SOAR Research Proposal -- Summer 2015

The Heat of Reaction of Luminol: Energy Flow in a Chemiluminescent Reaction

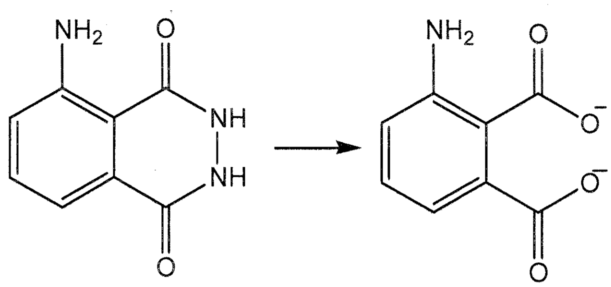
Faculty: **Carl Salter** Professor and Chair, Chemistry Department

Student: **Alex Sestok** Senior
Start Date: June 1, 2015
End Date: August 7, 2015
Length: 10 weeks

Description:

The Heat of Reaction of Luminol: Energy Flow in a Chemiluminescent Reaction. Luminol is a remarkably simple organic compound that emits blue light when it reacts with hydrogen peroxide. Luminol is the compound most often used in classroom demonstrations of chemiluminescence, and it used by crime scene technicians to visualize trace amounts of blood at crime scenes. (It is not, however, the material responsible for the luminescence of commercial light sticks.)

$2\ OH^- + 2\ H_2O_2 +$



$+\ N_2 + 4\ H_2O$

The resulting product of the reaction, the aminophthalate anion, has been identified for several decades as the chemical that actually emits the blue light. The mechanism of this chemiluminescent reaction has been a subject of investigation since the early 1960's, and a great deal is known about how luminol gives off light; however, it appears that a basic piece of information about the reaction has never been measured: the total energy change. Probably because of this missing information, there is a common misconception among chemistry teachers that luminol "produces light *instead of* heat". Our experiments show that this is certainly not the case; the usual demonstration "recipe" using 100 ml of luminol solution and 1 ml of 3% hydrogen peroxide yields a 0.3°C temperature rise. Since there is a mere 40 mg of luminol in the solution, the small temperature rise indicates that a substantial amount of heat is produced by the reaction *per molecule*, and in fact only a small percentage of the energy produced by the reaction is emitted as light. A precise measurement of the total energy change in this reaction would give us a better understanding of how the partitioning of the energy into heat and light takes place.

Accomplishing the measurement is a significant experimental challenge. The reaction itself presents a problem: we have learned that when luminol reacts with hydrogen peroxide and the chemiluminescence is finished, the luminol is not used up, even when there is excess hydrogen peroxide available. Thus, to measure the heat of the reaction precisely, we must measure both the temperature rise and **at the same time** how much luminol actually reacted. Fortunately we know the amount of luminol at the start; if we can measure the amount of luminol that remains after the chemiluminescence is finished, then we can determine by difference how much luminol reacted.

Previous Progress:

During the summer of 2006 Josh Beri worked on the luminol reaction. He quickly learned how to use the calorimeter to measure the temperature rise of the reaction, and he did an excellent job of controlling the conditions of the reaction so that a reproducible temperature rise could be observed. We knew that the key to completing the project would be to measure the amount of unreacted luminol leftover from a run, so that we could calculate the exact energy release per molecule. Unfortunately, our plan to use the GC-MS to measure the unreacted luminol was thwarted that summer because the GC-MS was broken and remained unrepaired throughout the summer. Last fall the department acquired a new GC-MS that will be better able to perform the needed analyses. In addition, we now have several HPLC s that can be used to analyze the reaction mixture, and they might be better suited than the GC-MS. In 2008 Josh explored an alternative method of measuring the extent of the reaction: the organic byproduct of the reaction, called aminophthalate, fluorescences when exposed to UV light. The department had just received a new fluorimeter, and Josh was able to demonstrate that he could measure the amount of aminophthalate using the fluorimeter.

Roles:

Alex Sestok is a rising senior chemistry major (math minor) who will have finished taking my physical chemistry classes, where she will learn to use both the calorimeter and the fluorimeter. In her Organic lab class she used the GC-MS for simple analyses, but she will need to learn more about both GC-MS and HPLC. Her first goal will be to prepare samples of the luminol reaction mixture, both real and simulated, and analyze them using the fluorimeter, the GC-MS, and the HPLC. As an important control experiment, she can prepare simulated reaction samples using aminophthalic acid that we purchase. She will need to assess which analytical instrument is the best-suited to measure the amount of remaining luminol, the amount of aminophthalate product, or ideally both. We also need to perform control experiments to determine whether or not the aminophthalate is undergoing subsequent reactions with the excess hydrogen peroxide.

Benefits:

Alex will gain tremendous experience in designing a sequence of experiments and control experiments that answer a basic chemical question, and in bringing an investigation to completion. I will benefit from having a student who can devote her full attention to the problem. In particular, it is important that several control experiments are run **on the same day** that the key measurements are made. The luminol reaction is so well known and so important in the chemical education literature that any new information and measurements that we can make about the reaction will be publishable in a research journal. In addition, if we can find a better catalyst, the heat of reaction of luminol can become a routine experiment in my physical chemistry lab course--this was the original motivation for my initial investigation of the reaction with Nicole Savino (independent study Fall 2005). This opens up the possibility of a follow-up publication of the lab experiment in the *Journal of Chemical Education*.

SOAR Budget Proposal -- Summer 2015

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Budget:

For the project, we will need 55$ for 5 grams of 97% luminol and 135.50$ for 5 grams of 90% 3-Aminophthalic Acid. These chemicals are necessary to run the experiments. We will also need 500$ for an anion exchange column to separate charged reaction mixtures in the HPLC.