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Kinetics of the photosubstitution of cis-bis(benzonitrile)dichloroplatinum(II) in chloroform

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Kinetics of the Photosubstitution of cis-Bis(benzonitrile)dichloroplatinum(II) in Chloroform

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Under 254 nm irradiation cis-[Pt(C$_6$H$_5$CN)$_2$Cl$_2$] is converted to H$_2$PtCl$_6$. Absorption of light by both the metal complex and the solvent contribute to the first step of this process, suggested to form HPt(C$_6$H$_5$CN) Cl$_3$. A linear dependence of the reaction rate on light intensity appears to rule out chlorination by trichloromethyl radicals. However, at higher light intensities a higher order dependence on intensity develops, and under 313 nm irradiation is dominant, and a reaction between trichloromethyl radical and the excited state complex is proposed to account for this.

INTRODUCTION

Photochemical reactions of transition metal complexes normally proceed through an excited state of the metal complex, and have a rate law that can be expressed as

$$-\frac{d[R]}{dt} = k\frac{I_0 f_R}{V}[S],\tag{1}$$

where R is the reactant metal complex, S is the substrate, I_0 is the incident light intensity, and f_R is the fraction of light absorbed by the metal complex. If the substrate is the solvent, the dependence of the rate on the concentration of R is entirely through f_R. Recent results in halogenated solvents point to another possible mechanism, in which radicals produced through the absorption of light by the solvent react with the ground state metal complex [1].

It is difficult to distinguish a metal-initiated pathway from a solvent-initiated pathway other than by kinetic means. They can lead to identical products, and both can generate free radicals in solution. The reaction rate dependence of a typical metal-initiated reaction will be linear in light intensity and f_R. More complex mechanisms are possible, but in any case the concentration dependence will be through f_R, not f_S, the fraction of light absorbed by the solvent. In a solution containing the reactant and a product, P, these functions may be expressed as [1]

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

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

(3)

in which A_S is the absorbance of the solvent and ε_R and ε_P are the extinction coefficients of reactant and product, all at the irradiation wavelength. Under initial rate conditions the product concentrations may be ignored and a simpler dependence on $[R]$ results.

Several photoreactions in chloroform have recently been found to be solvent-initiated [2,3], including [Fe(dtc)$_3$] $\rightarrow$ [Fe(dtc)$_2$Cl] (dtc = diethyldithiocarbamate), which occurs as a radical substitution chain reaction under 254 nm irradiation [3]. In the present study cis-[Pt(C$_6$H$_5$CN)$_2$Cl$_2$] was also expected to undergo photosubstitution. However, in contrast to [Fe(dtc)$_3$] photolysis, a stable molecule, benzonitrile, was expected to be displaced, rather than a radical that could propagate a chain. Another platinum photoreaction, the photoreduction of [PtCl$_6$]$^{2-}$ to [PtCl$_4$]$^{2-}$ in CHCl$_3$, is metal-initiated under 297 nm irradiation [4], but is a chain reaction following a rate law proportional to $I_0^{1/2} f_R^{1/2} [R]$, and proceeding through a Pt(III) intermediate that functions as a chain propagator.

EXPERIMENTAL SECTION

cis-[Pt(C$_6$H$_5$CN)$_2$Cl$_2$], H$_2$PtCl$_6 \cdot x$H$_2$O ($x \approx 5$) and CHCl$_3$ were used as supplied by Aldrich Chemical Co. Chloroform was HPLC grade, stabilized with ethanol. Electronic spectra were measured on a Hewlett Packard Model 8453 diode array spectrometer, equipped with single and multi-component analysis software, or a Perkin Elmer Lambda 11 spectrophotometer. The concentration of [Pt(C$_6$H$_5$CN)$_2$Cl$_2$] in CHCl$_3$ solutions was determined from the extinction coefficient at 274 nm (1.92×10^4 M^{-1} cm^{-1}, from a Beer's Law plot), or from a multi-wavelength analysis on the HP 8453. The spectrum of the final product was determined by exhaustive irradiation of samples of known concentration.

Samples dissolved in CHCl$_3$ were irradiated at 254 nm with a 100-W mercury lamp in an Oriel Q

housing, passed through an Oriel 0.125-m monochromator, with slit widths between 0.5 and 2.5 mm. No induction period from the ethanol stabilizer was observed. Light intensities were measured in triplicate by ferrioxalate actinometry [5,6]. Reaction rates during the course of a reaction were estimated as $\Delta[R]/\Delta t$, where $[R]$ is the concentration of reactant.

RESULTS

Irradiation of cis-[Pt(C$_6$H$_5$CN)$_2$Cl$_2$] at 254 nm led to the spectral changes illustrated in Figure 1. The decrease in absorbance at 266 nm, followed by an increase is evidence that at least one stable intermediate is formed. Exhaustive photolysis yielded a spectrum that was identifiable (λ_{max} = 266 nm) as that of hexachloroplatinate(IV) [4], and matched that of H$_2$PtCl$_6 \cdot x$H$_2$O dissolved in CHCl$_3$. Though this appears unusual, because of the ease with which [PtCl$_6$]$^{2-}$ in chloroform is photoreduced to [PtCl$_4$]$^{2-}$ when the counterion is N$_4$Bu$^+$ [4], preliminary experiments indicated that H$_2$PtCl$_6$ undergoes only slow and partial photoreduction, and is regenerated thermally. The final product may, in fact, be a photostationary mixture of H$_2$PtCl$_6$ and H$_2$PtCl$_4$, the
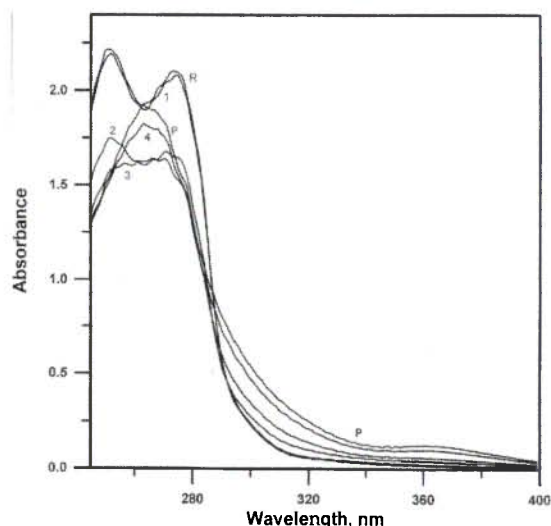

FIGURE 1 Sequential spectra from the 254 nm photolysis of [Pt(C$_6$H$_5$CN)$_2$Cl$_2$] ($= R$) to yield H$_2$PtCl$_6$ ($= P$).

former being greatly favored. The same spectral changes were found under 313 nm irradiation. An analogous complex, *cis*-dichlorobis(pyridine)platinum(II) was found to undergo only isomerization when irradiated in chloroform at 313 nm [7].

The spectrum of the intermediate was generated by a computer fit to sequential spectra from an irradiated solution, with the constraint that the total platinum concentration be constant. Photolysate spectra could be resolved reasonably well into reactant, intermediate, and product contributions, with fitting errors primarily at the lowest wavelengths recorded (250–260 nm). The irradiation of neat chloroform leads to several products that absorb in this region [2] and act as interferences. It was assumed that the bulk of the reaction involved these three platinum species, taking the form $R \rightarrow I \rightarrow P$, or

$$Pt(C_6H_5CN)_2Cl_2 \xrightarrow{h\nu} HPt(C_6H_5CN)Cl_3$$
$$\xrightarrow{h\nu} H_2PtCl_6 \qquad (4)$$
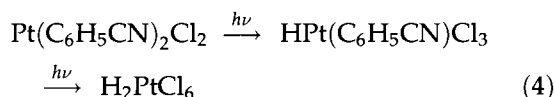
It was assumed that H$_2$PtCl$_4$ is initially generated in the second step, but is rapidly converted to the more stable H$_2$PtCl$_6$ thermally, photochemically, or by both means. We were unable to detect H$_2$PtCl$_4$ in absorption spectra.

Initial rates under 254 nm irradiation at constant initial concentration were measured as a function of light intensity. The results, in Figure 2, show a nearly linear relationship, with a higher order contribution, which could be a squared function. Only at the highest intensity used would the I_0^2 (or other) term be significant, making a contribution of less than a third to the reaction rate. Based on the linear part of the fit, the quantum yield would be 0.08 mol/einstein. A linear dependence on intensity implies a linear dependence on the fraction of light absorbed, either f_R or f_S, or conceivably $f_R^{1/2}f_S^{1/2}$.

Initial rates at constant light intensity were measured at different concentrations of Pt(C$_6$H$_5$CN)$_2$Cl$_2$. The rates were plotted against several trial functions consistent with a linear
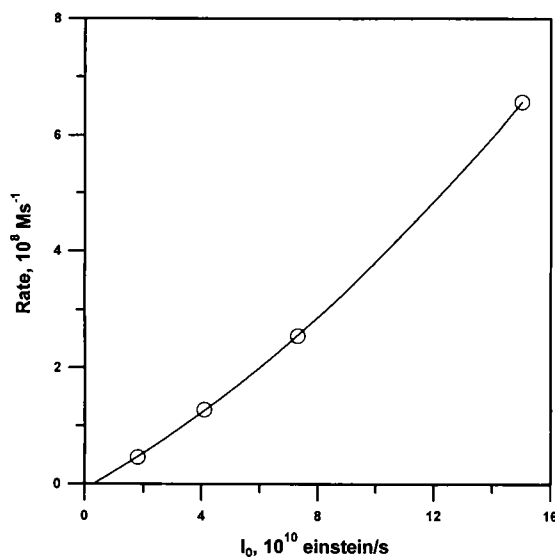
FIGURE 2   Initial rate, $-d[R]/dt$, of the 254 nm photolysis of 7.1×10^{-5} M [Pt(C$_6$H$_5$CN)$_2$Cl$_2$] as a function of light intensity. The best-fit quadratic function is 1.0×10^{10} $I_0^2 +$ $29I_0 - 9 \times 10^{-10}$.

dependence on I_0: f_R, $f_R[R]$, $f_R[R]^{1/2}$, f_S, $f_S[R]$, and $f_S[R]^{1/2}$. The actual rate law should lead to a straight line, ideally passing through the origin. The correlation coefficients ($\mathcal{R}^2$) and intercepts (b) of linear regression lines were compared. Only f_R and $f_S[R]$ yielded reasonable (though not good) straight lines ($\mathcal{R}^2 = 0.43$, $b = 4 \times 10^{-7}$). These two expressions are, in fact, functionally equivalent in their concentration dependence. Since rate laws depend on f_R in an overwhelming majority of instances, and since the reaction takes place with a similar quantum yield at 313 nm, we can presume that it is the correct function here. The plot is shown in Figure 3.

Similar plots were constructed based on point-to-point rates, $-\Delta[R]/\Delta t$, determined throughout the course of reactions carried out to 25–75% completion of the first substitution step. Again, the only reasonable straight lines were obtained when rates were plotted against f_R (or $f_S[R]$), yielding $\mathcal{R}^2 = 0.50$, $b = 8 \times 10^{-7}$. The scatter in Figures 2 and 3 is high in part because of the imprecision in rates derived from small differences in small concentrations and because of the presence of CHCl$_3$ photolysis products as
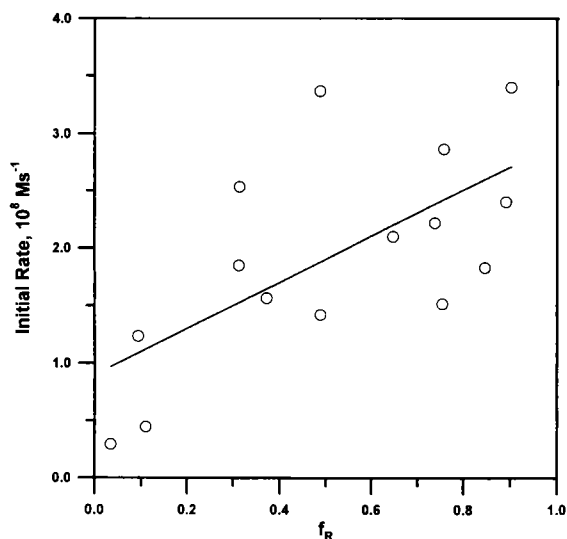
FIGURE 3 Initial rate, $-d[R]/dt$, of the 254 nm photolysis of [Pt(C_6H_5CN)$_2$Cl$_2$] as a function of the fraction of light absorbed by the metal complex. $I_0 = 5.0 \times 10^{-10}$ einstein/s. $\mathcal{R}^2 = 0.43$.

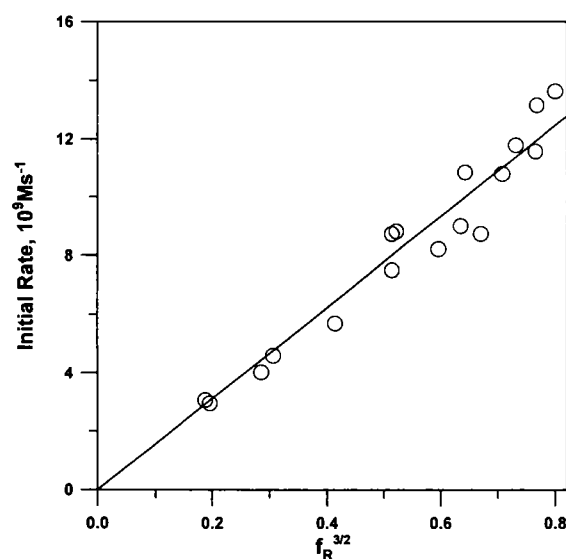FIGURE 4 Initial rate, $-d[R]/dt$, of the 313 nm photolysis of [Pt(C_6H_5CN)$_2$Cl$_2$] as a function of the three-halves power of the fraction of light absorbed by the metal complex. $I_0 = 10^{-8}$ einstein/s. $\mathcal{R}^2 = 0.94$. The slope is 2×10^{-8} M s^{-1}.

impurities, but also because f_R is not sufficient by itself to explain the dependence of the rate on concentration.

Initial rate data at constant light intensity were also acquired under 313 nm irradiation, under which conditions a solvent-initiated pathway is effectively excluded. Unlike the 254 nm results shown in Figure 3, a plot of rate against f_R was nonlinear. However, a reasonable linear plot was obtained when the rate was plotted against either $f_R^{3/2}$ or f_R^2. The former is shown in Figure 4, yielding $\mathcal{R}^2 = 0.94$ for a straight line fit through the origin.

Figures 3 and 4 refer to the formation of the initial product, presumably HPt(C_6H_5CN)Cl$_3$. It was expected that the second step, forming H$_2$PtCl$_4$ (initially), would behave similarly. However, plots of $\Delta[P]/\Delta t$ vs. f_I, the fraction of light absorbed by the initial product, were decidedly nonlinear. The best fit was to the function $f_S^{1/2}[I]$, which is expected for solvent-initiated chain reactions [3]. There was a considerable uncertainty in the concentration of HPt(C_6H_5CN)Cl$_3$, compounded by the difficulty in representing the

conversion of HPt(C_6H_5CN)Cl$_3$ to H$_2$PtCl$_6$ by a single step, despite the resolution of photolysate spectra into just three platinum species.

The reaction was compared in aerated and deaerated solutions, and no difference in rate or products was observed. Addition of Bu$_4$NCl greatly accelerated the reaction.

DISCUSSION

The intercept in Figure 3 (254 nm irradiation) is clearly nonzero, implying another pathway effective at low concentration of reactant. Supposing this to be a solvent-initiated pathway, one might formulate the net rate of reaction at constant light intensity as $af_R + bf_S$. This suggests that a plot of $(-d[R]/dt)/f_S$ vs. f_R/f_S would be linear. Such a plot for initial rates is shown in Figure 5. In fact, the fit is much improved ($\mathcal{R}^2 = 0.73$) over that in Figure 3 ($\mathcal{R}^2 = 0.43$). An analogous plot for rates during the course of reaction is shown in Figure 6, and is also much better ($\mathcal{R}^2 = 0.81$) than a plot of rate against f_R ($\mathcal{R}^2 = 0.50$).
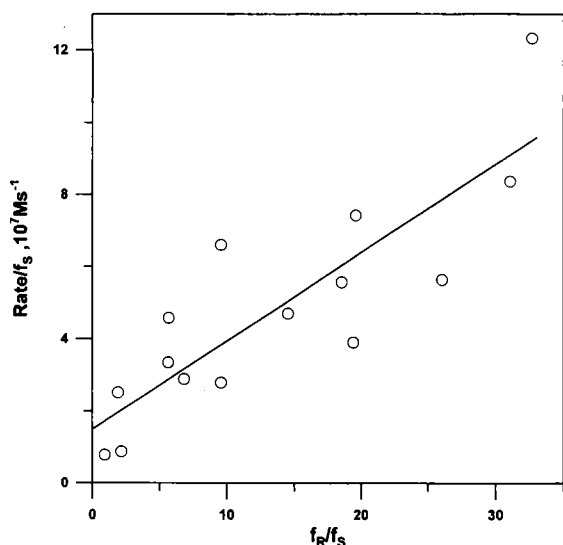
FIGURE 5 Plot from initial rates for the 254 nm photolysis of [Pt(C₆H₅CN)₂Cl₂], based on the equation $-d[R]/dt = af_R + bf_S$. From slope and intercept of best-fit line, $a = 2.5 \times 10^{-8} \, \mathrm{M \, s^{-1}}$, $b = 1.5 \times 10^{-7} \, \mathrm{M \, s^{-1}}$; $R^2 = 0.73$.
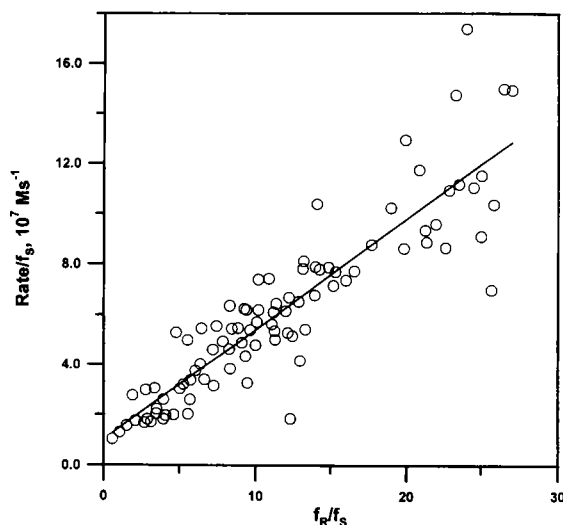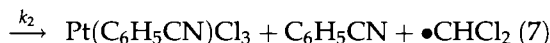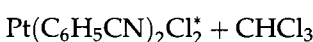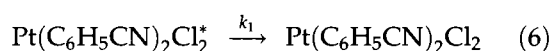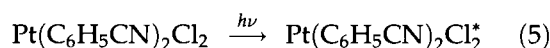

FIGURE 6 Plot from rates during the course of reaction of [Pt(C₆H₅CN)₂] ($\lambda_{exc} = 254$ nm), based on the equation $-d[R]/dt = af_R + bf_S$. From slope and intercept of best-fit line, $a = 4.4(\pm 0.2) \times 10^{-8} \, \mathrm{M \, s^{-1}}$, $b = 1.0(\pm 0.3) \times 10^{-7} \, \mathrm{M \, s^{-1}}$; $R^2 = 0.81$.

From the slope, $4.4 \times 10^{-8} \, \mathrm{M \, s^{-1}}$, and intercept, $1.0 \times 10^{-7} \, \mathrm{M \, s^{-1}}$, of Figure 6, we estimate that at a reactant concentration of $2 \times 10^{-6} \, \mathrm{M}$, half of the initial product would be formed through the

solvent-initiated pathway and half through the metal-initiated pathway. At a concentration of $2 \times 10^{-5} \, \mathrm{M}$ only 8% of the reaction would be solvent-initiated.
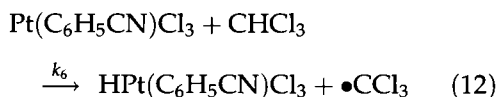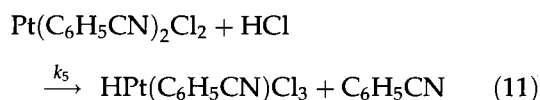
The following mechanism for the first step is consistent with the observed rate behavior under 254 nm irradiation, and assumes two entirely different pathways to form HPt(C₆H₅CN)Cl₃ to explain the dependence on both f_S and f_R,

$$\mathrm{Pt(C_6H_5CN)_2Cl_2} \xrightarrow{h\nu} \mathrm{Pt(C_6H_5CN)_2Cl_2^*} \quad (5)$$

$$\mathrm{Pt(C_6H_5CN)_2Cl_2^*} \xrightarrow{k_1} \mathrm{Pt(C_6H_5CN)_2Cl_2} \quad (6)$$

$$\mathrm{Pt(C_6H_5CN)_2Cl_2^* + CHCl_3}$$
$$\xrightarrow{k_2} \mathrm{Pt(C_6H_5CN)Cl_3 + C_6H_5CN + \bullet CHCl_2} \quad (7)$$

$$\mathrm{CHCl_3} \xrightarrow{h\nu} \bullet \mathrm{CHCl_2 + Cl\bullet} \quad (8)$$

$$\mathrm{Cl\bullet + CHCl_3} \xrightarrow{k_3} \mathrm{HCl + \bullet CCl_3} \quad (9)$$

$$\bullet \mathrm{CHCl_2 + CHCl_3} \xrightarrow{k_4} \mathrm{CH_2Cl_2 + \bullet CCl_3} \quad (10)$$
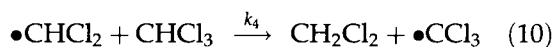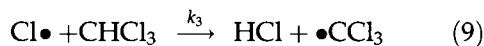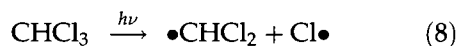
Equations (5)–(7) represent an initial reaction of the excited state Pt(II) complex with chloroform, leading to a Pt(III) intermediate, displacement of a benzonitrile, and the loss of a chlorine atom by chloroform to leave a dichloromethyl radical. Equations (8)–(10) represent bond homolysis by chloroform upon the absorption of light, followed by hydrogen abstraction to yield trichloromethyl radicals [8,9]. The rate of the first photochemical step (Equation 5) may be written as $I_0 f_R / V$, and that of the second (Equation 8) as $I_0 f_S \phi_S / V$, where ϕ_S is the quantum yield for carbon–chlorine bond fission.

We assume that the intermediate Pt(III) complex reacts directly with chloroform to yield HPt(C₆H₅CN)Cl₃, which constitutes the metal-centered pathway. In order to explain the solvent-initiated portion of the reaction, we postulate that the same product may also be formed directly from the ground state Pt(II) complex by reaction

with HCl, formed in Equation (9),

$$Pt(C_6H_5CN)_2Cl_2 + HCl$$

$$\xrightarrow{k_5} HPt(C_6H_5CN)Cl_3 + C_6H_5CN \qquad (11)$$

$$Pt(C_6H_5CN)Cl_3 + CHCl_3$$

$$\xrightarrow{k_6} HPt(C_6H_5CN)Cl_3 + \bullet CCl_3 \qquad (12)$$

The $\bullet CCl_3$ radicals would self-terminate, with no effect on the rate of formation of $HPt(C_6H_5CN)$-Cl_3. Under steady state conditions for HCl, $Pt(C_6H_5CN)_2Cl_2^*$ and $Pt(C_6H_5CN)Cl_3$, the reaction rate would be

$$-\frac{d[R]}{dt} = \frac{I_0}{V}(f_R\phi_R + f_S\phi_S), \qquad (13)$$

where $\phi_R = k_2/(k_1 + k_2)$. This is consistent with most of the experimental observations under 254 nm irradiation, as demonstrated by the linearity of Figure 6. However, the curvature of the actinometry curve, Figure 2, indicates that Equation (13) and the mechanism that generated it are not completely adequate, at least not at higher light intensities.

A critical point concerns the lack of a $\bullet CCl_3$ substitution step,

$$Pt(C_6H_5CN)_2Cl_2 + \bullet CCl_3$$

$$\longrightarrow Pt(C_6H_5CN)Cl_3 + C_6H_5CN + CCl_2 \qquad (14)$$
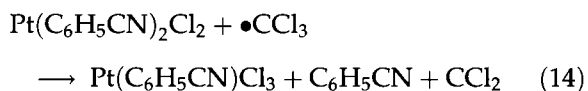
in the mechanism. In the $[Fe(dtc)_3] \rightarrow [Fe(dtc)_2Cl]$ substitution reaction, a $\bullet CCl_3$ substitution occurs as a chain propagation step, and leads to a square root dependence on the light intensity and fraction of light absorbed, because of the bimolecular termination of the trichloromethyl radicals [3]. However, in that process a direct radical substitution occurs, with no change in the oxidation state of the metal.

We have postulated a direct attack by HCl in Equation (11), because of the linear dependence of the rate on light intensity, and have ruled out chlorination by $\bullet CCl_3$ radicals because that

would lead to a square root dependence on light intensity and the fraction of light absorbed by the solvent. Experimentally, chloride ion (from Bu_4NCl) does accelerate the reaction substantially. An HCl addition reaction *might* also explain the partial dependence of the rate on I_0^2, or another higher power of I_0. HCl may be produced faster than it is used up, rendering the steady state approximation inaccurate. If the HCl concentration increases with time, an additional dependence of the reaction rate on f_SI_0 can be introduced [10].

Some light can be shed on this question by the results from 313 nm irradiation. Under these conditions absorption of light by $CHCl_3$, though not zero [2], can be neglected. Also, the considerably greater intensity of the 313 nm mercury line, compared to the 254 nm line, leads to more light absorbed by the Pt(II) complex, despite the lower extinction coefficient at that wavelength. Thus we can expect to be farther into the nonlinear region, which is confirmed by Figure 4, in which any linear dependence must be very small. From the experimental data it could not be established whether the reaction rate varied as the three-halves power or the square of the absorbed light intensity. A higher order dependence requires that two species formed photochemically react with each other.

One possibility consistent with the rate behavior is that $\bullet CCl_3$ radicals, though unreactive with the ground state complex, can attack the excited state complex. The reaction, otherwise the same as Equation (14), would be

$$Pt(C_6H_5CN)_2Cl_2^* + \bullet CCl_3$$

$$\xrightarrow{k_7} Pt(C_6H_5CN)Cl_3 + C_6H_5CN + CCl_2 \quad (15)$$
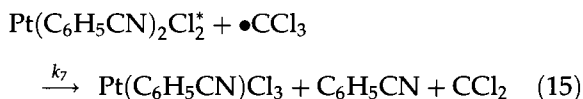
Equations (12) and (15) constitute a chain process, which allows us to consider the possibility that a reaction between two photoproducts can compete with one between a photoproduct and a bulk reactant, Equation (7). Given just the metal-initiated process, Equation (7), as an initiation step, the steady state approximation for

$Pt(C_6H_5CN)_2Cl_2^*$, $Pt(C_6H_5CN)Cl_3$, and all radicals, and the termination step,

$$2 \bullet CCl_3 \xrightarrow{k_8} C_2Cl_6 \tag{16}$$

lead to the rate law derived from Equations (5)–(7), (10), (12), (15) and (16)

$$-\frac{d[R]}{dt} = \left(\frac{k_2}{k_1 V}\right) I_0 f_R + \left(\frac{k_7 k_2^{1/2}}{k_8^{1/2} k_1^{3/2} V^{3/2}}\right) I_0^{3/2} f_R^{3/2}. \tag{17}$$

In Equation (17) the approximation was made that the nonradiative (or radiative) deactivation of the excited state, Equation (6), is much faster than the photochemical steps, Equations (7) and (15), which is consonant with the quantum yield. The first term is essentially identical to the first term of the rate expression for 254 nm irradiation, Equation (13).

The second term of Equation (17) supports the three-halves power dependence of the rate on the absorbed light intensity, illustrated in Figure 4. It is therefore tempting to characterize the first step of the photochemical substitution of $Pt(C_6H_5CN)_2Cl_2$ by the three unique terms in Equations (13) and (17): a metal-initiated pathway dependent on $I_0 f_R$, a solvent-initiated pathway, dependent on $I_0 f_S$, and a metal-initiated chain pathway dependent on $(I_0 f_R)^{3/2}$. The second term comes into play only at irradiation wavelengths short enough to cause significant light absorption by the solvent. The third term would be important at higher light intensities.

Despite the agreement with the experimental results, this mechanism must be regarded with caution. Other mechanisms can be devised in which two species produced photochemically react to form the product. The one proposed here, in which trichloromethyl radicals react with the excited state complex, even though the ground state complex is unreactive, is subject to severe, perhaps unreasonable, conditions on the rate constants. In order to achieve the observed rates

for the range of light intensities used, and in order for the rate of the 3/2-order path to equal or exceed the rate of the first-order path, the numerical value of $(k_1 k_2 k_8)^{1/2}$ should be within one or two orders of magnitude of k_7. If k_7 is significantly smaller, the 3/2-order reaction will not be competitive.

A diffusion-controlled rate constant of $\sim 10^{10} M^{-1} s^{-1}$ may be assumed for k_7, since one of the reactants is an excited state complex. One might also expect that k_8, the rate constant for the self-termination of $\bullet CCl_3$, would be diffusion-controlled, but experimental measurements place it between 10^7 and $10^8 M^{-1} s^{-1}$ [11]. From the quantum yield, k_2 is approximately $10^{-1} k_1$. This would permit k_1 to be at the most $10^8 s^{-1}$. Though one might expect a lifetime shorter than 10^{-8} s for a Pt(II) complex in solution, especially considering the lack of visible luminescence, a lifetime that long is certainly possible. The lifetime for solid K_2PtCl_4 at 20°C is 3×10^{-5} s [12], while that for dicyano(5,5'-dimethylbipyridine)platinum(II) in CH_3CN is 6×10^{-6} s [13], though both complexes are luminescent.

Regardless of the specific mechanism, we conclude from the data that at light intensities above 10^{-9} einstein/s, the photolysis of *cis*-[Pt(C₆H₅CN)₂Cl₂] proceeds in part through a metal-initiated pathway with a higher than linear dependence on the fraction of light absorbed by the reactant. We also conclude that a solvent-initiated pathway competes with metal-initiated pathways under 254 nm irradiation, but is significant only at very low concentrations.

Acknowledgements

References

[1] P.E. Hoggard, *Coord. Chem. Rev.* **159**, 235 (1997).

[2] S. Sathiyabalan and P.E. Hoggard, *Inorg. Chem.* **34**, 4562 (1995).

[3] J.M. Stegge, S.M. Woessner and P.E. Hoggard, *Inorg. Chim. Acta* **250**, 385 (1996).

[4] O. Monreal, T. Esmaeili and P.E. Hoggard, *Inorg. Chim. Acta* **265**, 279 (1997).

[5] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A* **235**, 518 (1956).

[6] A.D. Kirk and C. Namasivayam, *Anal. Chem.* **55**, 2428 (1983).

[7] L. Moggi, G. Varani, N. Sabbatini and V. Balzani, *Mol. Photochem.* **3**, 141 (1971).

[8] S. Hautecloque, *J. Photochem.* **14**, 157 (1980).

[9] I.G. Murgulescu and M. Weissman, *Rev. Roum. Chim.* **21**, 1275 (1976).

[10] E.M. Jaryszak and P.E. Hoggard, *Inorg. Chim. Acta,* in press.

[11] Z.B. Alfassi and S. Mosseri, *Reaction of CCl$_3$ and CF$_2$Cl Radicals,* in Z.B. Alfassi, ed., *Chemical Kinetics of Small Organic Radicals,* Vol. 3 (CRC Press, Boca Raton, 1988).

[12] J.N. Demas and C.M. Flynn, Jr., *Anal. Chem.* **48**, 353 (1976).

[13] C.M. Che, K.T. Wan, I.Y. He, C.K. Poon and V.W.W. Yam, *J. Chem. Soc. Chem. Comm.* 943 (1989).