

Sonochemiluminescence of Lucigenin in an Aqueous Solution Using Alcohol as Coreactant

アルコールを共反応物とする水溶液中でのルシゲニン超音波化学発光の観察

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1. Introduction

It is well-known that sufficient intensity of ultrasound to produce cavitation induces light emission in alkaline solution of luminol¹. The generation of cavitation can lead to the formation of reactive species, $\cdot\text{OH}$, $\cdot\text{H}$, and H_2O_2 in aqueous liquid, and secondary oxidation or reduction reactions can be induced by these species², which are referred to sonochemical reactions². The emission of luminol is believed to occur through an oxidative chemiluminescence process induced by sonogenerated $\cdot\text{OH}$. This sonogenerated chemiluminescence or sonochemiluminescence (SCL) is used to study the mechanics of cavitation.

We present a study on SCL of lucigenin (N,N'-dimethylbiacridinium dinitrate) (Luc^{2+}) as chemiluminescence (CL) probe. Luc^{2+} is one of efficient CL probe like luminol and used to detect superoxide ($\text{O}_2\cdot^-$). But SCL of Luc^{2+} has not been directly observed in aqueous solution. The CL of Luc^{2+} requires one-electron reduction of Luc^{2+} to form lucigenin cation radical ($\text{Luc}^{\cdot+}$). Due to the lack of reductive species in cavitation field, the observation of SCL of Luc^{2+} may have been failed. In our experiment, addition of a small amount of coreactant such as alcohols results appearance of SCL of Luc^{2+} . We proposed reductive pathways of Luc^{2+} SCL. This SCL can be used to monitor the reductive species generated in ultrasonic reaction field.

2. Experiment

A Sonochemical reactor for measurement was made of cylinder-shape acrylic chamber as shown in **Fig.1**. Quartz glass window was mounted in the side of chamber. The inner diameter of chamber was 6cm and the chamber was filled with water with 17.5 cm height. The transducer unit with frequency of 500 kHz was mounted on the bottom of the reactor, which was made of stainless steel. The waveform made by multifunction generator model WF1974 (NF Co., Japan) was amplified by RF amplifier model T145-5015A (THAMWAY Co., Japan) and applied to the transducer. A cylindrical

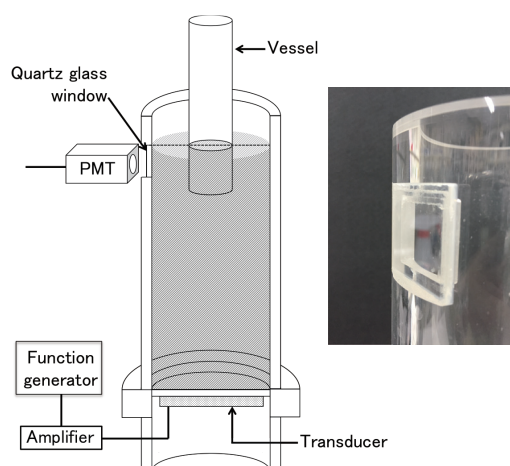


Fig. 1 A Schematic experimental setup of sonochemical reactor and picture of quartz glass window.

glass vessel with 3cm in diameter was used as sonochemical cell for SCL observation. The sample volume in the cell was 10 cm^3 , and the top of the cell was capped. The position of the cell was fixed above the transducer with a distance of 15.5 cm, and the sample liquid level in the cell was the same as surrounding water level in the chamber. The light emitting from sonochemical cell was measured by a H6780 photomultiplier tube module (Hamamatsu Photonics, Japan) placed beside the window. And the all experiment were conducted in a light proof box.

3. Results and discussion

The light emissions from samples under sonication are shown in **Fig.2** Strong emission was observed in the O_2 saturated solution containing 1mM NaOH, 50 μM Luc^{2+} and 52 mM 2-propanol. But absent of Luc^{2+} or 2-propanol resulted in very weak emission (Inset of Fig.2). This weak emission was considered to the sonoluminescence (SL) of water. Oxygen concentration also affected to the SCL intensity. When N_2 gas was saturated in the solution, very weak light same level as SL of water was observed.

The chemical effects of ultrasound are based

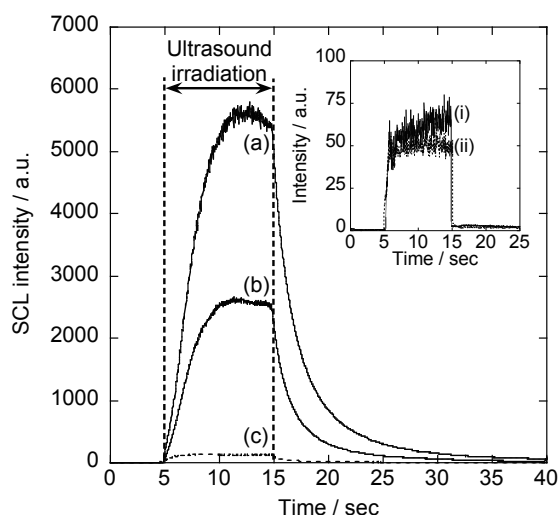


Fig. 2 SCL/SL signals under the sonication. The solution containing 50 μM lucigenin, 1 mM NaOH and 52 mM 2-propanol. (a) O_2 saturated; (b) Air saturated; (c) N_2 saturated. Inset: Signals in the O_2 saturated solution (i) without lucigenin; (ii) without 2-propanol.

on the formation of reactive species by acoustic cavitation. The alkyl alcohols tend to adsorb onto the cavitation bubble/solution interface and are able to scavenge the $\cdot\text{OH}$ produced during cavitation³. The reaction between 2-propanol and $\cdot\text{OH}$ leads to production of 2-propanol radical. This reductive radical diffused to the bulk solution and reacted with Luc^{2+} or O_2 . Luc^{2+} and O_2 are reduced to $\text{Luc}^{\cdot+}$ and $\text{O}_2^{\cdot-}$ respectively. The reaction between two radical species generated dioxetane type intermediate. This intermediate decomposed to the product in excited state and initiated the emission. Therefore the formation of 2-propanol radical is expected to induce the emission. This hypothesis was supported indirectly by the experiment of the addition of scavenger against $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$. Superoxide dismutase (SOD) is the enzyme that can catalyze the disproportionation of $\text{O}_2^{\cdot-}$, and salicylic acid is known as the scavenger to $\cdot\text{OH}$. The addition of these scavengers resulted in the quenching of the SCL. This means that two radicals, $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$, are necessary to emission and probably 2-propanol act important roll in the reaction with these radicals.

The effect of concentration of 2-propanol was shown in Fig.3. The greater the concentration of 2-propanol increased, the greater SCL intensity was observed. This is caused by the increase of $\text{Luc}^{\cdot+}$ and $\text{O}_2^{\cdot-}$ concentration. However SCL intensity did not further increase when concentration of 2-propanol was greater than 50 mM. This is probably due to the competition reaction by the 2-propanol radical or the evaporation effect. The radicals generated in sonication can react with 2-propanol or other radicals⁴. This reaction occurred competitively and probably light emitting

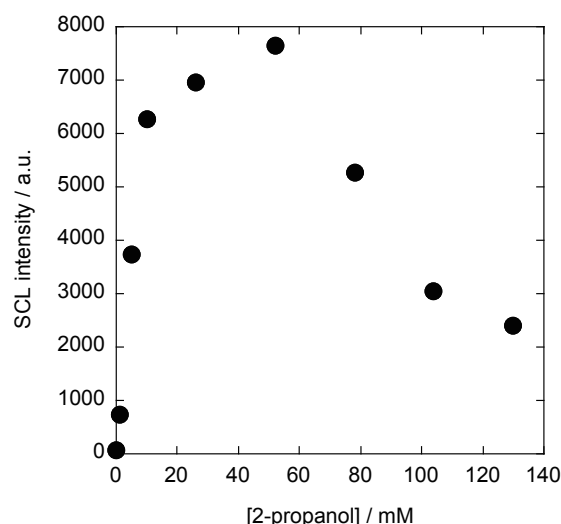


Fig. 3 The dependence of the concentration of 2-propanol on the SCL intensity.

reaction was prevented. In the ultrasonic field, 2-propanol can evaporate into the cavity and decrease the temperature of cavity⁵. And it probably affected to the reactions occurred in the cavity and at bubble/solution interface.

The kinds of alcohols are also important in SCL reaction. In the solution containing 10 mM alcohols, the degree of SCL were measured in order as 2-propanol > 1-propanol > ethanol > methanol. This order was caused by the reaction rate with the reaction of $\cdot\text{OH}$ ⁶, and consequently correlated to the amount of $\text{O}_2^{\cdot-}$ generated.

4. Conclusion

The efficient SCL of lucigenin was observed under coexisting alcohols. The reaction of SCL is complicated to characterize but the reaction between primary radicals formed in a cavity and alcohols led to the SCL in Luc^{2+} /alcohol system. This SCL has the advantage in simplicity because its emission is triggered by ultrasound without addition of reagents.

References

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