Photochemical Reduction of Uranyl Ion with Triphenylantimony

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Photochemical reduction of uranyl ions with triphenylantimony has been carried out in the visible region (>400 nm) using 125 watt mercury vapour lamp in dioxane-H$_2$O (6:1) medium. The photoredox products are uranium (IV) and triphenylantimony oxide. The rate of reduction is first order with respect to uranyl ion and triphenylantimony. The rate of reduction is independent of the temperature but varies with hydrogen ion concentration. The rate of reduction is also affected by the change of anions and follows the decreasing order: uranyl sulphate > uranyl acetate > uranyl nitrate. The absorption spectrum of uranyl ion in the presence of triphenylantimony does not show any ground state interaction between the uranyl ion and triphenylantimony. The quantum yield ($\phi$) for the uranium (IV) is less than one. A mechanism for photochemical reduction has been proposed.

Materials and Methods

Experimental details of reaction reactor have been described in our earlier papers$^{12}$ Uranyl acetate, uranyl sulphate, uranyl nitrate (all BDH, AR) were used. Triphenyl-antimony was used as such; oxide was prepared in the laboratory by hydrogen peroxide oxidation. The product of the photolysis were decomposed in concentrated hydrochloric acid, extracted with benzene, fractions separated with preparative TLC and characterised.

Results and Discussion

Photochemical reduction of uranyl ion with triphenylantimony was carried out in the visible region (>400 nm). Photolysis of solution of uranyl ion (10.20 x 10$^{-3}$ M) and triphenylantimony (18.20 x 10$^{-3}$ M) and those of products U(IV) and (triphenylantimony) oxide (TPSbO) have been carried out. Uranium (IV) was characterized by its absorption band at 660 nm. No characteristic band corresponding to U(V) was observed during the course of the reaction.

Photo reduction was studied at different concentration of uranyl ions (3.4 to 10.20 x 10$^{-3}$M). The rate of reduction of U(VI) to U(IV) is first order each with respect to uranyl ions and triphenylantimony. The overall rate is second order as revealed by the linear plots between [2.303 ($a-b$)] log ($a-x$) vs time. The rate of photoreduction is also dependent on [H$^+$] and the intensity of radiation. The rate of reduction is represented by the following equation.

\[
\frac{d[U(IV)]}{dt} = k [UO_2^+] [TP Sb] [H^+] \ldots (1)
\]

where $k$ is the second order rate constant and the values are reported in Table 1 and $[I]$ is the intensity of radiation. The rate of reduction of uranyl ions with triphenylantimony was studied at 30°, 35° and 40°C and found to be independent of temperature.

The quenching of fluorescence of uranyl ions can take place by the four possible mechanisms: (i) Intramolecular quenching by the excitation of uranyl ion and triphenylantimony complex via static electron transfer; (ii) Intermolecular quenching by the excited uranyl ion and triphenylantimony via intermediate complex formation—a dynamic electron transfer; (iii) Electronic energy transfer from the excited state to the substrate, triphenylantimony; and (iv) Radiationless deactivation or physical quenching where no redox product is obtained.

The absorption spectrum of uranyl ion (10.2 x 10$^{-3}$M) in the presence of triphenylantimony (18.2 x 10$^{-3}$M), in dioxane-H$_2$O (6:1) at [H$^+$] = 0.4 M H$_2$SO$_4$ does not show any shift in the absorption bands. Hence there is no ground state interaction and the quenching mechanism by the formation of

<table>
<thead>
<tr>
<th>[UO$_2^+$] $\times 10^3$</th>
<th>3.4 $\times$ 10$^{-3}$M; [H$^+$] = 0.4 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>[TP Sb] $\times 10^3$</td>
<td>(10$^4$ $I_{obs}$, sec$^{-1}$)</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>4.6</td>
<td>5.33</td>
</tr>
<tr>
<td>9.2</td>
<td>6.37</td>
</tr>
<tr>
<td>13.8</td>
<td>7.00</td>
</tr>
<tr>
<td>18.2</td>
<td>7.35</td>
</tr>
</tbody>
</table>

**Table 1 — Quantum Yields and the Rate Constants for the Photoreduction of Uranyl Ions with Triphenylantimony at 30°**
The ground state complex between the two (static process) is ruled out.

The photochemical reduction of uranyl ion by triphenylantimony gives uranium (IV) and triphenylantimony oxide. The electronic excited state level of uranyl fluorescence lies in the range 470–580 nm.4 The electronic energy transfer has been observed from the excited state of uranyl ions to Co(CN)₆³⁻ (ref. 5, 6) and Cr(en)₃³⁻ (ref. 7).

Matsushima and Sakuraba⁶ have reported the leading chemical quenching of the uranyl ion—benzene system, leading to deactivation of uranyl ion in the excited state. In the present case chemical quenching takes place leading to the redox product uranium (IV) and triphenylantimony oxide.

All these observations reveal that the quenching of uranyl fluorescence by triphenylantimony proceeds by dynamic mechanism (intermolecular). It is possible that quenching reaction occurs via the formation of an intermediate complex between the excited uranyl ion and triphenylantimony. The donor acceptor interaction can arise in the excited state even though there is no affinity in the ground state.

Mercantonatos⁷ has explained the quenching by substrates in terms of molecular orbitals. According to him the luminescence level of the uranyl ion is possibly a triplet state.⁸ Uranyl ion absorbs radiation of lower wavelength and excited to higher singlet state and deactivates to triplet state through inter-system crossing. The primary act of quenching involves simultaneous overlap of the triplet 3π, MO and one of the virtually atomic components of MO of (UO₂⁺) 3π, by an appropriate orbital of the quencher (triphenylantimony).

Uranium (IV) absorbs at (475, 550, 660 and 820 nm) and is responsible for the overall reduction process. The values of the quantum yield for U(IV) in the case of uranyl acetate, sulphate and nitrate are given in Table 1. The value of the quantum yield for uranyl sulphate, uranyl acetate and uranyl nitrate are 44.9, 40.0 and 28.3 respectively at [UO₂⁺] = 3.4 × 10⁻⁸M, [H⁺] = 0.4M and at 30⁰C. The life-time of the excited uranyl ion is 2.41 × 10⁻⁸ to 5 × 10⁻⁷ sec (ref. 12). K₄ is the quenching constant and is a measure of the rate of the bimolecular radiationless deactivation of the excited uranyl ions. Since the natural life-time (τ) of the excited uranyl ion is given by Eq. (11)

\[
\tau = \frac{1}{k_4 + k_5} \quad \text{(11)}
\]

the expression (10) can be written as

\[
K_q = K_q \tau \quad \text{(12)}
\]

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\]

The values of the second order rate constant for uranyl ion and triphenylantimony are given in the Table 1. This verifies the proposed mechanism and also the correlation between the second order rate constant and the quenching constant K₄. The plot of (φ)⁻¹ versus [TPSb]⁻¹ is also linear passing through the origin. This also supports the proposed mechanism. Bhat and Mathur have studied the rates of oxidation of uranium (IV) by NO₃⁻ in aqueous nitric acid and tri-n-butyl phosphate solution and by NO₃⁻ in aqueous HNO₃ solutions. Slade investigated the rate of oxidation of uranium (IV) by HNO₃ in aqueous nitric acid tri-n-butyl phosphate. They suggested the following reactions for oxidation of uranium (IV).

\[
\text{U}^{IV} + \text{NO}_3^- + \text{H}_2\text{O} \rightarrow \text{UO}_2^{IV} + \text{HNO}_3 + \text{H}^+ \quad \text{(13)}
\]

\[
\text{U}^{IV} + 2\text{HNO}_3 \rightarrow \text{UO}_2^{IV} + 2\text{NO} + 2\text{H}^+ \quad \text{(14)}
\]

\[
2\text{NO} + \text{H}_2\text{O} \rightarrow 3\text{HNO}_2 \quad \text{(15)}
\]
Bhat and Mathur during photolysis of uranyl ion in aqueous nitric acid-ethanol solutions suggested that the reaction mixture should be kept at low temperature to avoid oxidation of uranium (IV) produced. In our case the rate of photochemical reduction is least with uranyl nitrate. This may be due to oxidation of uranium (IV) produced during the reaction with nitrate ions which is in agreement with the results reported in literature.

The quantum yield (φ) for the photo-reduction of uranium (VI) to uranium (IV) for uranyl acetate, sulphate and nitrate is less than one. This indicates that deactivation of uranyl ions may be due to fluorescence (k₁), internal conversion (k₂), collision with another molecules of substrates (k₃), deactivation of exciplex (k₄), solvent molecules and physical quenching due to phenyl groups attached to the antimony as reported by Matsushima and Sakuraba.

The photoreduction of uranyl ions by triphenylantimony takes place via atom transfer and not by electron transfer. In order to verify this, the absorption spectra of the solution, exposed to radiations was recorded during photolysis. No band corresponding to uranium (V) was observed. In order to get further evidence for the atom transfer mechanism the products of the photolysis (green colour) were decomposed with hydrochloric acid and extracted with benzene. The compounds in the products were triphenylantimony and triphenylantimony oxide.

Dioxane also reduces the uranyl ion to a small extent as compared to triphenylantimony. The reaction with dioxane at uranyl ion concentration 3.4 x 10⁻³ M does not occur at all for twenty minutes and only at higher concentration of uranyl ion (10.20 x 10⁻³ M) some reduction is observed. The photo reduction was carried out for only 15 min only at low concentration of uranyl ion (3.4 x 10⁻³ M), for determining the quantum yield (φ) for the production of uranium (IV) in the case of uranyl acetate, sulphate and nitrate.

The rate of formation of U (IV) is affected by the change in [H⁺] and data for uranyl ion and triphenylantimony is presented in Table 2. The plots of k versus [H⁺] are linear for uranyl acetate and nitrate and obey Eq. (16)

\[ k = k' + k'' [H^+] \]

where \( k' \) is the second order rate constant at zero hydrogen ion concentration and \( k'' \) concentration dependent. The values of \( k' \) and \( k'' \) for uranyl acetate and nitrate have been obtained from the plots of \( k \) versus [H⁺] and the values are 1.39, 3.1 and 0.64, 3.9 min⁻¹ mol⁻¹ respectively. The change in the rate constants with the change in [H⁺] may be due to following factors : (a) variation in pH markedly affects the life-time of uranyl ion luminescence; and (b) the change in the nature of species present. It appears that the protonated uranyl ions are formed in a fast equilibrium which has higher oxidation potential (and larger absorption coefficient) in the excited state than the unprotonated uranyl ions.

The plot of \( k \) versus [H⁺] for reduction of uranyl sulphate with triphenylantimony is not linear (Fig. 1). The abnormal behaviour shown by uranyl sulphate is due to the formation of the complex species as reported by Patel and Ramakrishna.

The addition of uranium (IV) to the reaction mixture decreases the rate of reduction. This is due to the complex formation between U(IV) and triphenylantimony and triphenylantimony oxide, since complexation decreases the concentration of the substrate. The quantum yields for the uranyl ion by triphenylphosphine, arsine and antimony at [UOi⁺] = 3.4 x 10⁻³ M, [TPX] = 18.20 x 10⁻³ M and [H⁺] = 0.4 M (X = P, As and Sb) at 30° have the values 0.91, 0.63 and 0.57 respectively. These results show that the rate of reduction of uranyl ion with triphenylantimony follows the order : triphenylphosphine > triphenylarsine > triphenylantimony.

The variation in rates can be explained on the basis of electron donating capacity of the substrate (quencher). The electron donating capacity follows the order : triphenyl phosphine > triphenylarsine > triphenylantimony.

### References

### Table 2 — Effect of Varying [H⁺] on the Rate of Photo-reduction for Uranyl Ions with Triphenylantimony

<table>
<thead>
<tr>
<th>Substrate</th>
<th>10⁶(sec⁻¹ M⁻³) at [H⁺] (M)</th>
<th>Extinction coefficient (ε) at [H⁺] (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Uranyl acetate</td>
<td>2.95</td>
<td>2.47</td>
</tr>
<tr>
<td>Uranyl sulphate</td>
<td>3.43</td>
<td>4.18</td>
</tr>
<tr>
<td>Uranyl nitrate</td>
<td>1.30</td>
<td>2.78</td>
</tr>
</tbody>
</table>