

Photochemistry of Tris(2,2'-bipyridine)ruthenium(II) in Chlorinated Solvents

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Summary The photolysis of tris(2,2'-bipyridine)ruthenium(II) in chlorinated solvents at 436 nm and room temperature leads to the formation of *cis*-dichlorobis(2,2'-bipyridine)ruthenium(II) and 2,2'-bipyridine as the main products.

In spite of the large number of papers on photochemical and photophysical studies of tris(2,2'-bipyridine)ruthenium(II) published during the last decade,¹ the direct substitutive photochemistry of this complex has not been reported, although a recent report by Van Houten and Watts² mentioned that a direct photochemical release of one 2,2'-bipyridine ligand was obtained by irradiating $[\text{Ru}(\text{bipy})_3]^{2+}$ in dilute acid at 95 °C at 436 nm. No attempts were made to identify other photolytic products of the ruthenium complex or to determine the quantum yield of the process.

However, on dissolving $[\text{Ru}(\text{bipy})_3]^{2+}$ chloride in dichloromethane (and in several other chlorinated solvents such as chloroform, 1,2-dichloroethane, trichloroethane, 1,1,2,2-tetrachloroethane, *etc.*) containing a small percentage of ethanol to dissolve the complex, and irradiating the solution at 436 nm and room temperature, a photoreaction takes place leading to a colour change from yellow to violet. The spectral changes during irradiation of a solution of $[\text{Ru}(\text{bipy})_3]^{2+}$ in CH_2Cl_2 -EtOH (99.8:0.2 v/v) are shown in the Figure. The maxima at 288 and 455 nm characteristic of $[\text{Ru}(\text{bipy})_3]^{2+}$ decrease during photolysis; correspondingly three other maxima at 299, 375, and 555 nm appear, and isosbestic points are observed at 270, 296, 304, 350, 407, and 487 nm.

Spectrophotometric analysis of the photolysed solution shows that the absorption peaks at 299, 375, and 555 nm are due to the presence in the reaction mixture of the *cis*-dichlorobis(2,2'-bipyridine) ruthenium(II) complex. This can be concluded by comparing the u.v. and i.r. spectra of the photolysis product with those of the pure complex,

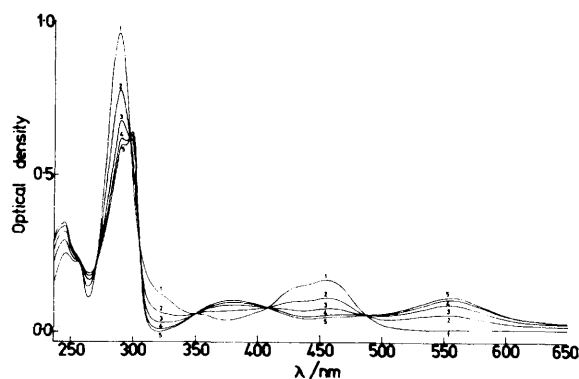


FIGURE. Spectral changes during irradiation at 436 nm and room temperature of a solution of $[\text{Ru}(\text{bipy})_3]^{2+}$ in CH_2Cl_2 -EtOH (99.8:0.2 v/v): (1) $t = 0$; (2) $t = 10$; (3) $t = 20$; (4) $t = 30$; (5) $t = 40$ min.

synthesized as in ref. 3. Elemental analysis of the photolysis product also agrees with the formulation $[\text{Ru}(\text{bipy})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

The presence of 2,2'-bipyridine in solution was confirmed by distilling off the solvent and subliming the solid residue over a 'cold finger'; a white powder was collected whose spectrum is very similar to that reported for 2,2'-bipyridine.⁴

The quantum yield for the formation of *cis*- $[\text{Ru}(\text{bipy})_2]\text{Cl}_2$, calculated on the basis of spectral changes, was found to be 0.02. It appears to be very sensitive to the amount of ethanol in solution and it is drastically reduced by increasing the ethanol concentration. Particular attention should be paid to the fact that commercial chlorinated solvents are normally stabilized with ethanol: therefore the dichloromethane we used for our studies was carefully purified by known procedures.⁵

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¹ For a review of the literature on $[\text{Ru}(\text{bipy})_3]^{2+}$ up to 1974, see V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Lawrence, *Co-ordination Chem. Rev.*, 1975, **15**, 321; since then nearly forty papers dealing with the photochemical and photophysical properties of $[\text{Ru}(\text{bipy})_3]^{2+}$ have been published.

² J. Van Houten and R. J. Watts, *J. Amer. Chem. Soc.*, 1976, **98**, 4853.

³ G. Sprintschnick, H. W. Sprintschnick, P. P. Kirsch, and D. G. Whitten, *J. Amer. Chem. Soc.*, 1977, **99**, 4947.

⁴ R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.*, 1961, **65**, 1196.

⁵ A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1970.