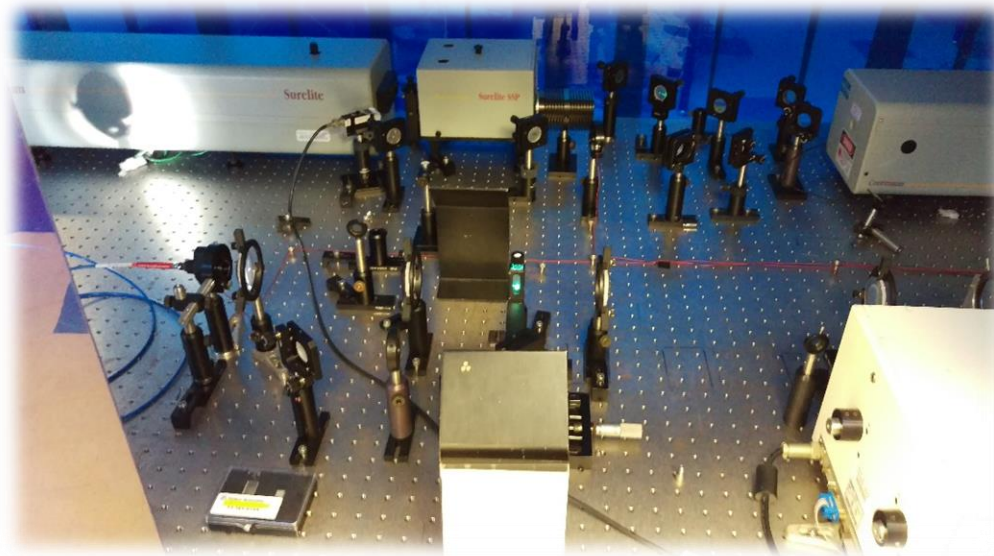
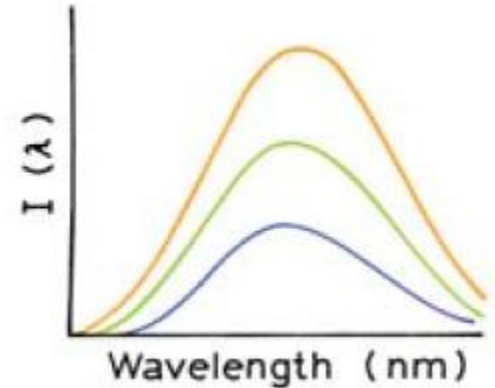


Instrumentation and Experimental Techniques



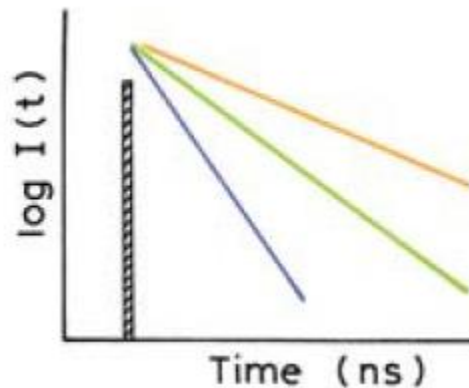
Steady-State vs. Time-Resolved Fluorescence

- Fluorescence measurements can be broadly classified into two types of measurements:
- **Steady-state measurements**, the most common type, are performed with constant illumination and observation
- The sample is illuminated with a continuous beam of light, and the intensity or emission spectrum is recorded
- Because of the ns timescale of fluorescence, most measurements are steady-state measurements
- When the sample is first exposed to light, steady state is reached almost immediately



Steady-State vs. Time-Resolved Fluorescence

- The second type of measurement is **time-resolved**, which is used for measuring intensity decays
- For these measurements, the sample is exposed to a pulse of light, where the pulse width is typically shorter than the decay time of the sample
- The intensity decay is recorded with a high-speed detection system that permits intensity to be measured on the ns timescale

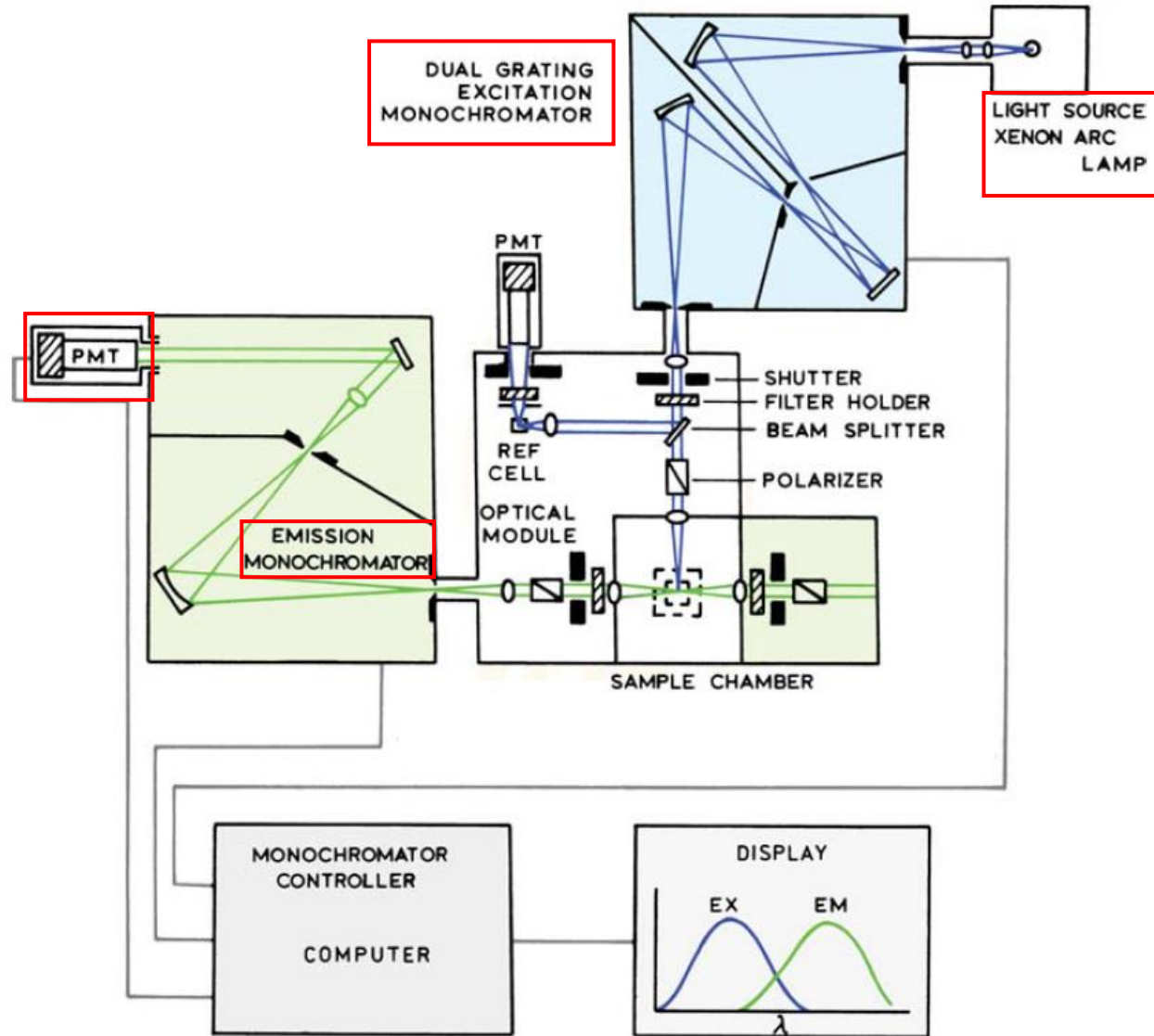


Spectrofluorometers

- For most spectrofluorometers it is possible to record both excitation and emission spectra
- An **emission spectrum** is the wavelength distribution of an emission measured at a single constant excitation wavelength
- Conversely, an **excitation spectrum** is the dependence on emission intensity, measured at a single emission wavelength, upon scanning the excitation wavelength
- Such spectra can be presented on either a wavelength scale or a wavenumber scale

Spectrofluorometers

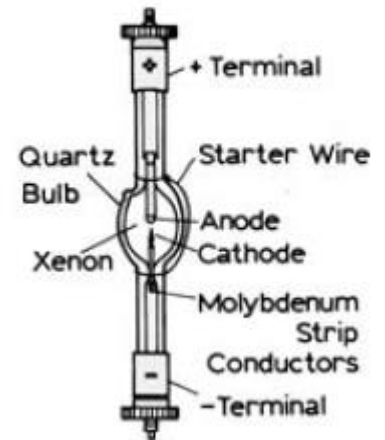
- Here is a schematic for a typical spectrofluorometer:



Spectrofluorometers

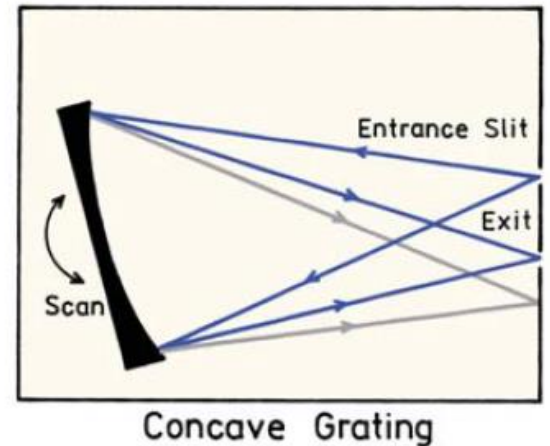
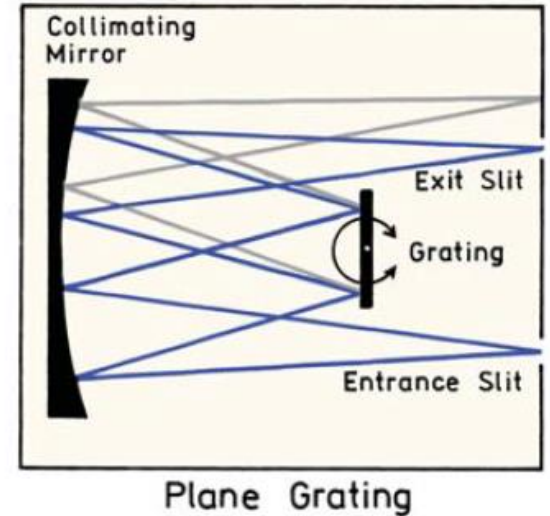
- For the source of exciting light, a **Xenon arc lamp** is typically used
- Such lamps are generally useful because of their high intensity at all wavelengths ranging upward from 250 nm
- Xenon arc lamps emit a continuum of light as a result of recombination of electrons with ionized Xe atoms
- These ions are generated by collisions of Xe atoms with the electrons that flow across the arc

Xenon Arc Lamp



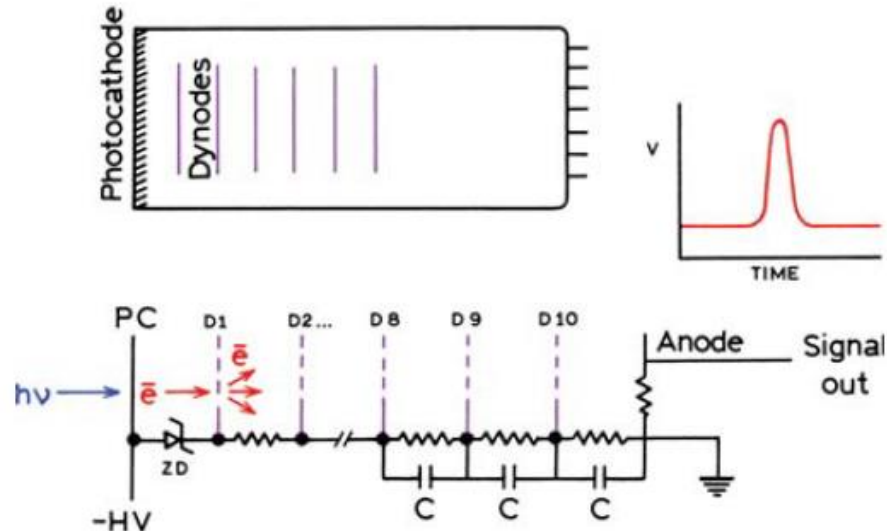
Spectrofluorometers

- The instrument is equipped with **monochromators** to select both the excitation and emission wavelengths using a diffraction grating
- In the prior diagram, the excitation monochromator contains two gratings, which decreases stray light, that is, light with wavelengths different from the chosen one
- Both monochromators are motorized to allow automatic scanning of wavelength
- Monochromators can have planar or concave gratings



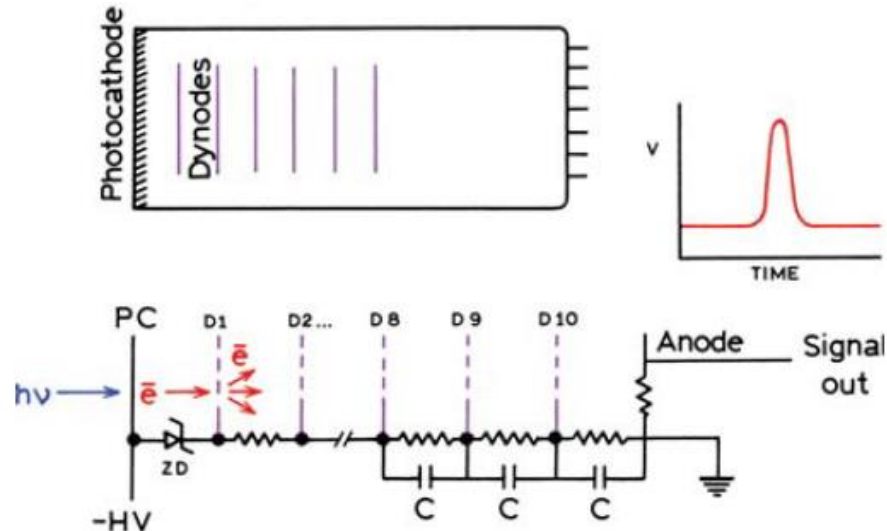
Spectrofluorometers

- The fluorescence is detected with a **photomultiplier tube (PMT)**
- A PMT is regarded as a current source, and the current is proportional to the light intensity
- A PMT vacuum tube consists of a photocathode and a series of dynodes which are the amplification stages
- The photocathode is a thin film of metal on the inside of the window
- Incident photons cause electrons to be ejected from the surface, and the generation efficiency of photoelectrons is dependent on the incident wavelength



Spectrofluorometers

- The photocathode is held at a high negative potential, and the dynodes are also held at negative potentials, but these potentials decrease towards zero along the dynode chain
- This potential difference causes ejected photoelectrons to be accelerated towards the first dynode, and this process continues down the dynode chain until a current pulse arrives at the anode



Chemical Actinometry

- A **chemical actinometer** is a chemical system that undergoes a light-induced reaction (at a certain wavelength, λ) for which the quantum yield $\Phi(\lambda)$ is accurately known
- Measuring the reaction rate allows for the calculation of the absorbed photon flux
- The **quantum yield** of a photochemical reaction is defined as $\Phi(\lambda) =$ the number of events (e.g., molecules changed, formed, or destroyed), divided by the number of absorbed photons of that particular wavelength in the same period of time
- In a chemical actinometer, photochemical conversion is directly related to the number of photons absorbed because the chemical action of light means reversible or irreversible chemical change, i.e., destruction or build up of molecules, and consequently, of their properties such as spectra

Quality Marks of a Chemical Actinometer

An established chemical actinometer should meet the following requirements (as outlined by IUPAC):

- The photochemical system should be simple and well studied. The photoreaction must be reproducible under well-defined and easily controllable experimental conditions
- Quantum yields should be accurately known for a wide range of wavelengths. A wide usable spectral range and wavelength-independent quantum yields are desired
- The chemical components should be thermally stable to exclude complications due to dark reactions

Quality Marks of a Chemical Actinometer

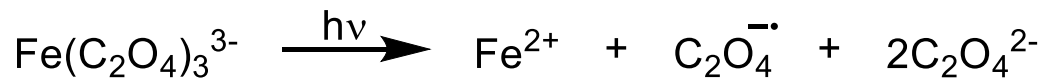
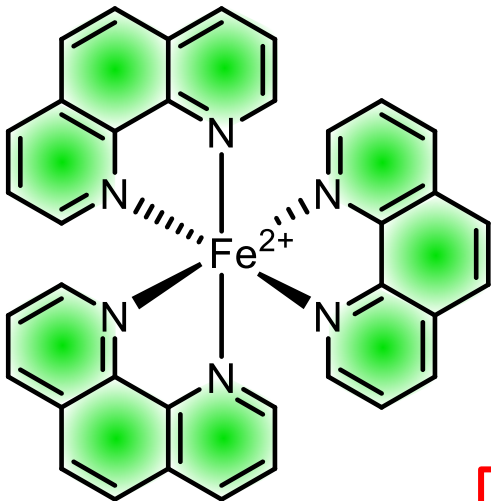
- The analytical methods should be simple. Direct spectrophotometric analysis is preferred
- The system should display large sensitivity
- The handling of the photochemical system and the evaluation of the photons absorbed should be simple and straightforward
- The actinometer material should be easy to synthesize and purify. Preferably, it should be commercially available. Disposal of waste should be straight forward

Using a Chemical Actinometer

- With chemical actinometers, it is generally easy to mimic the experimental situation of the sample
- By choosing strictly identical experimental setups for the actinometer and the sample, experimental errors due to differences in shape, surface, and spatial arrangement of the reaction vessel, light sources, etc. can be easily avoided
- The same solvent and equal absorbances should be chosen for the actinometer and reaction under study, whenever possible

Potassium Ferrioxalate

- The **ferrioxalate actinometer** ($\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$) is the most widely accepted standard actinometer
- Wavelength range: 250–500 nm; $\Phi = 1.25\text{--}0.9$
- Absorption measurement: absorbance at 510 nm of Fe(II)-1,10-phenanthroline complex in buffered acidic solution



Added after reaction is complete

Absorbs @ 510 nm

Calculating the Photon Flux

- Since the quantum yield of ferrioxalate is well-established for a range of wavelengths, by monitoring the amount of Fe^{2+} formed, which is indicated by the amount of $\text{Fe}(\text{phen})_3^{2+}$ observed upon the addition of 1,10-phenanthroline (complex absorbs @ 510 nm), the photon flux can be calculated
- In this example, a 3 mL solution of potassium ferrioxalate (0.15 M) was irradiated for 60 s in a standard 1 cm x 1 cm cuvette. The samples were then developed with a 500 μL buffered phenanthroline solution, and the absorbance at 510 nm was recorded
- The data from three trials is shown below:

	Irradiated Sample (A_{Light})	Dark Sample (A_{Dark})
Trial 1	1.402	0.121
Trial 2	1.400	0.134
Trial 3	1.381	0.148
Average	1.394	0.134

Calculating the Photon Flux

- Using these data, we can calculate the concentration of Fe^{2+} produced during the 60 s reaction using the Beer-Lambert law:

$$A_{\text{Light}}: 1.394$$

$$A_{\text{Dark}}: 0.134$$

Extinction coefficient of $\text{Fe}(\text{phen})_3^{2+}$ @ 510 nm ($\epsilon_{510 \text{ nm}}$): 11,100 $\text{M}^{-1} \text{cm}^{-1}$

From literature

Path length (l): 1 cm

$$[\text{Fe}^{2+}] = \frac{A_{\text{light}} - A_{\text{dark}}}{\epsilon_{510 \text{ nm}} l}$$

$$[\text{Fe}^{2+}] = \frac{1.394 - 0.134}{(11,100 \text{ M}^{-1} \text{cm}^{-1})(1 \text{ cm})}$$

$$[\text{Fe}^{2+}] = 1.135 \times 10^{-4} \text{ M}$$

Calculating the Photon Flux

- Since we know the volume of the sample was 3.5 mL, we can calculate the moles of Fe^{2+} produced after 60 s:

$$\# \text{ moles } \text{Fe}^{2+} = (3.5 \times 10^{-3} \text{ L})(1.135 \times 10^{-4} \text{ mol/L})$$

$$\# \text{ moles } \text{Fe}^{2+} = 3.97 \times 10^{-7} \text{ mol}$$

Calculating the Photon Flux

- Lastly, to determine the number of photons absorbed per unit time:

$$\Phi = \frac{\text{mol Fe}^{2+} \text{ Produced per unit time}}{\text{mol Photons Absorbed per unit time}}$$

$$\text{mol h}\nu \text{ Absorbed per unit time} = \frac{N h \nu}{t}$$

$$\Phi = 1.01 @ 440 \text{ nm}$$

From literature

$$\frac{N h \nu}{t} = \frac{\text{moles of Fe}^{2+}}{\Phi t}$$

$$\frac{N h \nu}{t} = \frac{3.405 \times 10^{-7} \text{ mol}}{(1.01)(60 \text{ s})}$$

$$\frac{N h \nu}{t} = 6.5 \times 10^{-9} \text{ mol h}\nu \text{ s}^{-1}$$

Calculating the Quantum Yield of a Reaction

- Now that the photon flux of the light source has been determined with the ferrioxalate actinometer, the quantum yield of a reaction can be determined
- The reaction should be performed in the same irradiation geometry (identical setup) compared to the actinometer, and it should absorb the same number of photons as the actinometer over the region of irradiation
 - Good rule of thumb is to have both the actinometer and the sample with absorbances greater than 2.0 in the region of irradiation
- The quantum yield of a reaction ($R \rightarrow P$) can then be calculated with the following equation:

$$\Phi = \frac{\text{moles of } P \text{ formed,} \\ \text{or moles of } R \text{ consumed}}{(6.5 \times 10^{-9} \text{ mol } h\nu \text{ s}^{-1})(\text{Irradiation Time, s})}$$

- Characterization of Chain Reactions

Chemical
Science



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Characterizing chain processes in visible light photoredox catalysis†

Megan A. Cismesia and Tehshik P. Yoon*

- Determination of Excited State Quenching Probabilities

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Understanding the Kinetics and Spectroscopy of Photoredox Catalysis and Transition-Metal-Free Alternatives

Published as part of the Accounts of Chemical Research special issue "Photoredox Catalysis in Organic Chemistry".

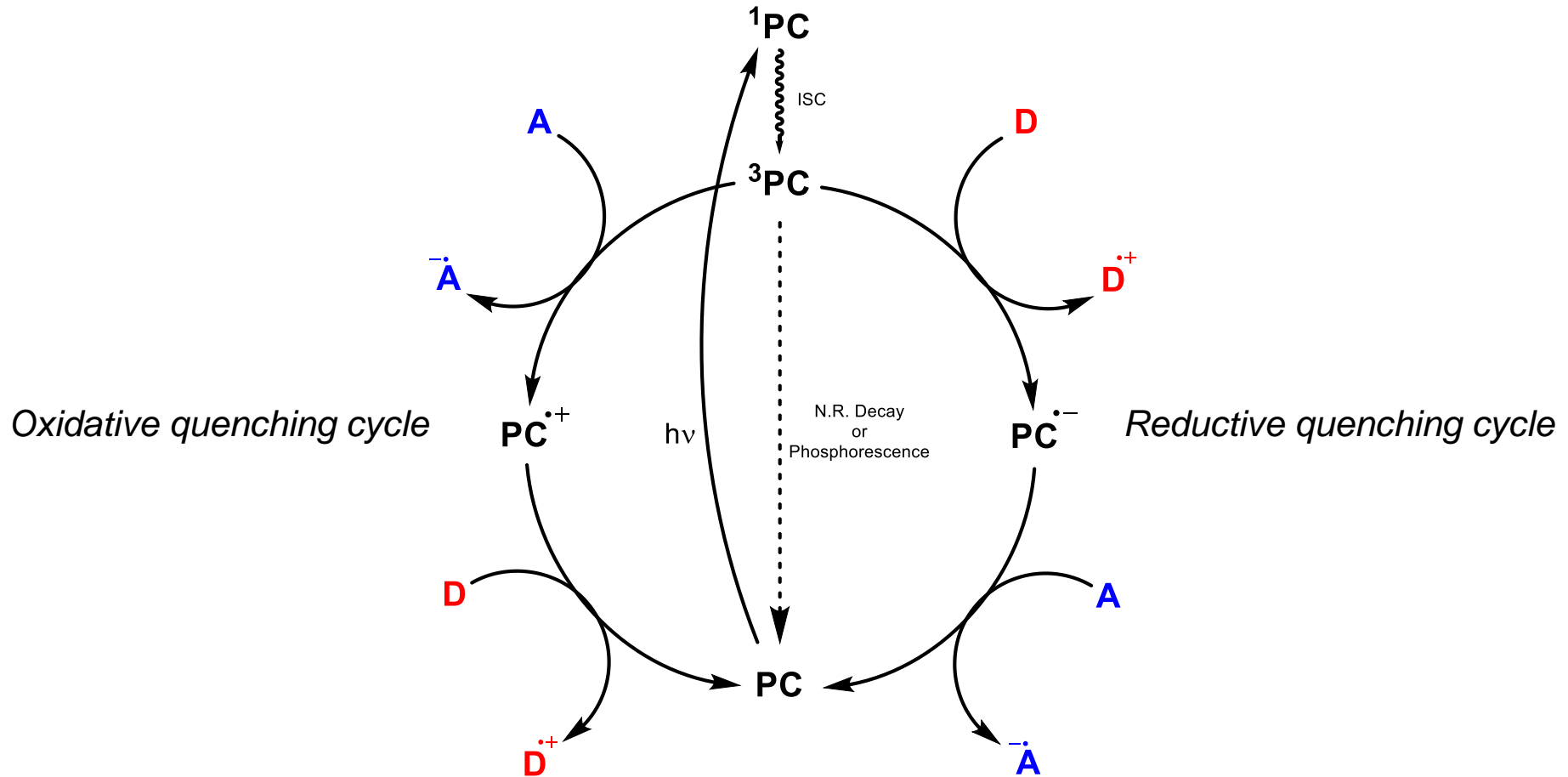
Spencer P. Pitre, Christopher D. McTiernan, and Juan C. Scaiano*

Photoredox Catalysis

PC: Photocatalyst

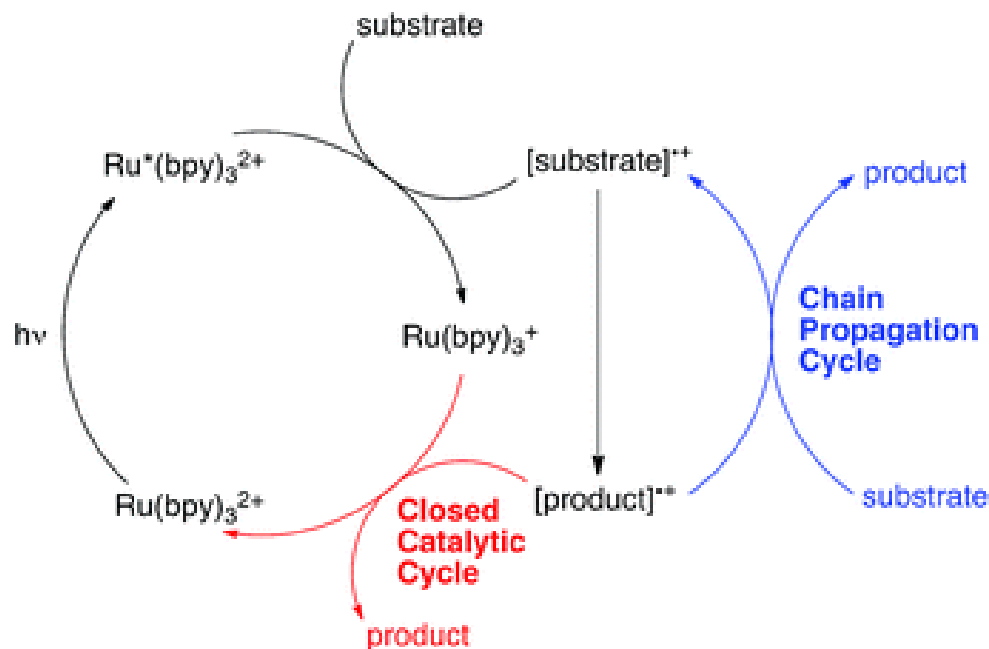
D: Electron donor

A: Electron acceptor



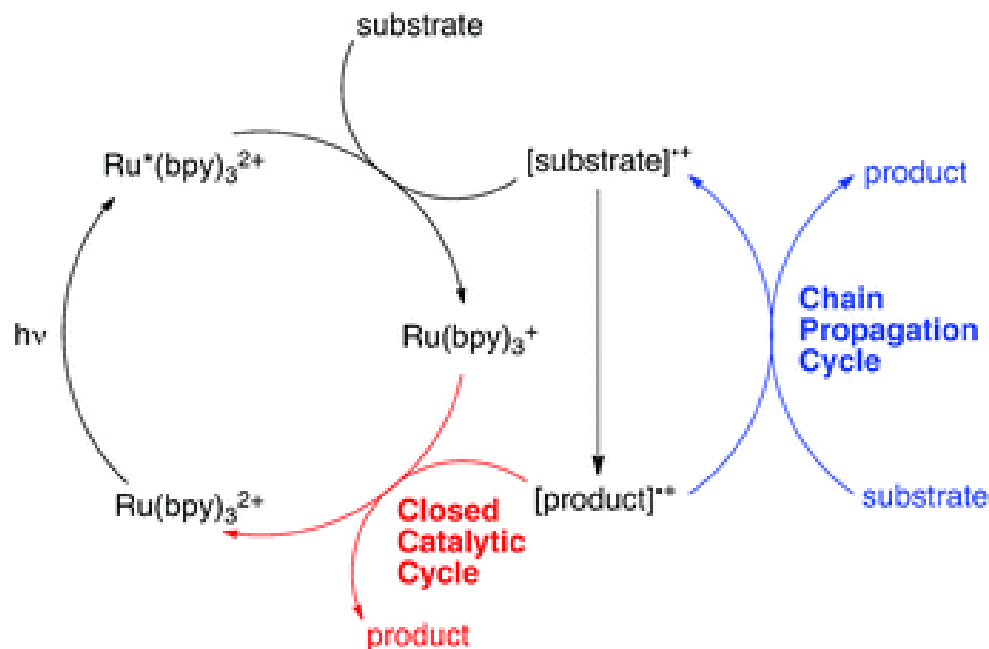
Chain Reactions in Photoredox Catalysis

- Let's consider the generic mechanism for an oxidatively induced photoredox transformation shown below
- Photoexcitation of $\text{Ru}(\text{bpy})_3^{2+}$ produces a relatively long-lived redox active triplet state that can be reductively quenched by a wide range of organic substrates
- The resulting radical cations ($[\text{substrate}]^{\bullet+}$) can participate in numerous possible reaction manifolds, resulting in the formation of an open-shelled odd-electron product ($[\text{product}]^{\bullet+}$)



Chain Reactions in Photoredox Catalysis

- Generation of the final neutral product can be achieved by proceeding through a closed catalytic cycle (**shown in red**) involving the reduction of $[\text{product}]^{*+}$ by the reduced form of the photocatalyst ($\text{Ru}(\text{bpy})^+$), which regenerates the $\text{Ru}(\text{II})$ ground state
- Another possibility is that product is formed via a chain propagation step (**shown in blue**) in which $[\text{product}]^{*+}$ interacts with another equivalent of neutral substrate, thereby generating the neutral product and another $[\text{substrate}]^{*+}$ in the process

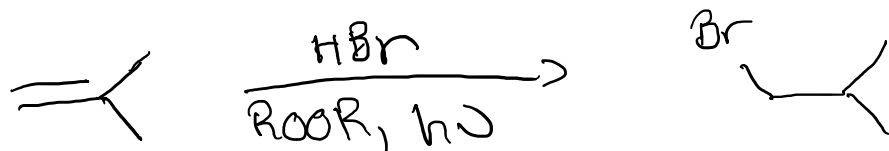


Chain Reactions in Photoredox Catalysis

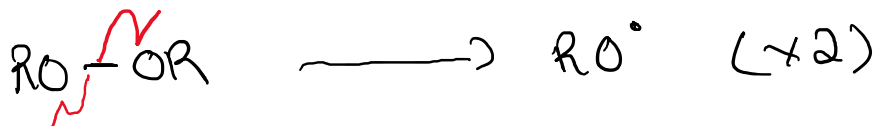
- Distinguishing between chain and non-chain mechanisms is important because strategies for optimizing these two classes of reaction can differ significantly
- For example, if product is only formed by a closed catalytic cycle, optimization of the chemical properties of the photocatalyst might be expected to strongly impact reaction efficiency
- On the other hand, if chain reactions dominate product formation, then the reaction variables that increase the rate of chain propagation or decrease the rate of chain determination should have a large effect

Review: Radical Chain Reactions

- Consider the following reaction below:

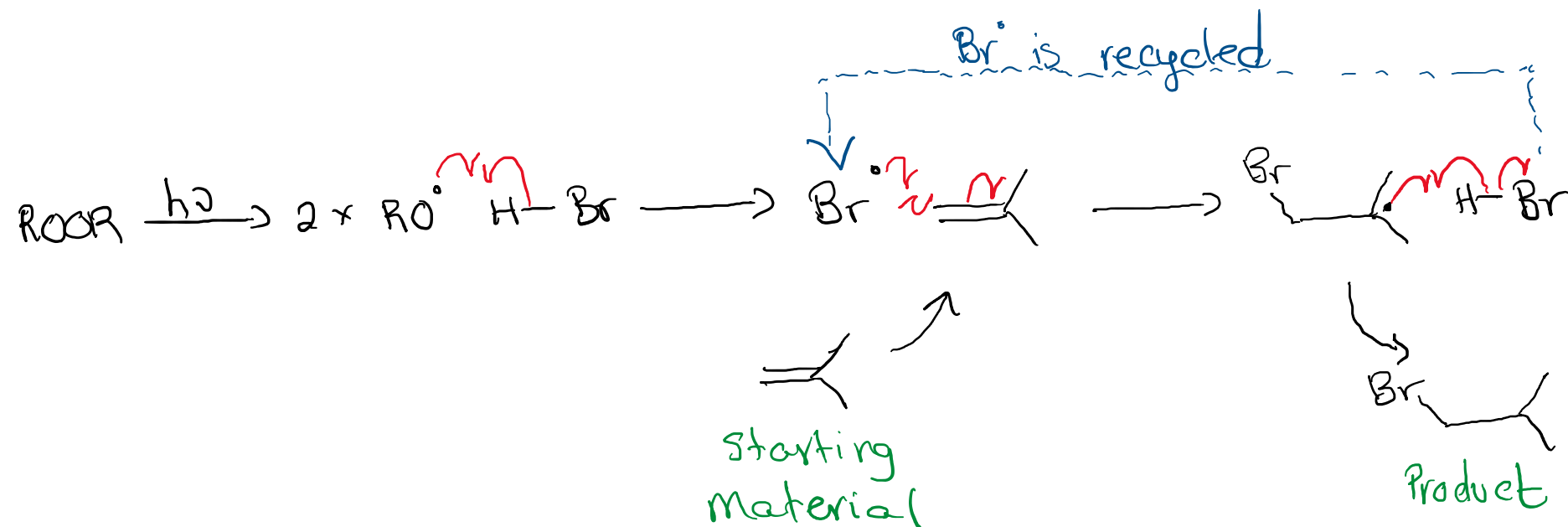


- The mechanism for this reaction is as follows:



Review: Radical Chain Reactions

- In each step of the cycle a radical is consumed and a new radical is formed

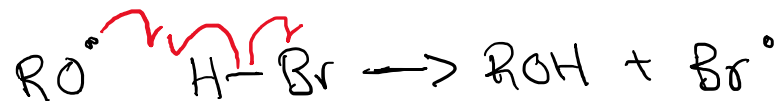


- This type of reaction is therefore known as a **radical chain reaction**
- The two steps that form the cyclic process that keeps the chain running are known as the **chain propagating steps**

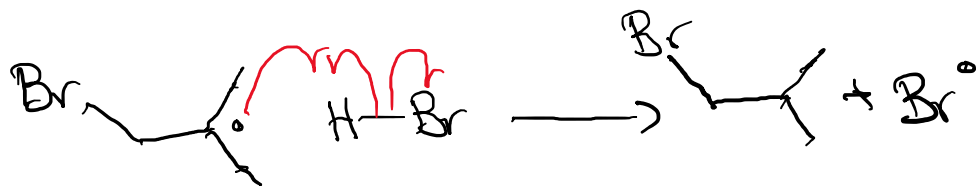
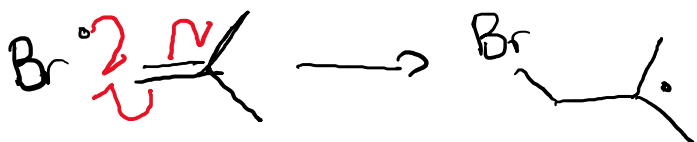
Review: Radical Chain Reactions

Radical chain reactions consist of:

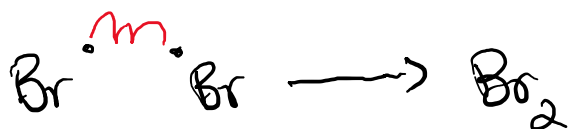
- Initiation steps



- Propagation steps

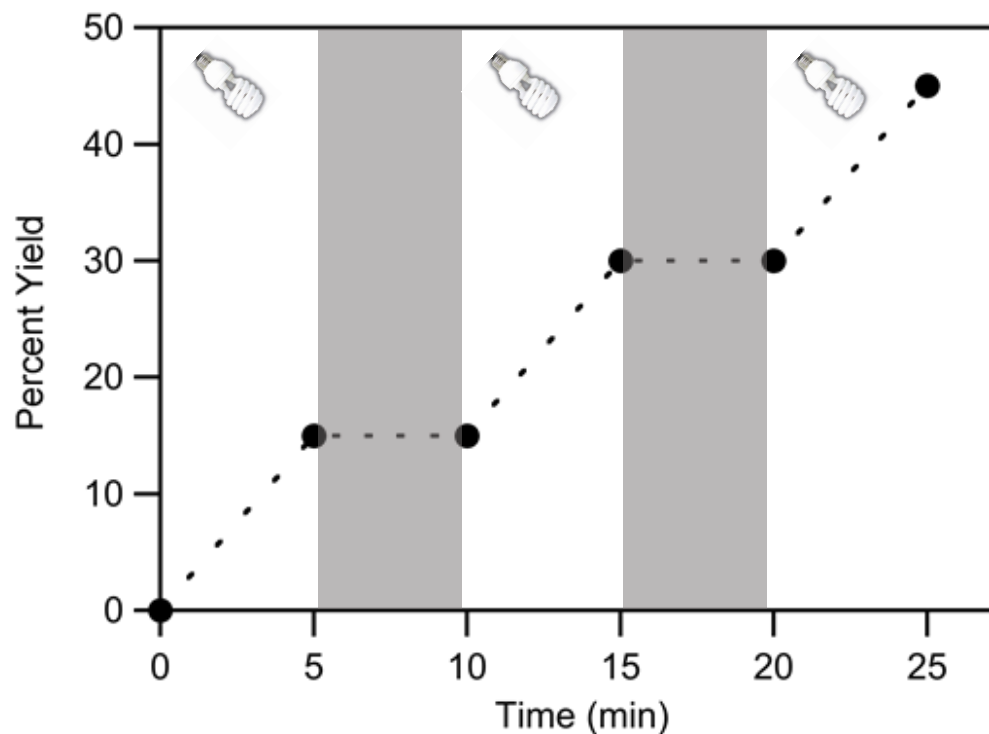


- Termination steps



Light/Dark Experiments

- One increasingly common method used to investigate the participation of chain processes in photoredox reactions is “light/dark” or “light on/off” experiments
- These experiments examine the progress of a reaction in alternating periods of irradiation and darkness

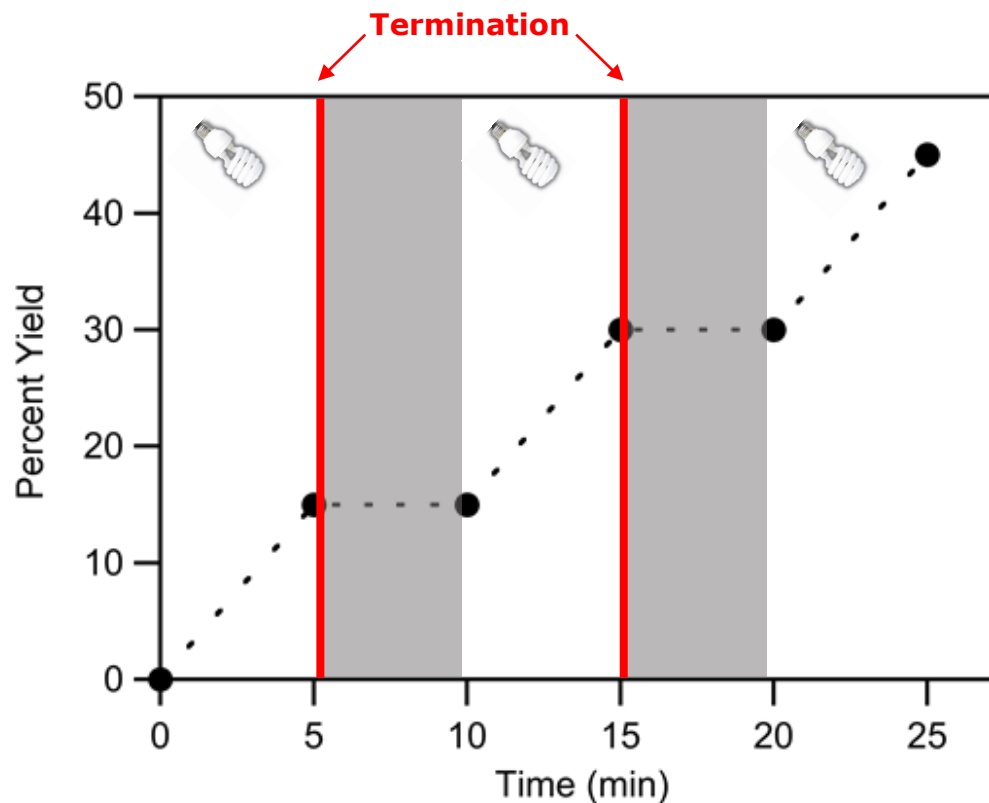


Light/Dark Experiments

- It is commonly concluded from these plots that if a productive reaction requires constant irradiation, chain reactions are not occurring
- However, typical lifetimes for radical chain processes can often be on the ms to s timescale
- The fact that conversion ceases during dark periods could also be consistent with chain processes that terminate faster than the timescale of analytical measurement used

Light/Dark Experiments

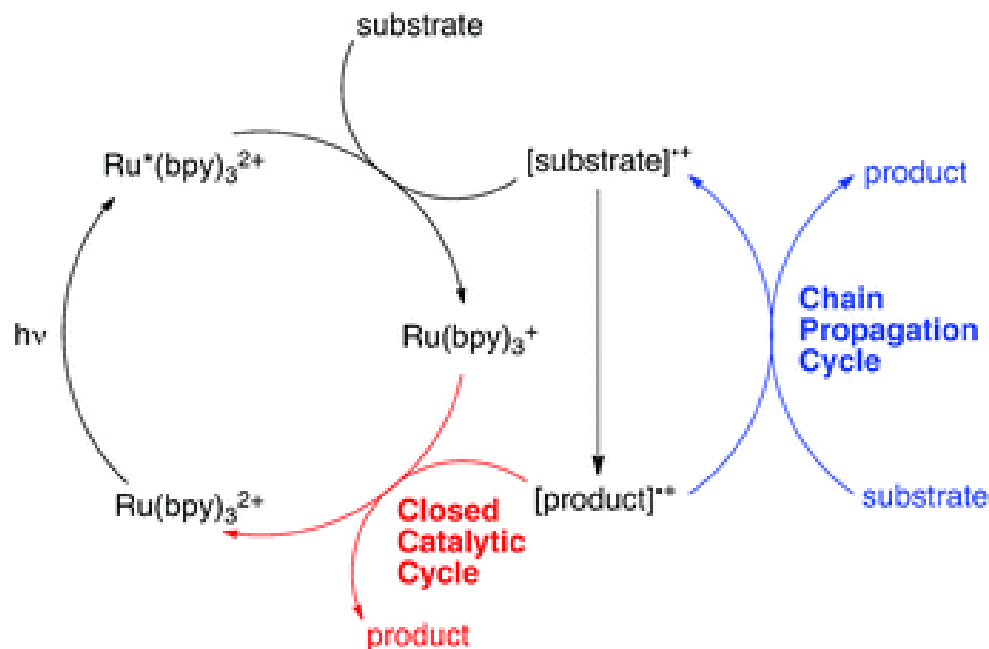
- Let's take another look at our light/dark experiment



- Due to chain propagation terminating *ms to s* after irradiation source is turned off, no observable difference can be measured on this timescale

Chain Reactions in Photoredox Catalysis

- In a system with a closed cycle (**shown in red**), the concentration of $[\text{product}]^{*+}$ must be the same as that of the reduced photocatalyst ($\text{Ru}(\text{bpy})_3^+$), which cannot be higher than the initial concentration of the photocatalyst
- Therefore, a non-chain cycle requires the encounter of two low-concentration reactive intermediates
- Therefore, if fast reaction times with low catalyst loadings are reported, a closed cycle is highly unlikely

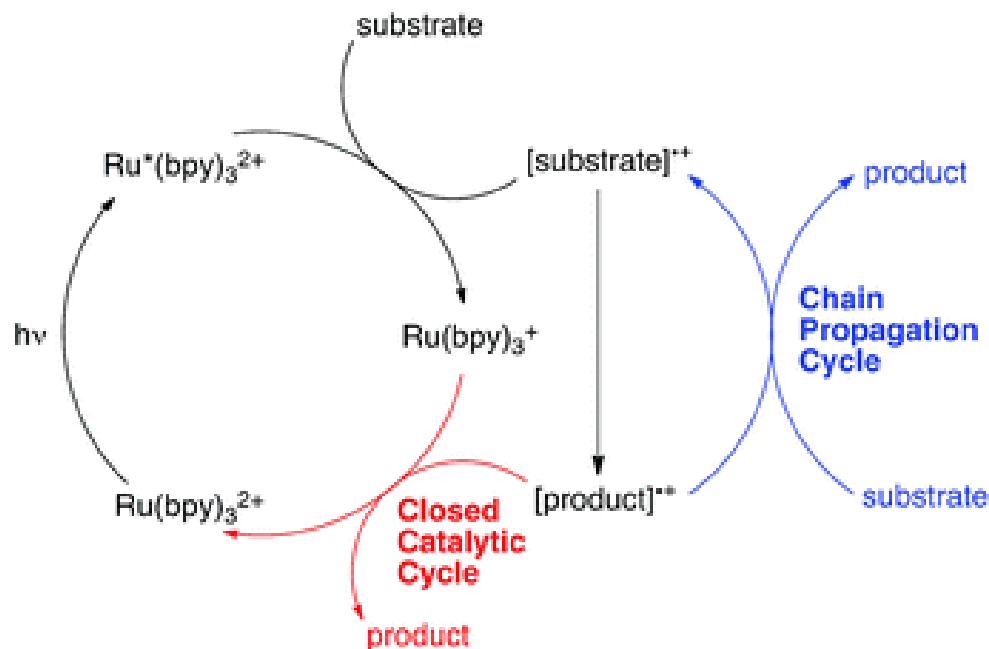


Chain Reactions in Photoredox Catalysis

- Quantum yield measurements are a great tool for identifying photochemical reactions that involve radical chains
- The closed photoredox cycle lacking chain propagation could exhibit a maximum theoretical quantum yield (Φ) of 1, which would indicate that every photon absorbed by the photocatalyst produced one molecule of product
- $\Phi = 1$ is the maximum value in this scenario because non-productive photochemical processes, like luminescence emission, non-radiative decay, or back-electron transfer would only lead to decreases in Φ

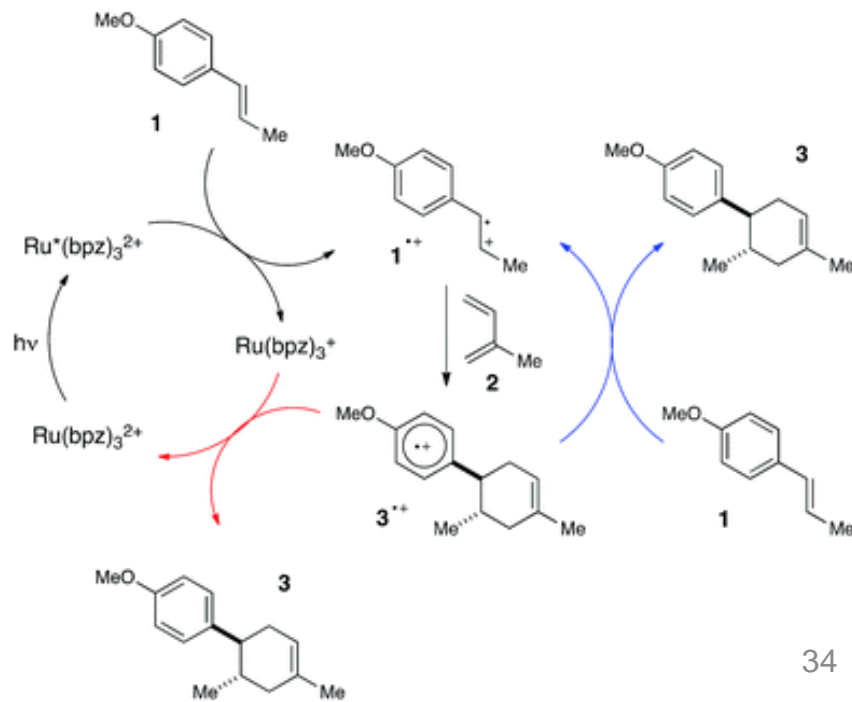
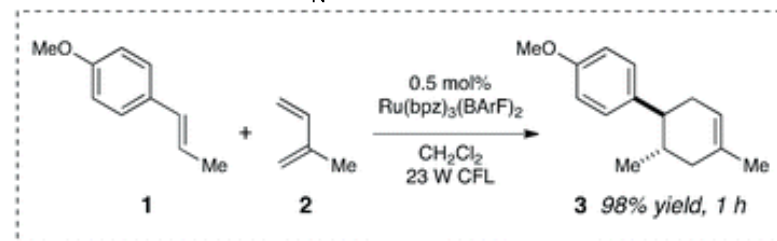
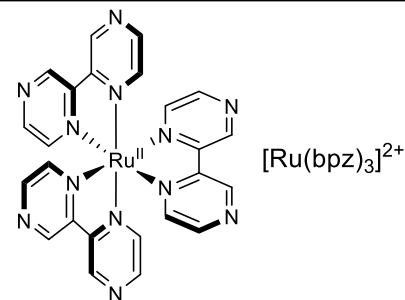
Chain Reactions in Photoredox Catalysis

- Chain processes (**shown in blue**), on the other hand, could potentially provide multiple equivalents of product from each photo-induced initiation step
- Therefore, a reaction with $\Phi \gg 1$ could only be consistent with a product-forming chain reaction



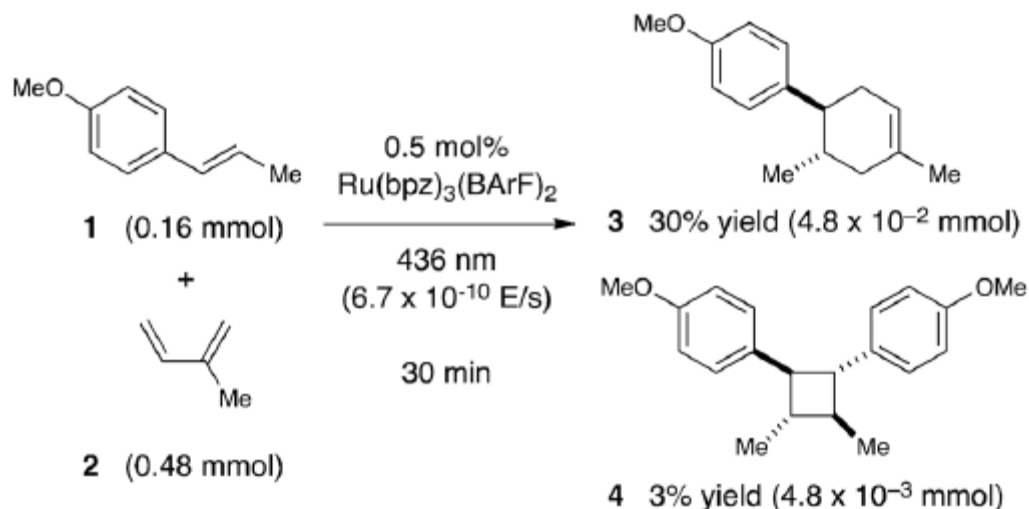
Chain Reactions in Photoredox Catalysis

- Yoon and coworkers chose to study a photocatalytic radical-cation Diels–Alder reaction previously reported by their group
- The proposed mechanism for the transformation is shown on the right
- In order to generate the neutral product (**3**), the product radical cation (**3^{•+}**) must be reduced by one electron
- This can either occur via a chain-terminating electron transfer from the reduced photocatalyst (**red**), or via a chain-propagating electron transfer from another equivalent of the starting material (**1**, **blue**)



Chain Reactions in Photoredox Catalysis

- In order to determine the quantum yield of the [4+2] cycloaddition, Yoon and coworkers employed the ferrioxalate actinometer
- An excitation wavelength of 436 nm was used as the photocatalyst absorbs strongly in this region, and the quantum yield of the ferrioxalate actinometer is accurately known ($\Phi = 1.01$)
- The photon flux was found to be 6.67×10^{-10} einsteins s^{-1}
- After 30 min of irradiation, they obtained 30% yield of the desired product (**3**) and 3% yield of a [2+2] homodimer side product (**4**)



Chain Reactions in Photoredox Catalysis

- The quantum yield can be calculated as follows:

$$\bar{\Phi} = \frac{\text{moles of product formed}}{\text{einsteins of light absorbed}}$$

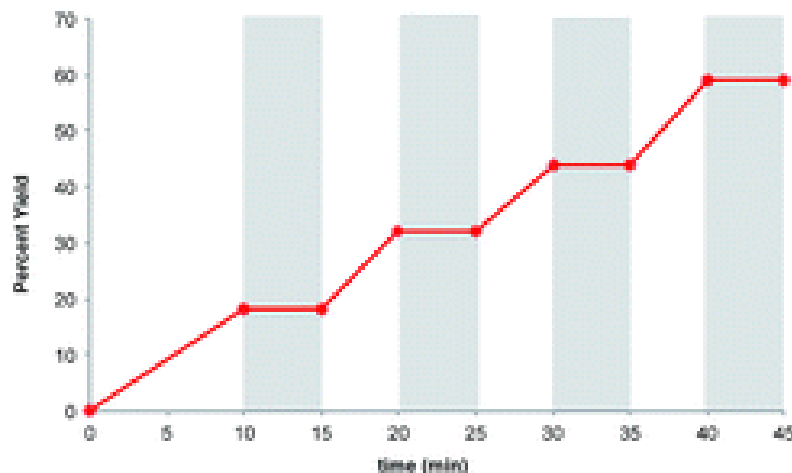
$$\bar{\Phi} = \frac{5.28 \times 10^{-5} \text{ mol}}{(6.67 \times 10^{-10} \text{ mol s}^{-1})(1800 \text{ s})}$$

$$\bar{\Phi} = 44$$

- This result can only be consistent with a chain mechanism

Light/Dark Experiments

- Now let's go back to the light/dark experiment
- Yoon and coworkers also performed a light/dark experiment for the radical cation [4+2] reaction, and observed that even though they had demonstrated the reaction has a long product forming chain ($\Phi = 44$), no conversion was observed in the dark periods
- Therefore, one needs to be cautious when drawing conclusions about chain propagation from light/dark experiments



Excited State Kinetics

- In Chapter 7, we discussed that the excited state of a molecule (photocatalyst) can act both as an electron donor or acceptor, depending on the thermodynamics of the electron transfer events
- To determine if an electron transfer event is thermodynamically feasible, we can employ the Rehm–Weller equation:

$$\Delta G_{et} \approx E_{(D^+/D)}^0 - E_{(A/A^-)}^0 - E(^*D \text{ or } ^*A) + \Delta E_{Coulombic}$$

- However, just because an electron transfer event is thermodynamically feasible does not necessarily mean it will occur
- One must also take into account competitive excited state quenching by other species in the reaction, as well as unimolecular deactivation of the excited state (radiative or non-radiative)

Excited State Kinetics

- If the excited state of the photocatalyst is emissive (fluorescence of phosphorescence), Stern–Volmer analysis can be used to determine the bimolecular quenching rate constants
- The Stern–Volmer equation is as follows:

$$\frac{I_0}{I} = 1 + K_{SV}[Q]$$

where I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively, $[Q]$ is the concentration of quencher and K_{SV} is the **Stern–Volmer quenching constant**

- The Stern–Volmer quenching constant (K_{SV}) is given by:

$$K_{SV} = k_q \tau_0$$

where k_q is the biomolecular quenching constant and τ_0 is the excited state lifetime in the absence of quencher

Excited State Kinetics

- Let's consider the hypothetical reaction below:



- Let's also assume that in order to promote the desired reaction, the excited state of the photocatalyst (*PC) must be quenched by A
- To determine if this is kinetically feasible, we can employ Stern–Volmer analysis to obtain the k_q values for A, B, and C with the PC
- While the k_q values indicate how efficient a particular quencher is, we need to account for the concentration of each quencher and the lifetime of the excited state in order to draw conclusions on how the reaction is proceeding

Excited State Kinetics



- To determine the probability that *PC is quenched by A, we can employ the following eq:

$$\% \text{ *PC quenched by A} = \frac{k_q^A[A]}{\tau_0^{-1} + k_q^A[A] + k_q^B[B] + k_q^C[C]} \times 100\%$$

where k_q^A is the bimolecular quenching rate constant for A (in $M^{-1} s^{-1}$), [A] is the concentration of A (in M) and τ_0^{-1} is the inverse of the excited state lifetime

- This equation is typically employed using initial reaction concentrations to give a rough estimate of initial electron transfer efficiencies

Excited State Kinetics

- From this equation, it becomes evident that although an excited state electron transfer reaction is thermodynamically feasible, it may not occur owing to time constraints and competition from other species
- However, one can use these data to optimize the desired reaction by modifying reactant concentrations or eliminating possible quenchers
- In practice, one of the simplest examples of such an optimization is removal of oxygen from a triplet-mediated photoreaction
- One can also see from the equation that using a photocatalyst with a longer excited state lifetime will help increase the probability of the desired electron transfer event

Up Next...

Photoredox Catalysis