7.3 Examples of homogeneous and nano-heterogeneous systems

A. Photo-oxidation of aromatic hydrocarbons by acridinium dyes

\[
\begin{align*}
\text{MA}^+ & & \text{CMA}^+ & & \text{APS}^0 \\
& & & & \\
\text{Dye} & \tau [\text{ns}] & \Phi_f & \phi(S/S^-) [\text{V/ SHE}] & \Delta E_{0,0} [\text{eV}] \\
\text{10-methyl-acridinium (MA}^+\text{)} & 42 & 0.71 & -0.184 & 2.66 \\
\text{9-chloro, 10-methyl-acridinium (CMA}^+\text{)} & 40 & 0.68 & -0.027 & 2.71 \\
\text{10-acridinium-3-propylsulfonate (APS}^0\text{)} & 36 & 0.65 & -0.350 & 2.74 \\
\end{align*}
\]

\[
(S + D) \xrightarrow{k_{et}} (1S^* + D) \xrightarrow{k_{sep}} (S^-/D^+) \xrightarrow{+ M} S^- + D + M^+
\]
Photo-oxydation of aromatic hydrocarbons by acridinium dyes

The quantum yield $\Phi_{M^+}$ for the production of the radical cation monitor $M^+$ is measured by ns laser transient absorption spectroscopy (laser flash photolysis). The reaction $D^+ + M \rightarrow D + M^+$ being quantitative, $\Phi_{M^+}$ can be expressed by:

$$\Phi_{M^+} = \Phi_{et} \cdot \Phi_{sep} = \frac{k_{et}}{\sum k_i} \cdot \frac{k_{sep}}{k_{sep} + k_{-et}}$$

where $\Phi_{et}$ is the quantum yield of the forward electron transfer process, and $\Phi_{sep}$ the yield of the separation of the ion pair ($S^-/D^+$).

The value of $\Phi_{et}$ is accessible experimentally by applying Stern-Volmer's method. The rate constant for back electron transfer $k_{-et}$ can then be simply estimated from the relationship:

$$k_{-et} = k_{sep} \cdot \left( \frac{\Phi_{et}}{\Phi_{M^+}} - 1 \right)$$

The separation rate constant $k_{sep}$ was measured separately and was found to be independent of the donor $D$:

$$k_{sep} = 2.5 \cdot 10^9 \text{ s}^{-1}$$

Transcript absorption spectrum of tri-p-tolylamine radical cation obtained upon ns pulsed laser irradiation of 10-methyl acridinium perchlorate 5·$10^{-5}$ M, m-xylene 5·$10^{-2}$ M, and tri-p-tolylamine 5·$10^{-4}$ M in degassed acetonitrile. Wavelengths for dye excitation and $M^+$ monitoring were $\lambda_{exc} = 408$ nm and $\lambda_{obs} = 670$ nm, respectively.
**Photo-oxydation of aromatic hydrocarbons by acrdinium dyes**

Ns laser flash photolysis

![Diagram of laser flash photolysis setup](image)

- Nd:YAG laser
- Dye laser
- SHG, THG
- Monitoring Diode
- Xe Lamp
- Filters
- Sample
- Monochromator
- PMT
- Transient Digitizer

$$\Delta A \quad \Rightarrow [M^+]$$

$$\lambda = 408 \text{ nm}$$

$$\lambda = 670 \text{ nm}$$
Photo-oxydation of aromatic hydrocarbons by acrdinium dyes

<table>
<thead>
<tr>
<th>Donor</th>
<th>$\phi(D^+/D)$ [V/ SHE]</th>
<th>$-\Delta G^0_{et}$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MA$^+$</td>
</tr>
<tr>
<td></td>
<td>2.64</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>2.40</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>2.48</td>
</tr>
<tr>
<td></td>
<td>2.16</td>
<td>2.34</td>
</tr>
<tr>
<td></td>
<td>2.05</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>1.98</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>1.86</td>
<td>2.04</td>
</tr>
</tbody>
</table>
Photo-oxidation of aromatic hydrocarbons by acridinium dyes

\[
\Delta G^0_{et} = -F \cdot [\phi^0(D/D^+) - \phi^0(S/S^-)]
\]

\[ S^- + D^+ \rightarrow S + D \]

\[ (S/S^-) \]

\[ (S^*/S^-) \]

\[ \phi [V/ SHE] \]

\[ \Delta G^0_{et} \]

\[ k_{et} \]

\[ S^* + D \rightarrow S^- + D^+ \]

\[ (D^+/D^-) \]

\[ (M^+/M^-) \]

\[ CH_3 \]

\[ N \]

\[ \text{hv} \]
**Photo-oxydation of aromatic hydrocarbons by acrdinium dyes**

<table>
<thead>
<tr>
<th>Donor</th>
<th>$-\Delta G^0_{\text{et}}$ [eV]</th>
<th>$\Phi_{\text{et}} / \Phi_{\text{M+}}$</th>
<th>$\log (k_{\text{et}} [s^{-1}])$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.82</td>
<td>0.487</td>
<td>9.47</td>
</tr>
<tr>
<td>m-xylene</td>
<td>2.58</td>
<td>0.339</td>
<td>9.74</td>
</tr>
<tr>
<td>p-xylene</td>
<td>2.48</td>
<td>0.158</td>
<td>10.17</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>2.34</td>
<td>0.092</td>
<td>10.44</td>
</tr>
<tr>
<td>Durene</td>
<td>2.23</td>
<td>0.061</td>
<td>10.63</td>
</tr>
<tr>
<td>Pentamethylbenzene</td>
<td>2.16</td>
<td>0.044</td>
<td>10.78</td>
</tr>
<tr>
<td>Hexamethylbenzene</td>
<td>2.04</td>
<td>0.037</td>
<td>10.86</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>2.41</td>
<td>0.363</td>
<td>9.69</td>
</tr>
<tr>
<td>Diphenylacetylene</td>
<td>2.27</td>
<td>0.277</td>
<td>9.86</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2.25</td>
<td>0.175</td>
<td>10.12</td>
</tr>
<tr>
<td>2-methylnaphthalene</td>
<td>2.13</td>
<td>0.125</td>
<td>10.29</td>
</tr>
<tr>
<td>2,6-dimethylnaphthalene</td>
<td>2.04</td>
<td>0.082</td>
<td>10.50</td>
</tr>
<tr>
<td>2,3,5-trimethylnaphthalene</td>
<td>1.95</td>
<td>0.061</td>
<td>10.63</td>
</tr>
</tbody>
</table>
**Photo-oxydation of aromatic hydrocarbons by acrdinium dyes**

\[ \log (k_{et})\text{[s}^{-1}] = -\Delta G_{et}^0 \text{[eV]} \]

- \( S = MA^+ \)
- \( S = APS^0 \)
- \( D \supset 1 \) ring
- \( D \supset 2 \) rings
Photo-oxydation of aromatic hydrocarbons by acrdinium dyes

Non-linear fitting of the parameters of Marcus-Dogonadze's equation

\[
k_{et} = |H_{DA}|^2 \cdot \frac{1}{\sqrt{2\pi} \cdot \lambda_{out} \cdot k_B T} \cdot \exp\left(-\frac{\lambda_{in}}{\hbar \nu}\right) \cdot \sum_{n=0}^{\infty} \frac{\left(\frac{\lambda_{in}}{\hbar \nu}\right)^n}{n!} \cdot \exp\left[-\left(\Delta G_r^0 + n\hbar \nu + \lambda_{out}\right)^2 \frac{4 \lambda_{out} \cdot k_B T}{\hbar \nu}\right]
\]

The vibrational frequency \( \nu \) is set to \( \bar{\nu} = \text{constant} = 1500 \text{ cm}^{-1} \)

<table>
<thead>
<tr>
<th>( S )</th>
<th>MA(^+)</th>
<th>APS(^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1 ring</td>
<td>2 rings</td>
</tr>
<tr>
<td>(</td>
<td>H_{DA}</td>
<td>^2 [\text{cm}^{-1}] )</td>
</tr>
<tr>
<td>( \lambda_{out} [\text{eV}] )</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>( \lambda_{in} [\text{eV}] )</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>
B. Light-induced heterogeneous ET from the conduction band of TiO$_2$ to an acceptor in solution

G

\[ \begin{align*}
E_C & & \quad (A/A^-) \\
\text{hv} \geq 3.2 \text{ eV} & & \quad (D^+/D) \\
\text{hv} \quad \rightarrow \quad \text{TiO}_2 (e_{cb}^- ... h_{vb}^+) & & \quad \text{TiO}_2 (e_{cb}^- ... h_{vb}^+) \rightarrow \text{TiO}_2 \\
\text{fast} & & \quad \text{fast} \\
\text{TiO}_2 (e_{cb}^- ... h_{vb}^+) + D & \rightarrow \text{TiO}_2 (e_{cb}^-) + D^+ \\
\text{4) Interfacial electron transfer} & \quad \text{ket} \\
\text{TiO}_2 (e_{cb}^-) + A & \rightarrow \text{TiO}_2 + A^- \\
\end{align*} \]

1) Intrinsec absorption of light
\[ \text{hv} \quad \text{TiO}_2 \rightarrow \text{TiO}_2 (e_{cb}^- ... h_{vb}^+) \]
2) Electron-hole recombination
\[ \text{TiO}_2 (e_{cb}^- ... h_{vb}^+) \rightarrow \text{TiO}_2 \]
3) Hole scavenging
\[ \text{TiO}_2 (e_{cb}^- ... h_{vb}^+) + D \rightarrow \text{TiO}_2 (e_{cb}^-) + D^+ \]

Dependence of $\Delta G^0_{et}$ upon the solution pH

\[ E_{f,n}^* \approx E_C = -\frac{F}{2} \left[ \phi_C (pH=0) - 0.059 V \cdot pH \right] \quad \text{where} : \phi_C (pH=0) \approx -0.210 \text{ V} / \text{SHE} \]

\[ \Delta G^0_{et} = -\frac{F}{2} \phi^0 (A/A^-) - E_{f,n}^* \]

\[ \Delta G^0_{et} \approx -\frac{F}{2} \left[ \phi^0 (A/A^-) - \phi_C (pH=0) + 0.059 V \cdot pH \right] \]
**Light-induced interfacial electron transfer**

Aqueous suspension of TiO$_2$ nanoparticles

Particle radius $\sim$ 5-10 nm

⇒ weak Rayleigh scattering
⇒ transparent colloid
⇒ allows for the application of ns laser transient absorption spectroscopy technique to monitor ET kinetics

**Electron acceptor A**

$\phi^0 (\text{MV}^{2+}/\text{MV}^+)$ = $-0.446$ V / SHE
**Light-induced interfacial electron transfer**

**Ns laser flash photolysis**

\[ \Delta A \]

**exponential fit \( \Rightarrow k_{et} \)**

- **Nd:YAG laser**
- **SHG**
- **THG**
- **Monitoring Diode**
- **Xe Lamp**
- **Filters**
- **Sample**
- **Monochromator**
- **PMT**
- **Transient Digitizer**

\[ \lambda = 355 \text{ nm} \]

\[ \lambda = 602 \text{ nm} \]
**Light-induced interfacial electron transfer**

![Graph showing log(kt) vs pH and other data points]

- **Tafel equation:**
  \[
  \ln i = \ln i_0 + \frac{\alpha \cdot F \cdot \eta}{RT}
  \]
  \[
  \ln \left( \frac{k_{et}}{k_{et}^0} \right) = \alpha \cdot \frac{-\Delta G_{et}^0}{RT}
  \]

- **[MV^{2+}]_0 = 10^{-3} \text{ M}**
The surface of titanium dioxide is amphoteric. In acidic medium, terminal $\text{–OH}$ groups, as well as oxygen bridges are protonated, yielding a positive surface charge. In alkaline medium, terminal hydroxyl groups are deprotonated, resulting in a negative surface charge. An isoelectric point, corresponding to a neutral surface, is found typically for $p\text{H} = 6$.

The zeta-potential of colloidal particles can be easily measured as a function of $p\text{H}$ by use of electrophoresis technique.
**Light-induced interfacial electron transfer**

Results displayed on page 51 are well fitted by Tafel linear equation with a slope $\alpha = 0.8$. The latter value ($\alpha \neq 0.5$) is not compatible with the assumption of a kinetically symmetric activated complex and thus with the classical Marcus theory.

Experimental results can be corrected for electrostatic interactions between the solid oxide charged surface and the acceptor cations in solution by using a semi-empirical function:

$$\alpha_{corr} = \alpha_{obs} - \frac{\gamma}{\sqrt{\mu}}$$

in which $\gamma$ is an adjustment factor and $\mu$ is the ionic strength of the liquid medium.
**Light-induced interfacial electron transfer**

Non-linear fitting of the parameters of Marcus classical relation applied to diabatic ET

\[
k_{et} = |H_{DA}|^2 \cdot \frac{\sqrt{\pi}}{\hbar \cdot \sqrt{k_B T \cdot \Lambda}} \cdot \exp\left(-\frac{(\Lambda + \Delta G_{et}^0)^2}{4 \Lambda \cdot k_B T}\right)
\]

\(|H_{DA}|^2 = 7.6 \text{ cm}^{-1}\)

\(\Lambda = 1.4 \text{ eV}\)