How additives affect the Light Emission of Peroxyoxalate Chemiluminescence

By William Wu

Introduction

The development of light sources represents the progress of human civilization, from the earliest reliance on natural light to the use of fire, then to Edison's invention of the electric light bulb. Nowadays, scientists have paid more and more attention to chemiluminescence as it does not rely on electrical power supplies, meaning that it can be used in emergency situations. Also, it releases little heat and produces no sparks, making it a suitable light source in combustible areas, such as mines. Chemiluminescence also has analytical and medical uses. For instance, peroxyoxalate chemiluminescence can be used to determine the glucose concentration in humans' body and form a visual image, by which even the early stages of cancer could be identified (Li *et al.*, 2019). The broad prospect of chemiluminescence has attracted many scientists, and many types of chemiluminescence reactions have been discovered, including Luminol, Lucigenin, ECL, singlet oxygen etc (Li and Miao, 1996).

Among all these types of chemiluminescence, the most efficient one is peroxyoxalate chemiluminescence (POCL). However, reaction conditions can further influence the light-emitting efficiency of a POCL reaction, like the use of specific catalysts has been suggested as a cost-effective and simple method of doing so. In this review, we will discuss and compare some of the proposed techniques.

Chemiluminescence and POCL

Chemiluminescence

Chemiluminescence is the emission of light during a reaction in which fluorescent molecules are excited by absorbing the energy produced by the reaction, and then falling back to the ground state, releasing the energy in form of light (Maruyama, 2013). The energy of photons should be in the range of 167-300 kJ mol^{-1} to be seen by humans, which exactly fits the energy of free radical oxidation reactions. Therefore, oxygen, peroxides and oxidizing agents are involved in most chemiluminescence reactions, as is the case in POCL (Xue, 2009).

Peroxyoxalate Chemiluminescence

A POCL reaction requires the mixing of two solutions to perform: the first one is bisoxalate dissolved into dibutyl phthalate, and the second one is a mixture of hydrogen peroxide and t-butyl alcohol. In the presence of a fluorescent dye (such as Rhodamine B), the system will emit light. The proportion of each chemical can be changed to obtain different light-emitting effects. Different bisoxalate can be used in the experiment as well, with the most common one being bis(2,4,5-trichloro-6-carbopentoxyphenyl) oxalate (CPPO in short).

The mechanism of this experiment is simple. Hydrogen peroxide acts as a nucleophile to attack the carbonyl group on bisoxalate to form an intermediate with high energy, which then breaks up to release energy. The fluorescent dye absorbs this energy and comes to its excited state, and then falls back to the ground state and emits the energy in the form of light (Yu, 2002).

Catalysts' effect on POCL reactions

To quantitatively describe catalysts' effect on the light emission of POCL reaction, a good way is to plot a graph of light intensity of the chemiluminescent system against time. This can clearly demonstrate the luminescent lifetime, peak intensity and how its intensity decays. The total energy output is described by the area under the curve.

A potential limitation of such an analysis is that the systematic conditions, such as the type of bisoxalate and the concentration of solutions, used in different papers are not exactly the same. However, as POCL reactions share the same core mechanism, and the same kind of catalysts have similar effects on the light emission of such systems despite different concentrations and types of bisoxalate may be used. This is proven in an experiment carried out by Xu and her colleagues, in which the same catalysts are added to POCL systems with different bisoxalate used, and the effects of catalysts on the light intensity curve turn out to be similar (Xu, 2007). Additionally, the concentrations and proportions of reagents must be in a certain range to perform POCL reaction successfully (Li and Miao, 1996), so the divergence of such systematic conditions is very little in different experiments from different papers. Therefore, I would argue that it is reasonable to compare across different papers to demonstrate different catalysts' effect on POCL reaction.

Catalysts that are used in the POCL reactions can be divided into four types: positive catalysts (or called "catalysts" directly), negative catalysts (inhibitors), polymers and compound additives. Each of these impact the light emission properties of the reaction in a distinct way.

Positive catalysts

Positive catalysts are what one might refer to as conventional catalysts. They increase the rate of reaction by providing an alternative reaction pathway with lower activation energy. In POCL reactions specifically, catalysts can promote the nucleophilic addition step and the leaving of the substituted phenyl group, and therefore make the reaction faster (Xue, 2009). To achieve this effect, common catalysts that can be used in POCL reactions are weak alkaline substances and some metal ions, such as salicylates, copper ions and sodium ions.

When different amounts of sodium salicylate are added to the POCL system, the light intensity curves change in the way below (Xu, 2007).

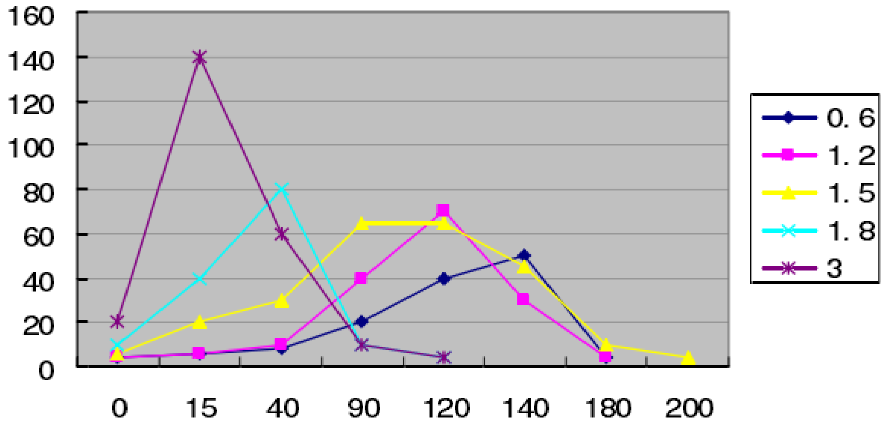

Figure 1. The effect of varying sodium salicylate concentrations of POCL light intensity curves (adapted from Xu, 2007).
The y value is the relative light intensity (without unit) and the x-axis is time in minutes. The colour of the curve indicates the concentration of sodium salicylate in the system in 10^{-5} mol/mL.

Figure 1 shows that as the amount of catalyst added increases, the luminescent lifetime and the time for the occurrence of the maximum light intensity decrease, but the maximum light intensity has enhanced greatly. However, when the concentration of the catalyst is too high, the total energy output would decrease as the luminescent lifetime is too short. The optimal concentration of sodium salicylate, in this case, is $1.5 \times 10^{-5}\ mol/mL$.

A similar phenomenon happens to the addition of sodium ions, here in the form of sodium chlorate(V), in the POCL system. From Figure 2, we can see that as the concentration of sodium ions increases, the light intensity of chemiluminescence also increases in all wavelengths of the emission spectrum (Maruyama, 2013).

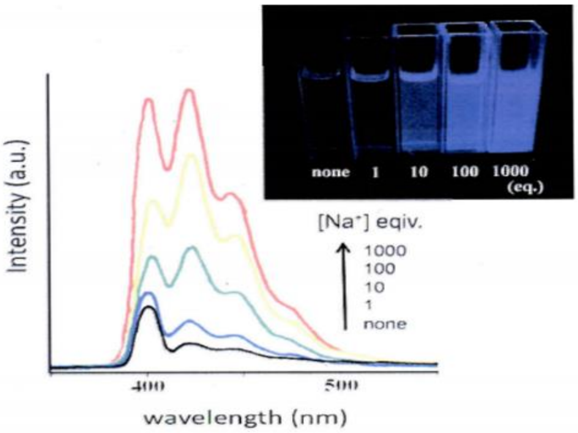

Figure 2. The effect of varying sodium ion concentrations of POCL light intensities in different wavelengths (adapted from Maruyama, 2013)
The x-axis in this graph is the wavelength of light emission in nm and the y-axis is light intensity. The colour of the curve indicates the concentration of sodium.

Different metal ions also have different catalysing abilities. The y axis for Figure 3 is the quantum yield for chemiluminescence, Φ_{CL}, a parameter indicating the efficiency of the chemiluminescent reaction. A higher quantum yield indicates a better efficiency of the reaction and higher total energy output. From the graph below, we can see that copper and zinc ions are the two best catalysts among them (Maruyama, 2013).

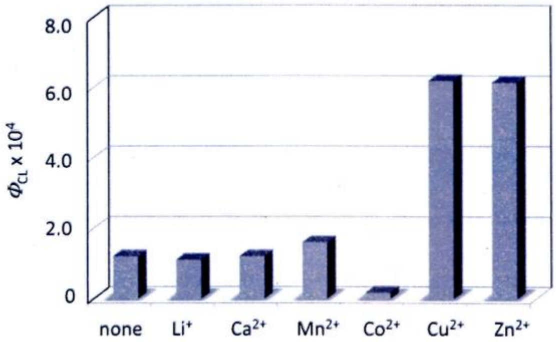

Figure 3. The quantum yield of POCL reaction under different metal ions (adapted from Maruyama, 2013)

Negative catalysts (Inhibitors)

Negative catalysts on the other hand, unlike the name would suggest, are not a direct opposite of a positive catalyst and so they do not introduce a reaction path with higher activation energy. Instead, inhibitors slow the reaction by removing reaction intermediates such as free radicals. In POCL reactions, inhibitors play their role by hampering the leaving of the substituted phenyl group to make the reaction proceed slower (Xue, 2009). By slowing the reaction down, negative catalysts have the benefit of extending the reaction time, so light is emitted over a prolonged period. This, however, comes at a price of reduced intensity. Common inhibitors used in POCL reactions are weak acids including oxalate acid and citric acid.

Different weak acids have different inhibiting abilities, and the effect of some most common ones are shown below (Xu, 2007).

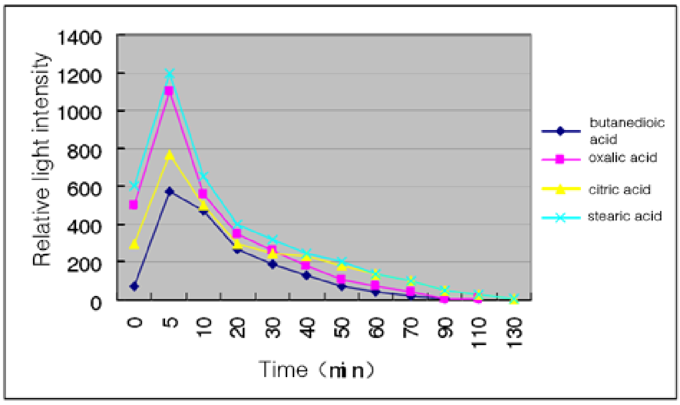

Figure 4. The effect of varying inhibitors of POCL light intensity curves (adapted from Xu, 2007). The y value is the relative light intensity (without unit) and the x-axis is time in minutes. The colour of the curve indicates the kind of inhibitor used in the experiment

From Figure 4, we can see that although 4 different inhibitors have generally the same dampening effect of the POCL reaction (the shape of the curves and the time for maxima are similar), stearic acid and oxalic acid have better ability to maintain the light intensity, which means less energy loss. Importantly, stearic acid has the largest molecular mass among them, which makes the whole system turn to a gel, so it is not often used practically. Therefore, oxalic acid, as an alternative, has been considered as one of the best inhibitors in POCL reaction.

Also, the concentration of inhibitors affects the POCL reaction. There are two experiments about how the amount of oxalic acid added to the system affects the light emission of the POCL system, and the light intensity graphs are shown below (Xue, Du and Sun, 2008).

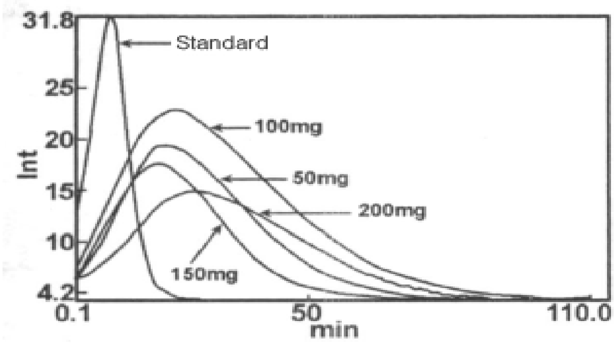

Figure 5. The effect of varying concentrations of inhibitors of the POCL system (adapted from Xue, Du and Sun, 2008)
The y-value is the light intensity in lumens and the x-value is time in minutes. The amount of oxalic acid added is indicated on the curve. 'Standard' means that no inhibitor is added to the system.

From Figure 5, we can see that generally, when oxalic acid is added, the luminescent lifetime will expand to a great extent, and the time for maximum light intensity is delayed. Although the peak value of light intensity is decreased, the total energy output is increased. We can also see that there is an optimal amount of addition, which is 100 mg in this case. For both less than or more than this value, the total energy output will decrease.

The same trend can also be seen in another experiment performed with different bisoxalate ester used as shown below in Figure 6. There is also an optimal concentration of oxalic acid in the system with the highest energy output, which is $6.3 \times 10^{-5}\ mol/mL$.

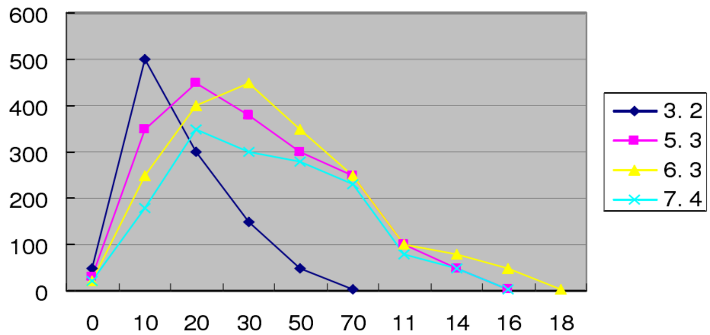

Figure 5. The effect of varying concentrations of inhibitors of the POCL system (adapted from Xu, 2007)
The y-value is the relative light intensity and the x-value is time in minutes. The amount of oxalic acid added is indicated on the curve. 'Standard' means that no inhibitor is added to the system.

Polymers

Polymers can also enhance the light emission intensity of the POCL reaction, which is first reported in a series of experiments held by Maulding *et al* in 1976. In their investigation, they have compared the effect of various polymers with different molecular mass and concentration on the POCL system. They concluded that multifarious kinds of polymers can enhance the light emission intensity as well as the luminescent lifetime of POCL reaction, and also a wide range of molecular mass (from 1000 to 600000) and concentration (0.1% to 1%) of polymers are effective. However, due to analytical limitations, they were not able to figure out why such a wide range of different polymers have such effects on POCL reaction (Maulding and Pauhut, 1976). Several years later, the mechanism of polymers affecting light emission of POCL reaction is finally revealed. During the process of high-energy intermediates passing their energy to fluorescent molecules by collisions, they may collide with other molecules as well, which leads to the waste of energy in the form of heat rather than light. Polymers increase the viscosity of the system and therefore decrease the occurrence of ineffective collisions, so the overall efficiency of the reaction increases (Du, Xue and Sun, 2009).

Several polymers have been proposed with the potential to affect POCL reaction dynamics. The specific choice of polymer added to the reaction mixture can have different effects on the light emission characteristics as demonstrated below. When PS (polystyrene) is added to the POCL system, both the light intensity and the luminescent lifetime have increased as shown in Figure 6. The optimal amount of addition of PS is 50 mg in this case, which has a total energy output of 1232.58 lumens ·h/L. This is 74.5% higher than that of the system without adding PS, which is 706.43 lumen·h/L (Xue, Du and Sun, 2008).

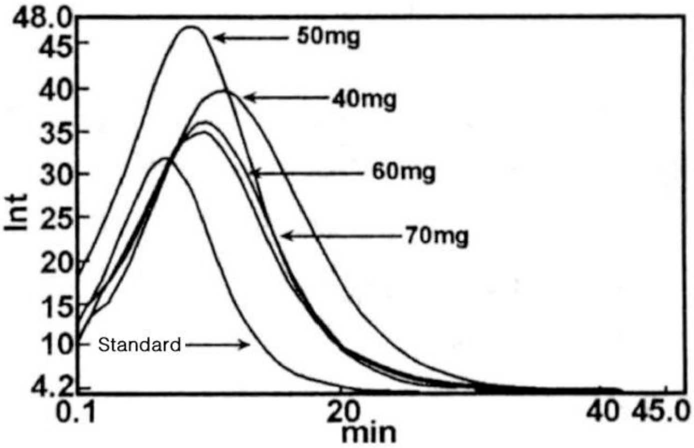

Figure 6. The effect of varying amounts of polystyrene of the POCL system (adapted from Xue, Du and Sun, 2008)
The y-value is the light intensity in lumens and the x-value is time in minutes. The amount of polystyrene added is indicated on the curve. 'Standard' means that no polystyrene is added to the system.

PMMA (polymethyl methacrylate), cannot increase the maximum light intensity like PS, but it can significantly increase the luminescent lifetime of POCL as shown in Figure 7 (A) and Figure 7 (B). Therefore, the total energy output has increased to a very large extent, from 751.71 lumens ·h/L to 2074.32 lumens ·h/L when 30 mg of PMMA is added (Xue, 2009).

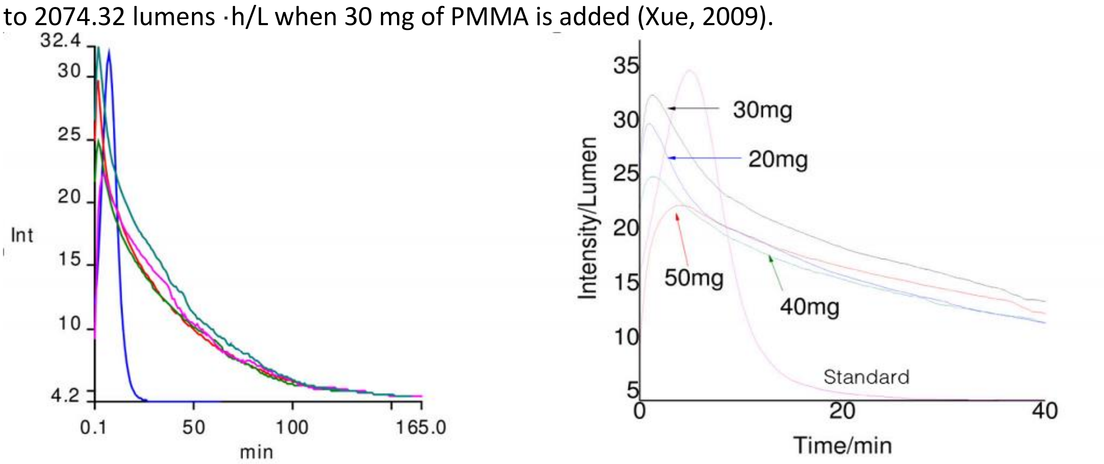

Figure 7 (A) and 7 (B). The effect of varying concentrations of inhibitors of the POCL system (adapted from Xue, 2009)
Picture 7 (B) magnifies Picture 7 (A). The y-value is the relative is the light intensity in lumens and the x-value is time in minutes. The amount of PMMA added is indicated on the curve. 'Standard' means that no PMMA is added to the system.

PEG (poly ethyl glycol), however, can both increase the maximum light intensity like PEG and prolong the luminescent lifetime greatly like PMMA as shown in Figure 8. The optimal amount of PEG is 70 mg in this system, for which the total energy output increases from 706.43 lumens ·h/L to 3095.60 lumens ·h/L (Xue, 2009).

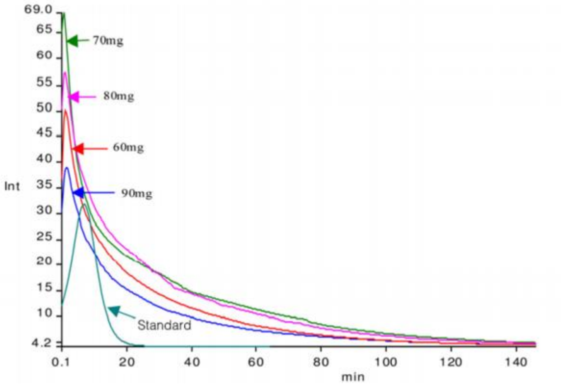

Figure 8. The effect of varying amounts of PEG of the POCL system (adapted from Xue, 2009)
The y-value is the light intensity in lumens and the x-value is time in minutes. The amount of PEG added is indicated on the curve. 'Standard' means that no PEG is added to the system.

Although different polymers have a different effect on the POCL system, all of them increase the luminescent lifetime due to the increased viscosity of the system. Another similarity between these experiments is that when excessive amounts of polymers are added, the total energy output of the POCL system would decrease. This is because when too much polymer is added to the system, fluorescent molecules will form complex compounds with polymers, which decreases the quantum yield of POCL reactions (Xue, 2009).

Compound Additives

Finally, compound additives refer to the inclusion of two or more of the above-mentioned additives, like an inhibitor and a polymer. This usually results in a better effect than simply adding only one kind of catalyst. Compound additives achieve an outcome that can be seen as the addition of the effect of its individual components. For instance, sodium salicylate can increase the light intensity and decrease the time for the maximum light intensity as well as the luminescent lifetime, while PS increases the light intensity and slightly increases the luminescent lifetime. Therefore, when two additives are added together into the POCL system, the effect would be just as shown in Figure 9 (Xue, 2009).

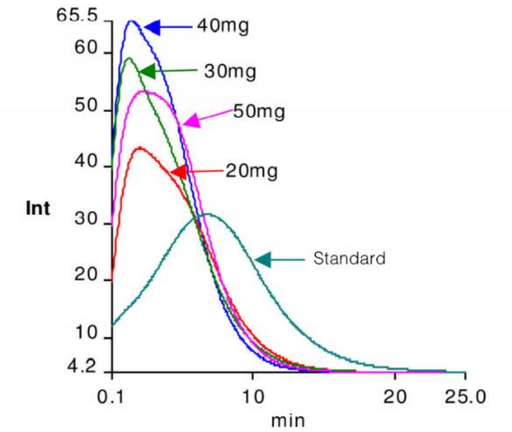

Figure 9. The effect of varying amounts of PS-sodium salicylate compound additive of the POCL system (adapted from Xue, 2009)
The y-value is the light intensity in lumens and the x-value is time in minutes. The amount of PEG added is indicated on the curve, while the amount of sodium salicylate added is 100mg unchanged. 'Standard' means that no additives are added to the system.

We can see that 40 mg PEG plus 100mg of sodium salicylate is the best compound additive with the highest energy output. However, this combination is not widely used as the total energy output have only increased from 706.43 lumens ·h/L to 894.12 lumens ·h/L.

This superimposed effect of two additives can be described as PS pulling the curve upwards and slightly to the right, while sodium salicylate is pulling the curve upward and to the left, as shown in Figure 10 below.

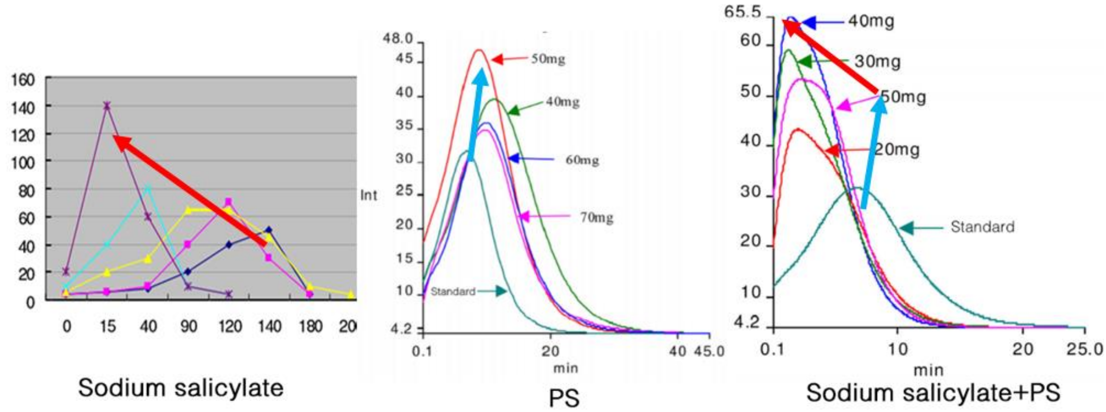

Figure 10. The effect of PS-sodium salicylate compound additive of the POCL system
The red arrow indicates the effect of sodium salicylate and the blue arrow indicates the effect of PS on POCL.

Similarly, the effect of another commonly used compound additive can be analysed using the method above as well. Oxalic acid can prolong the luminescent lifetime and reduce the maximum light intensity by slowing the speed of reaction. When added to the system with PS, which increases the light intensity and slightly increases the luminescent lifetime, the change of the light intensity curve will change as shown in Figure 11.

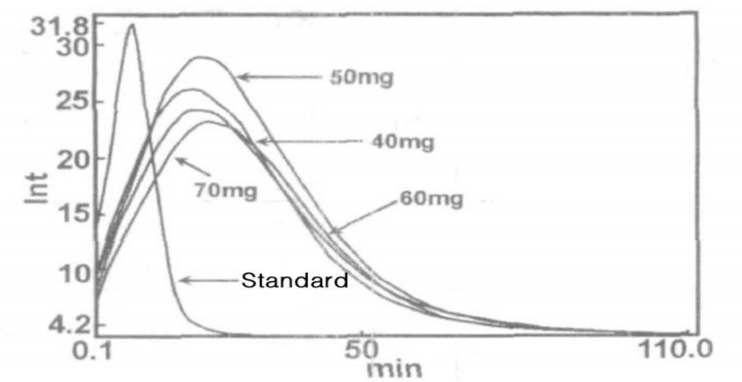

Figure 11. The effect of varying amounts of PS-oxalic acid compound additive of the POCL system (adapted from Xue, Du and Sun, 2008)
The y-value is the light intensity in lumens and the x-value is time in minutes. The amount of PEG added is indicated on the curve, while the amount of oxalic acid added is 100mg unchanged. 'Standard' means that no additives are added to the system.

It can be seen that 50 mg PEG plus 100 mg oxalic acid is the best, which increased the total energy output from 706.43 lumens ·h/L to 2224.47 lumens ·h/L.

This effect can be explained in Figure 12 as well, in which PS pulls the curve upwards and slightly rightward, and oxalic acid pushes the curve downward and rightward.

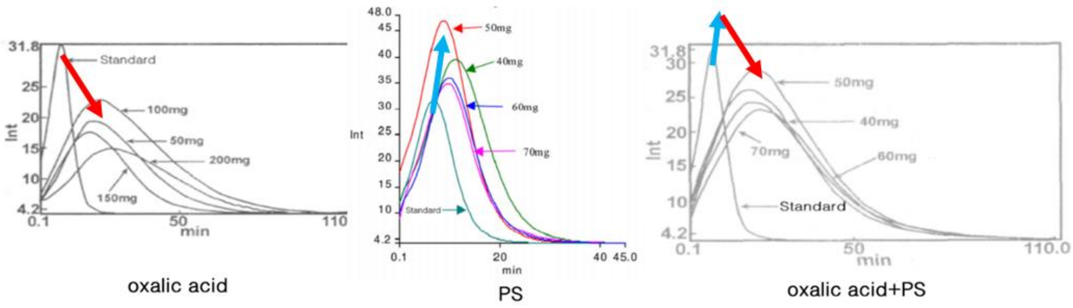

Figure 10. The effect of PS-oxalic acid compound additive of the POCL system
The red arrow indicates the effect of oxalic acid and the blue arrow indicates the effect of PS on POCL.

Conclusion

Overall, various types of catalysts open up an avenue to fine control reaction dynamics as desired for any particular use case. In cases for which a prolonged luminescent lifetime is required, such as the light source for emergencies, inhibitors with polymers could be added to the POCL system. Also, in circumstances for which the brightness of chemiluminescence is more significant than lifetime, such as the glowsticks used in parties and live shows, catalysts solely, or with some polymers can be added. Furthermore, a type of very fast peroxyoxalate chemiluminescence with a luminescent lifetime of only seconds has been discovered, which would probably be useful in capillary-based separation and sample handling techniques in near future (Jonsson and Irgum, 1999). Designers of products using POCL reactions can now manipulate the ingredients in the POCL system to change the light-emitting effect to meet the requirement of their product. This will bring a broad prospect for the future development and practical application of chemiluminescence.

References

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