Photolysis of Alkaline Earth Metal Tris(oxalato)ferrates(III): A Mossbauer Study

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Received 19 April 1984; revised and accepted 30 August 1985

Photolysis of alkaline earth metal tris(oxalato)ferrates(III) in solid and liquid states has been investigated using Mossbauer and electronic spectroscopy. Iron(II) species is formed in solid as well as liquid state. The effect of outer cations, viz. Mg, Ca, Sr and Ba has been observed on the formation of intermediates and quantum yields for Fe(II) species in the liquid state.

In earlier papers the effect of outer cations (Li, Na, K, Cs) on the photolysis and radiolysis of alkali metal tris(oxalato)ferrates(III) and alkali metal bis(citrato)ferrates(III) in solid and liquid phases was reported. The photolysis of hexamminecobalt(III)tris(oxalato)ferrate(III) has also been reported. As an extension the effect of outer cations, viz. Mg, Ca, Sr, and Ba on the products of photolysis of alkaline earth tris(oxalato)ferrates(III) and a comparison of results with those of potassium ferrioxalate are reported in this paper. The feasibility of its use in actinometer for the measurement of intensity shall be discussed.

Materials and Methods
Tris(oxalato)ferrates(III) of Mg(II), Ca(II), Sr(II) and Ba(II) were prepared as reported in our earlier publication. The experimental details of photodecomposition in solid and liquid states were the same as described earlier. The details of Mossbauer setup were also same as reported earlier. Photolysis in liquid state was investigated under inert O₂-free nitrogen atmosphere. The reaction mixture, taken in a quartz photochemical reactor (200 ml) was irradiated at 20°C with 300 nm radiations using a 125 watt medium pressure mercury lamp (Hanovia). Doubly distilled water and 0.2 M sulphuric acid were used for each run. Oxygen-free nitrogen gas was bubbled both for deoxygenation and stirring the mixture, prior to and during the reaction. The intensity of the lamp which was found to be 2 × 10¹⁷ quanta ml⁻¹ s⁻¹, and quantum yield was measured using potassium ferrioxalate actinometer. Thermogravimetry (TG) Stanton thermobalance at a heating rate of 10°C/min was used to study the thermal behaviour. Magnetic measurements were made on a Guoy balance using Hg complex as the calibrant. Infrared spectra were recorded in KBr matrix on a Perkin-Elmer 570 B model spectrophotometer.

Results and Discussion
Mössbauer parameters, IR data and magnetic moments of tris(oxalato)ferrates(III) of alkaline earth

Mössbauer spectra of the alkaline earth metal tris(oxalato)ferrates(III) of Mg, Ca, Sr and Ba are broad, due to spin-lattice relaxation effect. The isomer shift value for magnesium, calcium, strontium and barium tris(oxalato)ferrates(III) are 0.24, 0.26, 0.25 and 0.31 mms⁻¹ respectively, the values for strontium and barium tris(oxalato)ferrates(III) being close to those reported by Gallagher and coworker. The isomer shift values indicate these complexes to be high-spin, with +3 oxidation state of iron in an octahedral symmetry.

Infrared spectra of magnesium and calcium tris(oxalato)ferrates(III) exhibit bands at 3300 (vOH), 1650 (vC=O) and 1425 and 1260 cm⁻¹ (v₁ C=O), respectively. The elemental analyses of these ferrioxalates indicate the presence of water of crystallization which is further confirmed by TG. Reflectance spectra of these complexes exhibit a continuous absorption band from 200 to 550 nm, which is presumably due to ligand to metal charge transfer, and a very weak (d-d, spin-forbidden) band in the range of 650-690 nm. These values are in agreement with the values reported in literature for tris(oxalato)ferrate(III) complexes.

Magnetic moments for magnesium, calcium, strontium and barium tris(oxalato)ferrates(III) are 5.65, 5.64, 5.78 and 5.76 B.M. respectively, indicating that iron in these compounds is in +3 oxidation high spin state.

Solid state photolysis
All the alkaline earth tris(oxalato)ferrates(III) were
Table 1 — Mössbauer Parameters of Solid State Photolysis of Alkaline Earth Tris(oxalato)ferrates(III)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex</th>
<th>Isomer shift† (mms⁻¹)</th>
<th>Quadrupole splitting (mms⁻¹)</th>
<th>Tentative assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg₃[Fe(C₂O₄)₃]·6H₂O</td>
<td>0.24 ± 0.03</td>
<td>—</td>
<td>Parent complex</td>
</tr>
<tr>
<td>2</td>
<td>Ca₃[Fe(C₂O₄)₃]·8H₂O</td>
<td>0.26 ± 0.03</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Sr₃[Fe(C₂O₄)₃]·12H₂O</td>
<td>0.25 ± 0.03</td>
<td>0.40 ± 0.03</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Ba₃[Fe(C₂O₄)₃]·10H₂O</td>
<td>0.31 ± 0.03</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>5</td>
<td>Product I*</td>
<td>1.20 ± 0.03</td>
<td>1.80 ± 0.03</td>
<td>FeC₂O₄·2H₂O</td>
</tr>
<tr>
<td>6</td>
<td>Product II*</td>
<td>1.20 ± 0.03</td>
<td>1.96 ± 0.03</td>
<td>FeC₂O₄·2H₂O</td>
</tr>
<tr>
<td>7</td>
<td>Product III*</td>
<td>1.18 ± 0.03</td>
<td>2.30 ± 0.03</td>
<td>Fe²⁺[C₂O₄]₂(H₂O)²⁻</td>
</tr>
<tr>
<td>8</td>
<td>Product IV*</td>
<td>1.20 ± 0.03</td>
<td>2.68 ± 0.03</td>
<td>Fe²⁺[C₂O₄]₂(H₂O)²⁻</td>
</tr>
</tbody>
</table>

*Products I-IV are obtained, respectively on irradiation of Mg₃[Fe(C₂O₄)₃]·6H₂O, Ca₃[Fe(C₂O₄)₃]·8H₂O, Sr₃[Fe(C₂O₄)₃]·12H₂O and Ba₃[Fe(C₂O₄)₃]·10H₂O for 300 hr.
†All isomer shift values are with respect to natural iron.

Fig. 1 — Mössbauer spectra of photolysis of calcium tris(oxalato)ferrate(III) [(a) Unirradiated; (b) irradiated for 100 hr; and (c) irradiated for 300 hr]

Table 2 — Quantum Yields for Formation of Iron(II) Species During Photolysis of Alkaline Earth Tris(oxalato)ferrates(III) in Solution Phase

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg₃[Fe(C₂O₄)₃]·6H₂O</td>
<td>0.47</td>
</tr>
<tr>
<td>2</td>
<td>Ca₃[Fe(C₂O₄)₃]·8H₂O</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>Sr₃[Fe(C₂O₄)₃]·12H₂O</td>
<td>0.91</td>
</tr>
<tr>
<td>4</td>
<td>Ba₃[Fe(C₂O₄)₃]·10H₂O</td>
<td>0.91</td>
</tr>
</tbody>
</table>

tris(oxalato)ferrate(III), [Fe₂(C₂O₄)₅]⁶⁻ has been reported to be formed. This shows that outer cation affects the nature of intermediates and stability of products to a great extent.

**Photolysis in solution phase**

The quantum yields for the formation of iron(II) species during the photolysis of alkaline earth tris(oxalato)ferrates(III) are given in Table 2. The quantum yield for the formation of Fe(II) species in the case of potassium tris(oxalato)ferrate(III) in acidic medium is (i.e. φ = 1.20). The quantum yields for the photoreduction of alkaline earth tris(oxalato)ferrates(III) are in the range of 0.91 to 0.47. This may be due to the use of polychromatic radiations and change of outer cation. The quantum yields are higher for strontium and barium complexes and compared to those for magnesium and calcium complexes. The quantum yields of magnesium as calcium complexes show that physical deactivation is predominant in these complexes. The quantum yields less than unity clearly indicate that there is no possibility of chain reaction. The quantum yield for photoreduction to iron(II) species is less than that of potassium tris(oxalato)ferrate(III). So it is not desirable to replace potassium ferrioxalate as a chemical actinometer. The intermediates formed in solid state photolysis are stable in air. The rates of photochemical reduction follow the order Sr ≈ Ba > Ca > Mg, showing thereby that the size of the cation affects the rate of photochemical reduction of alkaline tris(oxalato)ferrates(III).
Isomer shift values are dependent on the nature of the outer cation. This shows the change of s-electron density at iron nucleus. The changes in electron density and size of outer cation affects the photochemical reduction of complexes in the solid and liquid states.

References