The Photoredox Decomposition of a Platinum(II) Complex Ion

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Summary The excitation of azide-to-platinum charge-transfer transitions in the azidodiethylenetriamineplatinum(II) complex ion causes the formation of N_3 radicals.

THE excitation of co-ordination compounds with light corresponding to ligand-to-metal charge-transfer transitions is expected to cause the reduction of the metal centre and the oxidation of the ligand(s).[1] This type of photoreaction has till now only been obtained for co-ordination compounds (such as those of Co^{III} or Fe^{III}) whose central atom has a relatively stable one-electron reduction product (either free or complexed).[2] Thus, the only types of photoreaction which have been observed until now for Pt^{II} complexes are ligand photosubstitution[3-5] or geometrical photoisomerization,[6,7] no matter whether the excitation was performed in ligand-field or charge-transfer bands. We report here what appears to be the first documented case of photoredox decomposition in Pt^{II} complexes.†

The spectrum of $[Pt(dien)N_3]NO_3$ (dien = diethylenetriamine) shows an intense absorption below 320 nm which can be attributed to azide-to-platinum charge-transfer transitions. The irradiation of aqueous solutions of the complex with light of 254 or 313 nm (absorbed light intensity of the order of 10^{-7} einsteins/min, volume of the solution 3 cm^3) causes spectral changes with two isosbestic points at about 250 and 325 nm. Simultaneously, evolution of nitrogen is observed. When the 313 nm irradiation is performed on deaerated solutions containing 1 M-acrylamide, nitrogen evolution is completely quenched and polymerization of the acrylamide monomer occurs. If the irradiation is performed in the presence of iodide ions, the characteristic absorption of the I_3^- ion is observed. These results clearly indicate that the observed nitrogen formation is the result of the photochemical oxidation of the azide ligand to N_3 radicals. Also, the presence of the two isosbestic points suggests that the formation of the N_3 radicals occurs in the primary photochemical process as a direct consequence of the electronic rearrangement induced by azide-to-platinum charge-transfer transition. As for the fate of the platinum-containing moiety, the primary photochemical process requires that the unstable $Pt(dien)^+$ ion is initially formed. The spectral variations show that the stable product which immediately originates from such an intermediate is not the $Pt(dien)H_2O^{2+}$ ion.

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† In a recent communication (ref. 8) a photodecomposition of oxalatobis(triphenylphosphine)platinum(II) yielding CO_2 is reported, but it is unknown whether such a result is due to the primary photochemical process or to a secondary thermal reaction.

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