A new kinetic law in the recombination of photodissociated carbon monoxide-haemoglobin

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The autocatalytic binding of molecular oxygen to haemoglobin has been much studied because of its great physiological importance. In particular, flash photolysis techniques have been used to investigate the kinetics of binding after photodissociation of the ligand–haemoglobin complex. We report a study on the recombination occurring after photodissociation of carbon monoxide–haemoglobin by 530 nm laser pulses of 1 - 7 ns duration in aqueous solutions of pH 6 - 9.5. It has previously been shown that a rapid phase (of about 100 ns duration) in this recombination is due to the reaction of photodissociated ligand with its geminate haem. The probability of this reaction is high during the time that the ligand remains imprisoned in the protein matrix. We have now found that this recombination has the square-root-of-time dependence that is characteristic of geminate fragment rebinding during diffusive displacements. We compared the experimental data with the kinetics calculated from theoretical treatments of various simplified model systems. With these it was possible to separate the probability of reaction during ligand–haem encounters from the process of carbon monoxide diffusion in the protein. Rate constants and activation enthalpies were determined for these two processes. Similar studies were performed on the isolated α and β haemoglobin subunits.