A Photochemical Reactor for the Study of Kinetics and Adsorption Phenomena

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A photochemical experiment irradiating an organic compound, such as a dye, can be used to examine the interaction between light and matter. As a commercial application, this type of experiment can be used to study the color stability of painted walls or the natural degradation of dyes in wastewaters *(1, 2)*. In this article we irradiate a dye, brilliant green (BG), with near-UV radiation introducing a novel photochemical reactor. The kinetics of photodegradation are examined in the presence and absence of anatase TiO_2 suspended in solution. The dye is adsorbed to the surface of the TiO_2 creating an additional photochemical degradation pathway.

The presence of a small quantity of anatase TiO_2 broadens the educational value of the experiment. The experiment could be used to investigate topics in physical chemistry, such as heterogeneous catalysis *(3, 4)*, semiconductor properties, and adsorption phenomena.

Theory

In semiconductor materials, electrons occupy energy bands. The highest energy band occupied by electrons is called the valence band. The next band higher in energy, which is empty, is called the conduction band. The bands are separated by an energy gap, known as the forbidden zone, which represents a range of energies that electrons do not have. For TiO_2, this gap corresponds approximately to 3.23 eV, which is the energy of a photon with a wavelength of 388 nm (near-UV range). When a TiO_2 particle is irradiated with a wavelength less than 388 nm, the energy provided is great enough to promote an electron from the valence band to the conduction band. This electron can migrate through the semiconductor surface and be transferred to an adsorbed molecule, for example, a dye molecule, thus generating a charge pair between the adsorbed molecule and the semiconductor *(5)*. As a consequence, the dye reactivity can be increased, creating a new photodegradation pathway and accelerating the process.

The Reactor

We have designed a novel photochemical reactor intended to be used for the kinetic study of dye photodegradation using spectrophotometric analysis. A distinctive characteristic differentiating this reactor from other devices *(6)* is that the sample is not irradiated in an isolated box but continuously flows around the UV source. Unlike static reactors, our apparatus works with a minimum irradiance power (preventing heating problems) and shows greater efficiency. Since it works as a closed system, it avoids problems of vaporization. The design is simple and is based on the use of readily accessible, low-cost materials.

The main element of the reactor (Figure 1) consists of a Pyrex glass Liebig or West condenser 40-cm long, with an external diameter of 3.5 cm, and an internal diameter of 2.0 cm. The transparency coefficient for Pyrex glass (borosilicate type) reaches a peak level of 0.95–0.99 from 360 to 500 nm, exceeded only by quartz *(7)*; thus it is an excellent and inexpensive material to use in photochemical experiments within the near-UV range. A commercial 8-W fluorescent actinic lamp (black light mercury) is placed inside the condenser. This lamp, which produces an intense emission at 366 nm (Figure 2), is similar to the ones used in systems designed to

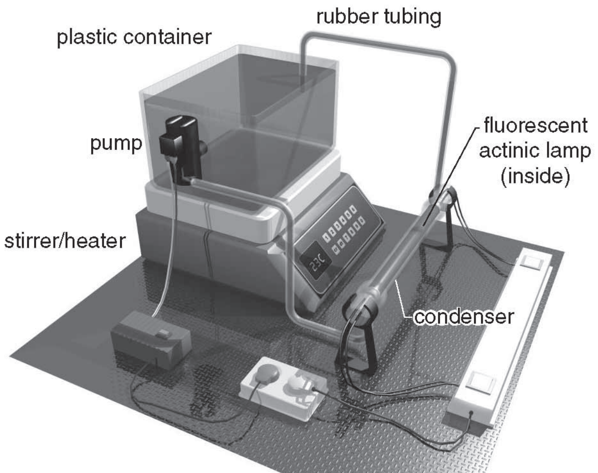

Figure 1. Experimental reactor configuration.

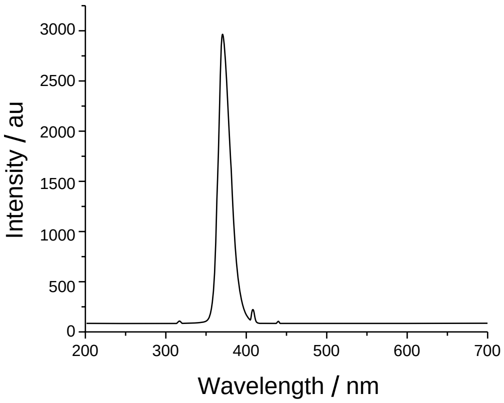

Figure 2. Black light mercury lamp emission spectrum.

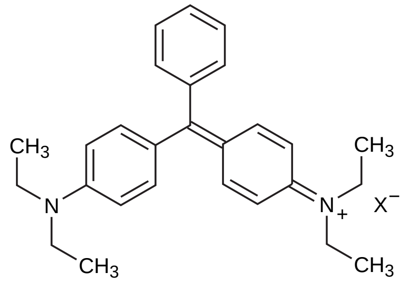

Figure 3. Structure of BG.

detect counterfeit money or fake credit cards, and to systems used in mineralogy and philately *(8)*. The condenser's external walls are completely covered with aluminium foil to prevent exposure to radiation and to improve the reactor's efficiency.

A dye solution is pumped via flexible rubber tubing through the condenser jacket from a 1500-mL plastic container equipped with a stirrer. The pump is like those used in cars to spray the windshield washer fluid. It is originally designed for 12-V dc operation, however it is driven by a 5-V dc power supply to avoid overheating.

Hazards

Optimal eye UV-A protection is advised. Lamp accessories, such as switches, sockets, ballast, and capacitor, must be inside an isolated box to prevent contact with the aqueous solution (not shown in Figure 1).

Some of the chemicals used in this experiment (brilliant green, malachite green, and potassium oxalate monohydrate) are classified as harmful. Avoid contact, inhalation, and ingestion. Gloves must be used.

Experiment

The usefulness of the reactor has been evaluated by means of two experiments, both using 750 mL of a 10^{-5} M aqueous solution of brilliant green (BG; Figure 3), and in one of the experiments 30 mg of TiO_2. To stabilize adsorption equilibrium and photon fluxes, the magnetic stirrers and the lamps were turned on 30 minutes before starting the pumps and taking the first samples. The samples were centrifuged and filtered before measuring their absorbances at 625 nm (wavelength of maximum absorbance). The reactor worked in continuous flow for two hours and the samples were collected every ten minutes. Along with the experiments, two samples (one for each experiment) were placed next to the reactor and exposed to room light. After two hours, these samples showed no significant changes in their absorbances.

The photodegradation kinetics of many organic compounds in TiO_2 dispersions under UV radiation follows the Langmuir–Hinshelwood equation *(9–11)*,

$$r = \frac{dc}{dt} = \frac{k_{ph} K_{ad}\, c}{1 + K_{ad}\, c} \qquad (1)$$

where k_{ph} is a rate constant that provides a measure of the intrinsic reactivity of the photoactivated surface, K_{ad} is the adsorption equilibrium constant, and c is the dye concentration. At low concentrations, when $K_{ad}c << 1$, the kinetics is first order and eq 1 may be expressed as,

$$r = k_{ph}K_{ad}c = k_{app}c \qquad (2)$$

where k_{app} is the apparent first-order rate constant.

A graph plotting the natural logarithm (ln) of the absorbance data versus time in minutes is shown in Figure 4. The regression coefficients (R^2) corresponding to the linear best-fits for the experiments with and without TiO_2 were both 0.99, confirming that the photodegradation reaction follows first-order kinetics. The reaction with the TiO_2 is faster than the reaction without it. This is shown in Figure 4, where the apparent rate constant calculated from the slope of the linear fit, is 15 times greater in the presence of the TiO_2 (5.62×10^{-4} s^{-1}), than in the absence of it (3.67×10^{-5} s^{-1}). It should be noted that BG photodegradation in the presence of the TiO_2 is not only due to the catalytic reaction but also to the noncatalyzed reaction.

Apparent versus Observed Rate Constant

The reaction mixture is never entirely exposed to the radiation at any one time. At any given instant, if only a 10% volume aliquot of the reaction mixture is exposed with a 50% degradation efficiency and then mixed with the remaining 90% volume of unexposed reaction mixture, it would seem that only 5.0% degradation has occurred. As a consequence, the observed rate constant, k_{obs}, must be related to k_{app} through the relationship,

$$k_{obs} = k_{vol}k_{app} \qquad (3)$$

where k_{vol} is the quotient between the radiated volume and the total volume of the reaction mixture. This relationship may be estimated measuring the condenser volume or carrying out two experiments with different total volumes. In our case, the estimated value for k_{vol} is 0.144 and the apparent rate constants based on the ones observed for the experiments

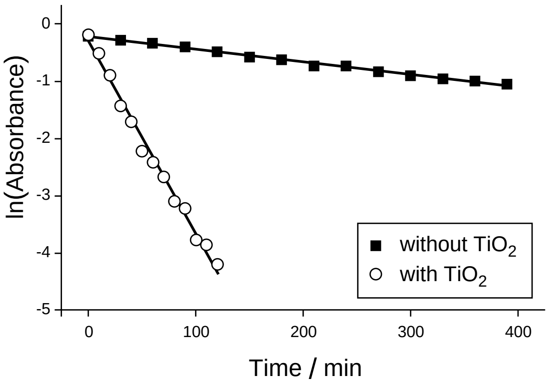

Figure 4. Photodegradation of BG by UV-A radiation with and without TiO_2. The absorbance of the experiment with TiO_2 advances quickly to the zero absorbance value at equilibrium, whereas in the experiment without TiO_2 it progresses much more slowly.

with and without TiO_2 were 3.93×10^{-3} s^{-1} and 2.50×10^{-4} s^{-1}, respectively.

An Actinometry Measurement

Photochemical experiments are usually designed to incorporate actinometry measurements to obtain the irradiance value, I_0. These measurements help the interpretation of kinetics data, since the value of the rate constant is proportional to the quantum yield Φ, (ratio of molecules that react divided by the number of photons absorbed) and to the light absorbed, I_{abs}, which itself is a fraction of I_0 *(12)*.

An actinometer is a chemical whose photochemical behavior has been precisely studied and quantum yields are accurately known. Potassium ferrioxalate, $K_3Fe(C_2O_4)_3$, is a commonly used chemical actinometer that absorbs UV and visible light up to 500 nm. When this compound is dissolved in a sulfuric acid solution and radiated with light within this wavelength range, a photochemical reaction takes place producing Fe^{2+} *(13)*:

$$2Fe^{3+} + C_2O_4^{2-} \xrightarrow{h\nu} 2Fe^{2+} + 2CO_2 \qquad (4)$$

The amount of ferrous ion generated is measured via spectrophotometric determination of its 1,10-phenanthroline complex at 510 nm. Using the absorbances obtained at this wavelength, the irradiance calculated for the reactor is 1.23×10^{-8} einstein cm^{-2} s^{-1}.

Other Applications of the Reactor

Many modifications could be made on the experiment described above to explore other concepts. For example, different dyes, catalysts (e.g., ZnO, CdS), and irradiation wavelengths could be used for this reactor.

In connection with these modifications, we propose an interesting experiment based on the use of another dye, malachite green (MG). Structure of MG is very similar to that of BG (Figure 3), except that the four ethyl groups in BG are replaced by methyl groups in MG and the counter ions are different. In the absence of surfactants, MG is difficult to degrade in aqueous TiO_2 dispersions as a result of its poor solubility in water and low adsorption on the surface of TiO_2 particles. The addition of surfactants enhances the solubility and adsorption ability of MG, thus significantly accelerating the MG degradation rate in aqueous TiO_2 dispersions *(14)*. According to this, the influence of several surfactants could be evaluated as another useful application of the photochemical reactor.

Finally, a further interesting experiment is to use a higher concentration of MG (or BG) to verify the Langmuir–Hinshelwood equation, using the linear transformation of eq 1, that is,

$$\frac{1}{r} = \frac{1}{k_{ph} K_{ad}\, c} + \frac{1}{k_{ph}} \qquad (5)$$

Acknowledgment

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ʷSupplemental Material

Comments and suggestions for the experiment and details of the actinometry experiment are available in this issue of *JCE Online*.

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