Light-Induced Transformations of the $C_{60}$ Derivative, Fullereneol: Interactions with Natural Organic Matter

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Outline

• Background
• Direct photolysis of fullerenol
• NOM effects on C60 and fullerenol photoreactions
• Spectral studies of NOM and fullerenol
• ROS reactions with fullerenol: \(^1\text{O}_2, \text{OH}\)
Definition of Fullerenes

- **Fullerenes** are a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, or plane. Spherical fullerenes are also called **buckyballs**, and cylindrical ones are called carbon nanotubes or **buckytubes**.
Molecular Structures of Carbon Nanomaterials (Fullerenes)

- C$_{60}$
- Single wall nanotubes (SWNT)
- Fullerol isomers

(a) (b)
(c) (d)
(e) (f)
Fullerenol Degradation under Simulated Solar Irradiation

![Graph showing the degradation of fullerenol over time under different conditions. The x-axis represents time in hours ranging from 0 to 500, and the y-axis represents the ratio of concentration C to initial concentration C₀, ranging from 0.0 to 1.2. Two lines are plotted: one for N₂ saturated conditions and another for air saturated conditions. The graph demonstrates a decrease in concentration over time.]
Fullerenol Monochromatic and Solar Irradiation Kinetics (22°C)

Equations:

\[ C = C_0 (0.2068e^{-0.3995t} + 0.7793e^{-0.0044t}) \]
\[ C = C_0 (0.1376e^{-1.336t} + 0.8627e^{-0.0065t}) \]

Quantum yield:

fast: \(1.55 \times 10^{-3}\), slow: \(1.71 \times 10^{-5}\)
**pH Dependence of Kinetic Parameters for Direct Photoreaction of Fullerenol**

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_{fast}$ (hr$^{-1}$) ($±1sd$)</th>
<th>$f_{fast}$ ($±1sd$)</th>
<th>$k_{slow}$ (hr$^{-1}$) ($±1sd$)</th>
<th>$f_{slow}$ ($±1sd$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>1.093 ± 0.310</td>
<td>0.154 ± 0.193</td>
<td>(3.94 ± 0.55) × 10$^{-3}$</td>
<td>0.844 ± 0.011</td>
</tr>
<tr>
<td>6.6</td>
<td>0.314 ± 0.085</td>
<td>0.212 ± 0.193</td>
<td>(3.20 ± 1.12) × 10$^{-3}$</td>
<td>0.772 ± 0.027</td>
</tr>
<tr>
<td>10.4</td>
<td>0.027 ± 0.0084</td>
<td>0.466 ± 0.109</td>
<td>(2.70 ± 1.03) × 10$^{-3}$</td>
<td>0.516 ± 0.109</td>
</tr>
</tbody>
</table>
Fullerenol Constituents Include pH Dependent Hemiketals
Direct Photomineralization Kinetics of Fullerenol (Simulated Solar Irradiation)
SRNOM Effect on $C_{60}$ Photolysis

Implication: NOM Enhances Dispersion & Persistence
Natural Organic Matter (NOM) Effect on Simulated Solar Irradiation of Fullerenol

\[ \text{pH} = 6.9 - 7.2 \]

\[ \frac{C}{C_0} \] (%)

Irradiation Time (hr)

DIC photoproduction also is enhanced
Calculation of the Enhancement/Attenuation Factor

Apparent enhancement factor of NOM, $EF$

$$EF = \frac{k_{obsd}}{k_{ful}}$$

$k_{obsd}$ and $k_{ful}$ is the first order rate constant of fullerenol solution in the presence and absence of SRNOM, respectively.

Light attenuation factor of NOM, $S$

$$S = \frac{1 - \exp(-a_{330}l)}{a_{330}l}$$
Effect of NOM on the Photodegradation of Fullereneol

<table>
<thead>
<tr>
<th>SRNOM (mg C /L)</th>
<th>$k_{obsd}$ (hr$^{-1}$)</th>
<th>EF</th>
<th>$a_{330}$ (m$^{-1}$)</th>
<th>initial S</th>
<th>EF Corr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0074</td>
<td>1.00</td>
<td>0.12</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>2.5</td>
<td>0.0095</td>
<td>1.28</td>
<td>31.16</td>
<td>0.85</td>
<td>1.51</td>
</tr>
<tr>
<td>5.0</td>
<td>0.0085</td>
<td>1.15</td>
<td>38.89</td>
<td>0.81</td>
<td>1.42</td>
</tr>
<tr>
<td>10.0</td>
<td>0.0057</td>
<td>0.77</td>
<td>55.65</td>
<td>0.75</td>
<td>1.03</td>
</tr>
</tbody>
</table>
Possible Mechanisms for Light-Induced NOM Interaction

- Intramolecular photoreactions of NOM-Full Aggregates –
  \[ \text{NOM} + \text{FUL} \rightleftharpoons \text{NOM:FUL} \xrightarrow{h\nu} \text{Products} \]

  Site saturation leads to plateau in EF vs [NOM]

- NOM is both source and sink for reactive transients that mediate fullerenol photoreaction

  \[ \text{NOM} \rightarrow \text{ROS} \text{ (e.g. OH)} \]

  \[ \text{ROS} \rightarrow \text{FUL} \rightarrow \text{NOM} \]
Agglomeration

\[ \text{FU} \xrightarrow{\times \text{FU}} (\text{FU})^x \]

Sorption/Complexation

Natural organic matter \[\leftrightarrow\] Sediments
Mixtures of SRNOM and Fullereneol Have Additive Absorption Spectra

No Evidence of Charge Transfer
Reactive Oxygen Species
Photoproduced From NOM

\[ \text{NOM} \xrightarrow{h\nu} \text{NOM} \xrightarrow{\text{heat}} \cdot \text{OH} \]

\[ e^- + \text{NOM}^+ \xrightarrow{O_2} \text{RO}_2^- \]

\[ \text{O}_2^- \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]

\[ \text{NOM} \rightarrow \text{RO}_2^- + ^1\text{O}_2 \]
Steady state conc. of $^{1}O_2$ increased an order of magnitude with no effect (within exp error); Same effect on overall transformation.

However, singlet oxygen reaction within NOM/Ful aggregates could be involved.
**Determination of 2nd Order Rate Constant (k_{ful}) for OH Reaction with Fullereneol**

\[
\begin{align*}
\text{NO}_3^- & \xrightarrow{h_v} \text{OH}^* \\
\text{Scavenger, Octanol} & \\
\text{Fullerenol} & \\
\end{align*}
\]

First-Order Method

\[k_{ful} [FUL] \ll k_{oct} [OCT]\]

- predominant reaction of OH is with octanol scavenger

Kinetic equations:

\[v_{OH} = k_{a,\lambda} \phi_{OH} [NO_3^-]\]

\[k_{exp,t} = \frac{v_{OH} k_{ful}}{k_{oct} [OCT]}\]

Slope of \(k_{exp,t}\) vs \(1/[OCT]\) used to compute \(k_{ful}\)

Fullerenol Reaction With OH Radical Nitrate/Octanol System at 313 nm

\[ k_{\text{ful}} = \left( \text{slope} \right) \left( k_{\text{oct}} \right) / \nu_{\text{OH}} \]

\[ k_{\text{FUL}} = 1.2 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \]
Conclusions

• Fullerenol photoreaction is enhanced in presence of NOM; \( \text{C}_6\text{O}_3 \) photolysis is retarded

• Photomineralization is a primary pathway for direct and NOM-enhanced photoreaction

• Dependence of enhancement on NOM concentration suggests either site saturation involving NOM-fullerenol aggregates or NOM scavenging of NOM-produced ROS

• Reaction via singlet oxygen in bulk water not likely but intramolecular pathway in aggregates possible.

• OH radicals react with fullerenol rapidly (\( k = 1.2 \times 10^9 \text{ M}^{-1} \text{s}^{-1} \)) so NOM may degrade fullerenol via OH mediated path.
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