Fireflies in the Kamo River

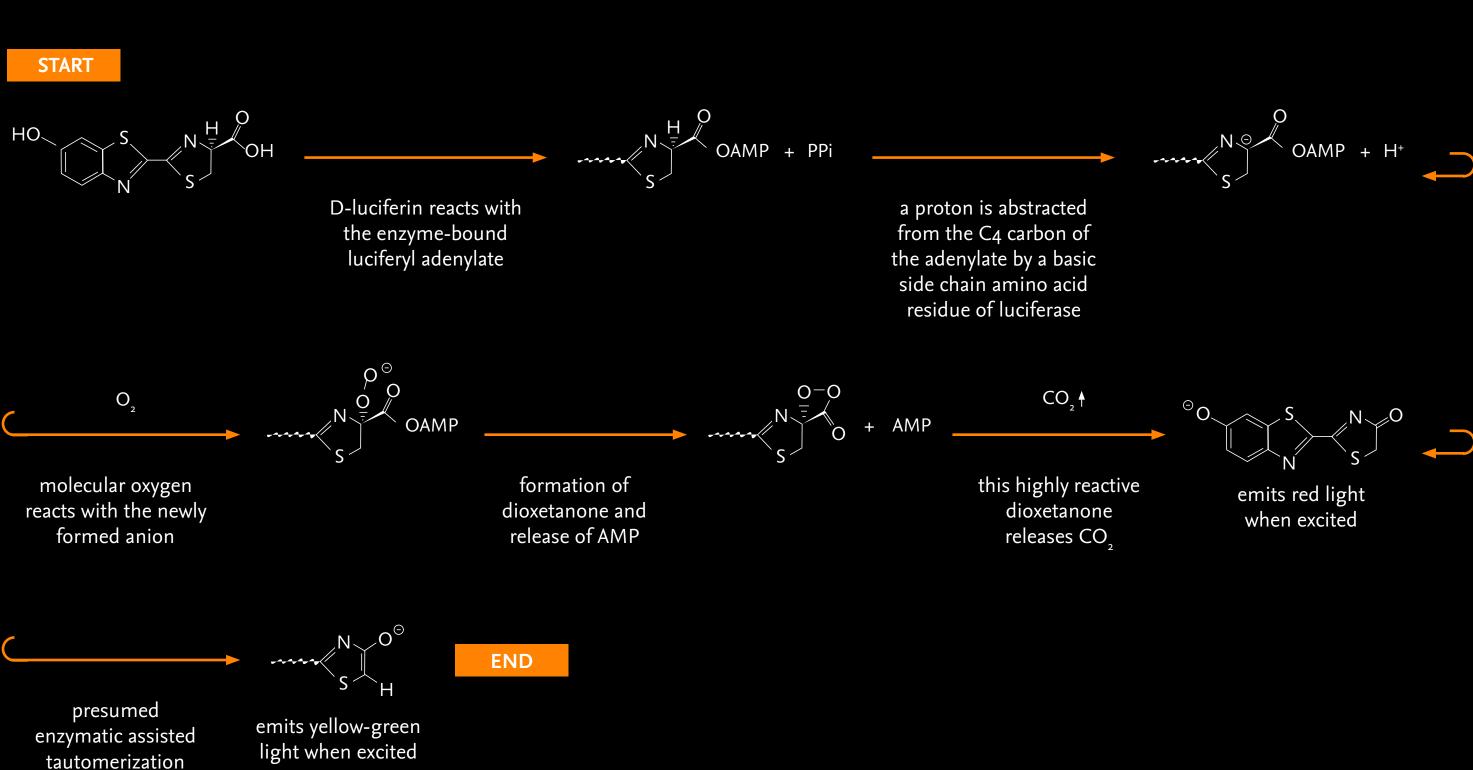
It is the middle of June and you are walking along the Kamo River in Japan, on your way home and enjoying a summer evening breeze. The riverbank is one of the most popular walking spots in the Kyoto Prefecture, but today you can see just a few people around. As daylight fades and your surroundings get dark, small green light flickers suddenly appear and begin to drift around you and the other nearby people.

The light flickers become more and more frequent as you and everyone else look around in wonder and delight. Soon, everyone is surrounded by a beautiful green glimmer. This green light is emitted by fireflies.

Fireflies or lightning bugs make light within their bodies. This process is called bioluminescence and is shared by many other organisms, mostly sea-living or marine organisms. Fireflies light up to attract a mate. To do this, the fireflies contain specialized cells in their abdomen that make light.

Generally Accepted Mechanism of Bioluminescence

The generally accepted mechanistic details of the overall process of firefly bioluminescence.



Biochemical Reactions of Bioluminescence

Firefly bioluminescence is a multi-step process that is outlined in Eqs 1-3



Luc + D-LH₂ + ATP Luc^{*}

Luc*LH2- AMP +PPi

corresponding enzyme-bound luciferyl adenylate. In fact, synthetic D-LH2-AMP reacts with oxygen in the presence of luciferase emitting a wavelength of light identical to that obtained with the natural substrates D-luciferin and Mg-ATP; this experimental

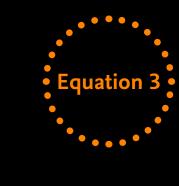
Luciferase converts firefly D-luciferin (LH2) into the

observation helped indirectly confirm the structure of D-luciferin and its role in firefly bioluminescence.



Luc*LH₂ - AMP + O₂ Luc*Oxyluciferin* + AMP + CO₂

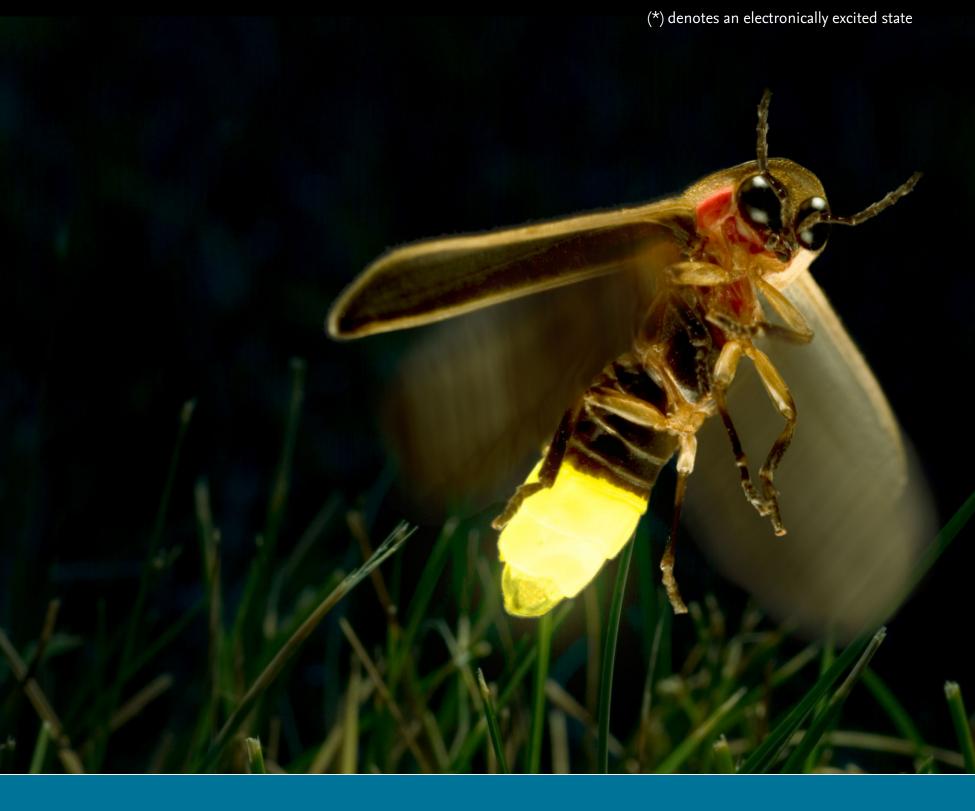
The luciferase enzyme functions as a monooxygenase, although it does so in a very unusual
manner without the apparent involvement of a
metal or cofactor. Luciferase amino acid residues
are recruited to promote the addition of molecular
oxygen to the D-luciferin adenylate, which is then
transformed to an electronically excited state
oxyluciferin and carbon dioxide is released.



Luc*Oxyluciferin* —→ Luc*Oxyluciferin + light

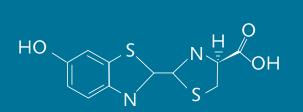
Visible light emission results from the rapid loss of energy of the excited state oxyluciferin via a fluorescence pathway. The very high quantum yield of ~0.4-0.6 for this process (the emission of photons from oxyluciferin) reflects very efficient machinery developed through evolutionary means. This is also a highly favorable reaction pathway which prevents the loss of this energy gained from the electronically excited state by non-light emitting pathways.

(*) denotes an electronically excited state

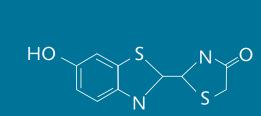


Compounds

D-Firefly Luciferin (LH₂)



Oxyluciferin



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Fireflies or lightning

START

bugs make light within

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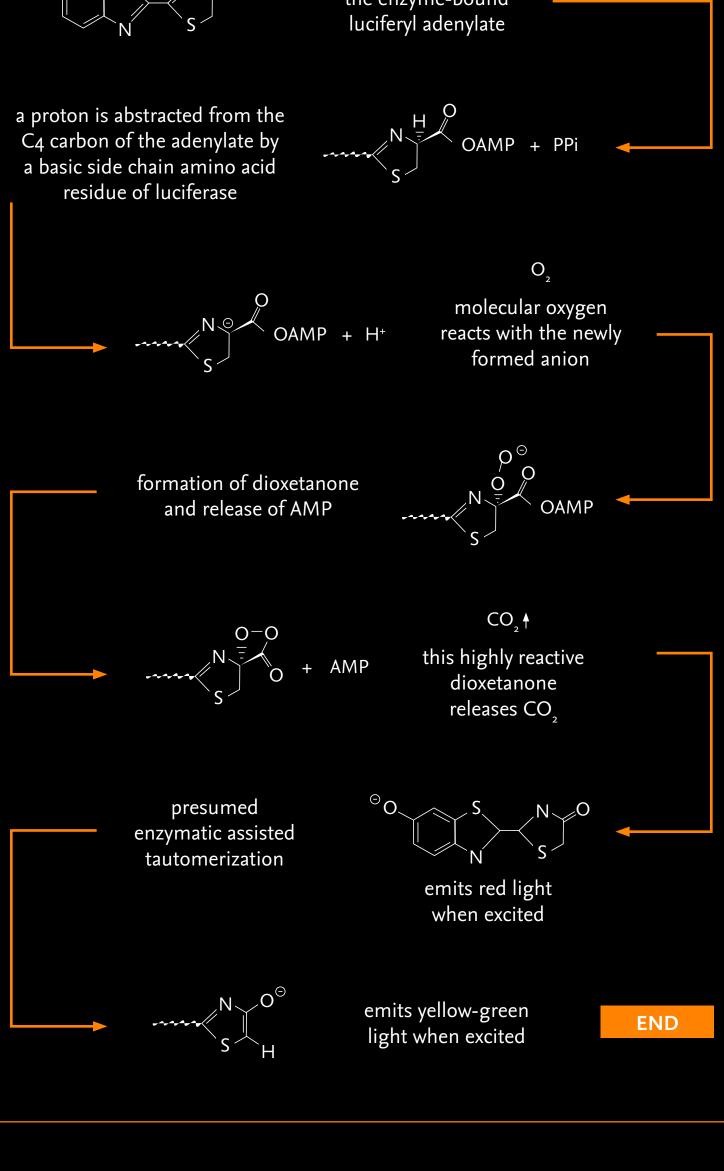
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The generally accepted mechanistic details of the

overall process of firefly bioluminescence.

D-luciferin reacts with the enzyme-bound



Mg²⁺

Luciferase converts firefly D-luciferin (LH2) into the corresponding enzyme-

bound luciferyl adenylate. In fact, synthetic D-LH2-AMP reacts with oxygen

in the presence of luciferase emitting a wavelength of light identical to that

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Luc*LH2- AMP +PPi

Luc + D-LH2 + ATP

Equation

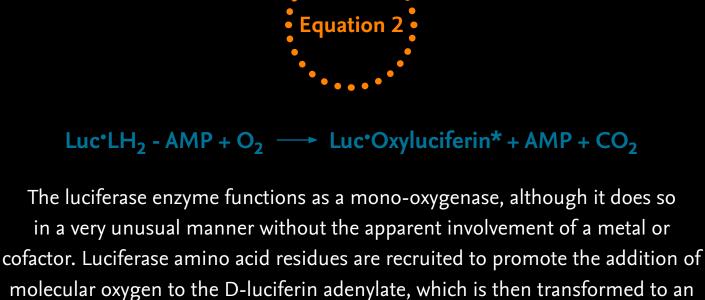
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electronically excited state oxyluciferin and carbon dioxide is released.

(*) denotes an electronically excited state



Compounds

D-Firefly Luciferin (LH₂)

$$\begin{array}{c|c}
N & \downarrow \\
N & \downarrow \\
O - P - O \\
\parallel & \downarrow \\
O & \downarrow \\$$

Luciferyl-AMP

Oxyluciferin

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