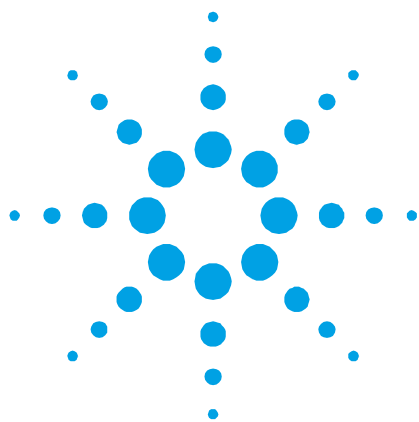




The investigation of the photo-kinetics of a platinum organoamine complex using the Cary 50/60

Application Note

Chemical

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Introduction

A photochemical reaction is a reaction that is initiated by the absorption of light. The reaction may then proceed with or without continuous irradiation. Reactivity arises from the absorption of light, which places the reactant molecules into an excited state. These molecules may then undergo a variety of subsequent reactions to form products. This reactivity is generally not observed in the ground state, i.e., when no light has been absorbed, however, very slow thermal reactions may occur¹.

In order to investigate a photochemical reaction *in situ*, using UV-Vis spectrophotometry, it is essential that the analyzing beam from the instrument does not degrade the sample, especially if the irradiating wavelength differs from that of the analyzing wavelength/s. This exemplifies the problem encountered with commercial diode array spectrophotometers, where the sample is analyzed with white light.

Another requirement of the spectrophotometer is that it must accommodate a second external source used for irradiation. Light from this source may be introduced to the sample via a fiber optic bundle, which means that the instrument must be able to operate with the sample compartment open. A black cloth is usually used to prevent unwanted degradation from room light. A subsequent consideration then becomes the stray light interference from the irradiating beam with the analyzing beam from the spectrophotometer. If the instrument is not room light immune, then the intensity of the irradiating beam can cause instrument problems, such as deviations from instrument photo-linearity specifications.



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The Agilent Cary 50 and Cary 60 takes into consideration all of the aforementioned points. It is room light immune, so stray light is not a problem, and it does not degrade even the most photo-sensitive samples. Figure 1 shows the absorption at 366 nm vs time profile for the irradiation of a photoactive platinum compound, [N,N'-Bis(2,3,5,6-tetrafluorophenyl)ethane-1,2-diaminato(2-)]dipyridineplatinum(II) in acetonitrile (quantum yield of photosubstitution in acetonitrile of 0.96)², performed on a Cary 50 and a commercial instrument. As can be seen, significant photo-degradation is caused by the other spectrophotometer.

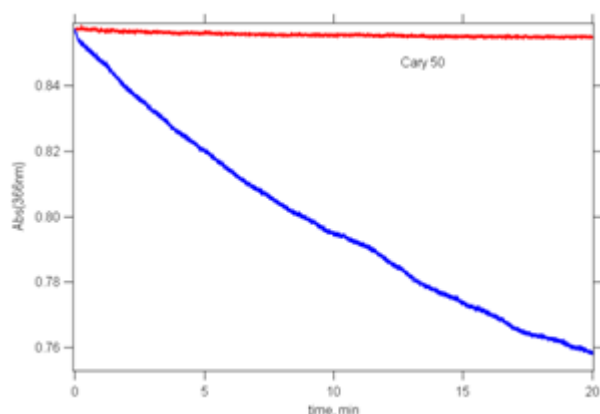


Figure 1. Absorbance(366 nm) vs time of platinum complex

This paper demonstrates the advantages of the Cary 50/60 UV-Vis when used to monitor photochemical reactions, by investigating the kinetics of [N,N'-Bis(2,3,5,6- tetrafluorophenyl)ethane-1,2-diaminato(2-)]dipyridineplatinum(II) in acetonitrile.

Background

The photochemistry of [N,N'-Bis(2,3,5,6-tetrafluorophenyl)ethane-1,2-diaminato(2-)]dipyridineplatinum(II)ⁱ, referred from now on as **1a**, has been investigated in previous studies^{2,4}. When irradiated with UV/blue light, solutions of **1a** undergo photochemical substitution in which a pyridine ligand is replaced by a solvent molecule (Figure 2). Continued irradiation sees the loss of a second pyridine and

finally the formation of a tetrakis-platinum solvent species.

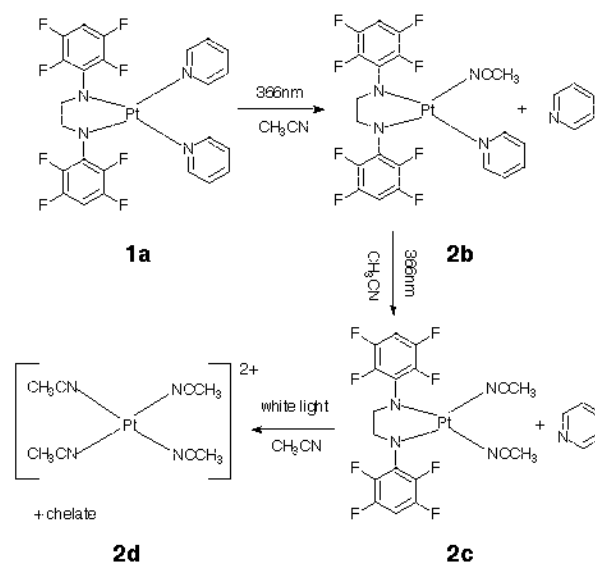


Figure 2. Schematic for the photosubstitution of **1a** in acetonitrile

The quantum yield of photoproduct formation for the mono-solvento complex has been determined in acetonitrile, DMSO and THF². In fact, the quantum yield measured in acetonitrile is the highest ever reported for a platinum photosubstitution reaction. The mechanism of photosubstitution is shown in Figure 3.

Irradiation with light of 366 nm populates a ligand-ligand charge transfer (LLCT) excited state, which is in thermal equilibrium with a ligand field (LF) excited state. High pressure photochemical experiments support a dissociative mechanism, in which the formation of the mono-solvento species occurs via a three coordinate transition state intermediate².

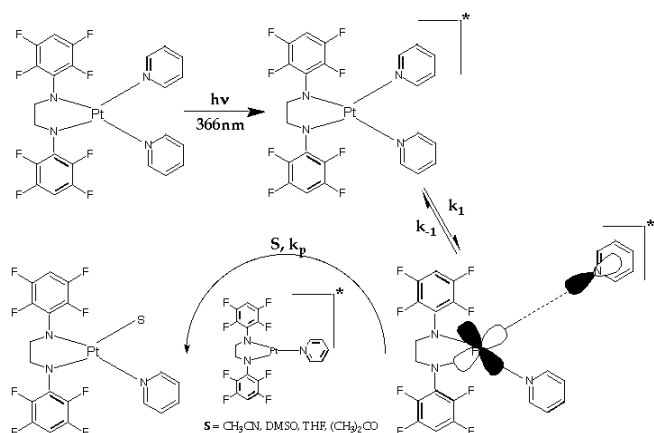


Figure 3. Mechanism of photosubstitution of 1a in solution

Experimental

Reagents:

- Acetonitrile (BDH, HPLC grade)
- [N,N'-Bis(2,3,5,6- tetrafluorophenyl)ethane-1,2-diaminato(2-)] dipyrindineplatinum(II)
- Potassium ferrioxalate (0.0114 M)
- Buffer (CH₃COONa/H₂SO₄ pH 3.5)
- 1:10 phenanthroline (0.1% w/v)
- MilliQ water

Apparatus:

- Agilent Cary 50 (Cary 60) UV-Vis
- WinUV Software
- Single cell Peltier temperature accessory
- 10mm pathlength quartz cuvette
- 100W Hg arc lamp/housing
- 366 nm bandpass filter
- 3' quartz fibre optic bundle

Figure 4 shows the setup used for irradiation.

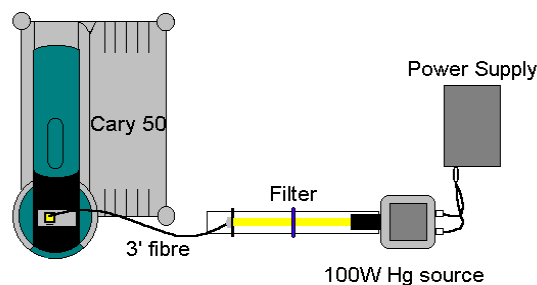


Figure 4. Setup of apparatus used for irradiating sample

White light from a 100W Hg source passes through a bandpass filter isolating the intense 366 nm Hg line, and is directed via a 3 foot fibre optic bundle into the top of a quartz cuvette. The solution in the cuvette, which is continuously stirred, immediately undergoes photochemical change upon irradiation from the Hg source. The solution is analysed using a Cary 50 UV-Vis with the WinUV Scanning and Kinetics software packages. A Cary 60 UV-Vis can also be used for this experiment.

Discussion

The intensity of the 366 nm irradiating beam from the Hg lamp was measured through chemical actinometry⁵. The method used is a modification from Hatchard and Parker's original procedure⁵, the details of which are fully described in References 2 and 4 and summarised below.

Potassium ferrioxalate (0.0114M, 1.30 cm³) was added to the quartz cuvette, immediately followed by CH₃COONa/H₂SO₄ buffer solution (pH 3.5, 0.70 cm³) and 1:10 phenanthroline (0.1% w/v, 0.50 cm³). The cuvette was placed in the thermostatted cell holder (25 °C) and allowed to equilibrate for 5-10 minutes in the dark. The solution was then irradiated with 366 nm Hg light and the absorbance at 510 nm monitored in the absence (no change in Abs, Figure 5) and presence (change in Abs, Figure 5) of the irradiating beam.

The instrument parameters used are outlined below.

Wavelength (nm)	510
Ave Time (s)	0.1
Y Min	0
Y Max	1.0
Cycle (min)	0
Stop (min)	30

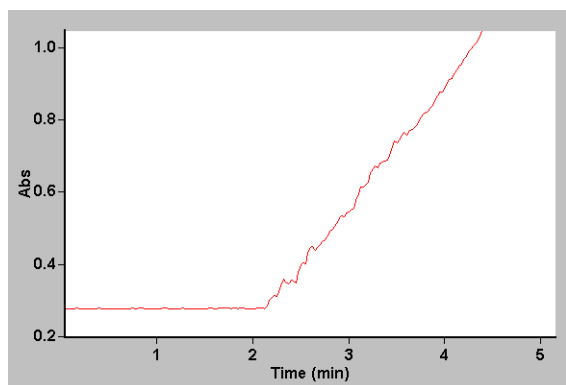


Figure 5. Absorbance(510 nm) vs time during irradiation with 366 nm Hg light

The change in absorbance only occurs in the presence of the irradiating beam. The intensity of the irradiating beam, in einsteins s⁻¹ dm⁻³, is calculated from this change in absorbance with time using Equations 1 and 2 below⁶.

$$\frac{n[\text{Fe(phen)}_3]^{2+}}{dt} = \frac{d\text{Abs}_{510}}{dt} \frac{V}{\epsilon_{510} l} \quad \text{Equation 1}$$

Where :

V = volume of solution irradiated (dm³)

ϵ_{510} = molar extinction coefficient at 510 nm of [Fe(phen)₃]²⁺ (M⁻¹cm⁻¹)

l = pathlength (cm)

$$I_0 = \frac{n[\text{Fe(phen)}_3]^{2+}}{\phi_{\text{Fe}^{2+}, \lambda} \frac{dt}{dt}} \quad \text{Equation 2}$$

Equation 1 calculates the change in the number of moles of [Fe(phen)₃]²⁺ with respect to irradiating time, which is used in Equation 2 to determine the intensity of the irradiating beam, I₀. The quantum yield for Fe²⁺ formation is 1.21, as determined by Hatchard and Parker⁵. The intensity of the irradiating source is determined before and after the photolysis of **1a**, and the result averaged to account for any intensity fluctuations in the Hg lamp over the course of the experiment. The lamp used is relatively stable over a period of days. The average intensity of the irradiating beam incident on the platinum solution is 9.32(2) × 10⁻¹⁰ einstein sec⁻¹ cm⁻².

Compound **1a** in acetonitrile (2.5 cm³) was then irradiated with the Hg source. The change in spectra over a 250 nm range (Figure 6) and the absorbance at 366 nm (Figure 7) were recorded in two separate experiments using the WinUV Scan and Kinetics packages respectively.

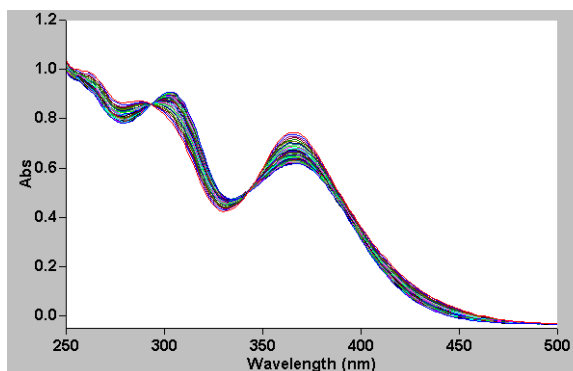


Figure 6. Change in absorption spectra of 1a in CH₃CN during irradiation with Hg light

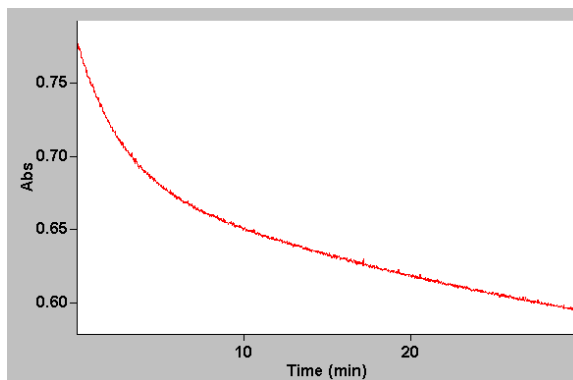


Figure 7. Change in absorbance(366 nm) as a function of time during irradiation

Figure 6 shows the formation of 2 isosbestic points, at 293 nm and 344 nm, during the initial stage of photolysis. During this time, only the mono-CH₃CN complex is being formed. The extremely fast scanning speed of the Cary 50/60 allows the fifty overlaid spectra in Figure 6 to be collected in less than 2 minutes.

The change in absorbance(366 nm) with time, $Abs_{\lambda,t}$, was used in Equation 3 to calculate the change in concentration of **1a**, $[A_t]$. The molar extinction coefficients at 366 nm of **1a** (ϵ_A) and **2b** (ϵ_B) have been previously determined², hence, $d[1a]/dt$ can be calculated.

$$[A_t] = \frac{Abs_{\lambda,t} - (\epsilon_B [A_0] l)}{l(\epsilon_A - \epsilon_B)} \quad \text{Equation 3}$$

Where :

l = pathlength (cm)

$[A_0]$ = the initial concentration of **1a**

The quantum yield of photoproduct formation (Φ_{PR}) of **2b** is defined as the amount of **2b** formed (or the amount of **1a** depleted), with respect to the amount of light absorbed by **1a**. The amount of light absorbed by **1a** over the course of the experiment (I_{abs}) is given by Equations 4-7⁷.

$$I_{abs} = \int_0^t I_{abs}(t) dt \quad \text{Equation 4}$$

$$I_{abs}(t) = I_{sol}(t) \alpha(t) \quad \text{Equation 5}$$

$$I_{sol}(t) = I_0 \left(-10^{-Abs_{\lambda,t} l} \right) \frac{S}{V} \quad \text{Equation 6}$$

$$\alpha(t) = \frac{\epsilon_A [A]_t l}{Abs_{\lambda,t}} \quad \text{Equation 7}$$

Where:

I_{sol} = the amount of light absorbed by the solution

$\alpha(t)$ = the fraction of light absorbed by **1a**

S = the area exposed to irradiation (cm²)

V = the volume of solution irradiated (dm³)

The quantum yield of formation of **2b** is then determined by plotting the change in concentration of **1a** against I_{abs} (Figure 8), and fitting a linear regression over the first 10% of the reaction. The quantum yield is given by the gradient, as defined in Equation 8.

$$-\frac{d[A]}{dt} = \Phi_{PR} I_{abs} \quad \text{Equation 8}$$

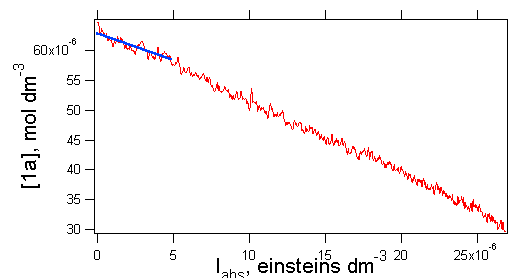


Figure 8. [1a] vs I_{abs} in acetonitrile

The WinUV software allows data to be exported as ASCII *.csv files. These files were imported into the mathematical analysis program IGOR PRO⁸, where Equations 3-8 were calculated. Figure 8 was also generated in IGOR PRO. A calculated quantum yield of (0.92 ± 0.04) molecules per photon of light absorbed is in excellent agreement with the literature value of (0.96 ± 0.03) ².

Conclusion

The Agilent Cary 50 and Cary 60 UV-Vis, with its room light immunity and fast scan speeds, has revolutionized the world of UV-Vis spectroscopy. Coupled with the powerful and versatile WinUV Kinetics and Scanning software, the Cary 50/60 UV-Vis is ideal for the study of photochemical kinetics. In analysing photochemical reactions, it allows the use of an irradiating light source without the problems associated with stray light. Also, studying even the most light-sensitive of compounds *in situ*, does not cause photodegradation from the analysing beam, which generally occurs when white light is used for analysis.

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