An Easily Visible Photochemical Oscillating Reaction

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The photochemical decomposition of $[Ru(bpy)_2(N_3)_2]$ (bpy = bipyridine) in $CHCl_3$ leads to a solution that oscillates between two visibly distinct products.

Photochemical oscillating reactions have been the subject of both theoretical[1—5] and experimental[6—9] investigations. The physical manifestation of the few reactions that have been observed experimentally has generally been in the form of a periodic variation in the intensity of light emitted by the reacting solution. We report a reaction of a different kind, in which the system oscillates, apparently totally, between two quite distinct chromophores. Furthermore, the system may be frozen in either of the two states by removing the source of illumination.

Solid diazidobis(bipyridine)ruthenium(II),[10] $[Ru(bpy)(N_3)_2]$, was dissolved in chloroform to a concentration of about 1×10^{-4} M. The solution was placed in a cylindrical cell in a water bath at 15 °C and irradiated with an unfiltered 500 W mercury lamp operating at about half power. Within one minute the solution turned from purple to a lighter violet as the spectrum of $[Ru(bpy)_2(N_3)_2]$ (λ_1 572 nm, λ_2 394 nm) was replaced by that labelled **A** in Figure 1 (λ_1 558 nm, λ_2 378 nm). On continued irradiation the colour of the solution changed after 2 min to a yellowish tan, with the spectrum labelled **B** in Figure 1 (λ_1 382 nm). Further irradiation caused an oscillation between **A** and **B**, **A** persisting for about one minute and **B** for two minutes. This was observed for more than 10 periods, during which time the oscillation periods increased somewhat. In the dark the solution was thermally stable in either state for at least 24 h.

The solution temperature is important. The fraction of time during which the violet product **A** was present increased with temperature, as did the overall oscillation period. Above about 60 °C the only product was **A**. It is interesting that Nitzan and Ross predicted that the temperature would have to be below a certain threshold in order for photo-induced oscillation to occur.[1]

Although a complete characterization of the products has not been completed, the electronic absorption spectra tentatively identify the two products as an Ru^{II} and an Ru^{III} species: $[Ru(bpy)_2Cl_2]$ (**A**) and $[Ru(bpy)_2Cl_2]^+$ (**B**).[11] Crystalline samples of the latter were insoluble in $CHCl_3$, and it is possible that it appears as a colloidal suspension during its part of the cycle. We are still investigating the mechanism by which the

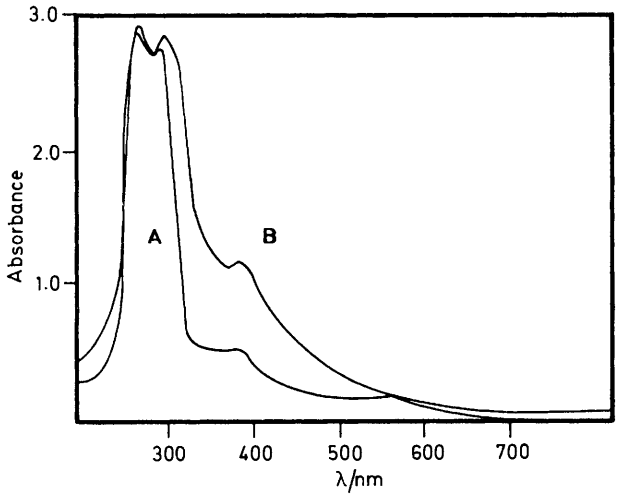

Figure 1. U.v.-visible absorption spectra of the two products formed during the irradiation of $[Ru(bpy)_2(N_3)_2]$ in $CHCl_3$.

oscillation occurs. The photodecomposition of $[Ru(bpy)_2(N_3)_2]$ and $[Ru(bpy)_2(N_3)_2]^+$ has been studied previously,[13,14] but not in chlorinated solvents, and the photoreactions taking place involved displacement of azide by solvent in both cases, with reduction to Ru^{II} when Ru^{III} was the substrate.

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