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New light from an old reagent: Chemiluminescence from the reaction of potassium permanganate with sodium borohydride.

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Abstract

When aqueous sodium borohydride (50 mM) is added to a solution of potassium permanganate (1mM, in sodium hexametaphosphate) at acidic pH, bright red-orange emission is easily visible in a darkened room. This chemiluminescence emission is due to an excited state of manganese (II) that undergoes solution phase phosphorescence and provides an excellent opportunity for students to explore the relationship between the initial oxidation state of the manganese and the likelihood of luminescence. Not surprisingly Mn(VII), Mn(IV) and Mn(III) all give rise to chemiluminescence where as Mn(II) fails to react.

Introduction

Since its first observation by Glauber (1659), and subsequent characterisation by Forchhammer (1820) and Mitscherlich (1832) the deep violet colour of potassium permanganate has held a fascination for most chemists (1). Now established as an oxidant, especially in volumetric analysis (2), potassium permanganate is well known to most high school students. Surprisingly in Harvey's (3) detailed account of the history of luminescence prior to 1900 there is no mention of this common oxidant being used as a chemiluminescence reagent. Although largely ignored in the classroom demonstrations, (the oxidation of siloxene (4, 5) is the only well-known demonstration of chemiluminescence involving the permanganate ion), potassium permanganate has a history as a chemiluminescent reagent in analytical chemistry (6). Under certain circumstances, higher oxidation states of manganese can be reduced to form an excited state Mn(II) species which undergoes solution phase phosphorescence to emit red chemiluminescence (7).

In this paper we describe what is undoubtedly one of the simplest of all chemiluminescent reactions, namely the reaction of potassium permanganate with sodium borohydride in aqueous solution. The demonstration provides an excellent opportunity for students to explore the relationship between the initial oxidation state of the manganese and the emission of light. Not surprisingly Mn(VII), Mn(IV) and Mn(III) all give rise to chemiluminescence whilst Mn(II) fails to emit. This demonstration has the potential to be further developed as a high school experiment where students can not only explore the oxidation state of the manganese but also the effect of variables such as reagent concentration and pH on the intensity of the light emitted. Furthermore all of the chemicals and equipment required are readily available in a high school laboratory and the only other thing required is the human eye, a most sensitive detector.

Experimental Procedure

Materials and Equipment

Potassium permanganate
Manganese sulfate
Sodium borohydride
Sodium hexametaphosphate (Calgon)
Sodium hydroxide (0.001 M)
Sulfuric acid (2 M)
Phosphoric acid (3 M)
Ultrasonication bath
Deionised Water
1 × 500 mL beakers
3 × 200 mL beakers
several extra 500 mL beakers to pour solutions into

Preparation of solutions

Manganese(VII): Dissolve 0.079 g (0.5 mmol) of potassium permanganate and 10 g of sodium hexametaphosphate (Calgon) in 1.0 L of deionised water. Adjust the pH of the solution to 2.0 with 2 M sulfuric acid. This solution is stable for more than 24 hours.

Sodium borohydride: Dissolve 0.2 g (ca. 11 mmol) of sodium borohydride in 500 mL of aqueous sodium hydroxide (0.2 g in 5.0 L).

Manganese(II): Dissolve 0.5 g (3.3 mmol) of manganese(II) sulfate and 1.0 g of sodium hexametaphosphate in 100 mL of deionised water.

Manganese(III): Dissolve 0.5 g (3.3 mmol) of manganese(II) sulfate and 2.5 g of sodium hexametaphosphate in 250 mL of deionised water. Adjust the pH to 2.0 with 2M sulfuric acid. Add 0.025 g (0.158 mmol) potassium permanganate to this solution and allow to react for thirty minutes. This resulting solution contains approximately 0.05 M Mn(III).

Manganese(IV): Solutions of manganese(IV) can be prepared from manganese dioxide synthesised by the method of Jáky and Zrinyi (8). Wet manganese dioxide

(0.04 g) is dissolved in 100 mL of phosphoric acid (3 M) assisted by ultrasonication.

Demonstration

When you wish to begin the demonstration turn out the room lights. Slowly pour some of the sodium borohydride solution into a 500 mL beaker containing some of the potassium permanganate solution. An intense and rapid red-orange chemiluminescence emission that fills the entire beaker is observed.

The potassium permanganate can be replaced with solutions of manganese(II), (III) or (IV) to demonstrate the effect of manganese oxidation state on the reaction. The light emission from the manganese(IV) reaction is low and therefore not recommended unless the room is entirely darkened, and not surprisingly the manganese(II) fails to emit chemiluminescence.

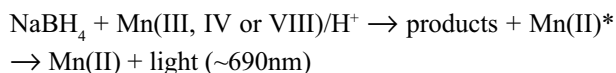
Hazards

Potassium permanganate is a strong oxidant whilst sodium borohydride is a powerful reductant and the reaction is a potential source of hydrogen gas. Therefore goggles, gloves and a laboratory coat should be worn whilst preparing the solutions and performing the demonstration. Care must be taken to exclude all sources of ignition, and the reaction should be conducted in a well-ventilated space.

Discussion

Chemiluminescence, or the emission of light as a result of a chemical reaction, has fascinated and enchanted young and old alike for centuries (3). No longer a laboratory curiosity, the number of applications of chemiluminescence in analytical chemistry has increased in recent years (6, 9, 10) whilst the novelty industry has marketed the phenomenon in the form of Cyalume® lightsticks.

In this demonstration the chemical reaction that produces the chemiluminescence involves the reduction of potassium permanganate by sodium borohydride. An electronically excited species of manganese (II) is formed, which de-excites to the ground state to yield light around 690nm (see equation 1).



Equation 1

It can be seen by the naked eye that all three manganese oxidation states result in chemiluminescence of the same colour (and therefore wavelength), these observations have been confirmed spectrophotometrically (See Figure 1). Comparison of the chemiluminescence emission spectra with the phosphorescence spectra of manganese (II) at 77K confirms the formation of an excited state manganese (II) species (See Figure 2). It is not surprising that manganese (II) does not emit as it is in the ground 2+ oxidation state and consequently unable to form the excited state species upon reaction with sodium borohydride.

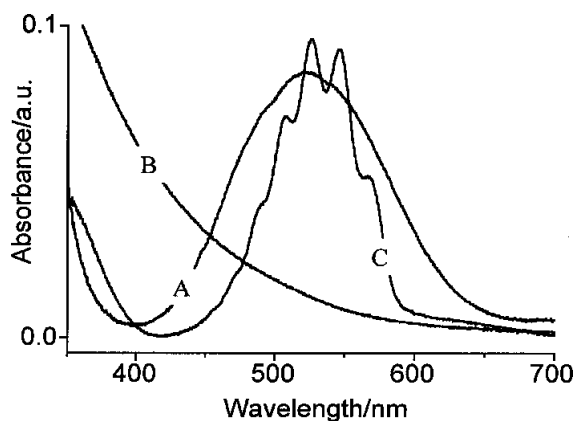


Figure 1. Absorbance spectra of manganese(III), manganese(IV) and manganese(VII) solutions, where A = manganese(III), B = manganese(IV) and C = manganese(VII)

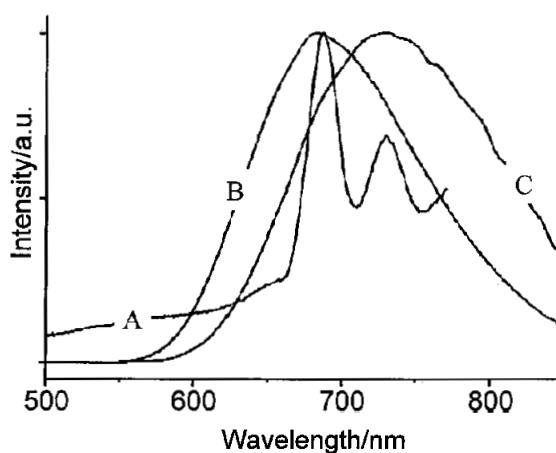


Figure 2. Luminescence spectra for potassium permanganate chemiluminescence and manganese(II) phosphorescence, where A = manganese(II) phosphorescence at 77 K, B = potassium permanganate chemiluminescence in the presence of sodium hexametaphosphate and C = potassium permanganate chemiluminescence in the presence of sodium orthophosphate

Further manipulation of the reaction conditions including the mixing order, reagent concentrations and pH allow the student to explore their impact on the resultant chemiluminescence intensity and longevity (some examples of this are depicted in Tables 1 - 4) and hence add a discovery aspect to their work.

Table 1. Effect of pH on the chemiluminescence reaction of manganese(VII) with sodium borohydride

pH	Observations
2.0	Brightest and fastest
2.5	Slightly weaker and slower
3.0	Weakest and slowest

Table 2.

Effect of reactant concentrations on the chemiluminescence reaction of manganese(VII) at pH 2.0 with sodium borohydride

NaBH 4/M	Manganese(VII)/M			
	0.0001	0.0005	0.001	0.005
0.001	Dull	Dull	Not Obs.	Not Obs.
0.005	Dull	Brighter	Brighter	Not Obs.
0.01	Dull	Brightest	Brighter	V. Dull
0.05	Dull	Brightest	Bright	V. Dull
0.1	Dull	Brightest	Bright	Not Obs.

Table 3. Effect of pH on the chemiluminescence reaction of manganese(III) with sodium borohydride (0.05M)

Manganese(III)/M	Observations
0.0001	V. Dull
0.0005	Bright
0.001	Brightest
0.005	Brightest
0.01	Bright

Table 4.

Effect of pH on the chemiluminescence reaction of manganese(IV) with sodium borohydride (0.05M)

Manganese(IV)/M	Observations
0.001	Not Observed
0.005	Very Dull
0.001	Dull

Conclusions

The reactions of manganese(III), (IV) or (VII) with sodium borohydride are some of a small group of purely inorganic chemiluminescent reactions. Whilst not as spectacular in intensity as the oxidation of white phosphorus or the combustion of carbon disulfide in nitrous or nitric oxides, it is our opinion that this simple demonstration is considerably superior to the oxidation of siloxane. As a demonstration it is devoid of toxic or corrosive by-products and sufficiently cheap to make it readily accessible to high school classrooms.

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Continuation from page 23:

The determination of the best separation conditions for a mixture of preservatives of varying polarity using HPLC: An ACELL experiment.¹

3.9 Are there any other features of this experiment that made it a particularly good or bad learning experience for you?

S1: I am easily distracted, so I found the small amount of "hands on" work to be not engaging enough. This may just be me, however.

S2: Like practicing, injecting, purging, conditioning column.

S3: This kind of experiment is one where I would need to take my own time to work on the machine etc.

In this way, group work is quite frustrating – I wanted to go slowly at one point, and they rushed ahead.

S4: Nice clear demonstration – can see on paper that peaks separate.

S5: No time to comment.

S6:

3.10 What improvements could be made to this experiment?

S1: No real comments/suggestions

S2: Actually using real life samples eg. cosmetic or food.

S3: Don't know.

S4: None.

S5:

S6:

3.11 Other Comments

Demonstrator was v.good and explained things clearly and concisely.

Not sure if the design of the experiment is meant to be so demonstrator-centred. As a student, that would drive me nuts!

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