Luminescence from Protoporphyrin IX Dimethyl Ester

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Summary Two excited states of protoporphyrin IX dimethyl ester have been identified using pulse radiolysis techniques.

SINGLET oxygen could be involved in the mechanism of photo-damage found in some types of the human disease porphyria,[1,2] the singlet oxygen being formed from ground state molecular oxygen ($^3\Sigma_g$) by energy transfer from triplet excited protoporphyrin IX, formed following exposure to sunlight. An excited state of protoporphyrin IX which exhibited an intense red emission with a maximum at 635 nm in tetrahydrofuran solution was postulated,[2] on the basis of biacetyl sensitisation and oxygen quenching, to be the triplet responsible for energy transfer. Earlier workers had assumed[3] that this emission was fluorescence. We have now applied pulse radiolysis techniques[4] to a study of this system.

Protoporphyrin IX dimethyl ester exhibits the same intense red emission as protoporphyrin IX. The species responsible for this luminescence has now been shown to have a very short lifetime (23 ns) at 25 °C in benzene, a solvent which supports excited states on radiolysis. This lifetime agrees with values published recently[5,6] by other workers using quite different techniques. In addition, the oxygen quenching of the red emission[2] has now been shown to occur with an approximate rate constant of $(1{\cdot}8 \pm 0{\cdot}1) \times 10^{10}\ \mathrm{s^{-1}\ mol^{-1}\ dm^{3}}$. This value is similar to typical rate constants observed for oxygen quenching of singlet excited states, those for triplets usually being an order of magnitude smaller.[7]

A longer-lived ($> 240\,\mu s$) non-emitting excited state was also detected in the pulse radiolysis experiments by its absorptions at 460 and 700 nm. It could also be formed by energy transfer from biacetyl. Under these conditions no sensitisation of the red emission at 635 nm was observed. Oxygen quenching of this non-emitting excited state occurred with a rate constant of $(2{\cdot}7 \pm 0{\cdot}2) \times 10^9\ s^{-1}\ mol^{-1}\ dm^3$.

These observations lead to the conclusion that the emitting species is a singlet excited state of protoporphyrin IX dimethyl ester, whilst the longer-lived non-emitting species is a triplet state.

The triplet excited state was quenched by both β-carotene ($E_T < 94$ kJ mol^{-1};[8] $k_q = 1{\cdot}8 \times 10^9\ s^{-1}\ mol^{-1}\ dm^3$) and naphthacene ($E_T = 122$ kJ mol^{-1};[9] $k_q = 0{\cdot}5 \times 10^9\ s^{-1}\ mol^{-1}\ dm^3$) but not by perylene ($E_T = 151$ kJ mol^{-1};[10] $k_q < 0{\cdot}2 \times 10^9\ s^{-1}\ mol^{-1}\ dm^3$). This suggests that protoporphyrin IX dimethyl ester has a triplet energy of 122—151 kJ mol^{-1}, in agreement with the value of 150 kJ mol^{-1} determined by Gouterman and Khalil[5] from low-temperature phosphorescence measurements. Such a triplet energy is in accord with the suggestion[2] that protoporphyrin IX acts as a triplet sensitiser for the generation of $^1\Delta_g$ oxygen ($E_S = 94$ kJ mol^{-1}).[11]

β-Carotene has been shown[12] to have a photoprotective function in erythropoietic porphyria. It may possibly quench triplet protoporphyrin IX and so prevent formation of $^1\Delta_g$ oxygen. Alternatively it may act as a quencher of singlet oxygen following formation of the latter.

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