Quenching of excited uranyl ion during its photochemical reduction by triphenylphosphine: Part I—Effect of monosubstituted benzene derivatives

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The relative rates of quenching of excited uranyl ion by benzonitrile, acetophenone, bromobenzene, chlorobenzene, biphenyl and aniline have been measured during photochemical reduction of uranyl ion by triphenylphosphine. The quenching of excited uranyl ion increases in proportion to the inductive effect of the substituent group on benzene ring.

Aromatic hydrocarbons\(^1\), substituted arylaldehydes and acetophenones\(^2\) and benzoic acids\(^3\) efficiently quench uranyl ion luminescence and substituents on the aromatic ring show a linear relationship between the relative rates of quenching and Hammett substituent constants. Luminescence quenching studies have so far been made using fluorescence spectrometer\(^4\)-\(^6\). However, the Stern-Volmer type quenching constants have been measured using a UV-visible spectrophotometer by quenching the photochemical reaction, where the quenchers, simply quench the excited species through physical deactivation. The title investigation is an extension of earlier work from our laboratory\(^7\).

Materials and Methods
Uranyl acetate, triphenylphosphine, sulphuric acid, acetone, aniline, biphenyl, chlorobenzene, bromobenzene, acetophenone and benzonitrile (all AR reagent) were used as such. Electronic absorption spectra of all the solutions irradiated in sunlight for 10 min, were recorded on a UV-visible Shimadzu 240 recording spectrophotometer. Other experimental details are described in the earlier publication\(^7\).

Results
Like simple aromatic hydrocarbons\(^1\), these monosubstituted benzene derivatives do not interact with ground state uranyl ion in aqueous acetone solution. However, the presence of these aromatic compounds reduces the quantum yield of photochemical reduction of uranyl ion (see Fig. 1). Decrease in the absorbance at 650 nm (the \(\lambda_{\text{max}}\) of \(\text{U(IV)}\) formation) is used to evaluate Stern-Volmer quenching constants \(K_v\) from the slope of the linear relationship (1).

\[
\frac{\phi_R}{\phi_{R0}} = 1 + K_v [Q] \quad \ldots (1)
\]

Where \(\phi_R\) and \(\phi_{R0}\) are quantum yields of photochemical reduction of uranyl ion with triphenylphosphine in the absence and presence of the quencher (Q) respectively. The values are given in Table 1.
Table I—Stern-Volmer type quenching constants of excited uranyl ion with monosubstituted benzene derivatives

\[
\left[\text{UO}_2^{2+}\right] = [\text{PPh}_3] = 0.01 \text{ mol dm}^{-3}, \quad [\text{H}^+] = 0.10 \text{ mol dm}^{-3}
\]

at 30 ± 2°C

<table>
<thead>
<tr>
<th>Derivative</th>
<th>(K_q) (dm³mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>80.0</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>50.0</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>6.66</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>4.44</td>
</tr>
<tr>
<td>Acetophenone</td>
<td>3.90</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>4.10</td>
</tr>
</tbody>
</table>

Discussion

The positive charge of uranyl ion localized on the uranium atom, is well protected and is not involved in the interaction with benzene derivatives in the ground state. However, exposure to light delocalizes the positive charge on the axial oxygen atoms of the uranyl ion, as a result of which excited uranyl ion forms donor-acceptor type complex with benzene derivatives. This in turn reduces the efficiency of photochemical reduction of uranyl ion by triphenylphosphine (Fig. 1).

Monosubstitution on the benzene ring of aromatic quenchers plays a very significant role in the quenching of the electronically excited uranyl ions. Due to negative inductive effect of substituents on the ring, and resonance stabilization of acetophenone, benzonitrile, chlorobenzene and bromobenzene, positive charge is delocalized over the ring, resulting in decrease in \(\pi\)-electron density. Consequently there is poor interaction with positively charged excited uranyl ion. Like anisole, the high value of \(K_q\) with aniline may be due to positive inductive effect and resonance stabilization of aniline.

The delocalization of negative charge over the ring helps in faster donor-acceptor complex formation with electronically excited uranyl ion leading to enhanced physical deactivation.

Biphenyl slightly deviates from linear Stern-Volmer plot (intercept = 0.93, less than unity). If the two phenyl groups were coplanar, the extension of the aromatic \(\pi\)-electron cloud would have quenched electronically excited uranyl ion very strongly. However, non-coplanarity due to free rotation of the phenyl groups may be responsible for its milder quenching action in comparison to that of aniline, but much stronger quenching action in comparison to that of other quenchers. Physical deactivation of excited uranyl ion due to aromatic \(\pi\)-electron cloud competes with its photochemical reduction with triphenylphosphine.

Acknowledgement

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References