

The chemiluminescence of luminol | lab report



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Introduction

Chemiluminescence is the process whereby light is produced via a chemical reaction with the evolution of little or no heat. Chemiluminescence, unlike phosphorescence and fluorescence, does not need to absorb an external source of photons to reach an excited state. Instead chemiluminescence occurs when a molecule is excited through a series of chemical reactions. The molecule, usually in the lower excited singlet state, can spontaneously lose its electronic energy in the form of a photon. In fluorescence the electronic spin ($\hat{S}=0$) is preserved, while the radiant intensity of chemiluminescence can be expressed as:

This equation holds true since the rate of chemiluminescence depends both on the quantum yield ϕ_{CL} , and also the rate of chemical reaction, k . Thus one may note that the degree of chemiluminescence depends greatly on the quantum yield and the number of photons emitted per chemiluminescing molecule.

In the practical below luminol, a chemiluminescence molecule is to be prepared from 3-nitrothalic acid. Luminol is seen to have many applications in life. For example, male fireflies in search for a mate are able to produce certain chemicals to allow their lower abdomen to glow. The interaction of luciferin from the firefly, its enzyme luciferase together with adenosine triphosphate, oxygen and the magnesium ion allows for this natural chemiluminescence. First the luciferin is adenylated by the ATP:



The second reaction involved the product of the first reaction being oxidised to give decarboxylketoluciferin. This is seen to be a cyclic endoperoxide intermediate that results in an electronically excited decarboxylketoluciferin, that finally chemiluminesces.

Luciferyl Adenylate + O₂ → decarboxylketoluciferin* + AMP + CO₂

Decarboxylketoluciferin* → decarboxylketoluciferin + photon

The decomposition of the endoperoxide results in an excited carbonyl that leads to chemiluminescence.

Method

2.1 Chemicals

Chemical

Grade

Brand

3-nitrophthalic acid

98 % Pure

Fluks

Hydrazine 8 % aqueous solution

GPR

BDH

Digol

GPR

Hopkin and Williams

Sodium hydroxide

GPR

Timstar

Sodium dithionite

Lab Reagent Grade

Fisher Scientific

Glacial acetic acid

GPR

BDH

Potassium Ferricyanide

GPR

Riedel de Hean

3% Hydrogen peroxide

GPR

BDH

2. 2 Apparatus

Analytical balance Tripod

Weighing boat Gauze

Spatula vacuum pump

Filter tube (dimensions 20 X 150 mm) Filter funnel

10 mL measuring cylinder Hirsh funnel

100 mL measuring cylinder Filter paper

Stirring rod conical flask with side arm

Thermometer test tube (20 c 150 mm)

Rubber bung 50 mL beaker

Bunsen burner 100 mL beaker

Erlenmeyer flask stirring rod

2. 3 Procedure

A) Preparation

1. 000g of 3-nitrophthalic acid were weighed on an analytical balance and placed in a filter tube of approximate dimensions of 20 x 150 mm.

2 mL of 8% v/v aqueous solution of hydrazine was added with care.

This solution was gently heated over a Bunsen flame until the solid dissolved. (The test tube placed about 20 cm away from the flame and periodically moving it away from the flame)

3 mL of Digol was added and stoppered using a rubber bung fitted with a thermometer.

The side arm was connected to the vacuum pump and boiled to disill off excess water in the solution

The solution was heated to 110-130 OC then rapidly heated to 200 OC.

The reaction mixture was kept at this temperature for two minutes.

The mixture was then cooled to 100 OC and 15 mL of hot water was added

The solution as cooled under running water and the intermediate product (II) collected by suction filtration using a Hirsch funnel.

The nitro-compound was transferred to a 20 x 150 mm test tube

5 mL of 10 % sodium hydroxide and 3. 000 g of sodium dithionite were added

Any remaining solids on the sides of the test tube was washed with a minimum amount of distilled water

The mixture was boiled gently for 5 minutes while stirring

2 mL of glacial acetic acid was added to the mixture and the solution cooled under tap water.

The amine (III) was collected by suction filtration using a Hirsh funnel

B) Chemiluminescence Demonstration (carried out in the dark)

2 mL of 10% sodium hydroxide solution was mixed with 18 mL of water

The 0.013 g of amine (III) was added to this solution and stirred until completely dissolved. (stock solution A)

The oxidising solution (stock solution B) was prepared by mixing 4 mL of 3 % w/v solution potassium ferricyanide to an equal volume of 3 % hydrogen peroxide.

The solution as made up to 200 mL using distilled water

Chemiluminescence was observed by diluting 5 mL of stock solution A to 40 mL distilled water.

Stock solution B was poured simultaneously with the solution prepared into a funnel placed on a large Erlenmeyer flask

The flask was swirled and small portions of alkali were added to increase the brilliance.

2. 4 Precautions

Care was taken when using the Hydrazine due to its toxicity

The 3-nitrophthalic acid solution was heated with periodic removal from the flame.

Care was taken to transfer all the solid from the filter paper, without adding any filter paper to the solid.

The chemiluminescence demonstration was carried out in a dark room so for better observation of illumination

2. 5 Sources of error

Some losses due to transfers may have been present leading to a lower yield

Some filter paper may have been transferred with the amine thus leading to a higher yield.

3. Results

Mass of amine(III) produced= 0. 13 g

Observation- Blue fluorescence was observed upon combination of the solutions as described above

4. Discussion

Nitrophthalic acid was added to hydrazine, and with the presence of heat the nitro derivative, Luminol, is formed. This may be described as a dehydration reaction.

Luminol may then form the Dianion by oxidation using the hydrogen peroxide, sodium hydroxide, and the use of the potassium ferricyanide as the catalyst. The dianion is oxidised to the triplet excited state then due to a slow intercrossing system is converted to a singlet dianion excited state. This compound eventually decays to its ground state and emits a photon of light per molecule.

The energy released in the reaction is therefore seen to cause the excitation of electrons in the products of the reaction thus the excited electrons return to the ground state, and blue visible light is emitted. Since blood is seen to have the metal ion Fe^{2+} , it may be used to oxidise the hydrogen peroxide into oxygen and water. Thus the oxygen may be used to oxidise the luminol in the same way as seen above. Thus blood can be seen to luminate with the addition of luminol

The yield of the amine produced was seen to be quite low. This may be caused by the overall entropically unfavourable reaction. This thus would cause low reaction efficiency. The reaction above is seen to require consecutive intermolecular and intramolecular condensations, which are likely to have, and entropy less than zero. Thus with the net negative entropy and high temperatures, the reaction is seen to be unfavourable.

Conclusion

From this practical one may see that a bright blue luminescence was observed. This thus confirms the production of luminol. The relatively low yield was due to the fact that the reaction was entropically unfavourable.