4.1 Photochemical techniques

Ground state reactants → Excited state reactants → Reaction intermediates → Ground state products

LASER TECHNIQUES
- Luminescence
- Transient absorption (UV, Vis, IR)
- Time resolved diffuse reflectance
- Photoacoustic spectroscopy
- Transient conductivity
- L.I.F. of reaction intermediates
- Mirage spectroscopy
- Time resolved light scattering
- Time resolved resonance Raman
As part of a method to study photoinitiated chemical reactions

As a light source, to initiate the same chemistry as with conventional sources

To induce new chemistry, different from that initiated by conventional sources

**Pulsed lasers**
## Pulsed nanosecond lasers

<table>
<thead>
<tr>
<th>LASER</th>
<th>WAVELENGTH, nm</th>
<th>PULSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>337</td>
<td>8 ns, ≤ 10 mJ</td>
</tr>
<tr>
<td>Excimer</td>
<td>193 (Ar/F)</td>
<td>5-50 ns, ≤ 300 mJ</td>
</tr>
<tr>
<td></td>
<td>248 (Kr/F)</td>
<td>5-50 ns, ≤ 1 J</td>
</tr>
<tr>
<td></td>
<td>308 (Xe/Cl)</td>
<td>5-50 ns, ≤ 500 mJ</td>
</tr>
<tr>
<td></td>
<td>351 (Xe/F)</td>
<td>5-50 ns, ≤ 300 mJ</td>
</tr>
<tr>
<td>Ruby</td>
<td>694</td>
<td>≥ 10 ns, 1 J</td>
</tr>
<tr>
<td></td>
<td>347 (x2)</td>
<td>≥ 10 ns, 300 mJ</td>
</tr>
<tr>
<td>Nd/YAG</td>
<td>1064</td>
<td>5-10 ns, 0.5-5 J</td>
</tr>
<tr>
<td></td>
<td>532 (x2)</td>
<td>5-10 ns, ≤ 500 mJ</td>
</tr>
<tr>
<td></td>
<td>355 (x3)</td>
<td>5-10 ns, ≤ 300 mJ</td>
</tr>
<tr>
<td></td>
<td>266 (x4)</td>
<td>5-10 ns, ≤ 150 mJ</td>
</tr>
<tr>
<td>Diode</td>
<td>&gt; 700 nm</td>
<td>low</td>
</tr>
<tr>
<td>Dye</td>
<td>&gt; 300 nm</td>
<td>5-20 % of pump</td>
</tr>
</tbody>
</table>
Lindqvist's 1966 laser set-up

Determining transient absorbances

\[ \text{PMT output} = P_{\text{out}} = I_0 - \text{Signal} \]

\[ T = \frac{P_{\text{out}}}{I_0} \]

\[ \Delta \text{O.D.} = -\log T = \log \left[ 1 - \frac{\text{Signal}}{I_0} \right] \]
4.6 Laser flash photolysis technique

Typically 266, 308, 337, 355 nm
Laser photolysis sequence

- Pre-pulse
- Pulse
- Post-pulse

- Laser shutter opens
- PMT output (mV)

60 Hz AC sine wave (from line synchronizer)

1 Hz laser pulses

- A/D laser detection monitoring

Time (ns)
Conditions and capabilities of laser flash photolysis

**FAST PRECURSOR PROCESSES**
**SLOW DECAY OF PRODUCTS**

Process under study
A → B

Reagents → \( ^{hv} \) fast → A

A → 10 ns - 500 µs → B

B → slow → final products
Kinetic analysis for visible systems

\[
\begin{align*}
\text{Bu}^\cdot & \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3^\cdot \\
\text{Bu}^\cdot + \text{solvent-H} & \rightarrow \text{Bu}^\cdot \text{OH} + (\text{solvent})^\cdot \\
\text{Bu}^\cdot + \text{Ph}_2\text{CHOH} & \rightarrow \text{Bu}^\cdot \text{OH} + \text{Ph}_2^\cdot \text{COH} \\
\end{align*}
\]

\[ k_{\text{growth}} = k_0 + k_{\text{rxn}} [\text{Ph}_2\text{CHOH}] \]

**PROBLEM:** Most systems of interest do not involve reactants or products that can be readily detected in the UV-Vis region

**E.g.**:

\[
\begin{align*}
\text{Bu}^\cdot & \rightarrow \text{Bu}^\cdot \text{OH} + \cdot \\
\end{align*}
\]
Some background on alkoxyl radicals

Alkoxyl radicals can be readily prepared by thermal or photochemical decomposition of the corresponding peroxide. Typical examples are di-tert-butyl peroxide and di-cumyl peroxide. While the extinction coefficients at $\lambda > 300$ nm tend to be small, it is usually possible to use enough peroxide to overcome this. Tert-butoxyl radicals are essentially invisible to laser flash photolysis, while cumyloxyl can be detected.

Alkoxyl radicals tend to abstract hydrogen readily; to a lesser extent, they also add to unsaturated systems. In addition, they undergo cleavage reactions which are very sensitive to the polarity of the medium (see below).

$$\begin{align*}
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\quad & \quad \\n\text{O}^\cdot & \quad \text{H}_3\text{C} \quad \text{O} \\
\quad & \quad \\n& \quad \text{H}_3\text{C} \quad \text{C} & \quad \text{CH}_3^\cdot
\end{align*}$$
An example of cumyloxyl reactivity towards HP-136

![Graph showing reactivity](image)

The graph illustrates the reactivity of HP-136 towards cumyloxyl. The peaks at various wavelengths indicate the absorption characteristics of the reagent. The inset shows the molecular structures of HP-136 and the reactant, highlighting the chemical changes during the reaction.
The technique allows the determination of the absolute rate constant for a reaction where all the reagents and all the products are invisible to the technique employed.
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**Is there a catch?**

- The method provides no information on the nature of the reaction; for example the mode or site of attack cannot be established by this method.
- The signals observed get weaker as the reactant is added. The rates are largely derived from conditions where the growth is fast and the signal weak.

It is essential to select probes that overcome the second problem by giving intense, readily detectable signals.
The significance of growth rates

All products from a reaction grow-in with a lifetime that is identical to the decay lifetime of their precursor. It is this characteristic that makes the probe technique possible.

This characteristic also implies that when two spectral bands grow-in with the same kinetics they have the same precursor.

It does not mean that the two bands necessarily belong to the same species.
Bromine atoms can be readily generated, but are invisible to the technique of laser flash photolysis.

\[
\text{RCHBr-CH}_2\text{Br} \quad \overset{h\nu}{\longrightarrow} \quad \text{Br}^\bullet + \text{RCH-CH}_2\text{Br}
\]

\[
\text{RCH-CH}_2\text{Br} \quad \longrightarrow \quad \text{Br}^\bullet + \text{RCH=CH}_2
\]

\[
\text{Br}^\bullet + \text{RH} \quad \longrightarrow \quad \text{HBr} + \text{R}^\bullet
\]
\[ \text{Br}^\bullet + \text{Br}^- \rightarrow \text{Br}_2^\bullet \]

Wavelength, nm

\[ 340.0 \quad 460.0 \quad 580.0 \quad 700.0 \]

Time

\[ 0.2 \, \mu\text{s} \]

growth of \( \text{Br}_2^\bullet \)
Analysis of the growth kinetics for $\text{Br}_2^{-}$

$$k_{\text{growth}} = k_0 + k_{\text{rxn}}[\text{Rt}_4\text{NBr}]$$

$$k = 1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$
The kinetics for *invisible reactions* can be determined by using the absorption from Br$_2$ as a probe.

\[ k_{\text{growth}} = k_0 + k_{\text{Br}^-}[\text{Br}^-] + k_X[X] \]

\[ k_X = 3.9 \times 10^7 \text{M}^{-1}\text{s}^{-1} \]

\[ [\text{Br}^-] = 50 \mu\text{M} \]
Reate constants for reactions of bromine atoms

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$k_q \times 10^6 \text{ M}^{-1} \text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.93</td>
</tr>
<tr>
<td>Ethanol</td>
<td>16</td>
</tr>
<tr>
<td>1-Pentanol</td>
<td>11</td>
</tr>
<tr>
<td>1-Octanol</td>
<td>12</td>
</tr>
<tr>
<td>2-Octanol</td>
<td>35</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>39</td>
</tr>
<tr>
<td>3-Pentanol</td>
<td>12</td>
</tr>
<tr>
<td>2-Methil-1-propanol</td>
<td>17</td>
</tr>
<tr>
<td>Dioxane</td>
<td>1.2</td>
</tr>
<tr>
<td>Ether</td>
<td>17</td>
</tr>
<tr>
<td>Toluene</td>
<td>66</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>29000</td>
</tr>
<tr>
<td>p-Cresol</td>
<td>30000</td>
</tr>
</tbody>
</table>
One step further in the probe technique
Examining triethylsilyl radicals

\[
\begin{align*}
\text{Bu}^3\text{O}^- & \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3^+ \quad \{k_0 \} \\
\text{Bu}^3\text{O}^- + \text{solvent-H} & \rightarrow \text{Bu}^3\text{OH} + (\text{solvent})^- \\
\text{Bu}^3\text{O}^- + \text{Et}_3\text{SiH} & \rightarrow \text{Bu}^3\text{OH} + \text{Et}_3\text{Si}^- \quad (k=5.7\times10^6\text{M}^{-1}\text{s}^{-1}) \\
\text{Et}_3\text{Si}^- + \text{Probe} & \rightarrow \text{Signal carrier} \quad \{k_{\text{probe}} \} \\
\text{Et}_3\text{Si}^- + \text{R-Br} & \rightarrow \text{Et}_3\text{SiBr} + \text{R}^- \quad \{k_{\text{xn}} \}
\end{align*}
\]

Signal carrier derived from benzil
Time resolved diffuse reflectance

an alternate approach for opaque samples
Decay of diphenylmethyl on silicagel

Diffuse reflectance under nitrogen

\[ \text{hv} - \text{CO} \rightarrow 2 \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{Ph} \]

\[ \text{H} \]

\[ \text{A} \]

\[ \text{B} \]

\[ \Delta I / I_0 \]

Time

5 µs

100 µs
Complex kinetics are common in heterogeneous systems

(LEFT) Decay trace in different time domains of TMT+/HY film. The traces were monitored at 350 nm and the 2, 5, 10 and 20 µs time scales were used. Note the logarithmic time scale.
(RIGHT) Distribution analysis of the TMT+/HY film.
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