × 10^{-3}	~0·4	

All the solutions, apart from those with air and oxygen, were deaerated with N_2.

The spectrum and reactivity of $[Ru(cp)_2]$ limits the possible organic quenchers which can be used, but experiments were tried with *trans*-stilbene, glyoxal, and biacetyl. The results are shown in Table 4. Together with the absence of an effect with biacetyl, it was found that there was no sensitised fluorescence or phosphorescence of biacetyl.

Fluorescence Quenching.—Ruthenocene was added to solutions of fluorescent compounds in 50% CCl_4–CH_3OH mixtures, and to solutions in methanol, and the decrease in fluorescence was observed. Plots were made of F_0/F, the ratio of fluorescence in the absence and presence of

$[Ru(cp)_2]$ *versus* concentration. In all cases the lines were straight; the quenching constant, which is the product of the lifetime of the excited state and the second-order rate constant for the quenching reaction, was determined from the slope. The values are recorded in Table 5. It can be seen that there is little difference between $[Ru(cp)_2]$ and the charge-transfer complex in quenching ability. It is also evident that the several singlet levels present in ruthenocene[15] can accept energy from the sensitisers of widely different singlet energies.

TABLE 5

Fluorescence quenching by ruthenocene

	Solvent system		
Compound	50% CCl_4–CH_3OH Constant/ l mol^{-1}	100% CH_3OH Constant/ l mol^{-1}	Singlet energy (in kJ mol^{-1})
Anthracene *	250	—	317
9,10-Diphenylanthracene	290	250	296
Acridine orange	20	—	230
Biacetyl	50	45	271

* Experiments made on the small fluorescence of anthracene in the presence of CCl_4.

Photosensitisation by Naphthalene at 313 *nm*.—Several sensitisers were tried, but for either analytical or reactivity reasons experiments with azulene, pyrene, benzpyrene, and anthracene were not successful. It was possible to sensitise the photo-oxidation with naphthalene at 313 nm, using concentrations adjusted so that naphthalene absorbed more than 90% of the light. That the naphthalene was sensitising the photo-oxidation of the charge-transfer complex rather than the ruthenocene is indicated by Figure 5, where the relative yield of formation for the ion is shown as a function of the volume of CCl_4 in the mixture, for constant sensitiser and $[Ru(cp)_2]$ concentrations. The relative yield varies with concentration of complex as shown in Figure 6. It can be seen that there is a peak at low concentrations, and an apparent self-quenching reaction at higher concentrations. When acrylamide was added to solutions of the same concentrations, no change in yield was observed. Some experiments were also made using 9,10-diphenylanthracene (DPA) as a sensitiser. Using 6×10^{-3}M-solution of DPA and 1—5 $\times 10^{-3}$M-solutions of $[Ru(cp)_2]$ in 50% CCl_4–CH_3OH sensitisation was observed and a small decrease with concentration of ruthenocene was noted, similar to that with naphthalene.

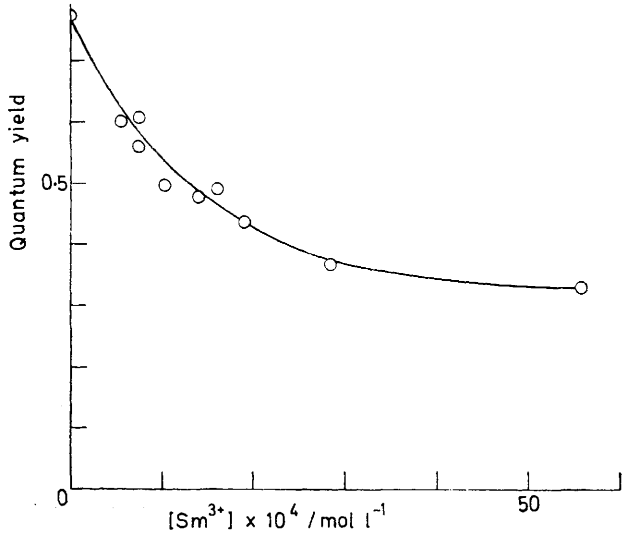

FIGURE 4 Quenching of the photo-oxidation of the charge-transfer complex by $SmCl_3$. Concentration of ruthenocene 0·01 mol l^{-1}. $CH_3OH : CCl_4 = 1 : 1$ by volume

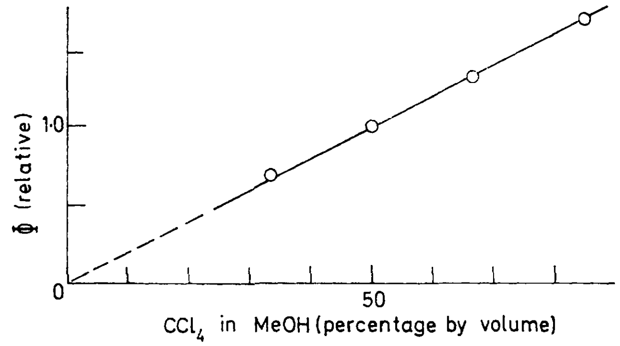

FIGURE 5 The yield of the photosensitised oxidation of ruthenocene as a function of solvent composition in mixtures of CCl_4 and CH_3OH. Concentrations: naphthalene, 0·23 mol l^{-1}; $[Ru(cp)_2]$, 2×10^{-3} mol l^{-1}; $\lambda = 313$ nm

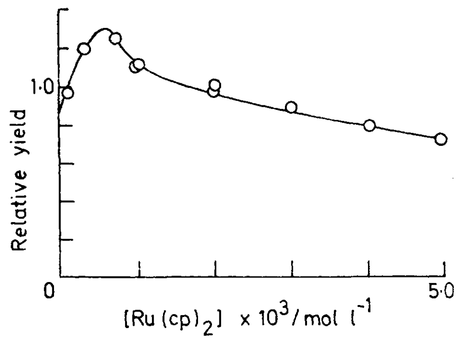

FIGURE 6 The yield of photosensitised oxidation of ruthenocene as a function of ruthenocene concentration at 313 nm. Solvent mixture: $CH_3OH : CCl_4$; 1 : 1 by volume

DISCUSSION

The value of the dissociation constant for the charge-transfer complex between $[Ru(cp)_2]$ and CCl_4 (0·012 l mol^{-1}) is similar[1,4] to that for $[Fe(cp)_2]$ (0·015 l mol^{-1}), and slightly less than those for aromatic hydrocarbons[16] with CCl_4 (benzene, 0·043—0·076 l mol^{-1}; xylene, 0·112 l mol^{-1}; and hexamethylbenzene 0·64 l mol^{-1}). The values perhaps illustrate the slightly reduced aromatic character of the cyclopentadienyl ring. The estimate of the binding energy of the complex (<7 kJ mol^{-1}) is also similar to the low values found for complexes between CCl_4 and aromatic hydrocarbons.

The spectrum of $[Ru(cp)_2]^+Cl^-$ (Figure 2) is similar in form to other metallocene spectra, but without the detail obtained in low-temperature studies. The strengths of the two bands (<250 nm and 330 nm) are consistent with charge-transfer transitions rather than

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[15] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3603.

[16] R. Foster, 'Organic Charge Transfer Complexes,' Academic Press, New York, 1969.

d–d absorptions.[15] They are lower in energy than the corresponding transitions in ferrocenium chloride.

Comparison of the photo-oxidation results with those from electrochemical [13] and chemical oxidation allows us to set up the scheme in Figure 7, relating $[Ru(cp)_2]$, $[Ru(cp)_2]^+$, and $[Ru(cp)_2Cl]^+$.

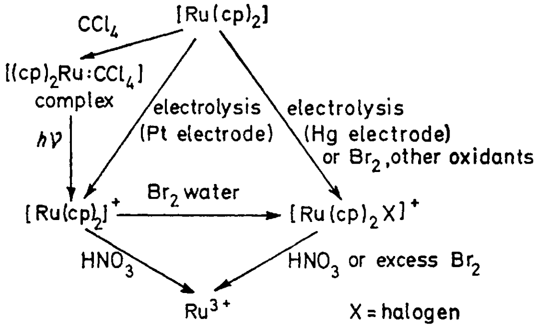

FIGURE 7 Oxidation scheme for ruthenocene

The small increase in quantum yield of the photoreaction with concentration (Figure 3) and the reduction of yield with the addition of acrylamide (Table 4) suggests that some secondary free-radical reactions consume part of the reactant. In the photolysis of the $[Fe(cp)_2]$ complex, it is thought that trichloromethyl radicals are formed, leading ultimately to the formation of a tetrachloroferrate of ferrocenium. It is probable that a similar reaction occurs here

$$[Ru(cp)_2] + h\nu \longrightarrow [Ru(cp)_2]^+ + CCl_3\cdot + Cl^- \qquad (2)$$

followed by attack by some of the radicals on further substrate molecules. The secondary consumption would be increased by concentration and reduced by addition of acrylamide. Therefore we think that the primary quantum yield is that in the presence of acrylamide, *i.e.* ϕ (total, 313 nm) = 0·64.

The behaviour in the presence of oxygen (Table 4) and excess Sm^{3+} (Figure 4) suggests that decomposition can occur from two excited states, only one of which can be quenched. It is probable that these are the excited singlet and triplet states and if so the following scheme can be set up

$$C \longrightarrow {}^1C^* \qquad (3)$$
$${}^1C^* \longrightarrow C \qquad (4)$$
$${}^1C^* \longrightarrow \text{Products} \qquad (5)$$
$${}^1C^* \longrightarrow {}^3C^* \qquad (6)$$
$${}^3C^* \longrightarrow C \qquad (7)$$
$${}^3C^* \longrightarrow \text{Products} \qquad (8)$$
$${}^3C^* + M \longrightarrow C + M \qquad (9)$$

where C is the complex, ^1C and ^3C are its singlet and triplet states, and M is a quenching agent. Steady-state analysis gives the quantum yield of the product formation, $\phi[M]$, in the presence of a concentration of [M] to be:

$$\phi[M] = (k_4 + k_5 + k_6)^{-1}\{k_5 + k_6k_8/[k_7 + k_8 + k_9[M]]\} \qquad (ii)$$

At higher quencher concentrations the triplet reaction is totally inhibited so the yield becomes constant.

$$\phi[M = \infty] = k_5/(k_4 + k_5 + k_6)$$

The results with Sm^{3+}, Figure 4, can be linearised by plotting $(\phi[M] - \phi[M = \infty])^{-1}$ *versus* [M] as shown in Figure 8. The ratio of slope/intercept for this plot gives the ratio of the quenching constant k_9 to those for deactivation k_7 and product formation k_8 of the triplet state: $k_9/(k_7 + k_8) = 1400 \pm 200$ l mol^{-1}. If, as is likely, the quenching reaction (9) is diffusion controlled, it shows that the effective lifetime of the state $(k_7 + k_8)^{-1}$ in this solvent mixture is shorter than 1 ms. The metallocenes do not luminesce, so there is no data for comparison, but the quenching and lifetime values are similar to those found for organic molecules.

The limiting yield $\phi[M = \infty, 313\text{ nm}] = 0{\cdot}28$ is the singlet yield. Allowing for the proportion of reactant consumed in secondary reactions, at zero quencher concentration ϕ (singlet, 313 nm) = 0·24 and ϕ (triplet, 313 nm) = 0·40. The results at 366 nm are similar, with similar proportion of quenching by air as at 313 nm, so that the approximate values for the quantum yields are: ϕ (total, 366 nm) = 0·41, ϕ (singlet, 366 nm) = 0·15, and ϕ (triplet, 366 nm) = 0·26. The error limits cannot be sensibly estimated in view of the uncertainty in the absorptivities of the ion.

Although the primary process seen here is analogous to that occurring in ferrocene, the quantum yields for the photo-oxidation, based on the light absorbed by the complex, are less than values found at several wavelengths for ferrocene by Traverso and Scandola.[4] The effect of acrylamide in reducing the overall yield is similar but we differ in the effect of paramagnetic quenchers, particularly oxygen. Traverso and Scandola found that oxygen increased their yield. Oxygen certainly decreased the yields from $[Ru(cp)_2]$ and this type of decrease is exactly analogous to that commonly observed in photochemical systems where oxygen acts as a quencher for both radicals and excited-state intermediates.

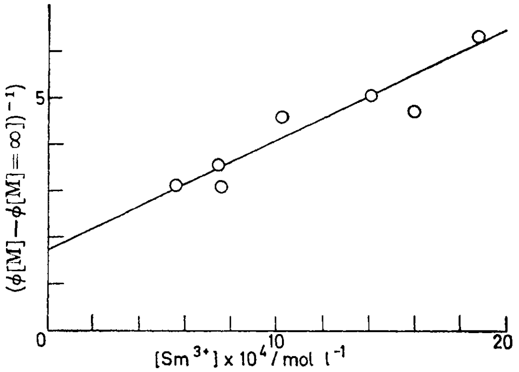

FIGURE 8 Linearised plot for the quenching of the photo-oxidation of ruthenocene by $SmCl_3$. Conditions as for Figure 4

A mechanism for the naphthalene-photosensitised reaction must take into account the maximum in the yield/concentration plot (Figure 6) and the variation of the yield with solvent composition (Figure 5):

$$N \longrightarrow {}^1N \qquad (10)$$
$${}^1N \longrightarrow N \qquad (11)$$
$${}^1N \longrightarrow {}^3N \qquad (12)$$
$${}^1N + M \longrightarrow N + M \qquad (13)$$
$${}^3N + C \longrightarrow \text{Products} \qquad (14)$$
$${}^3N + R \longrightarrow N + R \qquad (15)$$
$${}^3N \longrightarrow N \qquad (16)$$

Here N, ^1N, ^3N represent naphthalene in its ground, excited singlet, and excited triplet states; C is the complex $[(cp)_2Ru{:}CCl_4]$ and R is $[Ru(cp)_2]$. M is a quencher for the singlet state and may be either C or R. If the quantum yield of singlet naphthalene formation is ϕ_{10}, then the quantum yield of product formation, ϕ_{14}, is given by:

$$\phi_{14}(C,R,M)^{-1} = \phi_{10}^{-1}(1 + k_{11}/k_{12} + k_{13}[M]/k_{12})$$
$$(1 + k_{15}[R]/k_{14}[C] + k_{16}/k_{14}[C]) \quad \text{(iii)}$$

The rapid increase in yield with $[Ru(cp)_2]$ concentration (Figure 6) suggests that above *ca.* 10^{-3} mol l^{-1} all the ^3N is being transferred to either C or R (*i.e.* $k_{16}/k_{14}[C] \ll 1$) so that the effect of solvent composition (Figure 5) where the yield increases with proportion of CCl_4, is due to competition between R and C for the triplet energy [reactions (14) and (15)]. As Traverso and Scandola[5] found with ferrocene[5] only the complex can be oxidised. With these conditions

$$\phi_{14}(C,R,x_c,[M] > 10^{-3}\ \text{mol l}^{-1})^{-1} =$$
$$\phi_{10}^{-1}(1 + k_{11}/k_{12} + k_{13}[M]/k_{12})(1 + k_{15}/k_{14}K_1x_c) \quad \text{(iv)}$$

since $[M] = [C] + [R]$ and $[C] = K_1x_c[M]/(1 + K_1x_c)$, where x_c is the mole fraction of CCl_4. Figure 9 shows that ϕ^{-1} *versus* x_c^{-1} yields a straight line. The ratio of slope/intercept gives $k_{15}/k_{14}K_1$ to be (0·82 ± 0·15) mol fraction or k_{15}/k_{14} to be 1·48 ± 0·2. Thus the probability that $[Ru(cp)_2]$ will receive singlet energy from naphthalene is slightly greater than that for the complex; the difference probably reflects the differing diffusion rates. For constant solvent composition $k_{15}/k_{14}K_1x_c$ is constant so that

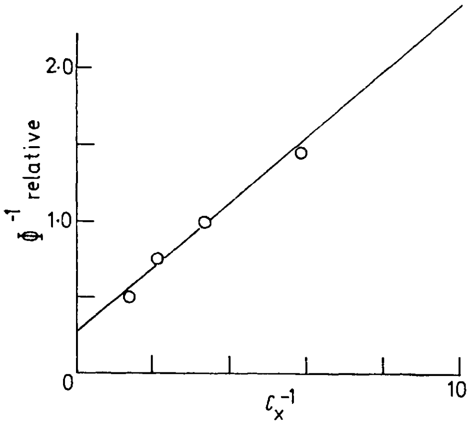

FIGURE 9 A plot of the reciprocal relative yield *versus* solvent mol fraction for the photosensitised oxidation of ruthenocene by naphthalene. Conditions as for Figure 5

$$\phi_{14}(C,M,x_c = 0{\cdot}29)^{-1}$$
$$= \phi_{10}^{-1}(3{\cdot}77 + k_{16}/k_{14}[C])(1 + k_{11}/k_{12} + k_{13}[M]/k_{12}) \quad \text{(v)}$$

Again at higher concentrations, when $k_{16}/k_{14}[C] \ll 1$, a plot of ϕ^{-1} *versus* [M] should give a straight line—Figure 10 shows that it does so. The naphthalene-triplet yield in the absence of transfer has been shown to be 0·71 in ethanol[17] so that $k_{11}/k_{12} \simeq 0{\cdot}41$, and therefore the slope/intercept ratio for Figure 10 gives $k_{13}/(k_{12} + k_{11})$ directly. The value found for this is 107 ± 20 l mol^{-1}, which compares reasonably with the value found (200 l mol^{-1}) by Traverso and Scandola[5] for the quenching of naphthalene fluorescence by ferrocene. It also compares well with the values noted in Table 5 for fluorescence quenching by ruthenocene of various compounds. Regrettably we omitted to measure the value for naphthalene itself.

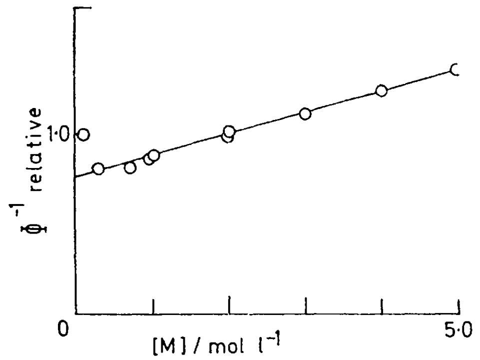

FIGURE 10 A plot of reciprocal relative yield *versus* ruthenocene concentration for the photosensitised oxidation of ruthenocene by naphthalene. Conditions as for Figure 6

Thus the fall in yield at higher concentrations (Figure 6) is due to quenching of the singlet state competing with transfer to the triplet state. It is clear that in our case quenching of the singlet state does not lead to photo-oxidation.

The ratio k_{16}/k_{14} cannot be determined accurately from the data in Figure 6, but the position of the maximum shows that $k_{16}/k_{14} \gg 10^4$ l mol^{-1}. If reaction (16) is diffusion controlled, then the lifetime of the triplet state of naphthalene is greater than 1 ms which is reasonable in this mixed solvent system.

There is a clear difference between ruthenocene and ferrocene. Traverso and Scandola[5] observed, over a similar concentration range to Figure 6, a growth in the product yield. By correlation of the growth with the quenching of the naphthalene fluorescence by ferrocene, they were able to show that the sensitisation was due to a singlet-state transfer. Our results indicate that the sensitisation of ruthenocene is a triplet-state reaction and also that the transfer from the singlet state does

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[17] C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, Amsterdam, 1968.

not apparently cause decomposition. The differences can probably be attributed to the different juxtapositions between the electronic energy levels of naphthalene and those of ferrocene and ruthenocene. However, as the triplet levels of the metallocenes are not well known, it is not possible for us to point to any clear correlation here.

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