1,3-스쿠아레인 염료의 산화환원 변색효과

"박 수열" "오 세화" "J. Griffiths*"
"응용화학연구부, 한국화학연구원" "*염료학과 리즈대학교(영국)"

Colour Change Redox Behaviour of the 1,3-Squaraine Dyes

"Soo-Youl Park" "Sew-Wha Oh" "J. Griffiths*"
"Dep. of Applied Chemistry, Korea Research Institute of Chemical Technology,
Taejon, Korea" "*Dep. of Colour Chemistry, University of Leeds, U.K"

ABSTRACT
The 1,3-bis(4-aminoaryl)squaraines showed colour change behaviour, they were found to undergo reduction with sodium borohydride in solution to give colourless leuco compounds, which oxidised readily in air back to the coloured squaraine dye. We have investigated this possibility, and have found that reduction can, in most cases, be achieved readily in organic solvents with sodium borohydride, and moreover, the resultant colourless reduced species (leuco dyes) are generally chemically stable and can be oxidised back to the coloured dye with air or common inorganic oxidants. This meant that the 1,3-squaraines could be used as redox indicators, with possible functional applications in enzyme assays, oxygen detection, or reprographic systems, and thus the chemistry of the leuco-1,3-squaraines was investigated in detail in order to determine their potential value in such areas.

Introduction

General considerations:
These symmetrical structures were prepared from squaric acid and the appropriate N,N-dialkylanilines. The now standard technique involves heating squaric acid in a mixture of toluene and n-butanol under azeotropic conditions, so that the mono-n-butyl squarate ester is formed. This then undergoes in situ nucleophilic substitution by the arylamine, giving the half-condensate. A second condensation reaction then gives the 1,3-bis(4-aminoaryl) squaraine. The efficiency of this reaction is determined by the nucleophilicity of the arylamine and the solubility of the product in the reaction medium. In those cases where the dye had low solubility in the solvent, the product could be filtered off directly and the purity was generally high.
The redox properties of 1,3-squaraine derivatives:
The redox properties of 1,3-squaraine derivatives have been the subject of several investigations since this class of chromophore was first discovered.[1,2,3]
Previously, Law et al. had also noted that 1,3-bis-arylsquaraines showed two reversible oxidation waves in dichloromethane, and the oxidation potential decreased as the donor strength of the substituted aryl residues increased.[4] Other redox studies have concentrated on the photochemistry of the squaraine dyes, where laser excitation can lead to radical cations and anions derived from the patent chromophore.[5,6,7]

**Results and Discussion**

*Synthesis and characterisation of the leuco-1,3-bis(4-aminoaryl)-squaraine dyes.*

Preliminary experiments showed that the 1,3-bis(4-aminoaryl)squaraines were readily decolourised by a variety of reducing agents, and the colour could be regenerated by leaving the solutions in air, or by adding oxidising agents such as ferric chloride. The most convenient method of reduction involved using excess sodium borohydride in a mixture of a dichloromethane and methanol at room temperature, most of the squaraine dyes being soluble in this medium. A reaction time of 2 hours was sufficient to effect complete reduction. Isolation of the leuco dye could be achieved by removal of the solvent on a rotary evaporator, adding water and acetic acid to the residue, and filtering off the precipitate. The white, or lightly coloured solid, could then be dried in vacuum over calcium chloride. This method was not always successful in producing pure products, as most leuco dyes were particularly susceptible to air oxidation and it was not possible to prevent partial reoxidation once the excess sodium borohydride had been destroyed by acidification. The leuco compounds were, in marked contrast to the parent dyes, generally low melting solids, readily soluble in non-polar solvents. They were also acidic, being insoluble in water but readily soluble in dilute aqueous alkali.

**Table 1.** Yields and physical data for leuco-1,3-squaraine dyes.

<table>
<thead>
<tr>
<th>Leuco dye</th>
<th>Structure</th>
<th>Yield / %</th>
<th>m.p. / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>R₁R₂N</td>
<td>R₂</td>
<td>R₃</td>
</tr>
<tr>
<td>b</td>
<td>Et</td>
<td>Et</td>
<td>H</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Leuco dye</th>
<th>Structure</th>
<th>Yield / %</th>
<th>m.p. / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>R₁R₂N</td>
<td>R₂</td>
<td>R₃</td>
</tr>
<tr>
<td>b</td>
<td>n-Bu</td>
<td>n-Bu</td>
<td>H</td>
</tr>
</tbody>
</table>
The most probable structure for the leuco compounds is (2), which would arise by direct transfer of hydride ion from the borohydride anion to the squaraine ring. A probable mechanism is shown in Scheme 1, in which one of the carbonyl groups of the ring becomes attached to boron. Treatment of the resultant complex with aqueous acid would then generate (2).

![Diagram of chemical structures](image)

Scheme 1. Formation of leuco 1,3-squaraines.

**Oxidation characteristics of the leuco-1,3-bis(4-aminoaryl)-squaraine dyes:**
The ability of the leuco squaraine dyes to undergo facile air-oxidation places them on a par with the leuco- indigoids, leuco-thiazinium and oxazinium dyes, and this means that they have many potential applications as colour-change oxidation-sensitive molecules.

An indication of the relative ease of oxidation of a range of leuco 1,3-squaraine dyes was obtained in the following way. A solution of each squaraine dye (10^-4 M) in dichloromethane/methanol was reduced fully with a slight excess of sodium borohydride, and after destroying any excess borohydride with a little acetic acid, the solution was diluted rapidly to ca. 10^-5 ~ 10^-6 M with dichloromethane, *(the concentration of this solution would give an absorbance of ca. 1.0 ~ 1.5 at max of the oxidised dye when fully oxidised, if oxidation were 100% efficient)*. The rate of coloration of the solution at room temperature in air was then monitored in a spectrophotometer cell by measuring the increase in absorbance at the max of the oxidised dye. Oxidations typically took less than 1 hour to go to completion. Figure 1 shows the typical appearance of the visible absorption spectrum of a leuco squaraine solution as it is allowed to autoxidise in air.
Figure 1. Air oxidation of a solution of the *leuco* squaraine dye (2a) in DCM.

Absorbance/time plots were relatively complex and this method has too many uncertainties to provide meaningful kinetic data (*e.g.* autoxidation will be a chain reaction and the induction period for initiation and rates of propagation will depend on such factors as solvent and sample impurities, oxygen concentration, incident light etc.).

References