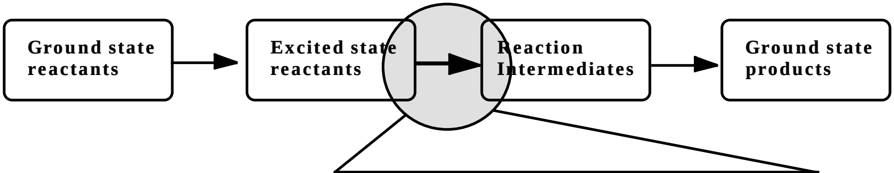
Conventional tools for the study of excited states



Competitive kinetics offer a very powerful tool to examine the behavior of excited staes using the conventional tools of the organic chemistry laboratory

Quantum yileds and conventional analysis were the tools historically used to establish <u>most</u> known photochemical mechanisms.

Quantum yields

From standard analytical techniques

$$\Phi = \frac{\text{Rate at which a process occurs of rate of formation of a product, or of disappearence of a reactant}}{\text{Intensity of light, i.e. rate of light absorption}}$$

Chemical systems or physical devices called actinometers allow the determination of the number of photons in an excitation beam

Note that the denominator refers to absorbed photons, not incident photons

Actinometry: physical devices

- **Primary standards**
  - **Thermal detectors (only *real* primary standards)**
    - **Convert incident photons to heat and measure the heat released**
    - **Requires monochromatic light or knowledge of the wavelength distribution**
  - **Quantum counters**
    - **Uses a dye, normally rhodamine B, to absorb the photons and emit fluorescence, ventually detected with a photomultiplier**

Ultimately the only standard is the optically black body

Actinometry: chemical systems

Chemical systems for which the quantum yield of a given process is accurately known and thus can be employed as a standard for the determination of the photon flux.

- wavelength dependent?
- temperature dependent?
- dependent on reactant concentration?
- affected by impurities?
- ease of analysis

Actinometry: chemical systems
common systems

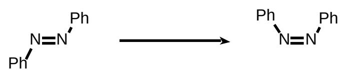
Potassium ferrioxalate

$K_3Fe(C_2O_4)_3$ converts to Fe^{2+} in acid solution

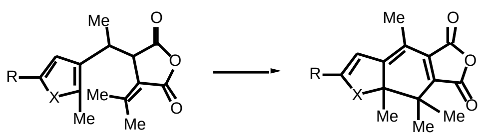
Uranyl oxalate

$$H_2C_2O_4 \xrightarrow{UO_2^{2+}} H_2O + CO_2 + CO$$

Azobenzene and its derivatives

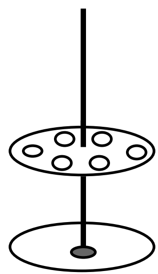


Fulgides (aberchrome)



Actinometry: keeping the same photon dose for sample and actinometer

- **Split side by side irradiation**
- **Sequential irradiation with established or assumed constancy of light dose**
- **'merry go round' irradiation**



Kinetics for conventional analytical techniques

The Stern-Volmer approach provides a valuable took to determine steady dtate kinetics from conventional analytical techniques, frequently gas chromatography or steady state luminescence.

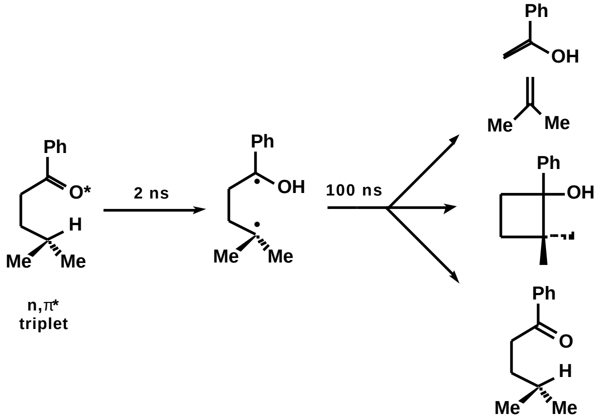
In most cases the '*clock*' reaction is one that approaches diffusion control; its rate constant is reasonably independent of the mechanistic details.

$$k_{diff} = \frac{8RT}{2000\eta} \quad 2 \times 10^{5} \frac{T}{\eta}$$

Debye's equation

Representative diffusion controlled rate constants in units of: 10^{10} M^{-1} s^{-1}	
isopentane	4.6
benzene	1.6
water	1.1

The Norrish Type II reaction
An example of intramolecular hydrogen abstraction



hν

γMeVLP → Acetophenone (ACP)

The Stern-Volmer equation

$$\gamma\text{MeVLP} \xrightarrow{h\nu} \text{Acetophenone (ACP)}$$

$$\gamma\text{MeVLP} \xrightarrow{h\nu} \gamma\text{MeVLP*} \qquad \Phi_{isc}$$

$$\gamma\text{MeVLP*} \xrightarrow{k\,=\,\tau^{-1}} \text{ACP}$$

$$\gamma\text{MeVLP*} + Q \xrightarrow{k_q} \gamma\text{MeVLP} + Q^*$$

with quencher

$$\Phi_{ACP} = \Phi_{isc} \frac{k}{k + k_q[Q]}$$

no quencher

$$\Phi^0_{ACP} = \Phi_{isc}$$

$$\frac{\Phi^0_{ACP}}{\Phi_{ACP}} = 1 + \frac{k_q[Q]}{k} = 1 + k_q\,\tau\,[Q]$$

Steady state emission

Steady state luminescence techniques, both fluorescence and phosphorescence, have been widely used in the study of organic reaction mechanisms. The same approach illustrated for valerophenone can be employed by monitoring the emission efficiency from a known excited state

Sandros in the 1950s studied the photochemistry of several carbonyl compounds, notably biacetyl, by performing steady state luminescence quenching experiments combined with Stern-Volmer analysis.