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Investigation of photochemical reactions using UV-Vis spectroscopy

UV-76
February 1998

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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. The 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 occur[1].

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 is a problem with commercial diode array spectrophotometers, where the sample is analyzed with white light. Significant photodegradation occurs over time.

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 fibre optic bundle, which means that the instrument must be able to operate with the sample compartment open. A black cloth may be placed over the instrument and sample to prevent unwanted degradation from room light. A subsequent consideration then becomes stray light interference from the irradiating beam with the analyzing measurement from the spectrophotometer. If the instrument is not room light immune, then the intensity of the irradiating beam can cause major problems, particularly with deviations from photo-linearity instrument specifications. This can result in significant errors with the data collected.

The Cary 50 is the first UV-Vis scanning spectrophotometer that 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 absorbance at 366 nm over time for the irradiation of a photoactive platinum compound in acetonitrile[2]. The experiment, performed on a Cary 50 and a commercial diode array spectrophotometer, shows significant photo-degradation by the diode array instrument.

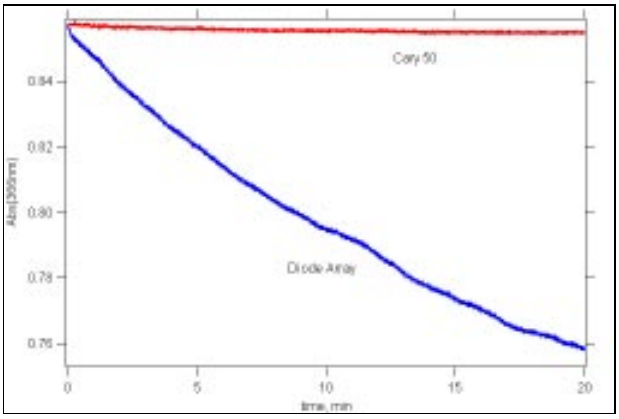

Figure 1: Absorbance(366 nm) vs time of platinum complex.

This paper demonstrates the advantages of the Cary 50 spectrophotometer when used to monitor photochemical reactions *in situ*, by investigating the photochemical degradation of the compound potassium ferrioxalate ($K_3[Fe(C_2O_4)_3]$).

Background

The efficiency of a photochemical reaction is defined by its quantum yield of product formation, i.e. how much product is produced with respect to how much light is absorbed. For a reaction where A⟶ B via the absorption of light, the quantum yield of photo-product formation (Φ_{PR}) is defined by Equation 1, where I_{abs} is the amount of light absorbed by the reactant, A, and d[A]/dt is the change in concentration of A with time.

$$-\frac{d[A]}{dt} = \Phi_{PR} I_{abs} \qquad \textit{Equation 1}$$

The change in concentration is followed by measuring the absorbance at a specific wavelength and using the Beer-Lambert law to convert this to a concentration. The intensity of absorbed light is calculated using Equations 2-5, which require the measurement of the absolute intensity, I_0, of the irradiating source.

$$I_{abs} = \int_0^t I_{abs}(t)dt \qquad \textit{Equation 2}$$

$$I_{abs}(t) = I_{sol}(t)\alpha(t) \qquad \textit{Equation 3}$$

$$I_{sol}(t) = I_0\left(1-10^{-Abs_{\lambda,t}\,l}\right)\frac{S}{V} \qquad \textit{Equation 4}$$

$$\alpha(t) = \frac{\varepsilon_A[A]_t\,l}{Abs_{\lambda,t}} \qquad \textit{Equation 5}$$

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 (cm^2)
- V = the volume of solution irradiated (dm^3)

The absolute light intensity of a source can be determined through actinometry. An actinometer is a substance or device that responds, in some measurable way, to the amount of light it absorbs. In the case of a chemical actinometer, the absorption of light leads to a photochemical transformation that is monitored by some analytical technique. The amount of reactant transformed is then used to calculate the intensity of irradiating light in units of Einsteins per unit time and area.

The sensitivity of the actinometer depends on the quantum yield for the photolysis reaction and the method of analysis. The latter is the most important as some analysis methods can cause significant degradation of the actinometer solution. Also, since most actinometers are extremely sensitive to room light, they must be protected and analyzed in a darkroom under red or yellow safelights.

Experimental

Reagents:

Potassium ferrioxalate (0.0114 M)

Buffer (CH_3COONa/H_2SO_4 pH 3.5)

1:10 phenanthroline (0.1% w/v)

Deionized distilled water

Apparatus:

Cary 50 Bio UV/Vis spectrophotometer

WinUV Bio software

Cary single cell Peltier

Water circulating bath

Magnetic flea stirrer

10 mm pathlength quartz cuvette

100 W Hg arc lamp/housing (Oriel)

366 nm bandpass filter

3' quartz fibre optic bundle (Dolan Jenner)

Potassium ferrioxalate (0.0114 M, 1.30 cm^3) was added to the quartz cuvette, immediately followed by CH_3COONa/H_2SO_4 buffer solution (pH 3.5, 0.70 cm^3) and 1:10 phenanthroline (0.1% w/v, 0.50 cm^3). 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. The instrument parameters used are listed below and Figure 2 shows the setup used for irradiation.

Wavelength (nm)	366
Av. Time (s)	0.1
Y Min	0
Y Max	1.0
Cycle (min)	0
Stop (min)	30

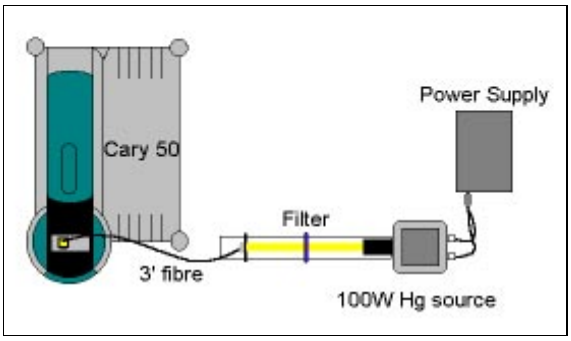

Figure 2: Setup of apparatus used for irradiating sample.

Light from a 100 W 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 of $K_3[Fe(C_2O_4)_3]$ in the cuvette, which is continuously stirring, immediately undergoes photochemical reduction upon irradiation from the Hg source and the change in absorbance is measured at 510 nm The solution is analyzed using a Cary 50 Bio spectrophotometer with the WInUV Kinetics software package.

Discussion

Potassium ferrioxalate is an extremely sensitive actinometer. Investigated by Hatchard and Parker[3] in the mid 1950s, $K_3[Fe(C_2O_4)_3]$ undergoes photochemical reduction from Fe^{III} to Fe^{II} upon absorbing UV-Vis (λ<500nm) radiation, as shown in Equations 6-8. The quantum yield of Fe^{II} formation is reported in Hatchard and Parker's paper, and the change in amount of Fe^{II} produced during irradiation is followed by UV-Vis spectrophotometry at 510 nm. The addition of 1:10 phenanthroline to the irradiated solution results in the formation of $[Fe(phen)]^{II}$, which has an absorption maximum at 510 nm.

$$[Fe^{III}(C_2O_4)_3]^{3-} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + C_2O_4^{-} \qquad \textbf{Equation 6}$$

$$[Fe^{III}(C_2O_4)_3]^{3-} + C_2O_4^{-} \rightarrow [Fe^{III}(C_2O_4)_3]^{2-} + (C_2O_4)^{2-} \qquad \textbf{Equation 7}$$

$$[Fe^{III}(C_2O_4)_3]^{2-} \rightarrow [Fe^{II}(C_2O_4)_2]^{2-} + 2CO_2 \qquad \textbf{Equation 8}$$

In the past, the amount of Fe^{II} produced has been determined by measuring the absorbance of $K_3[Fe(III)(C_2O_4)_3]$ at 510 nm before irradiation, irradiating the sample for a known time, adding 1:10 phenanthroline in a dark room, and then measuring the absorbance of $[Fe(II)(phen)_3]^{II}$ at 510 nm again.

The intensity of the irradiating source, I_0, is then calculated from the amount of Fe^{II} produced during irradiation.

The Cary 50 allows the above procedure to be slightly modified. Due to the room light immunity of the instrument, the change in absorbance at 510 nm can be measured *in situ* during irradiation of the $K_3[Fe(C_2O_4)_3]$ solution. This reduces the handling of solution during the reaction which, in turn, eliminates unnecessary exposure to ambient light. In order to avoid degradation during the reaction due to room light, a thick black cloth was placed over the entire instrument.

Figure 3 shows the change in absorbance at 510 nm in the absence (0 - 1.8 min) and presence (1.8 - 4 min) of the irradiating beam.

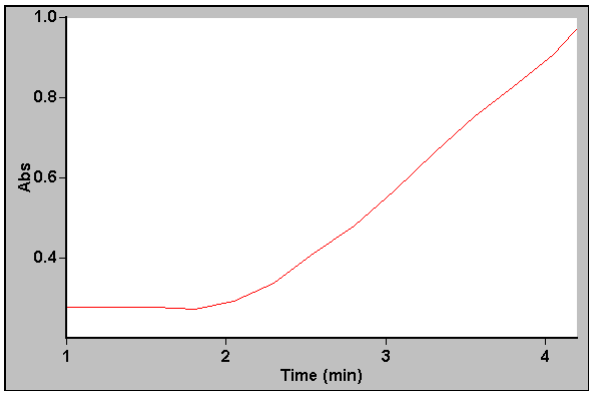

Figure 3: Absorbance(510 nm) vs time during irradiation with 366 nm Hg light.

The change in absorbance at 510 nm only occurs during irradiation and is linear. This linearity and absence of noise in the data, shows that stray light has little effect on the measurements and also confirms that stirring was extremely efficient. The intensity of the irradiating beam, in Einsteins s^{-1} dm^{-3}, was calculated from the change in absorbance using Equations 9 and 10 [4].

$$\frac{n\left[Fe(phen)_3\right]^{II}}{dt} = \frac{dAbs_{510}}{dt}\frac{V}{\varepsilon_{510}\,l} \qquad \textbf{Equation 9}$$

where

V = volume of solution irradiated (dm^3)

ε_{510} = molar extinction coefficient at 510 nm of $[Fe(phen)_3]^{II}$ ($M^{-1}cm^{-1}$)

l = pathlength (cm)

$$I_0 = \frac{\frac{n\left[Fe(phen)_3\right]^{II}}{dt}}{\phi_{Fe^2,\lambda}}$$ ***Equation 10***

Equation 9 calculates the change in the number of moles of $[Fe(phen)_3]^{II}$ with respect to irradiating time, which is used in Equation 10 to determine the intensity of the irradiating beam, I_0. Using the value of 1.21 for the quantum yield of Fe^{II} formation when $K_3Fe(C_2O_4)_3$ is irradiated with 366 nm light[3], the intensity of the irradiating beam incident upon the cuvette is $(9.32\pm0.02)\times10^{-10}$ Einstein s^{-1} cm^{-2}.

Conclusion

The Cary 50 spectrophotometer allows measurements to be performed whilst using an external light source to irradiate the sample. The problems of noise and deviations from photo-linearity, associated with stray light, are not observed. The Cary 50 is able to study even the most light-sensitive compounds *in situ* and does not cause photodegradation from the analyzing beam, which generally occurs when white light is used for analysis.

References

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